



Université catholique de Louvain - Ecole Polytechnique de Louvain

MANUFACTURE AND CHARACTERIZATION OF SELF-ASSEMBLIES OF FUNCTIONALIZED NANOWIRES

Thesis submitted by Guillaume Staelens to obtain
the Ph.D. Degree in Engineering Sciences

Thesis committee:

- Prof. **Bernard Nysten**
- Prof. **Alain Jonas**
- Prof. **Sophie Demoustier**
- Prof. **Tom Leyssens**
- Prof. **Gilles Bruylants**
- Prof. **Anne-Sophie Duwez**
- Prof. **Jacques Devaux**

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Abstract

In nature many organisms have the ability to adapt and change their structural configuration at the nanoscopic level, providing them an exquisite variety of properties and dynamic interactions with their environment. Mimicking such complex systems would open the path towards such properties and interactions. However the investigation of such systems requires first to understand and control the self-assembly of nanostructured systems and next to understand and control the reconfiguration mechanisms. This thesis aims at addressing the first part of this objective. Based on a "bottom-up" approach, the objectives of this work are the design, the manufacture and the characterization of self-assemblies of (multi)functionalized nano-building blocks. These self-assemblies should be thin films presenting an ordered structure at a scale close to the one of the building blocks ("supra-crystalline") dependent on the system conditions, such as the pH or the temperature. The nano-building blocks chosen in this thesis are functionalized nanowires (NWs) made of noble metals: mainly platinum, gold and palladium. The nano-objects were synthesized by electro-chemical deposition in nanoporous membranes, made of anodic aluminum oxide or polycarbonate, leading to NWs of controlled diameter, length and composition. This templating method simultaneously allowed to chemically modify specific parts of the nano-object surface, especially their bases. In this work, the chemical functionalization was achieved using either thiol assembly or polyelectrolyte adsorption. Homogeneously functionalized as well as homogeneously multi-functionalized NWs were obtained. The grafting of fluorescent dyes allowed to prove the successful functionalization of the nano-objects. The functionalized nano-objects were assembled using two different methods: drop-casting on functionalized substrates and assembly at the toluene-water interface. Different techniques (fishing, drain-to-deposit or PDMS stamp inking) were tested to recover the assemblies built at the toluene-water interface on appropriate substrates. The obtained assemblies were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The influence of several parameters such as the nature of the nano-object, the functionalization of the nano-objects or substrate, the pH, etc. on the compactness (density) and organization of the assemblies was studied.

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List of abbreviations

AAO: anodized aluminum oxide
AFM: atomic force microscopy
APS: ammonium persulfate
ATRP: atom transfer radical polymerization
CTAB: cetyl-trimethylammonium bromide
CV: cyclic voltammetry
CYS: cysteine
DAPI: 4',6-diamidino-2-phenylindole
DDT: dodecanethiol
DIPEA: N,N-diisopropylethylamine
DLVO theory: Derjaguin-Landau-Verwey-Overbeek theory
DMSO: dimethylsulfoxide
DNS: dinitrosulphatoplatinates
DRIE: deep reactive-ion etching
ECD: electro-chemical deposition
EIS: electrochemical impedance spectroscopy
FITC: fluorescein isothiocyanate
GSH: glutathione
ICP-AES: inductively coupled plasma - atomic emission spectroscopy
LbL: layer-by-layer
MAA: mercaptoacetic acid
Mph: mercaptophenol
MPPTS: 2-methoxy(polyethyleneoxy)propyl trichlorosilane

MUA: 11-mercaptoundecanoic acid
MUTAB: 11-mercaptoundecyl-N,N,N-trimethylammonium bromide
NM: nanomaterial
NP: nanoparticle
NR: nanorod
NW: nanowire
OTS: octadecyltrichlorosilane
PAA: poly(acrylic acid)
PAH: poly(allylamine hydrochloride)
PC: polycarbonate
PDADMAC: poly(diallyldimethylammonium chloride)
PDMS: poly(dimethylsiloxane)
PEG: poly(ethylene glycol)
PEI: poly(ethylene imine)
PI: polyimide
PMMA: poly(methyl methacrylate)
PSS: poly(styrene sulfonate)
Rhod: rhodamine
SAM: self-assembled monolayer
SEM: scanning electron microscopy
STEM: scanning transmission electron microscopy
SERS: surface enhanced Raman spectroscopy
UPD: under-potential deposition
UV-Vis: ultraviolet visible
THF: tetrahydrofuran
TEM: transmission electron microscopy
VLS: volume-liquid-solid

General introduction

Since several decades, the domain of the infinitesimal, the nanosciences, developed and grew in numerous directions from biology to electronics. This is mainly due to the discovery of new properties, arising from the reduction in size of bulk material close to the atomic level, which instantaneously raised many researches. In particular, metallic nanomaterials (NMs) have been extensively studied because of their fascinating physico-chemical properties [1, 2]. Indeed, by reducing the dimensions of metallic materials, confinement of the electrons at their surface takes place, granting these new objects with specific size- and shape-dependent properties such as electrical, optical or magnetic properties [3, 4]. At the beginning, spherical particles received most of the attention because of their ease to be synthesized, obviously due to their thermodynamically favorable shape [5]. But rapidly, anisotropic semiconductor and metal NMs gained increasing attention due to their unique chemical and physical properties [1, 6]. The shape anisotropy in these objects induces disturbance into the common characteristics associated with spherical nanoparticles (NPs) which gives rise to new properties or shift in the "classical" ones [7]. The synthesis of specifically sized and shaped NMs can then provide particular desired properties. However, with the constant development of nanotechnology, the integration of NMs in nano- or macro-devices to reach application objectives became essential and predominant. That is why recently, hot topic is gradually shifting from the synthesis of those individual (disordered) NMs or nanostructures to the nano-fabrication of macroscopic ensembles [8]. The NMs would not have to be integrated inside the device, they would become the device. This can happen by manufacturing nano-building blocks able to assemble themselves leading to novel two-dimensional (2D) or three-dimensional (3D) nanostructures [9]. This bottom up approach is actually not new: this is how natural macro-structures are made. They grow from elementary building blocks that assemble

themselves in a specific way to obtain a final macro-structure [10]. Thus mimicking Nature

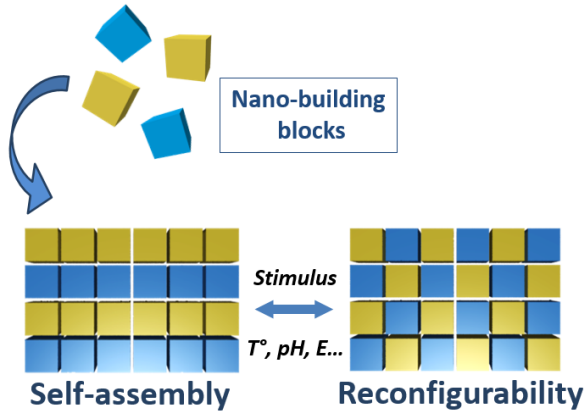


Figure 1.1: Schematic representation of the self-assembly of nano-building blocks and their reconfigurability upon stimulus.

by exploring self-assembly could lead to the design of new nano-devices and nanostructures but could also help to improve the comprehension of the mechanisms of elementary assembly. Moreover the use of nano-building blocks could open a new path to dynamic applications. Depending on the conditions of their environment, nano-building blocks could assemble in different ways and they may even change conformation in response to change of environmental parameters [11]. This is what is called reconfigurability (Figure 1.1). Eventually new desired nanostructures could be formed and reconfigured by self-assembly of smartly designed

nano-building blocks.

In this context the manufacture of thin films by self-assembly of NMs is a first important step on the path of smart assemblies. It allows the study of interactions, mechanisms and techniques enabling the optimization of large scale self-assemblies. Moreover, assembled thin films formed by metallic NMs can directly be valuable for some applications. Indeed thanks to the surface plasmonic effects of metallic NMs (and in particular gold), thin films can be used as "simple" optical filter [12]. But more interestingly they can be used as substrate for surface enhanced Raman spectroscopy (SERS) [13]. SERS consists in the enhancement of the Raman scattering of the molecules that are deposited on films made of NPs assemblies. Hence SERS allows better detection and discrimination between close looking molecules than classic Raman spectroscopy.

1.1 Objectives and strategy

The aim of this thesis is the manufacture and characterization of thin films (2D) made by self-assembly of NMs. The possible application for those films will not be investigated: the obtention of such films will already be a challenging objective. To reach this goal, this study was divided in three distinct parts. First, the manufacture of nano-building blocks. Second, the grafting of the main interaction inducers on the blocks. Third, the manufacture and the characterization of the

thin films (2D) made by self-assembly of the nano-building blocks. In particular, this thesis will focus on metallic nanowires (NWs) as nano-building blocks. They will be made of noble metals: gold, platinum or palladium. The manufacture will be done by electro-chemically depositing those metals inside the nanopores of membranes (polycarbonate or anodized aluminum oxide) [14]. This technique should allow the precise control on the dimensions of the nanowires and on their composition. It will also be possible to use this technique to obtain multi-segmented NWs if needed [7], as one can see in Figure 1.2. Moreover this deposition inside a template could be useful

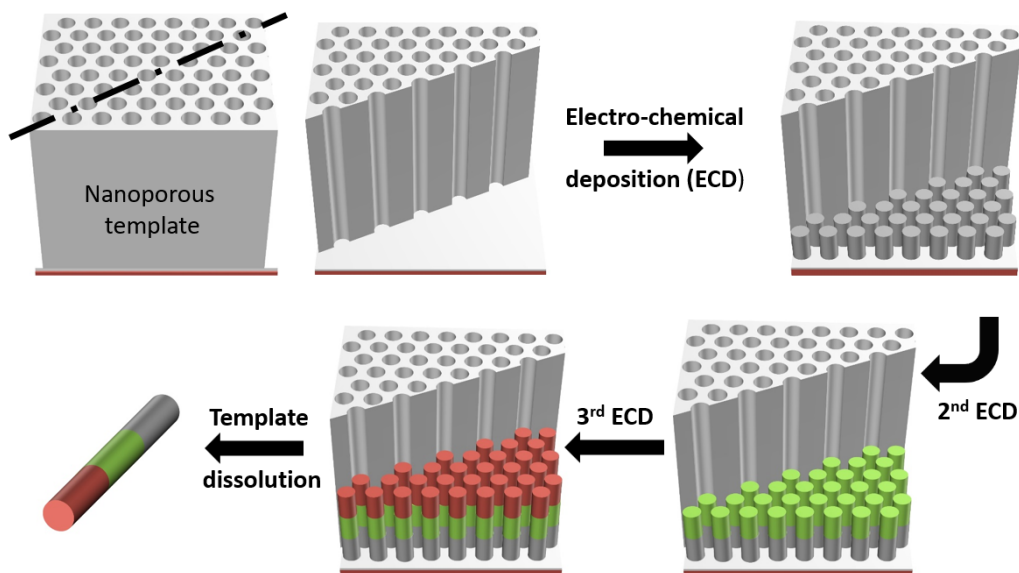


Figure 1.2: Schematic representation of the general strategy that will be adopted to obtain multi-segmented NWs by electro-chemical deposition (ECD).

for the second part of the thesis which is the functionalization of the NWs. Interactions between the NWs, hopefully leading to self-assembly, will be induced by chemical functions that will be grafted on the NWs. The functionalization can be homogeneous all around the NWs but to have a better control on the assembly and exploit at its maximum the anisotropic character of the NWs, it would be very exciting if this could be selectively done on localized part of the NWs. Especially one hopes to be able to functionalize the NW sides differently from the NW ends. This is where the electro-chemical deposition (ECD) within templates can be a supplementary advantage. As one can see in Figure 1.3, the template can mask for example the sides while one or both ends are functionalized. Besides, sacrificial deposited layers could also be used to mask specific parts of the NWs (the ends) while the other parts are being functionalized. The functionalization will be made thanks to thiols molecules that graft easily on noble metals (especially on gold) [15, 16] or thanks to layer-by-layer technique that allows successive deposition of polyelectrolytes, oppo-

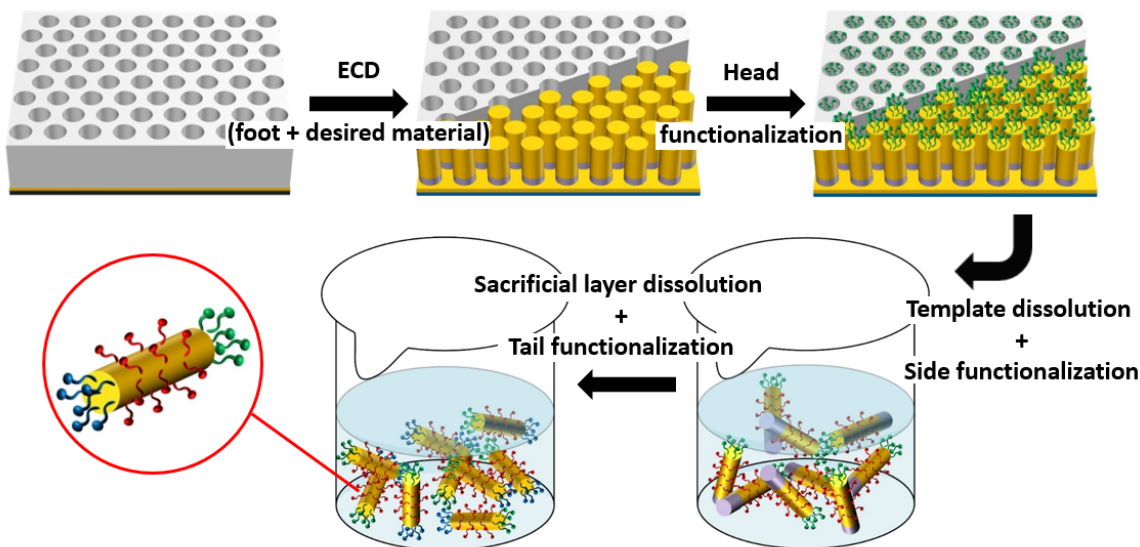


Figure 1.3: Schematic representation of the general strategy that will be adopted to obtain selectively multi-functionalized NWs. The 'foot' is a sacrificial layer deposited at the bottom of each NW

sitely charged [17]. Eventually self-assembly will be investigated by two techniques: drop-casting and fluid-fluid entrapment. The drop-casting simply consists in depositing of a droplet of NWs in suspension and let it evaporate [18] (Figure 1.4). During evaporation, the increasing concentration and some convection forces the NWs should be compacted allowing interactions between them to become predominant hence self-assembly. Fluid-fluid interface assembly consists in the

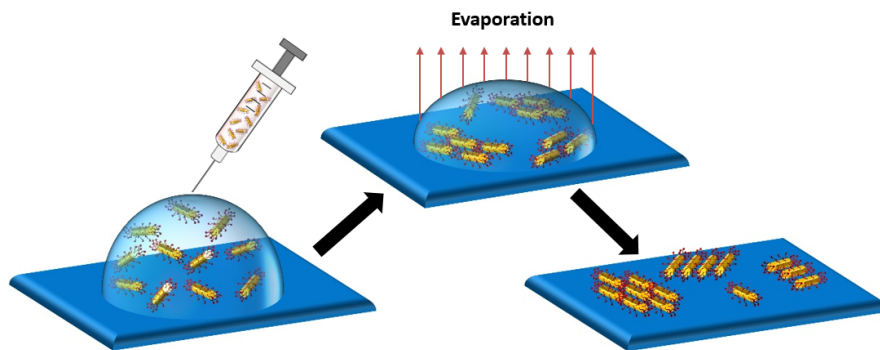


Figure 1.4: Schematic representation of the drop-casting technique.

confinement of the NWs at the flat interface between two fluids [19]. The schematic representation of this technique is presented in Figure 1.5. Once the NWs are at the interface they should naturally tend to shape as thin films. Moreover the compaction at the interface should enhance the interactions between them and therefore favor the assembly. Obviously since the objects that

are dealt with in this thesis are nanoscopic, every steps will have to be carefully checked thanks to characterization techniques and especially thanks to scanning electron microscopy (SEM) for the NWs body and the thin films, and epi-fluorescence microscopy for the functionalization grafting.

The present document will follow the steps of the thin films fabrication, beginning with the NWs manufacture, followed by their functionalization and finishing with the thin films self-assembled manufacture and characterization. Eventually conclusions on this study will be drawn and an additional chapter will precisely describe the materials and methods used to obtain the results. Before experimental and result chapters, the next chapter (Chapter 2) will be dedicated to literature review describing some of the important works that have already been published on this topic.

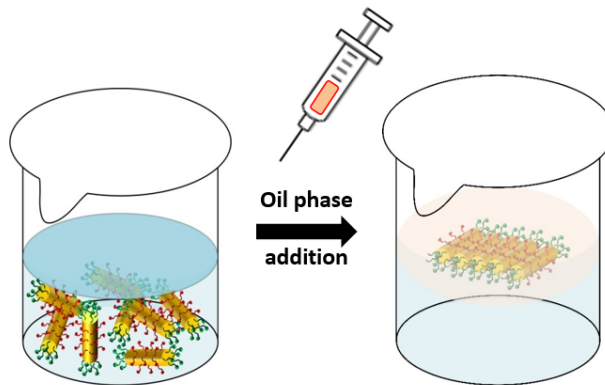


Figure 1.5: Schematic representation of the assembly at fluid-fluid interface.

State of the art

Self-assembled thin films are made of nano-objects. In researches, the most common of these objects are nanoparticles (NPs). Nano-objects have at least one submicrometer dimension while NPs are discrete objects with all of their dimensions in the nanometer range (1–100 nm). As a consequence of their nanoscopic scale, new and interesting properties can arise at the physico-chemical level, especially for metallic and semiconductive particles from the optical, magnetical, electrical or chemical point of views. NPs have thus attracted the interest of scientists and fastly a whole new domain was born. Initially only spherical (or quasi-spherical) particles were studied but rapidly anisotropic NPs gained in popularity thanks to their shape and size-dependent

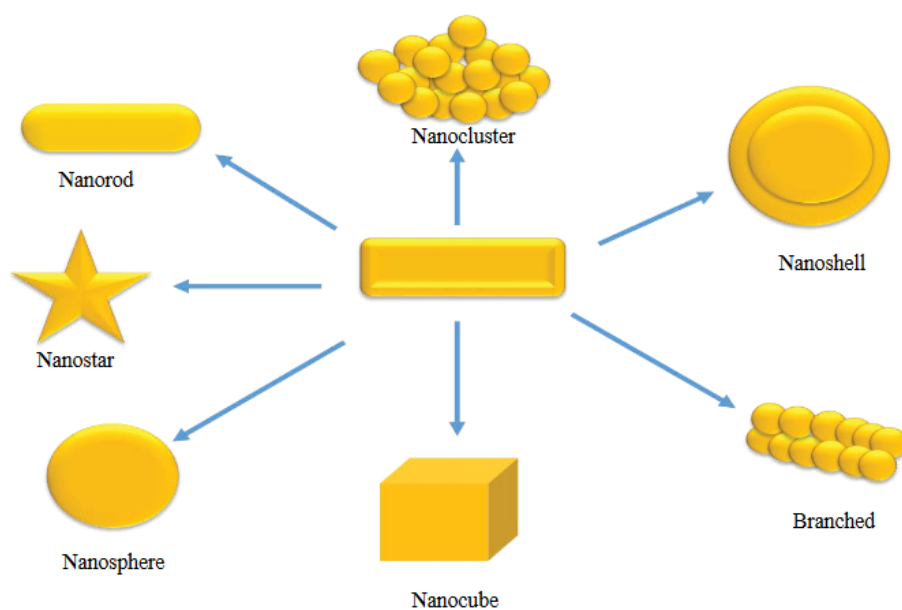


Figure 2.1: Various shapes of NPs. Reproduced from [20]

anisotropic properties [21]. Novel structures were able to be achieved and studied such as cylinders as in this thesis but also disks, tubes, cubes, prisms, nanoshells or even stars [20] and dumbbells [22] (Figure 2.1). Thanks to those studies and the better understanding of the physical nano-properties, NPs are beginning to be used in many applications: catalysis [23], nano-electronics [24], photonics [25] or biosensing [5]... To be properly used in those applications, these particles have to be functional at least to be able to "execute" one task. But rapidly scientists have thought about multifunctionalized NPs. If one could create NPs that bear several functionalities, they could perform many tasks/functions sequentially or even simultaneously. And indeed, the implementation of multifunctionalized particles has already been investigated, for example with Janus particles [26, 27]. This field is still in expansion and many other types of multifunctionalized NPs are under investigations. Although the goal of a particular application may be to create individual NPs, their assemblies can also be highly desirable to investigate the very essence of assembly in life and to study and try to understand the critical mechanisms behind the assembly of NPs in a ordered macro-structure, as well as the modulation of their physical properties arising when particles are brought together.

This chapter will try to give an overview of the studies that have mainly contributed to the development and progress of this latter particular topic: the manufacture of self-assembled nanostructures and especially thin films (2D). It will start with an overview of nanowires (NWs) and nanorods (NRs) manufacture techniques and in particular those made of noble metals, easily functionalizable. Following, the studies revealing how functionalization and multifunctionalization can be carry out will be reviewed. Finally the general systems of assembly and self-assembly of NPs existing in the literature will be described.

2.1 Synthesis of nanowires

One-dimensional (1D) nanomaterials (NMs) can be organic or inorganic (or hybrid) with properties specific to their composition and their aspect ratios. In addition to NWs, nanorods (NRs) and nanotubes are the two other shapes corresponding to 1D NMs. The distinction between NWs and NRs is not clear. By definition NWs should be nanocylinders long enough to be bendable while NRs have smaller dimensions and in particular smaller aspect ratios (length over diameter below 5) and also smaller diameters (about few to ten nanometers). But it seems also that the designation, NRs or NWs, also depends on the method to obtain the nano-objects. Indeed the 1D NMs obtained by wet chemistry seem to be generally called NRs whatever their size [28] while those obtained by template-assisted electrochemistry seem to be mainly called NWs [29].

In this project the nano-objects produced are on the edge between both definitions: they are not long enough to be bendable but will have rather large diameters and will be made by templated-assisted method. It has been chosen to call these nano-objects NWs but the NRs designation could be easily justified. Here one will only focus on conductive NWs or NRs, and especially on those made of noble metals, that possess very interesting properties, such as thermal and electrical conductivity but also surface plasmonic resonance. Their manufacture are now well studied and can be divided into four different main strategies and techniques: seed-mediated growth, template-assisted synthesis, vapor-liquid-solid (VLS) growth and synthesis by lithography. The three first strategies are bottom-up approaches consisting in the chemical reduction of metallic ions into NPs. The lithography synthesis is a top down approach that reduces larger piece of material to small pieces. Those strategies present some advantages and disadvantages, and the choice of the synthesis method should be based on the specific targeted applications. Self-assembly, for instance, requires high throughput, easily put in suspension NMs with highly similar morphologies, i.e. size and shape, to allow good organization.

2.1.1 Seed-mediated synthesis

The seed-mediated synthesis of 1D NM is a synthesis by wet-chemistry in solution. It is the most common method for noble metal NR manufacture, especially and mainly gold NRs. The process consists in the reduction of the targeted metal on small seed particles of about 3 nm made of that metal. The seeds in solution are capped with a surfactant that adsorbs on the surfaces, providing a shell (capping layer) that stabilizes the particles in solution and mediates their growth along a privileged axis leading to NRs formation. The premises of this technique were reported in the late 90's by Wang et al. [30] who achieved the manufacture of gold NRs using an electro-chemical cell in which the anode was made of gold, providing the gold source. In this method, the solution was a mixed surfactant system of cetyltrimethylammonium bromide (CTAB) and tetradodecylammonium bromide (TDTAB). A silver plate was also placed at the bottom of the cell. Its role is not clear but it has been theorized to produce silver ions in solution that may be part of a trans-metallic reaction [31]. Under the application of a constant current between the electrodes and constant sonication, one obtains single-crystalline gold NRs, grown along the (001) direction [32]. Although the complete growth mechanism is still unclear, it is believed that growth may have occurred on the surface of the electrode, with sonication responsible for freeing the rods into the suspension [1].

Based on these first results, the real seed-mediated synthesis has been developed by Murphy and coworkers in 2001 [33]. The source of gold was replaced by chloroauric acid and the electro-

chemical reduction by chemical reduction using ascorbic acid and silver nitrate. Only CTAB was used as surfactant and the addition of the seed particles allowed the complete reduction of metallic gold despite the high CTAB concentration and the low pH (~ 2.5). It lead to the gradual change in shape of the seeds from quasi-spherical to rod-like crystal. At the beginning the aspect ratio was relatively low (~ 1.5) and a large amount of spheroidal particles was present ($\sim 80\%$) but separation by centrifugation permitted to obtain correct results (Figure 2.2 (a)). Shortly after, clear improvements were made by El-Sayed et al. who used CTAB-capped seeds which gave rise to high yield of NR products [34]. Based on this technique, many other variation of the

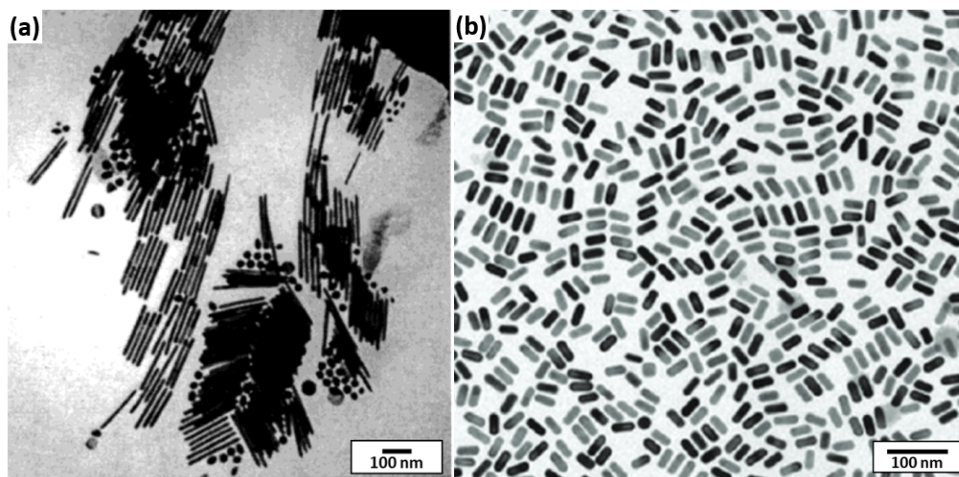


Figure 2.2: TEM images of gold NRs obtained, (a) by early seed-mediated synthesis, and (b) by improved seed-mediated synthesis thanks to aromatic additives. Reproduced from [33] and [35], respectively.

”standard” seed-mediated synthesis have been explored leading to many kind of single crystalline gold NRs (and even NWs) ranging from diameter of about tens of nanometers and aspect ratio between 1.5 and 10 [1]. The aspect ratio and the quality of the NRs greatly depends on the surfactants and the reducing agent. Therefore, although CTAB is a very common surfactant, many other molecules have been investigated. As example, high quality gold NRs were obtained using aromatic additives in the growth solution (Figure 2.2 (b)).

Besides, to increase the throughput, researches to manage one-pot process have been actively conducted. Indeed, in the ”standard” seed-mediated synthesis, the seeds have to be prepared (and capped if desired) prior to the growth in a different solution than the one where growth takes place. The so-called ”seedless” methods were thus developed, where the seeds are created *in situ* thanks to the addition of sodium borohydride [36]. However, the two-step method is often preferred because it allows to chose both the seed structure and the growth conditions since both processes occur separately [4], leading to better reproducibility.

The complete growth mechanism is still under investigation but it seems that it results from a mix of two phenomena that reduces the surface energy of certain facets of the NR crystals. The first one is the stronger binding affinity of CTAB on the side facets which have a higher surface energy due to larger interatomic distances in comparison with the tip side facets. The second one is the presence of metallic silver coating on specific facets of the rods. Ag ions could normally not be reduced by ascorbic acid in those conditions (in presence of CTAB and at low pH) but it can happen onto the gold surface at lower potential than expected: under-potential deposition (UPD). Growth along the side direction would be slowed as it would require re-oxidation of silver, leading thus to the unexpected growth along the more thermodynamically stable direction. It was demonstrated that up to several layers of metallic silver could be present on the surface of NRs [11]. One must add that even the exact crystal structure of those NRs during their growth is still under debate (see Figure 2.3 (a)). The combination of those two "surfactant" effects favored more complex growth mechanisms with different oxidation and reduction step as one can see in Figure 2.3 (b).

In addition to the "standard" seed-mediated synthesis, a widely spread variation, with the major difference being the absence of silver ions in the solution, is the so-called "three-step" process. It was also developed by Murphy et al. [33]. Three growth solutions are prepared (with adjusted concentration in gold, CTAB and ascorbic acid) and a series of sequential transfers of seeds, coming from the first growth solution, are carried out from the first to the second and from the second to the final [1]. It results in pentahedrally-twinned (and not single crystalline) gold NRs with diameter of about ~ 20 nm and high aspect ratio (from 20) with length that can reach the micrometer scale. The anisotropic growth is explained by the "zipping" process: CTAB molecules adopt a bilayer structure in aqueous media, where one layer interacts with the gold NP surface and the other layer extends toward the aqueous media, therefore stabilizing the bilayer via Van der Waals interactions. The surfactant specifically blocks the side crystal facets, therefore enabling the growth in a single direction, as depicted in Figure 2.4.

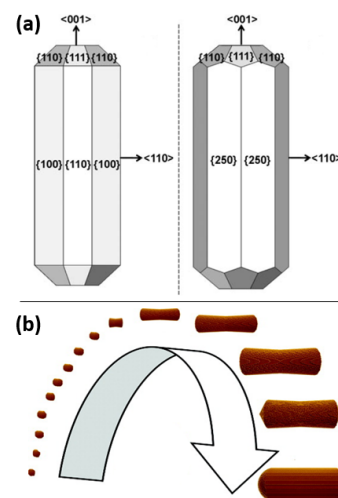


Figure 2.3: (a) Scheme of two possible crystallographic structures for gold NRs obtained by seed-mediated synthesis. (b) Schematic theoretical growth of gold NR due to CTAB surfactant and Ag UPD. Reproduced from [37] and [38], respectively.

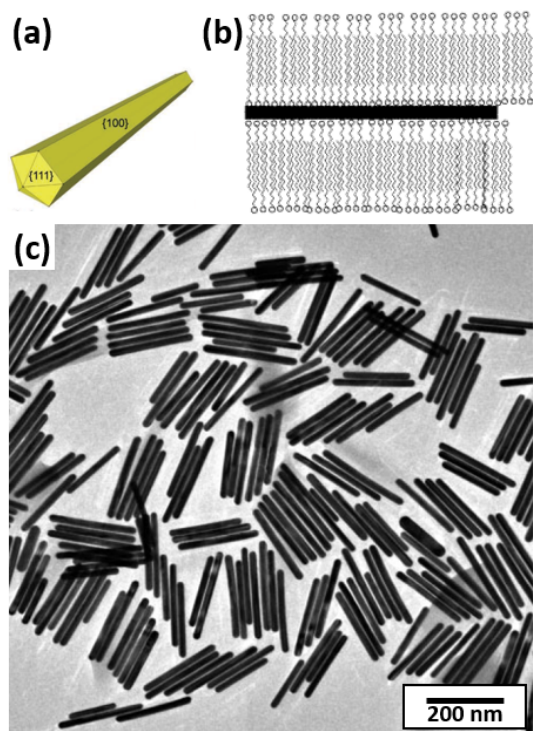


Figure 2.4: (a) Illustration of pentahedrally-twinned NR. Reproduced from [1]. (b) Schematic of surfactant "zipping" process directing anisotropic growth. Adapted from [39]. (c) TEM image of gold NRs obtained by the "three-step" seed-mediated method. Reproduced from [28].

NRs. The diameter and aspect ratio can be selected by finely choosing the reducing agent, the surfactants and the seeds, and carefully tuning their molarity in the growth solution. The diameter can be up to 20 nm and the length up to the micrometer. Nevertheless larger diameters can not be achieved and obtaining every diameter-length couple NRs requires often very different experimental parameters. Moreover the products of the seed-mediated synthesis are always coated with relatively high binding strength surfactants (most of the time CTAB) which can represent a major problem if one wants to obtain NRs bearing other functionalities.

Based on these techniques, several adaptation were developed to manufacture other metal NRs even if for now on it remains very exotic due to the larger attractiveness of gold NPs. The synthesis of other metal NRs with variation of the seed-mediated method is challenging due to the difficulties to manufacture new seeds and to adapt the surfactants. Noble metals were privileged because of their similar characteristics with gold. The manufacture of silver [40, 41] and palladium NRs [42, 43] was reported with variable success and reproducibility (Figure 2.5). Platinum NRs were not achieved by this method because Pt seeds only grow in complex shapes like tetrapods or octopods (Figure 2.6) [44]. Many core-shell NRs were also synthesized by seed-mediated-like approach such as Au@Pd core/shell nanobar [45] and Au@Ag core/shell nanorods [46].

To summarize, the seed-mediated synthesis allows the high volume manufacture of gold NRs, mainly and, in a lesser extent, of silver, palladium NRs and, Au@Ag and Au@Pd core/shell

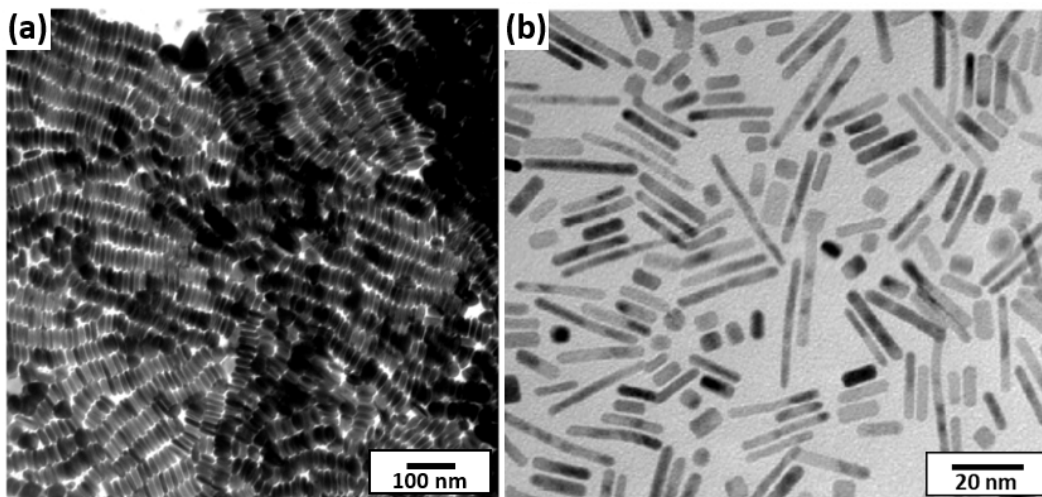


Figure 2.5: TEM images of (a) Ag NRs, and (b) Pd NRs (and nanobars). Reproduced from [40] and [42] respectively.

2.1.2 Template-assisted synthesis

The template-assisted synthesis consists in the deposition of a material inside a template giving the shape to the fabricated object. To obtain 1D nanostructures the template has to be porous with linear (cylindrical) pores. To obtain semi-conductors NWs, the sol-gel process can be applied. The driving force for the precursors to enter the pores is the capillary forces. But most of the time, template-assisted synthesis is performed via electro-chemical deposition (ECD) [47]. This method will be further described more deeply since it is the one used in this thesis.

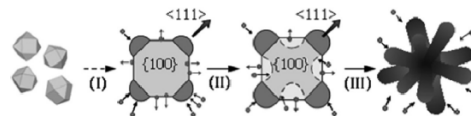


Figure 2.6: Schematic illustration of the growth mechanism for platinum nanocrystals: nucleation into cuboctahedral nuclei, growth into single-crystalline quasi-octapods. Then formation of etched octapods and finally transformation into porous nanocrystals Reproduced from [44].

There are two categories of templates: hard and soft templates. Whereas soft templates can be used for NW formation, hard templates are by far more common.

Soft templates are mainly surfactant in solution forming 1D-like shaped micelles allowing NR or NW reduction/deposition. As an example, Song et al. [48] used a soft template formed by CTAB in a two-phase water-chloroform system and borohydride as reducing agent, to form a platinum NW network. The scheme of the method and the SEM images of the resulting network are depicted in Figure 2.7.

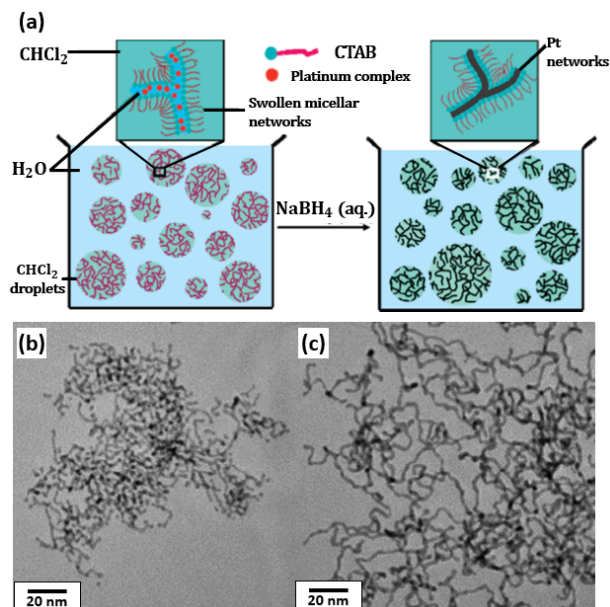


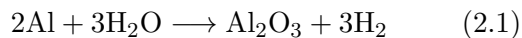
Figure 2.7: (a) Illustration of the soft template with the wormlike micellar network formed inside droplets of chloroform, on the left, and the developed platinum NW networks formed by reduction of Pt complexes within the template, on the right. (b) and (c) TEM images of the platinum nanostructures obtained using 1 mM (b) and 20 mM (c) Pt complexes in 10 mL of chloroform containing 40 mM CTAB. Reproduced from [48]

Hard templates are solid (micro- or) nanoporous material. They can be made of many different materials, such as zeolites, glass, nanoporous oxides, mica, and block copolymer films. However, ion-track-etched membranes and anodic aluminum oxide (AAO) templates are the most commonly used materials [7].

2.1.2.1 Anodic aluminum oxide template

AAO templates are nanoporous membranes that are obtained by the anodization of aluminum. The anodization process consists in the oxidation of an aluminum layer which spontaneously leads to the formation of nanoporous alumina (Al_2O_3). The aluminum layer must have been deposited on a conductive layer (most often Pt or Au) which will play the role of the anode. Between these two layers there is another thin layer (5 nm) needed to have a good adherence between both layer (most of the time titanium or chromium). The cathode is a cylinder or disk of pure aluminium dipped in an electrolyte solution poured in an electrolytic cell. The scheme of the setup is shown in Figure 2.8. Under an applied potential between both electrodes, the electrolyte solution must be able to both react with Al to form Al_2O_3 and dissolve the already formed oxide in order to obtain a

nanoporous Al_2O_3 template. Very few acidic electrolytes were reported to produce that template. Three were mainly reported: sulfuric, oxalic and phosphoric acids [49]. When the potential between the electrodes is activated several reactions happen at the cathode and at the anode. The overall reaction is:



At the beginning, a first layer of alumina is formed. Then pores nucleate on the places where the layer is thinner leading to an electric field enhancement (see Figure 2.9). The oxide is dissolved with an accelerated rate in the region where the field is higher. Due to the high electric field, the surface oxygen atoms of the Al_2O_3 prefer to be surrounded by water molecules rather than Al (the solvation rate of the surface oxygen atoms is higher). Afterwards, two reactions will compete: the oxidation of aluminum in alumina and the localized dissolution of the alumina where the electric

field is enhanced. The reaction finally reaches an equilibrium value corresponding to a balance between both reactions. In addition to these self-catalytic effect inducing the pore formation, there is a self-ordering of the pores tending to a "honeycomb" structure (Figure 2.10(b)). It is due to the volume expansion of the layer during the oxidation. Indeed the atomic density of alumina is larger than the one of aluminum. So there must be a volume expansion and as the bottom of the pores are dedicated to the dissolution of the oxide, the expansion took place on the walls toward the upper direction since the lateral expansion is blocked by the other pores (see Figure 2.10(d)). The relaxation of that stress favors the self-ordering. One can also note the important role of the adherence layer in this step which has to resist to that intense internal stress. For longer anodization (up to 30 hours) another aspect become predominant: the pore tip repulsion. Each pore tip can be seen as a charged tip, due to the presence of ions at the bottom of the pores, generating an electric field that repulses the neighboring tips (see Figure 2.10 (c)). That gives an additional self-ordering effect leading to the "honeycomb" structure. It has to be mentioned that the exact growth concept is more complicated and still under debate for some mechanisms. More details on the fabrication of AAO are presented in the review of Lee and Park [51].

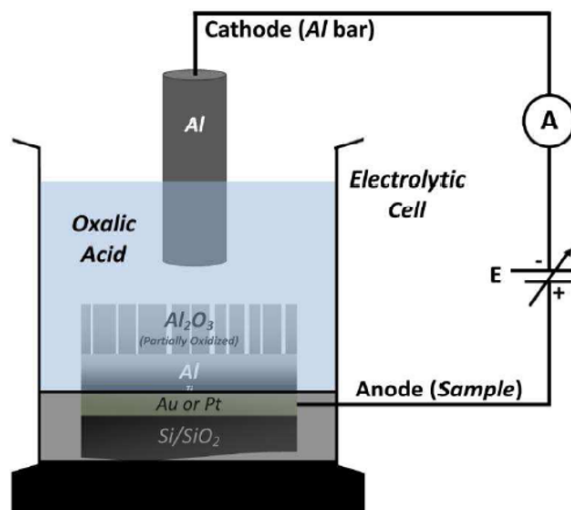


Figure 2.8: Scheme of the anodization setup performed in oxalic acid. The ultra-thin layer of Ti (or Cr) is not represented. Reproduced from [49]

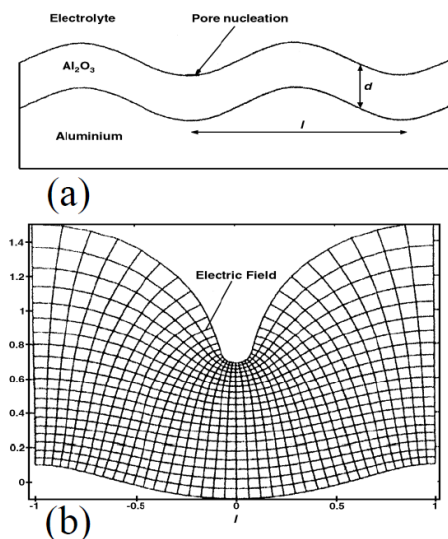


Figure 2.9: (a) Schematic representation of the pore nucleation. (b) Numerical simulation of the electrical field distribution during the pores formation. Reproduced from [50].

an additional isotropic etching step is added to slowly dissolve alumina and to suppress any remaining barrier layer preventing the pores to be in contact with the conductive electrode.

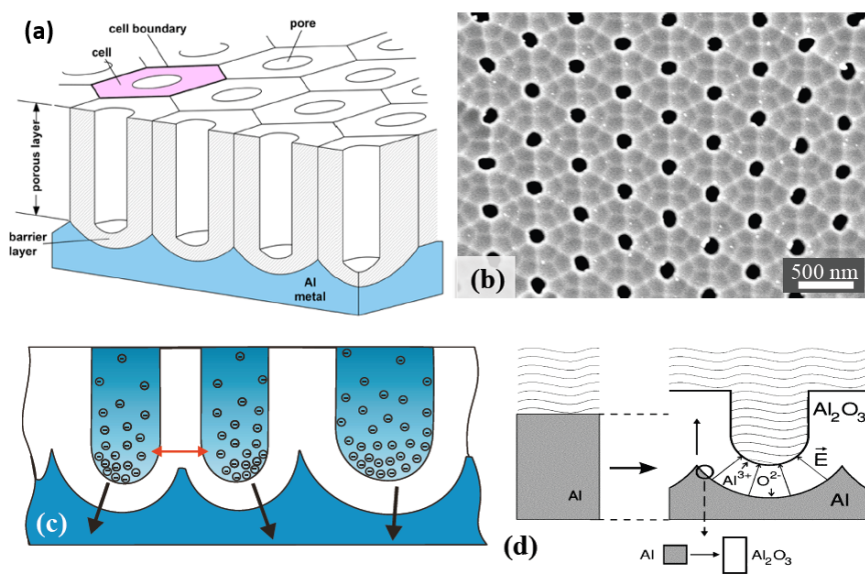


Figure 2.10: (a) Schematic representation of a supported AAO template on aluminum. (b) Top-view SEM image of an highly-ordered AAO template. (c) Schematic representation of the tips coulombic repulsion. (d) Illustration of the volume expansion during the Al_2O_3 formation. This expansion can only take place vertically. Reproduced (a) from [51], (b) and (c) from [49] and (d) from [52]

The AAO membranes that can be obtained with these techniques can be highly ordered nanoporous membranes with pores diameter, down to 5 nm, and with a really high pore density, up to 10^{11} pores/cm² [51]. Due to this high pore density, the pore diameter is usually limited to 250 nm. The tuning of the pore diameter is done during the isotropical etching of the alumina after the anodization. The self-supported membranes can be as thick as 100 μ m but are very brittle while supported template are usually limited to 5 μ m because of the aluminum sputtering step which can be difficult to control at higher thickness [49].

2.1.2.2 Ions track-etched membranes

Ion track-etched membranes are mainly used as filters and are usually prepared from polycarbonate (PC), polyester or polyimide thin films [54]. The ion track-etching consists in the irradiation of a polymer film with fragments from the fission of heavy nuclei such as californium or uranium or with energetic heavy ions from particle accelerators. In both cases it leads to the formation of linear damaged tracks across the irradiated polymer layer or film [55]. Thanks to the advances in particle accelerators, most of the time, the second method is preferred as it has the big advantage to be radioactive free. The damage tracks through the membranes are then chemically etched. They are revealed into pores using a particular wet chemical etching (for example, NaOH or a mix of CrO₂ and H₂SO₄) depending on the polymer. The combination of the process of membrane irradiation with the subsequent etching leads to nanoporous polymer membranes (see Figure 2.11) with versatile pore diameter, pore density and layer thickness. Diameters can range from 10 nm up to 30 μ m, with densities as high as 10^{11} pores/cm² for very small diameters. For diameters around hundred of nanometers, the highest density (without formation of "meta" pores made of several pores) is about 10^9 pores/cm². It is also possible to obtain very low density template (1000 pores/cm²). The thickness of such templates can go up to hundreds of micrometers [1, 56]. The most common ion track-etched polymer membranes used as hard template for NWs synthesis are PC membranes.

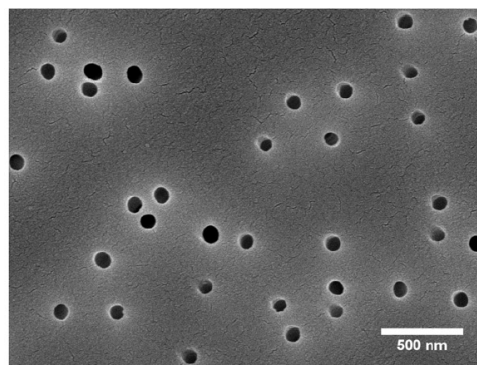


Figure 2.11: Top surface SEM image of a nanoporous track-etched PC membrane. Reproduced from [53].

2.1.2.3 Electro-chemical deposition within hard template

The electro-chemical deposition (ECD) of metals consists in the injection of an electrical current to reduce the ions of a diluted specific material from a certain electrolytic solution in order to crystallize them onto a conductive layer. As for the anodization setup, a current is generated by imposing a difference of potential between the sample, working as a cathode (or working electrode) and a Pt foil immersed in the solution, the anode (or counter electrode). The contact with the sample is made thanks to a thin metallic layer attached to the bottom part of the porous membrane. For ion track-etched and AAO self-supported membranes it is made by metallization of one side of the membrane while for supported AAO template it is the bottom electrode used for the anodization. In addition to these two "classical" electrodes a third one, composed of Ag/AgCl, is immersed in the electrolyte solution. A potentiostat controls the potential of the working electrode by comparing it with the reference electrode and it adjusts further the voltage level by injecting a current into the cell through the counter electrode. An example of setup is shown in Figure 2.12.

The NWs obtained have a polycrystalline structure [57]. Their diameter is dictated by the pore size of the template, while their length is directly related to the amount of charge passed through the system according to Faraday's Law. However, it is sometimes difficult to control the exact length of the wires with ECD within template. Indeed, deposition can be uneven and lead to a 30 % variance in length [1]. To ensure an ideal growth of the NWs with low length dispersity and with almost flat ends, several parameters have to be finely tuned such as the electrolytic composition, the potential and the temperature [3].

ECD within hard template was introduced by Martin and co-workers in 1994 [14, 54]. Since then, numerous types of NWs have been synthesized [7]: many metals (Au, Ag, Sn, Cu, Ni, Co, Pt, Pd, Pb, Fe, Zn, Bi), several metallic alloys (NiFe, CoFe, CoPt) [29], some semiconductors with small adaptations to the process (CdSe, CuSe, ZnO) [58] and even semi-conducting polymers (polypyrrole (PPy), polyaniline, and poly(3-methylthiophene) (P3MT)) [59]. In the case of the polymers, there are of course no crystallization of ions within the pores: electro-chemical polymerization occurs. The polymerization is induced by the application of the electro-

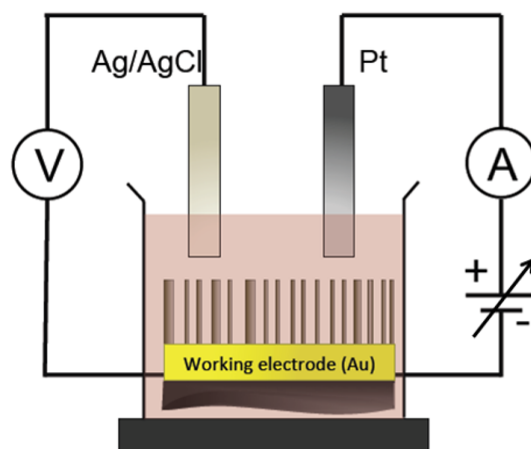


Figure 2.12: Schematic diagram of hard template assisted synthesis of NWs. Reproduced from [49].

chemical potential. Electro-polymerization being an oxidation process, the working electrode in that case is the anode and the counter electrode the cathode. Moreover, ECD within template allows easily the formation of multi-segmented NWs with several layers of different materials perpendicular to the axis of the NW. A layer can be produced with a specific electrolytic bath containing the targeted material and stopped at the desired length. Then the bath is switched to another electrolytic bath containing the second material to produce the second layer, and so on. One can see several examples of multi-segmented NWs in Figure 2.13 (a-c). A variant based on pulsed ECD has been developed specifically for the preparation of multi-segmented metal nanowires with precise interfaces [7]. In this technique, a single electrolytic bath, containing multiple metal ions, is used. For two component metals, the electrochemical potential is alternately pulsed for fixed durations between values above and below the reduction potential of the less noble component. At less negative potential, the more noble component is exclusively deposited. At more negative potential, the less noble component is deposited but also the more noble component, simultaneously: there is co-deposition. However, by selecting unfavorable diffusion conditions, mainly by keeping the more noble component concentration very low and keeping the less noble component concentration much higher, co-deposition will happen with only a small amount of the more noble component inside the less noble component layer [60].

The pulsed ECD is also used to improve the length uniformity of the NWs, the morphology (grains) or the tip-end morphology of the NWs [49]. A sequence of two pulses with different voltages is used during different times. During a short pulse, the ions in the solution are dissociated and possibly deposited. This pulse is followed by a pause that is usually a longer pulse with a smaller voltage. This pause allows the diffusion of the ions inside the pores of the template and also allows a partial relaxation of the system. One can add, or substitute the long pulse with, a short pulse with positive potential allowing very few oxidation of the forming NWs, so improving the flatness of the NW ends by etching the imperfections between each depositing pulses. Theoretically, pulsed ECD for single material NWs can bring many improvements to standard ECD but there are several difficulties to achieve them. Firstly, the parameters to be optimized simultaneously are more numerous. Secondly, the transitory nature of the pulses makes the predictions of the ECD behavior hazardous [63]. That is why the pulsed ECD is still not well spread for single material NW synthesis.

ECD within hard template produces NWs that are "attached" to the conductive layer and trapped inside the template. It is often required to detach the NWs and/or to remove the template, to collect the NWs in suspension or to have free-standing NW brushes (Figure 2.13 (d)). The dissolution of AAO can be done using NaOH that will completely and rapidly etch alumina. It can be so fast that, to avoid too harsh constraints on the deposited material, it

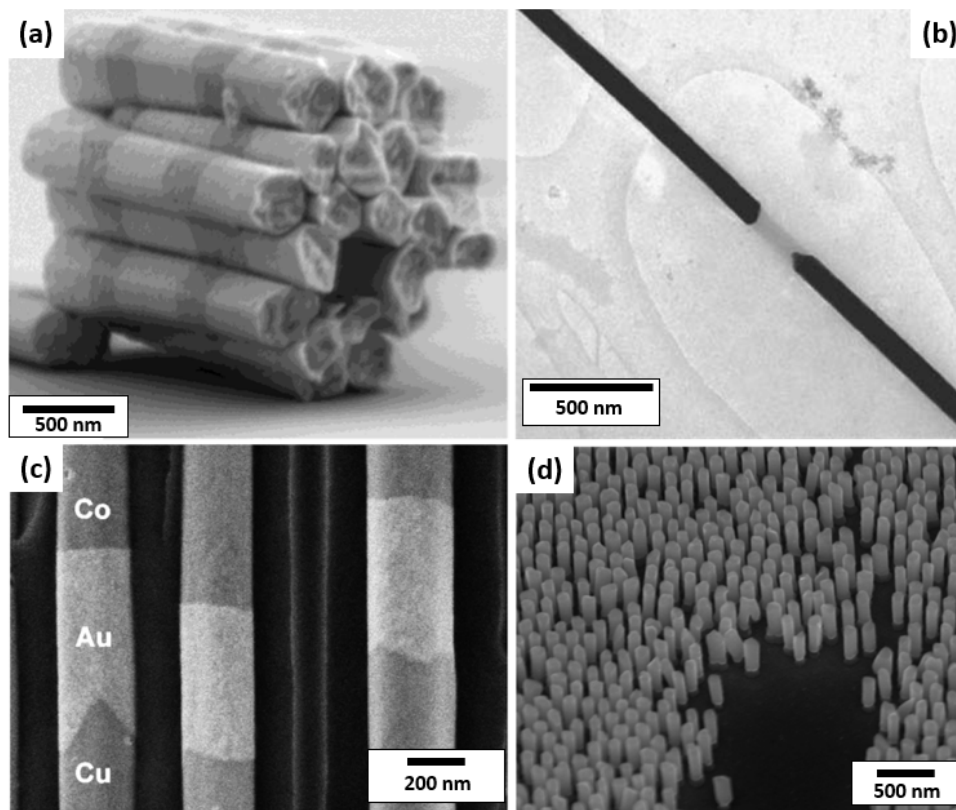


Figure 2.13: (a) SEM image of multi-segmented NWs composed of Au and Ni (b) TEM image of Au-Ppy-Au nanowire. (c) SEM image of cross-sectional view of multi-segmented NWs showing Cu- Au-Co sequence. (d) Free standing Ni NWs brush. (a) Reproduced from [15], (b) from [61] and (c) from [62].

is recommended to dissolve the template step by step in several NaOH baths, beginning by low NaOH concentration and finishing with high concentration to eliminate all the residues. Nanoporous PC membrane can be easily and softly dissolve in dichloromethane. To recover the NWs in suspension, the metallic film can be simply etched for self-supported membrane (preferably prior PC dissolution). For supported AAO membrane, the feet of NWs can be broken by ultrasonication or, alternatively, a sacrificial layer (foot) of a different material deposited prior the targeted material may be etched. Therefore it is extremely important to think about how NWs will be used before the deposition process.

2.1.3 Volume-Liquid-Solid growth

The volume-liquid-solid (VLS) growth consists in 1D nanostructures growth by chemical vapor deposition catalyzed by liquid alloy droplets. The direct adsorption of a gas phase onto a solid

surface in order to grow a new solid phase is generally very slow. To obtain a quicker result, the VLS method introduces liquid alloy seeds that will allow rapid vapor adsorption to supersaturation levels, and from which crystal growth can then occur at the liquid–solid interface. This method is privileged to manufacture single-crystalline semi-conductor NWs. The process can be divided into three steps: the alloying, the nucleation and the growth. Figure 2.14 shows schematics and TEM images of a NW growth.

Alloying A thin layer (1-10 nm) of gold is deposited on a substrate. The sample is placed in an environment saturated with the desired material vapor. The temperature is increased until the eutectic point of the Au–material phase diagram is reached. At this point droplets of liquid alloy containing gold and some of the material are formed. The size of those droplets depends on several parameters and especially on the thickness of the Au film.

Nucleation Once the concentration of the targeted material inside the liquid alloy exceeds a certain value it enters in a biphasic part of the phase diagram. There is coexistence of the liquid alloy phase with a solid phase composed of the targeted material implying the precipitation of this material at the bottom of the liquid droplets onto the substrate. The nucleation occurs at a higher concentration of the targeted material than what should thermodynamically happen, indicating that nucleation indeed occurs in a supersaturated liquid alloy [65].

Growth Once the nanocrystal nucleates at the liquid/solid interface, further condensation/dissolution of the targeted material vapor into the liquid alloy will increase the amount of material precipitation from it. If the substrate has been carefully chosen, nanostructure will epitaxially grow in the vertical direction. The droplet will go up with the NW growth and the existing interface will then be pushed forward allowing the process to continue until the decrease of temperature inducing the liquid solidification on top of the NW, hence stopping its growth.

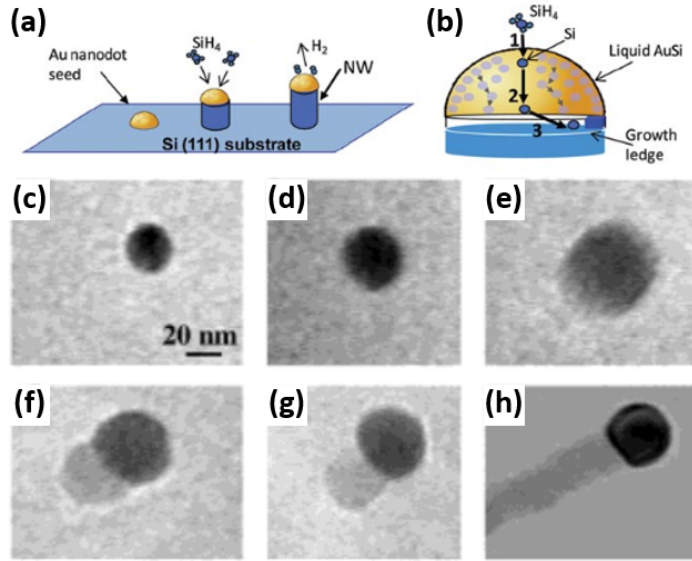


Figure 2.14: (a) Schematic of VLS Si NW growth. (b) Enlarged view of the mechanism near and inside the liquid alloy droplet. Reproduced from [64]. (c-h) TEM images of VLS Ge NW growth. (c) to (e) depicts the alloying process: Au solid seed turns into the liquid alloy, hence the color change. (f) to (h) depicts Ge axial growth "beneath" the liquid alloy droplet. Reproduced from [65]

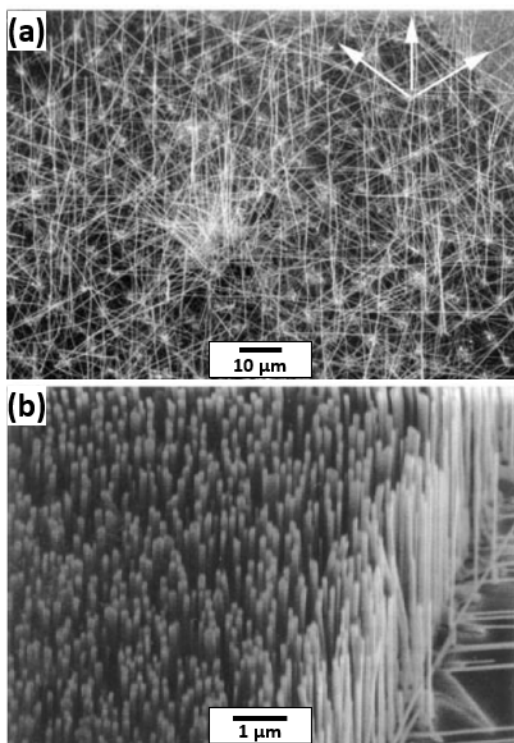


Figure 2.15: (a) Si whiskers grown on (100) substrate. The three preferential orientations are indicated by arrows. (b) Array of ZnO NWs epitaxially grown on *a*-plane sapphire substrate. Reproduced from [66] and [67] respectively.

In general micrometric NWs are easily obtained.

The VLS process was introduced by Wagner et al. in the 1960s to obtain single-crystalline whiskers [68] (usually silicon) with different orientations as the epitaxial growth conditions were not met (see Figure 2.15(a)). This process has been improved, especially thanks to P. Yang and his coworkers [65, 66, 67]. One can now control the NWs orientation, their morphology (diameter and length) and their position on the substrate. The diameter of the NWs directly depends on the size of the liquid alloy droplet that can be carefully chosen by dispersing Au clusters on the substrate surface instead of depositing a thin film. However, at very small droplet diameters, the chemical potential inside the droplet increases according to the Gibbs-Thomson effect, decreasing the overall growth rate, leading to a minimum NWs diameter of ~ 5 nm [64].

The diameter can go up to hundreds of nanometers. Concerning the length, the only limitation comes mainly from the collapse of the NWs at too high aspect ratio and especially at small diameters. In general micrometric NWs are easily obtained. The place where the NWs grow can also be selected

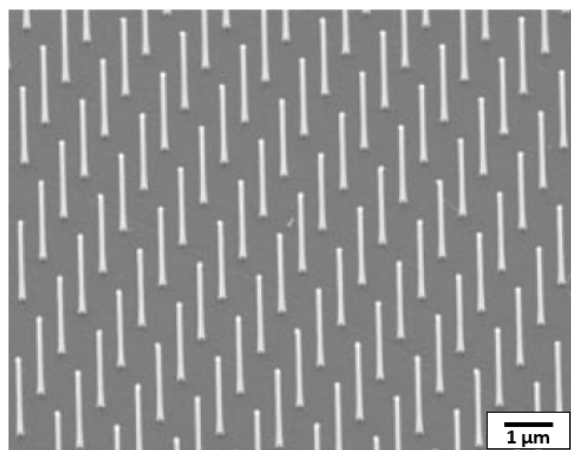


Figure 2.16: Ge NWs array grown by VLS with Au seeds obtained via electron beam lithography of a 20 nm Au film. Reproduced from [64].

by simple lift-off lithography process. The Au thin film is etched except at specific places that will allow nucleation (see Figure 2.16).

VLS method has been reported to enable synthesis of a wide variety of semiconductor NWs including Si, Ge, SiC, B, GaAs, GaP, InP, InAs, and ZnO [64]. Often physical methods (laser ablation, arc discharge, thermal evaporation) had to be used to generate the vapor species required for the NW growth [65]. Some multisegmented semiconductor NWs have also been synthesized such as Si/Ge or GaAs/GaP [69]. Those NWs are attached to their substrate and can only be roughly recovered by ultrasonication.

2.1.4 Synthesis by lithography

Lithography is one of the most popular top-down techniques for nanofabrication. Generally it is done thanks to a resist material, such as poly(methylmethacrylate) (PMMA), that acts like photographic film to produce a pattern after exposure and development using a patterned mask. This technique is not really suitable for NWs because of its limited resolution linked to the wavelength of visible light. However, patterns with higher resolution can be achieved with electron-beam lithography, which does not involve mask, the exposure being directly made by the electron-beam. To produce (vertical) NWs, the pattern will consist of circles or holes on top of a substrate of the desired material.

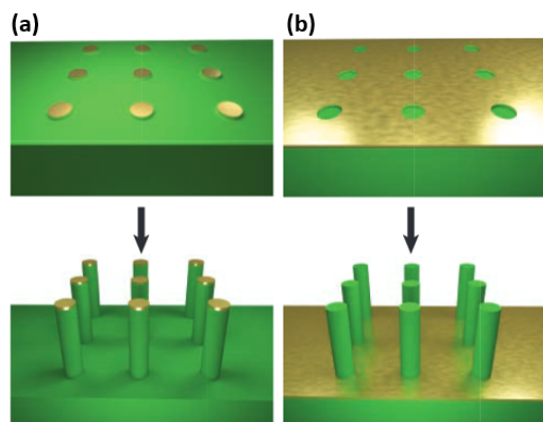


Figure 2.17: (a) Lithographic patterning of a metallic mask followed by anisotropic etching, such as DRIE. (b) Lithographic patterning of exposed regions followed by anisotropic metal-assisted chemical etching. Reproduced from [70].

desired material.

This pattern will then be used as a mask to etch the wafer outside the protected areas to finally obtain NWs (Figure 2.17(a)). Depending on the process, the resist may be used directly as the etching mask or may serve as template for the deposition of a more stable mask material, such as gold. Conventional chemical etchants, like potassium hydroxide, or electro-chemical etchants can be used but often produce tapered rather than cylindrical NWs due to the isotropic etching under the mask [70]. This problem can be minimized by the use of anisotropic etchants. Most of the time the wet chemical etchant is replaced with a highly anisotropic deep reactive ion etching (DRIE), which can produce NWs that are tens of microns in length. Briefly, DRIE alter-

rates cycles of etching in a flow of SF_6 and passivation in a flow of C_4F_8 . The first step etches the unprotected areas and the second step deposits fluorinated polymer to protect the side walls of the resulting etched structures [71].

Alternatively, the pattern can be inverted, with metal covering all the areas except the areas corresponding to the NWs to be grown. Then anisotropic metal-assisted etching is used which is a special process that etch only the area covered by the metal (Figure 2.17(b)). Typically, Si substrate partly covered by a noble metal is subjected to an etchant composed of HF and an oxidative agent. As a result, Si beneath the noble metal is etched much faster than the Si without noble metal coverage. So the noble metal "sinks" gradually into the Si substrate, generating the NWs [72].

Other methods have been developed to obtain differently templates (or masks) to improve the throughput and cost of the lithography process. Nanosphere lithography, for example, consists in the use of polystyrene nanospheres as mask for the deposition of a metal or other masking material. They are usually self-assembled on the wafer in closed-packed lattice and are removed after deposition [71]. An example of nanosphere lithography combined with anisotropic metal-assisted etching is shown in Figure 2.18. Nanoscale patterns can also be produced by nano-imprint lithography (NIL). A high resolution master pattern is produced by electron-beam lithography. This master is then pressed into the resist material to transfer the pattern. In practice NWs synthesis by lithography is almost exclusively limited to silicon NW manufacture although few others semiconductors NWs have been reported: Si/Ge, GaAs, GaN, and SiC.

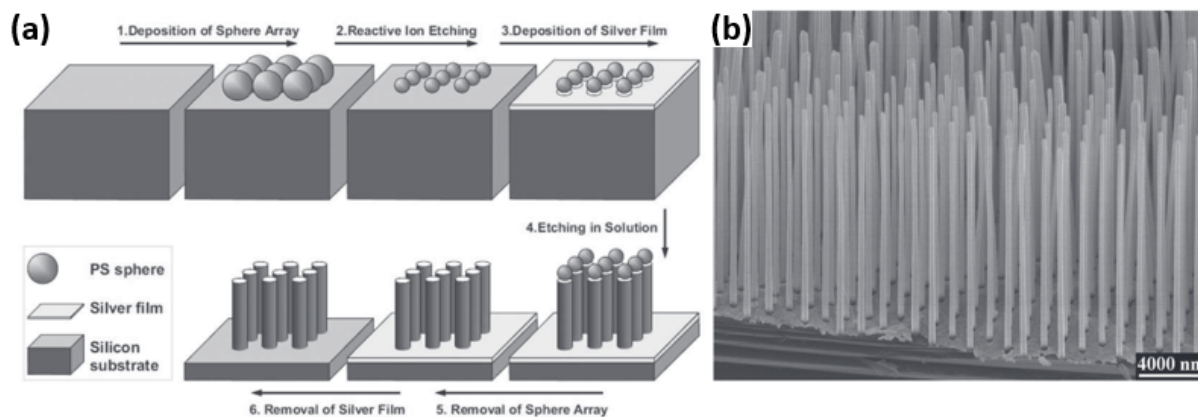


Figure 2.18: (a) Scheme showing the processes in a method combining nanosphere lithography and metal-assisted chemical etching. The sphere monolayer is first etched to obtain smaller NWs diameter and more spaced. (b) SEM image of the resulting Si NWs. Reproduced from [73].

2.2 Functionalization of inorganic nanoparticles

The functionalization of a NP consists in the grafting on its surface of molecules bearing particular chemical functional moieties. Functionalization of NPs can then enable interactions between them which can possibly lead to self-assembly. Functionalization can be done by several chemical or physico-chemical ways using covalent bonds or weaker bonds. The techniques usually adopted to functionalize NPs use self-assembled monolayers or layer-by-layer deposition. Moreover, NPs can be multifunctionalized by functionalizing them with different functions and, as described in the introduction, there is great interest in the localized functionalization of specific parts of the NPs. It could allow different interactions with the NPs that can take advantage of the anisotropy of the functionalization and/or of the NPs.

2.2.1 Self-assembled monolayer

Self-assembled monolayers (SAMs) are organic molecules that orderly assemble through spontaneous adsorption onto surfaces. The molecules are first grafted by chemisorption of their head group and afterwards, organization occurs thanks to interactions between the tail of each molecule. The most common head groups are thiols and silanes but SAMs can also form with carboxylic acids or amines. Of course the choice of the head groups will depend on the nature of the substrate, of the NPs. SAMs are very commonly used to functionalize NPs. SAM functionalization is often even performed during NPs manufacture to control their size and/or to allow their stabilization.

2.2.1.1 Thiols

Thiols are known to react with metallic atoms through their mercapto (-SH) group and form on surfaces very closely packed SAMs. Thiol SAMs were mainly studied on gold surfaces but their occurrence have also been widely reported on other noble metals, such as platinum, palladium and silver, as well as on copper and more anecdotally on mercury and some semi-conductors (GaAs, CdSe, CdTe) [15, 16, 74].

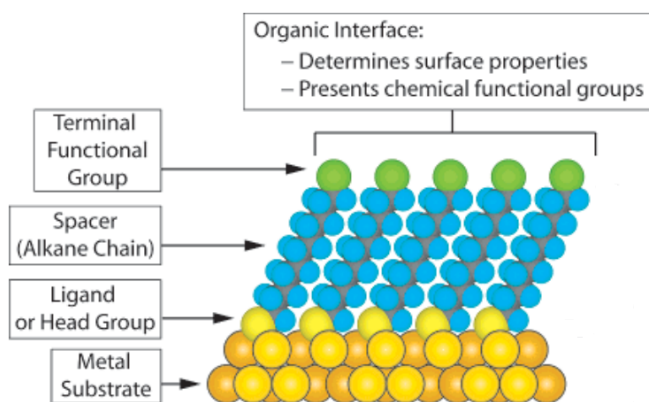


Figure 2.19: Schematic diagram of an ideal, single-crystalline SAM of alkanethiolates supported on a gold surface with a (111) texture. The anatomy and characteristics of the SAM are highlighted. Reproduced from [15].

Amongst all those possible bindings, the ones obtained between noble metals and thiols are the strongest, with a maximum value obtained for the S–Au link ($\Delta H_{\text{S–Au}} = 253.6 \text{ kJ/mol}$ [74]). Noble metals and especially gold are thus more suitable to be durably functionalized by these molecules. This property has been exploited to anchor numerous functional groups on noble metallic surfaces. Indeed thiols (as other SAM initiators) can be divided in three parts: the head group (here -SH), the tail which is most of the time an alkane chain (but some other groups can be added, like ether), and the functional group that ends the molecule (Figure 2.19). This last group will be on the outer surface of the SAM and will induce the external chemical interactions of the newly functionalized surface. The alkane backbone is also important as it allows the stabilization and the compaction of the SAM by Van der Waals interactions. It has even been demonstrated that under 8 carbon atoms in the backbone, SAMs obtained (on gold) have very poor quality with many defects [75]. A schematic model of the steps during the formation of thiol SAM is depicted in Figure 2.20 where one can see the close-packing formation stabilized through the tails.

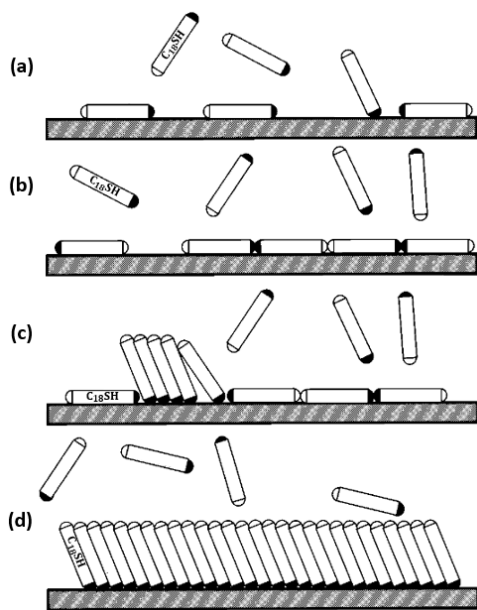
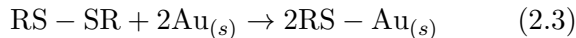


Figure 2.20: Naive schematic for the self-assembly of $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$ on gold, enlightening the tail SAM stabilization allowing closely packed monolayers formation. Reproduced from [75].

SAMs can also be obtained with disulfide molecules. It is an attractive alternative as disulfides are often easier to prepare and they are able to attach more easily larger biomolecules onto the surface [76]. When it has been discovered it was believed that the disulfide divided themselves into two parts and formed S–Au links [77]. This simple but outdated model describing the linking formation corresponds to the equations:



for simple thiol, and



for disulfide molecule [77].

However it does not reflect the reality. Many models were developed to fit more accurately the experimental data acquired about the metallic-sulfur interface but everything is still not fully understood. For example, the simple gold-sulfur interface is believed to result from a modification

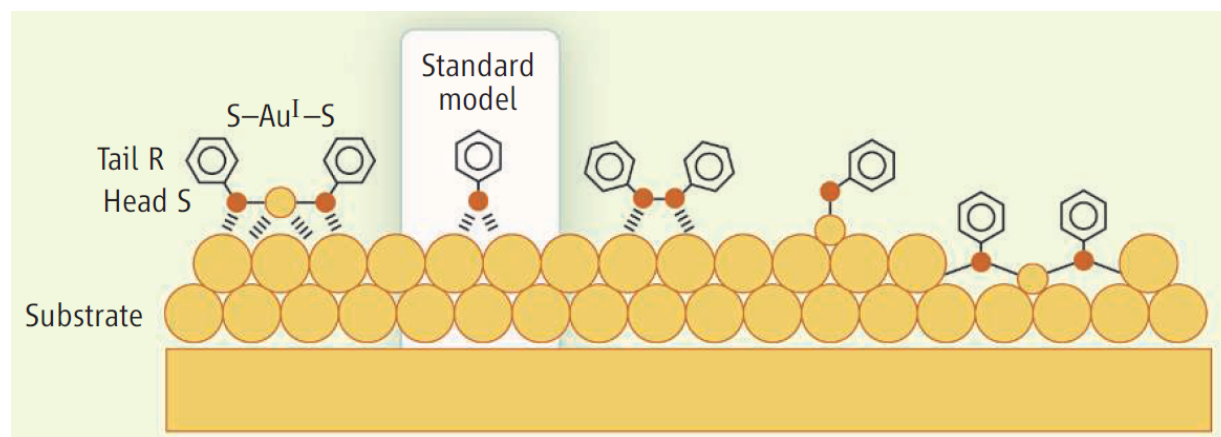


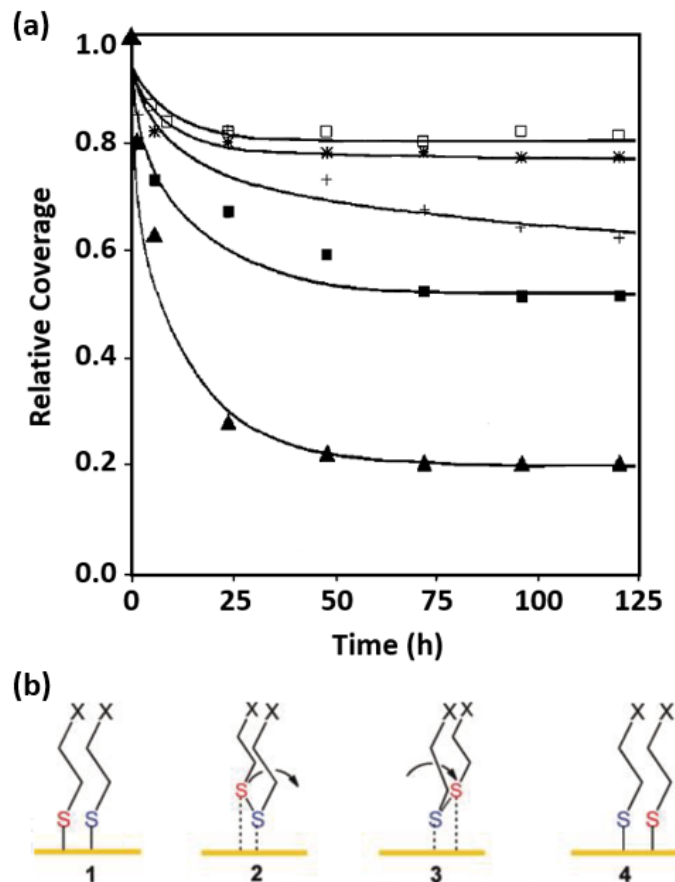
Figure 2.21: Several atomic structures for the gold–sulfur interface of the close-packed thiolate-SAM on Au(111) that were suggested over the past 20 years. The ‘standard model’ describing a monothiolate binding at atop, bridge or hollow site on an unreconstructed Au(111) surface has been challenged by (from middle to right): disulfide bonding, a complex involving an Au adatom and a thiolate (Au–SR), and a polymeric chain structure where monothiolates are bridging Au adatoms. New experimental and theoretical evidence shows that a key structural unit in the low- and medium-coverage SAM layer may be the complex RS–Au(i)–SR where the bridging gold atom is in a formal oxidation state of +1 (left). Reproduced from [79].

of the oxidation state of Au adatoms under the attack of a thiolate, giving rise to accessible electronic shell to induce only semi-covalent bonding with one or several sulfur atoms [78]. The disulfides are not believed to be cleaved any more. Several model of the Au–S (and possibly the disulfide-gold) bond are presented in Figure 2.21. Despite the good affinity between noble metals and thiols, the binding must only be considered as semi-covalent because there is a slight polarization of the link and therefore this link is not as strong as a covalent one. Moreover the strength of the sulfur-noble metal link is known to be better for gold than for platinum, palladium or silver [15].

Finally it is important to report that spontaneous desorption of thiols can happen with time on every surfaces and in every solvents leaving partially thiol-covered substrate. Those remaining thiols still allow a relative coverage of about 80 % in water (see Figure 2.22 (a)). In addition some exchange and self-exchange processes have been occasionally reported. It leads to the exchange of grafted thiols with free thiols in solution (depending on the excess of the solution). Thiols can also diffuse along the surface due to desorption and exchange processes. Diffusion may also be mediated through a so-called “disulfide walking” mechanism. This mechanism is schematically presented in Figure 2.22 (b).

Despite those stability problems, thiols still remain the preferred solution to functionalize noble metals surfaces and in particular gold. They have been successfully grafted on NPs (Au [17, 81] and Ag [82]) and even on NRs [83, 84], sometimes with more difficulty, depending mainly on the curvature of the surface that can prevent SAM stabilization by Van der Waals interactions.

The thiol functionalization process itself has the major advantage to be relatively fast. It does not require any advanced equipment or expensive products (except the thiols themselves). Functionalization is simply made by immersing the particles or the surface in a thiol solution for a few hours. The solvent is often ethanol but other organic solvent and even water can be used [17, 79].



2.2.1.2 Silanes

Functionalization of hydroxyl (OH) groups on surface with organosilanes to form SAMs grafted by covalent Si–O bonds is called silanization. It is

mainly used to cover silicon, mica and glass substrates but it can also be applied to metal oxide or metal with native oxide layer (especially aluminum). As Si–O bonds are strong and covalent ($\Delta H = 799.6 \text{ kJ/mol}$ [2]), the SAMs obtained are very stable. The functionalization components, organosilanes, are alkylsilane derivatives with the general structure RSiX_3 , R_2SiX_2 , R_3SiX where X is chlorine or alkoxy group and R is a carbon chain that can bear different functionalities. One can see a scheme of two different silanization mechanisms in Figure 2.23 (a-b). In the second one there is a so-called polymerization step that form Si–O–Si bonds between the silanes creating a network, ensuring an even better stabilization of the SAM. However this scenario cannot be

Figure 2.22: (a) Surface coverage of octadecanethiol monolayers on gold as a function of immersion time in various pure solvents at room temperature: water (*); hexane (+); ethanol (■); THF (▲); 0.1M aqueous HClO₄ (□). (b) Proposed "disulfide walking" mechanism for surface diffusion of thiolates on Au. Adapted from [80] and reproduced from [77], respectively.

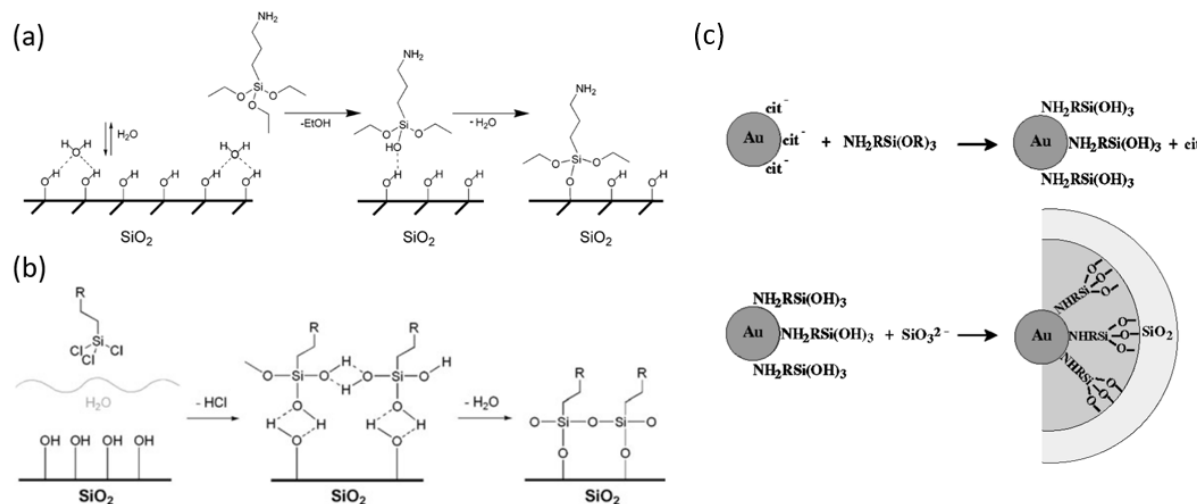


Figure 2.23: (a-b) Schematic silanization mechanisms at hydrated silica surface with (a) 3-aminopropyltriethoxysilanes (b) trichlorosilanes. (c) Schematic diagram of the surface reactions occurring during the formation of a silica shell on citrate-stabilized gold NPs. Reproduced (a) from [85] (b) from [86] and (c) from [2].

directly applied to full coverage monolayers. Indeed the distance required to have Si–O–Si bonds would not leave enough space for parallel, upright-standing hydrocarbon chains. It implies that cross-linked headgroups would prevent the formation of a full-coverage layer and, reversely, that a full-coverage layer cannot be fully cross-linked [87].

The silanization on a surface is commonly performed by two different methods: liquid phase deposition (LPD) or vapor phase deposition (VPD). In LPD the silane is dissolved in an organic solvent and the substrate stays in contact with the solution for a certain time and is dried afterwards. Typically one can deposit droplets of the solution on the surface to be silanized and wait for evaporation and drying of the solvent. In case of VPD, the silane is evaporated (by reducing the pressure and/or heating) and the sample is exposed to that vapor. Both methods should take place under an inert atmosphere or at least under vacuum (for LPD) to avoid any contamination and especially oxidation. It was found that the LPD tends to lead to clustered multilayers whereas high quality monolayers can be achieved by VPD. To functionalize NPs, LPD is often preferred to keep them in solution [88] but NPs silanization by VPD has also been realized [89]. To apply this technique to other kind of metals (and semi-conductor) one can make a silica coating. It is usually achieved by the Stöber method. It typically consists in the polymerization of tetra-alkylsilicates in a mixture of water, ethanol and ammonia. As the tetra-alkylsilicates polymerizes, silica seeds are formed and the shell grows around the solid metallic NPs. Another method of silica shell formation process on citrate-stabilized Au NP is depicted in Figure 2.23(c) [2]. In this case a

silane coupling agent (3-aminopropyl)trimethoxysilane reacts first. Then sodium silicate solution (pH 10-11) is added and the silica polymerizes onto the gold particle surface.

2.2.1.3 Other SAMs

As already mentioned, there are other molecules than silanes and thiols that can form SAMs. But since they were not used or are less prevalent they will not be thoroughly described.

Carboxylic acids Carboxylic acids can form SAMs on several metals such as gold, platinum and especially silver and copper [90]. The metal surface interacts with the negatively charged carboxylate groups, obtained by deprotonation of carboxylic acids.

Amines Amines can usually be used to stabilize metallic NPs such as gold or palladium [91]. The binding is made thanks to nucleophilic nitrogen atoms.

Isocyanides Isocyanides can make SAMs on several transition and noble metals. The bond with those metals can arise from multiple interactions. For example, several reports concluded that the (ArNC)–Au bond (with Ar an aryl group) is formed dominantly by σ -donation from the carbon lone pair of the isocyanide group to a gold atom, but when the metal has filled d orbitals, a sort of π -type bond also may form [92].

Others One can still add phosphines [81], that have electron donating groups, and selenols [93], that are an exotic alternative to thiols. Both can produce SAMs on metals, with better results (or at least more successful studies) on noble metals.

2.2.2 Layer-by-layer

The layer-by-layer (LbL) deposition is a thin film fabrication technique. It is widely used to functionalize various surface from silicon to metallic ones. The technique consists in the sequential immersion of a support into polyelectrolyte solutions of opposite charges. At each step, a polymer layer of a given charge, alternatively positive or negative, is added to the support surface which have to bear an opposite relative charge on its external layer to give rise to the polymer layer

deposition. It finally leads to multilayer structures made of oppositely charged polyelectrolytes. The process is not *stricto sensu* driven by electrostatic interactions since counterions already compensate the surface charges. Actually the process is entropically driven by the release of the counterions and their replacement with the polyelectrolytes. The functionalization thus relies on more than the multiplicity of electrostatic interactions, which are weak taken one by one. Eventually polyelectrolytes are strongly attached to the surface.

Between each immersion in polyelectrolyte solutions, intermediate washing steps are required to avoid an excess of residual polymers of the same charge at the surface. This could lead to disturbance in the alternating charge process.

The LbL was first demonstrated for planar substrates, but Caruso and coworkers demonstrated the possibility to coat acidic gold NPs with an homogeneous film of polyelectrolytes [17] (Figure 2.24). The main issue during LbL functionalization of NPs is that particles have to be extracted from the polyelectrolytes bath and washed while avoiding NPs irreversible aggregation. It is often made by centrifugation provided that the pellet can easily be redispersed.

The main advantages of LbL are the wide range of polyelectrolytes available and the relatively good and easy control over the film thickness. However, the duration of the process can be a limitation, since many purification steps are necessary. The main polyelectrolytes used for NP functionalization are poly(styrene sulfonate) (PSS), poly(acrylic acid) (PAA), poly(diallyldimethylammonium chloride) (PDADMAC), poly(ethyleneimine) (PEI) [94] and poly(allylamine hydrochloride) (PAH). PAH, PEI and PDADMAC are polycations while PAA and PSS are polyanions. On one hand, PDADMAC and PSS are two strong polyelectrolytes that are fully charged over a wide range of pH values. On the other hand, PAA, PAH and PEI are weak polyelectrolytes that are protonated at a pH smaller than their pKa, which are about 4.5, 8.5 and 7 respectively [95, 96].

Many parameters influence LbL deposition and particularly the conformation that polyelectrolytes adopt on the surface. The most relevant parameters are: the polyelectrolyte characteristics (molecular weight, charge density, steric properties), the solution parameters (pH, ionic strength, temperature) and the NP size. It is important to note that the pH of the solution only influences the conformation of the weak polyelectrolytes. The stoichiometry is of course also important (the relative amount of polyelectrolytes compared to the total surface of NPs should be taken into account) [94]. The influence of the pH on the film thickness has been thoroughly investigated for PAH/PAA couples on planar surfaces by Shiratori and coworker [98], which showed that a small change in pH can lead to large variations in the film thickness (between 4 to 80 Å, as depicted on Figure 2.25). An example of film thickness variation on polystyrene

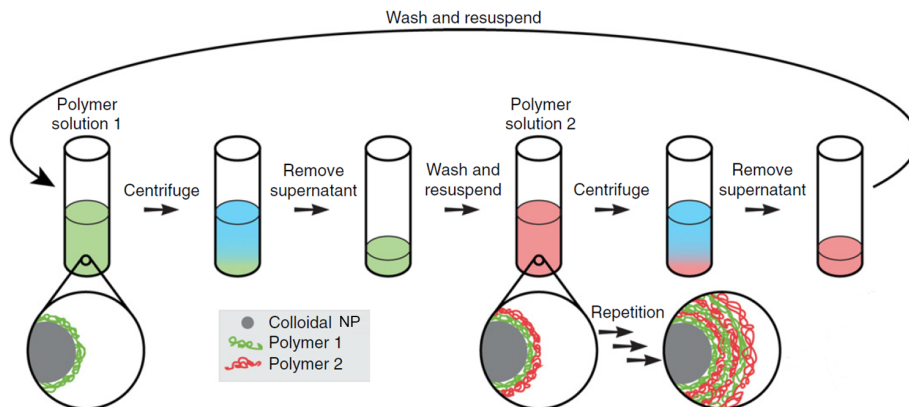


Figure 2.24: Scheme of a layer-by-layer assembly on colloidal NP. Adapted from [97]

NPs as a function of the number of deposited layers is depicted in Figure 2.26. The influence of the ionic strength and pH was also reviewed by Pereira et al. for Au NPs [95]. They concluded that each NP size/polyelectrolytes couple require an optimization of the ionic strength, pH and also polyelectrolytes concentration and NP concentration to obtain good LbL coverage without inducing flocculation and aggregation of the particles. In general low ionic strength decrease the flocculation rate while the choice of pH depends of the pKa of the polyelectrolytes.

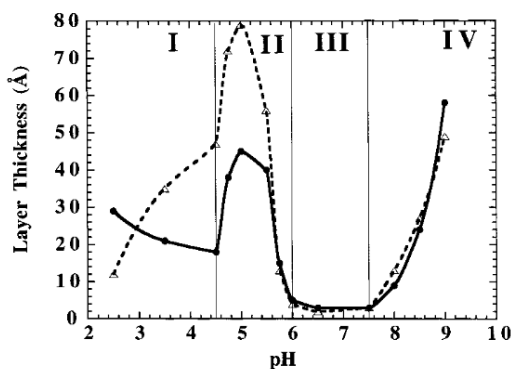


Figure 2.25: Average incremental thickness contributed by a PAA and PAH adsorbed layer as function of solution pH. Both the PAH and PAA dipping solutions were at the same pH. Solid line represents the PAA layer while the dashed line is the PAH layer. Reproduce from [98]

Number of layer	Film thickness [nm]	
	PAH/PSS	PDADMAC/PSS
1	1.2	1.4
3	3.4	3.3
5	5.6	6.6
7	8.4	8.5
9	11.5	11.7
11	15.0	—
15	24.8	—
21	33.9	—

Figure 2.26: Thickness of polyelectrolyte multi-layer films assembled onto polystyrene latexes NPs. Reproduced from [2].

2.2.3 Ligand exchange and post-functionalization

In most of the wet-chemical NP formation, NRs included, surfactants (SAMs or not) are used to stabilize the particles and/or control their shape. However those "functionalizations" are often not desired, because of their end-functional group or their weak bonds with the surface. They need thus to be replaced by desired functions. There are mainly two ways to achieve this: ligand exchange and post-functionalization. In addition to both techniques, researchers try to directly integrate the functionalization on the NPs by adapting their manufacture process.

Ligand exchange It consists in the exchange of ligand at the NP surface. The original surfactant or SAM, resulting from the manufacture process is exchanged by another molecule bearing the required group and/or having better grafting strength with the surface. Many factors affect ligand exchange and contribute to the characteristics of the resulting mixture of ligands on the NP including ligand-surface interactions, ligand-ligand interactions, ligand-solvent interactions, and particle morphology [83]. There are of course many limitations to this process and especially the new ligand must have a stronger preferential attraction with the NPs than the original ligand. Therefore it is relatively easy to replace some Van der Waals adsorbed surfactants but very

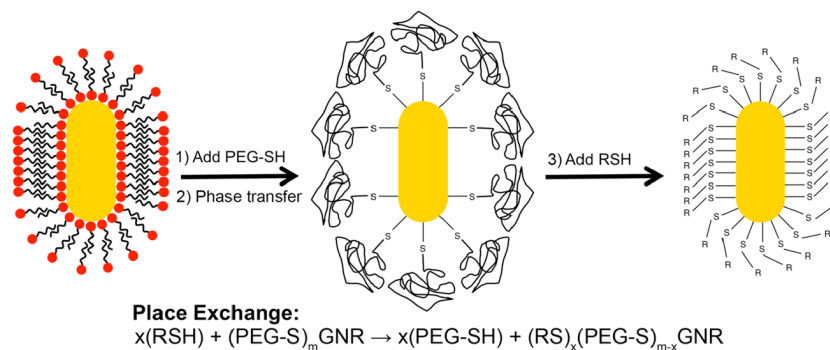


Figure 2.27: Schematic representation of the ligand exchange of CTAB for PEG-SH followed by the place exchange of PEG-SH for an alkanethiol. The reaction for the place exchange is also shown. Replacing CTAB with PEG-SH provides a facile means of transferring the Au NRs into an organic phase to functionalize the surface with RSH without causing particle aggregation. Images are not drawn to scale. Reproduced from [83].

difficult to replace alkyl chain thiols despite the semi-covalent nature of the bond. One of the common example is exchange of the CTAB on gold NRs, arising from seed-mediated method, with some thiols [99]. One can see an example of this process in Figure 2.27 where CTAB bilayer ligands stabilizing NRs are first exchanged by PEG-SH and afterwards PEG-SH is exchanged by short alkanethiols. The PEG-SH step is necessary to avoid the aggregation of the NRs [83]. The PEG-SH exchange with alkanethiols is possible thanks to the space left between PEG-SH

molecules on the Au NRs surface that allows progressive grafting of alkanethiols stabilizing themselves very efficiently by Van der Waals interactions between their tails. Eventually the PEG-SH is progressively removed and replaced by alkanethiols until nearly complete exchange.

Post-functionalization It consists in the exchange of the functional end-group of a molecule, functionalizing a NP by chemical ways. It does not change the nature of the grafting bond with the NPs but allows to obtain the desired end-functional group on the functionalizing molecules. The interactions induced by the NPs on each other and on the external world can thus be carefully chosen. Figure 2.28 shows some of the main chemical ways to post-functionalize NPs.

NWs can also be functionalized with polymers by starting polymerization from the initial end-functional group or from a newly added one that will play the role of the initiator. It is the "grafting from" polymerization. Conversely, the "grafting to" technique consists in the grafting of an already formed polymer by one of its end on a surface thanks to specific interactions just like SAMs. It is important to mention that each chemical process described in the Figure 2.28 is not suitable for every molecules grafted onto the NPs surface and especially for the grafting link. Some post-functionalization processes could alter the grafting link or even destroy it, leading to the loss of the functionalization. The chemical post-functionalization should thus be carefully handled by taking into account the characteristics of the already grafted molecules.

2.2.4 Multifunctional nanoparticles

The multifunctionality of NPs can be defined in different ways. For example, gold NRs coated with carboxyl-end groups SAMs could be called multifunctionalized NPs since the nature of the gold NRs induces particular optical properties (plasmonic effects) and the carboxyl groups on the SAMs induce particular chemical interactions. However, here one will only consider the chemical functionalization arising from grafted molecules on the NPs. A NP will thus need to bear several kinds of functional molecules on its surface to be defined as multifunctionalized.

The different molecules can either be homogeneously (or randomly) distributed over the surface or localized at specific positions on the surface.

2.2.4.1 Homogeneous multifunctionalization

Homogeneous surface multifunctionalization is achieved most of the time by grafting several kinds of molecules all in one step. Afterwards it is still possible to modify the end-functional

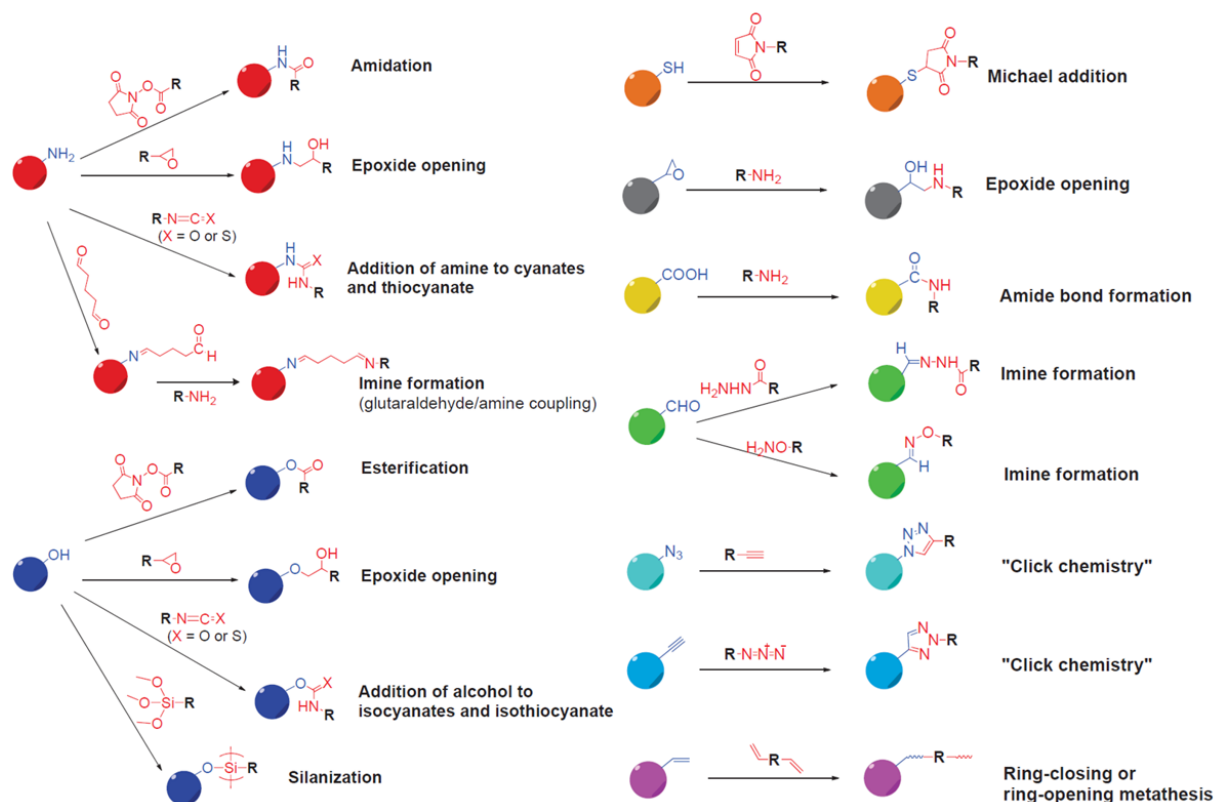


Figure 2.28: Main strategies for covalent post-functionalization of NPs. Reproduced from [100].

groups by post-functionalization if desired. This kind of process is illustrated in Figure 2.29 where two different kind of thiols are grafted onto Au NPs. The first kind of thiol is PEG-SH and the other is a thiol that will enable atom transfer radical polymerization (ATRP) to give the final structure to the newly multifunctionalized Au NPs. It is worth mentioning that this example associates "grafting to" and "grafting from" methods. The ratio between both kind of thiols during functionalization can be adapted to obtain NPs with different coverage percentage of each thiol species on the surface. Controlling the ratio between different kind of molecules, linking themselves identically to the surface, is a good way to control the number of active sites on the particles. The surface ratio between grafted functions will arise mainly from preferential bonding of some molecules on some spots (even in the same "SAM family"), related to steric hindrance, stabilization possibilities or surface curvature. The other parameter that can influence the surface ratio between grafted function is the ratio between the functional molecules within the functionalization solution [102]. One can see another example on Figure 2.30 where the desired active functions are in minority around the NP. Multifunctionalization of NRs or NWs by this mean has also been reported [6, 103]. Adding several func-

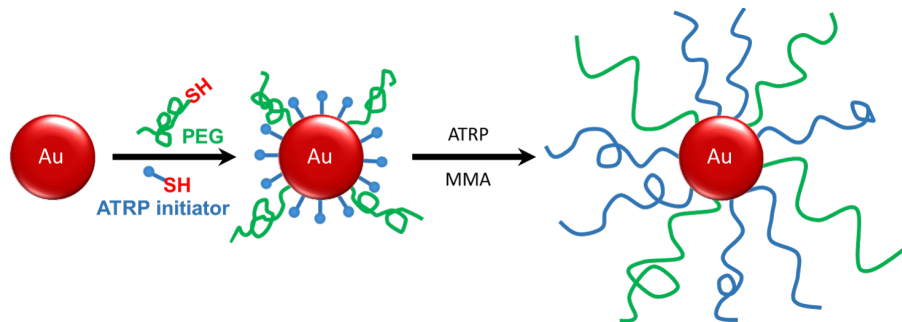


Figure 2.29: Schematic illustration of the synthesis of multifunctionalized gold NP in the sequentially combined “grafting to” (coadsorption PEG and ATRP initiator) and “grafting from” (surface-initiated ATRP of MMA) approaches. Adapted from [101].

tionalization with different grafting mechanisms (for example thiols with carboxylic acids) is not recommended since in most of the cases, one of them will have a better attraction with the particle and will graft at best preferentially and at worst solely to the surface. This is one of the largest limitation to this technique along with steric hindrance of bigger molecules that can perturb the homogeneous grafting and in particular the control on the ratio of the surface covered by one or another molecule. However there are some exceptions where steric hindrance can be taken as an advantage. Indeed some studies achieved homogeneous multifunctionalization by firstly functionalizing NPs with large molecules that let free spaces in between them on the surface. In a second step, smaller, and especially alkyl-like chains, can be used to functionalize the particle inside those remaining spaces without necessarily leading to ligand exchange, depending on the specific interactions of both molecules [83].

2.2.4.2 Selectively localized multifunctionalization

For some applications, it can be interesting to confine the different functionalizations in some limited regions of the NPs. Then functional-

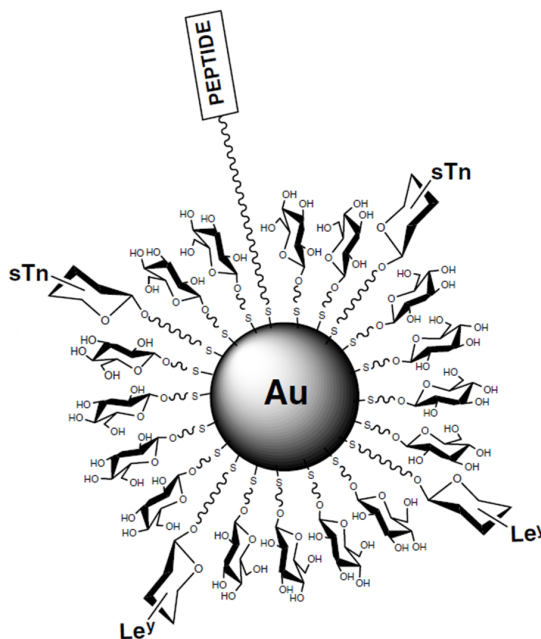


Figure 2.30: One-step synthesis of glyco NP incorporating neo-glycoconjugates and TT peptide ligands in a controlled way. Reproduced from [102].

izations promote specific or non-specific interactions between defined areas of the particles. The idea is that every "patch" of functionalizations provides "instructions" for the NPs to self-assemble. Therefore it can possibly lead to a higher-ordered and more complex structures than the one obtain with monofunctionalized NPs [104]. The most common example are the Janus particles but there exist several other types of selectively multifunctionalized NPs though their manufacture and use remain very marginal.

Janus nanoparticles. Janus NPs are nanospheres (or approaching shapes) with a different functionalization on each hemisphere. The synthesis of such NPs is still a major challenge often requiring ingenious strategies [26]. Most of the time the NP is made of one material and the multifunctionalization is performed by support-assisted formation. The idea is to mask one side of the nanosphere while functionalizing the other one. After removing this mask, the second half of the sphere is functionalized with another kind of molecule. The mask can be a solid substrate on which the NPs are deposited but the throughput is relatively low as it relies on NPs 2D monolayer. Moreover it can be difficult to recover the NPs in suspension after the first functionalization. Still, this technique is efficient. A typical example is illustrated in Figure 2.31 where citrate-stabilized Au NPs are immobilized on silanized surface and lift-off via sonication [105]. Another

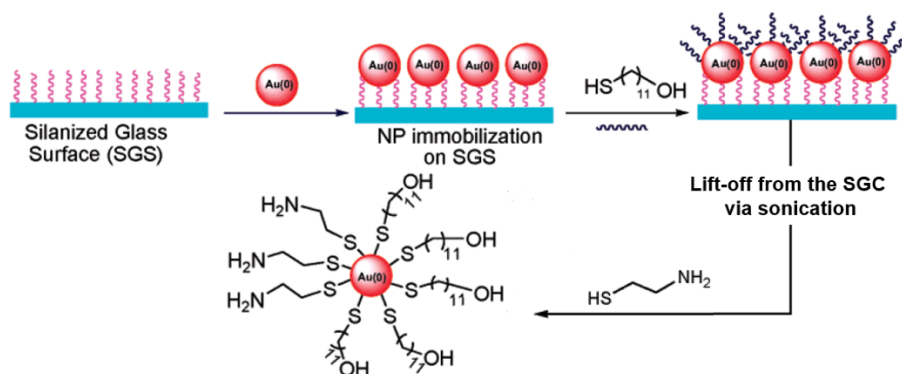


Figure 2.31: Immobilization of citrate-stabilized Au NPs on an amide-terminated silanized glass surface followed by generation of asymmetrically functionalized Au NPs. Adapted from [105].

privileged support to immobilize NPs is PDMS that can additionally be inked with functional molecules, inverting the process. It allows functionalization of the NPs surface when touching the immobilizing stamp (see Figure 2.32). The flat support can also be a polymer matrix that will be heated near glass transition to trap the NPs and protect one of their sides. By carefully choosing the temperature one can control the depth of penetration inside the matrix and so control the surface ratio between both functionalization [106].

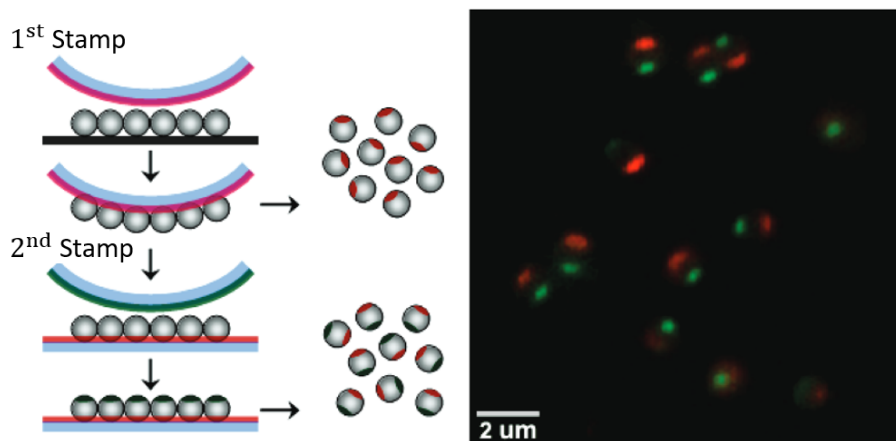


Figure 2.32: Left: Scheme to form "trivalent" colloidal NPs. A first PDMS stamp lifts outermost particles from the surface after they have been deposited as a monolayer onto a solid support. A second PDMS stamp does the same to the opposing pole of the NPs. The central surface area stays unmodified, and finally the "trivalent" particles are released via sonication. Right: Epifluorescence images of the resulting NPS with red dye attached to one pole and green dye attached to the other. Reproduced from [27].

Another approach is to use non-flat supports with larger particles. The mechanism is the same except that in this case there must be other interaction than gravity to immobilize the NPs onto those kind of surface. For example Lattuada et al. produced magnetic NPs that were first functionalized with monolayers of PAA [26]. These negatively charged NPs were adsorbed electrostatically onto positively charged silica beads. Amino-ended polymer were then anchored to the non-masked hemispheres of the NP using amidation chemistry. The Janus NPs were recovered by increasing the pH of the solution, which reversed the charge on the silica beads and repelled the adsorbed NPs. Figure 2.33 presents schematically this process.

Eventually a very appealing route to create Janus NPs is to use a fluid-fluid interface to immobilize the NPs. The interface is obtained by Pickering emulsion droplets, most of the time between oil and water phases. Pickering emulsion is an emulsion that is stabilized by solid particles which adsorb onto the interface between both phases. A transfer energy $-\Delta E$ should be overcome to remove a spherical particle from the interface. This energy depends on the contact angle $\theta_{w/o}$ between the oil-water interface and the particle, measured through the water phase, the particle radius r and the interfacial tension $\gamma_{w/o}$ at the oil-water interface:

$$-\Delta E = \pi r^2 \gamma_{w/o} (1 - |\cos \theta_{w/o}|)^2 \quad (2.4)$$

Equation 2.4 is exact for particles at a flat interface and valid for particles much smaller than the curvature of the interface (and when the gravity force is negligible). For larger particles or smaller droplets, the effect of the curvature should be taken into account. An expression including the

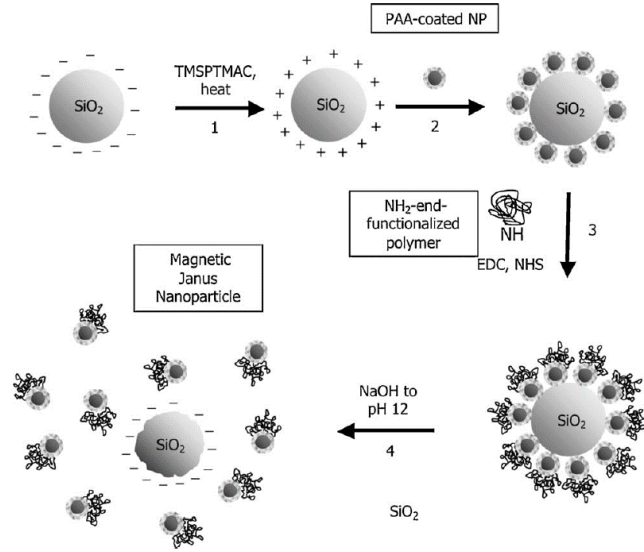


Figure 2.33: Schematic of the masking procedure for the asymmetric functionalization of PAA-coated magnetic NPs (TMSPTMAC is N-Trimethoxysilylpropyl-N,N,N-trimethylammonium chloride). Reproduced from [26].

curvature effects is given by:

$$-\Delta E = 2\pi\gamma_{w/o}[r^2(1 + |\cos \alpha|)\cos\theta_{w/o} - R_s^2(1 - \cos \beta)] \quad (2.5)$$

where $\alpha = \arcsin(x/r)$, $\beta = \arcsin(x/R_s)$, R_s is the resulting size of the swollen droplet after adsorption of particles and x is the radius of the three-phase contact line around the particle at the interface given by $x = \frac{rR_s \sin \theta_{w/o}}{\sqrt{r^2 + R_s^2 + 2rR_s \cos \theta_{w/o}}}$ [107].

During Pickering emulsion, the NPs will form a monolayer at droplet interface preventing the coalescence of the droplets. NPs stabilized at the oil-water interface could be directly functionalized with different molecules dissolved in each phase but they can often wiggle or rotate on themselves at this interface. This could perturbate the functionalization step and the clear demarcation between both functionalizations on the surface. A simple solution have been proposed by Granick and his team [108]: the use of parafine wax as the oil solution. Above a certain temperature the wax is liquid and can be used to induce droplets and Pickering emulsion but when temperature is decreased, solidification of the wax droplets occurs. The solid wax droplets can be recovered with the NPs trapped at their surfaces, ready to be functionalized. Afterwards, at higher temperature without the emulsion, the wax releases the NPs allowing the functionalization of their other side. Figure 2.34 shows a scheme of the whole process. The principal advantage of this technique is the fact that the interface monolayers are not only 2D, requiring large surface to obtain large amount of molecules, but 3D, around droplets, which highly improves the process

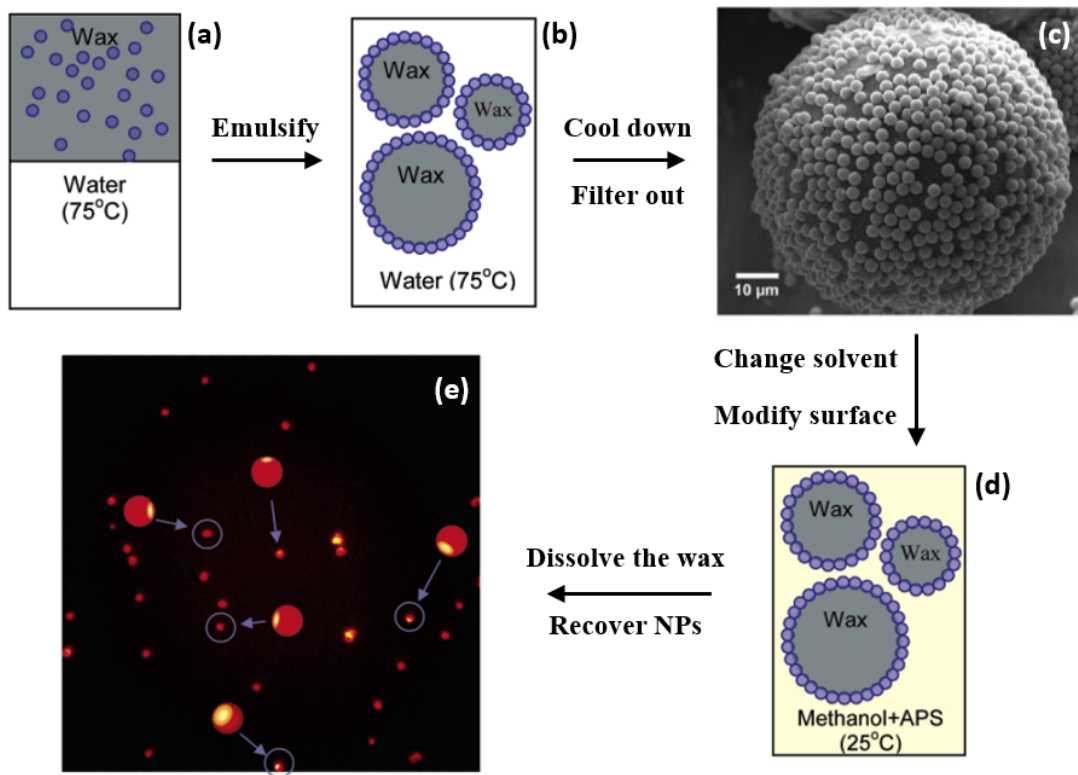


Figure 2.34: Schematic procedure to create Janus particles by functionalizing particles adsorbed onto a Pickering emulsion and then cooling the sample so that the oil solidifies to form a wax. (c) SEM image of a typical wax droplet (colloidosome). (e) Fluorescence images of Janus particles with wax protected area labelled with fluorescent dye. The fluorescence "anomaly" arises from the anisotropic coating of the NPs. (APS is (aminopropyl)triethoxysilane). Adapted from [108].

throughput. Moreover the technique allows the fine tuning of the surface ratio functionalized with one functionalization or the other. Indeed, adding some surfactant inside the emulsion can modulate the penetration of the NPs inside the oil-water interface (see Figure 2.35).

The (flat) air-water interface can also be used but in this case, the use of a Langmuir-Blodgett mechanical equipment can be essential to compact the NPs to prevent their rotation at the interface.

It is also possible to create Janus NPs by synthesizing heterodimers, i.e. NPs made with two different inorganic materials. The resulting particle has commonly the shape of two interconnected spheres. This result can be obtained by various ways such as direct heterogeneous nucleation or nonepitaxial deposition followed by thermally driven coalescence/crystallization. The synthesis mechanisms will not be explained here but the main informations can be found in the review written by Lattuada et al.[26]. The heterodimers can easily be multifunctionalized since they are made of two materials that can have selective grafting interactions allowing grafting

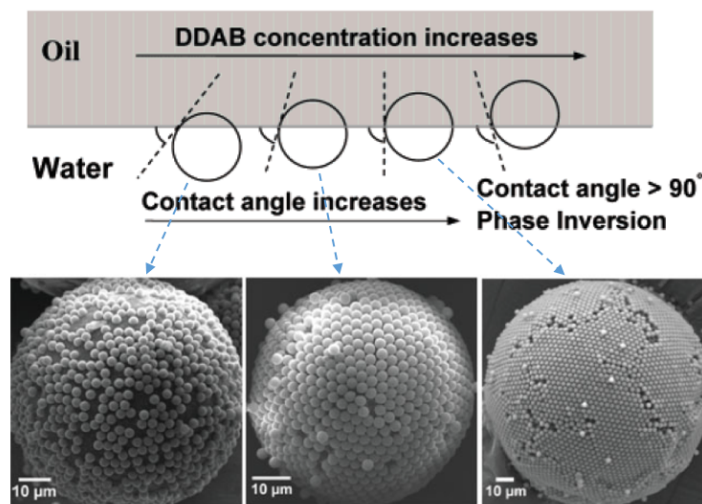


Figure 2.35: (above): Scheme of the surfactant effect on the particles adsorb to the water–oil interface of emulsions, determining a contact angle depicted by the dotted line, changing the distance that the particle penetrates the respective phases. (below): SEM images (colloidosome) of silica particles on wax droplets depending on the amount of cationic surfactant didodecyldimethylammonium bromide (DDAB) rendering the particle more hydrophobic, causing them to penetrate more deeply into the oil phase. Adapted from [109].

of different molecules on each of them.

Selectively multifunctionalized nanorods and nanowires. There are several techniques to obtain selectively multifunctionalized NRs and NWs but the most studied is the functionalization of multi-segmented NRs/NWs

By definition, multi-segmented NRs/NWs are composed of several materials and by carefully choosing the molecules to graft on them one can get relatively easily multifunctionalized NRs or NWs with different functionalization on each part of different composition. As explained in Section 2.2.1, several materials have specific attraction towards specific molecules leading to links more or less thermodynamically stable. For example Meyer et al. managed to multifunctionalize Au–Ni NWs with thiols and carboxylic acid on gold and nickel, respectively [110] (Figure 2.36 (a)). Both functionalizations are not performed at the same time to avoid possible disruptive interactions between them. Carboxylic acid is first added and preferentially adsorbed on the nickel parts. Second, thiols are added and link preferentially on gold leading if necessary to ligand exchange with the carboxylic acid. Another example has been given by Mallouk and its team who multifunctionalized Au–Pt–Au trisegmented NWs [58]. First isocyanides functionalized both materials and afterwards thiols were used to induce ligand exchange on the gold parts. The basic mechanism is depicted in Figure 2.36 (b).

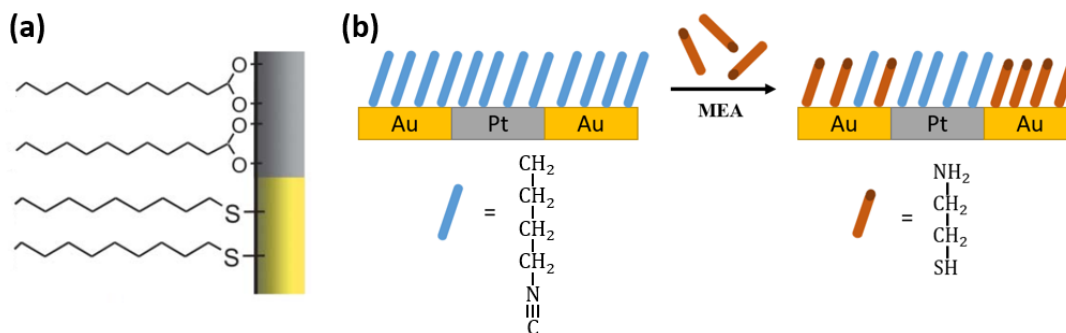


Figure 2.36: (a) Au-Ni NW multifunctionalized with carboxylic and thiols molecules. (b) Multifunctionalization of Au-Pt-Au NW that was first functionalized with isocyanide and after with thiols (2-mercaptoethylamine (MEA)). The isocyanides are exchanged by the thiols only on gold (nearly completely). Adapted from [110] and [58], respectively.

Another technique to selectively multifunctionalized takes advantage of what was explained in Section 2.1.1. The NRs synthesized by the seed-mediated method are crystals with different facets orientation. These facets do not have the same surface energy and do not induce the same interactions with molecules. One can especially mention the preferential binding of CTAB along the (100) facet of the longitudinal side of the NRs (which enable anisotropic growth of the NRs) leaving their ends (the (111) faces) deprived of CTAB. This allows and largely favors the binding of thiol-terminated molecules to the ends of the NRs [111]. In addition to the difference of facets orientation, the much larger curvature at the NR ends also plays an important role on the easier exchange of CTAB at those places. A typical example has been published by Rubinstein et al. [112] who have synthesized CTAB capped Au NRs with PS-SH on their ends (Figure 2.37 (a)). Although the conditions during the end-ligand exchange have to be finely tuned to avoid complete exchange of the CTAB all around NRs, this technique is appealing as it is suitable for seed-mediated synthesized NRs.

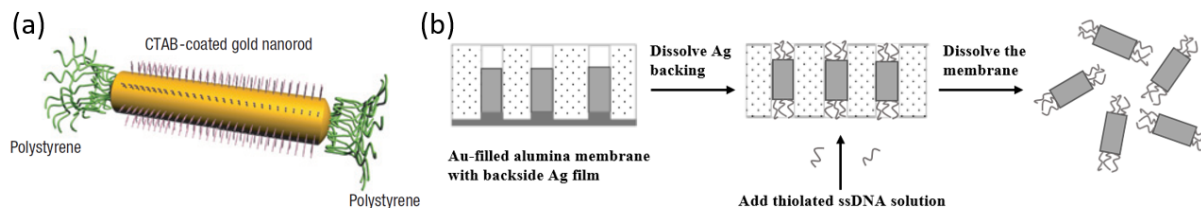


Figure 2.37: (a) Gold nanorod with double layer of CTAB along the longitudinal side and polystyrene molecules grafted (by S-Au link) to both ends. (b) Scheme for in-membrane functionalization of the ends of gold NWs with thiolated single stranded DNA (ssDNA). Adapted from [112] and [58], respectively.

A third method, that is less common but has still been reported few times [58], is the use of some

hard-template to partly mask the NWs. The typical example is the use of nanoporous template to synthesize NWs and to mask their sides. The NWs are electro-chemically deposited within the nanopores of the membrane then the bottom metallization is dissolved and the NWs are trapped inside the membrane with their ends free of access and their sides protected by the membrane. The selective functionalization of the ends is allowed before dissolution of the template. This process is schematically shown in Figure 2.37 (b).

2.3 Self-assembly of nanorods/nanowires

Self-assembly of NMs depends mainly on the interactions that can arise between the particles themselves, and possibly with the external medium. However it can also significantly depends on the techniques implemented to bring the NMs near each other, close enough to allow them to start interacting with each other. The typical interactions between the NMs depends on the synthesized NMs, on the nano-objects material and the functions present on their surface, and on external linkers, ligands or the external medium. It goes from van der Waals forces to solvophobic interactions through electrostatic interactions. The techniques that lead to compaction of the NMs depends on external conditions such as surfactants in solution, NM concentration but also mechanical or thermodynamical NM compaction and capillary forces. In addition to those parameters and techniques, it is essential to choose and discuss the method used to characterize the assemblies in order to avoid any mismatch between the characterized "assembly" and the real assembly. This section will concentrate on the assemblies of NRs and NWs by reviewing the interactions at stake, the techniques used and the characterization techniques developed as well as the typical results obtained in those conditions, corresponding to the state of the art on this topic. It is worth to mention that most of the studies on this topic were realized on NRs and not on NWs, likely because of the usually larger mass of the NWs and the higher throughput for NR manufacture by seed-mediated growth. Eventually a brief review of the main application of such NRs assemblies will be made.

There exist of course other interactions than the one that will be reviewed. One can especially cite the assembly of NWs by the application of magnetic or electrical external fields. Those types of assemblies will not be described in this thesis since they do not enter in the "self-assembly of NMs" but some typical examples are given in [113] (magnetically-assisted) and [114] (electrically-assisted). Moreover specifically nano-patterned surfaces acting as template to assemble NPs [115] will not be mentioned here either.

2.3.1 Interactions between nanorods/nanowires in suspension

The interactions between functionalized NWs or NRs (building blocks) in suspension that can eventually lead to self-assembly will now be discussed. Those inter-NMs forces are non-covalent and include especially Van der Waals interactions, coulombic forces, entropic forces, hydrophobic or solvophobic effects, and hydrogen bonding. These interactions can lead to the creation of large, discrete, ordered structures from relatively simple units [116]. This section will give some

examples of interaction forces between 1D NMs and the self-assemblies they can lead to.

2.3.1.1 Van der Waals interactions

Van der Waals interactions are weak interactions (when discrete) coming from instantaneously induced dipoles in non-permanently charged particles. In the case of NRs and especially heavier NWs those forces are often too weak to induce self-assembly alone in low concentrated NM solutions. However if the nano-objects are compacted by another mean, they can start interacting. This especially induces the aggregation of non-functionalized NRs with a preference to side-to-side assembly (smaller distance between extremities and larger surface). Stabilizing agent are thus usually added during NR synthesis to avoid their aggregation. Van der Waals interactions can weaken other interactions especially if they induce forces of opposite direction [117].

2.3.1.2 Electrostatic interactions

Electrostatic interactions are the attraction or repulsion effects between charged groups: the nano-objects themselves (ions, metallic NMs...) or molecules/polymers, grafted on the NMs, bearing charges (polyelectrolytes). Those interactions can be exploited to produce self-assembly. For example, since the Au NRs produced by seed-mediated method are already coated by a bilayer of CTAB, they have a positively charged surface. This has often been exploited. For instance, Orendorff et al. [11] studied the pH-triggered self-assembly of gold NRs, using adipic acid as linker. Self-assembly of the CTAB-capped Au NRs was achieved by mixing the NRs with adipic acid solution at pH 7 or pH 8. Due to the larger presence of CTAB molecules, Au NRs carry principally positive charges on their sides, which can interact electrostatically with the adipic acids end groups that are carboxylate groups at those pH. These molecules act as bridges between adjacent NRs, and it is thus critical that these linking molecules have two acidic functions as well as a short enough alkyl chain to prevent a looped adsorption. Obviously the self-assembly does not occur when the pH is low since the carboxylic groups are protonated. The assembly can thus be pH-triggered although the authors recognized that solvent evaporation and therefore translational entropy also likely contribute to NRs assembly. TEM images of the NRs assemblies can be seen in Figure 2.38 showing the compact assemblies in finite domains when the pH is fixed at 7 or 8 while the NRs are very dispersed at pH 3.

Other examples were described with other ligands such as lyotropic chromonic materials [19]. Several studies reported end-to-end assemblies by adding negatively charged ligands or reagents

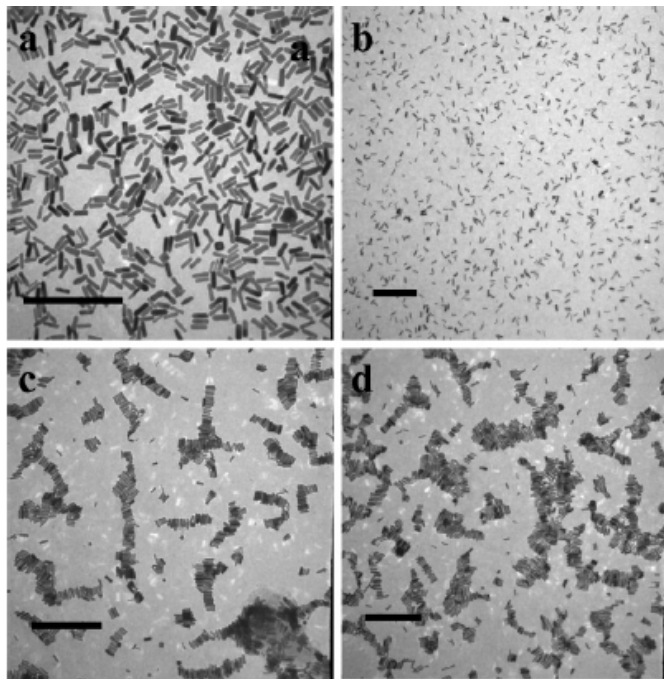


Figure 2.38: TEM micrographs of gold NRs assembled in (a) pure water, (b) 10-5 M adipic acid at pH 3, (c) 10-5 M adipic acid at pH 7, and (d) 10-5 M adipic acid at pH 8. The scale bar represents 500 nm. Reproduced from [11].

such as citrate anions [118] or Na_3PO_4 [73]. However the explanation of these last phenomena is still under debate and although there is no doubt on the impact of charge of the additives, the final assembly could arise from other interactions such as solvent affinity of the ultimate NRs surface.

2.3.1.3 DVLO theory

To try to take into account both previous interactions (Van der Waals forces and electrostatic forces) the Derjaguin, Landau, Vervy, and Overbeek (DLVO) theory has been developed in the 1940s. Since then it still represents the cornerstone of the understanding of interactions between colloidal particles and their aggregation behavior. It is also used to rationalize forces acting between interfaces and to rationalize forces between particles and planar substrates, for example, thin liquid films [119]. The DVLO theory considers only two sets of forces impacting the colloidal stability: the Van der Waals forces and the electrostatic (Coulombic) forces coming from the surface potential of the colloids. The Van der Waals forces comes from the dipole interactions whether it comes from permanent dipoles or induced dipoles. These forces depends mainly on

the Hamaker constants of the materials, the medium and on the geometry of the particles. The other forces comes from the electrostatic double layer that forms around particle interface, and so from the surface potential of the particles and from the medium (especially its ionic strength). In the case where Van der Waals forces are present in combination with electrostatic forces, the DLVO theory is based on the assumption that the electrostatic double layer forces and the Van der Waals forces are independent and therefore can be superimposed or added at each interacting distance for two particles. In addition to their specific dependence, both forces do not vary identically with the distance between particles (or interface). The Van der Waals attraction gives a negative term and is an inverse power law function of the separation distance while the double layer force decays exponentially with the separation distance. Therefore curves of the sum of the force and energy, that applied on identical particles, versus the inter-distance can be drawn for general cases (Figure 2.39). Note that the energy curve has two minima and one "kinetic" barrier. The Van der Waals forces between identical particles are always attractive and increase

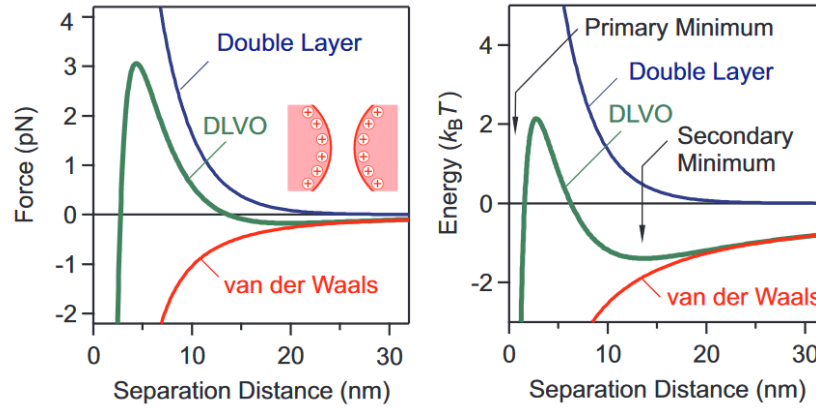


Figure 2.39: Force (left) and energy (right) coming from Van der Waals and double layer interactions, and DLVO profiles, corresponding to two spherical particles with radius of 250 nm, Hamaker constant of 5×10^{-21} J, surface charge density equals to 2 mC/m², in water with monovalent salt concentration of 8 mM. Reproduced from [120].

with the particle size and with the Hamaker constant. The double layer forces between identical particles are always repulsive and increase with the particle surface potential and decrease with the ionic strength of the medium. This double layer forces dependence leads to energy curves such as depicted in Figure 2.40. Although the DLVO theory gives an interesting approximation about the forces exerted on NMs, it does not take into account many other interactions. Among these interactions one can cite the H-bondings, the hydrophobic/hydrophilic interactions, the critical coagulation concentration or the forces induced by polymers (steric repulsion, bridging attraction...) [120].

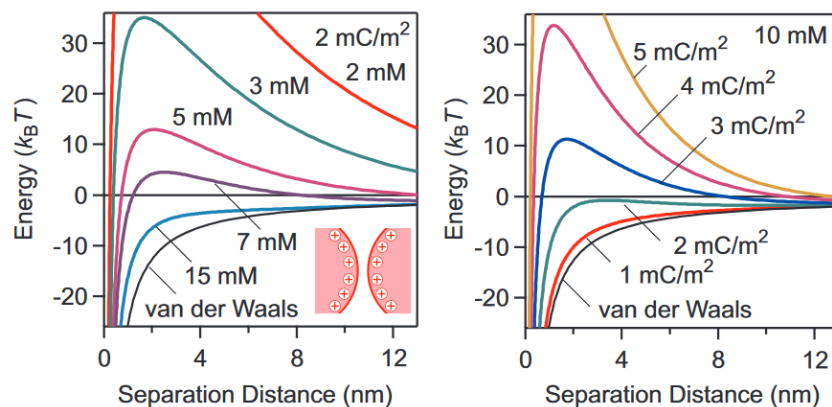


Figure 2.40: Energy DLVO profiles with dependence in (monovalent) salt concentration (left) and surface charge density (right), corresponding to two spherical particles with radius of 250 nm, Hamaker constant of 5×10^{-21} J. On left profiles, the surface charge density is 2 mC/m^2 while on right profiles the (monovalent) salt concentration is 10 mM. Reproduced from [120].

2.3.1.4 Hydrophobic/hydrophilic or solvophobic interactions

Molecules can be hydrophobic, hydrophilic or amphiphilic. In an aqueous solution, hydrophobic groups will tend to aggregate and to assemble to avoid contact with H_2O molecules. This phenomenon is well known for amphiphilic molecules that will form micelles to keep their heads and tails in their favorite solvent (oil or water). In the same way some molecules will tend to "like" some solvents and "dislike" others, defining their good solvents and their poor solvents. Although these interactions are not always very strong they can induce self-assembly of NRs and will often be an important parameter to play with. It has been demonstrated by Kumacheva et al. who synthesized tri-blocks Au NRs which assembled by hydrophobic interactions [112]. The NR sides were simply functionalized with a hydrophilic double CTAB layer arising from the synthesis and the NR ends were functionalized with hydrophobic polystyrene. Knowing that dimethyl formamide (DMF) is a good solvent for CTAB and polystyrene, and depending on the solvent used, different assemblies will occur. On the one hand, the NRs assemble in end-to-end fashion in mixture of water and DMF. On the other hand, in mixture of tetrahydrofuran (THF) and DMF the NRs assemble side-to-side, less well marked and limited to assemblies of two NRs or leading to mesosphere of NRs. This behavior is believed to be caused by the polystyrene folding around the NRs. Several kinds of these self-assemblies can be seen in Figure 2.41. Another example based on amphiphilic semiconductor CdSe NRs gave similar end-to-end assembly results in aqueous solution [117]. The whole NRs were functionalized with hydrophilic groups (2-(dimethylamino)ethanethiol (DMAET)) but after few days in aqueous solution it is believed

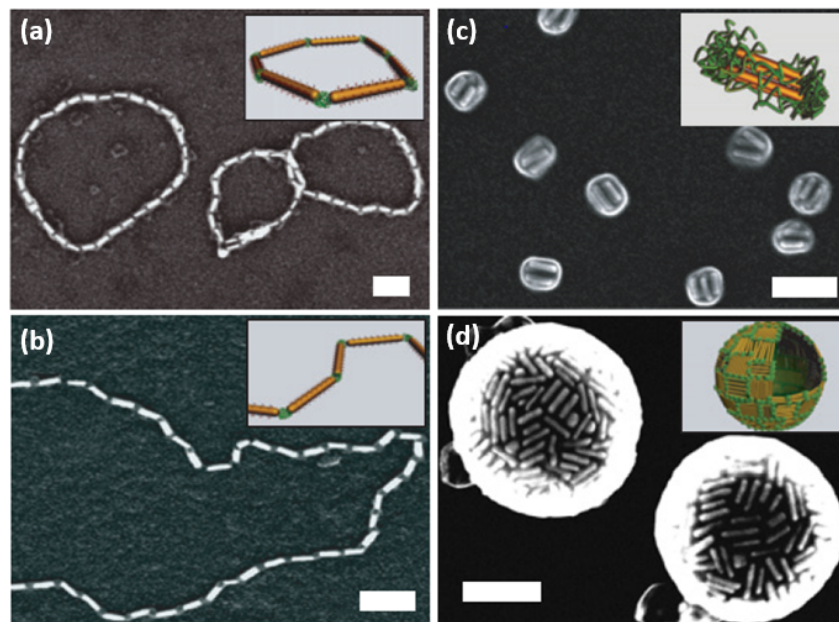


Figure 2.41: SEM images of the self-assembled NRs structures: rings (a) and chains (b) self-assembled in the DMF/water mixture at water contents of 6 and 20 wt%, respectively, side-to-side aggregated bundles of NRs (c) and nanospheres (d) self-organized in the THF/water mixture at water contents of 6 and 20 wt%, respectively. Reproduced from [112].

that there is a ligand desorption process, dominating at the NRs ends, which have a weaker binding affinity for thiolate ligands than the side surfaces, leading to the formation of uncapped hydrophobic inorganic ends and finally to end-to-end assemblies. Indeed after several days fibrous 1D end-to-end assemblies aggregated by strong interchain interactions, leading to the formation of 3D-network polymer-gel-like precipitates.

These two studies indicate that the complete mechanisms and especially the whole set of the forces that drive the assemblies are not yet completely understood nor controlled.

2.3.1.5 Hydrogen bondings

A hydrogen bond is an electrostatic attraction between a hydrogen atom (H), which is bond to a very electronegative atom such as nitrogen (N), oxygen (O) or fluorine (F), with another adjacent atom bearing a lone pair of electrons. The H-bonds are on average stronger than Van der Waals interactions. An example of a assembly based on hydrogen bonding was published by Ni et al. [121], who demonstrated the hydrogen-bonding mechanism responsible for the end-to-end assembly of gold NRs carrying thiol-grafted functions (see Figure 2.43 (d)). Some studies have already reported end-to-end self-assembly of Au NRs via H-bonds, especially thanks to cysteine (CYS) [122], but proof of H-bondings rather than solvophobic interactions were lacking. Ni and his coworkers tested three different bonding molecules: CYS (carrying amine and carboxylic groups), glutathione (GSH) (more complex but carrying among others amine and carboxylic groups) and 4-mercaptophenol (Mph) (carrying alcohol group). Each of these molecules were grafted on Au NR ends while the longitudinal sides already bore CTAB molecules. Thanks to UV-Vis spectrophotometry, extinction spectra were measured at different time and at different pH. It allowed to demonstrate that after a certain time a new peak appeared (around 950 nm) in a small pH window. This peak is supposed to correspond to the assembly of the NRs since some end-to-end assemblies could be imaged. The speed at which this peak appear and its height were recorded and found to be maximum at specific pH depending on the functional molecules. It appeared that this pH corresponds to the pKa of the chosen linking molecules. Some extinction spectra and the extinction modifications of the 950 nm peak for Mph functionalized Au NRs can be found in Figure 2.43. The results suggested that assembly between NRs occur via the so-called PU complexation, which is a H-bonding interaction between a protonated acid (P) and its unprotonated conjugated base (U). Of course this complexation occurs when the concentration of both P and U are high and therefore nearly equal, which is only the case at a pH close to the pKa of the linking molecules. This study suggested thus that H-bonding between NRs can occur and could be increased by choosing an appropriate pH regarding the pKa of the functional molecules. Moreover, increasing the temperature may lead to higher assembly rate since a higher temperature increases the probability of collisions between monomers and therefore the formation of PU complexes.

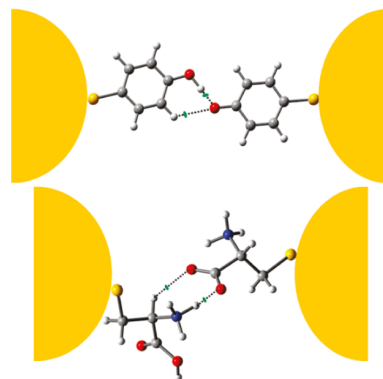


Figure 2.42: Representation of the H-bond between functionalized Au NWs ends. (above): Mph, (below): CYS. Reproduced from [121].

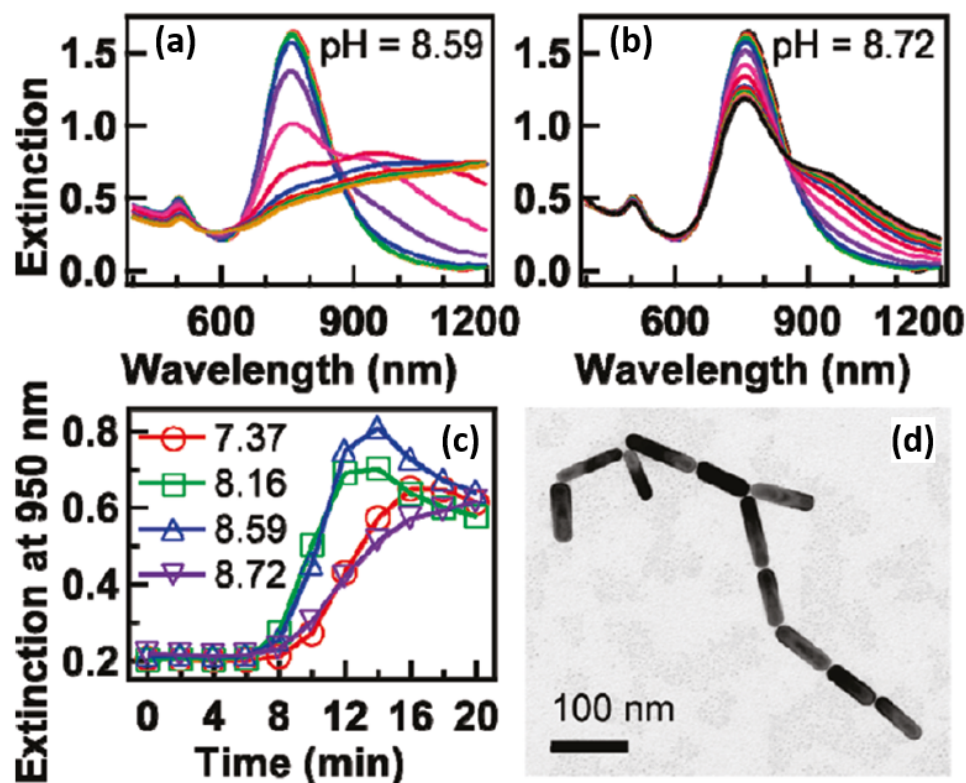


Figure 2.43: (a-b) Time-dependent extinction spectra acquired for the assembly of Au NRs at pH 8.59 and 8.72. The NRs were functionalized and maintained in an aqueous solution with 0.64 mM MPh and 0.1 M CTAB at 40°C. The spectra were acquired every 2 min. (c) Extinction changes at a wavelength of 950 nm as a function of time at different pH values. (d) TEM image of a Mph-assisted end-to-end assembly of Au NRs. Reproduced from [121].

DNA strands interactions Interaction between complementary DNA strands relies on specific H-bonding between complementary bases present on the strands. The main assembly mechanism is therefore not really different to the one explained before but thanks to the different H-bondings, the recognition between two DNA strands is highly selective and predictable. Moreover the link between the strands can be broken when increasing the temperature. All those reasons made self-assembly via DNA strands interactions a really hot topic. That is why, even if DNA is a particular functionalization, it seemed important

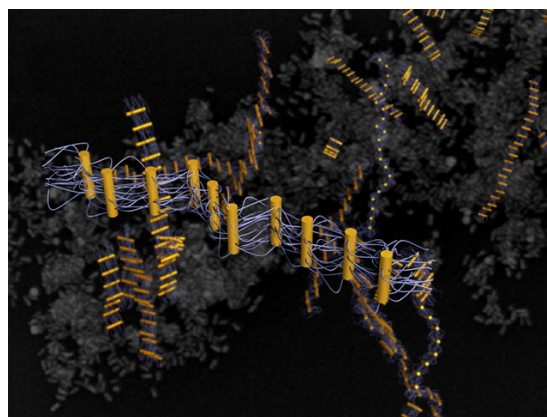


Figure 2.44: Illustration of the ribbon-like structure. Reproduced from [123]

to describe briefly some self-assemblies obtained like that.

In the early 2000's Mann et al. showed some results of DNA-driven 3D aggregation of Au NRs [124]. Several years later, Gang et al. [123] improved and completed that study by showing that DNA-functionalized Au NRs could assemble into ribbon-like structures, using direct or linker-induced hybridization. In both techniques, DNA strands were grafted on the NRs using thiol groups. The recognition could be achieved directly between two complementary DNA strands or via a linker. The ribbon structure and a scheme of the process are illustrated on Figures 2.44 and 2.45, respectively. Based on this study many others have been published [125, 126] describing

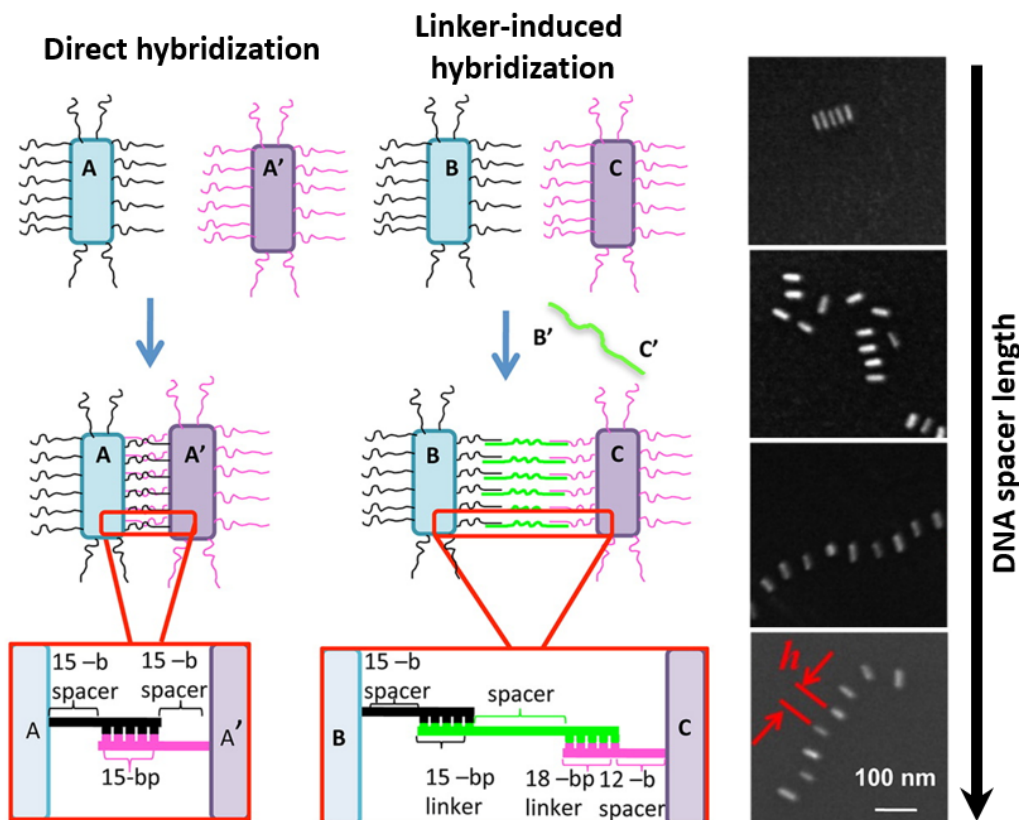


Figure 2.45: Links: Schematic of a Au NRs assembly generated via direct or linker-induced DNA hybridization, and the detailed structure of one interparticle linkage. Right: Representative SEM images of ribbons for the direct hybridization, linker-induced hybridization 33 bases (L33), L100, L200, allowing control of inter-rod distances, h . Reproduced from [123]

other 2D and 3D assemblies through DNA strands what clearly suggests that DNA could be an important step in the preparation of highly predictable assemblies.

2.3.2 Self-assembly strategies

Previous section showed the importance of functionalization in order to obtain self-assembly of 1D NMs. However, these interactions are not always sufficient to provide an ordered structure over long-range distance. Indeed, sometimes particles have to be brought close to each other before being able to interact through their specific functionalities. Sometimes assemblies can also even occur via other forces than the ones induced by the functionalizations. Moreover the characterization techniques of the assemblies can induce (inconveniently) new specific interactions. As an example, most of the assemblies shown in the previous section (Figure 2.41 for example) were obtained after complete solvent evaporation. Therefore it is difficult to know if the assembly in suspension was exactly identical to the one characterized since the SEM or TEM characterizations (normally) require dried samples. The problem is that solvent evaporation can change or even induce assembly. That is why this section will describe the main self-assembly strategies, namely assembly in suspension, drop-casting and assembly at the interface between two fluids, and their corresponding characterization techniques.

2.3.2.1 Assembly in suspension

The self-assembly of NRs/NWs can be driven while they are in suspension as it was described in the previous section. Since 1D NMs can adopt different organization more freely in suspension, various types of self-assemblies may be observed compared to surface-based methods. It can in particular enable assembly mechanism that are typically 3D and can (or not) lead to such 3D assembly, as it has been described by Pileni et al. with (reverse) micellar mechanisms [128]. However, as already mentioned, the difficulty of this method comes from the sample characterization. Techniques such as SEM, or AFM require the drying of the sample, therefore it is not possible to determine if the characterized assembly corresponds effectively to the in solvent assembly or if it comes from the drying process. Other techniques such as cryo-TEM can be used, but its difficulty to use and the uncertainty to avoid any assembly disturbance during freezing limited its application. As a consequence, liquid phase

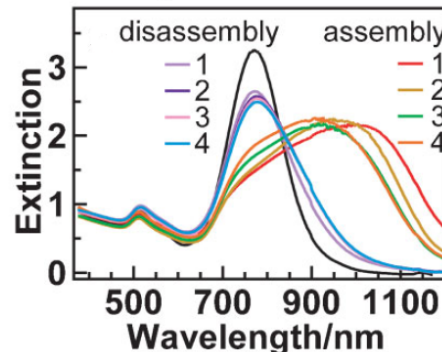


Figure 2.46: Extinction spectra corresponding to four cycles of assembly and disassembly of Au NRs functionalized by 3-mercaptopropionic acid. Assembly was induced by adjusting the pH solution to 9.6 and disassembly by adjusting the pH to 3.1. The assembly organization in suspension was believed to be end-to-end. Reproduced from [127].

measurements including dynamic light scattering or UV-Vis absorbance spectroscopy are common techniques to characterize the assembly directly in suspension. Although these techniques can readily establish shift of the NPs organization, it cannot precisely determine their organizations. One can see an example of self-assembly/disassembly pH-triggered in suspension characterized by UV-Vis in Figure 2.47. To have a better idea on the assembly morphology some complex theoretical simulations need to be performed. For example one can try to determine theoretically the absorbance peaks in UV-Vis corresponding to the believed assembly. The difficulty to do such calculations explains why UV-Vis is solely used to provide tangible proof of organizational change.

2.3.2.2 Drop-casting

Lately, self-assembly by drop-casting has attracted much attention because of its simplicity and its ease of characterization. This method consists in depositing a droplet of the solution containing the nano-building blocks onto a substrate and let it dry. During solvent evaporation NPs are brought together and concentrated inside macroscopic concentric circles called "coffee rings". This effect comes from the movement of the NPs inside of the droplet. When a droplet begins to dry, its edge presents a "stick-slip" motion because of the competition between the pinning and capillary forces to compensate the evaporation of the solvent. The pinning of the contact line induces a flow

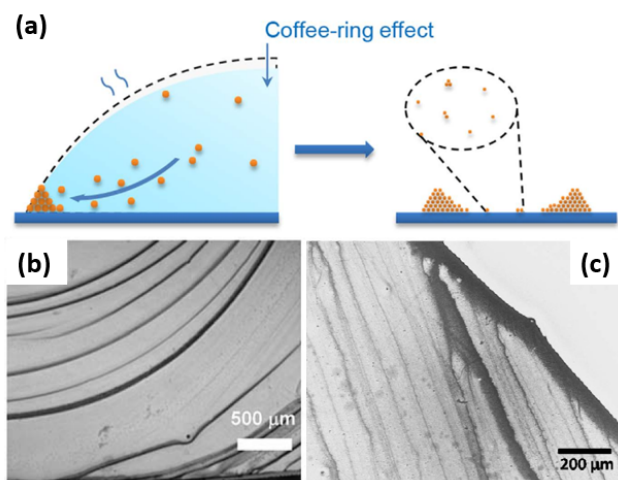


Figure 2.47: (a) Scheme of the coffee-ring effect. (b) and (c) Low magnification SEM images of part of coffee stains composed of NRs. Reproduced: (a) from [130], (b) from [131] and (c) from [129].

of NPs and solvent from the droplets center towards their edge, towards the contact lines [129]. At one point, as the solvent continues to evaporate, the pinning cannot sustain the capillary forces anymore and there is slipping of the contact line inward of the droplet until new pinning appears. Therefore, the coffee rings are often made of several concentric circles. Eventually the contact line is pinned until complete evaporation of the solvent. During this process the NMs are deposited with larger concentration at the pinning points compared to the inner regions because of the outward solvent flow. Inside those concentrated regions,

NRs and NPs can easily self-assemble into ordered phase, especially when the concentration of NRs attains a certain level in the substrate vicinity. Liquid-crystalline phases of NRs begin to form and precipitate at the droplet edge. These phases can finally lead to different types of dried assemblies: monolayer or multilayer, vertically or horizontally aligned, long- or short-range ordered [18, 129, 132, 133]. The various types of assemblies result from several interactions and forces: assembly is mainly driven by capillary forces, convection, hydrophobic interactions, electrostatic interactions (often repulsive coming from functionalization to avoid random aggregation) and weak attractive forces: Van der Waals forces between the NRs, which become important with the solvent evaporation and the NRs compaction [132]. Moreover gravity or thermal flow and thermodynamic or entropic effects can have a predominant role on the final equilibrium assembly. Faced with so many determining forces, it is difficult to predict in advance the kind of assembly that will be produced. Even with very simple model that does only take into account hard-core rods without any surfactants or solvent effect, the calculations are complex and need assuming many hypotheses [134]. However there are some parameters that can be adjusted to optimize the chance to obtain the desired assembly such as NRs concentration, solvent and surfactants, substrate, NRs morphology and evaporation rate.

Before reviewing those parameters, it is interesting to mention that above a certain aspect ratio this method gives worse results: NRs/NWs assemblies obtained then are very poor in terms of organization [135]. It is believed to be caused by the weight of those anisotropic particles that is too large to continue neglecting gravity. However some smectic-like phases (multilayered) were observed with NWs by simply drop-casting solution into wells glass and let the NWs precipitate by gravity without drying the solution [135]. The assemblies were examined from below using optical microscopy (to avoid any drying step). Still, the best results were obtain for the shortest NWs (2 μm long).

Nanorods concentrations. Martín et al. designated the NR suspension concentration as the main factor influencing the self-assembly process over other parameters including the temperature and the substrate [132]. They have performed Au NR assemblies into vertical arrays by droplet evaporation method, using NR organic suspensions of different concentrations, which varied from 1.4 nM to 14 nM. As one can notice from the Figure 2.48, the size of the dried droplet decreases while the decreasing NR concentration, even if the initial deposited droplet size was equal (10 μL). One could thus think that the compactness of the assembly will not be very different for compensated by the decreasing of the surface assembled. But it is not completely the case: the defects areas decreased while increasing NR concentration. Figure 2.48 (b) shows the variation of the surface coverage versus the NR concentration. At low concentration (1.4 nM, marked by

the number 1 in the graph and in the inset), small domains of NR arranged vertically (average size of $2 \mu\text{m}^2$) have been observed, occupying 34 % of the total area covered by the droplet. Remaining areas were empty or with few NRs deposited horizontally to the substrate. For higher concentration (14 nM, marked by the number 3 in the graph and in the inset), domains presented an average size of $20 \mu\text{m}^2$ and covered around 94 % of the surface.

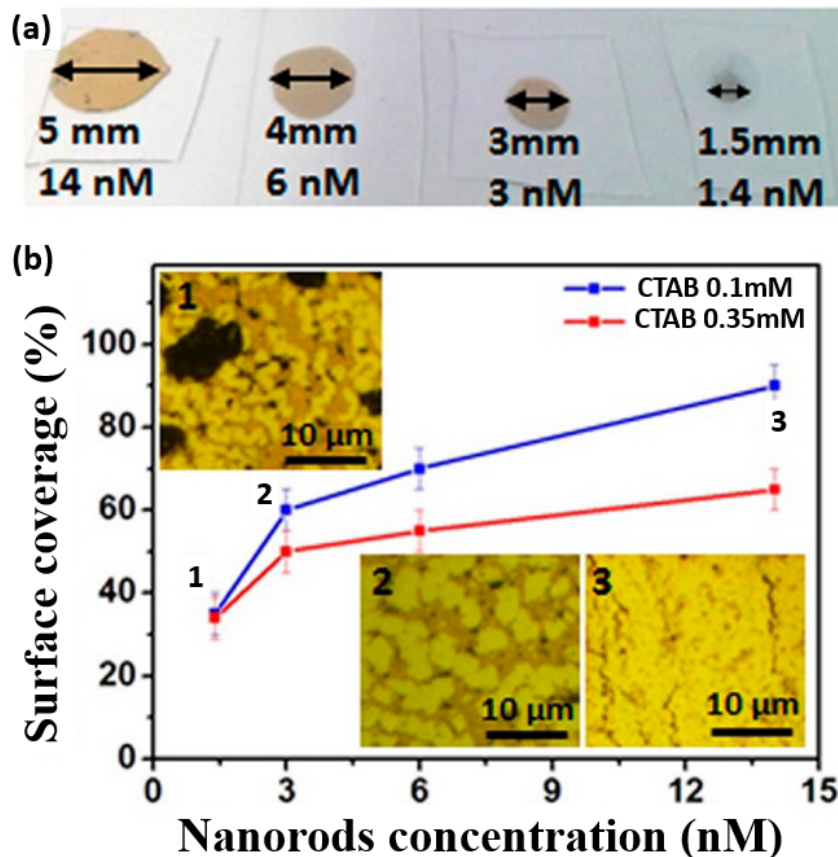


Figure 2.48: (a) Photographs of dried droplets obtained from Au NR chlorobenzene solutions for different concentrations. (b) Variation of the surface coverage versus the NR concentration for 2 different concentrations of CTAB. Reproduced from [132].

Nobile et al. have observed similar results but with horizontal assemblies: when the NR concentration decreases, the length and the density of the ordered fringes decreases [129]. One can even see in Figure 2.49 that the NR concentration increase allows transition from a nematic to a smectic phase. However, increasing the NR concentration tends to lead more easily to formation of multilayer assemblies. Besides, the determination of the mono- or multilayer nature of the assembly can be difficult if there is no defect in the surface. A defective assembly, where the 3D character of NR "leaves" is easily perceptible, is presented in Figure 2.49 (d).

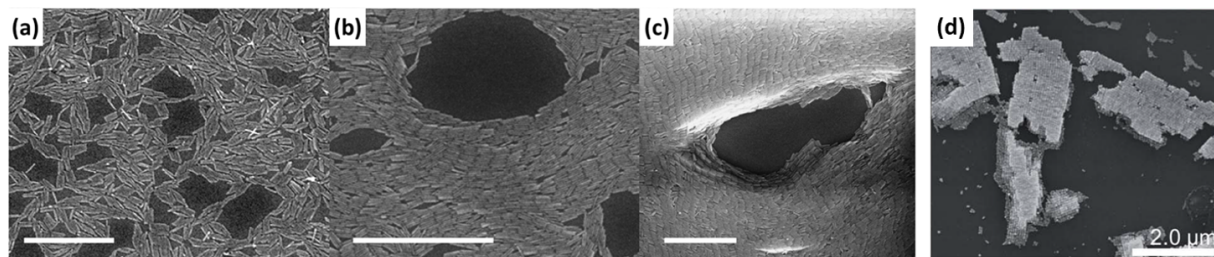


Figure 2.49: (a-c) SEM images of CdSe/CdS core/shell NRs deposited on GaAs substrates by drop-casting method at increasing NR density. The scale bar corresponds to 500 nm. (d) SEM image of gold NRs 3D "leaves" in the pinned edge area. Reproduced: (a-c) from [129] and (d) from [133].

Solvent and surfactants. Ordered close-packed assemblies have been obtained for several solvents especially for water and toluene. Although water seems adapted for several studies using CTAB-capped Au NRs, Martín and his coworkers reported the use of chlorobenzene as the best solvent for their system [132]. Indeed, in their case, chlorobenzene was essential to obtain the long-range ordering of monolayered NRs. By doing the same deposition with an aqueous solvent, they obtained accumulation of NRs at the periphery, forming dense multilayered arrays. They supposed the lower viscosity and surface tension of chlorobenzene compared to water contributed to the higher ordering. NRs were thus more mobile and could reach the equilibrium position more freely.

Of course the solvent effect is directly related to the surfactants or functionalizations that coat the NRs. According to Wang and coworkers, these stabilizing surfactants are essential for the ordered assemblies formation during droplet evaporation [18]. They have studied the self-assembly of Au NRs by solvent evaporation using CTAB as the cationic stabilizing surfactant. Their results revealed that CTAB concentration had to be higher than a critical value to lead to an ordered structure. For instance, for NRs with aspect ratio equal to 4.4, CTAB concentration had to be

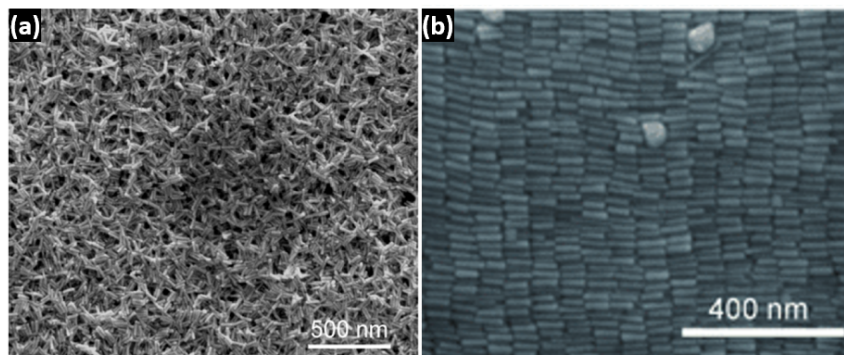


Figure 2.50: SEM images of droplet edges obtained after drop-casting of Au NRs (aspect ratio = 4.4) with CTAB concentration below (a) and above (b) critical concentration (1 mM). Reproduced from [18].

larger than 1 mM otherwise NRs tended to form a disordered structure (Figure 2.50). This critical concentration corresponds to the surfactant quantity needed to form a bilayer on the NR surface. When surfactants are adsorbed to the surface, NRs become positively charged, which enables them to stabilize in the aqueous phase. If NRs were not functionalized with surfactants such as CTAB, they tended to aggregate in a disordered way because of the Van der Waals attraction existing between them. Surfactants adsorbed onto the surface exert electrostatic repulsion to neighbouring NRs, leading to balance with the attractive forces. However, the concentration of surfactants has to be controlled to avoid disturbing the assembly formation because the NRs and the excess of cationic surfactants tend to phase-separate and generate their own structures [133]. Therefore, an appropriate concentration of surfactants is required for an ordered NR self-assembly. Similar results are presented in Figure 2.48 (b). The surface coverage occupied by NRs on the substrate was higher at 0.1 mM than at 0.35 mM [132].

Substrate. The substrate and its interactions with the drying solvent have obviously major impact on the final NR assembly. Depending on the solvent and the hydrophobicity or hydrophilicity of the substrate, the contact angle of the droplet on the substrate will change. One can easily understand the different consequences for the coffee stains hence for the NR assembly if the droplet makes convex or concave meniscus with the substrate. One example of difference induced by substrate is given by Min et al. that performed drop-casting on gold surfaces functionalized with different SAMs [131]. The results can be seen in Figure 2.51 and one can especially notice that the coffee-rings do not appear in the case of a hydrophobic surface (functionalized with hexadecane thiol). This behavior is attributed to constant droplet edge movement of the colloidal Au NRs during evaporation, induced by the hydrophobic surface with 90° (or more) contact angle of the droplet. There is no "stick-slips" process because pinning is not strong enough. However there are still numerous close-packed ordered islands of NRs in the "non-coffee ring" drop-casting. These results suggest that an appropriate functionalized substrate could lead to a larger scale ordered assembly if the conditions (in particular concentration) are properly adapted. Indeed, during "stick-slip" process, ordered assemblies only occur in the coffee-rings which are not very large and definitely not always homogeneous all along their thickness.

Nanorod size and polydispersity As already explained, too long aspect ratio NMs and especially NWs give rise to poorly ordered assemblies by drop-casting. Moreover different organization of NRs depending on their size (and aspect ratio) can appear. For example, Iacopino et al. did drop-castings of several Au NR sizes in chlorobenzene [136]. Au NRs of 16 nm in diameter and 41 nm in length gave rise to horizontal closely-packed side-by-side alignment (in

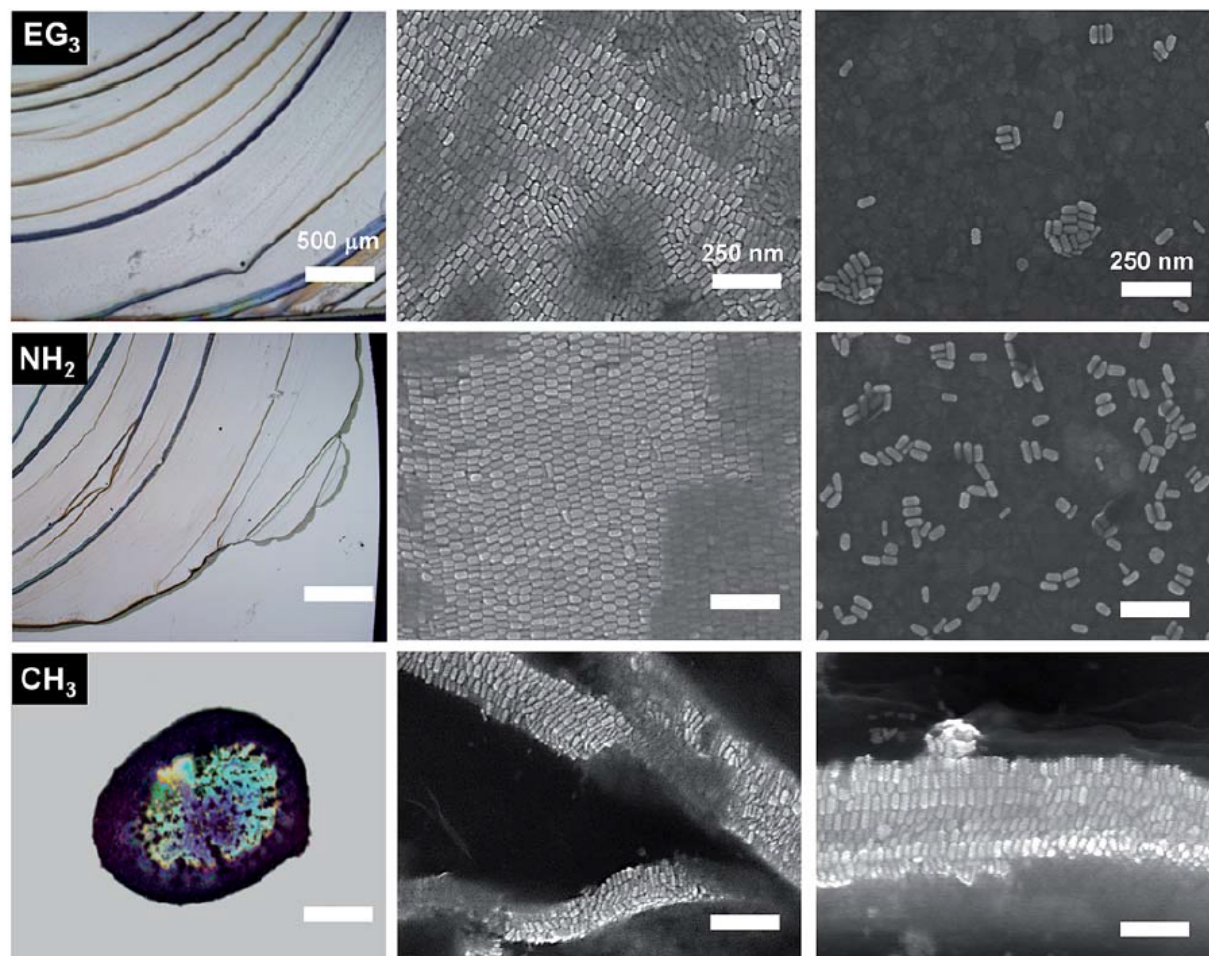


Figure 2.51: Images of Au NRs assembled by drop-casting on SAMs Au substrate with different end-functional group (EG_3 is tri(ethyleneglycol)). (First column) Bright field images, (Second column) SEM images of ordered assembly structures at the edge and (Third column) at the center. The scale bars are 500 μm in bright field images and 250 nm in SEM images, respectively. Reproduced from [18].

chlorobenzene). However, when the NRs were 23 nm in diameter and 55 nm in length, contrary to the previous case, they organized into vertical arrays onto the substrate (see Figure 2.52). It is believed that only NRs with very small aspect ratio (~ 2) are able to align vertically. It is therefore extremely important to have very narrow size distribution with such small NRs. In the same spirit, Wang and coworkers performed the self-assembly of NRs by drop-casting technique, using a binary mixture of Au NRs at a molar ratio close to 1:1 [18]. Two solutions of different NR sizes ($(16 \pm 2) \times (64 \pm 5)$ nm and $(11 \pm 1) \times (29 \pm 2)$ nm) were mixed and deposited onto a substrate. After drying, NRs separated from each other and formed their own smectic structure as presented in Figure 2.53. It seems that the NRs segregate depending on their size. Therefore

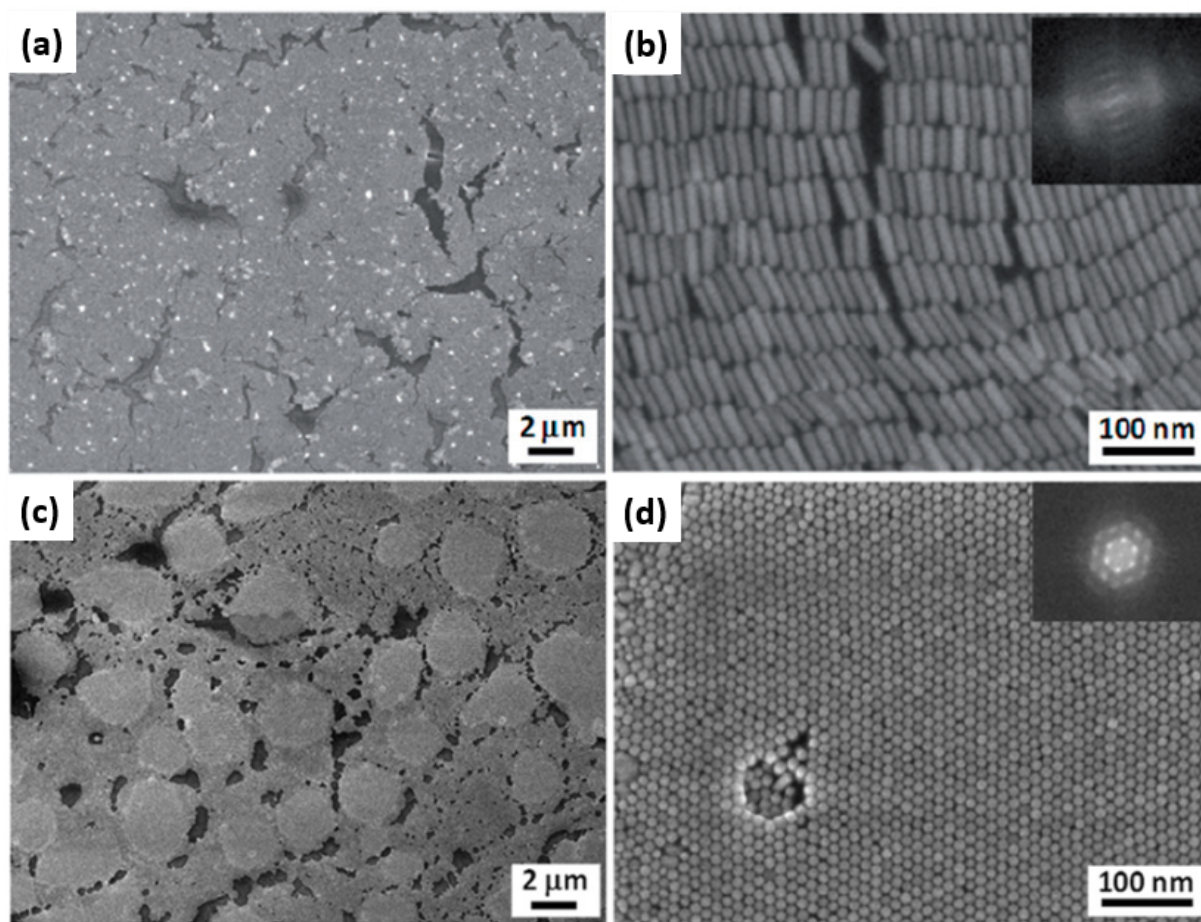


Figure 2.52: SEM images of ordered nanostructures obtained from Au nanorods, (a-b)) 15×41 nm and (c-d) 23×55 nm, inside chlorobenzene droplet deposited onto silicon substrate. Reproduced from [136].

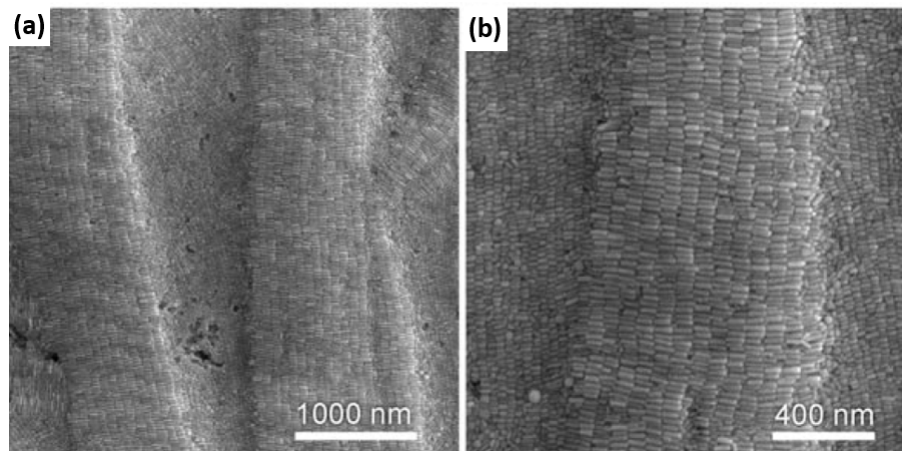


Figure 2.53: SEM images of structure formed by a binary mixture of Au NRs with different sizes: $(16\pm2)\times(64\pm5)$ nm and $(11\pm1)\times(29\pm2)$ nm, dropcasted in water onto silicon substrate. Reproduced from [18].

it seems logical to think that increasing the size polydispersity will be detrimental because assemblies of NRs with different sizes will disturb each other. On the other hand one could think of a regular porous pattern obtained with "large" NRs that could be stuffed by "small" NRs. This kind of assembly has not been found in the literature: almost all studies used very narrow size polydispersity, requiring sometimes long purification process to obtain NRs very similar in size. Drop-casting method has also been used to self-assemble other Au NMs of various shapes. And of course the results showed that ordered assemblies depend strongly on the shape of the NMs. For example, Au polyhedra assembled into a hexagonally packed superstructure, whereas Au nanocubes presented a tetragonally packed superstructure [18].

Evaporation rate. The evaporation rate is also an important parameter to take into account during the drop-casting technique. It has been described by Xie et al. and Lin et al. that a slow evaporation favors vertically aligned NRs on large surface and prevents the "coffee stains" effects [133, 137]. The pinning is believed to be less important during slow evaporation (especially in a solvent saturated atmosphere) and then the contact line moves back constantly without real accumulation of NRs on the pinning angle. Moreover the convection effect is less pronounced during slow evaporation which could induce a near-equilibrium environment hence the closely-packed vertically aligned NRs (see Figure 2.54). Consequently the surface covered during slow evaporation includes an outer edge filled with horizontally aligned NRs and a large surface center covered with close-packed vertical NR assembly. Figure 2.55 (a) presents a SEM image of such assembly. But very surprisingly, as one can see in Figure 2.55 (b), Martín et al. obtained an

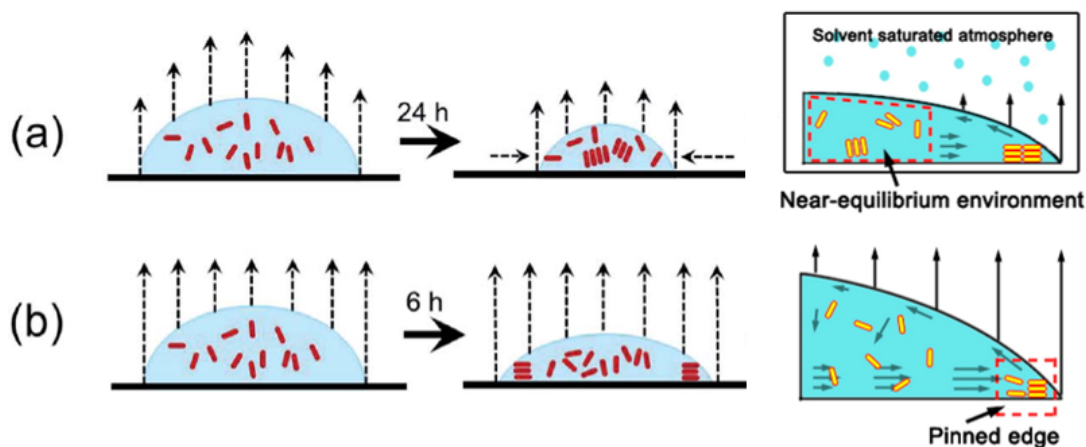


Figure 2.54: Self-assembly of gold NRs on silicon substrate induced by (a) Slow evaporation favoring large surface with NRs vertically aligned, (b) Fast evaporation favoring coffee stains surface with NRs horizontally aligned. Adapted from [133] and [137].

opposite structure during slow evaporation in chlorobenzene [132]. It may be due to the solvent that gives a different contact angle at the droplet edge. Anyway in the same study they compared several evaporation rate and concluded that defects decreased with evaporation rate, therefore the surface coverage increased.

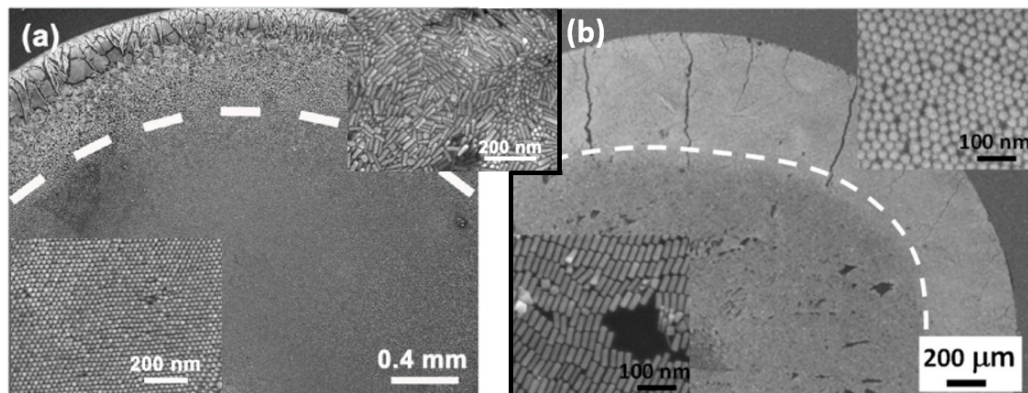


Figure 2.55: Self-assembly of gold NRs on silicon substrate induced by (a) Slow evaporation favouring large surface with NRs vertically aligned, (b) Fast evaporation favouring coffee stains surface with NRs horizontally aligned. Adapted (a) from [137] and (b) from [132].

Increasing temperature above a certain limit seems also to perturbate the assembly. Wang and coworkers could only obtain disorganized assemblies of Au NRs, when temperature was set to

a higher value than 60°C [18]. They believed this resulted from the fact that high temperature increases the speed of evaporation, hence NRs do not reach their equilibrium positions. However the thermal agitation may be the only reason that prevented close-packed assembly.

2.3.2.3 Assembly at the fluid-fluid interface

When two immiscible fluids such as oil and water are put in contact, they form two different phases. As it was already discussed in Section 2.2.4, the presence of NPs at the interface is often thermodynamically favored since it decreases the liquid-liquid surface area, leading to a decrease of the total free energy of the system [107]. The NPs confinement at the interface allows the formation of monolayers where the supramolecular forces between NPs can stop to be negligible. Eventually self-assembly can occur, taking different micro-structures, more or less ordered [138]. Before that, the first step remains the confinement of the NPs at the interface and the reasons why it happens will be described more deeply.

Nanoparticles confinement at fluid-fluid interface. When an interface is created, the surface tension (or surface energy) parameter can be determined. Thermodynamically it will tend to force the fluid to occupy the smallest surface area. As already seen in the case of the Pickering emulsion, NPs at this interface allow the decrease of this interface surface area, leading to stabilization of droplets of one phase inside the other. The same theory can be applied to flat interfaces. Despite the fact that here the emulsion can not be sustained by the NPs, the attraction and stabilization of the NPs at the fluid-fluid interface is still often thermodynamically favored. In that case the interfacial energy is decreased by this NPs confinement at this interface. Indeed usually, the sum of the surface tension between the solid and the oil ($\gamma_{s/o}$) and the solid and water ($\gamma_{s/w}$) is lower than the surface tension between the two fluids ($\gamma_{w/o}$).

To go further one can establish a model for a nanosphere where the contact angle ($\theta_{w/o}$) depending on the surface tension between the different elements is given by the Young-Dupre equation:

$$\cos \theta_{w/o} = \frac{\gamma_{s/w} - \gamma_{s/o}}{\gamma_{w/o}} \quad (2.6)$$

The different elements of this equation are sketched on Figure 2.56 (a).

With these elements, the interfacial energy E , mediated by NPs, can be determined as:

$$E = -\pi r^2 \gamma_{w/o} \quad (2.7)$$

where r is the radius of a spherical NP at the interface. So the attachment energy of the NP reaches the highest value when the particle presents the same affinity with both phases (i.e. $\theta_{w/o}=90^\circ$). A small deviation from 90° can sometimes lead to detachment of particles from the interface [139]. Eventually it leads to the calculation of the reduction in interfacial energy depending on the contact angle $\theta_{w/o}$:

$$-\Delta E = \pi r^2 \gamma_{w/o} (1 - |\cos \theta_{w/o}|)^2 \quad (2.8)$$

The absolute value arises from the fact that the NPs can come from one or the other fluid [107]. This is the same equation than the one presented during description of Pickering emulsions (Equation 2.4) but this time since the interface is flat, it is exact.

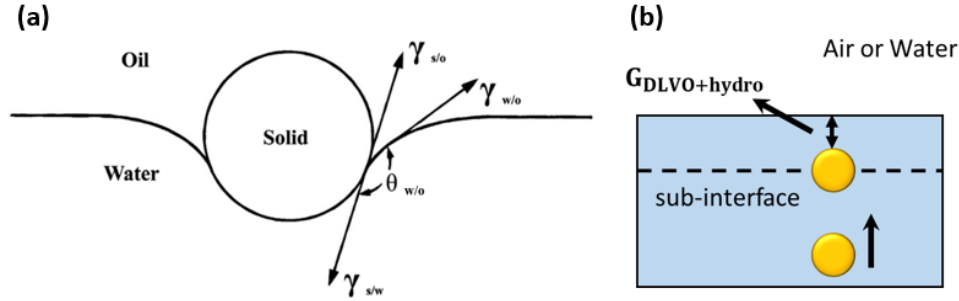


Figure 2.56: (a) Sketch of the surface tensions and contact angle at the liquid-liquid interface. (b) Schematic of the sub-interface model. Reproduced from [140] and adapted from [141], respectively.

The decrease in total interfacial energy is the main driving force for the NP movement towards the interface which results in a deep potential well enabling strong trapping of the NPs at the interface and their self-assembly. However, even if the NP adsorption at the interface is thermodynamically favored, it does not always occur. According to Xiang et al., this proves the existence of a sorption potential barrier ($G_{DLVO+hydro}$) inhibiting the particle adsorption kinetically [141]. The particle adsorption can be seen as a two-step process. First, the NP diffusion from the bulk to the sub-interface occurs due to the concentration gradient. The sub-interface corresponds to the location where the interactions between the interface and the NPs becomes non-negligible. Then, the NPs are adsorbed from the sub-interface to the interface. The sorption barrier makes the rate of the adsorption step much smaller than the rate of the diffusion step, so that the overall NP adsorption process is usually kinetically controlled. The Figure 2.56 (b) shows the schematic model revealing the sub-interface and the barrier to overcome, controlling the NP adsorption.

The sorption barrier $G_{DLVO+hydro}$ energy is the resulting addition of the hydrophobic interaction energy G_{hydro} , which corresponds to long-range attractive force between particle and interface [142], and the Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction G_{DLVO} , corresponding to the sum of the attractive Van der Waals forces and the repulsive electrostatic force (from the surface NPs and the solvents).

$$G_{DLVO+hydro} = G_{DLVO} + G_{hydro} \quad (2.9)$$

where the hydrophobic energy can be expressed as a function of the distance h from a flat air or oil surface and the force constant K_{132} for the particle (1) interacting with the second phase (2) across the first phase (3):

$$G_{hydro}(h) = -\frac{K_{123}}{h} \quad (2.10)$$

The force constant is dependent on the system (parameter a and b), the contact angle $\theta_{w/o}$ and the contact angle between the two phases θ_0 (usually set to 180°):

$$\log K_{123} = a\left(\frac{\cos \theta_{w/o} + \cos \theta_0}{2}\right) + b \quad (2.11)$$

The G_{DLVO} energy can be calculated thanks to DLVO theory which is mainly based on the Van der Waals interactions and so on the effective Hamaker constant A_{132} . It corresponds to a particle (1) interacting with the second phase (2) across the first phase (3) and it is based on the Hamaker constant A_{ii} for a material (i) interacting with itself in vacuum:

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (2.12)$$

So the sorption barrier $G_{DLVO+hydro}$ can vary depending on several intrinsic factors. Xiang et al. studied the effect of the NP hydrophobicity on the adsorption at the water-air interface. They made calculations by giving different hydrophobic character to the particles, resulting in different contact angle $\theta_{w/o}$. Moreover they made the assumption that the repulsive DLVO interactions are constant and not affected by the hydrophobic coating. The Figure 2.57 (a) shows the variation of calculated sorption barriers $G_{DLVO+hydro}$ versus the separation distance h between silver NP ($r = 50 \text{ nm}$) and water/air interface for different hydrophobicities expressed by the contact angle (20 to 55°). As one can notice, $G_{DLVO+hydro}$ decreases with the increasing contact angle, which seems logical since the hydrophobicity increased while the NPs come from the water phase. But one can also see that calculations predict a high sorption barrier for hydrophilic

particles (especially at $\theta_{w/o} = 20^\circ$), and hence adsorption of hydrophilic particles is kinetically disfavored. Consistently, they experimentally observed that it was difficult to induce movement of mercaptoacetic acid-modified silver and gold NPs to water–air and water–oil interfaces [141].

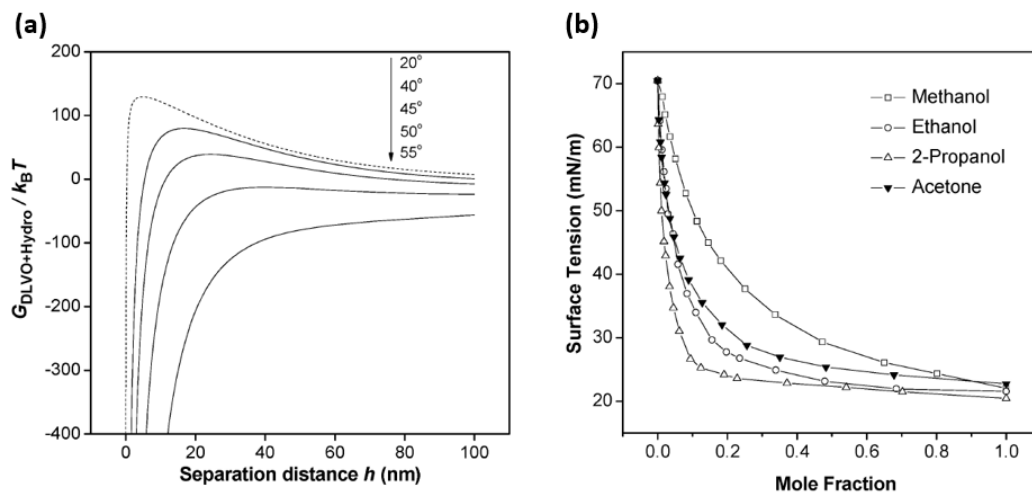


Figure 2.57: (a) Sorption barrier between a silver particle ($r = 50$ nm) with varying particle hydrophobicity and a water–air interface. (b) Surface tension of aqueous solutions of organic solvents as a function of organic solvent mole fraction. Reproduced from [141].

In addition some calculations have been made on the role played by solvents inside the system. It has been shown that addition of organic solvent (soluble inside water such as ethanol or acetone) decreases the attractive potential of G_{hydro} . Kokkoli et al. have experimentally observed this co-solvent induced reduction in the hydrophobic force [143]. However, these neutral organic solvents have been determined as surface-active, that is their positive adsorption at the interface dilutes the charges on the fluid–water interface and thus decreases the repulsive electrostatic forces to a larger extent than the attractive hydrophobic forces. One can see one effect of this solvent dilution into water in Figure 2.57 (b) where the surface tension of water drastically drops when solvent is added. This eventually means that G_{DLVO} is largely reduced by solvent addition, leading to a global decrease of the sorption barrier by adding diluted solvent in the system.

To summarize, NPs can be attracted more easily at oil–water or air–water interface if they are more hydrophobic and if surface-active solvents are added. This is the main reason why numerous studies add some ethanol during the oil–water or air–water self-assembly process [138, 144, 145, 146]. In the case of 1D NRs, the orientation of the particle has a strong influence on the reduction of the surface energy, which reaches a minimum when the long axis is parallel to the surface. However, the ligands also influence the orientation. Indeed, NRs functionalized with highly hydrophobic or hydrophilic ligands can have a perpendicular orientation since the

tip usually contains a lower density of ligands (Figure 2.58). Similarly, hydrophobic/hydrophilic Janus particles show a greater reduction in surface energy than homogeneous particles [147]. This illustrates well the benefits of surface functionalization for NP assemblies.

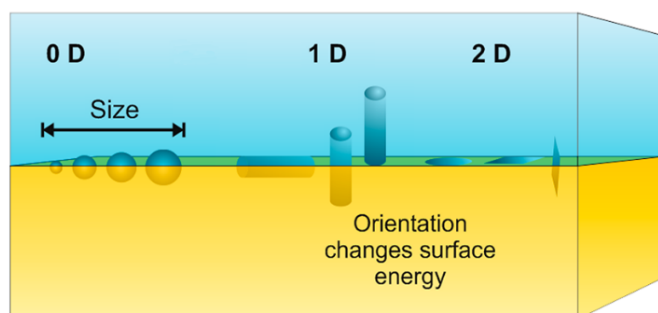


Figure 2.58: Schematic showing particles with different dimensionality assembled at liquid/liquid interfaces. Reproduced from [147]

Self-assembly results The first assemblies of NPs at the oil-water interface were performed by Vanmaekelbergh et al. (in 2004) that assemble Au NPs [138] at toluene-water interface. The film obtained was not completely close-packed but was clearly a monolayer (Figure 2.59 (a)). Later, Wang and his coworkers obtained similar results by doing the assembly at the water-pentanol interface and heating to evaporate the pentanol afterwards [148]. The assembly was thus floating at the air-water interface and when it was fished they noticed that the film was freestanding. It is believed that the pentanol functionalized the NPs and maybe heating allows a sort of film-gel development composed of the NPs and residue of the dried solvent. This assembly only occurs

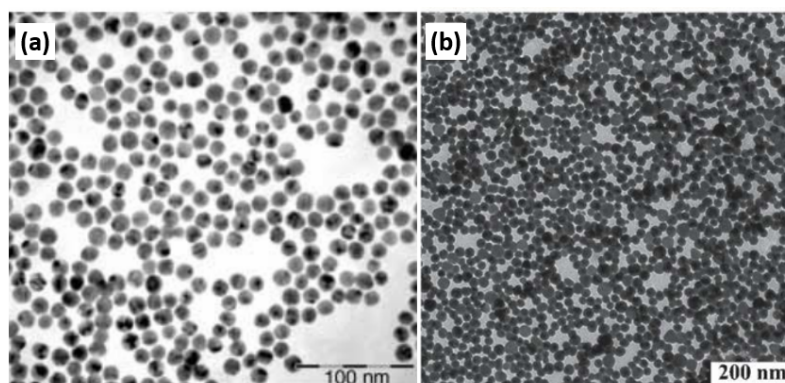


Figure 2.59: (a) TEM image of Au NPs self-assembly collected from heptane-water interface. (b) TEM image of freestanding monolayer film of 12 nm gold NPs obtained by self-assembly of the NPs at the water-pentanol interface in a Petri dish, followed by heating at 48°C for 3 h. Reproduced (a) from [138] and (b) from [148], respectively.

when heating treatment was performed: letting the pentanol evaporate at room temperature did not lead to such freestanding film. The resulting self-assembly can be seen in Figure 2.59 (b). Despite a good long-range surface order, the assemblies obtained were still not completely densely packed, the first close-packed assembly was obtained by Park et al. They had the idea, mimicking Langmuir-Blodgett process, to mechanically compact air/water floating Au@Pt core/shell NPs assembly until obtaining an optical mirror-like film surface [19]. However it led sometimes to multilayered assembly and, knowing when to stop the compression to obtain the number of layers desired was not easy. Eventually they concluded that results were better with Au NPs functionalized *in situ* [149] (Figure 2.60). The functionalizations were long alkyl-chain thiols but

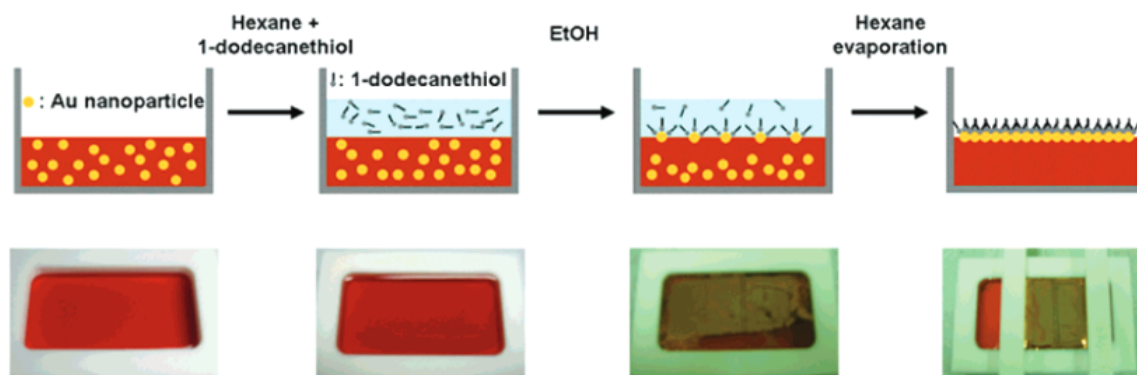


Figure 2.60: Schematic representation of the NP film formation with each corresponding side view of cartoon chemistry (the first row) and with optical images (the second row). Notice the compression step, by bringing two Teflon bars closer to each other. Reproduced from [149].

the particularity of the process is that thiols are placed inside the oil phase (hexane) while the Au NPs are originally in the water phase. By adding some ethanol the NPs are attracted and finally trapped at the interface where one of their hemisphere is functionalized and they self-assemble. This results in a highly ordered Au NP film. And as one can clearly see in Figure 2.61, the assembled film with the absence of 1-dodecanethiol shows large void areas equivalent to a range from one to five NPs, while the film prepared with an appropriate amount of 1-dodecanethiol (4.17×10^{-7} M) displays highly ordered hexagonal packing without voids. The adsorption of 1-dodecanethiol to the NPs surface decreases the surface charge density of these NPs, leading to a further decrease in their electrostatic repulsive force, thus favoring a close-packed assembly. Indeed several studies argued that charged particles did not lead to close-packed assemblies due to their self-repulsive interactions. One can still remark that the addition of too large quantity of 1-dodecanethiol results in NPs overlapping.

Recently a study led by Yang and Hallinan Jr, used the same *in situ* functionalization technique to assemble Au NPs partially coated with alkylamines [144]. The longer the alkyl chain was, the

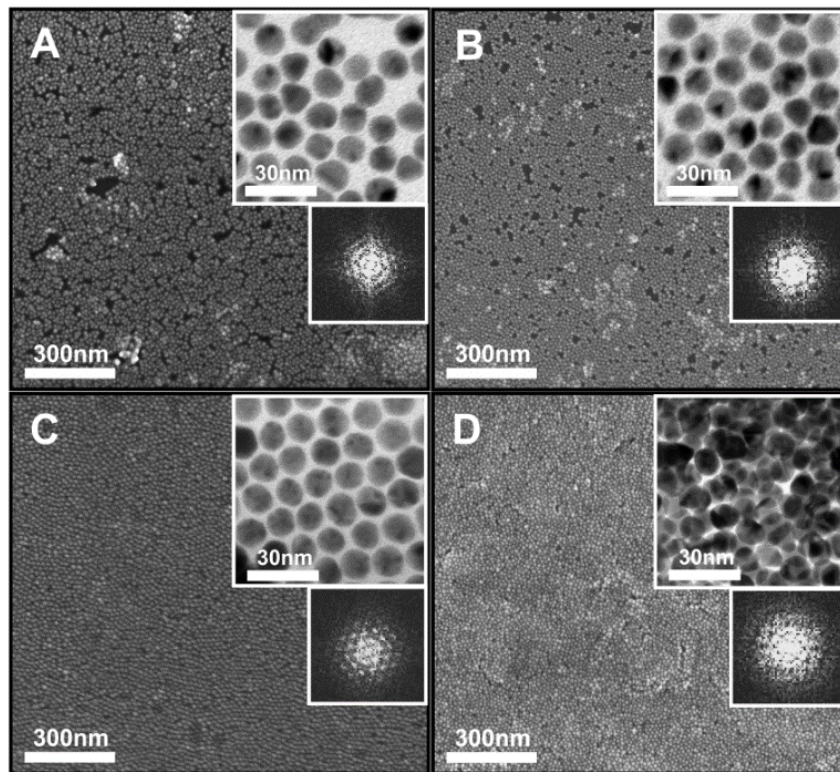


Figure 2.61: FESEM and TEM (upper right insets) images of NP films transferred on silicon wafers. The films were prepared in the presence of 1-dodecanethiol, (A) 0, (B) 4.17×10^{-9} , (C) 4.17×10^{-7} , and (D) 4.17×10^{-4} M in a hexane layer. Corresponding FFT images are shown in the lower right insets. Reproduced from [149].

better the order (and packing) obtained was. One can also cite a study that managed to obtain close-packed binary crystals superlattices from Fe_3O_4 and FePt NPs [150]. To obtain an ordered assembly with a low defect content, the ratio and size between the particles had to be carefully chosen. The assembly was performed at the diethylene-glycol hexane interface.

Some studies also used another compression technique when the assembly was floating at the air water interface. Sashuk et al. [151] demonstrated the possibility to compact amphiphilic NPs dispersed at a air-water interface by adding one droplet of tetrahydrofuran (THF) to the water surface by a syringe, causing a fast shrinking of the NPs into a compact film (see figure 2.62). Because of the asymmetry in the distribution of capillary forces hence surface tension gradient, the NPs move towards the higher surface gradient area. This process, called "capillary trap", is fully reversible if there is no strong irreversible interactions between the particles, but the relaxation is rather slow compared to the response to the onset of the stimulus because of hydrophobic interactions. It was therefore possible to analyze the assembly by SEM before and

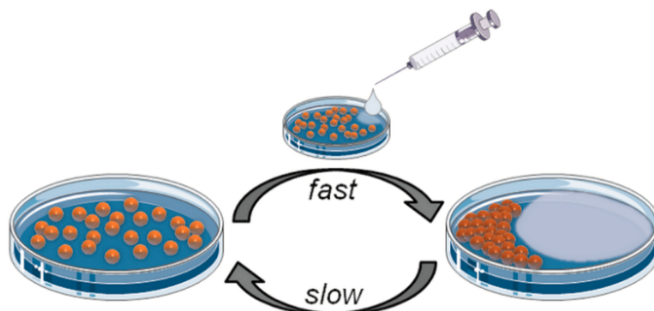


Figure 2.62: Illustration of dynamic self-assembly of the NPs at aqueous-air interfaces. Adding solvent to the fluid interface creates a surface tension gradient, making the NPs compress into dense film. When the external stimulus is discontinued, the NPs disperse throughout the interface. Reproduced from [151].

after the compression (on two separate samples).

Li et al. used a similar process to obtain (hexagonally) close-packed assemblies of Au NPs coated with poly(diallyldimethylammonium) (PDDA) [152]. They tried compression by "capillary trap" with several solvents and noticed that the best results were obtained with ethanol (results with methanol were also very densely packed but fragmented on "large area" as shown in Figure 2.63). Li and his coworker did not observe relaxation after the compression. It may be due to the coating of the NPs or perhaps relaxation time is very slow and they did not wait enough to complete it.

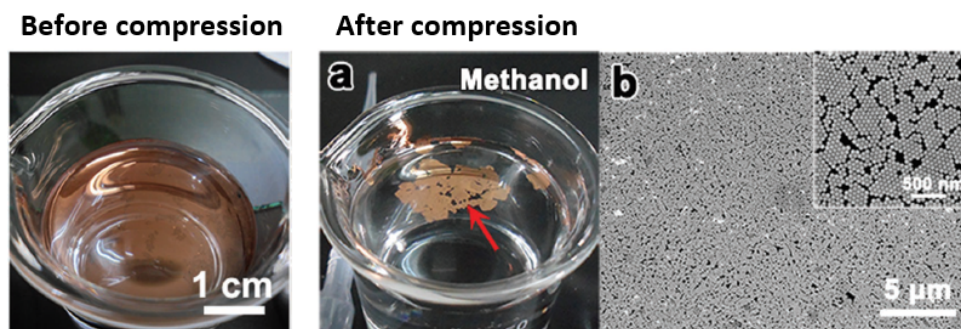


Figure 2.63: Photographs of Au monolayer floating on the water surface before and after compression (a) and SEM images of the compressed assembly (b). Reproduced from [152].

The assemblies of NRs at oil-water interface was very little studied but Park and his coworkers published several studies on this topic [13, 153]. They used their mechanical compaction technique on water-hexane interface with CTAB capped Au NRs. Their experiments were performed on several Au NRs with different aspect ratio. The self-assemblies obtained had poor order and were multilayered. The results are presented in Figure 2.64.

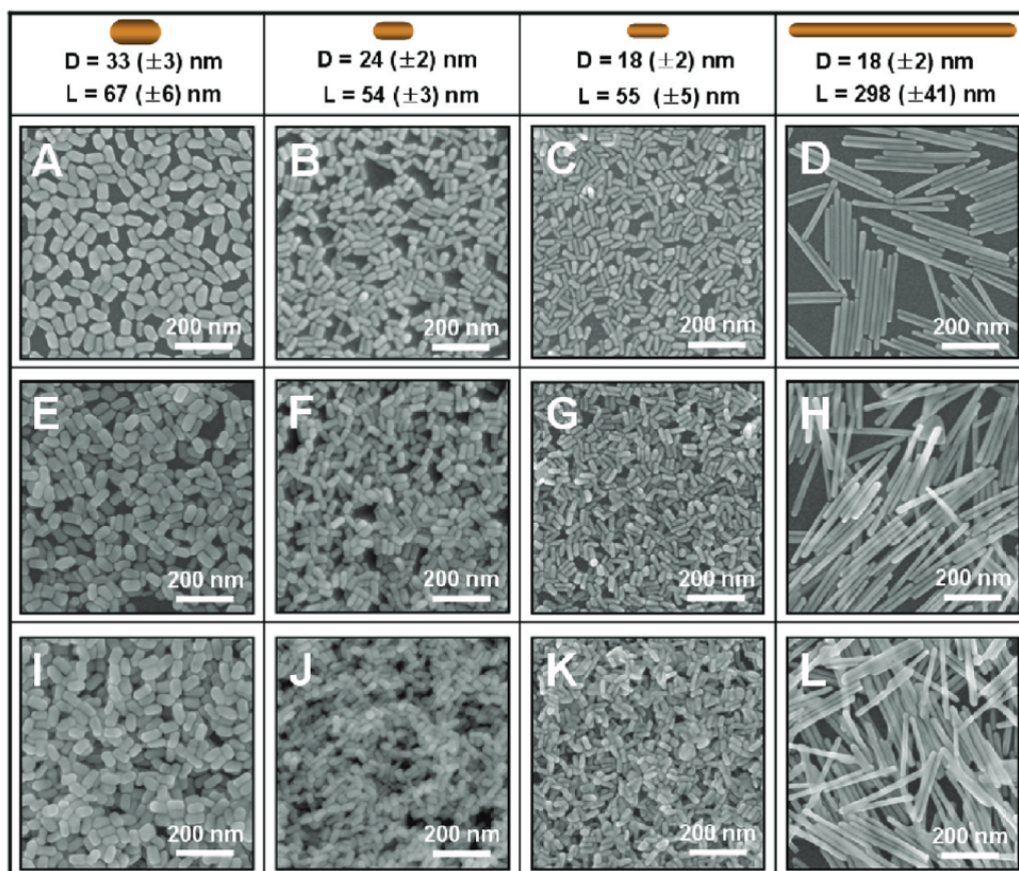


Figure 2.64: FESEM images for different aspect ratio gold NR films as a function of the estimated layer number. (A-D) Monolayer NR film for each sample. (E-H) Bilayer. (I-L) Four layers. Reproduced from [13].

Characterization techniques Once the particles are assembled at the interface, it is often required to transfer the assembly on substrates to characterize it. Indeed, some reflection or scattering techniques exist to partially characterize the assemblies at the interface and especially at the air-water interface but these techniques gave only vague results that cannot be sufficient to know the exact micro-structure of the assembly. SEM and TEM, for example, give way better results but require transfer and drying of the assembled films onto substrates. This transfer is not obvious at all, therefore the technique developed to manage it will be described here. The most common technique to transfer the assembly on a substrate is the "fishing" technique. It simply consists in recovering the assembly by immersing a substrate below the film and lifting it up (Figure 2.65). This technique has many disadvantages and especially its poor reproducibility since it is a manual technique with many parameters left uncontrolled such as the penetration angle of the substrate in the interface, the angle during lift off or the speed of the process. Moreover, a final drying step can also disturb the assembled films. However this technique is

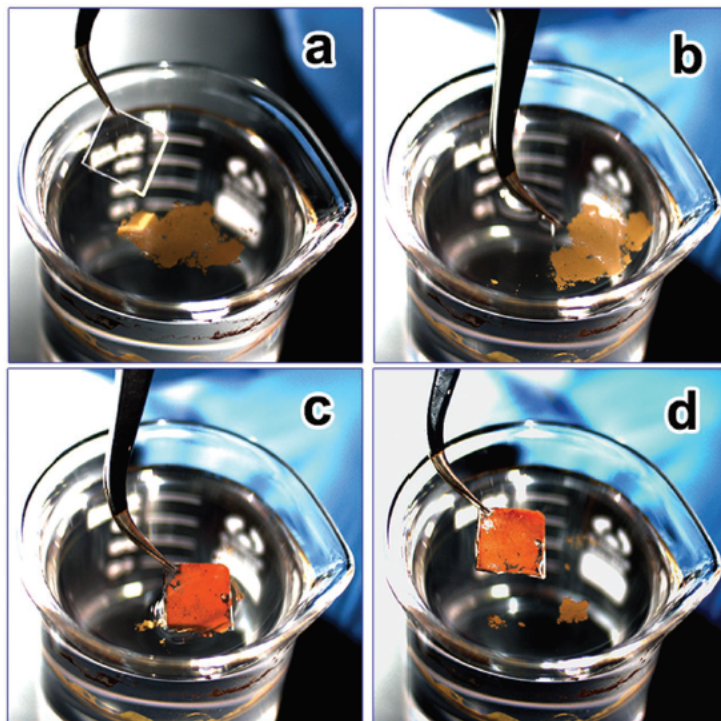


Figure 2.65: Photographs of the fishing process for the Au NPs monolayer film transferred onto a quartz substrate. Reproduced from [152].

very simple and therefore used in most of the studies, even if the authors are often elusive about this topic [13, 19, 149, 150, 153]. On the same principle, Langmuir-Blodgett methods have been developed but the film size is usually limited because of the mechanical perturbations during film transfer [8]. Moreover the implementation of such system is not easy nor inexpensive as it requires very precise mechanical compaction of the assembly during the slow lifting up of the transfer substrate.

Another technique consists in placing the substrate (silicon wafers or copper grids, for example) at the bottom of the lower liquid phase and draining this phase to allow the deposition of the NPs on this substrate. Yang et al [144] used this method, called drain-to-deposit, to form a large area monolayer gold NRs film. The whole process is depicted in figure 2.66, including the functionalization *in situ* of the Au NPs with alkylamine molecules. After hexane evaporation, the aqueous phase was slowly removed with a pump, leading to the progressive descent of the NP film until deposition on the substrate. The complete removal of the remaining solvent cannot be done only by pumping: a thin aqueous film remained and was evacuated by evaporation. This final evaporation may have serious impact on the assembly morphology. The inking of PDMS stamp seems also a good alternative to transfer assemblies. Liao et al. managed to obtain large (and

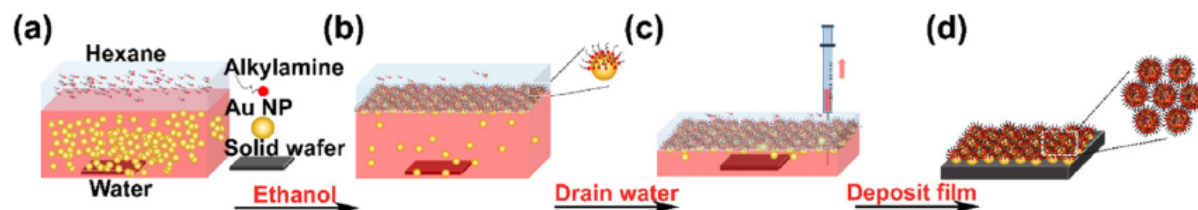


Figure 2.66: Schematic illustration of the Au NP film formation and the drain-to-deposit transfer. Reproduced from [144].

patterned) surfaces of close-packed Au NPs by inking some very hydrophobic PDMS stamp with NP assembly floating at air water interface [154, 155]. Their process is schematically depicted in Figure 2.67 where one can see that they perform a second transfer from the PDMS stamp to print the Au films on structured rigid surface. This technique almost prevent completely the drying disturbance because of the high hydrophobicity of PDMS. However the inking of the PDMS stamp is a very tricky process, where enough pressure/contact have to be done but not too much to avoid disturbance of the floating assembly. Moreover the meniscus at the water surface is often not completely flat which could also induce only partial printing of the assemblies or at least create minor defects.

Eventually some freezing or gelation techniques have been developed [8]. It goes from cryo-TEM to similar technique to Janus particles synthesis via Pickering emulsion: using oil phase at high temperature during assembly and cool down to solidify this phase afterwards [146]. The main problem with those techniques is that freezing or gelation, slow or ultra-fast, certainly induces

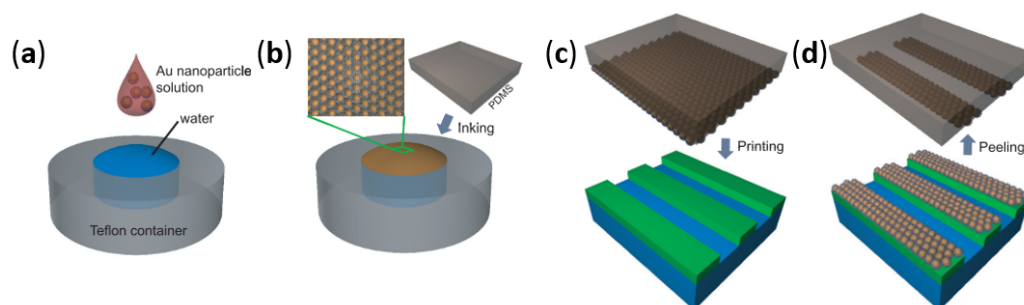


Figure 2.67: Schematic of the strategy to fabricate patterned close-packed NPs arrays. (a) Drops of dodecanethiol-capped gold NPs solution are cast onto slightly convex water surface in Teflon container. (b) After self-assembly and solvent evaporation, a flat PDMS stamp was inked with the NP monolayer(s) by conformal contacting the film for 10 s and lifting. (c) PDMS stamp inked with the NP film is then printed on a structured substrate. (d) Peeling off the PDMS stamp from the substrate left the protrusion structures covered with ordered NP arrays, whereas the complementary arrays stuck to the PDMS stamp. Reproduced from [154].

constraints on the assembly that may lead to reorganization, to cracks or even complete destruction of the assembly.

2.3.3 Applications

Applications of the self-assembly of NWs or NRs are numerous. The main ones will be briefly reviewed here. However as already explained several times the occurrence of NRs assembly being much more important than the ones of NWs, there are more applications implying NRs.

Due to their remarkable electronic and optical properties, metallic NRs (and especially gold ones) are envisaged for many applications. It mainly concerns self-assembly on substrate with applications ranging from simple lithography masks [79] to optical nano-antennas for white-light generation [156, 157] in solar panel materials and harvesting energy systems [158, 159]. One of these application is the surface enhanced Raman spectroscopy (SERS) which has already been mentioned in the introduction. It consists in using a substrate covered with closely-packed NRs assembly (preferentially gold) as holder for molecules to be characterized by Raman spectroscopy [160]. Thanks to the strong interparticle electro-magnetic coupling on such substrate it has been observed a strong enhancement of Raman scattering of adsorbed molecules [13]. SERS can thus more accurately analyze the molecules than the standard Raman spectroscopy because of its higher resolution.

Other applications concerns the NR assembly in solution. One can especially cite sensor applications [162]. The aggregation of NRs can be triggered by a modification in the suspension allowing the detection of this modification. Moreover, with multifunctionalized NWs, the detection could be followed by another action such as drug-delivery, directly linking the field to theranostics [163]. An example of bio-sensors has been developed by Kotov [161]. They manage to graft antibodies and antigens selectively, either on the sides or on the ends of CTAB stabilized Au NRs. By carefully choosing the pH, the antibodies or antigens graft directly onto the CTAB bilayer mainly on the sides of the NRs. To get the function-

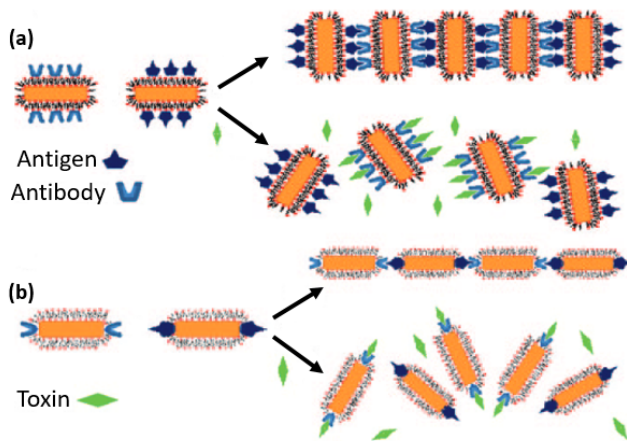


Figure 2.68: Toxin detection method with (a) side-by-side and (b) end-to-end NRs assemblies. Reproduced from [161].

alization on the ends of the NRs, thioctic acid was firstly add, with its thiol group preferentially grafted on the ends of the NRs where the CTAB amount was low. The antibodies and antigens were added to the thioctic acid using activated carboxylic groups and amine groups. Eventually, four types of NWs were obtained and could interact to form different assemblies and in particular end-to-end or side-to-side assemblies. Moreover, the effect of a toxin, microcystin LR, interacting with the antibodies grafted on the Au NRs was studied. When the NRs were placed in a solution contaminated by the toxin there was competition between NRs assembly, mediated by antibody-antigen reactions, and toxin immobilization by antibodies. The assembly did not occur in highly contaminated solution and this could thus be used to detect the contamination (Figure 2.68). Finally there are potential applications that can arise from the better understanding of the assembly process. It could help to mimick natural structures and thus replace it synthetically and maybe even improve it. This may also lead to programmable assemblies: by carefully tailoring NMs, they would assemble on demand and according to predefined but complex designs (Figure 2.69) [9].

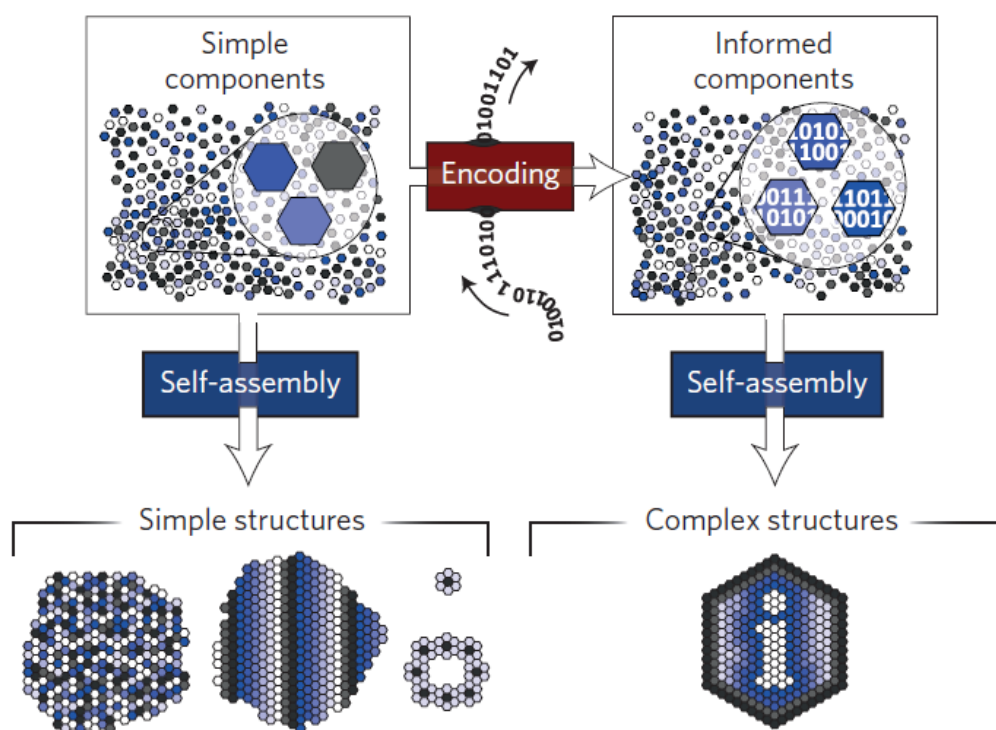


Figure 2.69: Self-assembly can be obtained by simple (with high-symmetry) components but will always leads to simple structures. However the self-assembly of complex structures can be obtained from information-rich building blocks (informed components). The synthesis of such components (or the “simple” encoding step) corresponds to programming the assembly. Reproduced from [9].

Unlike the previous studies that have been reviewed in this chapter, the present work aims at developing a versatile strategy allowing the easy production of metallic NWs for self-assembly. Those NWs will have specific dimensions corresponding to nano-objects whose self-assembly was not (or almost not) previously studied (large diameters around 100 nm and small aspect ratio around 3). Moreover their length should be extremely easy to adapt and multisegmented NWs should be easily feasible with adaptable segment lengths. Those NWs will be functionalized with thiols or LbL and selective multifunctionalization will be attempted using several strategies adapted from the literature. Eventually the assembly of such NWs will be tested for the first time to obtain thin films. The self-assembly will be done by drop-casting and especially at the fluid-fluid interface.

Nanowire Manufacture

3.1 Introduction and objectives

The first step towards the achievement of self-assembly of NWs is the manufacture of the NWs devoid of any functionalization with techniques compatible with selective multifunctionalization in a later step. As described in the previous Chapter (Section 2.1), there are several ways to obtain 1D NW, especially seed-mediated growth, volume-liquid-solid (VLS) growth and template assisted electro-chemical deposition (ECD). In this thesis, the latter technique has been chosen owing to its modularity and flexibility. It allows the manufacture of NWs of many metals (and even NWs of conductive polymers) and it is reported to provide access to multisegmented NWs. The NW size and diameter are controlled by the deposited charge and by the nanopore diameter, respectively. Moreover it should allow the local multifunctionalization of the NWs by masking some of their elements with the template itself, or by including sacrificial layers in the NW structure. Although the manufacture of NWs by ECD has already been widely studied, challenges remain, such as the production of very precisely sized and shaped NWs, the recovery of the NWs in suspension, free of all impurities, and finally, the production of a large number of NWs, which is limited by the 2D nature of the template. Indeed the throughput of template-assisted ECD is not as good as the one of seed-mediated growth which is the most common technique to obtain gold NRs (but is almost only suitable for gold). It is then important to try to increase the throughput of template-assisted ECD to make it more competitive and to obtain more rapidly NW stocks. It is also essential to insure that the NWs obtained are very reproducible from one batch to another; they should have a very narrow size distribution within a batch but also from one batch to another. Moreover the NWs should be cylinders with a smooth lateral surface and flat bases, which will provide better surfaces for the functionalization and subsequent NW assembly. As will be shown in the results of this section, the throughput was essentially increased by

increasing the area of deposition. However, the manufacture of well-shaped NWs of the different metals tried was less easy and required at least very finely tuned parameters. Moreover the recovery of the NWs in suspension (adapted for subsequent self-assembly) was not as straightforward as it would seem.

3.2 Strategies

The template-assisted ECD technique requires a nanoporous template within which metals will be deposited. The most common templates are either track-etched polycarbonate (PC) membranes or aluminum anodized oxide (AAO) membranes. The BSMA department has a relatively good experience in the homemade fabrication of supported AAO templates. This kind of template leads to membranes with mildly ordered nanopores having a diameter that can attain 150 nm and density as high as 10^{10} pores/cm² but their thickness is limited to max. 1.5–2 μ m. Thicker self-supported AAO templates with better pore order are commercially available but they are much more expensive than PC membranes and they are quite brittle. This is why they will not be used in this thesis. PC membranes can only have densities up to 10^9 pores/cm² with no ordering but their thickness is usually around 20 μ m. Considering the differences between those different templates, specific strategies have been developed and tested.

Self-supported homemade AAO templates can be exploited to obtain freestanding NW brushes after dissolution of the template. The NWs can then be functionalized while attached, leading to easy handling and washing processes. Besides, trisegmented NWs with the extremities made of sacrificial layers can be deposited within the template. After dissolution of the AAO, the freestanding NWs can be first functionalized on their side while their ends are still protected by the sacrificial layers. Finally to obtain a different functionalization on the ends, the sacrificial layers can be etched and, after redispersion of the NWs in suspension, the second functionalization should occur only on the ends. A schematic representation of this strategy is shown in Figure 3.1. It is interesting to add that during the formation of the AAO template a constriction of the nanopores develops at the bottom of the membrane requiring the deposition of a sacrificial foot, even for the manufacture of simple NWs (without functionalization); otherwise the constriction will be present on the NWs (Figure 3.2).

In the case of the track-etched PC membrane, the template is self-supported and needs to be metallized to host ECD, but more importantly it cannot generate freestanding NWs. Once the PC is dissolved the NWs have to be recovered in suspension or they will be lost. Moreover in this technique it is also recommended to deposit a sacrificial foot, as with the supported AAO

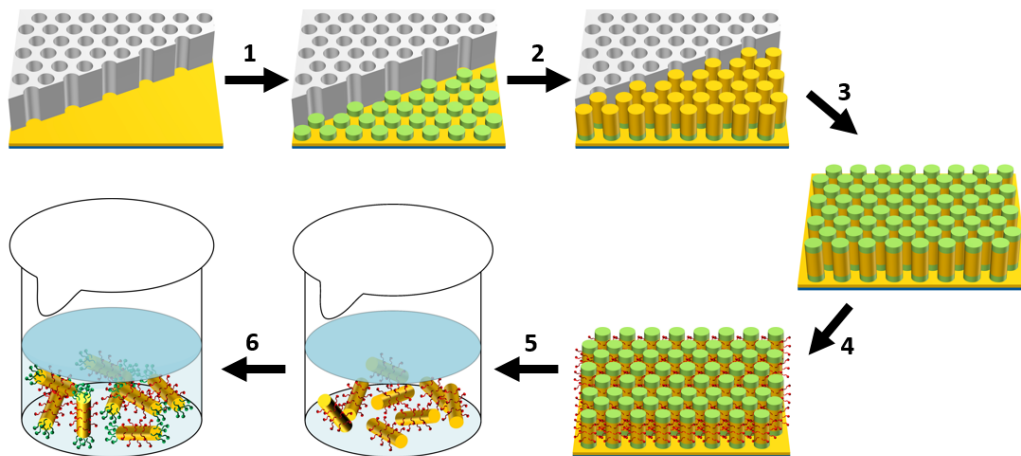


Figure 3.1: Scheme of the strategy used to manufacture selectively bifunctionalized NWs from a supported AAO template. (1) ECD of a sacrificial layer (foot), (2) ECD of the desired material, (3) ECD of the second sacrificial layer and dissolution of the template, (4) side functionalization, (5) sacrificial layer etching and recovery of the NWs in suspension, (6) end functionalization.

template, to prevent some deposition below the membrane at places where the metallization layer would adhere less. The self-supported character of the PC template leads to a specific strategy to enable multifunctionalization of the NWs using the template as the mask instead of the sacrificial layer(s) (see Figure 3.3). This time the aim is to trap the NWs inside the membrane letting the NW ends accessible for a first functionalization while this sides are masked by the template itself. This requires to deposit the desired material (after the sacrificial foot) and then to dissolve the metallization layer (and the sacrificial foot). Once the first functionalization performed, the NWs are released from the template by dissolving the PC and the second functionalization can be done.

In addition to those techniques corresponding to specific templates, it is possible to use any of both template to obtain trisegmented NWs in suspension having sacrificial layers at their extremities. To obtain this kind of NWs first a sacrificial foot has to be deposited, followed by the deposition of the the trisegmented part, with the sacrificial layers composed of another metal than the foot. Then, the membrane and the foot (and the metallization layer in the case of the PC membrane) are dissolved and the trisegmented NWs are recovered in suspension.

Afterwards, similarly to the technique specifically adapted to AAO templates, a first functional-

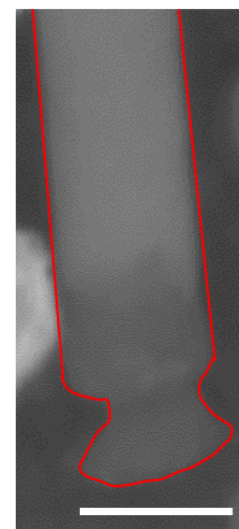


Figure 3.2: SEM image of the bottom of a Ni-Pt NW obtained from a supported AAO template. The outlines of the NW have been underlined in red. The scale bar represents 100 nm.

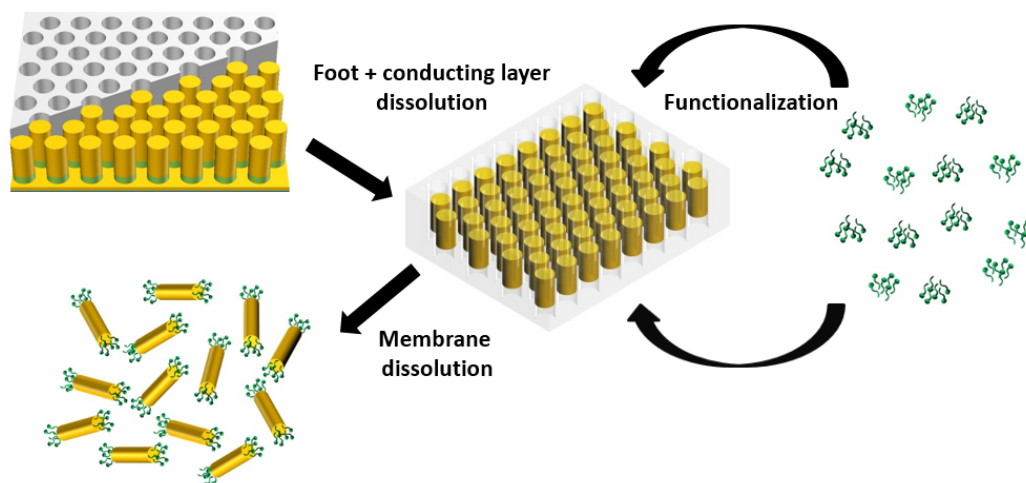


Figure 3.3: Scheme of the strategy to manufacture selectively end-functionalized NWs from a metallized PC template.

ization is performed on the side of the central segment. After etching the sacrificial layers, the end functionalization can be performed (Figure 3.4). Of course, it is also possible to use both templates to only obtain simpler NWs in suspension by first depositing a sacrificial foot, followed by the deposition of the desired material and finally the dissolution of the membrane and etching of the sacrificial foot. This latter technique will not allow selective multifunctionalization but is the simplest method to produce NWs. This is why it was first investigated in this work.

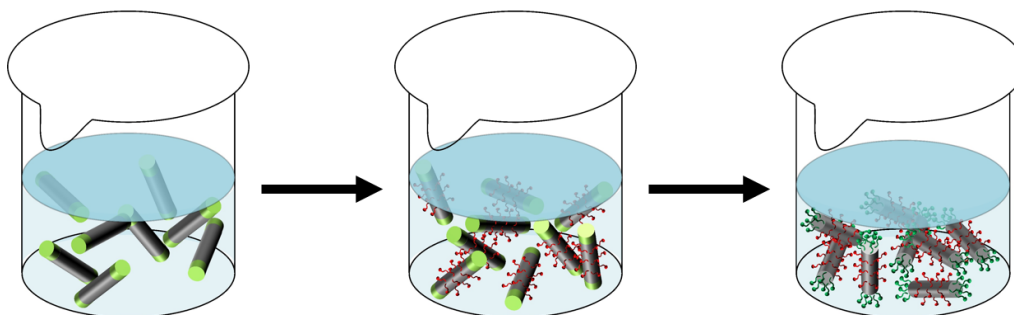


Figure 3.4: Scheme of the strategy to selectively multifunctionalize trisegmented NWs in suspension.

In this study the metals deposited for the non-sacrificial segments of the NWs are noble metals: gold, platinum or palladium. This choice has owing to their ability to bind with thiols. The metals used as sacrificial layers were copper and nickel because of the good experience acquired at the BSMA lab with those species (especially with Ni ECD) and their easy etching with ammonium persulfate (APS) for Cu and nitric acid for Ni [164]. However, APS being highly oxidant, it cannot

be used after functionalization with thiols because it would compromise the SAMs by oxidizing the thiol groups [165, 166]. In trisegmented strategies, the sacrificial protection of the NWs is meant to be dissolved after the first functionalization: in this case, nickel was selected as sacrificial layer. Finally, considering the available membrane, one selected a diameter of 100 nm for the NWs. Their length was set to 300-350 nm which gives a real anisotropy (~ 3) to the objects while limiting their size and therefore favoring Brownian motion and (supposedly) self-assembly.

3.3 Results

3.3.1 Homemade AAO templates

The AAO templates that were used in this thesis are homemade products. Their manufacture process is thoroughly described in Chapter 7 Section 7.2.1.1. Briefly, it implies first the deposition of an aluminum layer on a silicon substrate already covered with gold, leading to aluminum-gold-silicon system. Moreover there is a slight layer of titanium (5 nm) between the gold and aluminum. This layer is useful both for adhesion and as a stop layer of the anodization process. The aluminum layer will be anodized and become nanoporous alumina while the gold layer will be the conductive layer allowing a good electrical contact with the bottom of the aluminum layer. The precise deposition needed to obtain the adequate quality of this aluminum layer is performed by plasma sputtering. This technique and the required layer quality limit the aluminum thickness to max. 1.5-2 μm . When the proper Al-Au-Si substrate is obtained, it can be anodized by applying a potential between the gold layer and an aluminum bar dipped inside an oxalic acid electrolytic solution. When the nanopores form, a current passes through the system. Recording this current allows to follow the progress of the process. At the end, the pores attain the titanium layer which is also oxidized but at a slower rate. It results in the uniformization of the nanopores length, enabling most of the pores to reach the bottom conducting layer or at least the titanium layer. Finally a widening step is applied to make sure the pores are well open at the bottom, removing completely aluminum oxide or titanium at the end of the pores. Typical resulting membranes can be seen in Figure 3.5. However, one cannot be sure that these pores are fully open before deposition is performed, which is a major drawback. Top view images of freestanding NWs (obtained by ECD) after dissolution of the AAO are shown in Figure 3.6, giving the exact characteristics of the templates (at those places). The characterization process is described in Chapter 7 Section 7.2.1.1. Note that the places where there are no NW are the places where the pores did not reach the bottom conducting layer: the pores are not completely

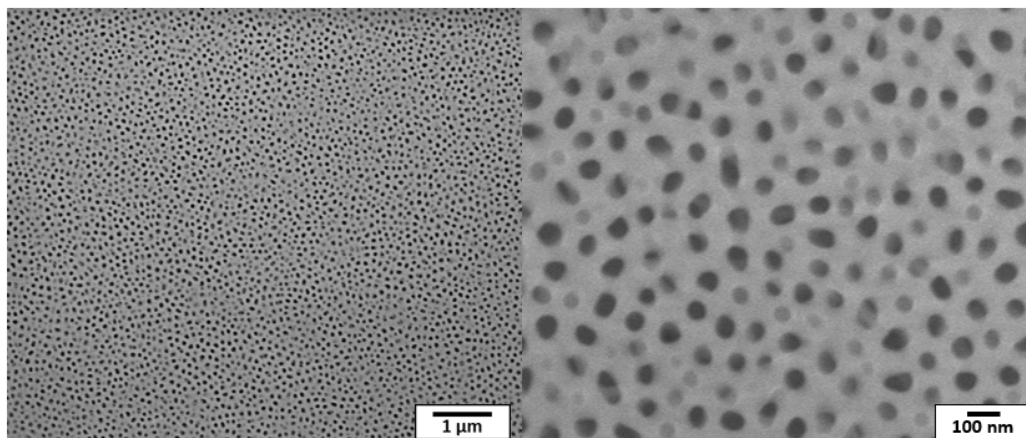


Figure 3.5: Top view SEM images of an AAO membrane at several magnifications. The insulating nature of the alumina leads to a "charging" effect blurring a bit the image.

open; hence no metallic reduction could occur there. One can also see that the characteristics of the homemade templates, and especially their porosity, are far from identical from one sample to the other despite having been synthesized in exactly identical conditions. This is certainly

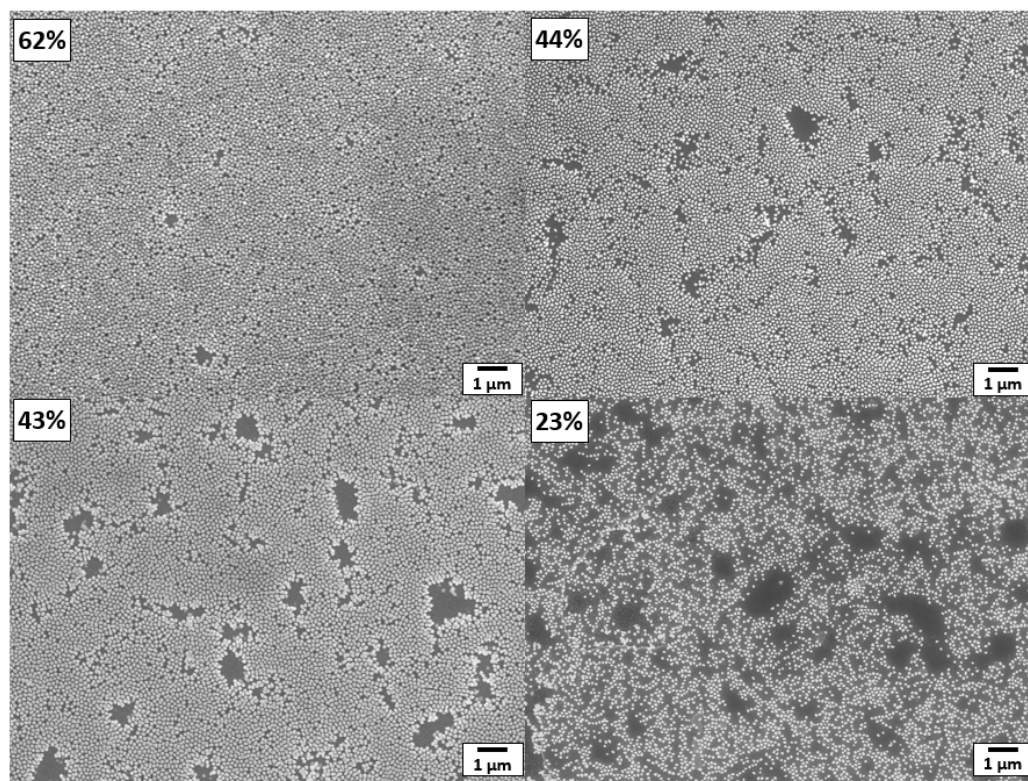


Figure 3.6: Top view SEM images of freestanding NWs deposited in different (but obtained with the same parameters) supported AAO templates, after dissolution of alumina. The porosity of the starting membrane is given in percentage.

due to small variations occurring during deposition of the layers on the silicon substrate. A very small change in the quality and thickness of the layers can have tremendous consequences [49]. Sadly, except for some severe defects, those differences can not be detected before use: about one every five wafers presents those severe defects allowing their discrimination even before anodization. This problem of reproducibility is represented in Figure 3.7 in which 50 measurements of template porosity (in percentage) are presented. It is important to remember that a porosity of 35 % corresponds approximately to 4.5×10^9 pores/cm² while a porosity of 60 % corresponds approximately to 7.5×10^9 pores/cm² (with a pore diameter of 100 nm). Finally as can be seen in Figure 3.8, the diameter of the pores is not completely cylindrical nor completely identical from one template to another. This last fact is not as problematic as the porosity: the diameters obtained are about 97 ± 13 nm.

The problem of reproducibility of supported AAO templates leads of course to a problem of reproducibility in the NW deposition and especially in the length of the NWs. Indeed, the charge (or equivalently the time) should normally control the length taking into account the opened pores surface able to produce NWs. But if this surface change, the charge and time to obtain a certain length also change. Yet, the advantage of the AAO template is its high porosity in comparison with PC membranes which are only 4.71 % open (6×10^8 pores/cm²).

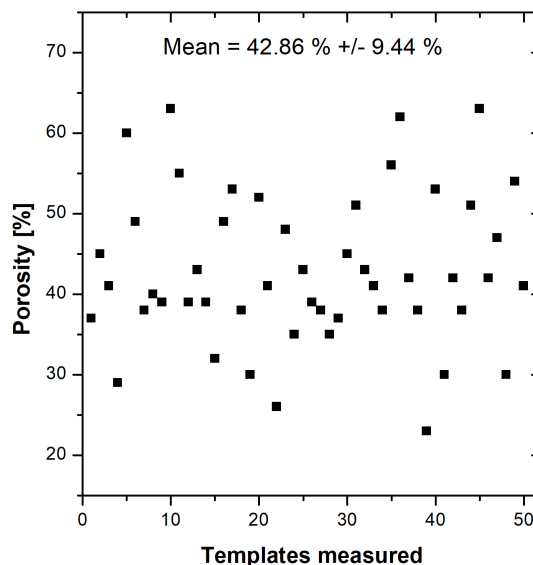


Figure 3.7: Graph of the porosity (in %) of 50 supported AAO templates synthesized in identical conditions. The mean and standard deviations are also given.

3.3.2 Simple nanowire deposition technique

The simplest way to obtain NWs by ECD from a desired material is to deposit a (rather) thin sacrificial foot, to get rid of the bottom membrane imperfections whatever the template, and then to grow the desired material. Afterwards, by dissolving the template and the sacrificial foot (and the metallization layer for PC membranes), one can liberate the NWs. There are three main parameters to take into account while depositing a metal: the nature and concentration of the electrolytic solution containing the material, the potential applied, and the temperature. The

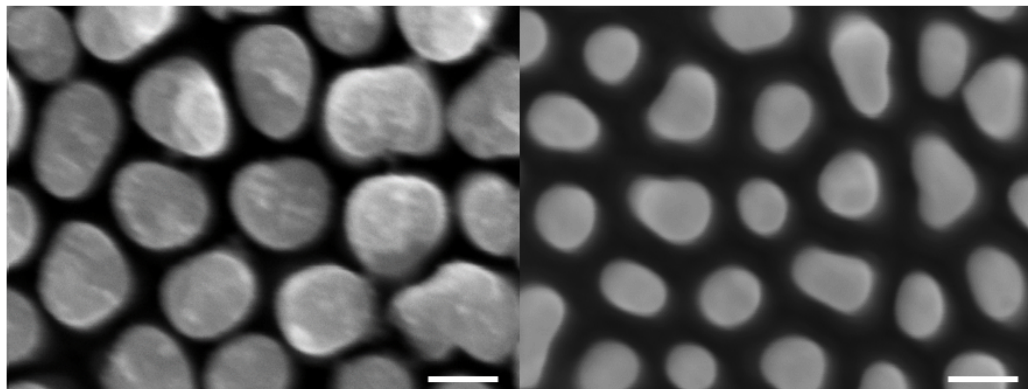


Figure 3.8: Top view SEM images at high magnification of freestanding NWs deposited in two different supported AAO templates (but obtained with the same parameters) after dissolution of the alumina. The scale bars are both 100 nm.

parameters used and how the NWs were characterized in this thesis are thoroughly described in Chapter 7 Section 7.2.1.2. Moreover, once those parameters are set, the final NW length will be determined by the deposited charge or the deposition time. The charge and the deposition time are equivalent control parameters (although not equal) and can be used when the surface of deposition, i.e. the number of opened pores allowing growth of NWs, is known. Indeed $Q = t \times I$ where I , the current, depends on the potential applied and on the total surface opened pores. Of course other parameters can play a determining role even if they are more subtle and sometimes difficult to control, such as the type of conducting layer, the pore density and diameter, the surface of deposition, the exact position of the electrodes, the defects of the conducting layer, the ageing of the electrolytic solution (in particular the change of concentration, complexes and pH), the height of the already deposited metals (decreasing the resistance), etc. Here, the surface area of deposition has been first fixed in agreement with the experience at the lab by using an existing and proven electrolytic cell. The template surface was 1.33 cm^2 (1.3 cm diameter). Regarding the diameters of the pore membranes hence of the deposited NWs, the AAO template pore diameter is $97 \pm 13 \text{ nm}$, as mentioned earlier, while the PC membrane pore diameter is $103 \pm 6 \text{ nm}$. Those close numerical values were approximated to 100 nm when the diameter value was needed as input for a computation. It is also important to mention that all the standard deviations that will be given in future were obtained from measurements performed on several samples and several membranes, and not only from one sample obtained with one membrane.

Electro-chemical deposition of sacrificial foot. The sacrificial feet have been made in nickel or copper. Nickel ECD has been studied in our lab for several years and the deposition of

this metal is well mastered. It gives very reproducible results with flat end NWs. This is due to the ease of deposition of Ni but also to years of fine-tuning of pulsed deposition parameters. The normal amount of nickel deposited to obtain the NW feet depends on the type of template because of the difference of pores density but also because of the constriction of the AAO template. The latter case requires a thicker layer deposited to get rid of that defect. For PC templates the charge deposited to obtain the foot has been fixed to 50 mC which leads to a length of 53 ± 11 nm in ca. 338 ± 13.5 s. The average deposition current is then about 148 nA. For AAO template the constriction at the bottom of the template requires a longer sacrificial foot (at least 65 nm to be sure to be above the constriction). The problem as described in the previous section is that the pore density is not constant from one sample to the other with this type of template. Still the charge deposited has been chosen to be 300 mC which leads to a length of 74.5 ± 23.5 nm by taking into account only the templates having a porosity comprised between 35 % and 45 % (the majority). This length can be related to the time of deposition that is also quite variable: $t = 570 \pm 67.5$ s, with an average deposition current ca. 526 nA. Finally this result can be compared to those obtained in the case of the PC which has a porosity of 6×10^8 pores/cm² (4.71 % since the diameter is 100 nm) while one took for AAO a mean porosity of 5×10^9 pores/cm² (~ 40 % by approximating the diameter to 100 nm). In the case of PC, the charge per number of pores per nm length of NW is ca. 1.18 pC/pore nm⁻¹ while for the AAO it is about 0.61 pC/pore nm⁻¹. These values theoretically correspond to the charges needed to obtain one single (100 nm diameter) NW of 1 nm "length". They thus correspond to the charge needed to grow a supplementary nanometer of a single NW. This calculated value is interesting to try and compare deposition rates between materials and templates.

This analysis allows a very rough comparison between the deposition strategy and materials. There is a factor two between the two values of charge per pore and length. This can be explained by several parameters. First the defects on the AAO template are difficult to take into account probably leading to a slight overestimation of the true pore density. Second the constriction drastically changes the diameter of the NWs over a non negligible length, reducing the area of deposition, leading to overestimation of the total "volume" deposited. Third maybe in the case of PC membrane some deposition can occur in between the membrane and the metallization layer if the latter does not perfectly adhere everywhere. The summary of the results obtained for the Ni foot deposition are given in Table 3.1.

Although nickel was easy to deposit, it was also important to have a second kind of sacrificial layer. This role has been played by copper. It is important to remember that this material cannot be dissolved once the NWs are functionalized, because the functionalization would be oxidized and certainly be degrafted. Copper deposition was made in continuous mode resulting in reproducible NW lengths. The deposition parameters were adapted from those of Antohe et

Table 3.1: Parameters and results obtained for the Ni foot deposition

	charge (Q)	length (L)	time (t)	average current ($\langle I \rangle$)	$Q/(L \times \# \text{ pores})$
PC	50 mC	53 ± 11 nm	338 ± 13.5 s	~ 148 nA	$1.18 \text{ pC/pore nm}^{-1}$
AAO	300 mC	74.5 ± 23 nm	570 ± 67.5 s	~ 526 nA	$0.61 \text{ pC/pore nm}^{-1}$

al. for copper deposition in our lab [167]. Unfortunately the deposition was not as good as nickel with respect to the flatness of the NW ends. This leads then to worse NW shapes after etching of this sacrificial layer (Figure 3.9). In the PC membrane the deposited charge has been imposed

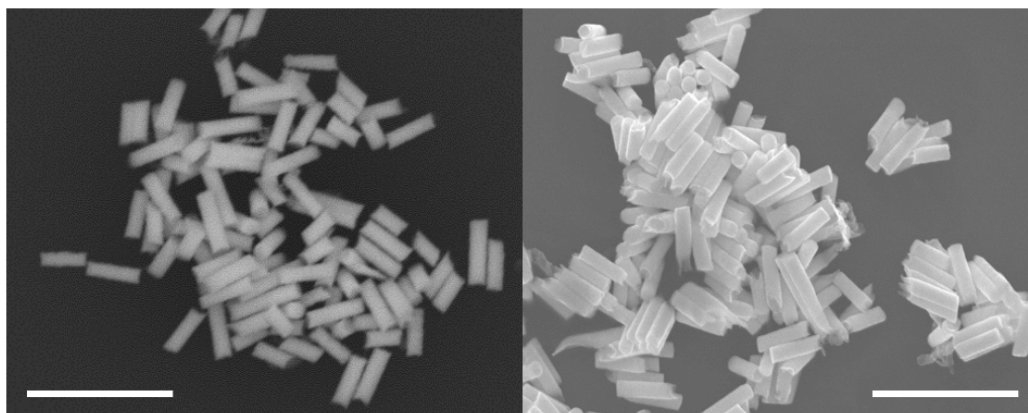


Figure 3.9: Platinum NWs obtained by depositing first a sacrificial foot made of (left) nickel and (right) copper. The sacrificial foot, the metallization layer and the PC membrane have been dissolved. Scale bars are $1 \mu\text{m}$.

to be 100 mC. It leads to NWs of ca. 142 ± 22 nm length. It is longer than with Ni but it was hoped that a longer deposition would induce a better near equilibrium deposition, consequently leading to a flatter end. The main results obtained for Cu foot deposition are given in Table 3.2.

Table 3.2: Parameters and results obtained for the Cu foot deposition

	charge (Q)	length (L)	time (t)	average current ($\langle I \rangle$)	$Q/(L \times \# \text{ pores})$
PC	100 mC	142 ± 22 nm	198 ± 20 s	~ 505 nA	$0.88 \text{ pC/pore nm}^{-1}$

Electro-chemical deposition of the core segment. The selected materials for the core of the NWs are noble metals: gold, platinum or palladium. Gold is the most often-used metal for thiol functionalization. Therefore it was the first metal to be tested. However, a reproducible

deposition was difficult to obtain using either continuous or pulsed deposition. Acceptable results could be achieved from time to time but the reproducibility was not reached. The final optimized ECD was at 55°C in pulsed mode with pulses of -0.35 V for 90 ms and of -0.55 V for 10 ms, with the commercial solution from METAKEM (15 g/l of gold). These parameters were adapted from the ones recommended by the supplier of the electrolyte solution. Preliminary tests had been done in our lab by V. Antohe with similar parameters. Part of the problem might be due to the fact that the commercial gold solution actually etches alumina (with a higher rate at higher temperature). This solution is a sulphite-based gold electroplating bath with a neutral pH-value. It leads to the widening of the pores during deposition and therefore to a thickening of the NWs along their length. One can see an extreme case in Figure 3.10 where the gold bath etched the AAO template over a period of 1h30. In addition, the electrolytic gold bath is

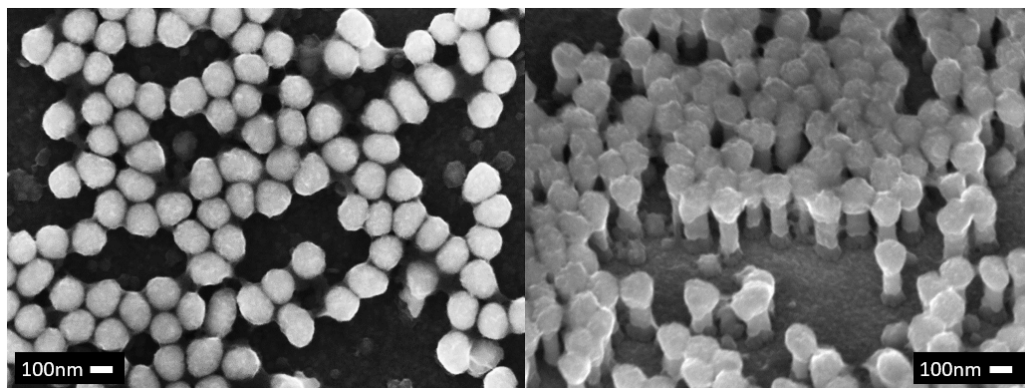


Figure 3.10: SEM images of freestanding Ni-Au-Ni NWs (left) top view, (right) tilted view at 45°. The Au deposition was made at 55°C and the electrolytic bath was left in the pores at that temperature for 1h30. Finally the bath was changed and the Ni deposition was made. It is clear that etching of the AAO membrane happened during the time the gold bath remained inside the pores, which explains the final "mushroom" shape.

photosensitive and easily oxidizable, leading to effects such as the formation of spikes or pores in the NWs. Poorly grown NWs are presented in Figure 3.11. However this electrolyte bath has been preferred over the more common HAuCl_4 because several other studies made in the lab (especially by C. Chattaway) with the hydrogen tetrachloroaurate were not very successful either. For all these reasons, gold NWs were eventually not extensively used in self-assembly experiments, because these experiments require a very large stock of identical NWs.

The length versus charge curves, depending on the nature of the template, are shown in Figure 3.12. One can notice the very large standard deviation due to the problem of reproducibility. Moreover, the deposition process can only be roughly approximated by a linear relationship. Table 3.3 displays a summary of the parameters and results for Au deposition. Based on these values the theoretical charges needed to obtain a 100 nm diameter NW with a "length" of 1 nm

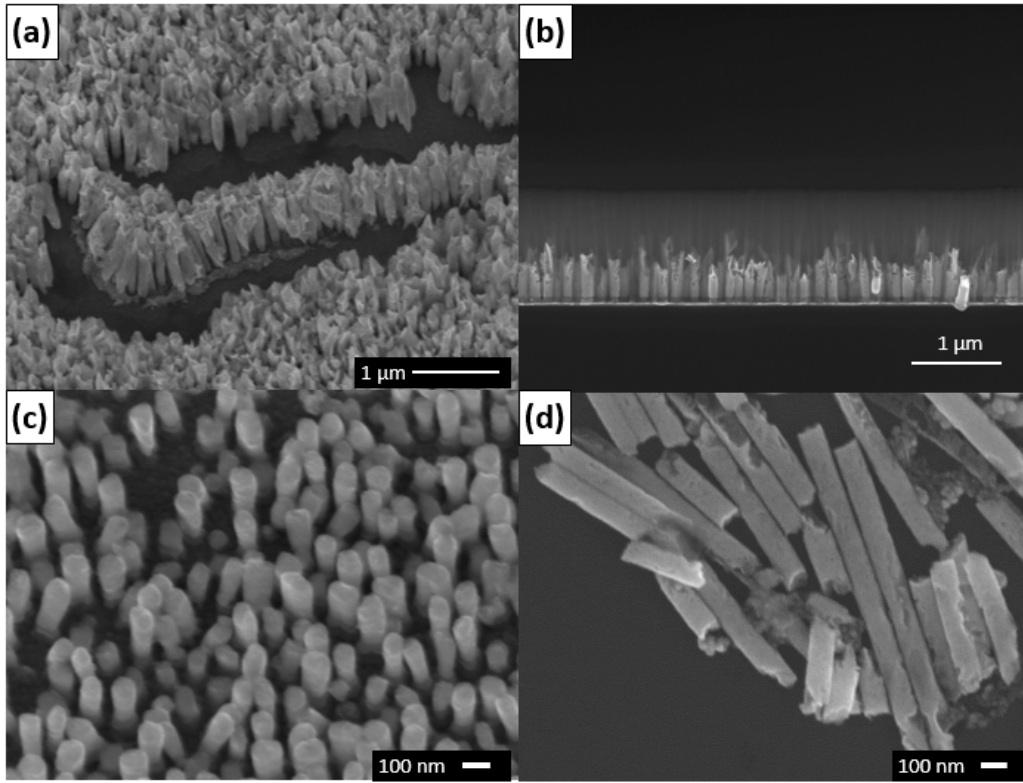


Figure 3.11: SEM images of typical "bad" Au NWs obtained from time to time. (a-b) Spiky NWs obtained in AAO template; (a) Tilted view at 45° and (b) section view. (c) Tilted view at 30° of small NWs with a large distribution of sizes. (d) Au NWs obtained in PC membrane where some porous parts can be spotted, hence the very long length.

would be $0.14 \text{ pC/pore nm}^{-1}$ for Au in AAO and $0.30 \text{ pC/pore nm}^{-1}$ for Au in PC. There is again a factor two between these two values. However if one uses the slope of the linear fits, very different results are obtained: $1.56 \text{ pC/pore nm}^{-1}$ for Au in PC, and $0.091 \text{ pC/pore nm}^{-1}$ for Au in AAO. The huge difference between those two values reflects clearly a difference between the templates. In the case of the Au ECD in AAO, the parallel slow dissolution of the template by the gold bath could perturb the measurements of the real charge deposited for a single diameter NW, overestimating the charge needed to obtain a certain length.

Table 3.3: Parameters and results obtained for Au deposition with the optimized condition

	charge (Q)	length (L)	time (t)	average current ($\langle I \rangle$)	$Q/(L \times \# \text{ pores})$
PC	75 mC	$\sim 310 \text{ nm}$	$\sim 650 \text{ s}$	$\sim 242 \text{ nA}$	$0.30 \text{ pC/pore nm}^{-1}$
AAO	300 mC	$\sim 330 \text{ nm}$	$\sim 275 \text{ s}$	$\sim 909 \text{ nA}$	$0.14 \text{ pC/pore nm}^{-1}$

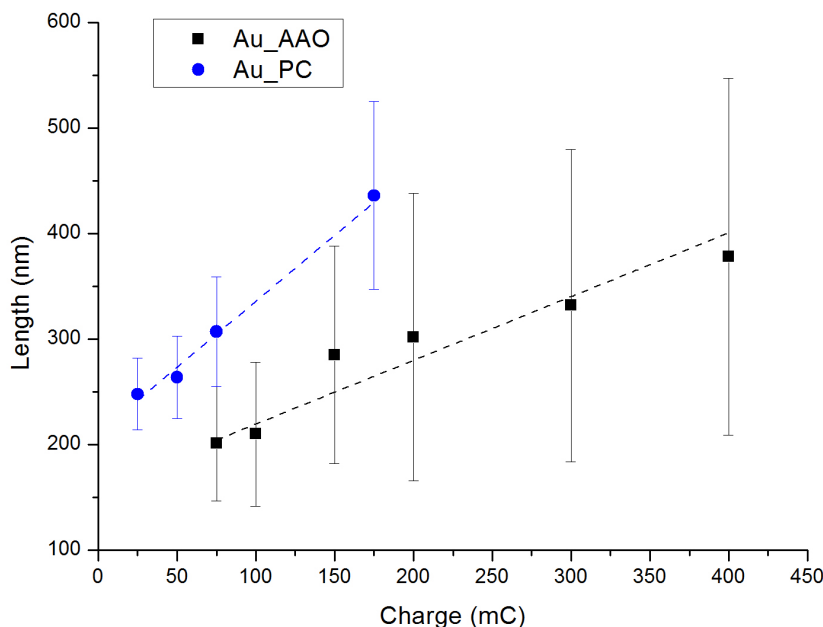


Figure 3.12: Diagram of Au NWs length distribution depending on the charge deposited and the type of templates. The dashed lines correspond to the linear fit of the results. The error bars correspond to the standard deviations between all the NWs coming from different samples.

Platinum was easier to deposit, best conditions being in continuous mode at -0.3 V, at 50°C . The variance on a sample surface was small and the length of the NWs for a given charge had a small standard deviation (Figure 3.13). To obtain the desired range of length, one used the parameters of Table 3.4. Additionally, Pt NW growth is faster than Au NWs which is an other advantage. Regarding the values corresponding to the theoretical charge needed to obtain a 100 nm diameter NW with a "length" of 1 nm, one needs $0.48 \text{ pC/pore nm}^{-1}$ for Pt in PC and $0.076 \text{ pC/pore nm}^{-1}$ for Pt in AAO. When values from the linear fits are considered, one finds $2.55 \text{ pC/pore nm}^{-1}$ for Pt in PC and $0.29 \text{ pC/pore nm}^{-1}$ for Pt in AAO. The difference between the AAO and PC templates is again surprisingly large. This might be due to an overestimation of the density of AAO templates.

Table 3.4: Parameters and results obtained for the Pt deposition with the optimized condition

	charge (Q)	length (L)	time (t)	average current ($\langle I \rangle$)	$Q/(L \times \# \text{ pores})$
PC	120 mC	$\sim 315 \text{ nm}$	$\sim 110 \text{ s}$	$\sim 381 \text{ nA}$	$0.48 \text{ pC/pore nm}^{-1}$
AAO	165 mC	$\sim 325 \text{ nm}$	$\sim 95 \text{ s}$	$\sim 507 \text{ nA}$	$0.076 \text{ pC/pore nm}^{-1}$

Finally, palladium was also tested in the aim of using the contrast between platinum and gold

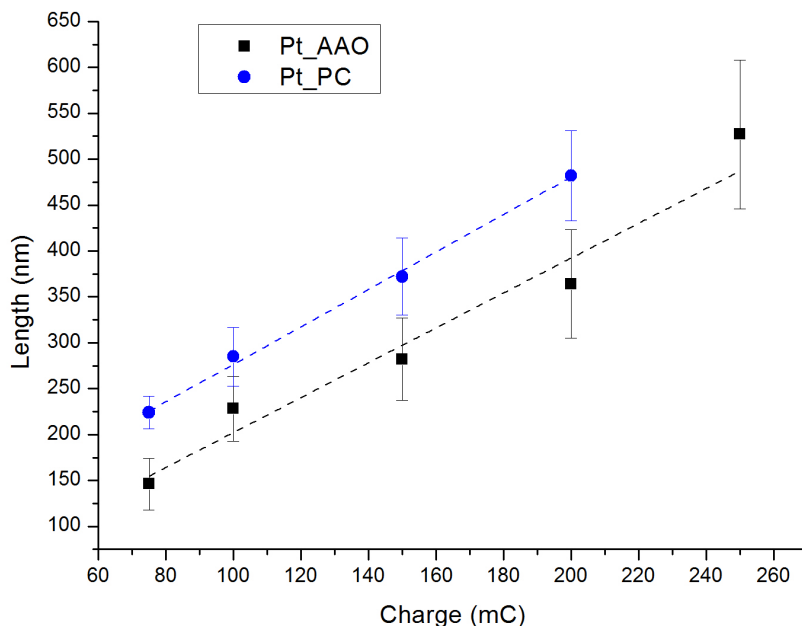


Figure 3.13: Diagram of Pt NWs length distribution depending on the charge deposited and the type of templates. The dashed lines correspond to the linear fit of the results. The error bars correspond to the standard deviations between all the NWs coming from different samples.

in SEM. Indeed the idea was to further try to self-assemble two types of oppositely charged NWs. Those NWs may then assemble side-to-side: one "positive" NW next to one "negative" NWs. The distinction by SEM between gold and platinum being very difficult since they have almost the same atomic number, it would have been easier to detect the arrangement between NWs made of palladium and gold or platinum. This will be more deeply discussed when presenting methods of higher throughput since the performed tests are specific to these methods (see the Section 3.3.6).

3.3.3 Freestanding trisegmented nanowires grown into homemade AAO templates

As described in the introduction of this chapter, one investigates the manufacture of freestanding trisegmented NWs that could be functionalized afterwards while still attached to the substrate (Figure 3.1). The first step in this particular strategy is to produce self-supported AAO templates. And as already described in this chapter, the reproducibility of this step was far from good. That is why freestanding NWs from supported AAO templates were finally only used as a proof

of concept and not as a regular production means. Nevertheless, a few good samples were manufactured by this technique when using templates with average porosities ($\sim 35\text{-}45\%$): Ni-Au-Ni and Ni-Pt-Ni freestanding NWs could be obtained by this way (Figure 3.14). The first

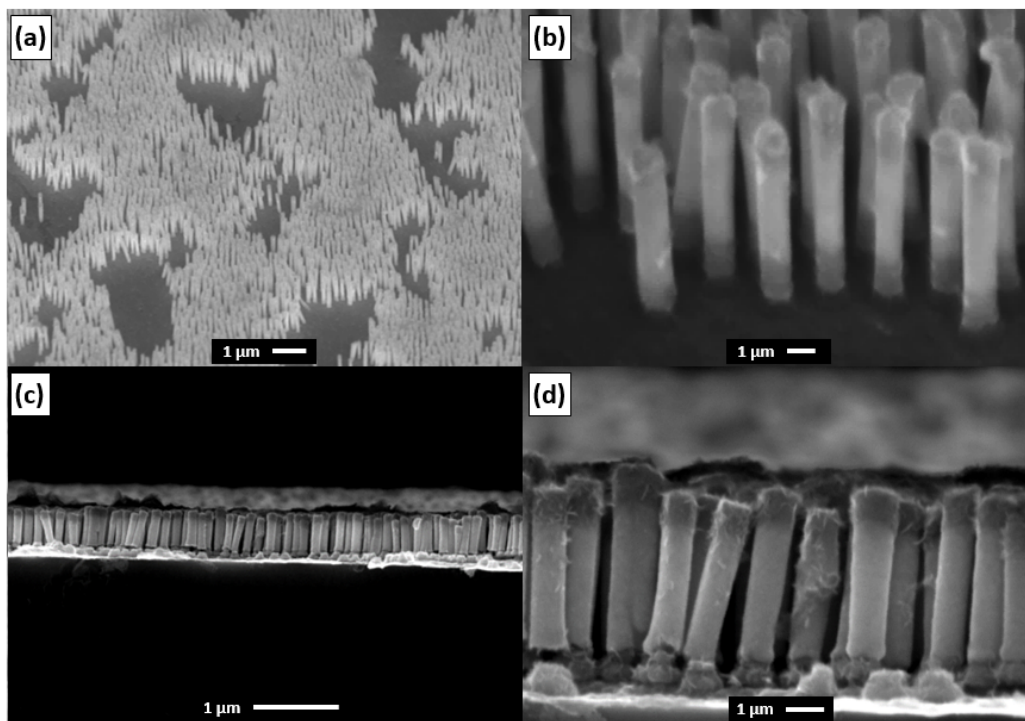


Figure 3.14: SEM images of freestanding trisegmented NWs. (a-b) Ni-Pt-Ni NWs; (a) top view and (b) tilted view (45°C). (c-d) Section view of Ni-Au-Ni NWs; when the foot constriction is too strong, the NWs detached from the substrate during the fracture made for imaging purposes. On all images some remains of alumina can be spotted, especially on the top Ni layer.

sacrificial layer was deposited under the standard conditions: 300 mC; while the second layer of nickel was added by depositing a charge of 200 mC. This is lower than the first sacrificial foot layer because of the absence of constriction after the first 100 nm. The time needed to deposit this second Ni layer was about ~ 400 s. The core Au or Pt were deposited under the previously described optimized conditions. It is also important to insist on the fact that complete NWs should not exceed ~ 600 nm length otherwise they will collapse as shown in Figure 3.15.

3.3.4 Trisegmented nanowires from PC membranes

The aim here is to produce trisegmented NWs liberated in suspension for functionalization of their sides prior to dissolution of the two end-capping segments followed by spatially-selective chemical

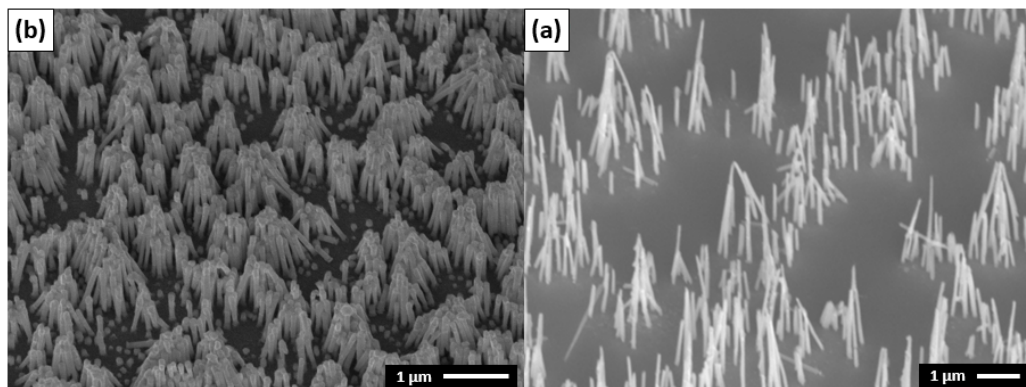


Figure 3.15: SEM images (tilted at 45°) of collapsed long NWs. Notice in (a) some sacrificial feet lacking the rest of NWs, indicating that the NWs often broke at the constriction.

functionalization of the NWs ends (see Figure 3.4). AAO templates could also be used but as seen the reproducibility problem which is getting even worse when adding a larger number of layers, each layer being subjected to a significant error, this strategy was finally limited to NWs grown in PC membranes only. To obtain such trisegmented NWs in suspension, one has to actually deposit quadri-segmented NWs: a sacrificial foot is first grown, followed by the standard trisegmented deposition with a different sacrificial material encapping the desired core material, such as in grown Cu-Ni-Au-Ni and Cu-Ni-Pt-Ni NWs. The charge for the copper sacrificial layer was the same as the one determined for the "standard" manufacture of simple NWs: 100 mC. For each sacrificial nickel layers the charge was set to 20 mC which is lower than the sacrificial foot in the "standard" strategy because the defects of the bottom of the membrane should already be passed over. The Pt and deposition charges were identical to the ones determined in the "standard" strategy, that is 120 mC and 75 mC, respectively. Figure 3.16 depicts typical trisegmented NWs obtained after dissolution of the copper foot.

3.3.5 Trapped NWs in PC membrane, and large diameter NWs

This strategy consists in keeping some NWs inside PC membrane after dissolution of the metallization layer and of the sacrificial foot. This allows the spatially-selective functionalization of their ends (see Figure 3.3). Functionalization of the lateral side of the NWs can then be selectively performed after membrane dissolution. The ECD is identical to the "standard" way of deposition in a PC membrane. However this section will specify some parameters to obtain high aspect ratio NWs with a larger diameter. Those NW types will be further used to ease the characterization and demonstrate selective NW functionalization at their ends and side. Indeed, larger aspect

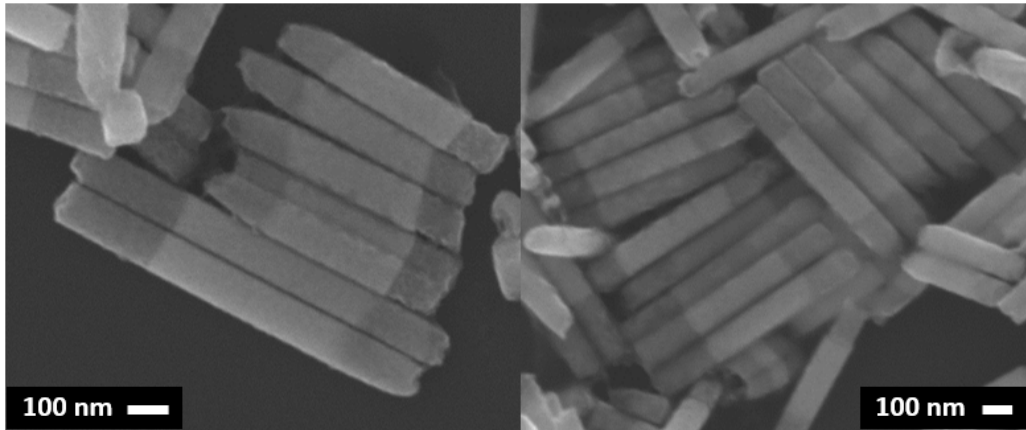


Figure 3.16: SEM images of trisegmented NWs obtained in PC membranes. (Left) Ni-Au-Ni NWs (note the difference of length between some NWs) and (Right) Ni-Pt-Ni NWs.

ratios and larger diameters allow for an easier characterization by optical microscopy. To do so, the PC membranes used had pores of about 600 nm diameter, with a density of 4×10^7 pores/cm² which corresponds to a porosity of 11.31 %. The feet of the NWs were made of copper since its dissolution is easier (see later). The deposition of the core material was designed to obtain NWs in the range of 10 μ m. The deposition and morphological parameters to obtain those NWs are presented in Table 3.5. SEM images of the resulting NWs, after the dissolution of the

Table 3.5: Deposition and morphological parameters for ECD of large NWs

	charge (Q)	length (L)	time (t)
Cu (foot)	400 mC	~ 200 nm	~ 1000 s
Au (core)	7 C	7-10 μ m	~ 1 h40
Pt (core)	10 C	7-10 μ m	~ 1 h

This information has to be taken with caution because the errors are large due to the large charge and time of deposition.

metallization layer and of the membrane, and the etching of the copper feet, are shown in Figure 3.17. It depicts an image of confocal microscopy showing well that thanks to those high aspect ratio the ends and sides can be optically resolved.

3.3.6 Increase of throughput

One of the main disadvantages of ECD in nanoporous templates is its low throughput. It is theoretically better when using AAO templates for this template is denser (more porous) than PC membranes. However, owing to the problem of reproducibility with AAO templates, other strategies have been developed with PC membranes to increase the throughput of this fabrication route. To do so, two strategies have been tested. The first technique is simply to increase the surface of deposition, which increases proportionally the number of produced NWs. This requires nanoporous membranes of larger area, and the deposition has to be uniform all over this surface. The second technique is to produce "long" multisegmented NWs in which segments of the desired material are interspersed with sacrificial layers, as in $\text{Ni}-(\text{Au-Ni})_x$. After the standard recovery of the NWs the sacrificial layers should be etched to finally obtain a large number of NWs. Eventually, if both strategies are efficient, it would also be logical to combine them to increase even more the throughput.

Increase of the area of deposition. The increase of the deposition area first requires a larger membrane area, which is not a problem for PC membranes are provided in A4 size. The real

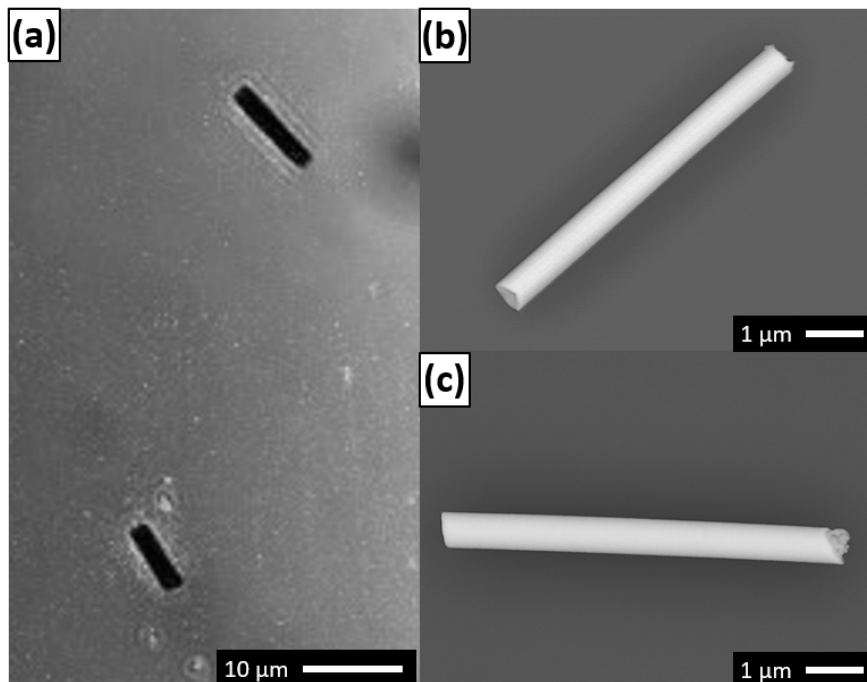


Figure 3.17: Images of high aspect ratio NWs obtained in PC membranes with 600 nm pore diameter. (a) Confocal microscopy image of Au NWs and (b-c) SEM images of Pt NWs where one can notice the non flat end corresponding to the previous sacrificial Cu foot.

difficulty is the deposition step that could be less homogeneous because of a less even distribution of the current lines on the whole sample during ECD. This is the principal limitation for this technique. One way to improve the uniformity of the electric field in ECD is to use special counter-electrodes called platinum gauze electrodes that form a tubular mesh surrounding the upper circumference of the deposition area [168, 169]. Here these special electrodes have not been used because they are expensive and anyway the potentiostat used to perform the deposition could only sustain a limited current. It should have been replaced if the deposition area would have been extremely increased and this would have been really expensive. Therefore one has simply increased the active diameter to 3.5 cm diameter surface (9.62 cm^2 area), which is 7.2 times larger than the usual "standard" area. In such large area membranes, only platinum NWs have been produced owing to their narrow distribution of length for a given charge and the reproducibility of the process. The deposition and morphological parameters for large area PC membrane are given in Table 3.6 This ECD process was reproducible in times, allowing pooling

Table 3.6: Deposition and morphological parameters for ECD on large area PC membrane.

	charge (Q)	length (L)	time (t)
Ni (foot)	500 mC	$\sim 75 \text{ nm}$	$\sim 300 \text{ s}$
Cu (foot)	1 C	$\sim 125 \text{ nm}$	$\sim 500 \text{ s}$
Pt (core)	10 C	$\sim 320 \text{ nm}$	$\sim 150 \text{ s}$

of the resulting NW to obtain a large stock of Pt NWs. Some NWs coming from this stock and the distribution of size within this stock are depicted in Figure 3.18. The results are slightly more polydispersed than the ones obtained in smaller PC membrane areas. Ni-Pt NWs have a length of $323 \pm 57 \text{ nm}$ and Cu-Pt NWs of $327 \pm 61 \text{ nm}$, to be compared to a standard deviation of 44 nm for an Ni-Pt NWs average length of ca. 325 nm in the case of the smaller membranes. The NWs obtained with the Ni feet have flatter bases after Ni dissolution, but required extensive purification steps as will be shortly described.

Additionally, many tests were also performed with palladium. Unfortunately the palladium NWs were most of the time of very poor quality whatever the conditions used. The tests were performed with feet of nickel and copper, at temperature from 30°C to 50°C and potential from -0.45 V to -0.65 V (in continuous mode). Some results are depicted in Figure 3.19 in which one can see that the palladium begins its growth tubularly or at least porously. This problem might be due to ageing of the Pd solution.

Large template areas have also been obtained for AAO templates, with the anodization process being adapted to obtain larger diameters (3.5 cm). Unsurprisingly this increase of surface did

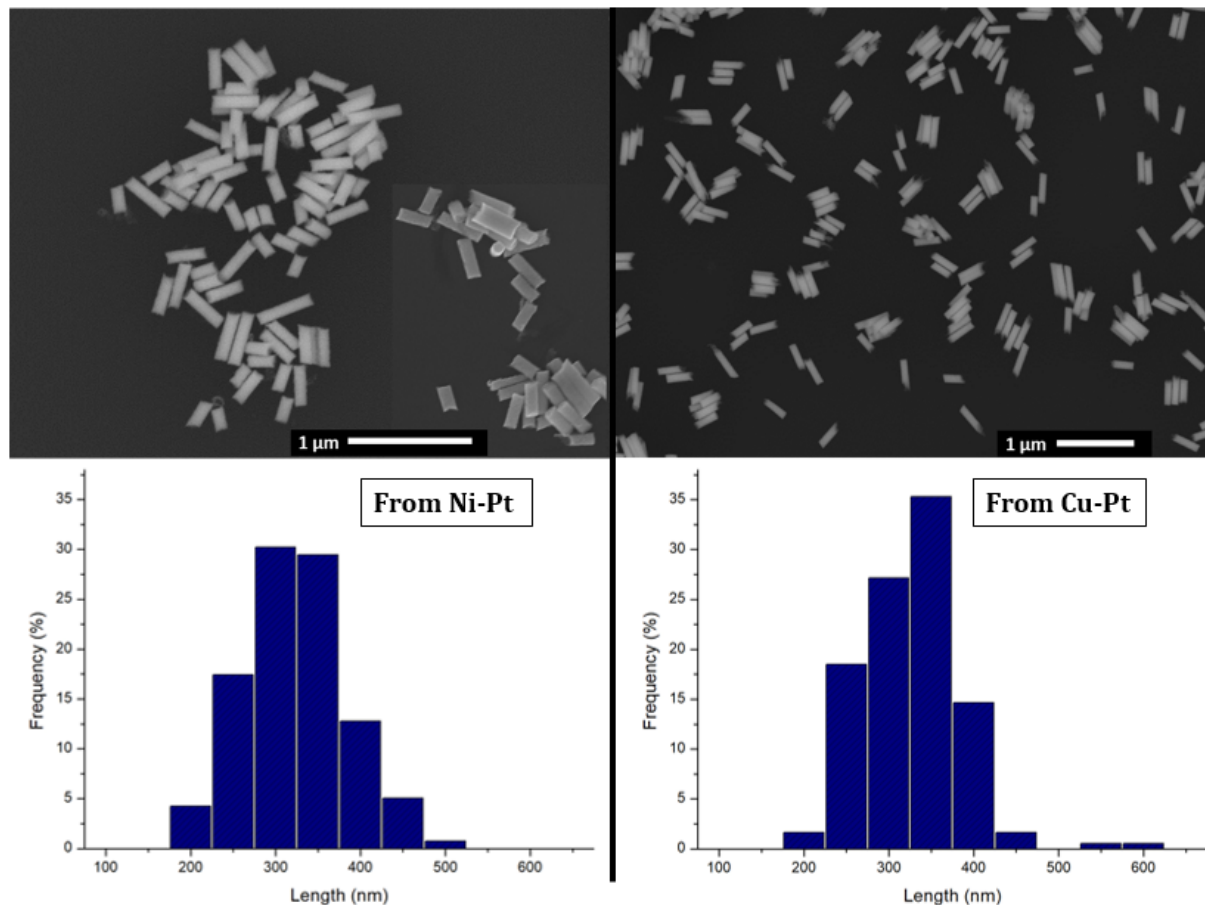


Figure 3.18: SEM images (top) and distribution of length of the NWs (bottom) coming from the stock solutions obtained from Ni-Pt NWs (left) and Cu-Pt NWs (right). (The number of counts equals 250).

not improve the reproducibility of those homemade templates which are therefore not discussed here. However some supplementary information about the scaling up of the anodization process can be found in Appendix 7.2.4.3.

Multisegmented nanowires. In the second strategy, long multisegmented NWs with intermediate sacrificial layers have to be deposited on the "standard" surface area (1.33 cm²). One can even think of multisegmented NWs separated by several sacrificial layers to obtain trisegmented NWs after dissolution of the template and of the main sacrificial "spacer". Therefore one manufactured NWs of type (Ni-Pt)_x, (Cu-Pt)_x and (Cu-Ni-Pt-Ni)_x. Some tests were also performed with gold instead of Pt but the problems of reproducibility encountered with Au were even worse since several successive deposition steps had to be performed. Therefore only Pt based systems

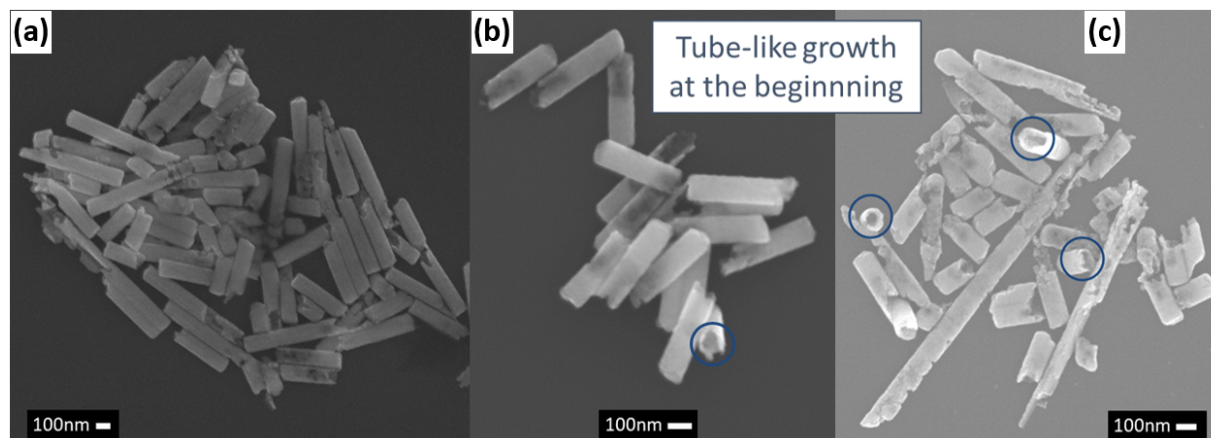


Figure 3.19: SEM images of Pd NWs obtained with the larger area processed at 45°C, with feet made of copper and by applying potential of (a) -0.6 V, (b) -0.55 V and (c) -0.5 V, until deposition of 1.5 C charge.

will be described next.

The first sacrificial feet were deposited with 50 mC for Ni or 100 mC for Cu. The other sacrificial and spacer layers were deposited with a lower charge, 20 mC and 40 mC for the Ni and Cu, respectively. ECD of Pt was performed in the standard condition (120 mC). Several multisegmented NWs obtained by this way are shown in Figure 3.20. The results were relatively reproducible regarding the total length, even though the more layers, the wider the length distribution and the more compromised the flatness of the layers. Moreover the NWs often broke at the intersection between two layers. This is not a problem when the expected final product is pure platinum NWs, but it is when end-protected trisegmented NWs are desired for one does not know where the NWs break. But the main problem with this high throughput methodology is the dissolution of the spacers or sacrificial layers. As will be described in the next section, those dissolutions were very difficult to achieve and sometimes even impossible. Although the inter-metallic nature of the segments was not proved, it is believed that there is either diffusion of atoms from neighboring segments (noble metals) inside the sacrificial layers, forming an alloyed material of lower solubility, or that co-deposition happens because of the successive electrodeposition steps requiring a change of electrolytic bath that could lead to residues of the previous bath despite vigorous rinsing. This could then lead to alloy deposition that will be clearly more difficult to dissolve. The characterization of the composition of remaining segments (after normal dissolution) could be useful to clarify their nature. To reduce the occurrence of this possible problem an additional neutral electrolyte could be used to rinse the cell in-between two successive electrolytic baths. A small deposition in the previous conditions could then be performed to hopefully deposit the remaining last residues of the previous metal ions bath. Despite this problem of dissolution, a large stock solution of Pt NWs could be produced by this strategy. But even after many etching steps

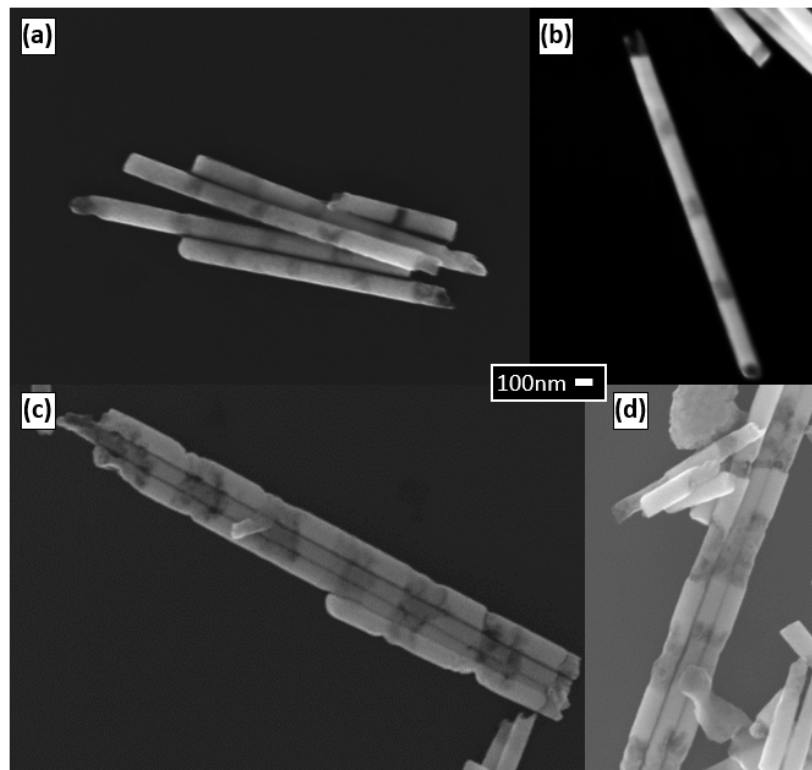


Figure 3.20: SEM images of multisegmented NWs (a) $(\text{Cu-Pt})_4$, (b) $(\text{Ni-Pt})_4$ and (c-d) $(\text{Cu-Ni-Pt-Ni})_8$.

and ultrasonications to try to remove all the sacrificial layers, a few very long NWs composed of platinum and nickel were still present. Pt NWs and their length distribution obtained by dissolving the Ni layers from $(\text{Ni-Pt})_8$ are shown in Figure 3.21. There are clearly many non-dissolved nickel layers despite the many etching and washing steps performed.

In addition some tests were performed with palladium to obtain $(\text{Ni-Pd})_{12}$ NWs. This time the results were more satisfactory, although the length distribution was very high. One observed that depositing longer Pd NWs leads to less porous NWs. Therefore the production of Pd NWs was focused on length of ca. 600 nm. The depositions were made at 45°C and at continuous potential of -0.6 V to deposit 100 mC. It took about $215 \pm 45\text{ s}$, leading to lengths of about $634 \pm 139\text{ nm}$. Some examples of the resulting NWs are given in Figure 3.22.

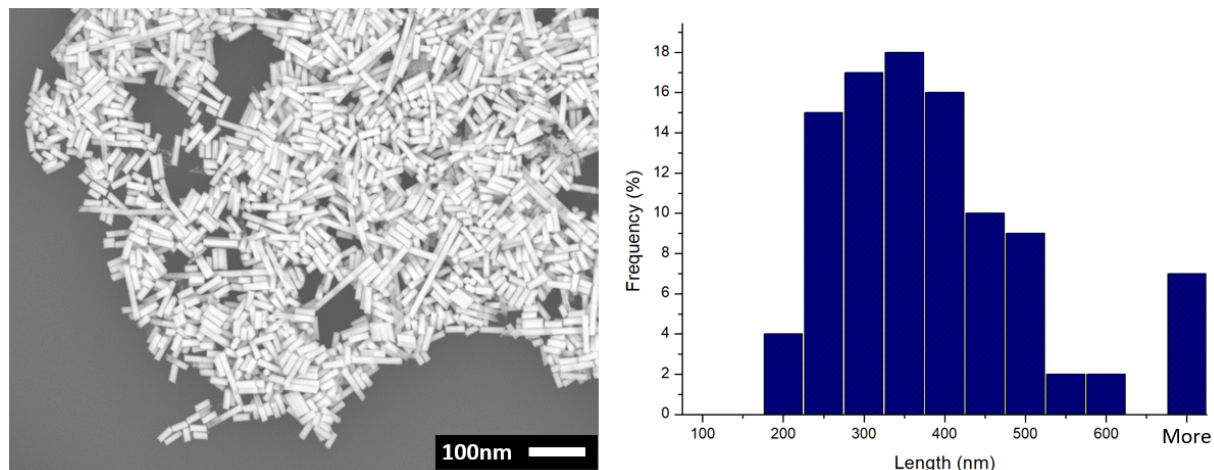


Figure 3.21: (Left) SEM image of the "Pt" NWs stock solution obtained from $(\text{Ni-Pt})_8$. (Right) D-Length distribution of these "Pt" NWs. (The number of counts equals 250). Compare the distribution with the ones of Figure 3.18.

3.3.7 Nanowire recovery

In order to recover the NWs in suspension there are several dissolution steps to perform in specific order depending on the chosen strategy. These steps are the dissolution of the template, the dissolution of the sacrificial feet, the dissolution of the metallization layer (for PC membrane), and the dissolution of the sacrificial layers (when appropriate). The complete processes that have been applied to the samples are thoroughly described in Chapter 7 Section 7.2.2.

When the ECD occurs in AAO templates, the alumina template has to be dissolved first to uncover the NWs. This is done by successive immersions of the sample in NaOH baths, increasing their concentration from bath to bath to progressively remove all the impurities. The tricky part is to completely remove all alumina without compromising the freestanding aspect of the NWs. This is why the first NaOH baths are of "lower" concentration (2M) to avoid the stress induced by too fast dissolution. Similarly, ultrasonication and even gas flashing (to dry)

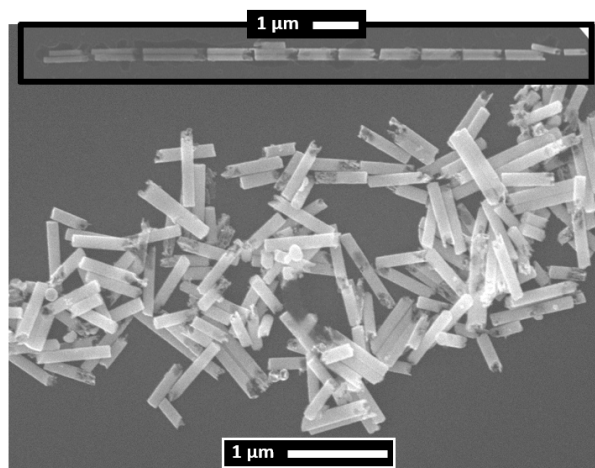


Figure 3.22: SEM images of (top) $(\text{Ni-Pd})_{12}$ NWs with Ni partially dissolved, (bottom) Pd NWs resulting from the previous multisegmented NWs with the best Ni etching obtained.

are prohibited. After that step the sacrificial feet have to be dissolved to recover free NWs in suspension. They are dissolved with ammonium persulfate (APS) for Cu and nitric acid for Ni, with addition of ultrasonication steps to improve and help the etching process. While the NWs are freestanding after the AAO dissolution, the etching of the feet makes them collapse and the NWs are recovered into the etchant solution in an Eppendorf tube.

When the ECD occurs in PC membranes, the metallization is first dissolved, then (usually) the feet are etched and finally the PC is dissolved to recover the NWs. The metallization is made by copper, mainly, and by a thin layer of chromium playing a role of adhesion. The copper layer is dissolved in APS and the chromium one in a specific chromium etchant solution. Then the sacrificial feet can be dissolved inside the membrane similarly to the method used in the AAO case, except that the use of ultrasonication has to be very limited to avoid fracture of the membrane. Next, the PC membrane is dissolved in successive dichloromethane (CH_2Cl_2) baths. Hence, during the etching of the metallization layer and of the sacrificial feet, NWs remain trapped inside the template. After dissolution of PC, similarly to AAO template, the NWs are recovered in suspension into an Eppendorf.

Once the NWs are recovered in the Eppendorf tube, further processing operations can be applied to the NWs in suspension. After each operation, the tubes are centrifuged to form a NW pellet, which can be easily rinsed.

This etching is often difficult or even impossible, especially when the sacrificial layers are in between two other segments. As regards the sacrificial feet, copper is relatively easy to dissolve while nickel often requires many acidic baths of increasing concentration with strong ultrasonication to dissolve them completely. The problem is more complex for multisegmented NWs which eventually gives rise to some "meta" NWs still containing several sacrificial segments, as discussed in Section 3.3.6. Consequently many baths (with often long immersing times) were usually required to completely eliminate sacrificial layers. Most of them were performed in Eppendorf tubes after NWs collection.

As a result of the difficult dissolution of the sacrificial layers, the fabrication process of the NWs remained sub-optimal:

1. multisegmented NWs did not lead to the complete collection of monosegmented NWs;
2. the use of Ni as sacrificial foot was not as efficient as Cu, which was therefore preferred;
3. the harsh etching conditions required for the complete elimination of sacrificial segments limited the prior functionalization of the NWs surfaces. This is especially true when Ni is used for which nitric acid is the standard etchant;

4. unavoidable loss of NWs was observed at each rinsing step, a problem which results in a significantly lower throughput for NWs requiring many extensive etching steps.

3.4 Summary

To summarize this chapter, the production of NWs by ECD within nanoporous templates was very successful in the case of platinum NWs inside the PC membranes but less reproducible for other noble metals, as well as within supported AAO homemade templates. However several concepts could be proven for platinum and gold NWs. Indeed, freestanding NWs with protected ends could be obtained in AAO template and trisegmented NWs in suspension could be obtained via PC membranes. Despite these successes, the supported AAO homemade templates were not reproducible enough to continue using this strategy to obtain NW stocks large enough to study self-assembly. After numerous experiments the same observation had to be done about gold NWs that are not reproducible enough to obtain easily large stock solutions. Palladium was less investigated and the results were not encouraging except for longer NWs such as used in the multisegmented strategy.

All these problems directed the production towards Pt NWs for the study of self-assembly. Three types of large stock solutions of bare Pt NWs could thus be obtained in this thesis: by the multisegmented approach, and by the ECD over large surfaces of Ni-Pt NWs and of Cu-Pt NWs. The differences between these three strategies are mainly due to the dissolution of the sacrificial layers (feet or separating layers). In general, the dissolution of the sacrificial feet is easier than the sacrificial intermediate layers which are sometimes impossible to dissolve. Moreover it is easier to dissolve copper than nickel. However the copper layers are less flat. There is thus no such thing as a perfect methodology. Nevertheless, balancing all advantages and drawbacks, the Cu-Pt ECD within large surfaces is the best strategy to obtain rapidly large stocks of NWs of narrow length distribution.

Functionalization of the nanowires

4.1 Introduction and objectives

The next step towards the self-assembly of functionalized NWs is their functionalization. As described in Section 2.2, there are several ways to functionalize NPs. The most common strategies are to use SAMs or LbLs. The usual SAMs are made of silanes and thiols. The latter can be easily grafted on several noble metals such as the NWs produced in this thesis. Thiols are particularly known for their strong interactions with gold surfaces and gold NWs, conveniently leading to their functionalization. In that case, the ω -functional end groups of the thiol molecules may engage into chemical interactions with other functionalized NWs. These interactions range from electrostatic interactions and H-bonds to hydrophobic/hydrophilic interactions. Functionalization by LbL is very different from SAMs for it relies on entropic and electrostatic interactions and not on specific grafting; this is why it can be used on many materials, contrarily to thiols. However, the fuzzy nature of LbL assemblies blurs interactions at their outer surface. Both techniques have thus advantages, and could be used for the homogeneous monofunctionalization of NWs, and for local multifunctionalization, i.e. the different functionalization of ends (bottom and top) and sides of NWs. Despite some studies on the multifunctionalization of 1D NMs [58, 111, 112], this kind of functionalization remains challenging. Additionally, another challenge towards this objective is the characterization of multifunctionalized NWs. This problem arises from the size of the nano-objects and the very thin layer of functional molecule. Common way to characterize is to add fluorescent dyes on thiols to detect them grafted on the nano-objects. Nevertheless, detecting the fluorescence at the nanometric scale, even with confocal microscopy, is still a difficult endeavor. These challenges will be tackled in this chapter.

4.2 Strategy

Several routes have been investigated to obtain functionalized NWs. First of all, the choice of noble metals for the body of NWs has been made owing to their easy modification by thiols. Homogenous functionalization will be made with thiols in NWs suspensions and should not be that challenging since it is a simple and common process. Functionalizing differently the ends and side of NWs is however a different story. As already described in the previous chapter several strategies can be considered. First, one could use trisegmented NWs with sacrificial layers on both sides of the desired noble metals either attached to the substrate, or not. Another technique is to trap the NWs inside a PC membrane and functionalize their ends before their sides. A scheme of these strategies is shown in Figure 4.1.

The two first techniques imply the dissolution of the sacrificial layers after the first functionalization being performed. As observed in the previous chapter these dissolutions are not easy. It is especially important to ensure that the grafted thiols stay grafted in spite of the etching steps. The third technique does not require such post etching what is a great advantage, since dissolving the PC membrane is not a harsh process. In addition to thiol grafting, route (a) and (c) of Figure 4.1 were also tested with LbL deposition.

Regarding the proof of functionalization, there are few ways to characterize *in situ* the functionalities grafted on the NWs: fluorescence from a grafted fluorescent dye, or high-resolution TEM to spot the organic coating around NWs. Fluorescence is limited to relatively low magnifications whereas TEM does not provide contrast between different functions. Moreover, residual organic coatings could be erroneously taken as a proof of success. This is why fluorescence microscopy has been selected in this thesis. To improve resolution, the NWs that will be used as proof of concept of the functionalization will have larger dimensions than the ones targeted for the final assemblies.

Cyclic voltammetry (CV) was also used on flat surfaces to follow the main steps of the grafting process, and the resistance of the grafted layers to etchants.

The functional layers tested during this thesis were thiol SAMs and LbLs able to engage different interactions with other functionalized NWs. Four thiols were tested (Figure 4.2):

- Dodecanethiol (DDT), for hydrophobic interactions.
- Mercaptoundecanoic acid (MUA), for pH-dependent interactions. At low pH (below its pKa), the carboxylic acid group is protonated and the MUA can form H-bonds. At high pH, the COOH group is deprotonated and the function is negatively charged and can be

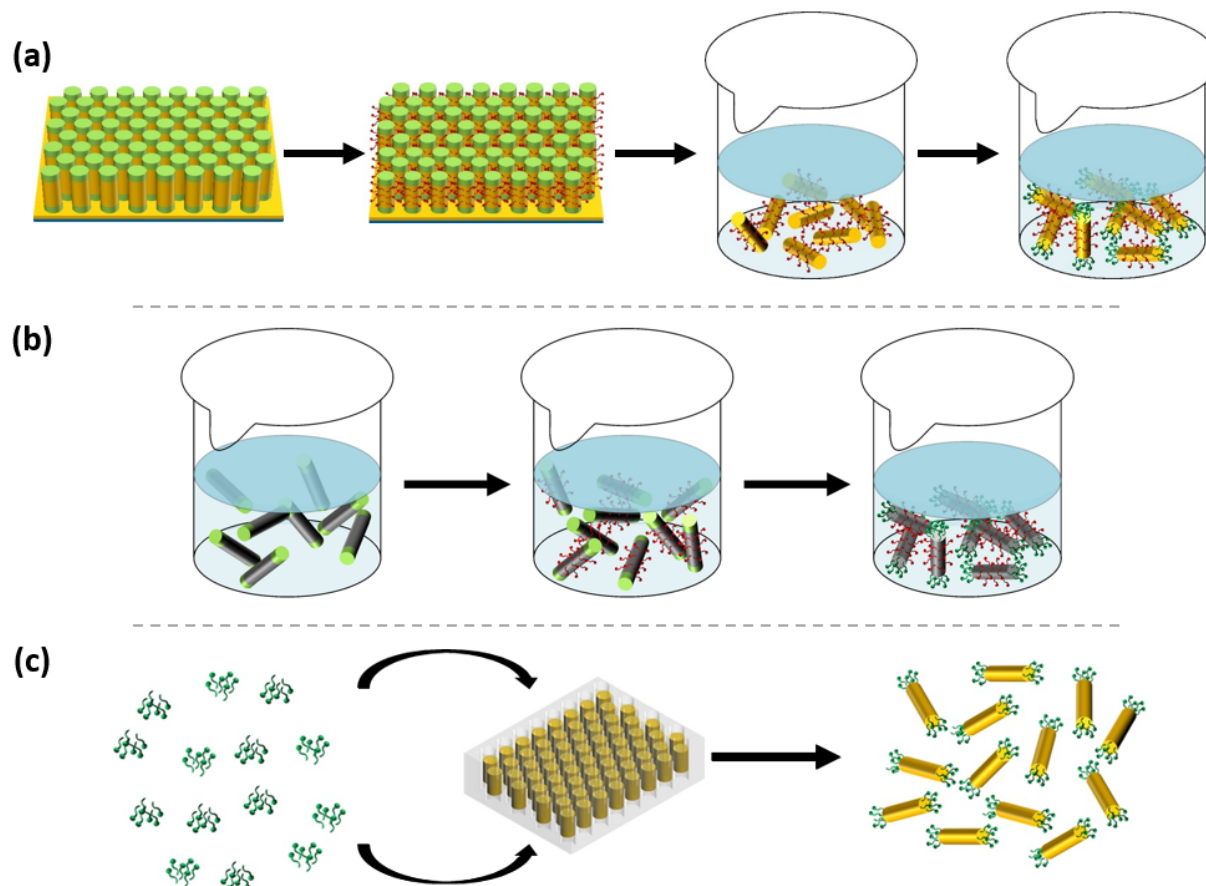


Figure 4.1: Scheme of routes used to obtain multifunctionalized NWs. Stepwise functionalization of (a) freestanding trisegmented NWs, (b) trisegmented NWs in suspension, (c) NWs trapped in PC membrane.

involved in electrostatic interactions.

- Mercaptoundecyl-N,N,N-trimethylammonium bromide (MUTAB), for electrostatic interactions (cationic).
- Poly(acrylic acid) with a thiol end group (PAA-SH), it should have similar properties as MUA except it is composed of many carboxylic acid groups and should thus have stronger interactions (its pKa is also slightly different).

For LbL assemblies, several polyelectrolytes were selected (Figure 4.3):

- Poly(allylamine hydrochloride) (PAH), a strong polycation.

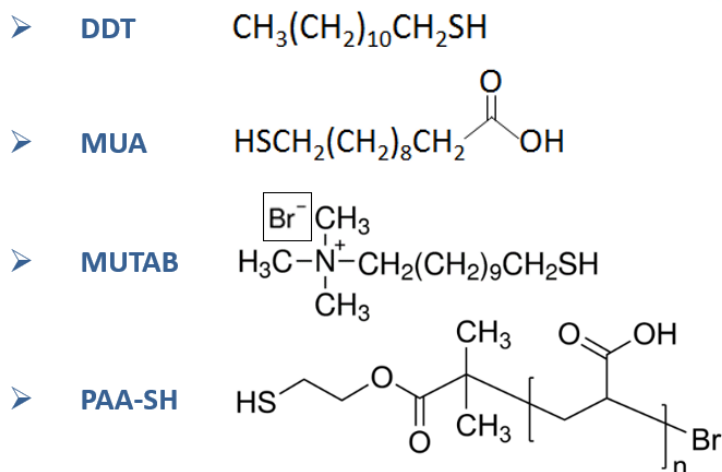


Figure 4.2: Semi-developed formula of the thiols used in this thesis.

- Branched poly(ethylene imine) (PEI), a polycation of strength dependent on pH due to its different amines.
- Poly(acrylic acid) (PAA), a weak polyanion (strength dependent on pH).
- Poly(styrene sulfonate) (PSS), a strong polyanion.

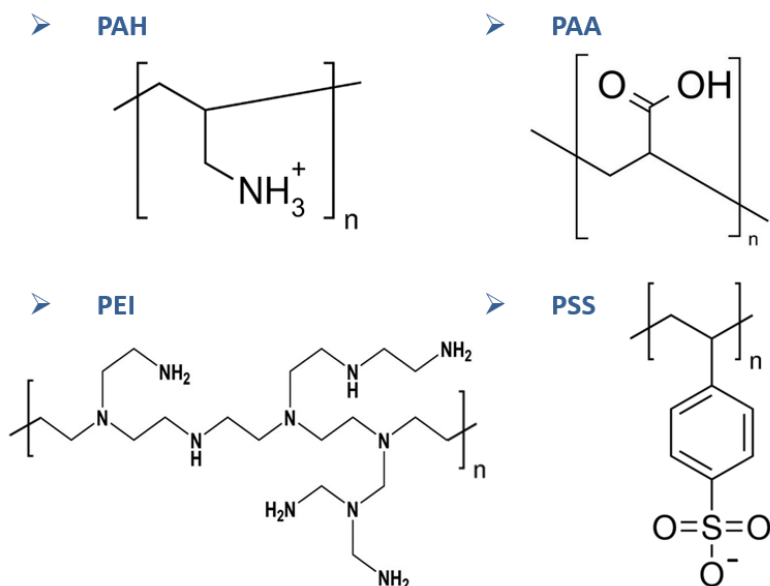


Figure 4.3: Semi-developed formula of the polyelectrolytes used in this thesis.

4.3 Results

4.3.1 Flat surface functionalization

The first tests of functionalizations were performed on flat surfaces. These tests intended to check the adherence of the functionalization in these conditions but they could also give information on the resistance of the grafting under harsher conditions, especially on the etching conditions.

4.3.1.1 Characterization of thiols SAMs by electrochemical means

Each thiol SAM has been tested on flat surfaces by electrochemical analysis to check that a homogeneous grafting was obtained. In addition, these analyses have also been used to study the resistance of the layers (on such flat surfaces) to the numerous etching processes required to dissolve the nickel sacrificial layers. The flat surfaces were silicon substrates coated with sputtered gold. The noble metals corresponding to the composition of the NWs (platinum, palladium or gold) were deposited by ECD, to obtain surfaces closer to the ones of the NWs. After deposition of the desired metals, the surfaces were immersed in thiol solutions (diluted in ethanol) for several hours and then rinsed with ethanol to remove the residual non-grafted thiols. Finally the functionalized surfaces are placed in an electrolytic cell (0.5 cm diameter) containing a metallic redox couple ($\text{Fe}^{2+}/\text{Fe}^{3+}$) that will allow probing the layer resistance by cyclic voltammetry (CV). Briefly, CV is a potentiodynamic electrochemical measurement, which consists of measuring the redox current, in a three-electrode electrolytic cell, while varying the voltage in cycles. A potential difference is imposed between a reference and a working electrode, and the current is measured between a working and a counter electrode [170]. This technique is widely used in order to explore the reaction kinetics or to study the electrochemical properties of an analyte in solution. In this thesis, the functionalized surface plays the role of the working electrode. When well functionalized, almost no current passes from the surface to the solution during the application of the voltage. In contrast, if non-grafted areas exist, the current can pass resulting in the oxidation and reduction of $\text{Fe}^{2+}/\text{Fe}^{3+}$. Consequently, a hysteresis loop is observed displaying the oxidation and reduction peaks of the redox couple. To summarize, when the surface is not fully covered by a SAM, a hysteresis loop is recorded, with a higher current; when the surfaces is completely coated by the SAM, the hysteresis loop is flat with almost no current passing. The complete description of the performed experiments is reported in Chapter 7 Sections 7.2.3.1 and 7.2.3.3.

SAMs on gold surfaces. Gold ECD was performed on surfaces of gold sputtered on silicon wafers. The ECD was made under the same conditions as the ones used to deposit NWs (pulsed mode at 55°C on 1.33 cm^2 surfaces) by applying a charge of 2 C. The surfaces were then diced ($\sim 1\text{ cm}^2$) and immersed in thiol ethanolic solutions ($2 \times 10^{-2}\text{ mM}$) for three hours. The surfaces were then recovered and thoroughly rinsed with ethanol. The thiols tested were DDT, MUA and PAA-SH. The results are given in Figure 4.4.

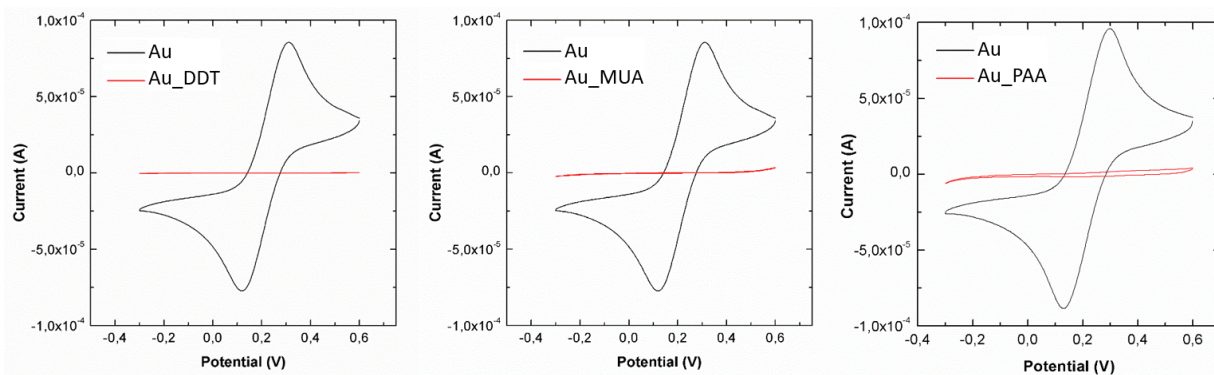


Figure 4.4: CV diagrams comparing bare gold surfaces and thiol-coated ones (DDT, MUA or PAA-SH).

One can see that the three thiols were well grafted, almost completely insulating the gold surfaces. There is almost no difference between the CV diagrams of DDT and MUA SAMs. On the other hand, the PAA-SH CV diagram is a bit less flat indicating that the layer is less compact and let some current pass. This is certainly due to the polymeric and amorphous nature of the layer.

Other tests were also performed to probe the resistance of the grafted SAMs to etching steps. Therefore, the surfaces undergone treatments similar to the one used to dissolve nickel sacrificial layers: immersion in nitric acid at several concentrations, for several times and including or not ultrasonication steps, which were performed in acid, every 15 min for 5 min. The results for DDT and MUA are given in Figure 4.5. The grafting layers resist to the etching conditions except for high concentrations of HNO_3 ($> 30\%$) or long time of immersion ($> 30\text{ min}$).

The functionalization prior to dissolution of Ni is thus possible but only when the Ni layers are promptly etched with acid of lower concentration. Unfortunately, as discussed in the last chapter, such conditions are not optimal for a complete dissolution of Ni in many cases. At the present time, the best not fully satisfactory etching conditions would be to dissolve Ni parts within 15% nitric acid for 30 minutes with ultrasonication steps, which avoids SAM degrafting.

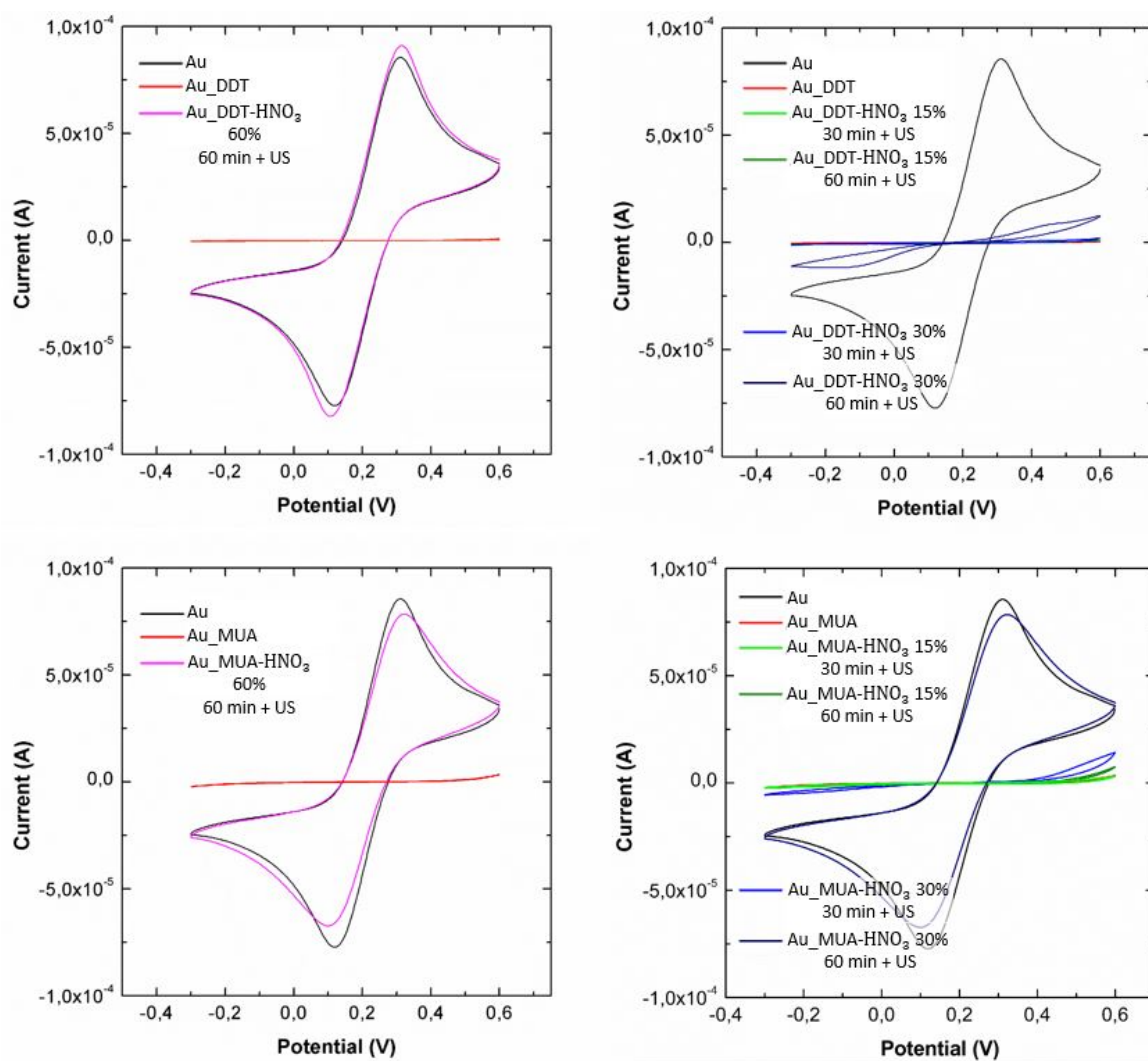


Figure 4.5: CV diagrams comparing bare gold surfaces and thiol SAMs-coated ones (with DDT or MUA) after undergoing or not nitric acid treatment. Concentrations are in mass and the "US" corresponds to the application of ultrasonication steps.

SAMs on platinum surfaces. Tests on platinum were performed very similarly to the ones on gold. The platinum was deposited on gold-silicon wafers in the same conditions as the ones used for NWs (continuous mode at 50°C; 1.33 cm² area) applying a charge of 3 C. The analyses were performed on DDT, MUA and PAA. It has appeared very quickly that there was an important

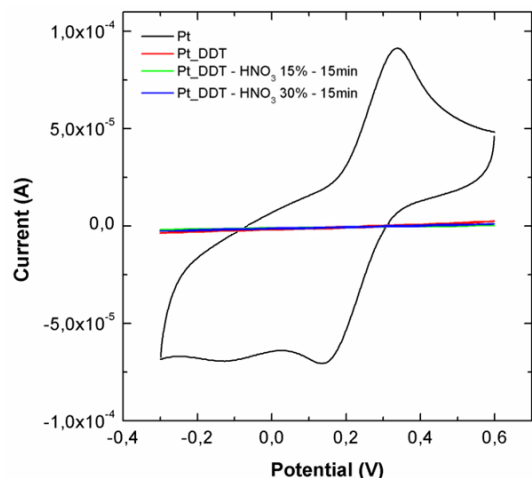


Figure 4.6: CV diagrams comparing bare platinum surfaces and DDT coated ones after undergoing or not acidic conditions.

difference with the previous results on gold. While DDT gave similar results (Figure 4.6), the MUA SAM was quickly destroyed by the conditions of the CV itself. In consequence the hysteresis cycles recorded were dependent on the number of cycles applied. Some of the resulting cycles are depicted in Figure 4.7. The results for the PAA-SH are very similar, except they were performed on platinum sputtered surfaces rather than Pt ECD surfaces. This change was done to check whether the problems of degrafting in CV were only dependent on the nature of the noble metal and not on a possible morphological parameter (such as roughness) specific to ECD. Both results prove that thiols are

much less strongly grafted on Pt than Au, as already described in previous publications [15, 17, 74]. Still, this does not mean that there is no grafting nor that the layer is not resistant to acidic conditions. It only means that the grafting

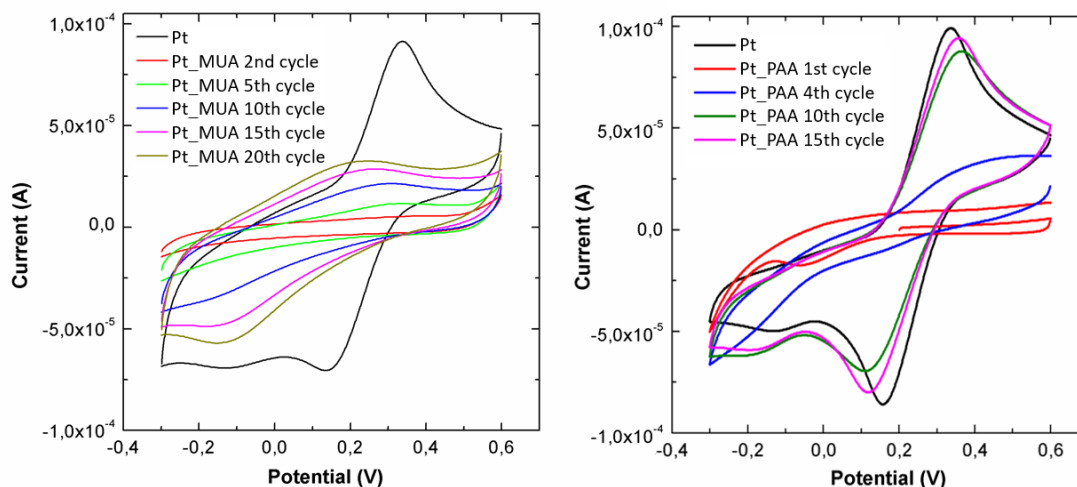


Figure 4.7: CV diagrams comparing bare platinum surfaces and thiols (MUA and PAA-SH) coated ones depending on the number of CV cycles (in the Fe²⁺/Fe³⁺ solution).

does not sustain the rather invasive CV analyses, which prevents from using this technique to follow the chemical resistance of given SAMs on Pt.

Therefore electrochemical impedance spectroscopy (EIS) was performed instead CV. In this three-electrode electrochemical analysis technique, the current is measured while a sinusoidal potential of small amplitude is applied over a wide frequency range. Then the impedance, which is the totally complex resistance, can be obtained by Ohm's law. Finally, the values of the impedance can be represented in a Nyquist diagram in which the imaginary part is plotted versus the real part. The results can be interpreted by modeling the electrochemical system as an equivalent electric circuit composed of resistances, capacitors (and other elements). One of the simplest and most used model for interfacial phenomena in electrochemical cells is the Randles electronic equivalent circuit [170]. It includes a capacitance (C_{dl}) corresponding to the double layer of ions at the electrode surface, the ohmic resistance of the electrolyte solution (R_s) and the charge transfer resistance (R_{ct}). A variation of this circuit is obtained by the addition of the Warburg element (Z_w) resulting from the diffusion from the solution to the electrode surface (Figure 4.8). These elements can be obtained from the Nyquist plot, and in particular R_s and R_{ct} . A bare surface without coating will have a very low R_{ct} , resulting in a quasi-linear Nyquist plot, while a surface with an insulating coating will have a large R_{ct} , resulting in a quasi semi-circular Nyquist plot.

The results of the EIS analyses on the platinum surfaces are given in Figure 4.9, indicating the good grafting of the SAMs on Pt surface. It also indicates that PAA-SH SAM can sustain acidic conditions (at least the ones suggested as the best to prevent degrafting for Au surface) even if R_{ct} is lower than when no acidic treatment is performed, displaying surely a slightly less covered surface.

SAMs on palladium surfaces. Palladium was less investigated due to the few NWs obtained by this technique. Palladium was deposited on Au-Si wafer in the same conditions as Pd NWs (continuous mode at 45°C; 1.33 cm² area) applying a charge of 1.5 C. The obtained results are depicted in Figure 4.10. MUTAB grafts well on Pd, and the MUA results are similar to the ones obtained with Pt. The CV curves depends on the number of cycles and each cycle degrafts a bit

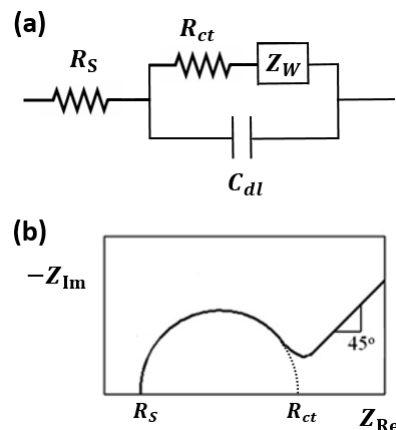


Figure 4.8: (a) Scheme of the Randles-Warburg circuit and (b) corresponding Nyquist diagram. Adapted from [170].

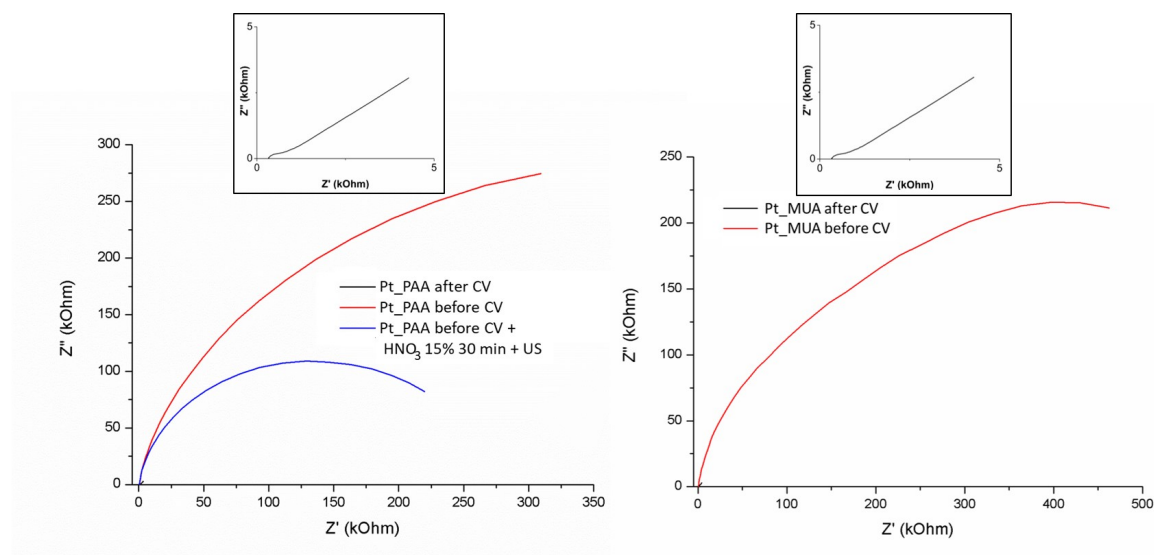


Figure 4.9: Impedance measurements on Pt surfaces coated with MUA (left) and PAA-SH (right). The results after CV are zoomed in inserts.

more MUA from the surface. The behavior of thiols on Pd seems thus similar to Pt even if in this case no EIS analysis was performed. Still the CV diagrams show that before the analyses the surfaces were at least partially covered.

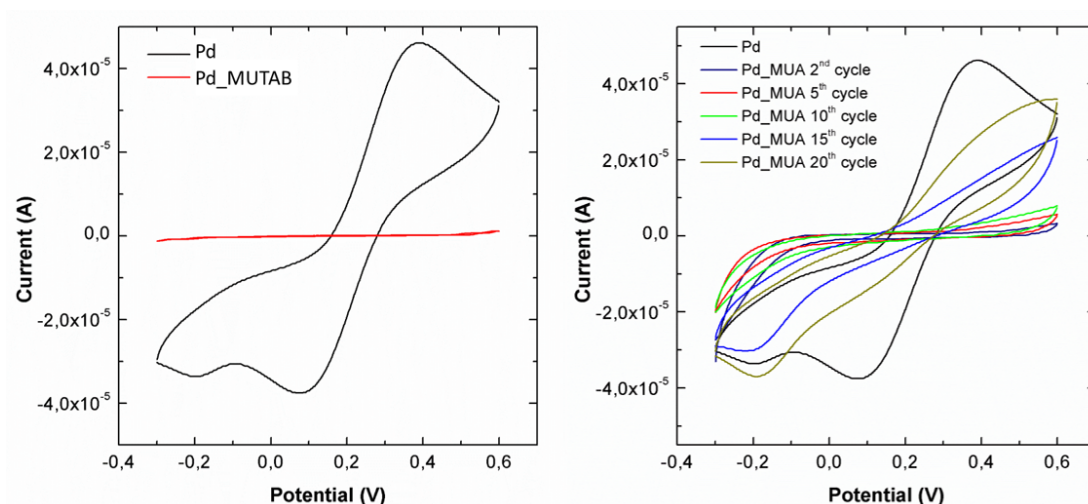


Figure 4.10: CV diagrams comparing bare palladium surfaces and thiols coated ones (MUTAB and MUA).

4.3.1.2 Characterization of layer-by-layer assemblies by fluorescence microscopy

LbL deposition was performed on platinum flat surfaces to follow layer assembly and to check the possible quenching of fluorescence with such metal. The manufacture of the Pt surfaces was identical to the one used when probing the thiol SAMs. A scratch was made on the sample surface (after LbL) with sharp tweezers (Figure 4.11), to remove the polyelectrolyte layers over

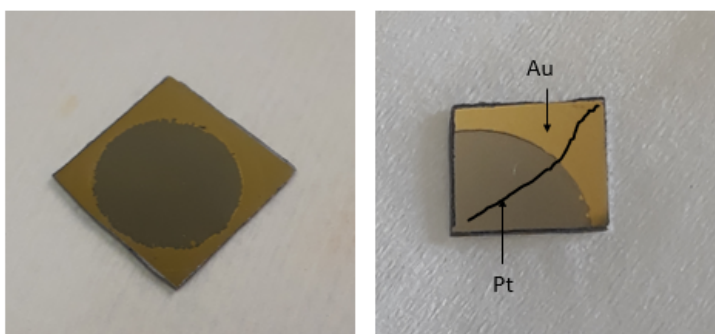


Figure 4.11: Result of the ECD of Pt on a Si/Au substrate. The black line represents the scratch achieved before fluorescence microscopy analyses.

a small part of the sample, allowing to compare between the background and the fluorescence of the sample covered by LbL. Therefore, the scratch served as a reference to evaluate the intensity of the fluorescence. Both Au and Pt surfaces could be imaged simultaneously, since Pt was only deposited over part of the sample (Figure 4.11). The selected LbL pair was PAH/PSS with a last layer composed of PAH-fluorescein isothiocyanate (PAH-FITC) which fluoresces in the green. The surfaces were successively immersed in PAH and PAA baths with intermediate rinsing steps to remove the excess of adsorbed polyelectrolytes. The surfaces were finally immersed in PAH-FITC and rinsed. The final products are then Pt surfaces coated with x (PAH/PSS) bilayers and one final layer of PAH-FITC. The technical details about the LbL can be found in Chapter 7 Section 7.2.3.1. The results are given in Figure 4.12. Below 4 bilayers, it is difficult to distinguish the scratch, suggesting that the polyelectrolyte layer is not thick enough to prevent quenching. From 4 bilayers on, the scratch can be distinguished from the fluorescent surface. When adding more bilayers, the contrast does not increase strongly. Therefore, the minimal number of bilayers on Pt surfaces that leads to a detectable fluorescence is four. Note that the results are identical for the gold part of the samples.

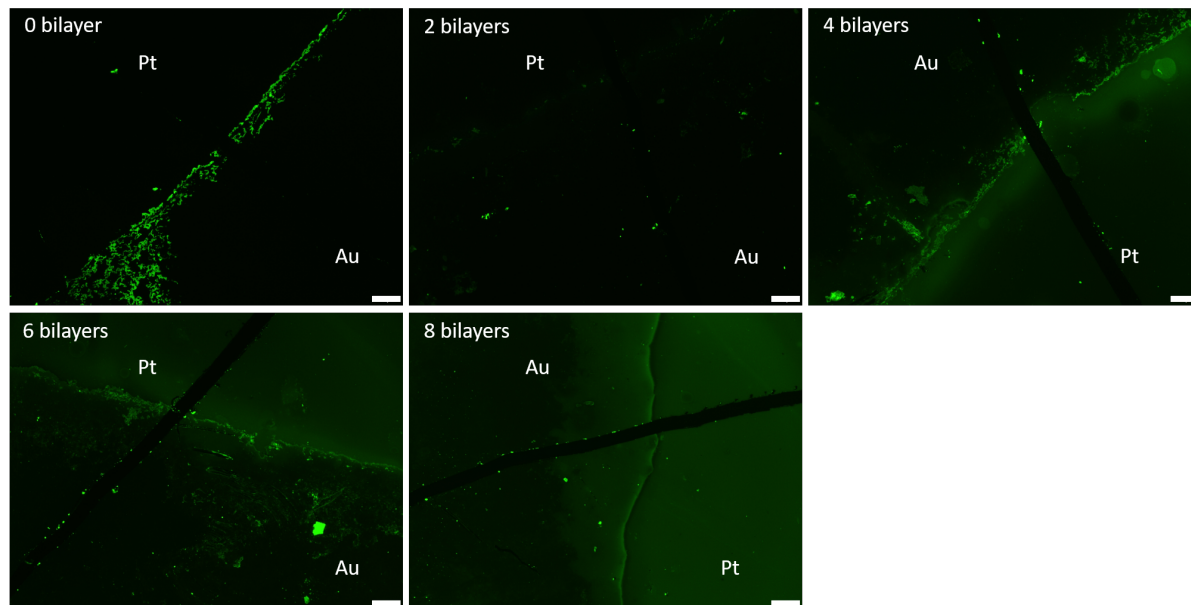


Figure 4.12: Fluorescence microscopy images of Pt/Au surfaces functionalized with 0, 2, 4, 6 or 8 PAH/PSS bilayers plus one PAH-FITC layer. Scale bar represent 100 nm.

4.3.2 Homogeneous monofunctionalization of nanowires

The functionalization of the NWs in a homogeneous way has been done mainly with thiols and NWs made of a single material in suspension. Because the characterization of such functionalized NWs is challenging, larger NWs were used and fluorescent dyes were added in the functionalization processes. In parallel, a few tests were performed aiming at functionalizing freestanding NWs from supported AAO templates. The functionalization was then made by LbL and characterized by scanning transmission electron microscopy (STEM).

4.3.2.1 Thiol functionalization of nanowire suspensions

Similarly to the functionalization of the flat surfaces, the standard NWs were immersed in an ethanolic thiol solution and left under agitation for one night (about 12 hours). This is a longer time than the one used on flat surfaces because the grafting is supposed to be more difficult hence more time may help to stabilize the thiols and to obtain a better coverage. Then, several rinsing steps were performed with ethanol via successive centrifugations. To allow easier characterization, some larger and longer NWs were grown (600 nm diameter and ca. 7-10 μm length). At those dimensions characterization with a standard equipment (epiflu-

orescence microscope or confocal microscope) is possible. The NWs were either functionalized with fluorescent thiols, or dyes were grafted on the thiol SAM. Several fluorescent thiols were used to have several colors of fluorescence available for the monitoring of multifunctionalization. In particular, FITC-poly(ethylene glycol)-thiol (FITC-PEG-SH) and rhodamine-poly(ethylene glycol)-thiol (Rhod-PEG-SH) were used. FITC fluoresces in the green whereas Rhod fluoresces in the red. For MUA and PAA-SH, some 4',6-diamidino-2-phenylindole (DAPI) was directly grafted on the COOH group(s) after the formation of the SAM/ This grafting was done in several steps involving 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and hydroxybenzotriazole (HoBt). Details on this grafting are in Chapter 7 Section 7.2.3.2. This allows the "direct" monitoring of MUA and PAA-SH SAMs. Moreover the DAPI fluoresces in blue and is thus complementary to FITC and Rhod.

Results for a fluorescent PEG-SH SAM on gold NWs are given in Figure 4.13, the images of DAPI grafted on MUA and PAA-SH SAMs on Au NWs are depicted in Figure 4.14. In

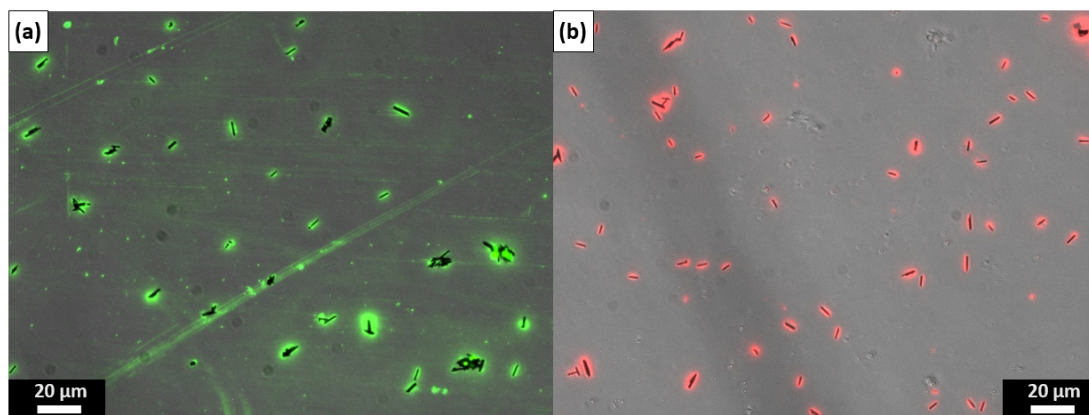


Figure 4.13: Epifluorescence microscopy images (combined with the bright field ones) of Au NWs functionalized by (a) FITC-PEG-SH and (b) Rhod-PEG-SH.

the images, fluorescence, characterized by the color (red, green or blue), can be detected all around the NWs. The NWs seem thus properly functionalized by PEG-SH, MUA and PAA-SH. However the finite resolution of the epifluorescence images prohibits to know whether the covering layers are continuous or defective; nevertheless, they demonstrate that many fluorescent thiols are grafted around the NWs.

In the case of platinum NWs, results were very similar for Rhod-PEG-SH and FITC-PEG-SH (Figure 4.15), but not for MUA or PAA-SH. The grafting of the PEG-SH occurred well but as for the gold NWs the quality of the coverage can not be extracted from these images. Anyway, no blue fluorescence could be obtained after DAPI grafting. Since the same reaction was successively used to post-modify MUA and PAA-SH SAMs on gold, and considering that the deposition of

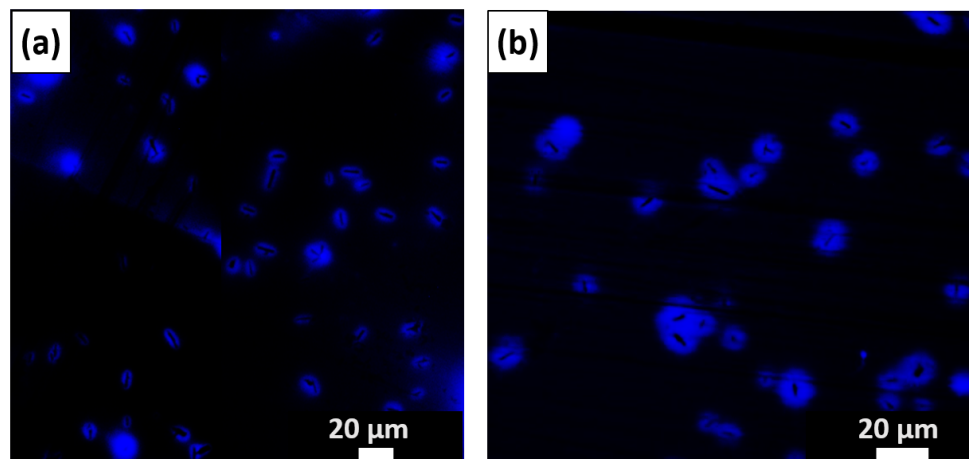


Figure 4.14: Epifluorescence microscopy images of Au NWs functionalized by (a) MUA and (b) PAA-SH, with post-grafting of DAPI on the carboxylic acid group(s).

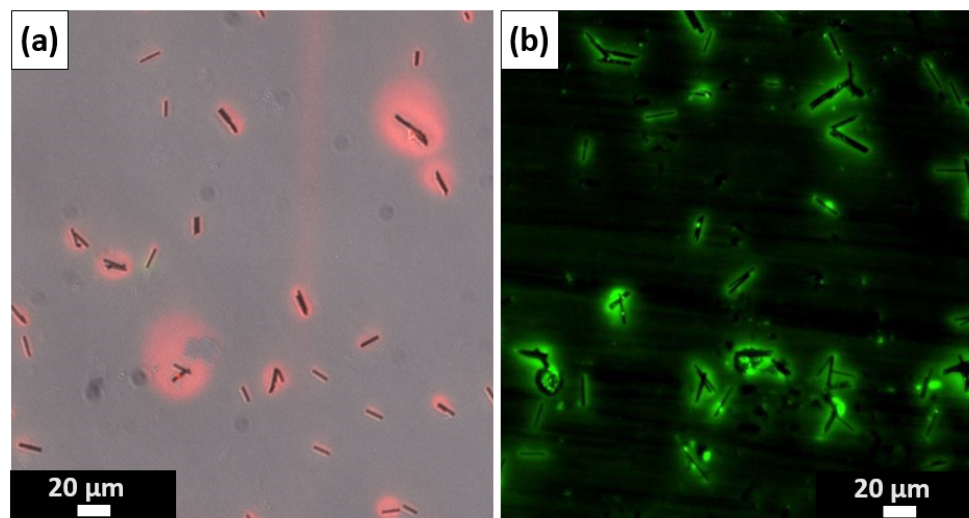


Figure 4.15: Epifluorescence microscopy images of Au NWs functionalized by (a) Rhod-PEG-SH (combined with the bright field image) and (b) FITC-PEG-SH.

these SAMs on Pt NWs leads to an assembly behavior very different from bare Pt NWs (Chapter 5), one concludes that either the DAPI fluorescence is quenched by Pt, or the DAPI grafting process destroyed the SAMs. This might be the case since one has seen previously that thiol SAMs are less stable on Pt than on Au. On the other hand, quenching of the fluorescence by Pt cannot be fully excluded, even though quenching is mainly reported for quantum dots or fluorescent ligands in presence of some Pt complexes or ions [171, 172, 173].

4.3.2.2 Layer-by-layer assembly on freestanding nanowires

Because freestanding NWs from ECD within supported AAO templates are easy to handle and wash, they are ideal candidates for LbL coating. The NWs tested were Au NWs with a Ni foot and the PAH/PAA pair of polyelectrolytes was selected. The number of bilayers was eight. Unfortunately, once the LbL performed, the NWs could not be recovered by etching the Ni part with nitric acid, possibly due to the protective effect of the LbL cushion. Eventually it was possible to recover the NWs by intense ultrasonication of the system until fracture of the NWs at their basis (or at their constriction). STEM results are shown in Figure 4.16: the organic cushion corresponding to the LbL coating is clearly apparent. This cushion appears in white in the images which might be due to the STEM detector being a dark field detector. Nevertheless NWs that were not coated by LbL did not present this cushion. This proves the possibility to functionalize NWs while they are freestanding, as already reported previously [174]. Although successful, this strategy was not pursued owing the reproducibility problems encountered when using homemade supported AAO templates.

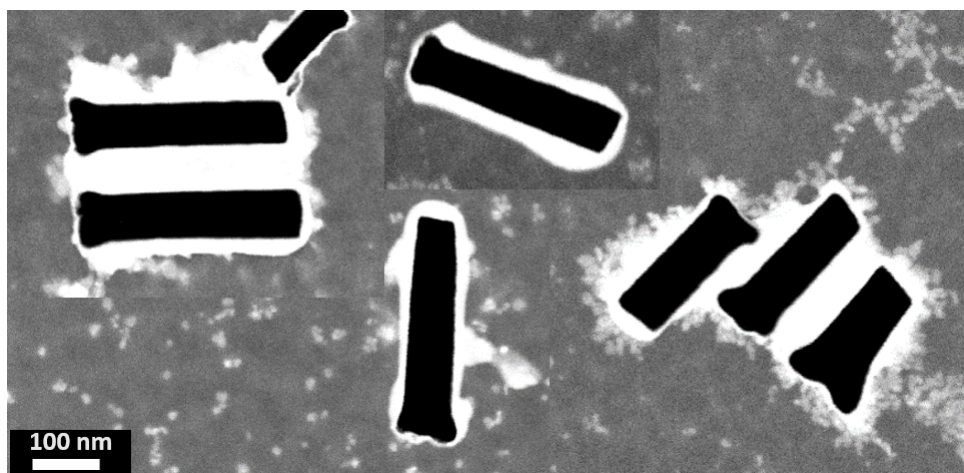


Figure 4.16: STEM images of Au NWs functionalized with $(\text{PAH/PAA})_8$ layers, obtained via the LbL of freestanding NWs from supported AAO templates.

4.3.3 Homogeneous multifunctionalization of nanowires

A few tests of homogeneous multifunctionalization were performed on NWs. This kind of NWs is not particularly interesting for this thesis, for they host several randomly dispersed functions; hence the interactions between the NWs are difficult to predict. Still multifunctionalizations

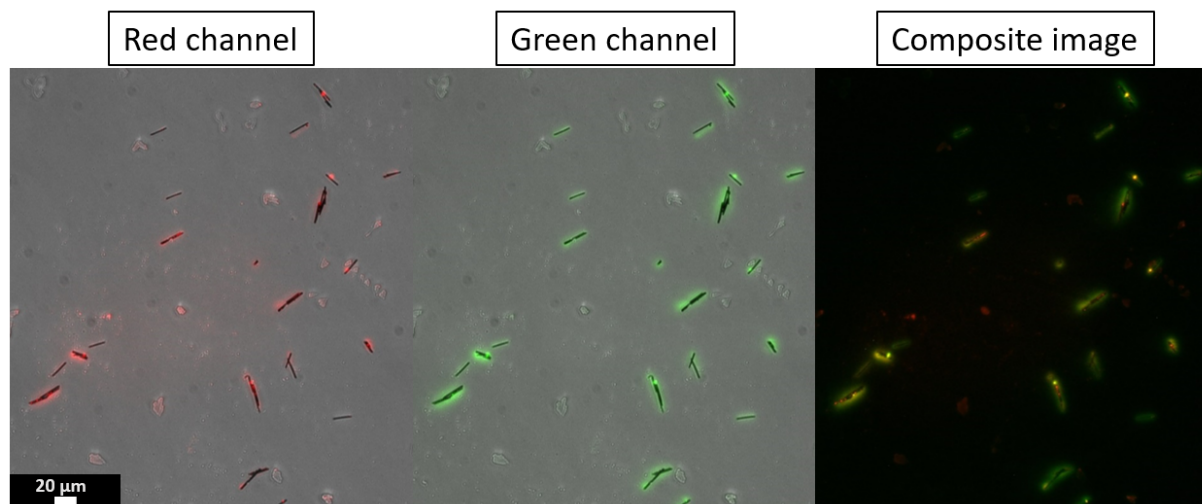


Figure 4.17: Fluorescence microscopy images of Pt NWs homogeneously bifunctionalized by FITC-PEG-SH and Rhod-PEG-SH.

was performed to check the wider applicability of the process. The NWs were immersed in ethanolic 1:1 solution of FITC-PEG-SH and Rhod-PEG-SH (each thiol concentration: 10^{-2} mM). It was decided to use two similar anchoring stems for the thiols (PEG-SH) hoping this would prevent preferential addition of one thiol, leading in the end to almost monofunctionalized NWs. The results are depicted in Figure 4.17. The red and green fluorescences are easily observable surroundings the NWs. It seems thus that NWs are grafted more or less equivalently by the two thiols although those images (due to the fluorescent resolution) do not allow to conclude on the spatial distribution of the fluorophores on the NW surfaces.

4.3.4 Spatially localized multifunctionalization of nanowires

When taking into account the difficulty to dissolve the nickel sacrificial parts and the relative resistance of the grafted layers, the best strategy to obtain spatially-localized multifunctionalized NWs is the one involving NWs trapped inside PC membranes. The process allows the different functionalization of the ends of the NWs and their sides, without any grafted layer being in contact with metal etchants. Again, the spatially-localized functionalization trials were performed on NWs of large diameter and high aspect ratio (gold or platinum). The functionalization was first performed with thiols for easy processing; then LbL was used because of diffusion problems discussed below.

4.3.4.1 Local functionalization of nanowires by thiol SAMs

The chosen thiols were FITC-PEG-SH and Rhod-PEG-SH. Functionalization was performed in the same way as usual: immersion of PC membrane in ethanolic thiol solutions. Then, after several rinsing steps, the NWs were recovered in solution by dissolving the PC. Eventually a second functionalization was performed to functionalize the sides of the NWs.

The first tests only implied the functionalization of the ends of the NWs without side functionalization. The results were irreproducible, although some experiments were positive: such results are depicted in Figure 4.18 and Figure 4.19 (left). One can see that the fluorescent response is concentrated on both extremities of the NWs and so at least a few thiols were grafted on these places. In addition, a test was performed to functionalize only one end of the NWs. It was successfully done with Rhod-PEG-SH on Pt NWs, by applying the thiol solution on one side only of the NW-entrapping membrane (Figure 4.19 (right)). The red fluorescence is well concentrated at one extremity of the NWs. This technique was investigated because it could be used to obtain locally tri-functionalized NWs, by modifying first the two ends of NWs separately (Figure 4.20), then performing the functionalization of the side of the NWs.

Despite the fact that localized grafting was sometimes successful, many experiments only gave rise to homogeneously-modified NWs. This could be due to a diffusion of the thiols between the NWs surface and the walls of the pores of the PC membrane, or to diffusion of the thiols along the surfaces of the NWs after SAM formation, as already described for flat surfaces [77, 78].

One thus attempted to functionalize differently the ends and sides of the NWs. Pt NWs were first functionalized with Rhod-PEG-SH on their ends, then with FITC-PEG-SH on their sides. One representative result is depicted in Figure 4.21, showing that the thiols are not spatially-localized. Yet, Rhod-PEG-SH was well grafted on the ends of the NWs as checked before the second functionalization. This is may be partly due to thiol exchange, occuring during the second functionalization step. This kind of exchange has already been described [77, 80]. If this exchange had occurred via the solution, it would have led to the loss of the red fluorescence on the head rather than spreading it on the whole NW surface. The exchange should thus happened where the NWs are already functionalized (the ends) and the thiols on those spots should have been replaced by the thiols in the high concentration solution during the second functionalization. Indeed, one can see green fluorescence on the head, confirming that the previously grafted thiols were displaced by the second thiols in solution. However, the fact that the red fluorescence is seen on the lateral surface of the NWs after immersion in the second thiol solution strongly suggests that a surface diffusion mechanism also occurred in parallel. It would be worthwhile to investigate

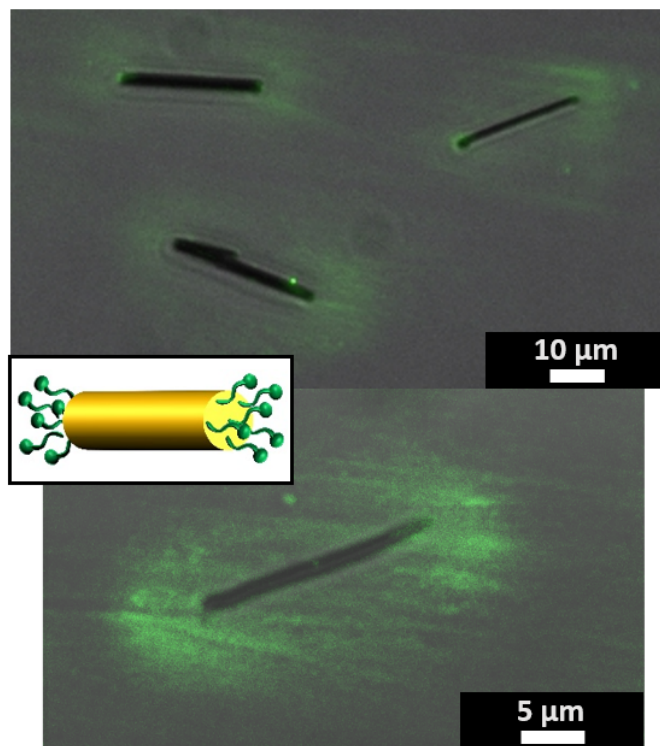


Figure 4.18: Confocal microscopy images of Au NWs end-functionalized with FITC-PEG-SH. Inset: schematic representation of the locally functionalized NWs

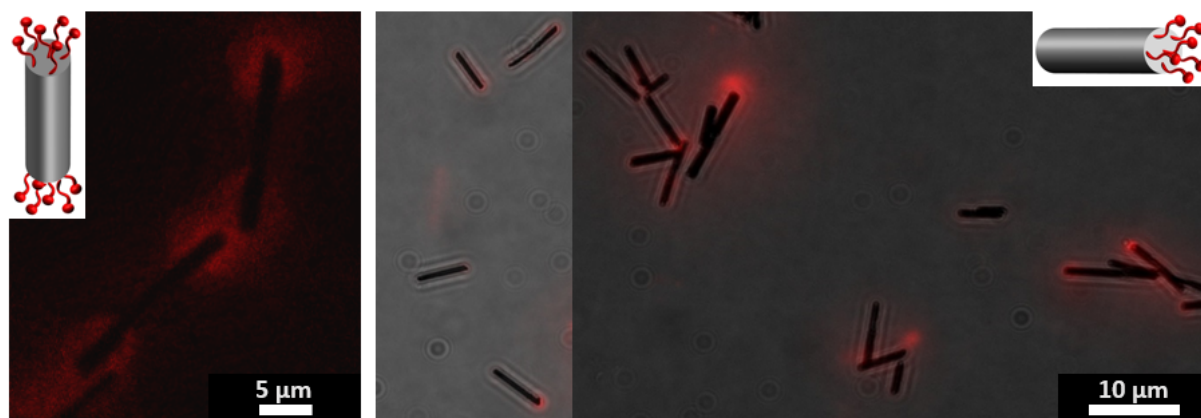


Figure 4.19: Images of Pt NWs locally functionalized with Rhod-PEG-SH. (Left) Confocal microscopy image showing functionalization of both ends. (Right) Fluorescence microscope images (combined with the bright field images) showing functionalization of only one end. Insets: schematic representation of the locally-functionalized NWs.

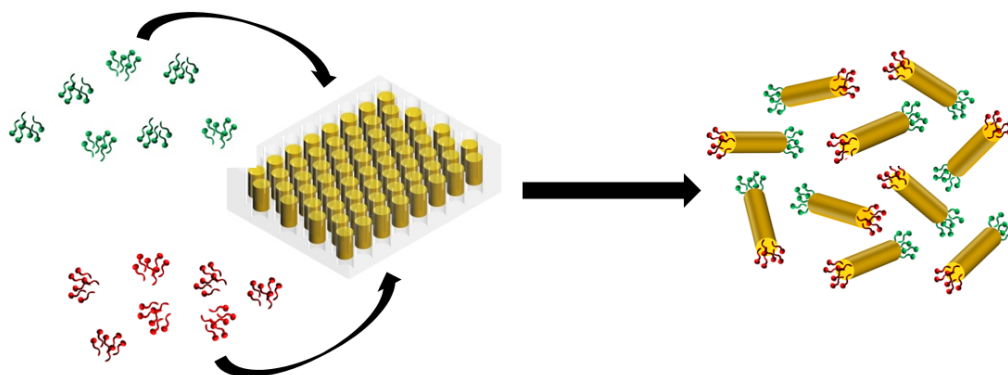


Figure 4.20: Schematic of the strategy to obtain NWs with both ends differently functionalized, that could eventually be used to obtain tri-functionalized NWs.

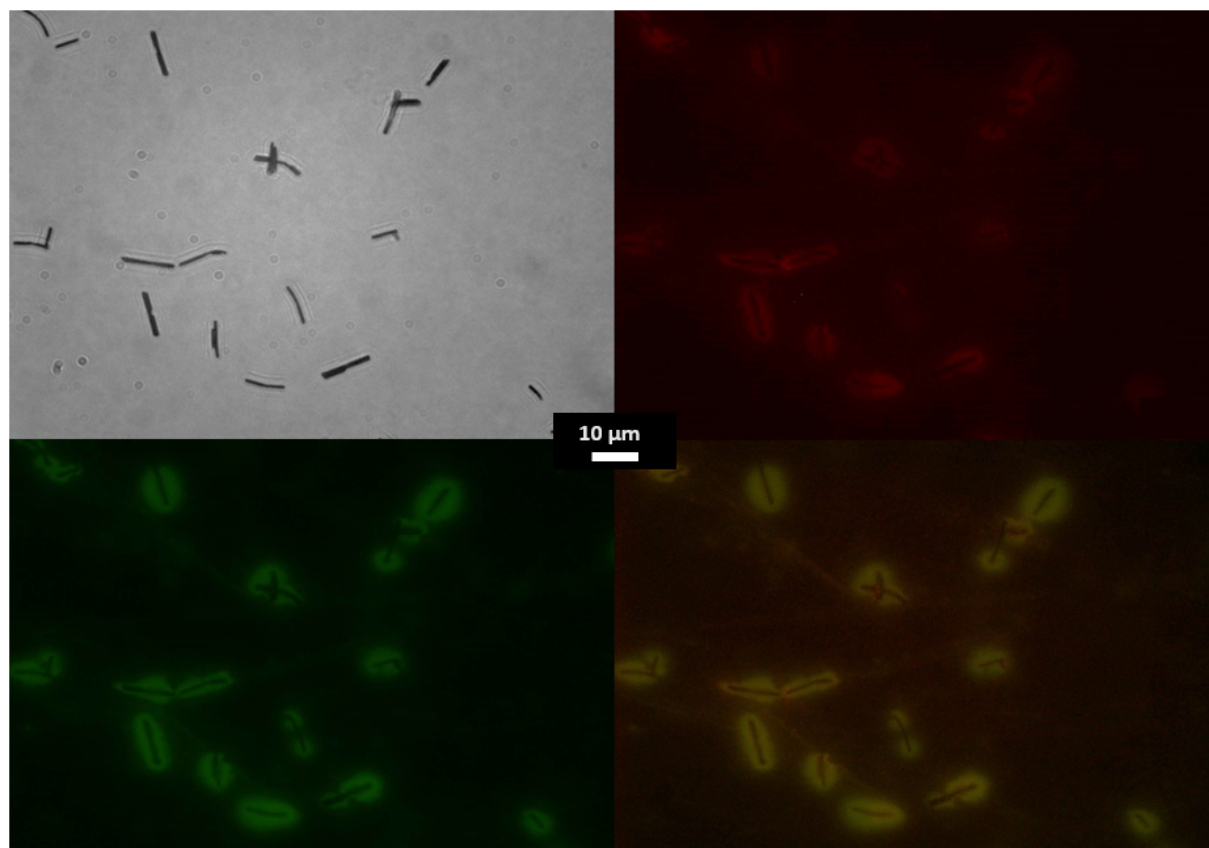


Figure 4.21: Results of fluorescence microscopy for multifunctionalized Pt NWs: ends were first functionalized by Rhod-PEG-SH, then sides were modified with FITC-PEG-SH. The first channel is the bright field image, the second and third are the red and green channel and the last one is the addition of both fluorescence channels.

further.

In those conditions because of this diffusion issue, the spatially-localized multifunctionalization of the NWs could not be achieved with thiol SAMs.

Some solutions that were not attempted could limit or prevent this problem. In particular, it would certainly have been beneficial to graft polythiols on the NW ends instead of the single thiol molecules. It would have created several anchoring points per molecule on the surface and should have reinforced the attachment at specific places of the NWs. Another approach would be to use another grafting mechanism leading to stronger links than thiols on gold (or other noble metals), e.g., diazonium grafting. Diazonium salts are a group of organic compounds sharing a common functional group $R-N_2^+X^-$, where R can be any organic group, such as an alkyl or an aryl, and X is an inorganic or organic anion, such as a halogen. These salts can be reduced on metals to make films alike SAMs [175]. The interest of this technique is that the link formed with the metal has been proven to be covalent. In particular, recent studies demonstrated the coating of gold NPs by this mean, leading to Au–C covalent bonds even if the reaction mechanism remains somehow unclear [176]. Finally a last approach would be to use LbL assembly and this will be described in the next section.

4.3.4.2 Local functionalization of nanowires by layer-by-layer assemblies

LbL assembly was tested to overcome the diffusion of thiols outside their primary grafting areas. LbL assembly of PAH and PSS was performed on the ends of platinum NWs embedded in the pores of PC membranes. After each immersion in solution of polyelectrolytes, the excess of polyelectrolytes at the membrane surface was removed using a cell scraper, and the membrane was washed into a salty solution at the same pH and ionic strength as the deposition solutions. The LbL assemblies frequently detached from the NW ends after release from the membrane (Figure 4.22 left). No fluorescence from the PAH-FITC could be observed, since the layer did not adhere to the NWs. A layer of branched PEI was then used to make a first adhesion layer, since amines are interacting with gold. The LbL process with the PEI gave slightly better results (Figure 4.22 right) since several green "tails" can be seen on some NWs. Nevertheless it was very rare when both ends of the NWs were functionalized after release.

It was then suspected that the LbL grafting could not sustain the conditions of dissolution of PC membrane and the washing/centrifugation steps needed to purify the NWs suspension. During the standard process of PC dissolution and transfer to ethanol, the NWs suffer in total five steps of centrifugation and ultrasonication. Indeed, if the NWs are directly observed after

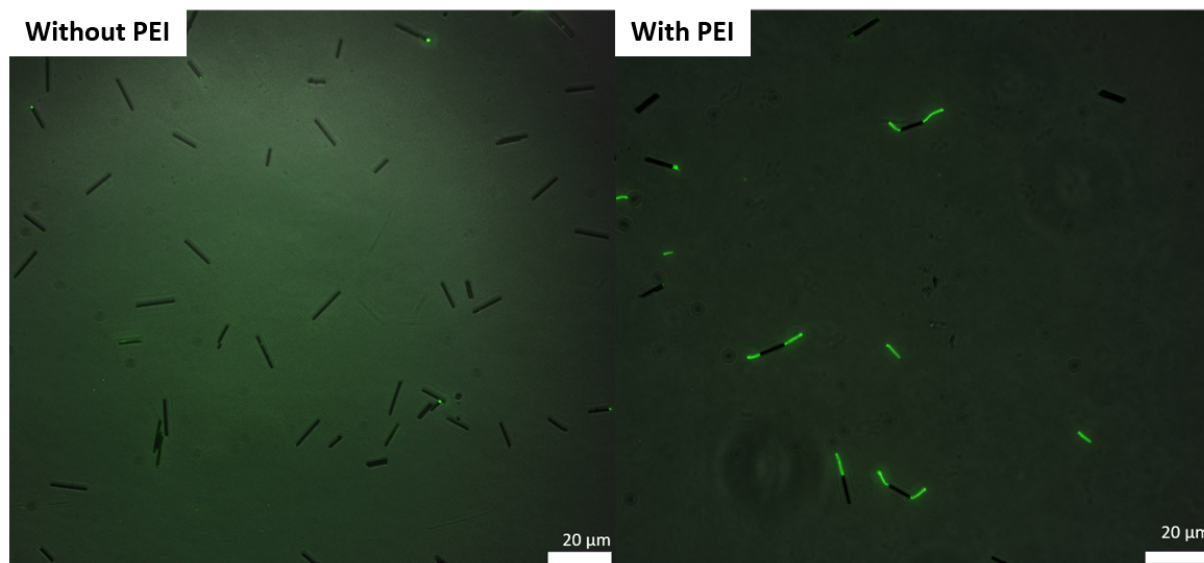


Figure 4.22: Fluorescence microscopy images of Pt NWs obtained after LbL coating of their ends. (a) $(\text{PAH}/\text{PAA})_4/\text{PAH-FITC}$. (b) $\text{PEI}/\text{PAA}/(\text{PAH}/\text{PAA})_3/\text{PAH-FITC}$.

one only dissolution step, many NWs appear to be functionalized on both sides (Figure 4.23 (a)). However, on other parts of the probed sample some PC residues remained attached to the NWs. Therefore, an alternative dissolution method was established to recover the NWs, by filtration on a nanoporous polyimide (PI) membrane. Additional dissolution of the remaining PC and rinsing steps can then be done on this membrane. Thanks to this method the NWs can be washed and rinsed without damaging processes (centrifugation or ultrasonication). Figure 4.23 (b) shows the results obtained with this alternative method: the NWs present fluorescence on both extremities, meaning they are functionalized on those points. The main issue with this dissolution technique is that the NWs stick to the PI membrane and cannot be re-suspended after collection. This issue might be resolved by replacing filtration on the PI membrane by a method based on the filtration of NWs in the presence of a powdered adjuvant, as in Jonas et al. [177].

This was not done because the NW ends are grafted with very thick organic layers, much thicker than the thickness of an equivalent multilayer grown on a flat substrates. This is due to the accumulation of the polyelectrolytes inside the pores. These adsorbed polyelectrolytes finally form a sort of organic cylindrical extension to the NWs. In order to prevent the adhesion of polyelectrolytes on the walls of the pores of the PC membrane, a surfactant, Pluronics[®], was added on the pore walls prior or after ECD. This was however not successful: the results were very similar with or without Pluronics[®].

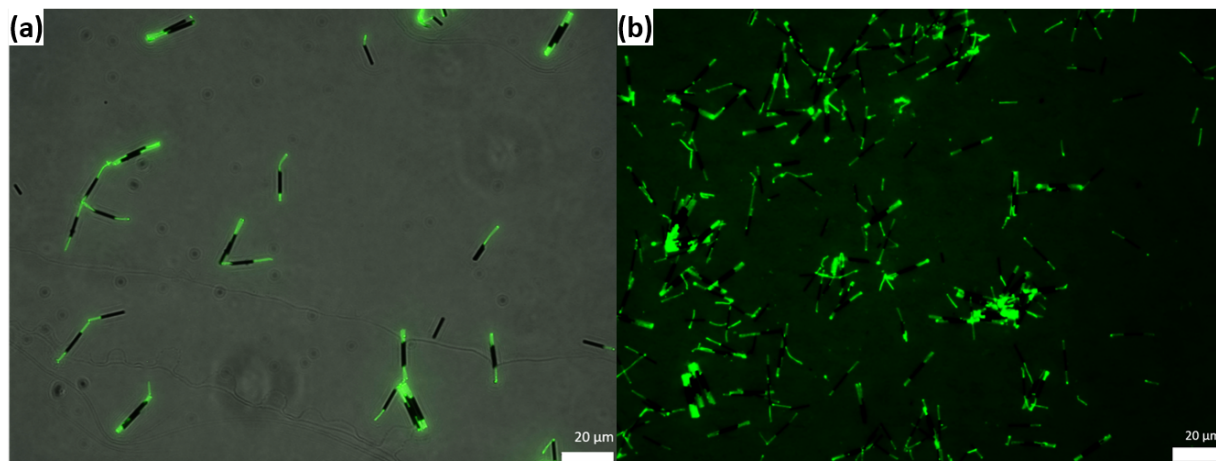


Figure 4.23: Fluorescence microscopy images of NWs obtained after LbL coating [PEI/PAA/(PAH/PAA)₃/PAH-FITC] (a) and recovery after one dissolution/washing step only, and (b) by the alternative dissolution technique.

LbL on the ends of NW entrapped in pores is thus possible but difficult to control precisely, and leads to hybrid wires which do not correspond to the goal of this study. Using such hybrid trisegmented NWs (organic-inorganic-organic) would be feasible, but is likely to be difficult due to the entanglement of the softer portions of the NWs. Nevertheless the hybrid nature of the NWs may direct their assembly in a way in which the organic parts entangle between each other. It may thus lead to kind of micellar structures when in suspension. The apparition of such micellar structure is supported by several samples (Figure 4.24).

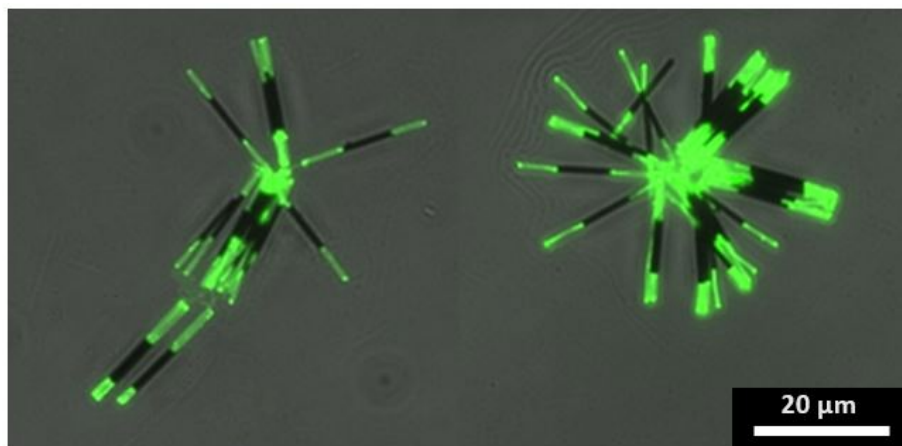


Figure 4.24: Fluorescence microscopy images of NWs obtained after LbL coating [PEI/PAA/(PAH/PAA)₃/PAH-FITC] and recovery after one dissolution/washing step only. The images were selected to emphasize the presence of some micellar-like structures.

4.4 Summary

The functionalization of NWs has been proven on gold and platinum NWs with thiols, even if the quality of the NW covering layer was not determined. Homogeneous functionalization was demonstrated with fluorescent thiols –FITC-PEG-SH and Rhod-PEG-SH– and also by post-grafting of DAPI on the carboxylic acid group(s) of MUA or PAA-SH. The presence of grafted DAPI could be shown on gold, not on platinum. This might be due to the less stable nature of thiol SAMs on Pt, which would not resist to the DAPI grafting conditions; or to fluorescence quenching by Pt.

The resistance of the layers was tested on flat surfaces. The resistance to acid treatment is generally good but not sufficient for the complete removal of nickel sacrificial layers. This led to the conclusion that the most viable strategy to manufacture selectively multifunctionalized NWs is the in-membrane functionalization strategy. A few successful trials of local functionalization have been performed in this way, especially with FITC-PEG-SH and Rhod-PEG-SH on the ends of Au and Pt NWs. Moreover an alternative strategy has been explored to functionalize one end only of the NWs, which was successful for Pt NWs with Rhod-PEG-SH. However, the functionalization of the ends by thiols often leads to the homogeneous functionalization of the NWs. This could be due to the thiols leaking in between the pores wall and the NWs. Eventually, no 100% efficient selective multifunctionalization could be achieved by thiol SAMs. The strongest issue is that the thiols do not stay on their original anchoring point. This is certainly due to diffusion (and exchange) of thiols. To overcome this problem, some tests were performed via LbL limited to the ends of in-membrane Pt NWs. Two problems arose with this technique: the grafting of the LbL was not strong enough to sustain the standard dissolution and washing steps of the membrane, and the polyelectrolytes clearly accumulated inside the pores, leading to formation of "long" organic tails at the ends of the NWs. This last problem was not resolved in spite of attempts to reduce the affinity of the polyelectrolytes with the PC membrane.

Eventually, locally multifunctionalized NWs could not be achieved. Nevertheless, the strategy proposed may be improved by the use of polythiols or diazonium salts as functionalization agents on the heads of the NWs. It should insure stronger link or multiple anchoring points hence better grafting on the NWs. These functionalizations were not tested here but homogeneously functionalized NWs were easily obtained by "simple" thiol grafting. Such NWs may thus be used to study the behavior of NW assembly depending on surface functionality. This will be performed in the next chapter.

Self-Assembly

5.1 Introduction and objectives

The assembly of the NWs is the last step and final objective of this thesis. In Chapter 2 (Section 2.3) several strategies were described to obtain self-assembly or to assemble NPs. The self-assembly of nano-objects in suspension seems to be the simplest to implement but the characterization of the obtained assemblies is often difficult to realize. The second most widely used technique is the drop-casting. It consists in the deposition of a droplet of NPs in suspension on a substrate and in waiting until the complete evaporation of the solvent. The objects can assemble themselves during the evaporation of the droplets and especially along the pinned edge of the droplet according to a slip and slick motion process. The great advantage of this technique is the ease of characterization of the resulting assemblies. At the end of the process assemblies are already dried on a substrate and can be analyzed without any difficulty by SEM. The third most used technique is the assembly of the NPs at a fluid-fluid interface. This special process requires a precise and smart execution to obtain reproducible results. Moreover the characterization problem also arises in this case. Many studies about fluid-fluid assembly have used characterization techniques that can have a huge impact on the assembly itself. So eventually the assembly characterized is not the original assembly floating at the fluid-fluid interface anymore. In the present work, the drop-casting and the assembly at the fluid-fluid interface have been used and strategies have been developed to collect the assemblies in a reproducible manner allowing their further characterization.

5.2 Strategies

To assemble the NWs two strategies with several variants have thus been chosen. The first strategy is the drop-casting (Figure 5.1). It is the simplest to implement and allows an easy char-

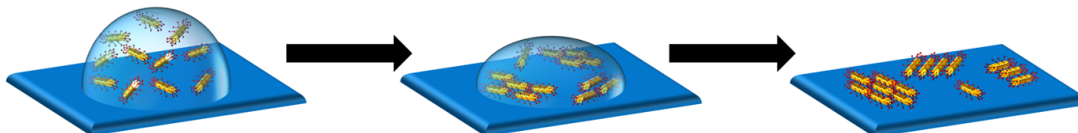


Figure 5.1: Schematics of the drop-casting method.

acterization of the obtained assemblies. The main drawback could be the rather strong forces that it implies. Indeed during the droplet evaporation local strong capillary forces should allow the compaction of the NWs. However if the compaction forces are too strong, the NWs will assemble whatever the interaction forces between them.

The second strategy is the fluid-fluid interface assembly. It may lead to a "more autonomous" self-assembly in comparison to the drop-casting. Indeed the NWs are concentrated at the interface thanks to a kind of Pickering emulsion. But once at the interface they should be free enough to organized themselves thanks to their mobility arising from the fluid interface. The major drawback of this method is the difficulty to recover the assemblies for further characterization. Here several strategies were developed to recover the assemblies the most efficiently possible to keep the original assemblies and to have reproducible results. The aim being to transfer the assembly on a substrate

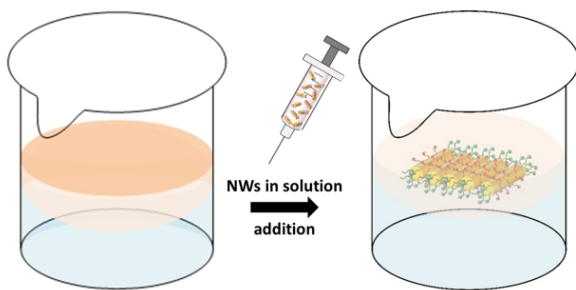


Figure 5.2: Schematics of the oil/water assembly method.

enabling characterization by SEM or AFM. Before recovery, to facilitate the transfer process, the upper phase (here toluene) was evaporated. Next, an additional compaction step was often performed by addition of ethanol as it was proposed by the study of Li et al. [152]. To recover the assemblies, the simple fishing method was first used. It consisted in holding the substrate with tweezers, immersing it inside the water phase, moving it under the floating assembly and lifting it to fish the NW layer. However it was soon abandoned because it strongly perturbed the assemblies.

The drain-to-deposit strategy, developed by Yang et al. [144], was more extensively investigated. It consisted in pumping off the water supporting the assembly until deposition of the assembly on

a substrate placed in the bottom of the beaker. The pumping was made with a peristaltic pump linked to a flat tip syringe. The peristaltic pump allowed a very slow pumping speed ($50 \mu\text{L}/\text{min}$) that should preserve the assembly from disturbing convection fluxes. To pump the maximum of the water phase, the tip of the syringe was carefully vertically inserted inside the beaker until the bottom after complete evaporation of the toluene. The scheme of the drain-to-deposit technique with the optional compaction step is presented in Figure 5.3.

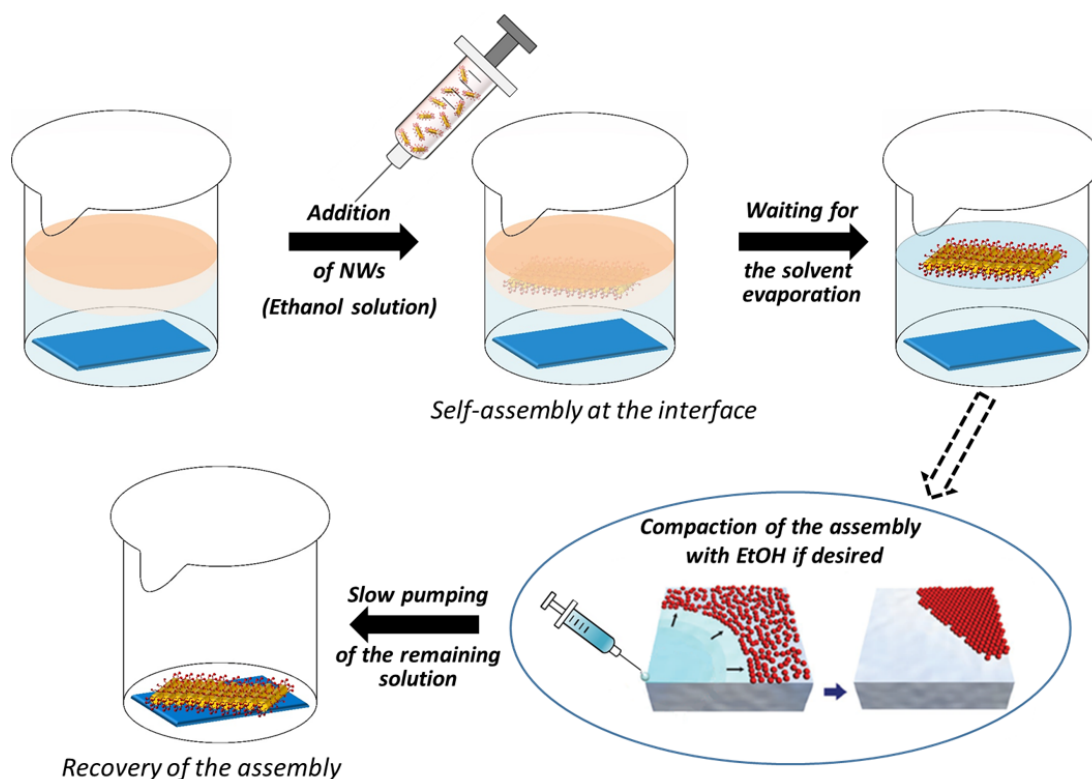


Figure 5.3: Complete scheme of the assembly at the toluene-water interface, the evaporation of the toluene, the optional concentration of the assembly with ethanol (the red marbles representing the NWs) and the drain-to-deposit characterization processes.

The last recovery method used a poly(dimethylsiloxane) (PDMS) stamp to recover the assembly. The PDMS is very hydrophobic and so metallic NWs easily stick on it. Therefore the NW assembly, floating at the air-water interface, could be inked on a PDMS stamp by gently pressing the stamp on the interface (Figure 5.4). The great advantage would be the very rapid gluing of the system on the stamp. It should avoid the draining or drying of remaining water thin layer. Indeed normally the NWs float at the surface and so the stamp should not have to break the water tension to recover the NWs. It could then prevent any perturbation of the assembly and would be a very direct and very accurate characterization technique of the real floating assemblies.

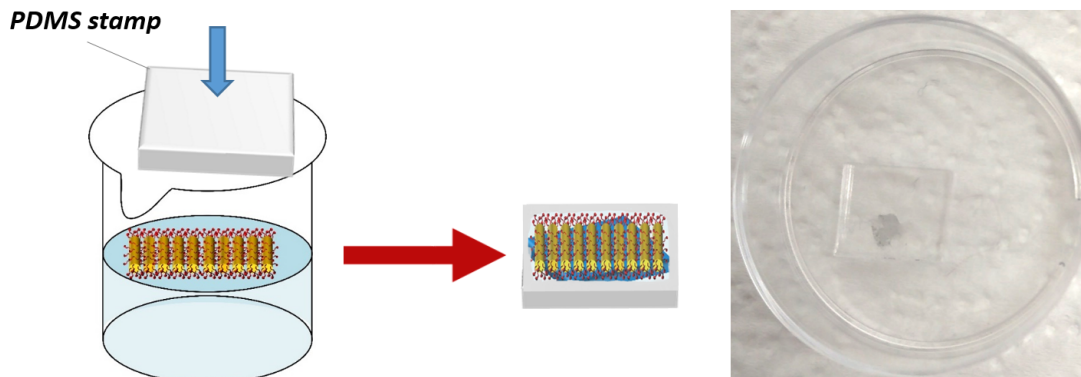


Figure 5.4: Scheme of the PDMS inking technique and photography of an inked stamp (inside a Petri dish).

5.3 Results

To obtain comparable results all the parameters had to be carefully controlled. First, the size and shape of the NWs had to be well controlled. Therefore, only Pt NWs that could be reproducibly synthesized were used (see Chapter 3). Second, the concentration of NWs in the suspensions had to be controlled. The first section of the results will thus describe how this concentration was determined and controlled.

5.3.1 Concentration of the nanowires

Harvesting the NWs resulting from one ECD followed by the washing steps and the optional functionalization steps did not give suspensions containing the same amount of NWs due to the loss of NWs at the various steps of the process. To solve this problem it has been decided to collect NWs into large stock suspensions of well controlled and quantified NW concentration.

The quantification of the concentrations have been done thanks to two analysis techniques: UV-Vis absorbance of NWs in suspension and the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The absorption intensity of NWs in

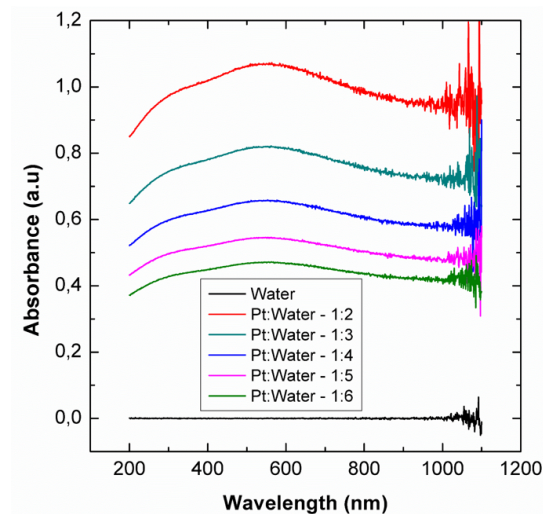


Figure 5.5: UV-Vis absorption spectra of NWs in suspension at different dilution.

suspension was function of the dilution factor. Starting from a very concentrated stock solution, the absorbance recorded decreased when the dilution of the solution increased. The correlation was especially good close to absorbance around 575 nm (Figure 5.5). In particular one can see in Figure 5.6 (a) that the absorbance doubled when the dilution factor went from 10 to 5 (doubled concentration). Here the dilution factor is defined as the ratio between the final volume (after dilution) and the initial volume of the solution (before dilution). It thus shows that at 575 nm the absorbance measured depends directly on the dilution factor hence on the concentration of the solution. At higher concentration this direct dependence may not be correct any more because of specific interactions between the NWs that could induce specific light diffusion.

In the case studied here, in order to have an absolute concentration, ICP-AES was performed. This analysis performed on suspensions with different dilutions allowed to build a diagram relating the absorbance values to the platinum concentration (Figure 5.6 (b)). The Pt molar concentration does not correspond to a precise NWs concentration but it could be theoretically calculated for NWs of known dimensions. Of course this calibration curve could only be used for NWs having similar dimensions to the ones used here, i.e. 100 nm diameter and 325-350 nm length. This calibration allowed to build the assemblies from suspensions having similar concentration of Pt NWs.

The typical suspension chosen for the self-assembly had an absorbance of 1 at 575 nm corresponding to a concentration around 0.88 mM of Pt.

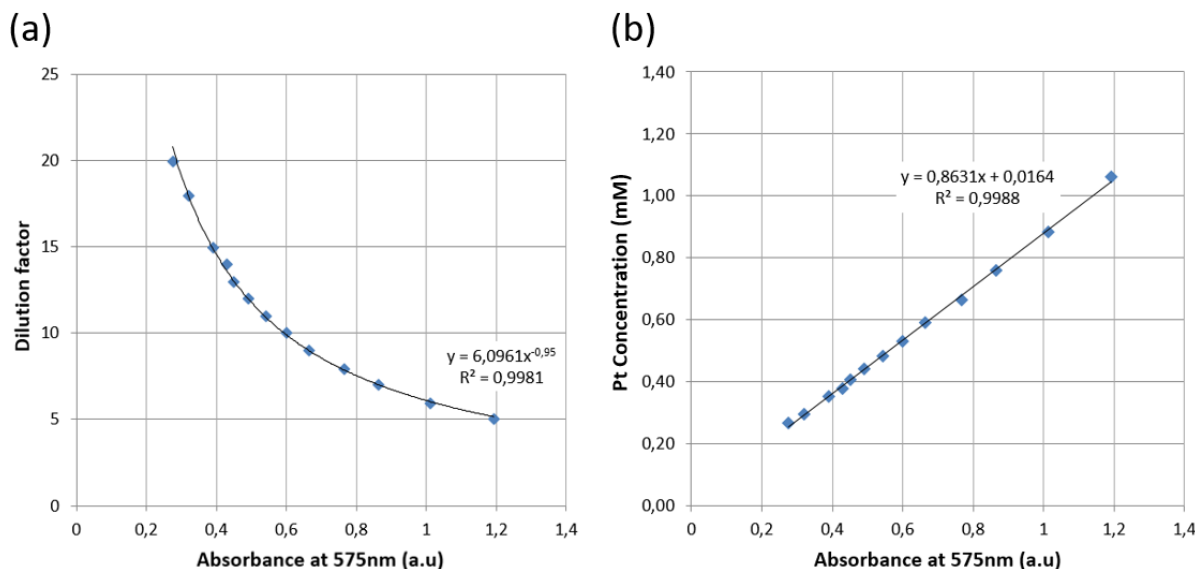


Figure 5.6: Diagrams of (a) the dilution factor versus the absorbance measurement at 575 nm and (b) the Pt concentration in mM versus the same absorbance. The blue diamond are the measurement and the black line is the fitting. The equation and the R^2 of the fitting are also displayed.

5.3.2 Drop-casting

The drop-casting assembly technique involves numerous parameters. All of these parameters have to be carefully chosen and controlled to be able to compare the produced results and optimize them. Of course the NW nature, bearing functionalization(s) or not, is one of those parameters as well as the concentration, that has already been mentioned. But in addition the nature of the solvent, the evaporation rate or the nature of the substrate can also have influences on the assemblies.

For drop-casting assemblies, the NWs used were Pt NWs resulting from the multisegmented NWs manufacture. Therefore in the assemblies there remained many "long" NWs that actually are multisegmented Ni-Pt NWs with non-dissolved Ni segments.

This section will only give and show the conclusions and major results obtained by drop-casting. A precise description on the assembly process with all the parameters and materials used can be found in Chapter 7 Section 7.2.4.1.

The first results quickly revealed that the NWs were only assembled in the outer edge of the pinned droplet (Figure 5.7). This is not surprising and was reported in most of the studies [130, 131, 129]. In this "ring", the assemblies were not exactly the same depending on the spots observed. It was thus decided to observe always the same region of the ring, i.e. 10 μm from the outer edge, where the NWs were the most concentrated without 3D aggregates.

As can be observed in Figure 5.14, the assemblies were not completely ordered nor compact. Chains (stacks) of side-to-side NWs are observed (up to 10 NWs). Sometimes, long NWs "break" these chains but, most of the time, the NWs tend to assemble in small stacks. These general results tend to conclude that the interactions between NWs is not strong enough to obtain very long and ordered chains or mesh of NWs.

The parameters of the drop-casting and their influence on the assemblies will be now reviewed. Of course the parameters are somehow interconnected so it is difficult to draw conclusions for each of them. The large number of parameters also prevent reviewing of all the possible combinations

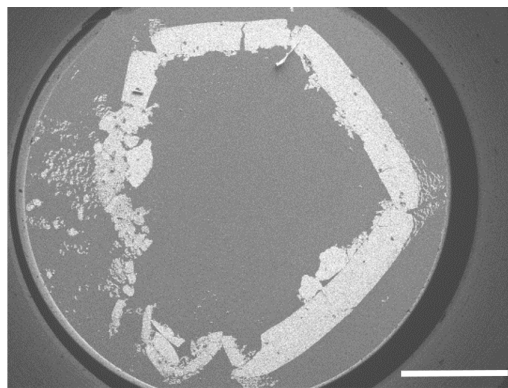


Figure 5.7: SEM image at low magnification of assemblies obtained by drop-casting. The perfect circle is the aperture of the microscope, visible at such low magnification. Scale bar represents 1 mm.

of parameters. One will then first cite all the parameters studied before getting to the results and the conclusions specific to each parameter. The parameters that were varied were:

- the concentration in nanowires: three different concentrations were tested.
- the relative humidity: two different relative humidity values were tested, near 40% and 80% relative humidity (RH).
- the agitation: the assemblies were performed with or without agitation.
- the nature of the solvent: water, toluene and a mixture of both were tested.
- the NW functionalization: NWs were functionalized with MUA or DDT (or PAA).
- the substrate type: hydrophilic or hydrophobic substrates, functionalized with silanes, were tested.
- the pH of water: the assemblies were performed above or below the pKa of MUA (at pH 3 or 9).

As a function of the obtained results, the experimental conditions were progressively adapted. The conditions that gave the best results were the ones with a Pt (NW) concentration of 0.88 mM, with the mixture of solvent where water had a low salt concentration ($\text{NaCl } 10^{-5} \text{ M}$). The tests were performed on both substrates even if all the results are not presented here. The results obtained will be reviewed depending on the parameters. First the parameters defining the drop-casting conditions are discussed. Then the results related to the NW parameters are presented and discussed.

Concentration in nanowires Several concentrations have been tested to chose a standard concentration that will be used for all the tests. In Figure 5.8, the results with three different concentrations are given. It shows that the assemblies always present defects: spots with no NW. These defects are more numerous when the concentration is low (left picture). However one can see that increasing above a certain point the concentration does not improve this point. Moreover the NWs are assembled side-to-side but the number of side-to-side NWs in a row does not increase with the increase of the concentration. It seems to indicate that below a certain concentration value, the assemblies obtained are less concentrated with more defects. But that does not prevent the side-to-side assembly of NWs even if it leads to slightly shorter chains of NWs. Increasing the NW concentration does not necessarily improve the assemblies. Above a

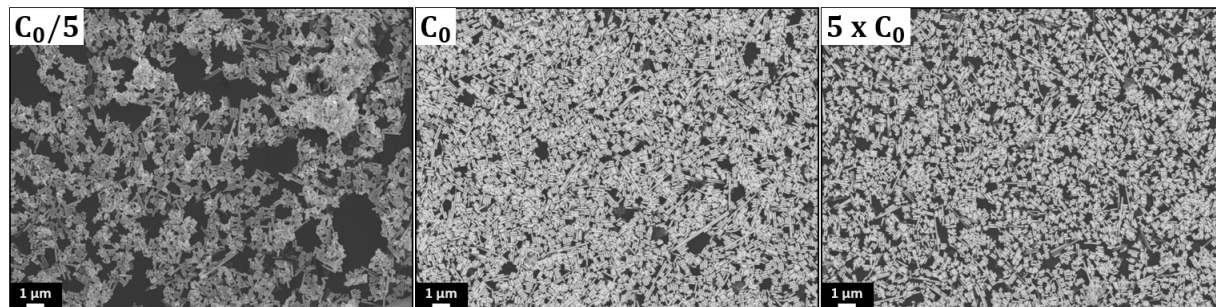


Figure 5.8: SEM images of drop-casted assemblies of Pt-DDT NWs depending on the concentration in NWs. The assemblies were performed with water-toluene droplet. The water was at $\text{pH} = 3$ and $\text{NaCl } 10^{-5} \text{ M}$, the substrate were Si-MPPTS (hydrophilic) and the relative humidity was set to 80% (with cover).

certain concentration (C_0), assemblies tends to adopt a similar morphology than the ones obtain at C_0 . Larger concentration certainly leads to a larger surface coverage of the substrate but since it necessitates larger amount of NWs, the C_0 concentration was further used. It was not possible to determine with a perfect precision this concentration but it was in the range of the concentration corresponding to UV-Vis absorbance equals to 1. This concentration corresponds to a concentration of 0.88 mM in Pt and it was thus taken to be the standard concentration for all the following assemblies.

Relative humidity The relative humidity (RH) was expected to have an important influence on the evaporation rate when water was used as a solvent. The relative humidity was thus varied inside a closed enclosure in order to change the evaporation rate. A small cover on the drop-casted surfaces in Petri dishes was also added in the higher humidity condition to further reduce the evaporation rate. Two types of evaporation conditions were thus studied: at ambient relative humidity (40%) inside the enclosure without additional cover on the Petri dishes (fast evaporation) and at 80% relative humidity with a cover (slow evaporation). Figure 5.9 shows SEM images of results obtained with Pt-DDT NWs. The difference between both conditions is not easy to catch: both images are pretty similar. In the case of Pt-MUA (Figure 5.10) there is a larger difference. The assemblies made under 40% relative humidity without cover presents a large dispersion of NWs on the substrate, contrary to the assembly made at 80% relative humidity with cover where the NWs are highly concentrated at the edge of the dried droplet (see low magnification images). At higher magnifications, the NWs seem to be more aggregated in the case of fast evaporation. Similar results were obtained with the opposite substrates (hydrophilic for the Pt-DDT NWs and hydrophobic for the Pt-MUA NWs). It could be explained by the fact that if the evaporation rate is too high, the NWs cannot reach their equilibrium positions

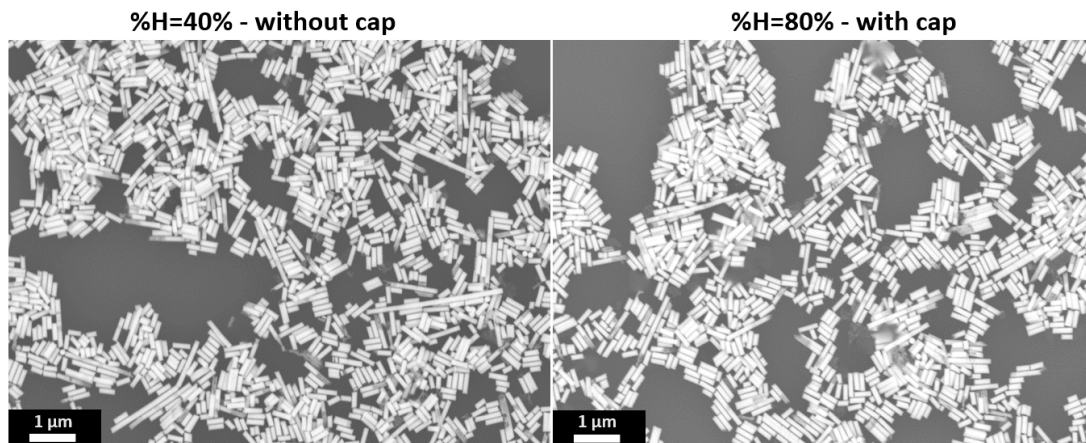


Figure 5.9: SEM images of drop-casted assemblies of Pt-DDT NWs depending on the humidity parameters. The assemblies were performed with water-toluene droplet and the water was at pH= 3 and NaCl 10^{-5} M. The substrate were Si-OTS (hydrophobic).

and tend to aggregate in 3D without ordering. Therefore, to obtain monolayers, the drop-casting should be performed at low evaporation rate in agreement with the publications of Xie et al. and Lin et al. [133, 137]. However the "high evaporation" conditions used here (40% RH) are already very low: it took one complete day to evaporate the droplet. The equilibrium may then already be reached for most of the samples.

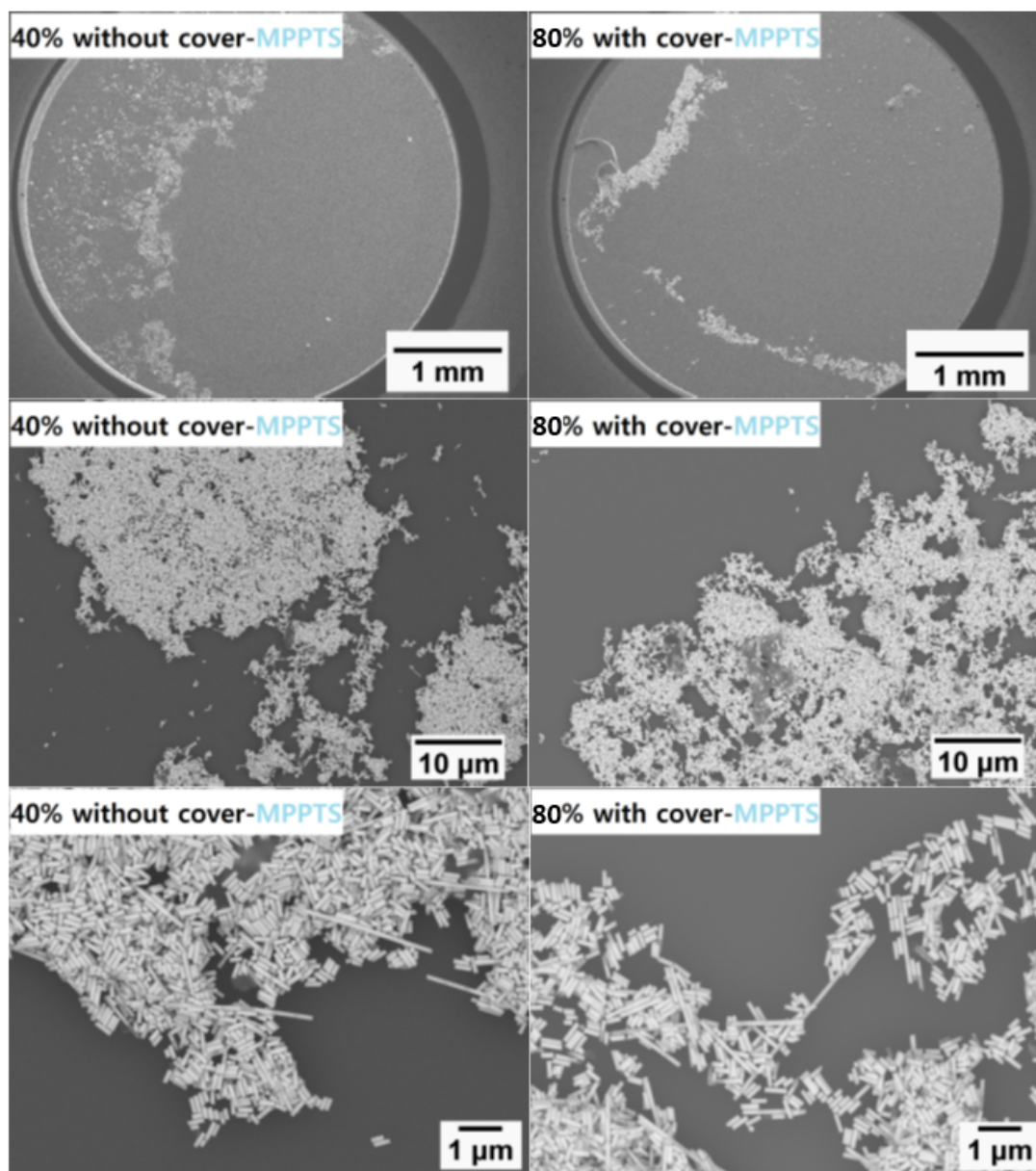


Figure 5.10: SEM images of drop-casted assemblies of Pt-MUA NWs depending on the humidity parameters. The assemblies were performed with water-toluene droplet and the water was at $\text{pH} = 3$ and $\text{NaCl } 10^{-5} \text{ M}$. The substrate is Si-MPPTS (hydrophilic).

Agitation Another parameter studied to improve the drop-casting method was the agitation of the substrate. After deposition of the droplet onto the substrate, it was put on a shaker to give a circular movement to the system. The idea was that NWs might gain some energy to move more freely inside the solution as Nobile et al. suggested [129]. Images of assemblies obtained in these conditions are shown in the Figure 5.11. The assembly obtained with agitation presents a

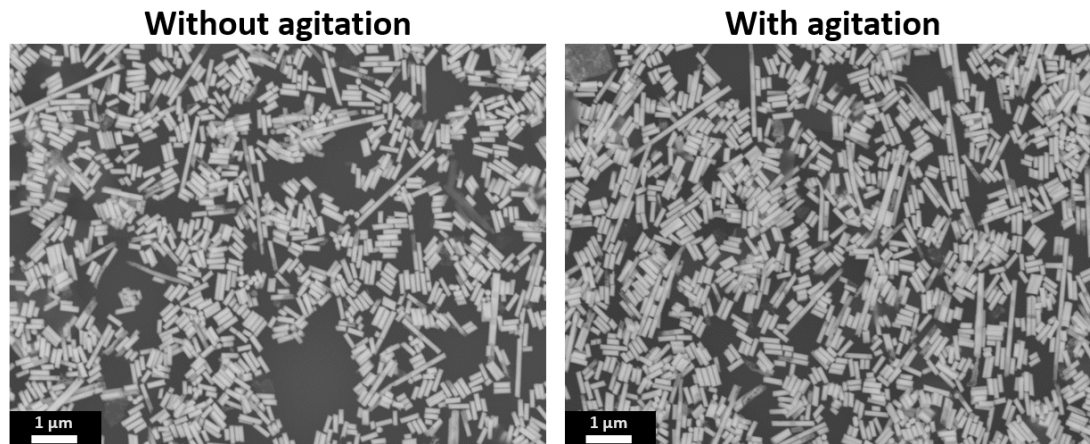


Figure 5.11: SEM images of drop-casted assemblies of Pt-MUA NWs depending on the circular agitation or not. The assemblies were performed with water-toluene droplet and the water was at pH= 9 and NaCl 10^{-5} M. The substrates were Si-MPPTS hydrophilic).

slightly higher concentration (with less void) but it is difficult to conclude in terms of alignment and organization of the NWs. This is why agitation was not performed on many samples.

Nature of the solvent Three types of solution were used for the drop-casting: water (with NaCl 10^{-5} M salt concentration), toluene and a mixture of both solution (1:1 vol:vol). The mixture between toluene and water was inspired by the common fluid-fluid assembly technique. The NWs were injected in an Eppendorf tube containing the mixture of toluene and water. They were then trapped at the interface between both fluids and a droplet of this mixture was deposited on a substrate. It was hoped that a "pre-organization" could happen at the interface between both phases, before evaporation of the droplet, in the same way as in the case of the fluid-fluid interface assembly. Finally it could lead to a better assembly. Since the mixture toluene-water was tested, some assemblies were tested with only toluene even if as seen the fast evaporation rate of the toluene, our expectations were not great. Images of assemblies obtained using these three different systems, with DDT-functionalized Pt NWs, are shown in Figure 5.12. Between the three images one can easily first discriminate the one obtained with toluene. The NWs are really aggregated in 3D and there are lots of defects (voids between aggregated spots. This must

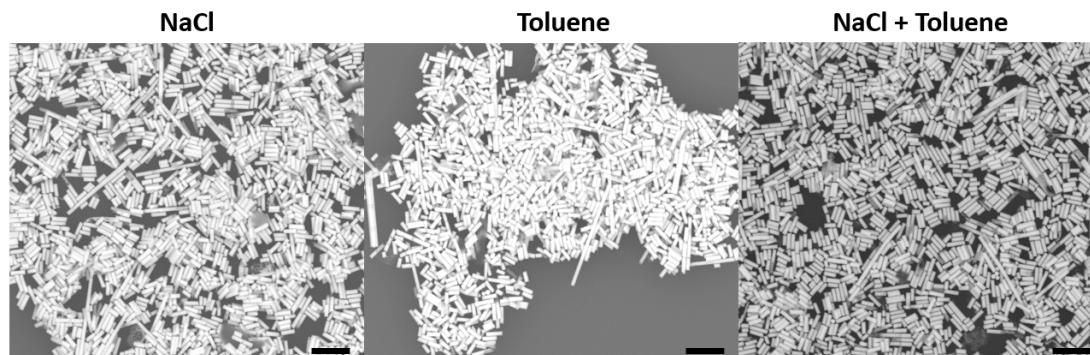


Figure 5.12: SEM images of drop-casted assemblies of Pt-DDT NWs depending on the nature of the solvent. NaCl is 10^{-5} M in water at pH= 3. The substrates were Si-MPPTS (hydrophilic) and humidity was set to 40%.

come from the very fast evaporation rate of toluene. Between the two other images the difference is more subtle. However one can clearly distinct a higher occurrence of 3D arrangements in the water (NaCl) assembly than in the toluene-water mixture. Moreover it seems that there are more chains of side-to-side NWs in the "mixture image". For these reasons it has been considered that the assemblies were better in the case of the toluene-mixture than the ones obtained with only water. The same results were globally also observed with MUA-functionalized NWs (Figure 5.13). In this case, toluene is a bad solvent for MUA. The hydrophilic MUA-functionalized NWs aggregated to minimize the contact surface with toluene. These results leads to the definitive choice of the solvent mixture system for all the following assemblies by drop-casting.

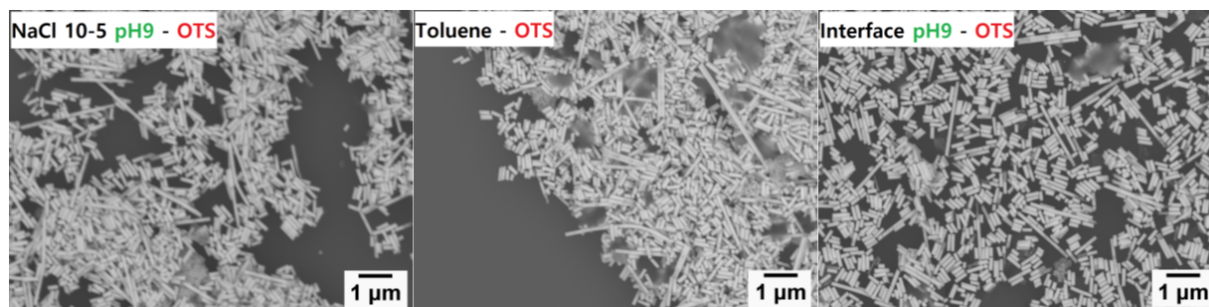


Figure 5.13: SEM images of drop-casted assemblies of Pt-MUA NWs depending on the nature of the solvent. The salty water was put at pH 9. The substrates were Si-OTS (hydrophobic) and the humidity ratio was set to 80% and a cover was added.

MUA (or PAA) vs DDT Pt NWs functionalized either with MUA (or PAA) or DDT were investigated. Most of the time, the best assemblies were the ones obtained with DDT functionalization, as one can see in Figure 5.14. The results for the MUA– and PAA–functionalizations

were less concentrated with more defects-voids. They were also more dependent on the parameters of the drop-casting. The assemblies with Pt-DDT NWs show less differences depending on the parameters of assembly such as the pH (3 or 9) or the relative humidity (40 or 80% RH). It is also important to notice that, unexpectedly, the MUA and PAA assemblies did not lead to

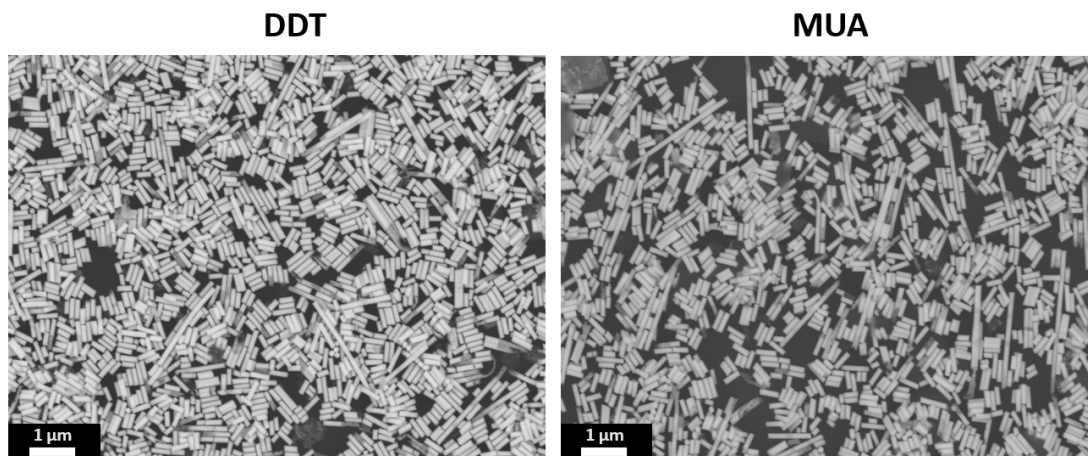


Figure 5.14: SEM images of drop-casted assemblies of Pt NWs depending on their functionalization. The droplet was composed of water (NaCl is 10^{-5} M) at $\text{pH} = 3$ and toluene. The substrates were Si-MPPTS (hydrophilic) and relative humidity was set to 40%.

long (side-to-side chains) and compact assemblies though H-bonding was possible at $\text{pH} 3$. The longer and compacter assemblies obtained were similar to the ones obtained with Pt-DDT.

Types of the substrate Two types of substrate were used: Si wafers functionalized with two different kind of silanes (2-methoxy(polyethyleneoxy)propyl trichlorosilane (MPPTS) and octadecyltrichlorosilane (OTS)). MPPTS is hydrophilic, while OTS makes the substrate hydrophobic. The idea was to use two extremely different substrates to see their influences on the assemblies. The results for DDT-functionalized Pt NWs are given in Figure 5.15. One can clearly see on the high magnification image but also on the low magnification image that the hydrophilic substrate gave more concentrated assembly. But the size of the chains of NWs assembled side-to-side is not clearly larger. The hydrophilicity of the substrate does not favor the sliding of the droplet during evaporation. It resulted in a stronger pinning of the edge of the droplet. Finally the NWs deposited on the substrate are more concentrated at the pinning edge. However it does not seem to mean that the order of the assemblies is favored.

For MUA-functionalized Pt NWs, one could expect that the hydrophilicity or hydrophobicity of the substrate would induce large changes in the NW organization. However, as one can see in Figure 5.16, no particular difference can be noticed between these two types of substrates. That is

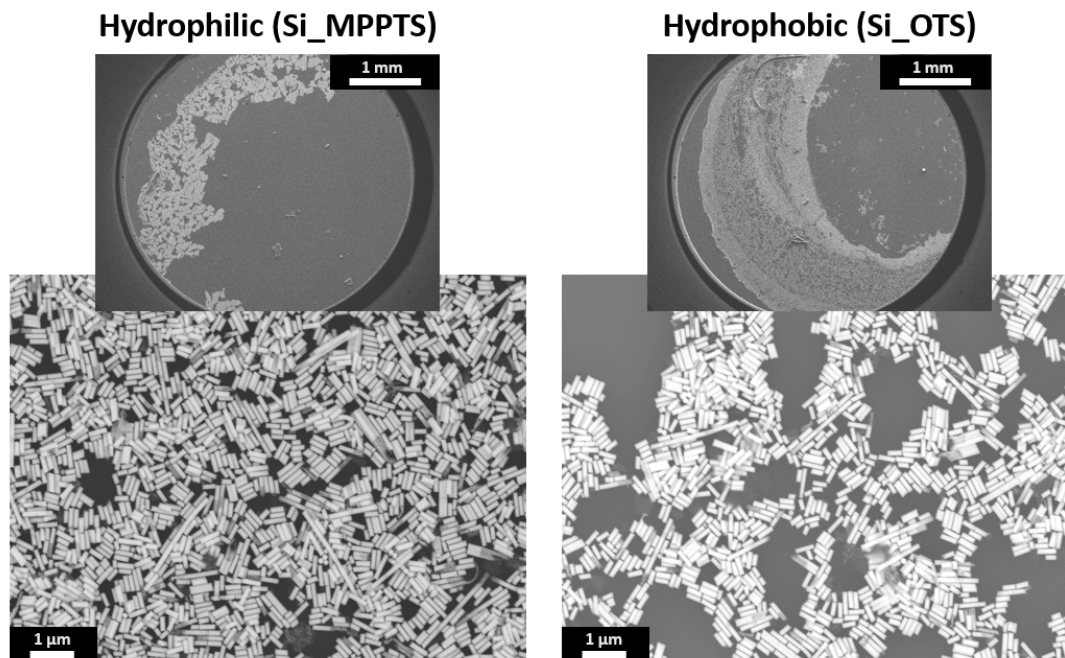


Figure 5.15: SEM images of drop-casted assemblies of Pt-DDT NWs depending on the nature of the substrate. The water was at pH= 3 and NaCl 10^{-5} M. The relative humidity was set to 80%

the reason why each experiment with Pt-MUA was performed with MPPTS and OTS substrates, even if all the results are not presented here.

pH of the medium As it has been mentioned previously, MUA and PAA can be charged or not by deprotonation, depending on the pH of the medium. Therefore, drop-casting was

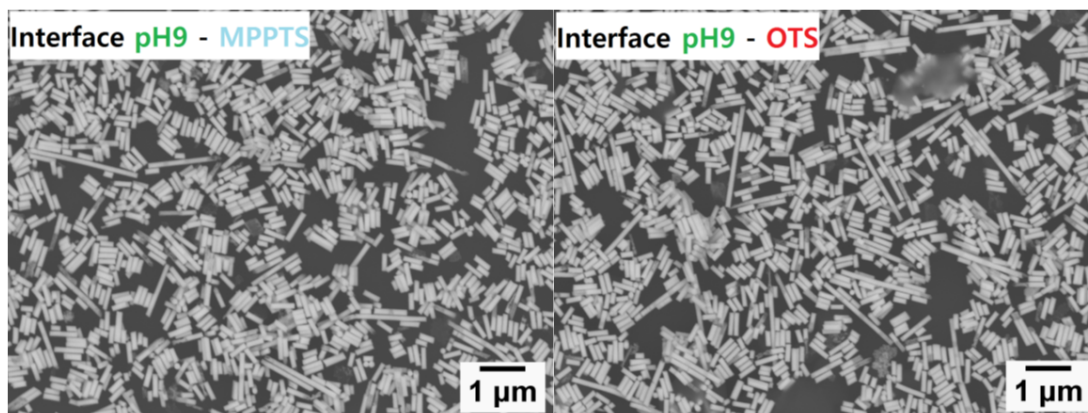


Figure 5.16: SEM images of drop-casted assemblies of Pt-MUA NWs depending on the nature of the substrate. The water was at pH= 9 and NaCl 10^{-5} . The relative humidity was set to 80%

performed with water-toluene using NaCl solutions (10^{-5} M) of two different pH, 3 and 9. These two values should allow the protonation or deprotonation of the carboxylic groups because MUA has a pKa of about 4.5 [178] and the PAA of about 4.2 [179]. Of course these pKa values have been measured with the (macro-)molecules in aqueous solution and they are not exactly valid in the case of SAMs. However the surface pKa of SAMs on gold flat surfaces and gold NPs have also been calculated in several studies. It seems that the pKa for MUA SAMs on gold flat surfaces is about 5.8 [180]. It is more difficult to find a precise value for the surface pKa of PAA SAMS on gold flat surfaces but it seems to be ranging between 4 and 7 [181]. Moreover the pKa depends on the curvature of the nano-objects on which the functions are grafted. Szleifer et al. showed that the surface pKa increases when the NP size is increased but it should be comprised between the pKa of SAMS on flat gold surfaces and the pKa of the free (macro)molecules in solution [182]. It is also important to note that the pKa also depends on the ionic strength but here the ionic strength is low and should not play a very important role on the pKa [181]. Eventually, pH 3 and 9 should thus be below and above the respective pKa of MUA and PAA grafted on the NWs.

The resulting assemblies obtained at those pH are presented in Figure 5.17. NWs seem to present less aggregation at pH 9 in both cases but especially with MUA. As explained previously, hydrogen bonds between COOH groups at pH 3 should lead to a more compact organization, whereas electrostatic repulsion between COO^- at pH 9 should result in a more spaced assembly. This could explain the results showing greater aggregation at pH 3 than at pH 9. However, it seems that the assembly at pH 9 with the PAA contains many defects (voids). Moreover, the assembly within a monolayer do not seem to be more ordered at pH 3 than pH 9. The results were similar with the OTS substrate.

Nature of the nanowires To investigate the influence of NW nature on the self-assembly, Pd NWs and Au NWs were used for drop-casting tests. These NWs were also synthesized using the multisegmented technique. Small amount of suspension of these NWs were prepared for the tests. The actual concentrations of these suspensions were not determined. The Au NWs were functionalized with DDT while the Pd NWs were functionalized with MUTAB. The assemblies were performed with water (NaCl is 10^{-5} M) and toluene, under 80% relative humidity with cover and with agitation. The water pH was fixed at 3 for the Au-DDT NWs while it was fixed at 9 for the Pd-MUTAB NWs. SEM images of Au-DDT NWs assemblies are presented in Figure 5.18. It seems that the NWs are less concentrated, with large voids without any NWs. This may be due to an insufficient concentration of the NW suspension. It also seems that there are more 3D aggregates with the Au-DDT NWs than with the Pt-DDT NWs.

SEM image of Pd-MUTAB NWs assemblies are presented in Figure 5.19. The average length

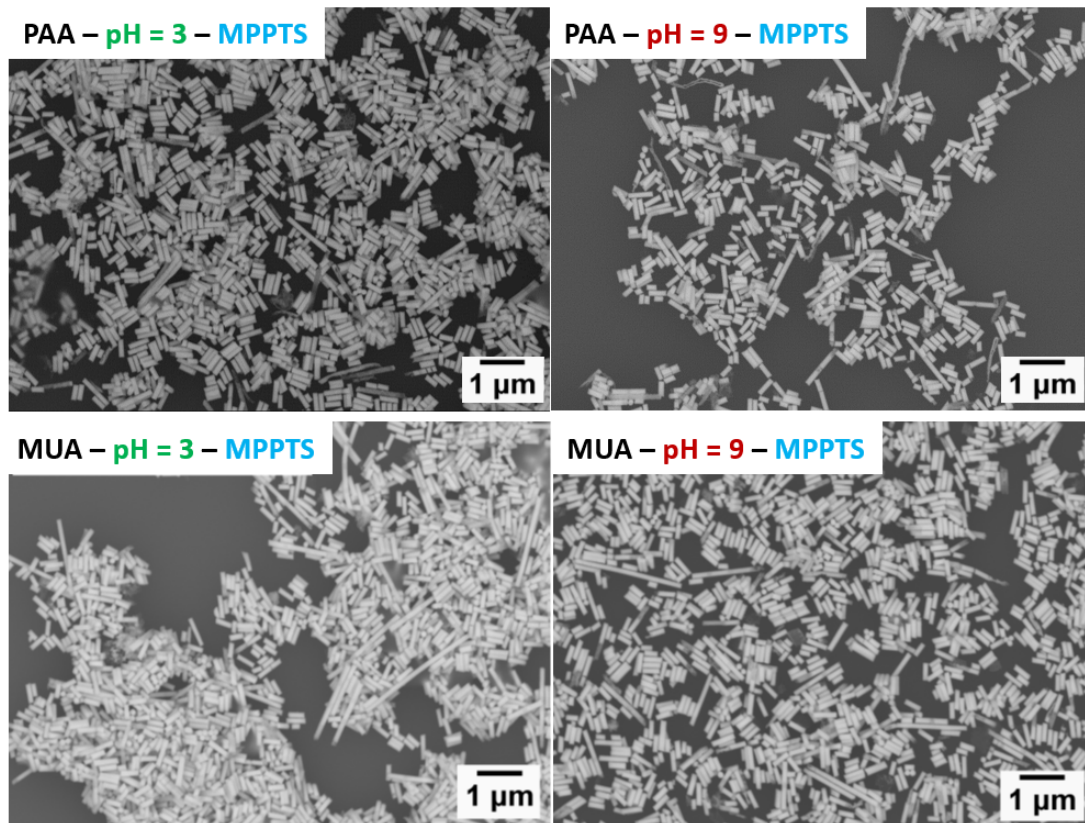


Figure 5.17: SEM images of drop-casted assemblies of Pt-MUA or Pt-PAA NWs depending on pH of the aqueous solution. The assemblies were performed with water ($\text{NaCl } 10^{-5} \text{ M}$)–toluene droplet. The substrates were Si-MPPTS and the relative humidity was set to 80% (with cover).

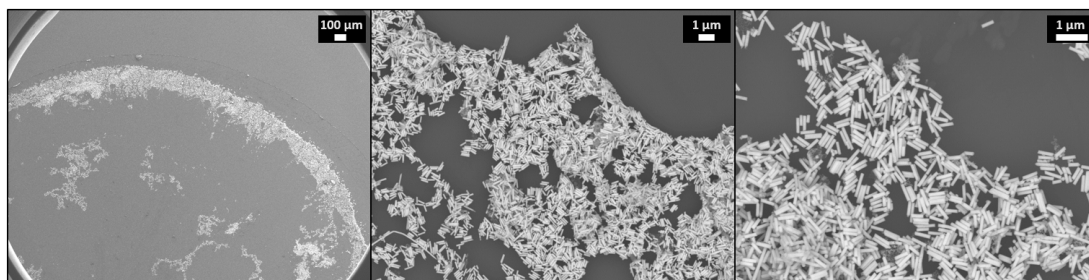


Figure 5.18: SEM images of drop-casted assemblies of Au-DDT NWs at different magnifications. The assemblies were performed with water-toluene droplet (NaCl is 10^{-5} M at $\text{pH} = 3$). The substrates were Si-OTS and relative humidity 80% (with cover). Drying under agitation

of these NWs was longer than the one of the Pt and Au NWs, around 630 nm. No particular difference can be noticed depending on the type of substrate used. In particular, it shows no clear repulsion between the positively charged Pd-MUTAB NWs.

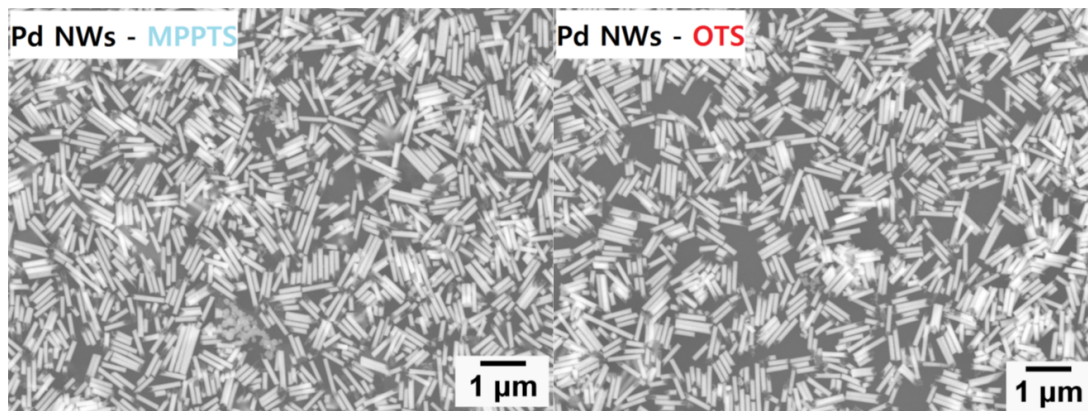


Figure 5.19: SEM images of Pd-MUTAB NW assemblies done by drop-casting using $\text{NaCl } 10^{-5} \text{ M}$ pH 9 and toluene, under 80% humidity with cover, onto Si substrate functionalized with MPPTS or OTS. Drying under agitation

Mixtures of nanowires Several assemblies were made by drop-casting a mixture of Pd and Pt NWs. An equal volume of both concentrated suspensions were mixed. Pt NWs were functionalized with MUA which is negatively charged at pH 9 and Pd NWs were functionalized with MUTAB which is always positively charged. An alternated organization of Pt and Pd NWs was thus expected due to electrostatic attractions between MUA and MUTAB. Two methods of mixing were carried out: Pt-MUA and Pd-MUTAB suspensions were either directly injected in the water-toluene solvent and drop-casted or they were first mixed in an ultrasonic bath before being injected in the water-toluene solvent. Drop-casting was done using water ($\text{NaCl } 10^{-5} \text{ M}$) at pH 9 and toluene, under 80% relative humidity with cover and agitation. The mixing method brought slightly different results as one can see in the Figure 5.20. Since Pt ($Z = 78$) presents a higher atomic number than Pd ($Z = 46$), they appear brighter on the SEM images.

When the NWs are added directly to the water-toluene system (Figure 5.20, images of the first line), they tend to form large aggregates of NW of the same metal. This may due to the fact that the NWs already adopt a certain organization in their respective suspension that is not broken during the drop-casting process. When the suspensions were mixed before injection in the solvent, the dispersion of the NWs is slightly better (Figure 5.20, lower row). However, the expected alternated organization of Pt-MUA/Pd-MUTAB NWs is not observed; small chains (stacks) of Pt-MUA NWs are dispersed within the Pd-MUTAB NWs. This may suggest that the attractive electrostatic interactions between the differently functionalized NWs are weaker than the Van der Waals interactions between NWs of similar material.

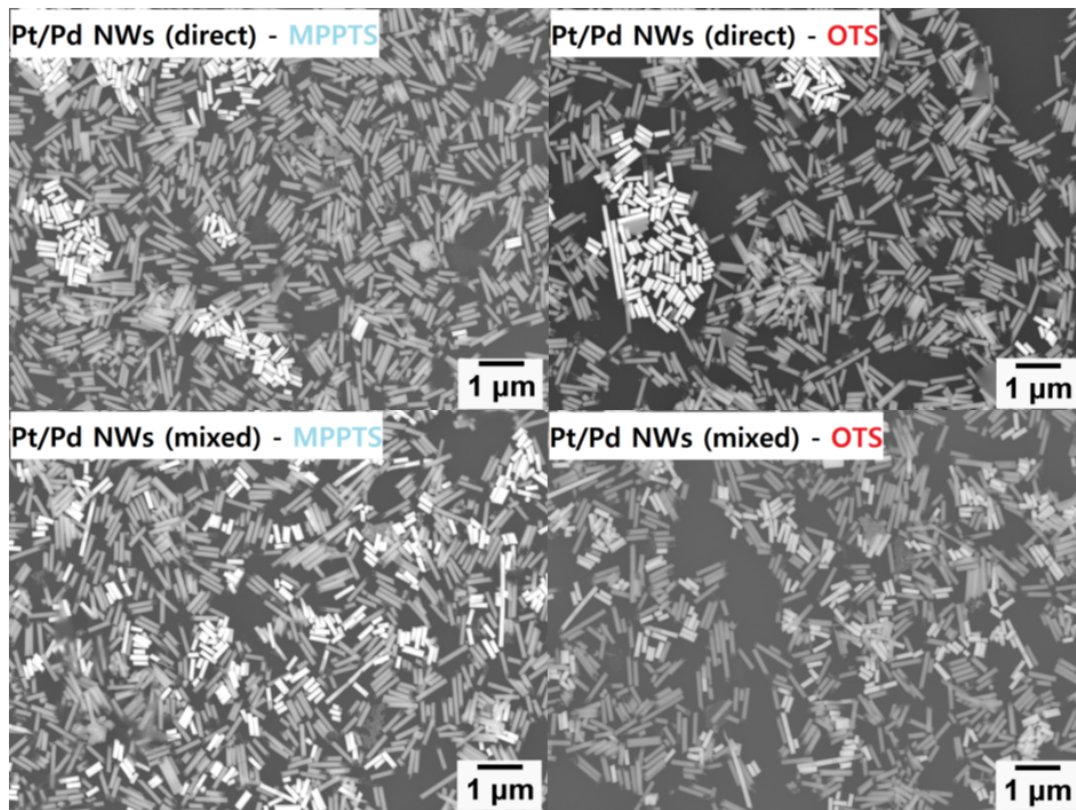


Figure 5.20: SEM images of assemblies done by mixing MUA functionalized Pt NW and MUTAB functionalized Pd NWs, by drop-casting using NaCl 10^{-5} pH 9 and toluene, under 80% relative humidity with cover. The indication "direct" means that each NW solution was mixed directly to the NaCl/toluene system, while "mixed" means that they were mixed before, using an ultrasonic bath, before being injected to the system. Assemblies were done onto Si substrate functionalized with MPPTS or OTS, with agitation.

5.3.3 Self-assembly at fluid-fluid interface

The second strategy that has been investigated to induce the self-assembly of NWs is the self-assembly at a fluid-fluid interface. It consists in trapping the NWs at the flat interface between two fluids. It should enable the concentration of the NWs and their assembly. The fluid states surrounding the interface should allow a minimum of mobility to the NWs while at this interface and may lead to a better assembly of the NWs governed by their mutual interactions due particularly to their surface functionalization.

As already mentioned, the drawbacks of this technique is the difficulty of direct characterization of the assembly at the liquid-liquid interface. Reliable techniques had thus to be developed to recover the assemblies for further characterization.

The assemblies took place at the interface between water and toluene inside a small beaker. Water was pure MilliQ water for non-pH dependent functionalized NWs (bare and DDT-functionalized NWs) and NaCl 10^{-5} M at pH 3 or 9 for MUA and PAA-functionalized NWs. Water and toluene were first added and then a smaller volume of NWs ethanolic suspension was quickly added. It led to an emulsion that rapidly stabilized with the NWs at the interface (Figure 5.21).

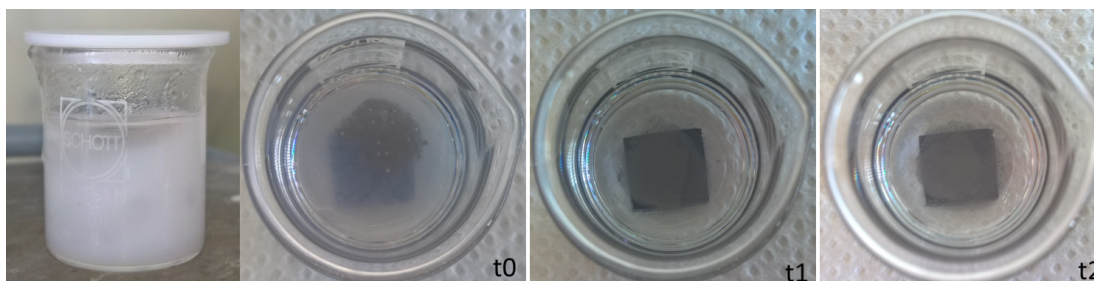


Figure 5.21: Self-assembly at the toluene-water interface at three different moments, chronologically.

Toluene was then allowed to evaporate until the NWs assemblies were floating at the water surface and became more accessible for recovery. However during the evaporation, the assemblies often tended to disintegrate or at least to become less dense. One of the extreme example is shown in Figure 5.22. To redensify the assemblies at the air-water interface, after complete evaporation of

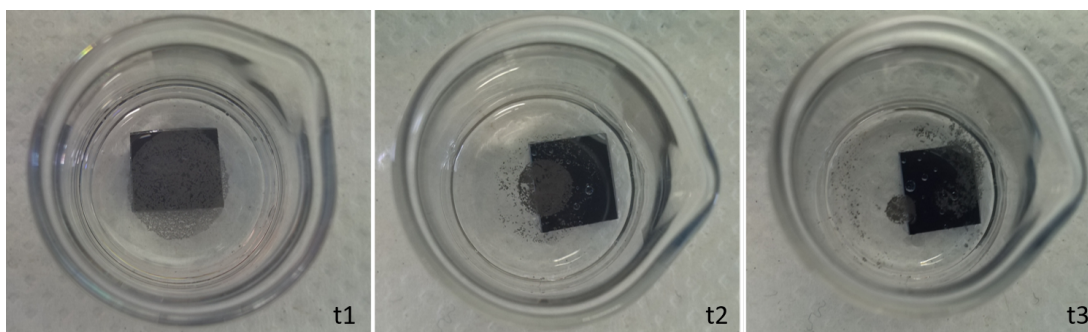


Figure 5.22: Self-assembly at the toluene-water interface at three different moments, chronologically.

toluene, ethanol was quickly injected at the water surface. It resulted in compacter assemblies as it can be seen in Figure 5.23 but with some loss of NWs against the wall of the beaker.

To further recover the assemblies, three methods have been investigated : the fishing technique, the drain-to-deposit technique and the stamp inking technique.

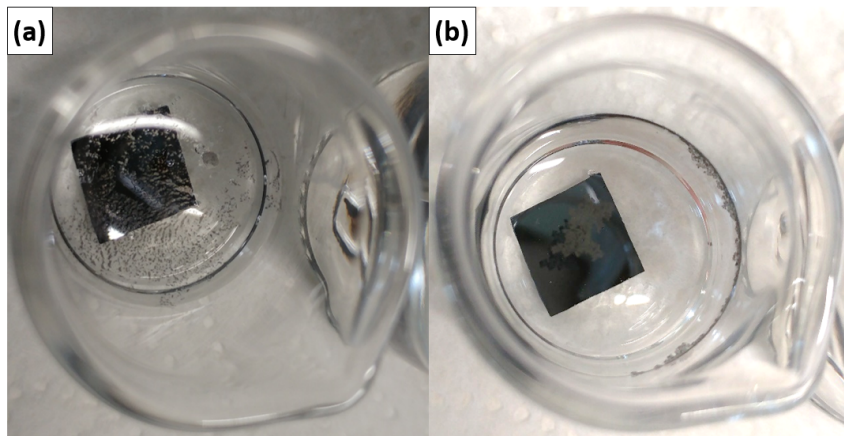


Figure 5.23: Pictures of assemblies floating at the air-water interface before (a) and after addition of ethanol (b). The assembly in picture (a) was intentionally disturbed by gently shaking the beaker, hence the "ripples" pattern.

5.3.3.1 Fishing technique

The fishing technique (described in Chapter 7 Section 7.2.4.2) is one of the simplest method to recover the NW assembly. However, this technique had different parameters that were difficult to control and it was thus very difficult to obtain reproducible results. It was first difficult to enter the substrate in the water phase with the same angle and the same speed. The same problems were encountered when lifting the substrate up. Especially, it often happen that the assemblies developed macro-cracks during the lifting process. However a more systematic and automated approach could maybe give reliable and more reproducible results.

Here, the fishing technique was not used extensively but enabled some first trials. Fishing tests were made with Pt NWs coming from the multisegmented strategy where "long" NWs were still present or with defective NWs. Some results are presented in Figure 5.24. One can see that the assemblies are not similar on every spaces and form horizontal monolayers or 3D aggregates, hence reproducibility problem. Nevertheless, it gave one intriguing result with short DDT-functionalized Au NWs about 200 nm long and with poor quality concerning one of their extremity: at some places NWs assembled in a compact and vertical way (Figure 5.24 bottom right). These kind vertical assemblies were only achieved that time. It is maybe due to the use of shorter NWs.

5.3.3.2 Drain-to-deposit

The drain-to-deposit technique allowed the recovery of the floating assembly by pumping the aqueous phase until deposition onto a substrate previously placed at the bottom of the beaker (Figure

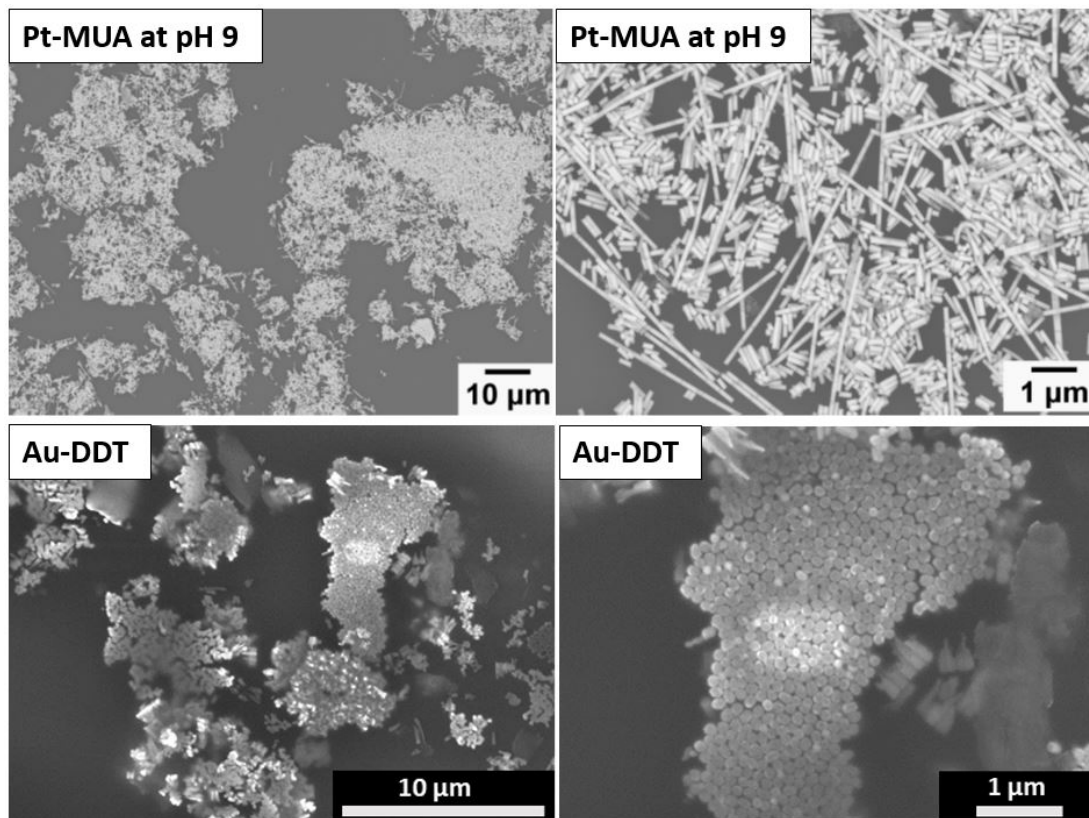


Figure 5.24: SEM images of self-assemblies at the toluene-water interface fished after toluene evaporation by a Si substrate. (a) Pt-MUA NWs with pH fixed at 9. (b) Au-DDT NWs (~ 200 nm long).

5.3). It is certainly not perfect. First, there always remains some water, and possibly ethanol, on the assembly after the pumping stage. This remaining solvent may perturb the assembly while evaporating. Second, the pumping of water may induce fluxes that could perturb the assembly. Finally, even after compaction with ethanol, the assembly may lose its compactness since the pumping stage took some times. The recovered assembly will thus have a morphology reflecting a dynamic state between a fully compact assembly and a fully relaxed assembly. However, the advantage of the drain-to-deposit technique is that most of the parameters can be controlled in order to obtain reproducible results. The complete description of the whole experimental setup is presented in Chapter 7 Section 7.2.4.2.

The experiments were performed with the Pt NWs coming from the Cu-Pt NWs to avoid the presence of long NWs. Only bare Si substrate were used because the functionalized substrates were found to perturb the flatness of the toluene-water interface, especially with the OTS-functionalized Si.

Figure 5.25 presents assemblies obtained with bare Pt NWs with and without the compaction step with the ethanol. The NW assemblies are not very compact but have already some long chains of NWs assembled side-to-side. The assembly is not particularly better with the ethanol compaction step. It just seems to include more 3D aggregates.

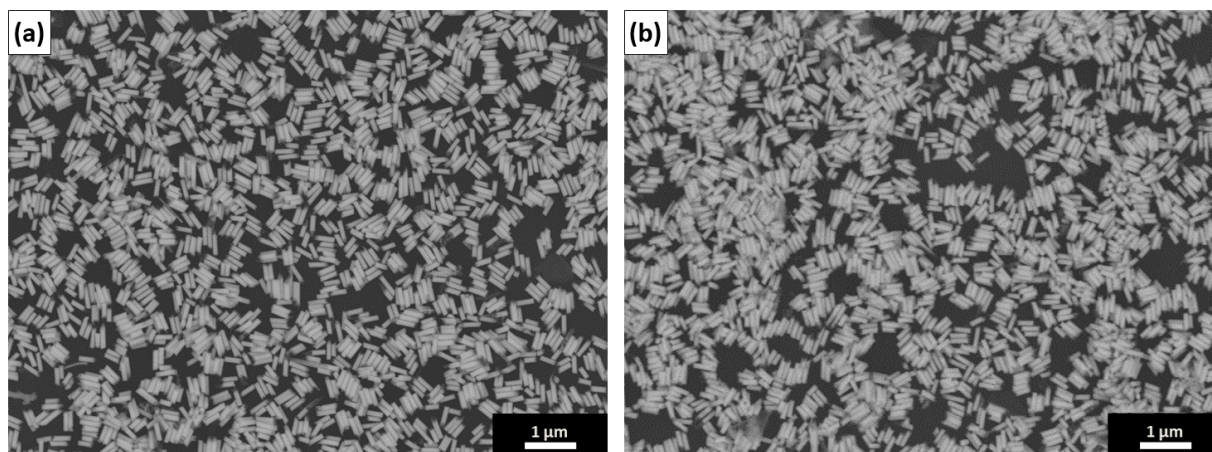


Figure 5.25: SEM images of Pt NWs assembled at the toluene-water interface and recovered by drain-to-deposit technique. (a) Without the ethanol compaction step and (b) with the ethanol compaction step.

Figure 5.26 presents assemblies obtained with Pt NWs functionalized with DDT without the ethanol compaction step (a-b), and with the ethanol compaction step (c-e). Without the compaction step, the assemblies are not very dense and the number of NWs assembled side-to-side are not more numerous in this case than with the bare Pt NWs. The NWs are more homogeneously distributed on the surface of the substrate. This was not expected since DDT is hydrophobic and the NWs were floating on water. So it seems that the hydrophobic forces are not strong enough to maintain the NW assembly. In the case of the recovery after the compaction step, the assemblies present a strong 3D aggregation of NWs at most places (Figure 5.26 (c-d)). This tends to prove that the DDT favors the aggregation and slow down the relaxing and "disassembly" of the NWs. At some places (Figure 5.26 (e-f)), a (sub-)monolayer of NWs was observed. The assembly there was rather compact but the number of side-to-side NWs was rather low.

The compaction step was performed by quickly injecting some ethanol with a syringe at the surface of the water. As suggested by the observation of (sub-)monolayers, it may be possible to obtain large monolayered assemblies of NWs by tuning the speed of addition of the ethanol. Some tests were performed by adding ethanol at different speeds. The new attempts were performed

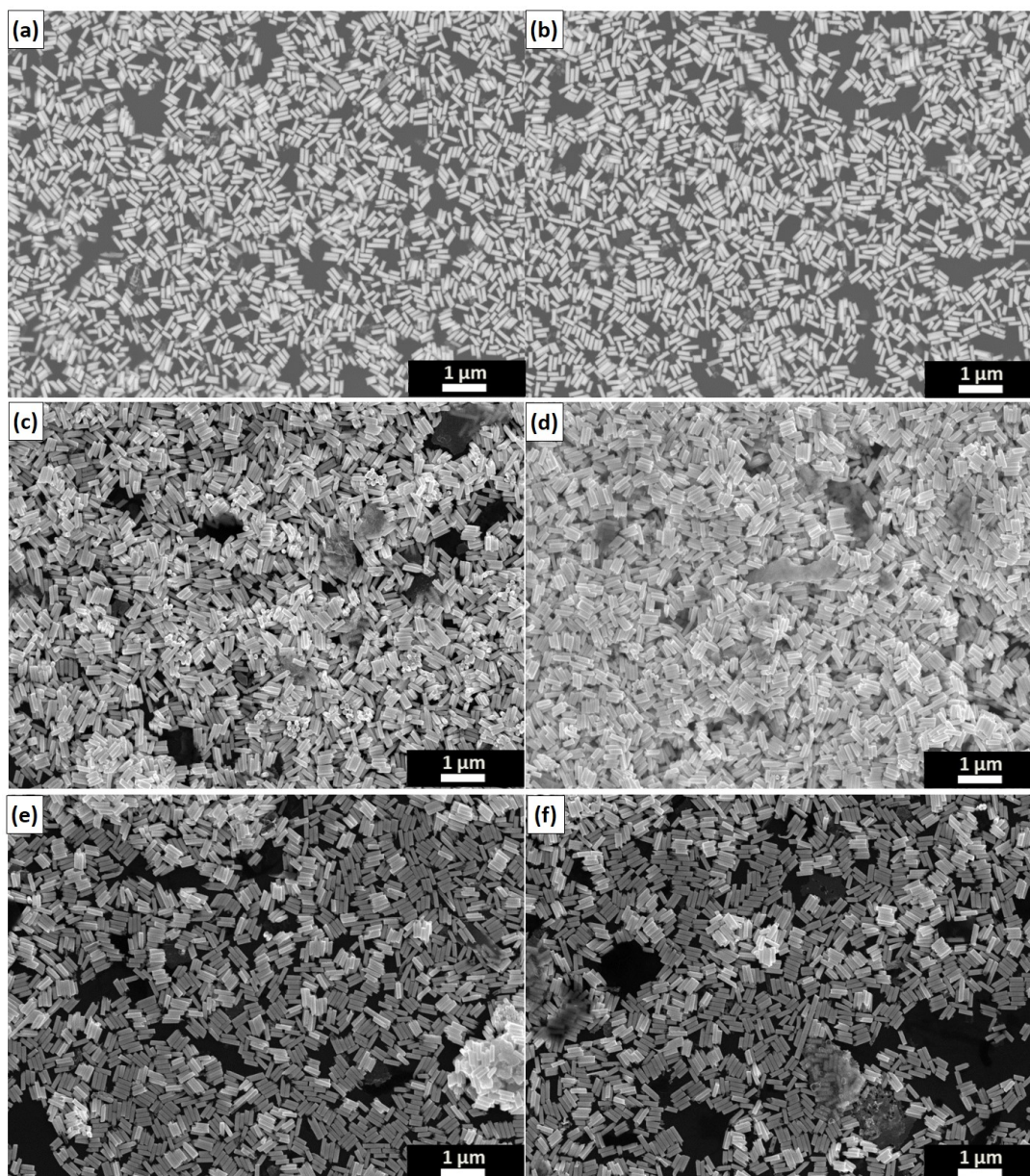


Figure 5.26: SEM images of Pt-DDT NWs assembled at the toluene-water interface and recovered by drain-to-deposit technique (a-b) without ethanol compaction step., and (c-e) with ethanol compaction step.

with two slower speeds: one was made thanks to the peristaltic pump with a flux of $100\text{ }\mu\text{L}/\text{min}$ and the other was made by simply pouring the ethanol inside a funnel linked to a flat tip syringe letting the gravity make flow the ethanol. The results are presented in Figure 5.27. The NWs were less aggregated and the assembly is monolayered at many places. But there was also a lot of places without any NWs. Therefore it seems to be difficult to obtain assemblies of Pt-DDT with only monolayer and without any defects whatever the speed of ethanol addition.

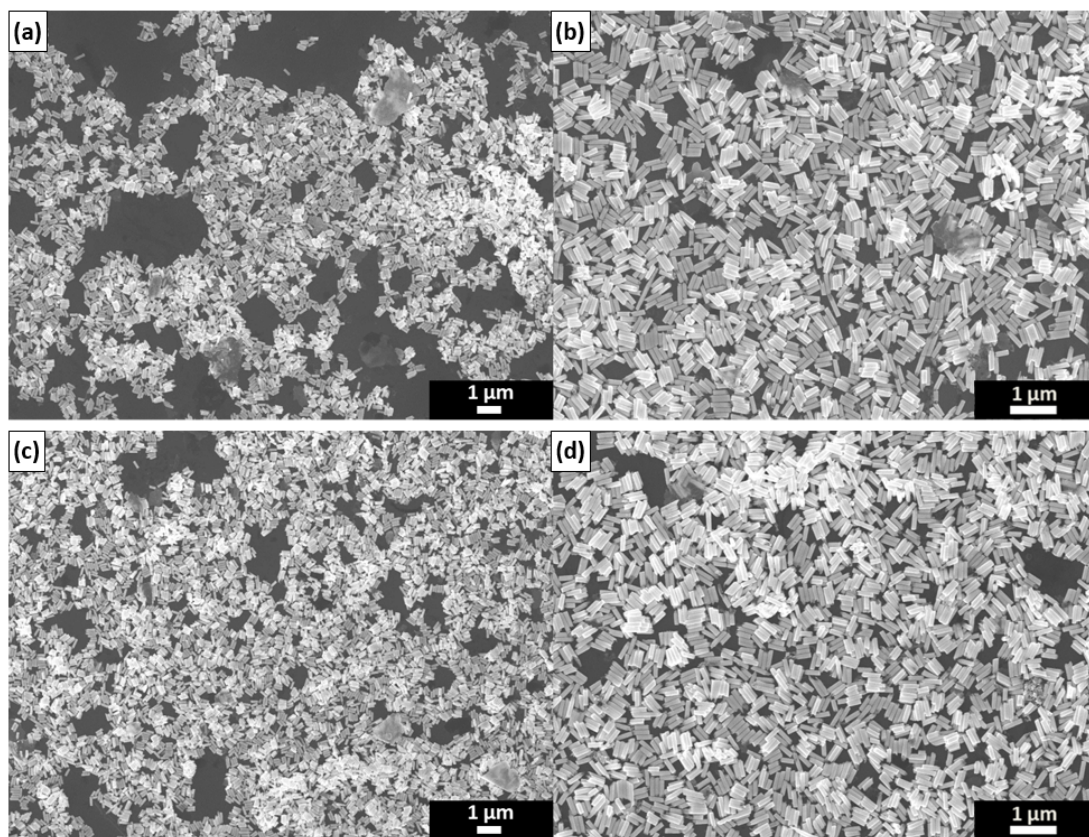


Figure 5.27: SEM images of Pt-DDT NWs assembled at the toluene-water interface and recovered by drain-to-deposit technique after ethanol compaction step performed (a) with a peristaltic pump ($100\text{ }\mu\text{L}/\text{min}$) and (b) by pouring the ethanol inside a funnel, linked to a flat tip syringe.

Assemblies obtained with PAA-functionalized NWs are presented in Figure 5.28. Without compaction step, there is almost no difference between the assembly obtained at pH 3 and pH 9. The assembly at pH 3 seems to be more concentrated with less spaces without NWs. But the NWs at pH 9 seem to form fewer long side-to-side chains. At pH 3 the carboxylic groups should be protonated and may induce H-bondings while at pH 9 they are deprotonated and should bear a negative charge. It was expected that the NWs would be more aggregated at pH 3 than pH 9 and

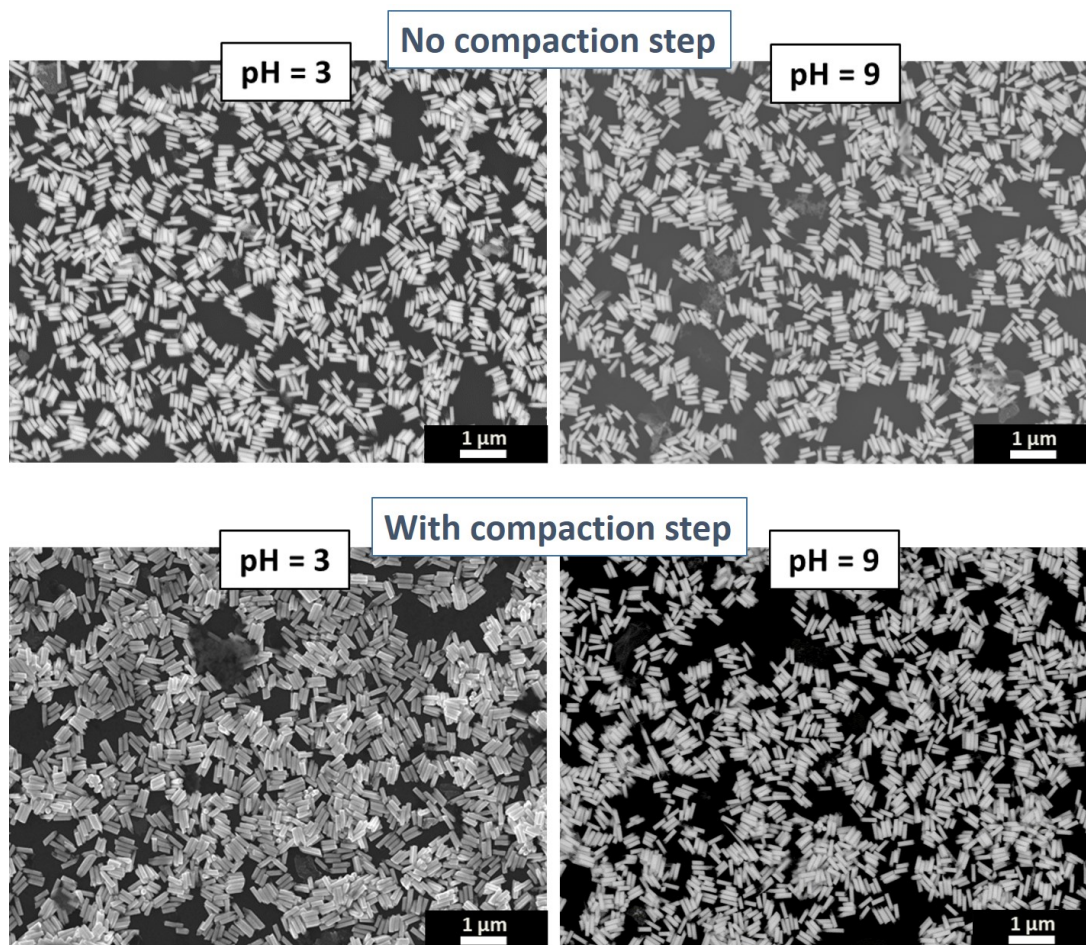


Figure 5.28: SEM images of Pt-PAA NWs assembled at the toluene-water ($\text{NaCl } 10^{-5} \text{ M}$) interface, at different pH, and recovered by drain-to-deposit technique without ethanol compaction step (first row) and with ethanol compaction step (second row).

that the NWs would form less side-to-side assemblies at pH 9 because of electrostatic repulsion. Obviously it is not the case. Maybe at pH 3 some H-bonds can be made with the water molecules while at pH 9 some interactions could happen with the counterions coming from the salt inside the water or the negative charges are simply very well solvated. Eventually this could just mean that the interactions between NWs (after toluene evaporation) are only very slightly impacted by the functionalization of the NWs. Or that the interactions coming from the NWs are not strong enough to prevent the relaxation of the assemblies after ethanol compaction.

After the ethanol compaction step, the NWs are more compact at both pH. The results at pH 3 are similar to the results of the Pt-DDT assemblies. The multilayer aspect of the assembly can easily be seen at pH 3. However one can guess the 3D aspect at some places when the pH was

fixed at 9. At pH 9 the NWs are also less compact but the number of long chains of side-to-side NWs does not seem very different from the assembly at pH 3.

In order to better characterize the assemblies, image analysis was performed on SEM images to characterize the compactness (density) of the layers and AFM images were made and analyzed to characterize the number of layers in the assemblies. These analyzes were not performed for the drop-casting owing to the lack of reproducibility on the whole sample and the large distribution of NWs length.

SEM images analyses The compactness (density) of the layers was evaluated by calculating the percentage of substrate surface covered by the NWs. The organization of the assemblies was evaluated by counting the numbers of NWs belonging to chains (stacks) of given number side-to-side NWs. The details on the compactness calculation and counting methodology are given in Chapter 7 Section 7.2.4.3.

Table 5.1 gives the mean compactness state of the assemblies at toluene-water interface recovered by drain-to-deposit technique (presented above in this Section). Only the compaction

Table 5.1: Compactness rate of the assemblies obtained at toluene-water interface recovered by drain-to-deposit technique.

	Bare Pt	Pt-DDT	Pt-PAA at pH 3	Pt-PAA at pH 9
Without compaction step	47.5 %	50.5 %	44.5 %	46.4 %
With compaction step	50.3 %	85.4 %	60.0 %	46.6 %

step made with syringe was taken into account in this table. The Pt-DDT assemblies with the compaction step using the funnel and the peristaltic pump were 65.0 % and 49.9 % compact, respectively. One can see that the compactness percentage are very similar in most of the cases except for the Pt-DDT and Pt-PAA at pH 3 with the ethanol compaction step. It suggests that the assemblies without ethanol addition are only little influenced by the functionalization of the NWs. The compaction at the toluene-water interface is not sustainable and the assemblies seem to relax whatever their nature. However, for the Pt-DDT NWs and Pt-PAA NWs at pH 3, the hydrophobicity of the surface functionalization seems to stabilize the assembly at the water surface when a compaction step is performed. This assembly is maintained a sufficiently long time to drain-to-deposit it on the substrate. The hydrophobic stabilization is as expected more effective for DDT than it is for PAA. On the contrary, the hydrophilicity of the bare Pt and, for the Pt-PAA NWs at pH 9, the electrostatic repulsion between the negatively charged NWs lead

to the recovery of the initial assembly at the water surface despite the compaction step.

The results of the analysis of the number of NWs in ordered stacks are presented in Figure 5.29. The results for the bare Pt NWs are very similar with or without the ethanol compaction step. On the other hand, the Pt-DDT NW assemblies present very few long side-to-side chains when no compaction step is performed. The distribution shifts towards longer chains when the compaction step is performed. For the Pt NWs functionalized with PAA, the analysis of the diagram is a bit more complex. The histograms are relatively similar for both pH when no compaction step is applied (a bit more chains between 5 and 9 NWs in a row for pH 9). With the compaction step, the number of very long chains is reduced at pH 3 as well as the number of very small chains. At pH 9, the entire histogram is displaced towards the shorter chains.

For the bare Pt NWs, the results are very similar with or without the compaction step with EtOH. For the Pt-DDT NWs, fewer long side-to-side stacks are observed when no compaction step is performed than when the compaction step is performed. When the compaction step is applied, the percentages of both long and short stacks decrease with an increase of the percentages of stacks of 3 and 4 NWs at pH 3. At pH 9, the electrostatic repulsion between the negatively charged NWs leads to a decrease of the percentages of long stacks of NWs and an increase of the percentages of short stacks (1 to 4 NWs). These observations are consistent with those made for the density of the layers and may also be explained by the hydrophobic interactions or the presence of repulsive electrostatic interactions.

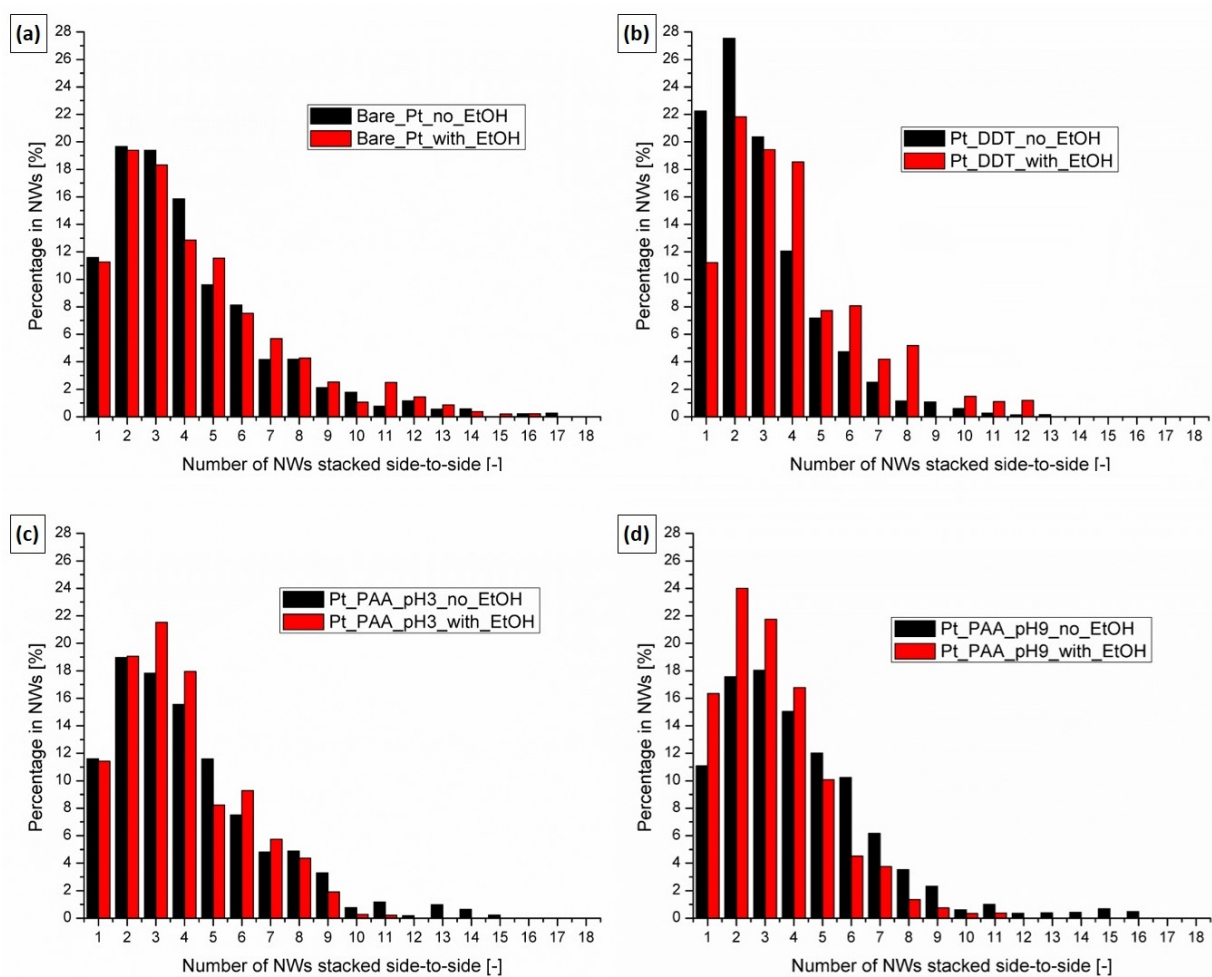


Figure 5.29: Diagrams representing the percentage in NWs of NWs inside chains of NWs assembled side-to-side. The assemblies were performed at the toluene-water interface and recovered by drain-to-deposit technique. N.B.: For Pt-DDT with compaction step, the counting was only performed on the (sub-)monolayer.

AFM images and analyses As for the SEM image analysis, the AFM images and their analysis were only performed for the assemblies obtained with drain-to-deposit method with or without ethanol compaction step. The AFM images obtained enabled to determine the percentage of monolayer, bilayer, tri and multilayer of NWs in an assembly. The method to determine those layers is presented in detail in Chapter 7 Section 7.2.4.3. But briefly, the height histograms of the images were calculated. Based on the peaks observed on the histograms, the images were thresholded to the height levels corresponding to the first, second, third and upper layers.

For example, Figure 5.30 presents two different AFM images of assemblies of DDT-functionalized Pt NWs, and Figures 5.31 and 5.32 corresponds to the different thresholding and Figure 5.33 shows the image from Figure 5.31 (b) with the layer represented.

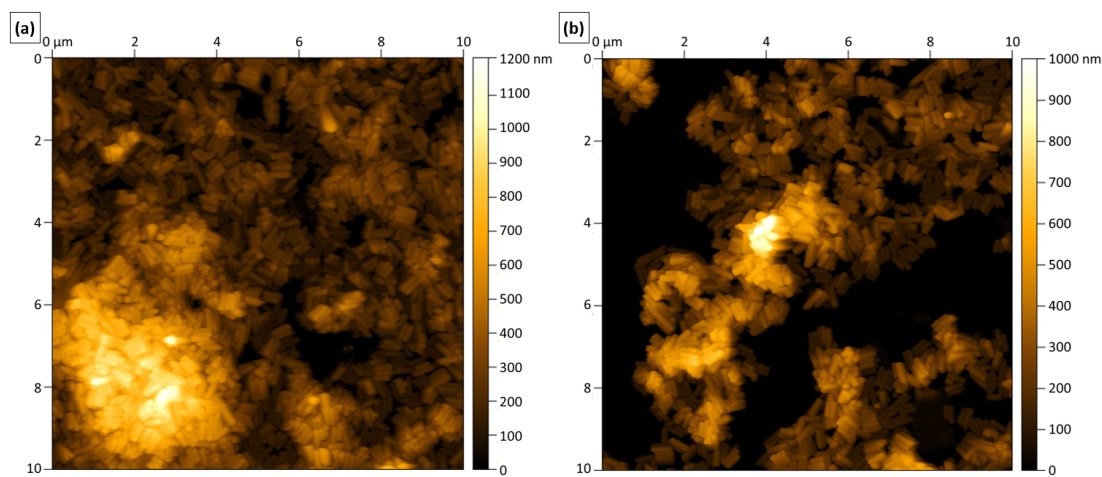


Figure 5.30: AFM images of Pt-DDT assemblies obtained at toluene/water interface with addition of ethanol (EtOH) with (a) a syringe and (b) a peristaltic pump.

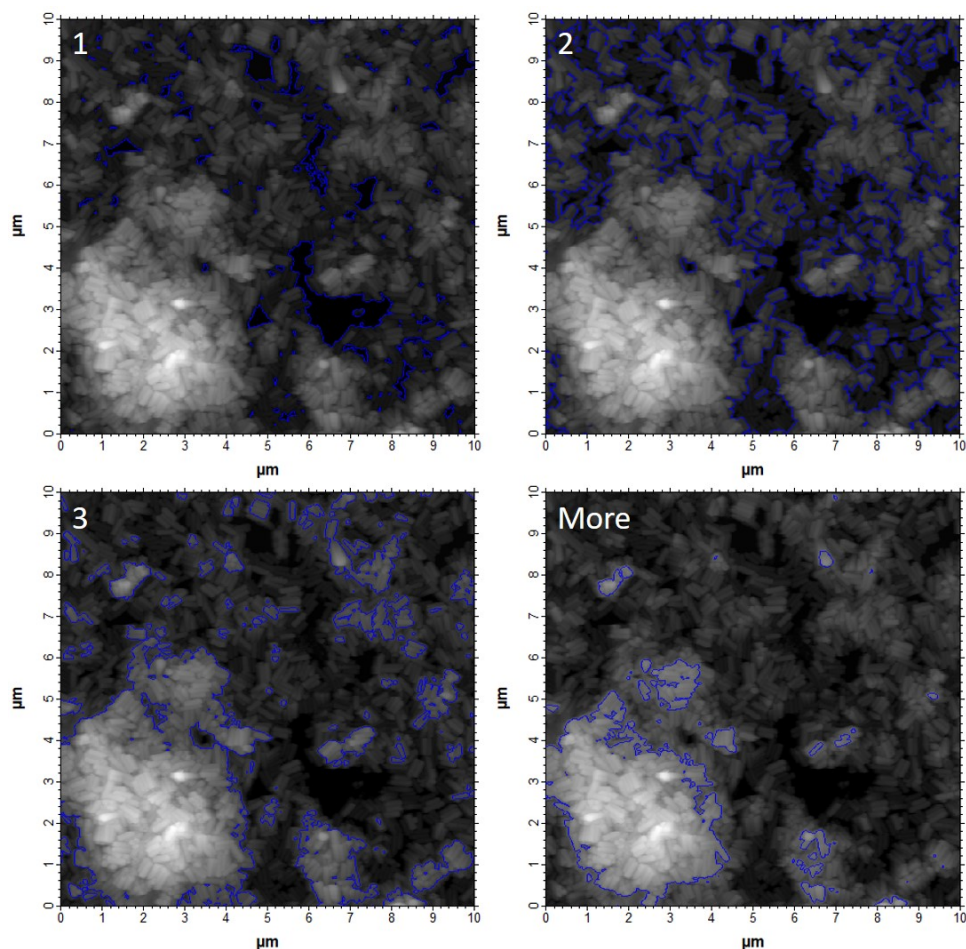


Figure 5.31: AFM images from Figure 5.30 (a) with the contours of the thresholding corresponding to the beginning of the 1st, 2nd, 3rd and more layers.

From these thresholded images, the percentage of surface covered by a monolayer, a bilayer, a trilayer and a multilayer were determined. The results are presented in Figure 5.34. It is important to note that the background, that is the place without NWs, were not considered in the percentages.

In general, the compaction step always favors a decrease of the monolayer areas. For the bare Pt NWs, the compaction step only slightly decreases the surface of monolayer and bilayer and increases the surface of trilayer and multilayer. For the Pt-DDT NWs, the compaction step drastically decreases the amount of monolayer at the expense of bi-, tri- and multilayer. This last result is similar but on a smaller extent for Pt-PAA NWs at pH 3. For Pt-PAA NWs at pH 9, the effect of the compaction is less important, similarly to the bare Pt NW assembly. Eventually these results are quite in agreement with what SEM images suggested and may also be explained by the hydrophobic interactions or the presence of repulsive electrostatic interactions.

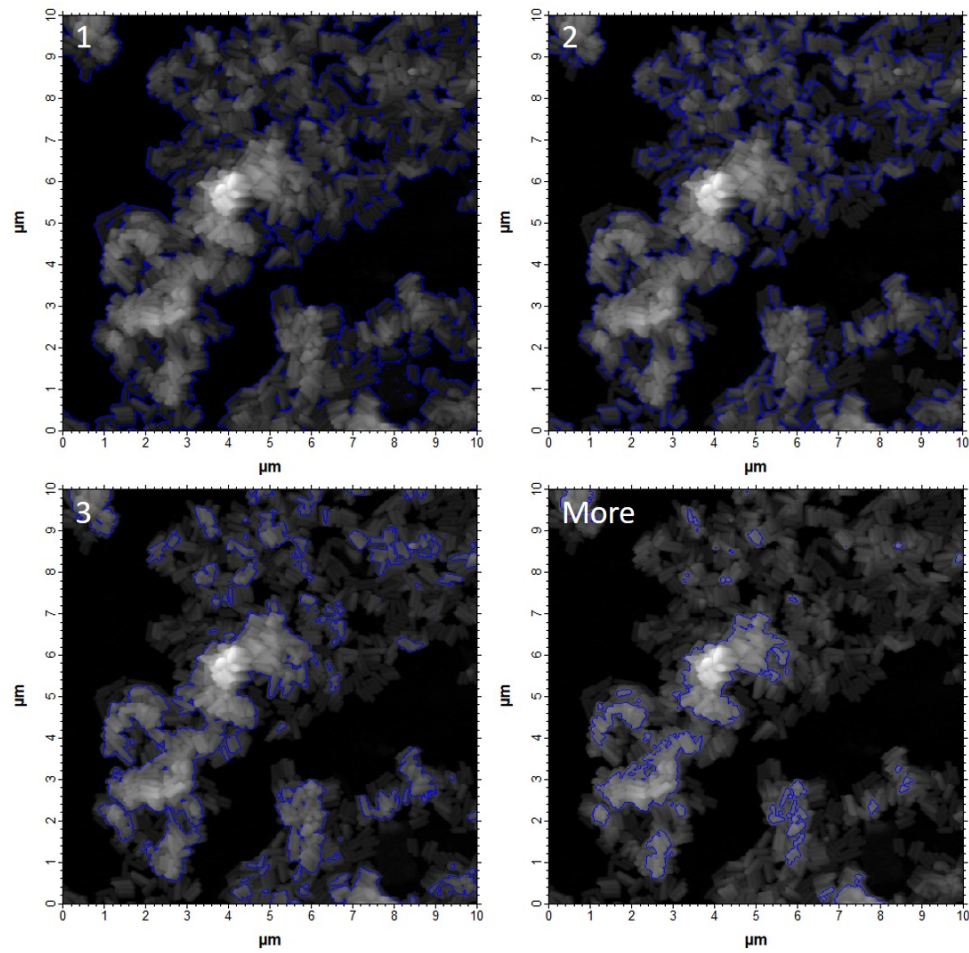


Figure 5.32: AFM images from Figure 5.30 (b) with the contours of the thresholding corresponding to the beginning of the 1st, 2nd, 3rd and more layers.

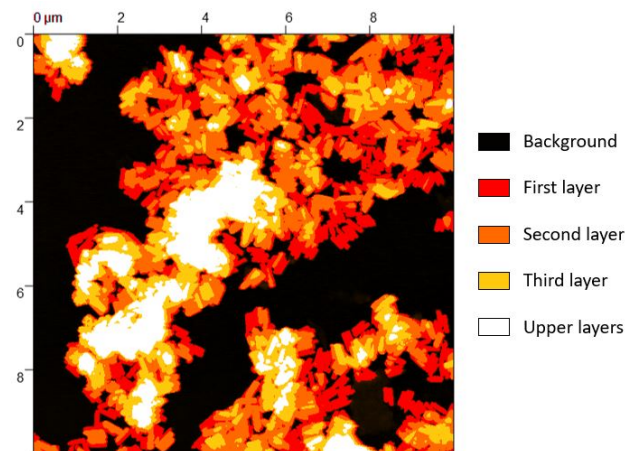


Figure 5.33: Image corresponding to AFM image from Figure 5.30 (b) with the different layers represented by different colors.

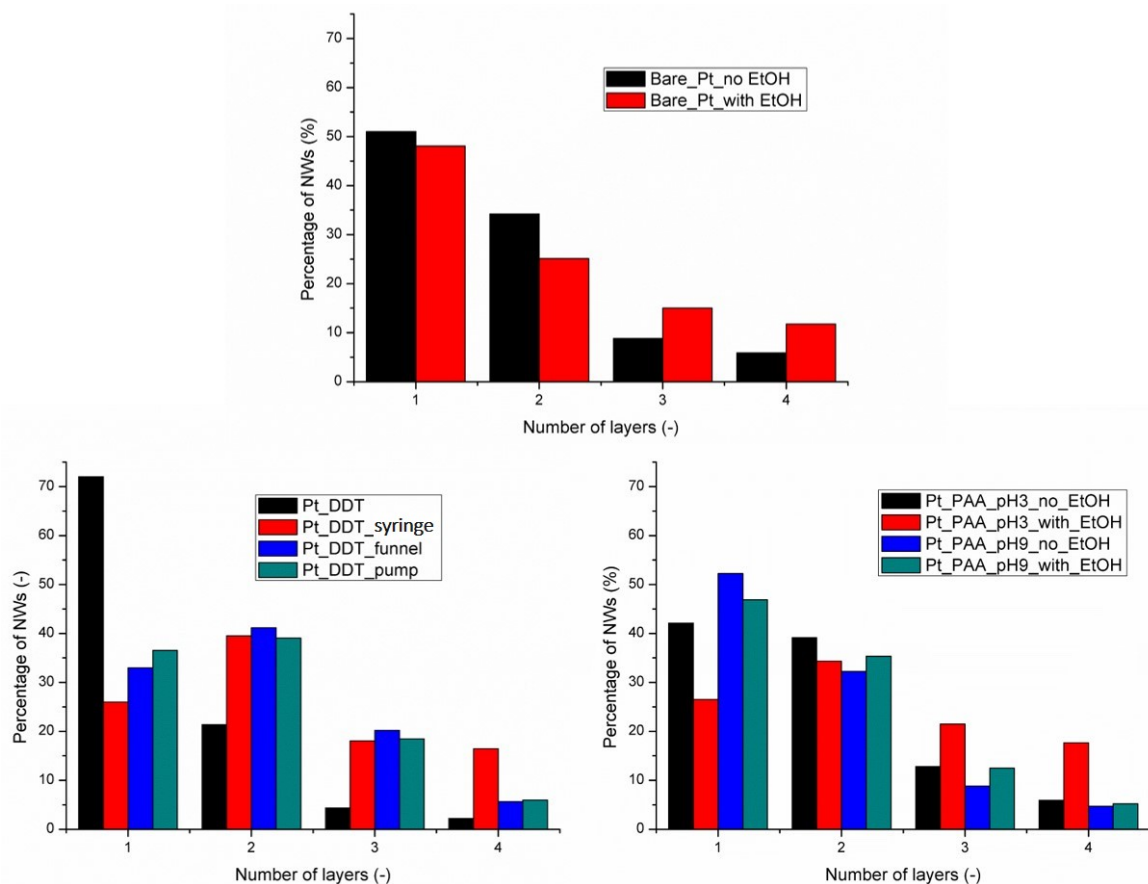


Figure 5.34: Diagrams giving the percentage of each NW layer in each assembly obtained by self-assembly at the toluene-water interface and recovered by drain-to-deposit technique.

5.3.3.3 Stamp inking

The stamp inking technique consists in inking a PDMS stamp with the assembly floating at the air-water interface, by gently pressing the stamp at the interface (Figure 5.4). It may give an exact characterization of the floating assembly for it should glue the NWs very rapidly. Of course there are several technical difficulty to obtain that completely accurate characterization. First the stamp should be completely flat and remain completely parallel to the plane of the interface. Second it is very difficult to know when pressing/pulling down the stamp. It could thus easily lead to destructive pressure on the assembly. Third on such small beakers the interface is not completely flat due to the capillarity of the water against the beaker walls. The interface is slightly concave (with respect with the air). So a flat squared stamp will first touch the interface with its corners. This first touchdown could perturb the assembly. The details on the parameters

and setup used in this work to make this kind of recovery are given in Chapter 7 Section 7.2.4.2.

In this work, tests with the stamp inking were performed with bare Pt NWs. First the stamp was gently manually pressed on the interface. The results are given in Figure 5.35. The assemblies

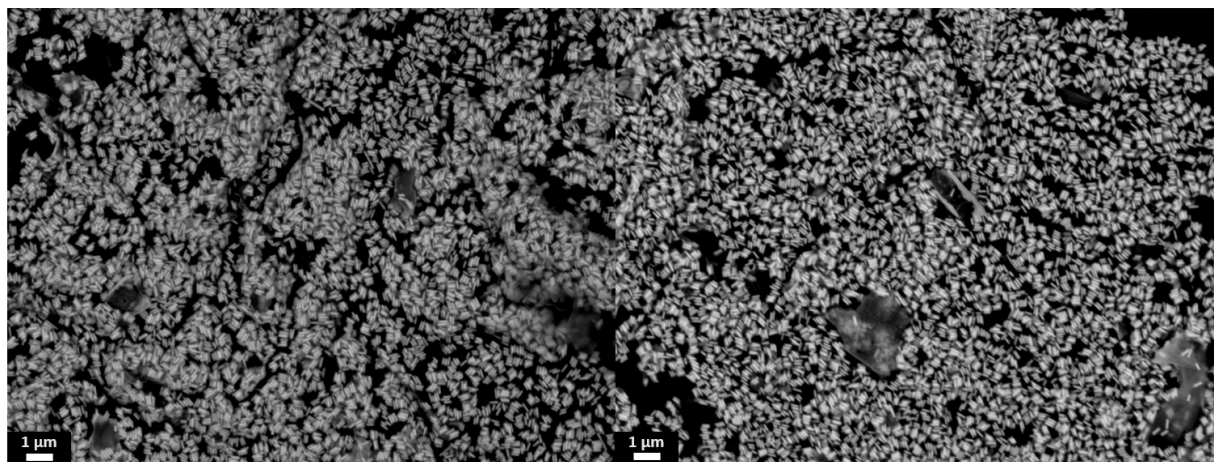


Figure 5.35: SEM images of bare Pt NWs assemblies at toluene-water interface, recovered manually by PDMS inking.

were characterized directly on the PDMS stamp after evaporation of a thin gold film. The results are still blurrier because of the insulating character of the PDMS. The NW assemblies seem to present 3D aggregates and lines without NW are observed which may be cracks that were formed during the manipulation of the soft PDMS stamp. A more automated system have been tried where the stamp was glued to a device that moved perfectly vertically and with a controlled speed. The only drawback of this method was that the vertical downward movement had to be stopped manually when the operator detected the contact of the stamp with the solvent surface. The results obtained with this setup are presented in Figure 5.36. The assemblies are better than those obtained manually but they still seem to present 3D aggregates. This is certainly due to the lack of precision that was inherent of the setup used here. The PDMS inking was not further investigated due to lack of time. However it is believed that if it was precisely adapted, with larger beakers or smaller stamps and a precise control on the pressure of the stamp on the surface and on the trigger of the stop of the vertical movement, the stamp inking could be a more powerful technique than the drain-to-deposit technique.

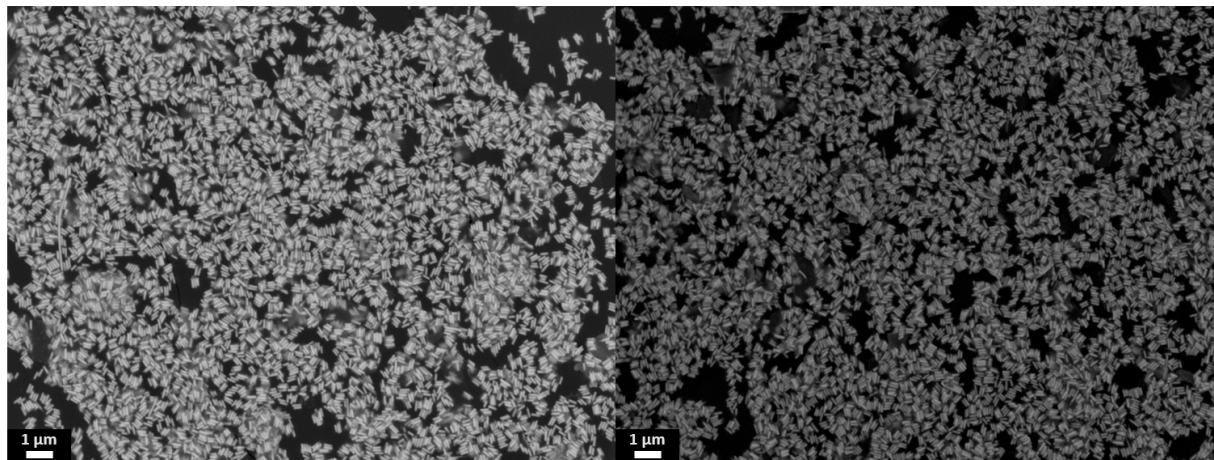


Figure 5.36: SEM images of bare Pt NWs assemblies at toluene-water interface, recovered by "automated" PDMS inking.

5.4 Summary and conclusions

Two techniques of self-assembly have been investigated: the drop-casting and the assembly at the fluid-fluid interface.

For the drop-casting, several parameters were varied to try to optimize the process. However, the morphology of the assembly could be very different depending on which distance of the center of the droplets one looks at. Indeed the assemblies were very localized on the ring of the pinned edge but even inside that ring the assemblies could vary depending on the distance to its edge. This is the major drawback of drop-casting and this could make difficult the drop-casting integration into an application. Nevertheless it has been shown that the better results were obtained when a mixture of toluene and water was used as a solvent and when the evaporation rate was rather slow. Unfortunately, none of the assemblies showed a long-range ordering of the NWs although a certain compactness and some side-to-side NW chains could be achieved.

The NWs functionalized with DDT gave the best assemblies but their compactness depended on the type of substrate; an hydrophilic substrate gave more concentrated assemblies than an hydrophobic one. The assemblies obtained with MUA- or PAA-functionalized NWs were less dependent on the substrate and were less compact. However many results showed side-to-side NWs packets. The pH of the water of the system induced a difference into the assemblies. At low pH (3), the assemblies were more compact and 3D aggregations often occurs while at high pH (9) the compaction was lower. However at pH 3, the number of NWs assembled side-to-side was not larger and, at pH 9, the NWs were not distant from each other. It seems that

the interactions due to the functionalization were not strong enough to produce such extreme assemblies. It is believed that the process of compaction of the NWs at the pinned edge was very strong (capillary and entropic forces) and could overcome at least partially the interactions due to the functionalizations of the NWs. Some tests were performed with a mixture of palladium NWs functionalized with MUTAB and platinum NWs functionalized with MUA. The expected ordering of alternating Pt and Pd NWs was not observed; Pt and Pd NWs segregated in clusters. It seems that Van der Waals interactions dominated the electrostatic interactions.

The assembly at the fluid-fluid interface was performed at the interface between toluene and water. Because the assemblies seemed to lose their compactness after toluene evaporation, an additional compaction step was sometimes performed just before the NW recovery. It consisted in adding some ethanol at the water surface.

The fishing technique to recover the assemblies was soon abandoned because it did not give reproducible results and perturb substantially the assemblies.

The main technique used to recover the assemblies was the drain-to-deposit method. The assemblies obtained by this technique were analyzed by SEM and AFM. The SEM gave a general view of the assemblies and allowed to count the chains of NWs assembled side-to-side and to determine the general assembly density or compactness. AFM enabled the determination of the number of layers in the assemblies. It appeared that the NWs assembled themselves preferentially side-to-side and into several horizontal layers. Most of the assemblies had a compactness around 50% and the number of side-to-side chains could be high but none of them presented a long-range ordering. The results for bare Pt NWs showed that the NWs assemble themselves even if they are not functionalized. The resulting assemblies were rather monolayered and compact. The assemblies with Pt-DDT NWs were very dependent on the compaction step. The addition of ethanol compacted the assemblies but created more multilayered areas without creating longer side-to-side NW chains. The Pt-PAA assemblies behavior at pH 3 was rather similar to the Pt-DDT assemblies even if the differences between each condition were less marked. At pH 9, the results were less impacted by the compaction of the NWs and tended to approach the ones obtained with bare Pt NWs.

Finally few tests were performed to recover the NWs with a PDMS stamp. This technique seems to be viable. The assemblies obtained by this method were similar to the one obtained with the drain-to-deposit method. The 3D character of the assembly was more pronounced and some cracks were visible certainly due to the soft and bendable nature of PDMS.

None of the assemblies was very compact and presented a long-range ordering. This could be due to several parameters. First, the dimension of the NWs and their weight. The NWs

had a rather small aspect ratio but they were much larger than the NRs already studied in the literature. The dimension and the mass of the NWs studied here might then have limited their mobility and hence their ability to self-organize. Second, the system that were used in this thesis were not saturated in NWs. It was hoped that the mechanisms to assemble the NWs would help to concentrate them but let the interactions between functionalized NWs to be a major driving force. It did not seem to be the case. However, by saturating in NWs the interface in the fluid-fluid interface assembly, as it was done in many previous studies, the NWs might assemble in a more long-range ordering way because of sterical reason: a NW mesh enabling more NWs in a surface than randomly distributed NWs. Thus, functionalization or nature of the NWs might be more incidental than the degree of compactness achieved at the interface and the method to obtain it.

Conclusions and perspectives

In this thesis, our main objective was to develop strategies leading to self-assembly of locally (multi-)functionalized NWs. To achieve this objective, three consecutive steps had to be explored: the manufacture of NWs, their functionalization and their assembly. These three steps are briefly reviewed below, before discussing the future prospects of our work.

NW manufacture was performed by ECD within nanoporous templates. After having explored different routes, we concluded that best results were obtained when depositing platinum NWs with a copper sacrificial layer in PC track-etched membranes. In contrast, less reproducible results were obtained when the deposition was performed within homemade AAO templates, or with gold and palladium NWs within PC membranes. Additionally, multi-segmented NWs were successfully produced. Besides deposition quality, the production throughput was another challenge to overcome, which could only partially be overcome by enlarging the deposition surface. Despite this improvement, large stocks of NWs could not easily be obtained and the manufacture of NWs remained a time-demanding step.

The functionalization of the NWs was mainly performed with thiols. It was confirmed that the thiol monolayers were less stable when grafted on platinum than on gold. Nevertheless, fluorescently-tagged thiols allowed us to confirm that grafting occurred in all cases. It was not possible to check the precise homogeneity of SAM layers but the fluorescence coming from FITC-PEG-SH and Rhod-PEG-SH was visible all around gold and platinum NWs. Moreover, we proved the possibility to install new functional groups on the thiol layers, as exemplified by the post-grafting of DAPI on PAA-SH and MUA layers on gold NWs. In the case of Pt NWs the blue fluorescence could not be observed, which we ascribed to the quenching of DAPI fluorescence on platinum, or thiol grafting weak resistance.

Regarding selective multifunctionalization, several initially-envisioned strategies could not be performed, due to the demanding conditions required to dissolve the sacrificial layer of the NWs. Therefore, another route was developed to alleviate this issue. In this new strategy, the NW ends are first functionalized while trapped inside the PC membrane. Next, the NWs are freed of the membrane and their sides are functionalized with a different compound. This route might even lead to tri-functionalized NWs if properly performed. This strategy indeed successfully selectively-grafted the thiols on the ends of the NWs. Unfortunately, when the second functionalization was performed, diffusion of thiols occurred, resulting in the blurring of the selective functionalization. We therefore investigated LbL deposition as a possibly more stable surface modification resulting from the multiplicity of anchoring points of polyelectrolyte macromolecules. However, the LbL layers accumulated inside the pores and formed long organic tails at the ends of the NWs, which was undesirable. Therefore, the spatially-selective multifunctionalization of the NWs could not be satisfactorily achieved.

As concerns the self-assembly of NWs, it was mainly performed via two strategies: drop-casting and assembly at a fluid-fluid interface. Drop-casting was investigated by depositing a droplet composed of toluene, water and the NWs in an ethanolic solution. Drop-casting was very easy to implement but gave heterogeneous results, with the deposition occurring only at specific places of the droplet. It was then difficult to know precisely where to characterize the assembly, since it was not identical all along the surface and not even all along the "coffee rings". Definitive conclusions on these assemblies were thus risky. Still, the obtained assemblies were neither ordered nor dense, contrasting to what has been reported in several studies. Though, the assemblies had a certain degree of compactness and there was a clear tendency for the NWs to assemble side-by-side in more or less long sequences. The assemblies with Pt NWs functionalized by DDT were more compact than the NWs functionalized with MUA or PAA, and the results were dependent on the type of substrate used (hydrophilic or hydrophobic). This substrate effect was especially strong for the Pt-DDT NWs. For Pt-MUA (and Pt-PAA) NWs the differences between assemblies at opposite pH conditions were not as extreme as initially expected, although the assemblies were more compact at pH 3 than at pH 9. However, the electrostatic repulsion at pH 9 seemed not strong enough to oppose assembling forces resulting from Van der Waals interactions and nematic ordering, resulting in the formation of small regions of side-by-side aligned NWs.

The second tested strategy was assembly at a fluid-fluid interface. By adding an ethanolic NW solution into a mixture of toluene and water, the NWs were trapped and 'floated' at the toluene-water interface. The high degree of freedom of the NWs should thus allow to reach a

more equilibrated self-assembly than with drop-casting, in which the stronger interaction of the NWs with the substrate could supposedly freeze the assembly process. However, a nagging issue with this strategy is the characterization of the assemblies. To recover the NWs, the toluene was let to evaporate, which often affected the assemblies even though a compaction step was added in some cases. Consequently the characterized assemblies did not reflect the toluene-water interface assembly but a hybrid one, after the organic solvent evaporation. To recover the assemblies, the classical but very imprecise fishing technique was first used. It was not reproducible but gave an amazing result with gold NWs of small aspect ratio: they were vertically aligned in some sort of flakes. This was the only time the recovered assemblies were vertical.

To obtain more reproducible results the drain-to-deposit method was implemented with a control over a maximum of parameters. It allowed the slow deposition of the floating assembly over a substrate. However the pumping of the water takes time, resulting in the relaxation of the assemblies even when the compaction step was added. Moreover, the residual solvent layer still needed to be evaporated after collection of the assemblies, which may disturb them compared to when they were at the toluene-water interface. Nonetheless the results obtained were quite reproducible from samples to samples. By analyzing the results, it appears that the NWs assemble themselves preferentially side-by-side and into several horizontal layers. The compactness of the assemblies was generally better than for drop-casting. The length of the chains of side-by-side-packed NWs was also higher, even though they did not form a highly ordered lattice. Results with bare Pt NWs showed that assemblies occurred even with non-functionalized NWs. These NWs formed compact (50 %) monolayered assemblies. We confirmed that the compaction step with ethanol plays well its compacting role but creates more multilayered assemblies without creating longer chains of side-to-side-packed NWs. Assemblies with Pt-DDT NWs were very dependent on this ethanol addition and on its experimental details. Pt-PAA assemblies at pH 3 were rather similar to Pt-DDT assemblies even if the differences between each conditions were less marked. This is not very surprising because the DDT should tend to aggregate the NWs due to hydrophobic-hydrophobic interactions whereas the PAA at low pH should tend to form H-bonds. At pH 9, the results with Pt-PAA NWs were less impacted by the compaction of the NWs and tended to approach the ones obtained with bare Pt NWs, again showing that the addition of the electrostatic repulsion was disruptive.

A third recovery technique was finally tested, consisting of the inking of the assemblies on a PDMS stamp. Only few tests could be performed due to time constraints. The assemblies were generally similar to the ones obtain with the drain-to-deposit method, except for a stronger 3D character and the presence of a larger number of cracks, which presumably arise from the softness

of PDMS and its associated bending.

Regarding NW manufacturing, it has thus appeared along this thesis that template-assisted ECD is not be the best mass-production method for self-assembly experiments. The throughput will always be intrinsically limited by the 2D nature of the membrane. Moreover, the reproducible deposition of metals is not as easy as sometimes described in the literature. A better reproducibility could probably be attained by a wider study of control parameters, which would require a more extensive and essentially incremental work (maybe by choosing another gold electrolytic bath). This might be worthwhile since, despite all its flaws, ECD remains unique in its capability to manufacture multisegmented NWs, which also permits to grow sacrificial segments that could be useful in the control of selective multifunctionalization. In this thesis, multifunctionalization was impeded by thiol diffusion all along the NWs. Moreover using LbL instead does not seem to be easy. The functionalization strategy was limited by the uncontrolled deposition of the LbL layers in the pores of the membranes, a problem which is not likely to be solved. Another approach based on LbL and ECD in membranes could be to first coat the pores of the membrane by LbL before ECD; in that way the NWs will be coated on their sides after ECD. Another solution that may solve the original diffusion problem would be to use other functionalization strategies with better or multiple anchoring points. Those functionalizations could thus be made of polythiols or diazonium salts.

Regarding NW assembly, drop-casting is the most easy technique to implement but it also seems to be the less adapted. Indeed the NWs are compacted but their freedom of movement is very limited during the whole process. At the last step of the evaporation process there is a significant chance that the NW assemblies are perturbed by capillary forces, and constrained to a very narrow space (the pinned edge). Therefore there is a reasonable doubt on the possibility to obtain a reproducible large-scale self-assembly by this method, despite previous reports in the literature. However, it cannot be theoretically excluded that a very careful tuning of the many parameters of drop-casting could result in a very slow evaporation of the droplet with a smooth sliding of the edge of the droplet and minimal convection currents in the droplet, with consequently a regular deposition of the self-assemblies on the whole substrate. This being said, the current conclusion of our work is that such a control would be very hard to achieve. To achieve assemblies, fluid-fluid interfaces seem more adapted. Indeed the NWs are already at a flat interface and the liquid character of the water phase allows NWs to move easily. It is thus

believed that if the interactions between the NWs are strong enough, they could be assembled in more equilibrated structures than in drop-casting. Nevertheless, this strategy has a big issue, namely the difficulty to characterize floating assemblies. One interesting solution to get access to the assembly is the drain-to-deposit technique. It first requires to let the organic phase evaporate, which however leads in our case to a loss of compactness of the assembly. During the toluene-water assembly the NWs are confined because of the "pressure" of the organic solvent. Thanks to this compaction, NWs can assemble and if the interactions are strong enough they should stay assembled even after evaporation of the toluene. This was not the case in our work but there exist ways to insure strong interactions between NWs. Some functions inducing strong and selective interactions could be grafted such as complementary DNA strands. Alternatively, the interactions arising from long polyelectrolytes of opposite charge should also be strong enough. In this thesis, we only tested NWs functionalized with PAA, for which interactions switch from repulsive at high pH due to the ionization of carboxylic groups, to attractive at low pH due to H-bonding. However, even at low pH, the NW assemblies were not locked in compact configurations; this might be due to the fact that only half of a NW is immersed in water at the toluene-water interface or on the contrary because the charges are well solvated. Hence, stronger interactions might be needed. Furthermore, it is probably required to have long chains with many interaction points, or very strong specific interactions, in order to obtain a close-packed and stable assembly.

This work also highlights the need to develop better methods to characterize the assemblies than drain-to-deposit that has some (minor) defects. The stamp inking of the assembly could be a very nice alternative to ease collection and characterization. This would require to improve our degree of control over the process, playing with parameters such as the parallelism between the interface and the stamp, as well as the applied pressure and its time of application. This has not been done here by lack of time but we believe this could be achieved after several adjustments and with the right equipment.

In a more applicative purpose, it is not excluded that some samples obtained during this work could display SERS. It may thus be interesting to do Raman spectroscopy. Eventually, obtaining self-assembled thin films deposited on substrates by our method could be used to test the SERS effect. Indeed our strategy could be used to easily test different materials and different dimensions of NWs to better understand the SERS effect and maybe finally optimize it.

In a longer-term perspective, the non-frozen character of the fluid-fluid interface may be better exploited. A very interesting study may be made by trying to achieve reconfigurable assemblies. One can for example use a thermoresponsive polymer on the NWs that could induce the assembly of the NWs while compacted at the toluene-water interface; these assemblies should remain

assembled after evaporation of the toluene if the temperature is above the collapse temperature of the polymer brush. Next, if the temperature is decreased the polymer layer should swell and the NWs should disassemble. By putting back the system to the assembling temperature the NWs should assemble again, possibly with the help of an ethanol compaction step.

Another approach would be to keep the assembly system at the liquid-liquid interface without any evaporation and characterize it by optical means. This may be done by trapping the system with a cover against the upper liquid phase without any air in between. This would allow to keep the assembly compacted at the interface (by the upper liquid phase) and would allow permanent fluidity of the NWs. By injecting light perpendicularly to the interface some polarization or scattering could occur. This may be useful to characterize the assembly performed at the fluid-fluid interface. Moreover, thanks to the optical properties and the reconfigurable characteristics of the confined assemblies, this may lead to applications very similar to the ones involving liquid crystals. For example, such a system could be used as a sensor to detect the temperature, pH or ionic strength of a given system. Another concrete application for this reconfigurable assembly setup could be the manufacture of panels and windows trapping such fluid-fluid interface assembly that could go from a transparent to a scattering state. Therefore the panels would become translucent or opaque. Depending on the scattering interactions it may also lead to color change, if desired.

Materials and methods

7.1 Materials

The following chemical products were used in this thesis:

- boric acid (H_3BO_3) (Sigma-Aldrich, 99.5+ %),
- copper sulfate penta-hydrate (CuSO_4) (Sigma-Aldrich 98+ %),
- 4',6-diamidine-2'-phenylindole dihydrochloride (DAPI) (Sigma-Aldrich, 90+ %),
- N,N-diisopropylethylamine (DIPEA) (Acros Organics, 98+ %),
- dichloromethane (CH_2Cl_2) (VWR, HPLC grade),
- dimethylsulfoxide (DMSO) (Sigma-Aldrich, 98 %),
- N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (Sigma-Aldrich, 98+ %),
- 1-dodecanethiol (DDT) (Sigma-Aldrich, 98+ %),
- ethanol (VWR, HPLC grade),
- fluorescein isocyanate-poly(ethylene glycol)-thiol (FITC-PEG-SH), (Gentaur bvba, $M_w = 1000$ g),
- gold solution (METAKEM SF-Bath, 15 g.l^{-1}),
- hydrogen peroxide (H_2O_2) (Sigma-Aldrich, 30 %),
- 1-hydroxybenzotriazole hydrate (HOBt) (Sigma-Aldrich, 97+ %),
- 11-mercaptoundecanoic acid (MUA) (Sigma-Aldrich, 98 %),
- (11-mercaptoundecyl)-N,N,N-trimethylammonium bromide (MUTAB) (Sigma-Aldrich, $M_w = 326.380$ g),
- 2[methoxy(polyethylenoxy)propyl] trichloro-silane (MPPTS) (abcr, 95 %),
- nickel (II) sulfate hexahydrate (NiSO_4) (Honeywell Fluka, 99 %),
- nitric acid (HNO_3) (Acros Organics, 60 % wt),
- octadecyl-trichloro-silane (OTS) (Sigma-Aldrich, 90+ %),

- palladium solution (METAKEM AS-3, 3 g.l⁻¹),
- perfluorodecyl- 1H,1H,2H,2H -trichloro-silane (fluorosilane) (abcr, 97 %)
- Pluronics[®] F68 (average $M_w = 8350$ g),
- poly(acrylic acid) (PAA) (Sigma-Aldrich, , $M_w = 100000$ g, 35 % wt in water),
- poly(acylic acid- α -thiol- ω -bromo-terminated (PAA-SH) (Polymer Sciences, $M_w = 1000$ g),
- poly(allylamine hydrochloride) (PAH) (Sigma-Aldrich, $M_w \sim 15000$ g),
- poly(ethyleneimine) solution (PEI) (Sigma-Aldrich, $M_w \sim 750000$ g),
- poly(fluorescein isothiocyanate allylamine hydrochloride) (PAH-FITC) (Sigma-Aldrich, poly(allylamine hydrochloride) : fluorescein isothiocyanate 50:1, based on PAH polymer $M_w \sim 15000$ g),
- poly(sodium-p-styrenesulfonate) (PSS) (Acros Organics, $M_w \sim 70000$ g),
- potassium chloride (KCl) (Acros Organics, 99+ %),
- potassium hexacyanoferrate (II) trihydrate ($K_4Fe(CN)_6$) (Sigma-Aldrich, 99.5+ %),
- potassium hexacyanoferrate (III) $K_3Fe(CN)_6$ (Sigma-Aldrich, 99+ %),
- platinum solution (METAKEM DNS-Bath, 10 g.l⁻¹),
- rhodamine B-poly(ethylene glycol)-thiol (Rhod-PEG-SH) (Interchim, $M_w = 3400$ g),
- sodium chloride (NaCl) (Acros Organics, 99+ %),
- sodium hydroxide (NaOH) (Chem-Lab, 99+ %),
- sodium hydroxide solution (NaOH) (Merck, 2 M or 5 M),
- sulfuric acid (H_2SO_4) (VWR, technical 95 %),
- sulfuric acid solution(H_2SO_4) (Merck, 0.5 M),
- Sylgard[®] 184 (curing agent and monomer) (Dow Corning),
- toluene (Acros Organics, 99.8 %).

Milli-Q water (resistivity 18.2M Ω .cm) was obtained from a Merck Millipore system (Milli-Q[®] Reference). Water refers always to Milli-Q water unless told otherwise.

All glassware used for surface modification and assembly was cleaned using piranha solution (1:2 v/v mixture of hydrogen peroxide (30 %) and sulfuric acid (95 %); *caution: piranha solution is extremely reactive and should be handled carefully*).

The PC membranes were purchased from it4ip. The diameter of the pores was announced to be 100 nm and 500 nm and the density was 10⁸ pores/cm² and 5 $\times$ 10⁷ pores/cm², respectively. However, the membranes announced with 500 nm diameter pores were actually measured as having pores of 600 nm diameter. The thickness of the PC membranes was always 21 μ m. The PI membranes used as filters were from it4ip and their pores were of 200 nm diameter (5 $\times$ 10⁷ pores/cm²). The PI membranes were 25 μ m thick.

Silicon wafers (100) were purchased from TOPSIL (diameter 10 cm).

The Eppendorf tubes used were always 2 mL volume unless said otherwise.

Ultrasonication was made in a BioBlock Scientific ultrasonic bath at 45 kHz unless told otherwise.

Centrifugations were made inside a Minispin Eppendorf at 10000 rpm.

7.2 Methods

7.2.1 Nanowire manufacture

7.2.1.1 Homemade AAO and PC templates

The AAO templates used in this thesis were supported. To obtain them, a freshly cleaned Si wafer was first coated with a Au/Al (50/1000 nm) bilayer by magnetron sputtering (Plassys MP500S). An ultra-thin Ti film (5 nm) was also deposited between the substrate and the successive metallic layers to act as an adhesion promoter. The as-prepared substrate was next sealed in an electrochemical cell of 1.3 cm diameter and exposed to a single step anodization process. This process was achieved in 0.3 M oxalic acid at 2°C, by applying 60 V between the substrate and an Al barrel dipped inside the electrolytic solution. Temperature control was achieved thanks to a Peltier device (linked to a Kepco power supply) at the bottom of the cell, via a temperature controller (Omega Cyc91) linked to a thermocouple probe and a resistance. The probe was inserted just below the substrate and the resistance was at the same height as the Peltier. The anodization potential was applied from a Keithley 2400 sourcemeter that also recorded the current during the process. The anodization was stopped when the current attained 20 mA. The section of the used electrolytic cell can be found in Figure 7.1 (a). The obtained nanopores were then chemically widened in 0.5 M H₂SO₄ at 40°C for 90 min (inside the cell). The membrane was then immersed in water for 10 min, then let to dry.

The characterization of the AAO porosity membranes was made by analyzing the SEM images (top view) of samples after ECD and after template dissolution. The images were analyzed in a software (ImageJ®) in which they were first turned into black and white (without grey shadow). The black pixels correspond to the background and the white pixels correspond to the NWs hence to the place where the membrane was porous (reaching the conductive layer). The total porosity

is then obtain by calculating the percentage of white pixels in the images.

The PC membranes were metallized (on one side) with a Cr/Cu bilayer in a metallizer-evaporator chamber Pfeiffer Vacuum 500. The bilayer thickness was (5/500 nm) for membranes of 100 nm pore size and (5/2000 nm) for membranes of 500 nm pore size.

7.2.1.2 Electro-chemical deposition of nanowires

ECD of NWs within the nanoporous templates was performed in an electrolytic cell. The sample was sealed at its bottom and the cell was filled with an electrolytic bath containing the desired material to deposit. The cell was either the same as the one used to obtain the AAO template (1.33 cm²) or a larger one (9.62 cm²) (Figure 7.1 (b)). In the latter case the temperature control was performed by circulating a fluid in a helicoidal copper tubing passing the copper base of the cell. The tubing was connected to a Ministat 230 chiller.

The ECD process was carried out in a "three-electrodes" potentiostatic configuration using a potentiostat (Princeton Applied Research 263A) by applying to the working electrode (the substrate) a potential versus a double-junction Ag/AgCl reference electrode (KCl saturated, $E = 0.197\text{ V}$), while a Pt foil was installed in the bath as a counter-electrode.

The parameters imposed were different for each materials deposited:

- For Ni ECD, the electrolytic bath was composed of 0.5 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.4 M H_3BO_3 . The potential applied was pulsed with a long pulse imposed at -1.05 V for 90 ms and a

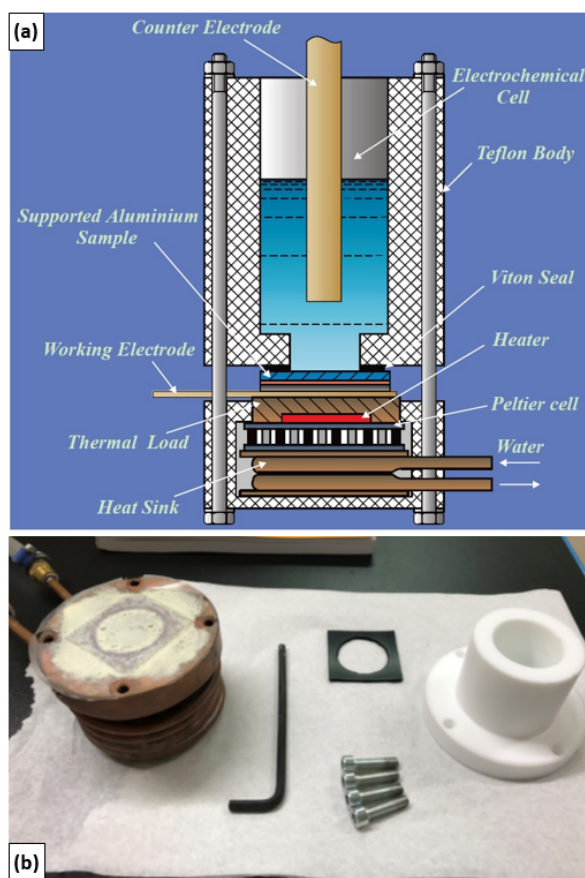


Figure 7.1: (a) Drawing of the "small" electrolyte cell (from [49]). (b) Picture of the elements of the "large" cell (including the allen key).

short pulse at -0.7 V for 10 ms. The temperature was set to 30°C.

- For Cu ECD, the electrolytic bath was composed of 15 mM $\text{CuSO}_4 \bullet 5\text{H}_2\text{O}$ and 0.5 M H_3BO_3 . The potential was continuously maintained at -0.2 V. The temperature was set to 30°C.
- For Au ECD, the electrolytic bath was a commercial one from METAKEM (15 g/L). The potential applied was pulsed with a long pulse varying from -0.3 V to -0.4 V for 70 ms to 90 ms and a short pulse varying from -0.5 V to -0.6 V for 10 to 30 ms. Eventually the best results were obtained with -0.35 V during 90 ms and -0.55 V during 10 ms. The temperature was then set to 55°C.
- For Pt ECD, the electrolytic bath was a commercial one from METAKEM (10 g/L). The potential was continuously maintained at -0.3 V. The temperature was set to 50°C.
- For Pd ECD, the electrolytic bath was a commercial one from METAKEM (3 g/L). The potential was continuous and was varied between -0.45 V and -0.65 V. The temperature was also varied between 30 and 50°C. Eventually the best depositions were made at -0.6 V and 45°C.

After deposition the cell, was emptied and rinsed with water. For rinsing, the cell was filled with water and shaken twice for 30 seconds, then was filled again with water and let to rest for 5 min. Finally the cell was emptied again and another fast rinsing step was performed. Eventually the sample was recovered or the next ECD was performed.

Seeing the difficulty to perform gold ECD, some voltammetry measurements were performed with electrolytic bath on AAO and PC templates. Typical results are provided in Figure 7.2 where one can clearly see that reduction occurs at -0.55 V when the temperature is raised to 55°C even if its intensity is not tremendous on PC templates. Note also that the current is almost zero at -0.35 V indicating that no reduction or oxidation really occurs. Pulses at such potential allow relaxation of the system and ion diffusion through the pores.

7.2.2 Dissolutions

7.2.2.1 Dissolution of the AAO template

The dissolution of the AAO template, i.e., the dissolution of the alumina layer, has to be realized gently to prevent the NWs from collapsing, and keep the NWs freestanding on the substrate. To

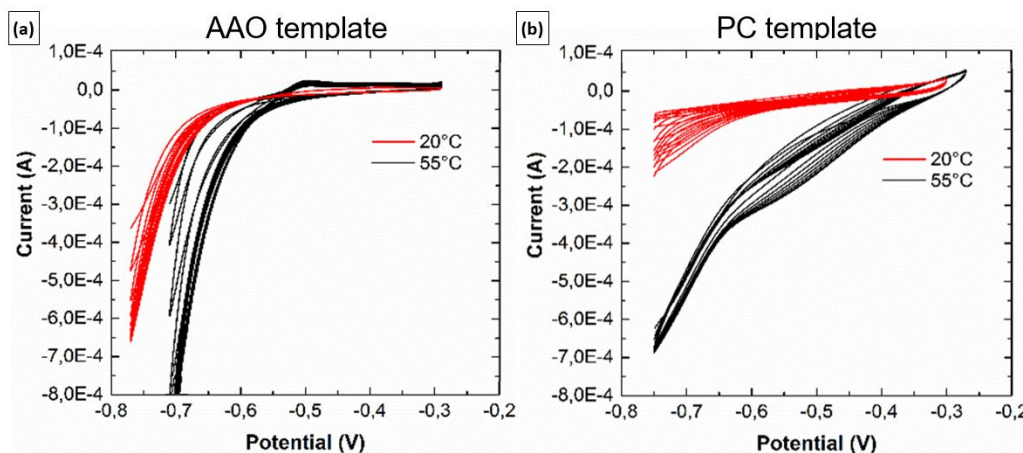


Figure 7.2: Cyclic voltammetry diagrams for the electrolytic gold bath at different temperatures on (a) AAO template and (b) PC template. The diagrams correspond to ten cycles between different potentials for each condition.

realize this soft dissolution, the sample was immersed in successive NaOH baths inside crystallizing dishes. In each bath, the sample was tilted at 45° to limit redeposition of the dissolved alumina on the sample. Six immersions in NaOH were performed: three in 2 M NaOH for 5, 4 and 3 min and three in 5 M NaOH for 3, 2 and 1 min. Next the sample was immersed in two successive baths of ethanol for 3 min each. The sample was then immersed for 5 min in water. Eventually the sample is let to dry under ambient conditions. Flashing the sample with N_2 is to avoid for it could make the NWs to collapse.

7.2.2.2 Dissolution of the PC template

Before dissolving the PC membrane itself, the metallization layer had to be etched. Therefore, the template was immersed in 0.2 M APS solution inside a crystallizing dish for 3 min (100 nm pore diameter) or for 5 min (500 nm pore diameter). This enables the dissolution of the Cu layer. Next the sample was thoroughly rinsed with water. The chromium layer was then dissolved by immersing the sample into the chromium etchant for 30 s in a crystallizing dish. Finally, the sample was rinsed with water.

If desired, the sacrificial feet can also be dissolved at that stage. Obtaining this complete dissolution inside the membrane could be obtained when using Cu as sacrificial layer (foot). In this case, the membrane was immersed in 0.5 M APS solution during 30 min under orbital agitation (75 rpm) (Edmund Bühler KS-15). The sample was then rinsed in water and dried in a N_2 flow.

The dissolution of the membrane itself was performed in an Eppendorf tube (2 mL). For small samples (ECD in 1.33 cm^2 area) the complete membrane was put in one tube. For the large samples (ECD in 9.62 cm^2) the samples were cut in four pieces and placed in four separate tubes. Each Eppendorf tube (coming from the small or large samples) was filled with CH_2Cl_2 and placed in an ultrasonic bath for 2 min. Then, the tube was centrifuged at 10000 rpm during 90 s and the supernatant was removed. The addition of dichloromethane and the following steps (ultrasonication, centrifugation and removal of the supernatant) were repeated twice. Directly after the first addition of CH_2Cl_2 the PC was dissolved but the two additional baths were found useful to eliminate all residues. Eventually the NWs were rinsed/transferred to ethanol. To perform this rinsing/transfer, the tube was filled with ethanol, placed in an ultrasonication bath for 2 min, centrifuged at 10000 rpm during 3 min and the supernatant was removed. This rinsing step was repeated twice.

When the sample was functionalized by LbL assembly within the membrane, an alternative dissolution of the membrane was performed. The membrane was dipped into an Eppendorf tube filled with dichloromethane. Then, the solution was filtered with a 13 mm swinny filter unit using a porous PI membrane as filter (pore diameter $200\text{ }\mu\text{m}$)(Figure 7.3). Similarly to the usual procedure, the PI membrane was finally rinsed with ethanol.



Figure 7.3: Picture of the material used for filtration on a PI membrane.

7.2.2.3 Etching of the sacrificial layers

NWs from the AAO strategy are freestanding on the Si substrate. The dissolution of the sacrificial layer leads to their liberation. The dissolution was performed in HNO_3 15% (trials were made for concentrations up to 60%) for Ni layers, and in 0.5 M APS for Cu layers. The samples were immersed in those solutions in a crystallizing dish of diameter just above the one of the sample. During the immersion the samples were placed in an ultrasonication bath for at least 15 min. Next, the samples were briefly flashed with water. All the liquid used in the process was then recovered in an Eppendorf tube, then centrifuged at 10000 rpm for 5 min and the supernatant removed. Most of the time an additional etching of the NWs in suspension was then performed

to try to remove completely the sacrificial layers.

The etching of Ni or Cu layers in suspension was performed inside an Eppendorf tube. The tube was filled with HNO_3 15 to 60 wt% or 0.5 M APS for Ni or Cu, respectively. In the case of Ni, the suspension in Eppendorf tube was first transferred to water if it was composed of ethanol. Indeed nitric acid and ethanol can react violently. To transfer the NWs, the Eppendorf tube was filled with water, placed in an ultrasonication bath for 2 min, centrifuged at 10000 rpm during 5 min and the supernatant was removed. Three water baths are advised to remove all traces of ethanol.

Then, the etching bath is added. The Eppendorf tube is placed in a ultrasonication bath every 15 min for 5 min. This cycle was repeated as many times as desired. For APS and nitric acid, when no constraints on the harsh conditions were imposed, four ultrasonication steps were made (60 min in total). When the dissolution was really difficult, several (up to five) successive etching baths were performed (60 min each), with centrifugation and supernatant removal between each bath. At the end, according to the resistance of the functionalization, the etching of Ni layer was made into HNO_3 15 wt% with one ultrasonication cycle.

After the etching bath(s) the sample was rinsed by water. Finally the NWs were transferred into ethanol. For each transfer, three successive baths were usually required with ultrasonication during 2 min to redisperse the NWs inside the solution, centrifugation to remove the supernatant and addition of the new bath. The centrifugation with aqueous and ethanolic solutions were for a least 5 min and 3 min, respectively.

7.2.2.4 Production and characterization of nanowire stock solution

The NWs coming from several samples were placed together in one single Eppendorf tube by adding 0.5 mL of ethanol inside each tube sample. Then the liquid were syringed and injected in a new tube. In case more more than four samples were to be collected, a centrifugation step was performed to remove the supernatant and make room for the extra samples.

After addition of many samples inside a single tube, the concentration in NWs of the suspension needed to be characterized. First a small amount of the suspension was analyzed by ICP-AES (Earth and Life Institute, UCLouvain). Next, the suspension was characterized by UV-Vis analysis in a Varian Cary 50 UV-Vis Spectrophotometer. It was then possible to correlate the UV-Vis absorbance obtained to the concentration obtained by ICP-AES for calibration purposes.

The morphological characterization of the NWs was made by depositing a droplet (10 μL) of NW ethanol solution on a Si substrate. The Si substrate was then imaged by SEM (FEG 7600 F from JEOL). It allows in particular the measurement of the length and diameter of the NWs. These measurements were made one by one and collected "manually".

7.2.3 Functionalization(s)

7.2.3.1 Flat surface functionalization

The metallic flat surfaces were obtained from a freshly cleaned Si wafer which was first coated with a Au (50 nm) layer by magnetron sputtering (Plassys MP500S). An ultra-thin Ti film (5 nm) was also deposited between the substrate and the metallic layer to act as an adhesion promoter. Exceptionally, the Au layer could also be replaced by a Pt layer (50 nm) to test assembly on sputtered Pt surfaces. In general, the Au-Si surfaces were then diced (1.5 cm^2) and coated with the desired material by ECD. The depositions were performed inside the small cell (1.33 cm^2) as described above. The charges deposited were 2, 3 and 1.5 C for Au, Pt and Pd, respectively. All surfaces were exposed under UV-ozone (20 min in a UVO-cleaner n° 42-220 (Jelight)).

Thiol SAMs The flat surfaces were immersed for 3 h into a thiol solution. For every simple thiol (DDT, MUA, MUTAB) the solution was 2×10^{-2} mM in ethanol. The PAA-SH was diluted in water (1 g/L) at pH 9 whereas the Rhod-PEG-SS and FITC-PEG-SH were also diluted in ethanol (1 g/L). The samples were finally thoroughly rinsed with ethanol and dried with a nitrogen flow.

Layer-by-layer assembly The flat surfaces were successively immersed into polycation (PAH or PAH-FITC) and polyanion (PSS) aqueous solution. After each immersion, the sample was washed in a NaCl solution having the same pH and ionic strength as the polyelectrolyte solutions. The solutions were 0.035 M in NaCl at pH 5 with PAH, PAH-FITC and PSS concentration of 1, 1 and 1.5 g/L, respectively.

The surfaces were first dipped into the polycation solution for 5 min. The samples were then rinsed in three different rinsing solutions: 15×1 s in the first one, 7×3 s in the second and 30 s in the third one. Afterwards they were dipped into the polyanion solution for 5 min then rinsed the same way. The previous steps were repeated as many times as the desired number of bilayers. Eventually the surfaces were dipped in the PAH-FITC solution for 5 min and then rinsed. Finally the samples were rinsed with water and dried with a nitrogen flow.

7.2.3.2 Nanowire functionalization

Nanowires in suspension. The functionalization of NWs in suspension was made as follows. 0.5 mL of NW concentrated solution in ethanol are sampled in an Eppendorf tube. In the case of Pt NWs, the concentrated solution corresponded to a UV absorbance of 1, whereas in the case of NWs from other nature, the concentrated solution corresponded to gathering of five samples obtained by ECD in the small cell. Then the tube was centrifuged for 3 min and the supernatant was removed. Next, the tube was filled with the thiol solution (2×10^{-2} mM in ethanol for DDT, MUA, MUTAB; 1 g/L in water for Rhod-PEG-SH, FITC-PEG-SH; and 1 g/L in water pH 9 for PAA-SH). The Eppendorf tube was then placed in an ultrasonication bath for 1 min and let under orbital agitation (100 rpm) for 12 h. The tube was then rinsed in ethanol (3 successive baths with centrifugation (3 min), withdrawal of the supernatant and redispersion by ultrasonication). Eventually, the NWs were concentrated back to 0.5 mL of ethanol to keep the same starting concentration.

Freestanding nanowires. The freestanding NWs were functionalized by LbL with PAH and PAA. A 0.035 M NaCl aqueous solution was used (pH = 5.5). PAH and PAA were both dissolved in this solution (1 g/L) and the pH was adjusted again to 5.5. Then, the whole substrate with the freestanding NWs was dipped into the PAH solution for 5 min. Next the sample was rinsed as previously described. Afterwards the sample was dipped into the PAA solution for 5 min and then similarly rinsed. The above steps were repeated as many times as the desired number of bilayers (most of the times, 8 bilayers).

Eventually the sample was immersed in three successive ethanol baths for 2 min and let to dry under ambient conditions.

The recovery of the NWs was first done similarly to the normal recovery of freestanding NW but this was not very efficient. Therefore, the NWs were finally recovered by immersing the sample inside water and applying strong ultrasonication conditions (37 kHz) for 10 min (inside a ElmaSonic P 120 H).

In-membrane functionalization The in-membrane functionalization of both NWs end was done by immersing the NW-filled PC membrane after dissolving the sacrificial feet.

For thiol functionalization, the immersion was done inside the standard fluorescent thiol solution used in this work (1 g/L in water for Rhod-PEG-SH, FITC-PEG-SH; and 1 g/L in water

at pH 9 for PAA-SH). The immersion was performed for 5 h. Eventually, the membrane was rinsed in ethanol by immersing the membrane in three successive baths for 5 min each.

When only one end of the membrane had to be functionalized, the membrane was sealed into a cell (originally used to perform ECD) of 1.2 cm diameter. The cell was then filled with the thiol solution to cover the membrane, for 5 h. Then the cell was filled by three successive ethanol baths for 5 min each, corresponding to the rinsing step. Eventually the membrane was taken out of the cell.

For the functionalization by LbL assembly (on both NW ends), the membrane was immersed in successive baths of polyelectrolytes and water. The aqueous solutions were 0.035 M NaCl at pH 5, with 1, 1.5, 1 or 2 g/l PAH, PSS, PAH-FITC or PEI, respectively.

The membrane was first dipped into a polycation solution for 5 min, then dipped into NaCl solution and a cell scraper was used to scrub each side of the membrane during one minute to remove the excess of polycation on the membrane. Next the sample was rinsed thrice as described previously. The same procedure was then repeated with the polyanion solution these steps (for which the experimental equipment is presented in Figure 7.4) were repeated as many times as the desired number of bilayers

Eventually the sample was dipped in the PAH-FITC solution for 5 min and scrubbed and rinsed. Finally the sample was rinsed with water and dried with a nitrogen flow.

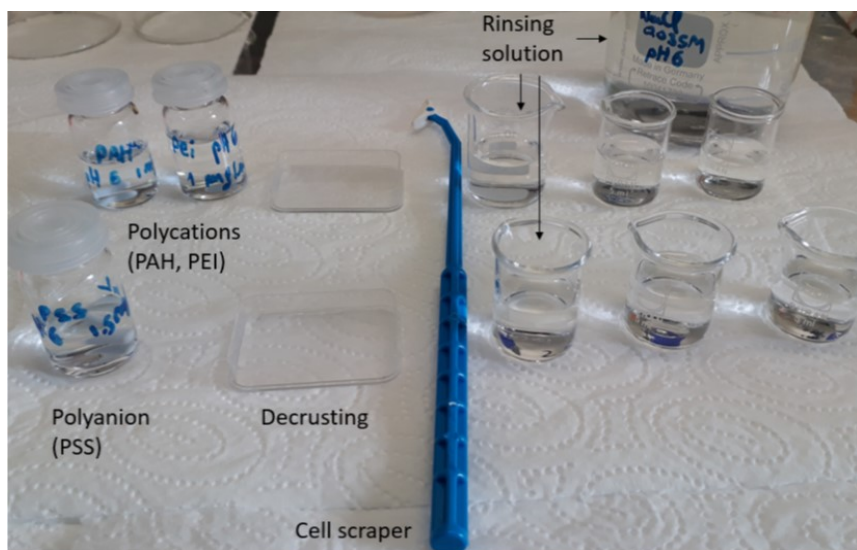


Figure 7.4: Layer-by-layer equipment to functionalize the NWs in-membrane.

DAPI grafting Grafting of DAPI onto MUA or PAA functionalized-NWs has been performed in Schlenk tubes under Ar atmosphere (Figure 7.5). First the NWs coming from the functionaliza-

tion step are transferred into DMSO inside an Eppendorf tube (with three cycles of centrifugation (for 90 s), removal of the supernatant, addition of DMSO and redispersion by ultrasonication) to finally obtain the NWs inside 0.5 mL of DMSO in the tube. This solution was injected in a Schlenk tube under Ar atmosphere. Next 0.5 mL of a solution containing DAPI and DIPEA was injected (3×10^{-2} M in DMSO each), followed by the injection of 0.5 mL of HOBt (2.4×10^{-2} M in DMSO) and finally by the injection of 0.5 mL of EDC (2.4×10^{-2} M in DMSO). In between each injection, a cycle of vacuum/gas treatment was applied. The mixture was then let to react for 18 h. Next the mixture was transferred to a new Eppendorf tube and rinsed in DMSO (with 2 cycles of centrifugation (90 s), removal of the supernatant, addition of fresh DMSO and redispersion by ultrasonication). Then it was transferred and rinsed in ethanol (with three similar cycles) to finally obtain the NWs inside ethanol, ready for fluorescence characterization.

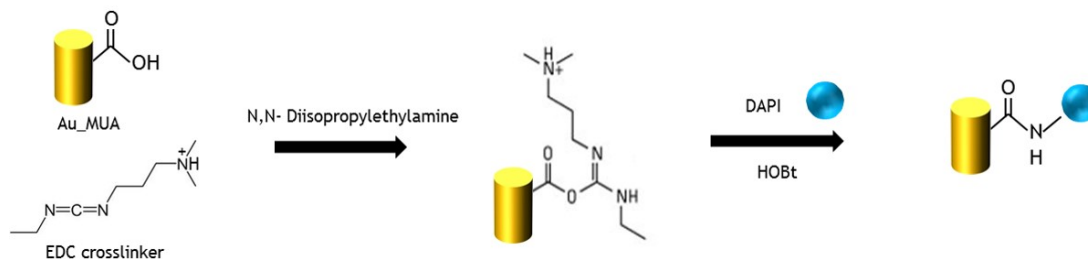


Figure 7.5: Schematic representation of DAPI grafting on MUA functionalized Au NWs.

7.2.3.3 Functionalization characterization

Electrochemical analyzes Electrochemical characterizations of the grafted layers were performed with a CHInstrument potentiostat 660B. The measurements were carried out at room temperature in a one-compartment Teflon cell (0.5 cm diameter) equipped with a platinum counter electrode, an Ag/AgCl reference electrode and the modified metal-coated surface as the working electrode. The barrier properties of the grafted layers were evaluated by measuring the electron transfer reaction on the modified surface using a potassium ferrocyanide redox probe. The electrolytic solution contained equal concentrations of both oxidized and reduced forms of the redox couple, namely 1 mM potassium ferrocyanide (II) ($\text{K}_4\text{Fe}(\text{CN})_6$) and (III) ($\text{K}_3\text{Fe}(\text{CN})_6$) in 0.1 M KCl. All electrolyte solutions were purged with N_2 for at least 10 min prior to measurements.

CV characterizations of the grafted layers were carried out by sweeping the working potential between -0.3 and 0.6 V at a scan rate of 0.1 V s^{-1} . This potential window should allow a clear detection of the grafting quality without oxidizing the thiols and so degrading the SAMs. Of

course it could have been also interesting to increase the potential window until this oxidation to see if one or another thiol resists to higher potential. It would then mean that its resistance (at least to electric potential) is higher.

EIS measurements were performed at the open circuit potential with a sinusoidal perturbation voltage of 10 mV amplitude in the frequency range from 1×10^{-1} to 1×10^{-5} Hz.

Fluorescence characterization Fluorescence was analyzed by epifluorescence microscopy (optical inverted epifluorescence IX71 microscope (Olympus, Japan)) or confocal microscopy (Zeiss LSM 710). The flat surfaces were directly imaged whereas the NWs in suspension were deposited on microscopy glass slides (droplet of 100 μ L).

Layer-by-layer on freestanding NWs The NWs modified by LbL while they were freestanding were recovered in suspension then deposited on a TEM grid (CF200-Cu 200 mesh from EMS). The grid was analyzed by STEM using a specific transmitted detector inside the SEM (FEG 7600 F from JEOL).

7.2.4 Nanowire self-assembly

7.2.4.1 Drop-casting

Drop-casting was performed with a very small amount of liquid to avoid wasting NWs. A mixture of 40 μ L solvent(s) and 10 μ L concentrated NW solution (in ethanol) was pipetted. The solvents were either NaCl 10^{-5} M in pH 3 or 9 water, toluene, or a mix of both (20 μ L each). The pipetted sample was dropcasted on a wafer in a small crystallizing dish of size tuned to the wafer in a desiccator. A cover can be added to the crystallizing dish and the desiccator can be placed on a stage with orbital motion (Edmund Bühler KS-15) at 50 rpm. Moreover, the relative humidity was controlled by a hygrometer and was measured to be 40%, or 80 % when adding a beaker of salt-saturated solution in the desiccator (40 g NaCl in 60 mL water). The wafers used were either hydrophobic or hydrophilic. The setup used to perform the drop-casting can be found in Figure 7.6

Substrate modification The modification of the substrates to render them hydrophobic or hydrophilic was made by silanation in the liquid phase. Si wafers were first washed in piranha

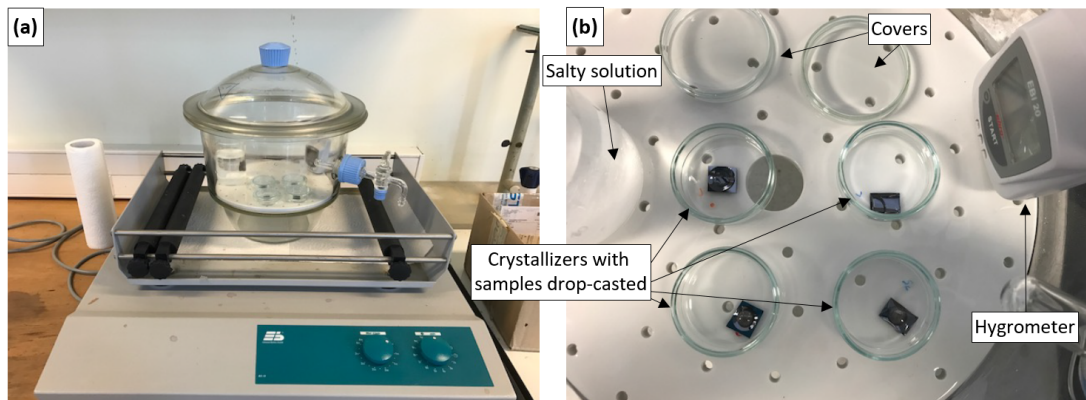


Figure 7.6: Setup used to perform drop-casting. (a) Desiccator on the stage with orbital motion. (b) View inside the desiccator.

solution and then exposed to an air plasma (EMITECH K1050X) for 10 minutes in order to activate them. Next the wafers were placed in Teflon crystallizing dishes inside a glove box. Then a solution, made of 40 mL of toluene and 0.4 mL of OTS (or 0.6 mL of MPPTS), was poured onto the wafers, and let to rest for 18 h. Then the wafers were recovered and rinsed with toluene, then ethanol, then water in an ultrasonication bath (2 min for each bath). Eventually the wafer were dried by nitrogen flow.

7.2.4.2 Self-assembly at the fluid-fluid interface

The fluid-fluid interface self-assembly was performed inside a small beaker of 5 mL volume. The water phase (1.5 mL) was first added and next, followed by the toluene phase (1 mL). Water was pure Milli-Q water for non-pH dependent functionalized NWs (bare and DDT-functionalized NWs) and NaCl 10^{-5} M at pH 3 or 9 for MUA and PAA-functionalized NWs. Finally the concentrated NWs in ethanol (75 μ L of concentrated solution added with 425 μ L of pure ethanol) were injected with a syringe inside the water/toluene mixture. The toluene was let to evaporate under ambient conditions. It usually took one day for the complete removal of the toluene.

If a compaction step with ethanol was performed, it was made by adding some ethanol (250 μ L) at the surface of the water, near one edge of the beaker. The addition was made thanks to a flattened needle according to three methods: by promptly pressing a syringe linked to the needle; by pouring the ethanol into a funnel linked to the needle; or via a peristaltic pump (MasterFlex C/L – HV-77120-42) linked to the needle with a speed of 100 μ L/min. The recovery methodology was then applied within 30 s after the addition of ethanol.

To characterize the assemblies they had to be recovered on substrates. To do so, several techniques were tried.

Fishing technique The simplest recovery technique was fishing. The substrate was held tilted with tweezers and immersed below the assembly to collect it by lifting the substrate. In this work the substrates were pieces of Si wafers (previously washed into piranha solution). An example of this process can be seen in Figure 7.7.

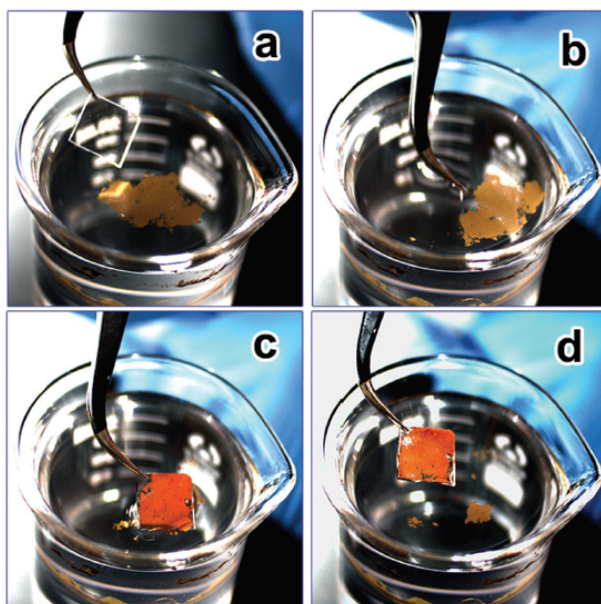


Figure 7.7: Picture of the fishing process for an Au NPs monolayer film transferred onto a quartz substrate. Reproduced from [152].

Drain-to-deposit technique For the drain-to-deposit method, a Si wafer (previously washed into piranha solution) was placed on the bottom of the beaker before the beginning of the assembly process (i.e., before the addition of any liquid inside the beaker). Then, after evaporation of the toluene and the compaction step (if wished), a flattened needle linked to the peristaltic pump was dipped vertically into the liquid, taking care to be very perpendicularly to the interface surface, until reaching the bottom of the beaker, close to the previously added wafer (but not touching it). Next the solution was pumped out at a rate of $50 \mu\text{L}/\text{min}$ until completely emptying the beaker. Then, the pump was stopped and the very last drops remaining in the beaker and on the wafer were let to evaporate under ambient conditions. The setup of the drain-to-deposit process is shown in Figure 7.8.

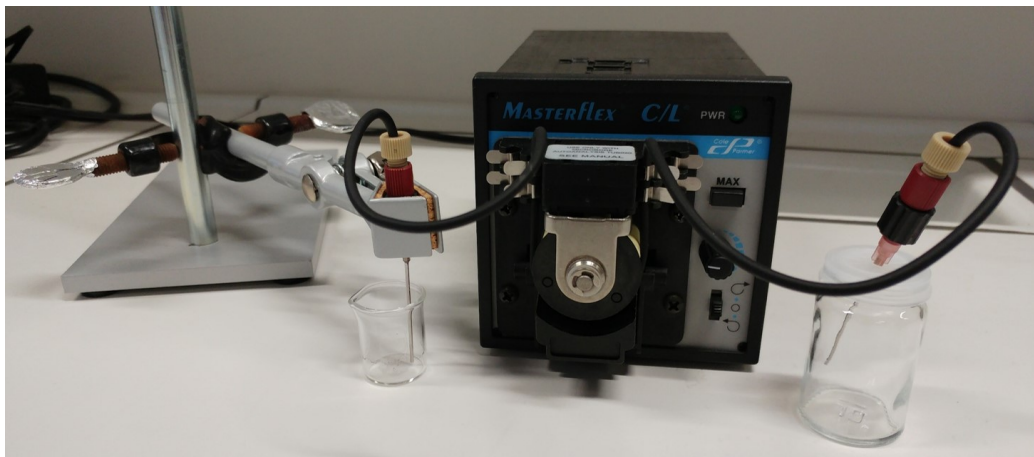


Figure 7.8: Picture of the drain-to-deposit setup. The pump was linked to a flat needle placed at the bottom of the 5 mL beaker, while the other end of the tubing is linked to a disposable waste container.

Stamp inking The last recovery technique was the stamp inking. The PDMS stamps were made via PDMS pouring (before crosslinking) on a fluoro-silanized Si wafer.

The fluorosilanation was performed as described previously (with OTS and MPPTS) using a fluorosilane solution 0.6:40 vol:vol.

Next, 6.5 g of curing agent was poured inside 65 g of monomer (Sylgar[®] 184). The solution was vigorously stirred for 2 min (with a plastic spoon) and then degassed in an ultrasonication bath (3×5 min with 30 s break in between). The fluorosilanized Si wafer was placed in a Teflon crystallizer (perfectly fitting the size of the wafer). Then the PDMS was carefully poured on the wafer, to finally obtain a layer of ~ 0.2 cm thickness. The system was let to rest under ambient condition while perfectly horizontal for 1 h. Next, it was placed in a stove at 60°C for 12 h. Eventually, the PDMS layer could be easily peeled off the fluorosilanized wafer and some squared stamp were cut off with a scalpel (0.5 cm side).

Those stamps could be used to press the floating assembly manually or more accurately thanks to an experimental setup. In this latter case, the stamps were fixed on a linear translation stage (LTS 150 from ThorLabs) fixed itself on a vertical rail. The beaker was placed at the bottom of this rail before doing the assembly. The stage was then slowly moved towards the beaker (at 10 $\mu\text{m/s}$). As soon as the stamp was in contact with the floating assembly, the stage was quickly ascended back.

7.2.4.3 Assembly characterization

Scanning electron microscopy The self-assemblies were always characterized by SEM (FEG 7600 F from JEOL). The assemblies transferred onto Si substrates were imaged as such. However, assemblies transferred on PDMS stamp had to be metallized with gold (5 nm). The metallization was performed in a Sputter Coater (Cressington 208HR).

When the global compactness rate (for one condition) was calculated, it was made by taking 4 images (magnification 5000 X) in the center of the assemblies. Each rate comes from 3 different samples (12 images in total). On every image, the compactness rate was calculated by taking the percentage of substrate surface covered by the NWs. This was made via ImageJ[®] routine *Analyze particles area*.

The SEM images were also often analyzed by counting the NWs that were side-to-side. The aim was to determine the number of NWs on the assemblies that are alone, part of a chain of two NWs side-to-side, part of a chain of three NWs side-to-side, and so on. This counting was made according to several rules. The images used to do the counting were always images obtained at a magnification of 5000 X. Two NWs were considered as part of the same chain if they were distant from each other by less than the diameter of one NW and if the angle they formed was below 30°. When a NW could not be distinguished from another it was not counted. However if some NWs were clearly visible and obviously side-to-side on a superposed level (second or third layer) those NWs were counted. Even if some NWs could be partially seen under those multilayered NWs, these lower NWs (partially hidden) were not counted. An image and its counting results can be seen in Figure 7.10.

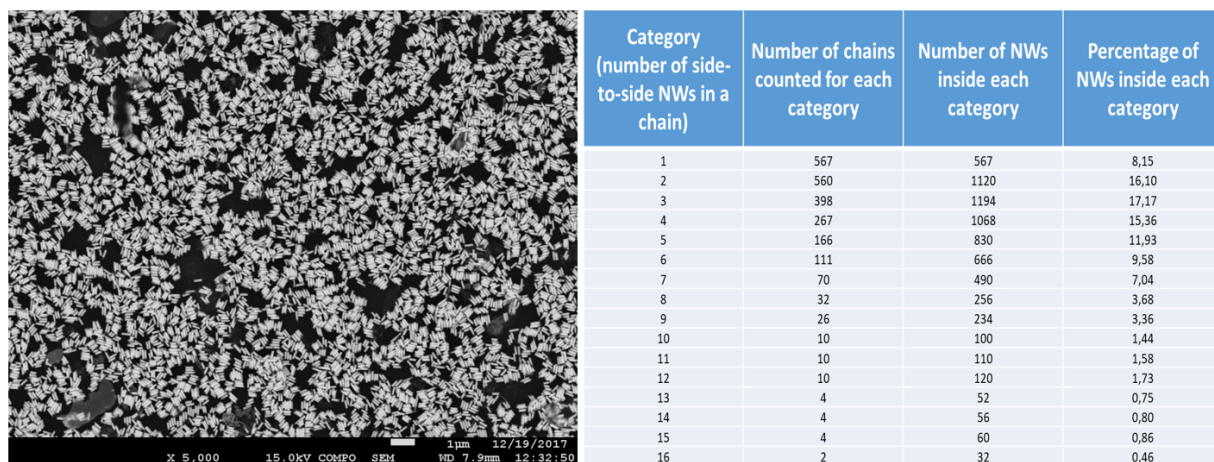


Figure 7.9: SEM image of a NW self-assembly (left) and results table of the counting (right).

Atomic force microscopy AFM characterization were performed on Si wafers. The imaging was performed in soft-tapping mode with SSS-NCHR tips from NANOSENSORS, in a Bruker Icon Dimension AFM.

AFM images were analyzed to determine the multilayered nature of the assemblies. First, all the images were flattened by subtracting a plane. Then the histogram of all the points of the image was traced. On this histogram (in the majority of the cases) there were some peaks corresponding to the different layers, and in particular, there often were three clear peaks. The first one corresponds to the background hence to the part of the sample where there is no NW. The second peak corresponds to the NWs organized in a monolayer, the third peak to the NWs in a bilayer. After that, a broader fourth peak could only sometimes be observed. Therefore this fourth peak was often extrapolated from the three first peaks by placing the sampling limit in the histogram at a distance similar to the ones in between the previous peaks. By sampling the images at different heights selected according to the location of the peaks in the histograms, the area corresponding to each type of layer could be determine. Eventually the percentage of each layer on an assembly could be determined. The sampling of an image is described graphically in Figures 7.10 and 7.11.

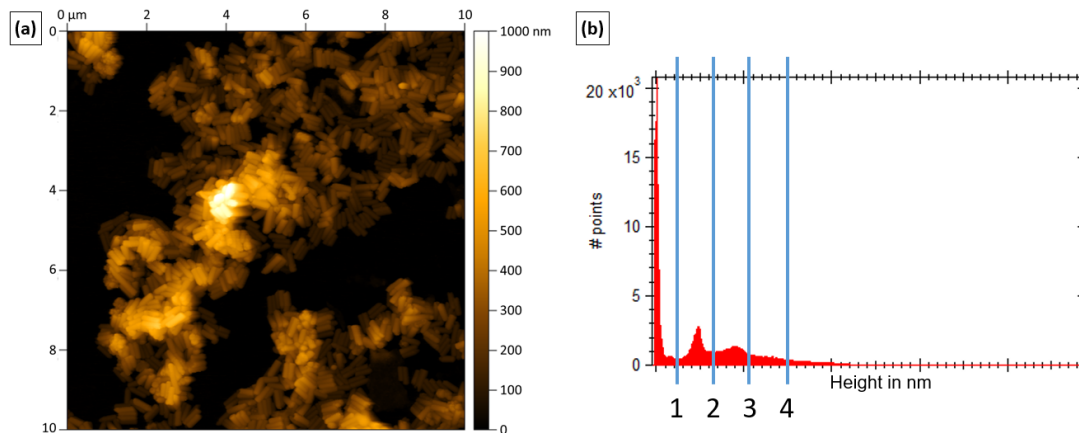


Figure 7.10: (a) AFM image of a NW self-assembly and (b) histogram with the limits applied to determine the limits of each layer.

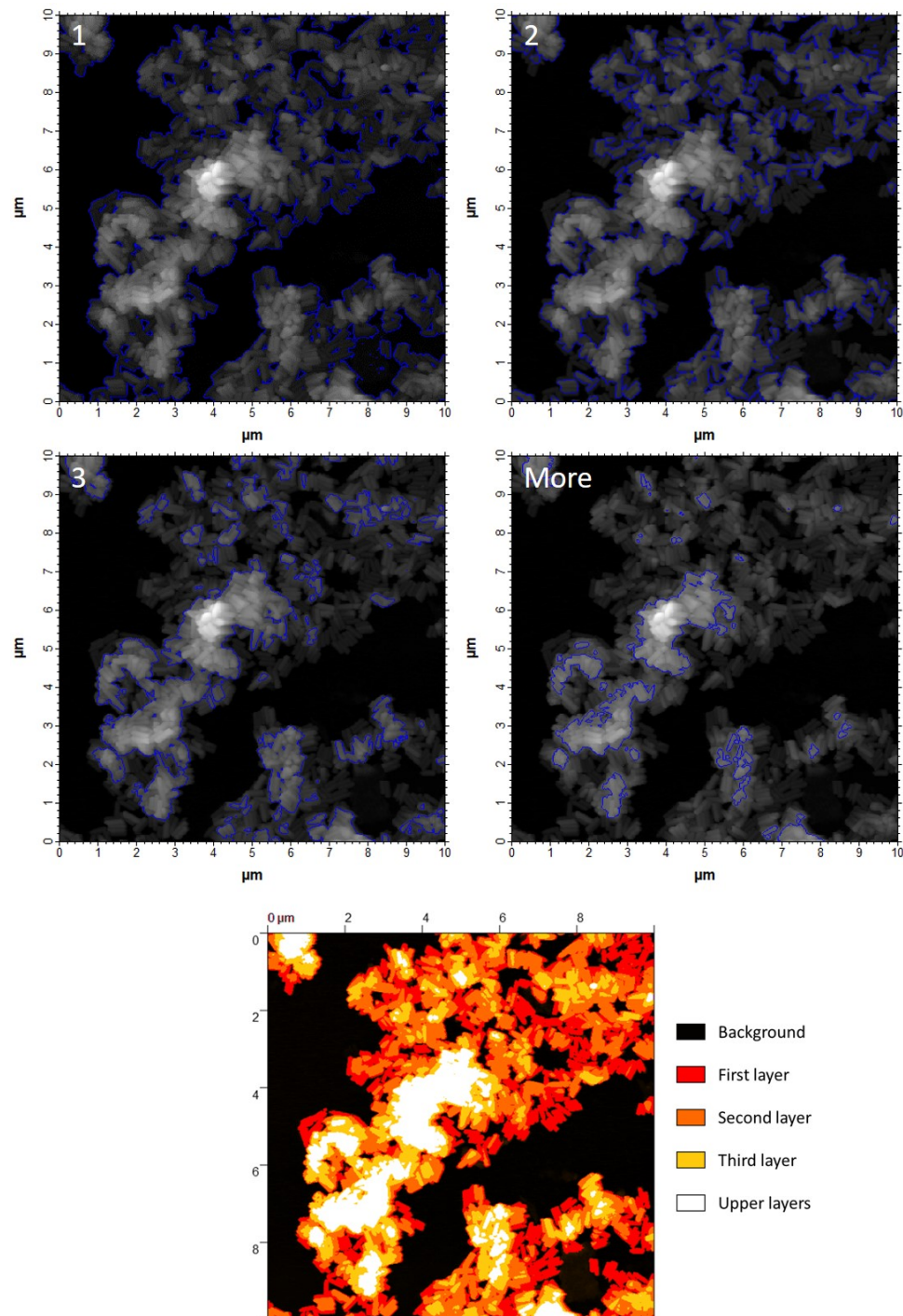


Figure 7.11: Images corresponding to the AFM image from the previous Figure, (top) with the contours of the thresholding corresponding to the beginning of the 1st, 2nd, 3rd and more layers, (bottom) with the different layers colored.

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Appendix: Anodization scaling up process

To obtain a higher throughput when manufacturing NWs by ECD, the scaling up of the anodization setup was investigated. Indeed a larger area on such high pore density template would allow the ECD of much more NWs at one time. Of course, owing to reproducibility problem with the homemade AAO template, this strategy was rapidly abandoned. Nevertheless the scaling up had been performed. The information gathered during this investigation will be presented here.

The new large anodization cell had the same copper basis than the large ECD cell with the same diameter (3.5 cm). The Teflon upper part of the cell was replaced by a double sided glass enabling the circulation of a cooling liquid. This double sided glass cell was useful to try to keep the oxalic acid at anodization temperature (2°C) during the whole process. Indeed, since the area to anodize was larger (times 7.25) the current passing through the cell would be higher, hence the heat arising from it. Some tubings were thus linked from a Ministat 230 chiller to the double sided glass and from the glass cell to the tubing at the basis of the cell (helicoïdal copper tubing). A thermocouple probe could be injected at the basis of the cell (just under the sample) and enabled feedback by PID (proportional-integral-derivative) control of the chiller. Thereby, the temperature could be controlled during the anodization process and kept approaching to 2°C. The anodization cell used is presented in Figure A.1.

To perform anodization, the sample is playing the anode while an aluminum bar is put in the oxalic acid. Here this bar had a smaller diameter than the one of used in the standard cell but was terminated by an aluminum disk of almost the large cell diameter. This disk should help distributing the electrical field all around the sample to obtain the most homogeneous template possible. Therefore, this disk had to be the flattest and the most horizontal possible to avoid defects and in particular half-anodized template (Figure A.2). Moreover it was discovered that



Figure A.1: Pictures of the large anodization cell, disassembled and assembled.

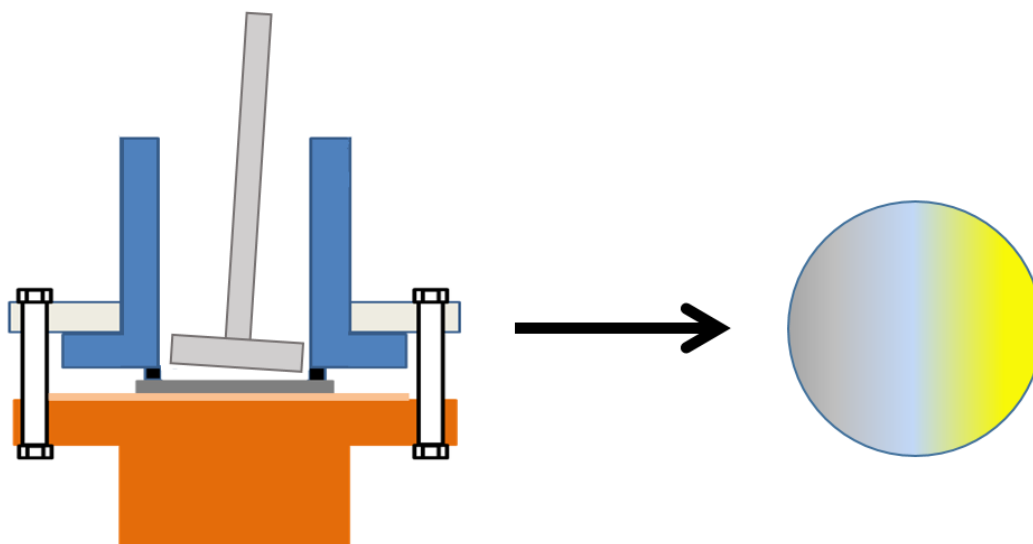


Figure A.2: Scheme of a wrong anodization process with the Al disk tilted, and the resulting supported template; the non-anodized parts are grey while the anodized parts are gold, hence the alumina is transparent and the sub-layer is gold.

the distance between the aluminum disk and the sample was of great importance. The bigger the distance, the higher the starting-current, which could lead to damage the sample. The starting-current is the current necessary to start the anodization process at the standard potential applied (60 V).

Finally the aluminum disk was placed at 5 mm of the sample to obtain a starting-current of ~ 250 mA. The starting current was about 750 mA when the distance was about 10 mm. To sustain such current another sourcemeter had to be used (Keithley 2460). The anodization lasts around 700 s for a 1 μm Al thick substrate and the end-current had to be set to 70 mA. The template were then exposed to a widening step identical to the one performed for "small" AAO template. Eventually, the templates obtained with these parameters had a good homogeneity all around the anodized area. They were very similar to the ones obtained with the standard anodization cell, except they sometimes had slightly more angular pores. The results obtained are presented in Figure A.3.

Unfortunately, the results were not better about the reproducibility and, as already announced, this path was not pursued.

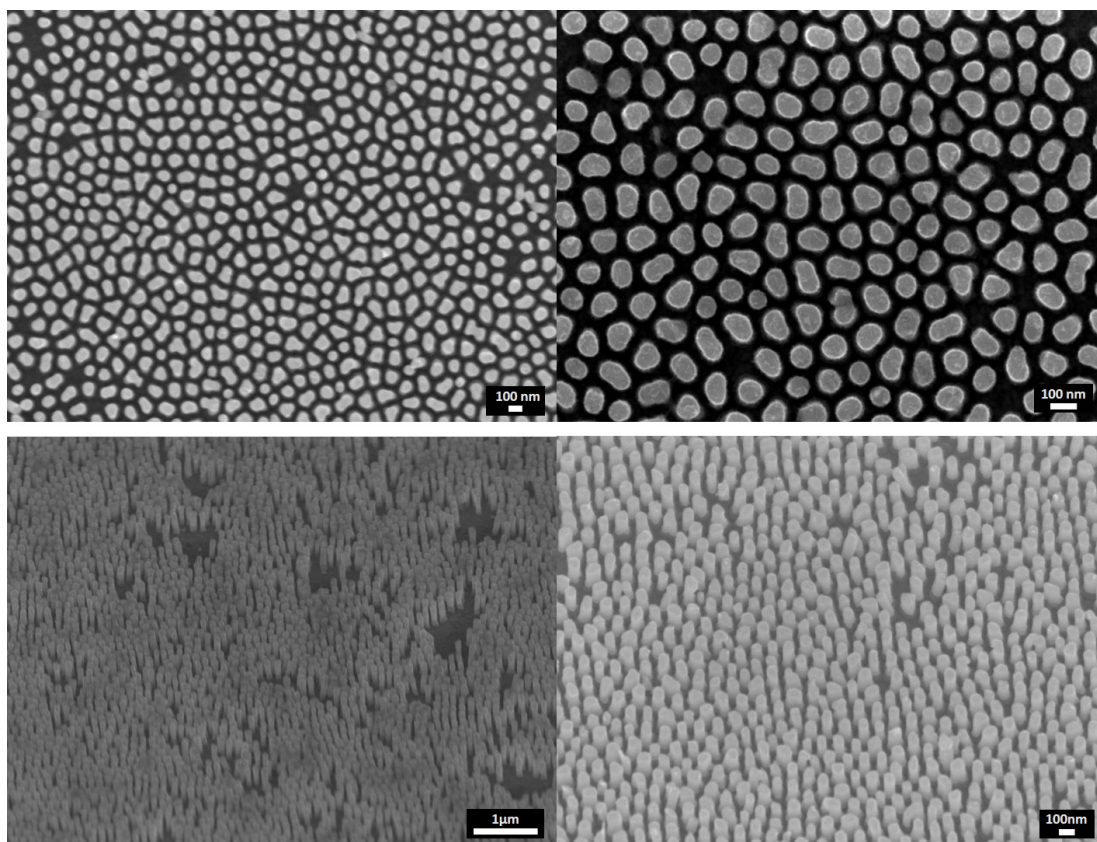


Figure A.3: SEM images of Ni NWs deposited within large supported AAO template. (First row) Top view. (Second row) Tilted view (45°).