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Multi-walled carbon nanotubes : decorated with metal
nanocrystals and incorporated into metal matrices

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**Multi-walled carbon nanotubes: decorated with metal nanocrystals and
incorporated into metal matrices**

By Praveen Martis

Abstract:

Since their discovery, carbon nanotubes have attracted the attention of researchers world wide in the field of nanoscience and nanotechnology, mainly due to their remarkable properties and potential applications. Though, we are entering into the third decade of intense research on carbon nanotubes, there is still so much to be discovered about their nature, growth and modification to realize the potential applications. Carbon nanotubes are largely inert and call for surface modification to disperse in many solvents to be further manipulated to decorate them with metal or metal oxide nanoparticles for various applications. These surface modified carbon nanotubes can also be incorporated into metal matrices. In the present research work, we have made a fundamental study to optimize the conditions to decorate the multi-walled carbon nanotubes with metal and metal oxide nanocrystals and also to incorporate the multi-walled carbon nanotubes into metal matrices.

In the first part of the work, we have decorated the multi-walled carbon nanotubes with metal and metal oxide nanocrystals. There are several methods of decoration of multi-walled carbon nanotubes and it is easier to decorate them with noble metals such as platinum, gold, silver etc., whereas, it is difficult to decorate them with transition metals and metal oxide nanocrystals. In this present study, we have designed a simple and efficient method to decorate the multi-walled carbon nanotubes with copper and nickel nanocrystals and optimized the conditions to achieve homogeneous decoration of those metals and their metal oxide nanocrystals.

In the second part of the work, we have incorporated the multi-walled carbon nanotubes into metal matrices. In this work, we have explored several methods and a new solvent to efficiently and uniformly incorporate the multi-walled carbon nanotubes into metal matrices. This was achieved by electrodeposition, mainly because it is a cost effective method to obtain the high purity of deposits. In our case, we have demonstrated that it is possible to incorporate multi-walled carbon nanotubes on copper substrate into nickel matrices. We have used different kinds of multi-walled carbon nanotubes, such as pristine, oxidized and amino-functionalized, to incorporate them into nickel matrices in aqueous solutions. Thereafter, we have used oxidized and pristine multi-walled carbon nanotubes as they showed better incorporation into nickel matrices compared to amino-functionalized multi-walled carbon nanotubes. This was done in ionic liquid, mainly because multi-walled carbon nanotubes showed better dispersion stability in ionic liquids.

The different methods, strategies opened us to new ways of surface modification of carbon nanotubes. We believe that these optimized conditions of decorating carbon nanotubes with metal and metal oxide nanocrystals and incorporating carbon nanotubes into metal matrices will lead to a lot of potential applications in the fields such as catalysis, nanocomposite reinforcement materials, sensors etc.

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Table of Contents

Multi-walled carbon nanotubes: decorated with metal nanocrystals and incorporated into metal matrices

Table of Contents

I. General Introduction	1
Chapter 1 : State of the art bibliography	4
1.1. Carbon nanotubes	4
1.1.1. Structure of carbon nanotubes	5
1.1.2. Production methods	7
1.1.2.1. Arc-discharge method	7
1.1.2.2. Laser ablation method	11
1.1.2.3. Catalytic chemical vapour deposition method	14
1.1.3. Properties	19
1.1.3.1. Electronic properties	20
1.1.3.2. Mechanical properties	21
1.1.3.3. Thermal properties	22
1.1.4. Applications	23
1.2. Modification of carbon nanotube surfaces	31
1.2.1. Surface functionalization of carbon nanotubes	31
1.2.1.1. Covalent functionalization of carbon nanotubes	32
1.2.1.2. Non-covalent functionalization of carbon nanotubes	37
1.2.2. Decoration of CNTs with metal and metal oxide nanocrystals	39
1.3. Incorporation of carbon nanotubes into metal matrices	40
1.3.1. Incorporation of carbon nanotubes from aqueous solutions	41
1.3.2. Incorporation of carbon nanotubes from ionic liquids	43
II. Proposed research strategies	45
Chapter 2 : Decoration of multi-walled carbon nanotubes with copper and copper oxide nanocrystals	48
2.1. Introduction	48
2.2. Preparation of Cu/CuO_x nanocrystals on MWCNTs	49
2.2.1. Impregnation of CPA with MWCNTs by reflux method	51
2.2.2. Impregnation of CPA with MWCNTs by IR irradiation	53
2.2.3. Calcination of CPA-MWCNTs	55
2.3. Results and discussion	56
2.4. Conclusion	72
Chapter 3 : Decoration of multi-walled carbon nanotubes with nickel and nickel oxide nanocrystals	73
3.1. Introduction	73

3.2.	Preparation of Ni/NiO _x nanocrystals on MWCNTs	74
3.2.1.	Impregnation of NAA on MWCNTs	74
3.2.2.	Calcination of NAA-MWCNTs	75
3.3.	Results and discussion	76
3.4.	Conclusion	86

Chapter 4 : Incorporation of multi-walled carbon nanotubes into nickel matrices

4.1.	Introduction	87
4.2.	Preparation of Ni/MWCNTs coatings	89
4.2.1.	Preparation of Ni/MWCNT coatings from aqueous solution	90
4.2.2.	Preparation of Ni/MWCNT coatings from ionic liquid	92
4.3.	Results and discussion of composites from aqueous solution	94
4.4.	Results and discussion of composites from ionic liquid	109
4.5.	Conclusions	119

III. Conclusions and perspectives

121

IV. References

126

V. Annexes

138

V.1.	Materials and methods	138
V.2.	Characterization techniques	141
V.3.	Ionic liquids	160
V.4.	References	165
V.5.	Publications and conferences	166

I. General Introduction

I. General introduction

“There’s Plenty of Room at the Bottom”, these are the revolutionary words uttered at the annual meeting of the American Physical Society, California Institute of Technology in December 1959 by Richard Feynman in his visionary talk, which revolutionized the thinking of modern engineers [1]. He proposed a completely new facet of miniaturization namely the “bottom up” approach. Although there was no experimental backup for his ideas that day, he proposed several ideas of nanoscience and nanotechnology obeying the basic physics and fundamental laws of chemistry. This was the starting point of the great revolution of “Nanotechnology”, which is influencing and going to influence human civilization in the decades to come.

Carbon, an element of prehistoric discovery, is widely distributed in nature. It is found in abundance in the sun, stars, comets and atmospheres of most planets. For centuries, it was believed that the element carbon existed in only two different forms, soft, conductive graphite and hard, transparent, insulating diamond. However, this was proven to be wrong with the discovery of Buckminster fullerene molecule [2] (named after the engineer and architect Richard Buckminster Fuller as the molecules resemble the architecture of his geodesic domes) in 1985 by a group headed by R.E. Smalley from Rice University, which received Nobel Prize in Chemistry in 1997. C_{60} is a soccer ball-like molecule made of pure carbon atoms bonded in hexagon and pentagon configurations. Besides diamond, graphite and C_{60} , quasi one dimensional nanotube is

another form of carbon first reported by Iijima in 1991 when he discovered multi-walled carbon nanotubes (MWCNTs) in carbon-soot made by an arc-discharge method [3]. About two years later, he made the observation of single-walled carbon nanotubes (SWCNTs) [4]. Since then, carbon nanotubes (CNTs) have captured the attention of researchers worldwide. A significant amount of work has been done in the past decade to reveal the unique structural, electrical, mechanical and chemical properties of carbon nanotubes and to explore what might be the key applications of these novel materials.

In order to create functional systems at the nanoscale, novel materials with useful properties (structural, electrical, mechanical, thermal....) are highly desirable. CNTs fall into those set of novel materials with extremely useful and unique properties [5,6]. The motivation behind the current research is a desire to efficiently modify the surface of MWCNTs by decorating them with low cost transition metals such as copper and nickel and incorporating the surface modified MWCNTs into metal matrices by electrogeneration to enhance their properties for various applications. As is the case with any other field, there is a lot to be explored about the dispersion of MWCNTs in solvents and metal solution for their efficient incorporation into the matrix. In conclusion, science has always been mysterious and exciting and so it is in the case of these novel materials.

The organization of this thesis is as follows: the first chapter introduces carbon nanotubes, its structure, production methods, properties and applications. It also gives the state of the art bibliography for the present research work, explaining the significance of decorating MWCNTs with metal nanocrystals and incorporating MWCNTs into metal matrices from aqueous solutions and ionic liquids. The second chapter is dedicated to the

decoration of MWCNTs with copper and copper oxide nanocrystals and the third chapter is devoted to the decoration of MWCNTs with nickel and nickel oxide nanocrystals. In both those chapters different methods of impregnation and the results are discussed in detail. The fourth chapter deals with the incorporation of MWCNTs into nickel matrices from aqueous solutions and from ionic liquids. This chapter elaborately deals with the challenges of incorporating MWCNTs and then incorporating different kinds of MWCNTs into nickel matrices to determine the homogeneous dispersion of MWCNTs in metal matrices giving rise to the most stable composites.

Chapter 1: State of the art bibliography

Chapter 1: State of the art bibliography

1.1. Carbon nanotubes

Carbon nanotubes may be classified as single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs).

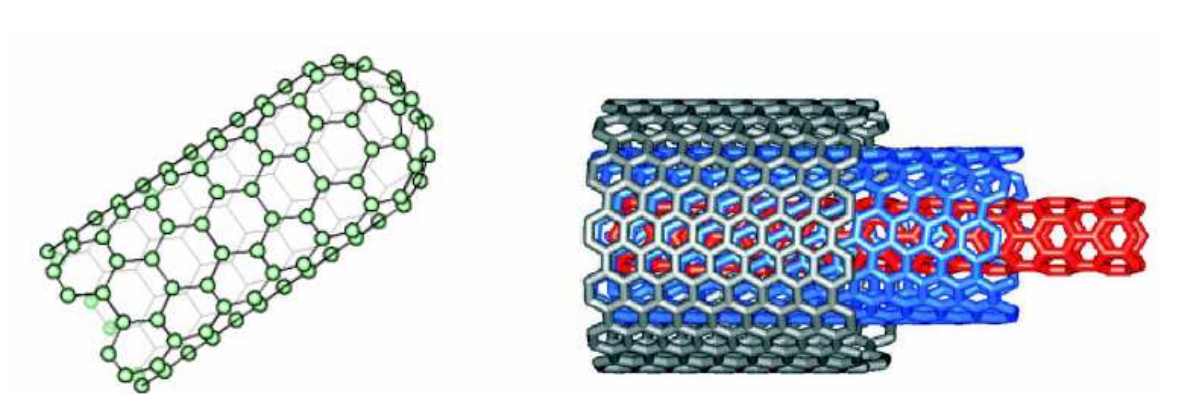


Figure 1 : Structure of a single and multi-walled carbon nanotube [7].

SWCNTs consist of a single graphene layer rolled up into a seamless cylinder [5] and DWCNTs with two concentric cylindrical shells of graphene sheets [8], whereas MWCNTs consist of more than two concentric cylindrical shells of graphene sheets (Figure 1) coaxially arranged around a central hollow core with van der Waals forces between adjacent layers [9]. The cylindrical nanotube has at least one end capped with a

hemisphere of fullerene structure. The lengths of the tubes can be up to hundreds of microns or even centimeters.

1.1.1. Structure of carbon nanotubes

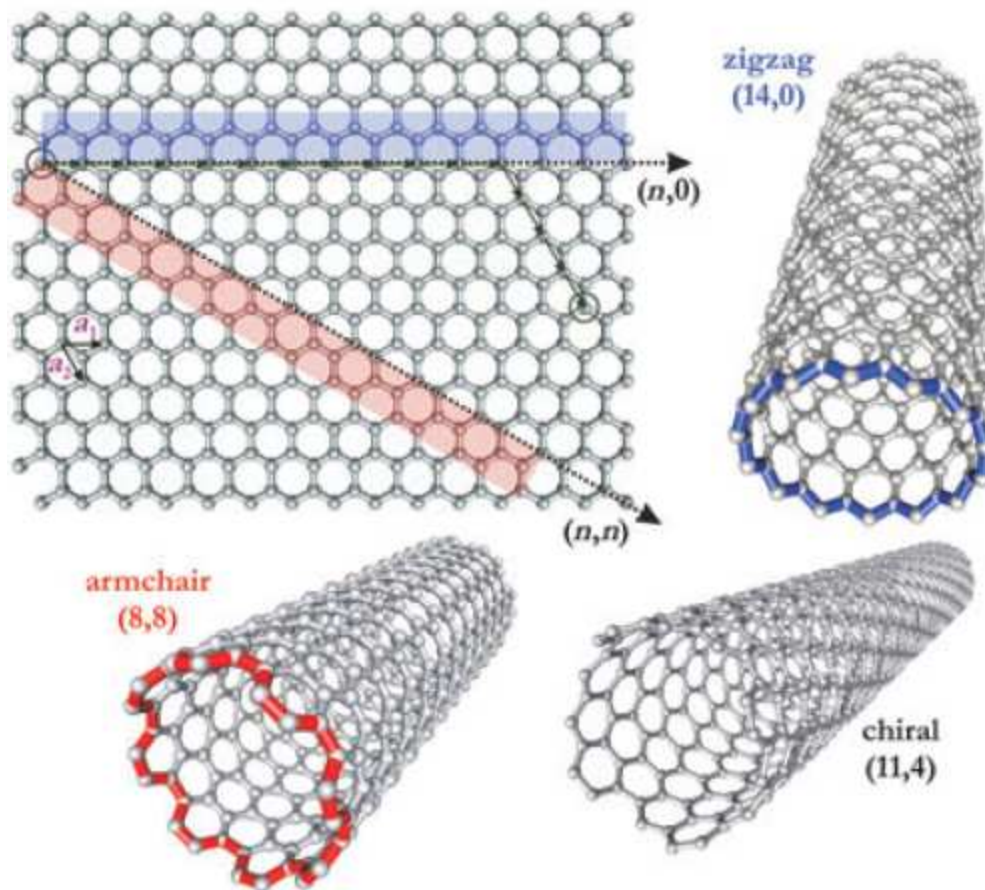


Figure 1.1 : Roll-up of a graphene sheet leading to the three different types of CNTs [7].

The exact structure of a nanotube depends on the different angles and curvatures in which a graphene sheet can be rolled into a tube and is determined by a single vector,

which is called a chiral vector and discriminates CNTs into ‘zigzag’, ‘armchair’, and ‘chiral’ [10] forms as shown in Figure 1.1. By folding a graphene sheet into a cylinder the beginning and end of a (n, m) lattice vector in the graphene plane join together to form an (n, m) nanotube. The (n, m) indices determine the diameter of the nanotube and also the ‘chirality’ [11]. ‘Armchair’ tubes with (n, n) indices form a tube are so named since the atoms around the circumference are in an arm-chair pattern. $(n, 0)$ nanotubes are termed ‘zigzag’ in view of the atomic configuration along the circumference. All the other types are ‘chiral’, having rows of hexagons spiraling along the nanotube axes.

In terms of mechanical properties, CNTs are known to be the strongest and most resilient materials to exist in nature. The electrical properties of a nanotube change in correspondence to its structure; thus ‘armchair’ nanotubes are metallic, while ‘zigzag’ and ‘chiral’ can be either metallic or semiconducting [11]. In general, SWCNTs are a mixture of metallic and semiconducting material, depending sensitively on their geometrical features, while MWCNTs are regarded as metallic conductors [12]. Different from other carbon materials, such as graphite, diamond and fullerene (C_{60} , C_{70} , etc.), CNTs are one dimensional carbon materials with unique tubular structures of nanometer diameter, which can have an aspect ratio (large length/diameter) greater than 1000 [13,14]. The MWCNTs may consist of one up to tens and hundreds of concentric shells of carbons with adjacent shells separation of 0.34 nm and diameter typically on the order of 10-20 nm. The carbon network of the shells is closely related to the honeycomb arrangement of the carbon atoms in the graphene sheets [11]. However, CNTs possess variety of diameters, length distribution and structures within the same sample.

1.1.2. Production methods

The MWCNTs were first reported by Iijima when he discovered them in the soot of the arc-discharge method. It took two years to Iijima and Ichihashi [4], and Bethune et al [15] to synthesize SWCNTs by use of metal catalysts in the arc-discharge method in 1993. A significant progress was achieved by Smalley and co-workers [16] when they synthesized bundles of aligned SWCNTs with small diameter distribution by laser-ablation method. Catalytic growth of nanotubes by the catalytic chemical vapor decomposition (CCVD) method was first used by Yacamán et al [17]. The industrial application of the carbon nanotubes requires the development of techniques for large-scale production of defect-free nanotubes. In this sub-section the three main production techniques will be considered separately, although there are few other miscellaneous techniques these are considered as the most important and reliable ways of synthesizing carbon nanotubes, which are briefly described.

1.1.2.1. Arc-discharge method

Arc-discharge is an important method of nanotube synthesis and will be discussed in this sub-section. Iijima reported the preparation of a new type of finite carbon structures consisting of needle-like tubes in 1991 [3]. The tubes were produced using an arc-discharge evaporation method similar to that used for the fullerene synthesis as shown in Figure 1.2. This method involves the condensation of carbon atoms generated from evaporation of solid carbon source such as graphite. In the arc-discharge method

carbon atoms are evaporated by plasma of an inert gas ignited by high currents passed through opposing carbon anode and cathode.

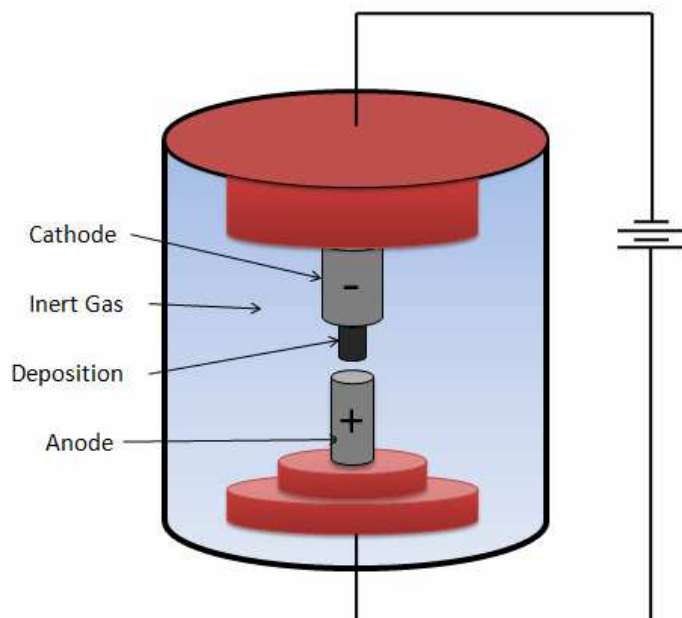


Figure 1.2 : Schematic representation of an arc-discharge setup [18].

Carbon nanotubes can be obtained by controlling the growth conditions such as the pressure of inert gas in the chamber and the arcing current [19]. An example of high resolution transmission electron microscope (HRTEM) image of MWCNT produced by arc-discharge method is shown in Figure 1.3. The TEM study of the growth morphology of the carbon nanotubes synthesized by arc-discharge [20] revealed that there were many variations in shape, especially near the tube tips.

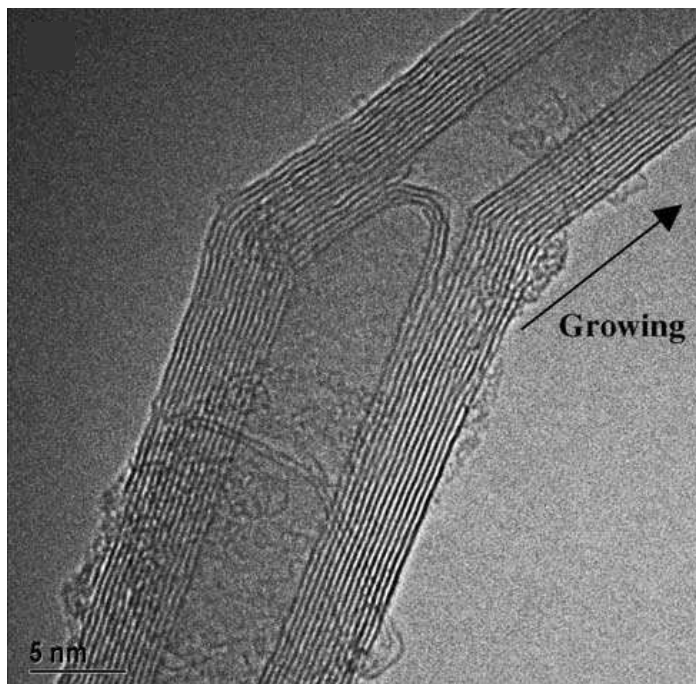


Figure 1.3 : HRTEM image of a MWCNT produced by arc-discharge [21].

A topological model was constructed in which pentagons and heptagons played a key role in the tube tip shapes. In the arc-discharge growth process the product contains CNTs and also other carbon species mainly constituted by multi-layered graphitic particles in polyhedron shapes. Ebbesen and Ajayan [22] reported large scale synthesis of MWCNTs by a variant of the standard arc-discharge technique. In a typical experiment, a potential of ~ 18 V dc was applied between two thin graphite rods in helium atmosphere. The yield of nanotube was maximal of ~ 75 % relative to the starting graphitic material, at helium pressure of ~ 500 Torr. The as obtained CNTs had diameters between 2 to 20 nm, and lengths of several micrometers and the tubes were capped with pentagons.

In a significant development, Iijima and Ichihashi [4] and Bethune et al. [15] almost simultaneously reported the synthesis of SWCNTs by catalyst assisted arc-discharge method. In the case of Iijima, the arc-discharge was generated by running a dc current of 200 A at 20 V between the electrodes in 40 Torr argon. It was found that the use of the three components argon, iron and methane were critical for the synthesis of SWCNTs. The TEM analysis revealed the presence of SWCNTs, which were curved and tangled together to form bundles. In the case of Bethune, the electrodes were vaporized with a current of 95-105 A in 100-500 Torr of He in the presence of a mixture of powdered metals (Fe, Ni or Co) and graphite. TEM analysis showed that only cobalt catalyzed nanotubes had SWCNTs. Journet et al [23] showed that large quantities of SWCNTs could be generated by the arc-discharge method. The SEM and TEM images revealed large amounts (~ 80 %) of entangled carbon ropes.

There have been number of variations on the 'classic' arc-discharge method since the original work in 1991. Many groups have experimented with alternative gases such as H₂ [24], N₂ [25], CF₄ [26] and organic vapours [27]. Some of these experiments have produced interesting results, for example, Iijima and colleagues [28] claimed to have produced the 'smallest possible carbon nanotube' with a diameter of 0.4 nm under H₂. It was suggested that the tube had a (3, 3) armchair structure and was capped with half of a C₂₀ molecule. In general, there is little evidence that using alternative gases produces major benefits in terms of nanotube yield. Another modification to the arc-discharge method is the use of magnetic fields. The Fuji Xerox group [29] showed that situating four cylindrical Nd-Fe-B magnets around the electrodes greatly increased the yield of nanotubes.

1.1.2.2. Laser ablation method

The laser ablation method was initially used for the production of C_{60} molecule [2], which was considered as the parent molecule in the fullerene family. Figure 1.4 illustrates the principle involved in the preparation of carbon nanotubes by laser ablation. A graphite target doped with a catalyst is placed in the middle of a noble gas filled quartz tube. The laser beam is focused on to the graphite source and this focused laser vaporizes and sublimates the graphite by uniformly bombarding the surface [30].

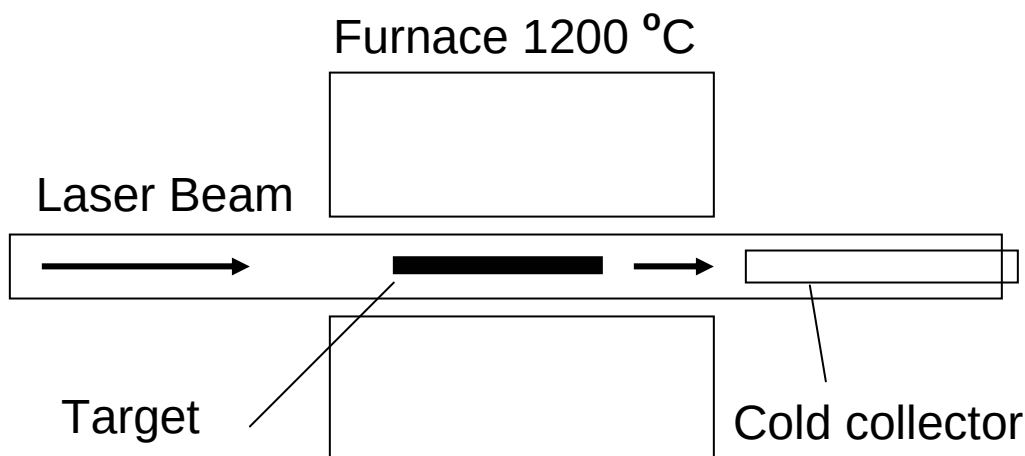


Figure 1.4 : Schematic diagram of a laser-ablation setup [11].

The nanotubes are collected on the cold collector placed in the quartz tube. When a carbon source without catalyst material is used in laser ablation multi-walled carbon nanotubes are formed. Figure 1.5 depicts the TEM micrograph of typical synthesized MWCNT by laser ablation method. In 1995, Smalley's group [31] at Rice University

reported the synthesis of carbon nanotubes by laser vaporization. A pulsed [32,33] or continuous [34,35] laser was used to vaporize a graphite target in an oven at 1200 °C. The main difference between continuous and pulsed laser, is that the pulsed laser demands a much higher light intensity (100 kW cm^{-2} compared with 12 kW cm^{-2}). Smalley and co-workers [16] after a year produced high yields ($> 70 \%$) of SWCNTs by laser ablation of graphite rods with small amounts of Ni and Co at 1200 °C. The TEM images showed that nanotubes were remarkably uniform in diameters and that they formed ropes or bundles. Several groups have explored the possibility of scaling up the laser vaporization process. In 1999, F. Kokai and colleagues [36] produced SWCNTs by irradiating a graphite-Co/Ni target with a 1 kW CO₂ laser and later in 2002, Peter Eklund and colleagues [37] used a 1 kW free electron laser to produce SWCNTs with a production rate as high as 1.5 g h^{-1} .

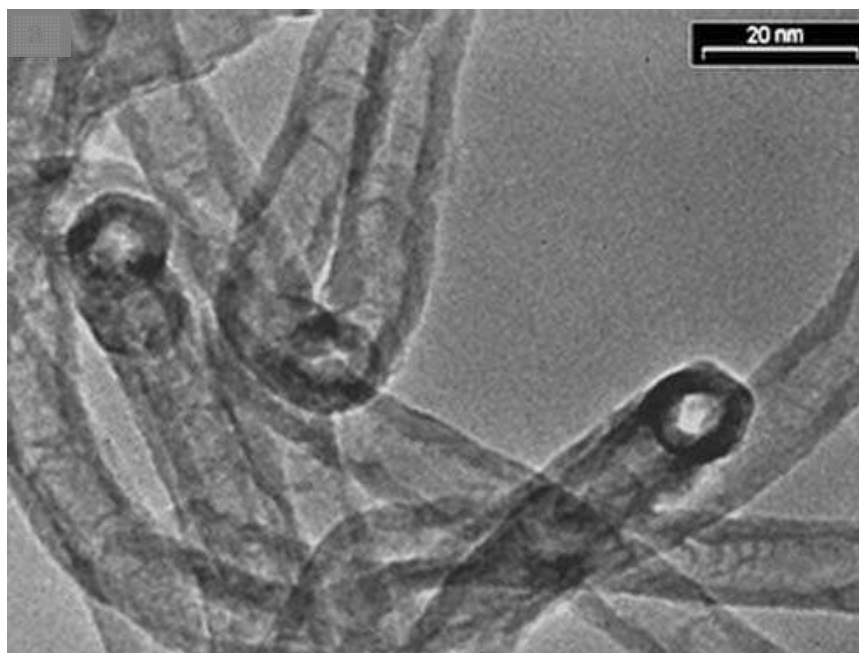


Figure 1.5 : TEM images of carbon nanotubes produced by laser ablation method [38].

Arc-discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality CNTs. Both arc-discharge and laser ablation methods have two things in common. Firstly, a high temperature requirement and secondly, the carbon originates from the erosion of solid graphite. Among the two methods, the arc-discharge has the advantage of being much cheaper than the laser ablation method. However, both methods suffer from drawbacks. As both methods involve evaporating the carbon source, so it has been unclear how to scale up production to the industrial level using these approaches. And also the vaporization methods grow CNTs in highly tangled forms, mixed with unwanted forms of carbon and metal species, creating difficulties in purification and in their potential applications.

As far as growth mechanisms in the arc and laser methods are concerned, it still remains obscure. In the case of MWCNTs, three types of model have been put forward, which could be labeled as ‘gas’ [39], ‘liquid’ [40] and ‘solid’ [41] growth but there is no consensus on which one is correct. For the SWCNTs produced by arc or laser vaporization, two types of growth model have been proposed, namely, vapour-liquid-solid mechanism [42] and solid state mechanism [43]. Of these, the former is more widely accepted and has been the subject of far more theoretical modeling, whereas, there appears to be experimental support for a solid state mechanism. The lack of understanding of the growth of both MWCNTs and SWCNTs by these methods is a serious impediment to progress in producing tubes with a defined structure. Clearly there is a need for an alternative method for producing the best quality MWCNTs. This will lead us to another important method of synthesis of MWCNTs.

1.1.2.3. Catalytic chemical vapor deposition method (CCVD)

One more effective method of generating carbon nanotubes is based on the CCVD of hydrocarbons over supported transition metal particles, which constitute the active species. This is a successful way to synthesize CNTs, because of the lower growth temperature (below 1000 °C) compared to arc-discharge or laser ablation methods and of the possibility to control inner diameter and length of the tubes. This method is based on the decomposition of the gaseous form of carbon (hydrocarbons like methane) on catalyst particles inside the chemical vapor deposition chamber [44] as shown in Figure 1.6. The catalytic species are typically transition-metal nanoparticles that are formed on a support material such as porous aluminum oxide (alumina) materials with large surface areas.

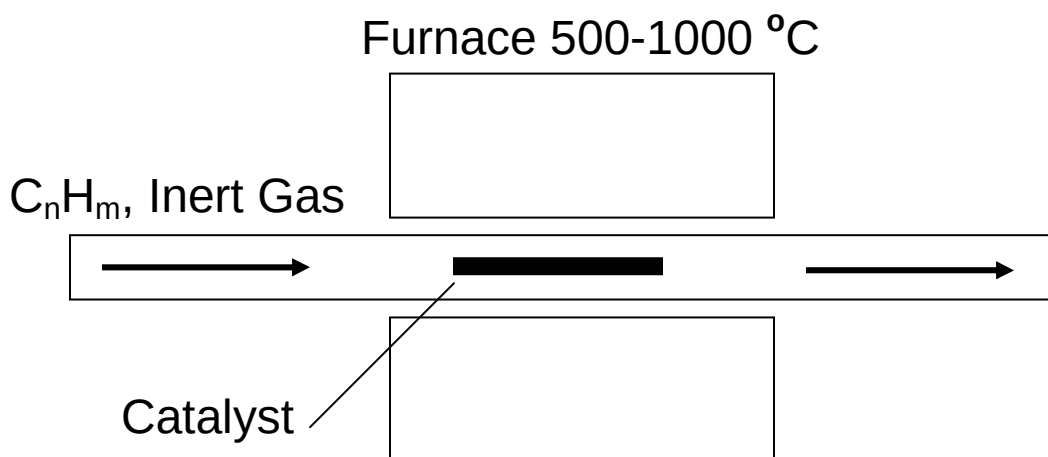


Figure 1.6 : Schematic representation of a CCVD experimental setup [11].

The general nanotube growth mechanism in a CCVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, and dissolution and saturation of carbon atoms in the metal nanoparticle. TEM images of raw CNTs

produced by CCVD method are shown in Figure 1.7, where we can clearly see the catalyst particles and agglomerated CNTs. The precipitation of carbon from the saturated metal particle leads to the formation of tubular carbon solids in sp^2 structure.

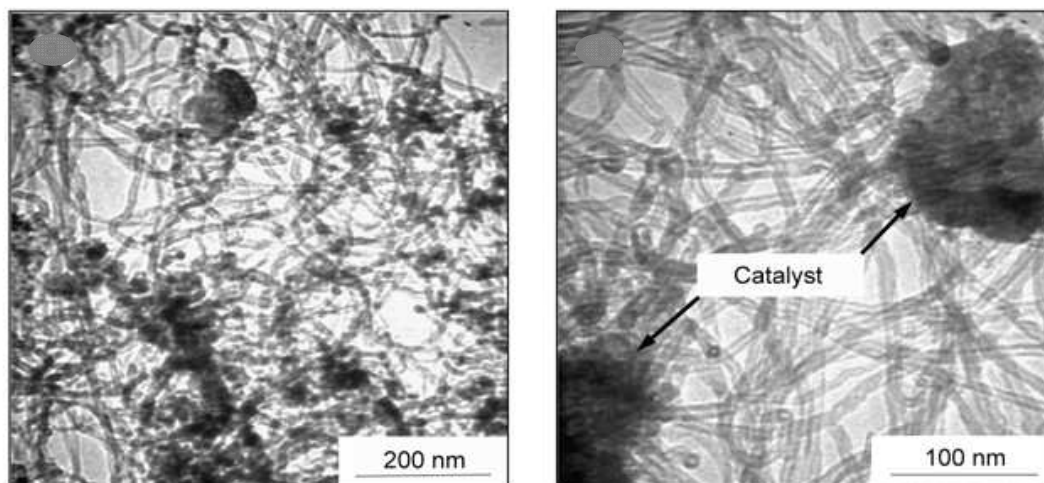


Figure 1.7 : TEM image of CNTs produced by CCVD method [45], (a) low-magnification and (b) high-magnification

Tubule formation is favored over other forms of carbon such as graphitic sheets with open edges. This is because a tube contains no dangling bonds and therefore is in a low energy form. For MWCNT growth, most of the CCVD methods employ ethylene or acetylene as the carbon feedstock and the growth temperature is typically in the range of 550–750 °C [46-48]. The catalyst particles usually used are iron, cobalt and nickel. In 2006, Christian Deck and Kenneth Vecchio [49] described a detailed study of the catalytic growth of MWCNTs using a wide variety of transition metal catalysts. They found that Fe, Co and Ni were the only active catalysts, with Cr, Mn, Zn, Cd, Ti, Zr, La, Cu, V and Gd showing no activity. They suggested that the rationale for choosing these

metals as catalysts for CCVD growth of nanotubes lie in the phase diagrams for the metals and carbon. At high temperatures, carbon has a finite solubility in these metals, which leads to the formation of metal–carbon solid state solutions and therefore to the aforementioned growth mechanism.

Kong et al [50] showed that high quality SWCNTs could be grown on silicon wafers by the CCVD technique. It was found that high reaction temperatures in the range of 850-1000 °C were necessary to form small diameter of SWCNTs. Methane was used as carbon feedstock. An abundance of individual and bundled SWCNTs were seen on TEM images. J.F. Colomer and co-workers [51] reported the large scale production of SWCNTs using a catalyst metal particle supported on MgO. Perhaps the most important method for the large scale catalytic synthesis of SWCNTs is the high pressure CO disproportionation (HiPco) process introduced by the Smalley group [52]. This process is based on the decomposition of $\text{Fe}(\text{CO})_5$ to form Fe clusters for the catalytic production of SWCNTs from CO at about 1000 °C.

The huge volume of research on the catalytic production of MWCNTs has resulted in significant improvements in quality. The use of metal complexes to produce CNTs has become increasingly popular. Gary Tibbetts et al [53] reported the gas-phase synthesis of carbon fibres in flowing mixtures of CH_4 or hexane with organometallics including ferrocene and iron pentacarbonyl. C.N.R. Rao and colleagues [54] have also described the production of nanotubes by the pyrolysis of pure metallocenes and of metallocene-hydrocarbon mixtures. The advantages of using organometallic compounds are that the carbon source and catalyst are in the same phase and that there is no catalyst support to remove at the end of the reaction.

A number of techniques for the catalytic synthesis of DWCNTs are now available. They can also be produced by arc-discharge method. A somewhat higher yield of DWCNTs was reported by Sishen Xie and colleagues [55]. Their method involved pyrolyzing C_2H_2 on a floating iron catalyst at 900-1100 °C. An interesting aspect of this work was that the growth of DWCNTs was promoted by the presence of sulphur in the reaction mixture, although the reasons for this are unclear. Cheol Lee and co-workers [56] described in 2003 the production of high quality of DWCNTs in good yield by the catalytic decomposition of alcohol over a Fe-Mo/ Al_2O_3 catalyst at 800 °C. Using an ethylene feedstock under similar conditions produced mainly SWCNTs, for reasons that are not well understood.

A significant growth area in CNT development since the late 1990s has been the catalytic synthesis of aligned nanotubes on substrates. The first report of aligned growth of CNTs was given in 1996 by a Chinese group [57]. They used a technique in which Fe nanoparticles were embedded in mesoporous silica and then used to catalyze the decomposition of acetylene at 700 °C. This resulted in the formation of straight MWCNTs growing in a direction perpendicular to the surface of the silica. A slightly different method to obtain aligned nanotubes was developed by Mauricio Terrones and colleagues [58]. They used laser etching to prepare a patterned cobalt catalyst on a silica substrate, which was then heat treated to break up the Co films into discrete particles. The patterned catalyst was used to pyrolyse an organic compound at 950 °C, resulting in the formation of aligned nanotubes growing approximately parallel to the substrate.

The way in which nanotubes are formed is not exactly known. Baker [59] obtained detailed insights into the mechanism of CNTs growth from the skilful

application of controlled atmosphere electron microscopy. They proposed mechanisms for both the tip and base growth (root growth) of CNTs. These are demonstrated in Figure 1.8. In the Tip growth process the decomposition of the carbon containing gas occurs on the front surface of the metal particle, producing carbon, which then dissolves in the metal as shown in Figure 1.8. The dissolved carbon then diffuses through the particle and deposits on the trailing face, forming the filament. They proposed that temperature and concentration gradients were the main driving forces for this process. In the case of base growth, there need to be a strong interaction between the metal particles and the support material so that the particle remains anchored to the surface.

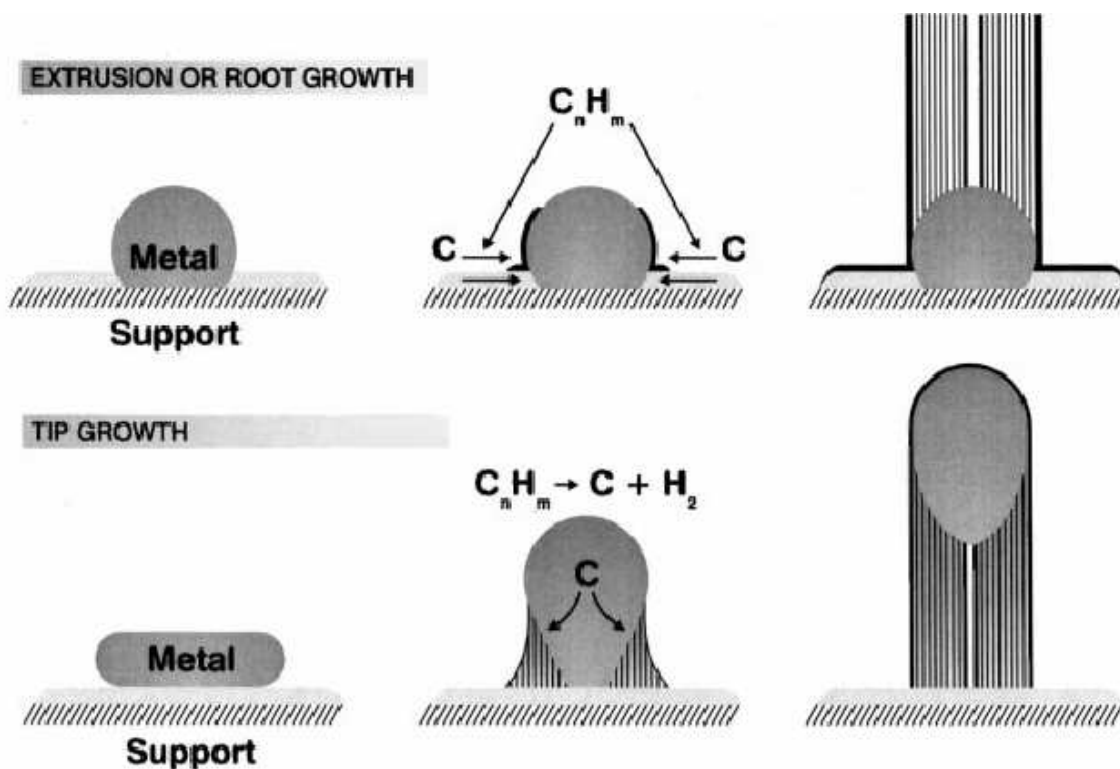


Figure 1.8 : An illustration of growth mechanism of MWCNTs [60].

Thus base growth occurs as shown in Figure 1.8. The diameter of MWCNTs produced by catalysis appears to depend largely on the size of the catalytic metal particles [61]. For SWCNTs, the vapour-liquid-solid mechanism [62] is widely accepted but this has not been definitely established.

Amazing progress has been made in the catalytic synthesis of nanotubes since the early 1990s. Bulk production of MWCNTs has advanced to the point where several companies claim to make more than 100 tons per year. SWCNTs can also now be produced in bulk using CCVD method. The advantage of CCVD process is that it is a low temperature process compared to the other two methods and it also has great potential for scaled-up nanotube materials synthesis. Carbon nanotubes produced by this method are much longer compared to the arc-discharge methods. For our research studies we have employed MWCNTs produced by CCVD method. CCVD method to produce CNTs has been actively pursued in recent years because of their significant potential for materials scale-up. All the known methods of fabricating carbon nanotubes give a wide variety of tubes with different properties.

1.1.3. Properties

Carbon nanotubes possess unique electronic, mechanical and thermal properties, which make them the most promising nanostructured materials. The exact magnitude of these properties depends on the diameter and chirality of the nanotubes and whether they are single-walled, double-walled or multi-walled form [11]. Few properties, which place

carbon nanotubes in the foremost place in the field of nanotechnology, are discussed here.

1.1.3.1. Electronic properties

One of the most amazing characteristics of CNTs is that they can be metallic like copper, or semiconducting like silicon, depending on their structure. These properties were first predicted theoretically and then confirmed experimentally by scanning tunneling microscopy. Carbon nanotubes exhibit metallic properties when $n-m = 3q$ where q is an integer. For all other values of n , m the nanotubes behave as semiconductors [10]. All armchair nanotubes (i.e. tubes for which $n = m$) behave as metals. It is well known that the conduction band and the valence band of the single graphene sheet superimpose at six corners of Brillouin zone. When this sheet of graphene is rolled to form a tube, the periodic boundary conditions overlap to form one-dimensional sub-bands. This particular phenomenon makes carbon nanotubes ideal systems for the study of quantum confinement effects and 1-D charge transport [63].

Nanoscale structures often have dimensions smaller than electron scattering lengths [64]. Carbon nanotubes are the best examples of such kind of materials and that makes them exhibit ballistic transport properties. This implies that the electrons with a large phase coherence length experience no scattering from phonons during ballistic transport in CNTs. Therefore, electrons encounter no resistance and dissipate no heat in CNTs [65]. In other words, the material can conduct a large current without getting hot, a highly desirable characteristic for the construction of nanoscale circuits. Depending on

their chirality carbon nanotubes behave as metals and moderate band gap semiconductors. In fact carbon nanotubes are the only molecules known to science that exhibit metallic behaviour at single molecule level. Carbon nanotubes can transport very high current densities like 10^9 A cm^{-2} [66]. This current density is very high compared to even best conductors like copper.

1.1.3.2. Mechanical properties

The mechanical properties of CNTs have attracted just as much interest as their electronic properties. The mechanical properties are strongly dependent on the structure of the nanotubes and this is due to the high anisotropy of graphite. Although, tubular morphology at nanoscale is observed for many 2-D solids, CNTs are unique because of the sp^2 hybridization. This bonding structure is stronger than the sp^3 bonds found in diamond and it provides CNTs with extremely high mechanical properties. Even though, there is no consensus on the exact mechanical properties of CNTs, theoretical and experimental results have shown unusual mechanical properties of CNTs. The tensile strength of carbon nanotubes is very high and it is almost 20 times higher than steel and it has been measured to be 45 Gpa [67]. Tensile young's modulus of MWCNT is highest recorded so far for any material, the value being 1 Tpa [68,69], approximately five times higher than steel.

The carbon nanotubes are expected to have high stiffness and axial strength as a result of the carbon-carbon sp^2 bonding [70]. Since this early work, the mechanical properties of MWCNTs have been widely studied using AFM [71,72], TEM [73,74] and

SEM [75,76]. All of these studies have confirmed that CNTs have exceptional stiffness and strength. The combination of these exceptional mechanical properties along with the low density, high aspect ratio and high surface area make CNTs an ideal candidate for reinforcement in composite materials. The CNT reinforced nanocomposites can be considered as a kind of particulate composites with the filler dimensions on the nanometer scale and a high aspect ratio. Unlike the microscopic particulate composites, the mechanical properties of nanocomposites depend strongly on the dispersion state of nanofillers, apart from the properties of fillers and matrix material. The aspect ratio must be sufficiently large to maximize the load transfer between the CNTs and matrix material and thus to achieve enhanced mechanical properties [77,78]. It is well known that the mechanical properties of CNTs exceed those of any existing materials.

1.1.3.3. Thermal properties

The thermal properties of carbon nanotubes are directly related to their unique structure and small size. Because of these properties, nanotubes are proved to be an ideal material for the study of low-dimensional phonon physics, and for thermal management, at nanoscale. The thermal properties of carbon nanotubes are not completely understood as yet. There is some disagreement into the exact nature of thermal conductivity of CNTs, although most of them agree that thermal conductivity seems to change depending on temperature and possible also on current and vacancy concentration [79,80]. It was suggested that the conductivity was linear in temperature from 7 K to 25 K [81]. From 25 K to 40 K, the line increases in slope and it arises monotonically with temperature to

above room temperature. The thermal conductivity of CNT competes with diamond or a single sheet of graphite, which are regarded as the best heat conductors.

1.1.3.4. Applications

Progress in nanotube growth has facilitated the fundamental study and applications of nanotubes. Gaining control over challenging nanotube growth issues is critical to the future advancement of nanotube science and technology, and is being actively pursued by researchers. CNTs can find applications in many different fields with such highly desirable properties described above. In fact, apart from being the best and most easily available one-dimensional model system, carbon nanotubes show strong application potential in nanoelectronics, photovoltaic devices, electrochemical actuators, electrochemical capacitors, nanowires, field emission, conducting plastics, thermal conductors, energy storage, conductive adhesives, thermal interface materials, structural materials, fibers, catalyst supports, scanning probe microscopy, chemical and biological sensing, reinforced composite materials, and in many more areas [82-90].

Some time after the publication of Iijima in Nature, theoretical studies appeared which demonstrated that the electronic properties of nanotubes were a function of both tube structure and diameter. By the late 1990s, however, studies were appearing which confirmed these predictions, and the first nanotube based electronic devices began to be produced. Among the landmarks in this field are the direct correlation of electronic properties with SWCNT structure by producing the carbon nanotube field effect transistor, demonstrated by Dekker and co-workers in 1998 [82]. The ‘Science, 2001’

cover picture shown in Figure 1.9(a) accompanied an important article on nanotube logic circuits by Dekker and co-workers [91].

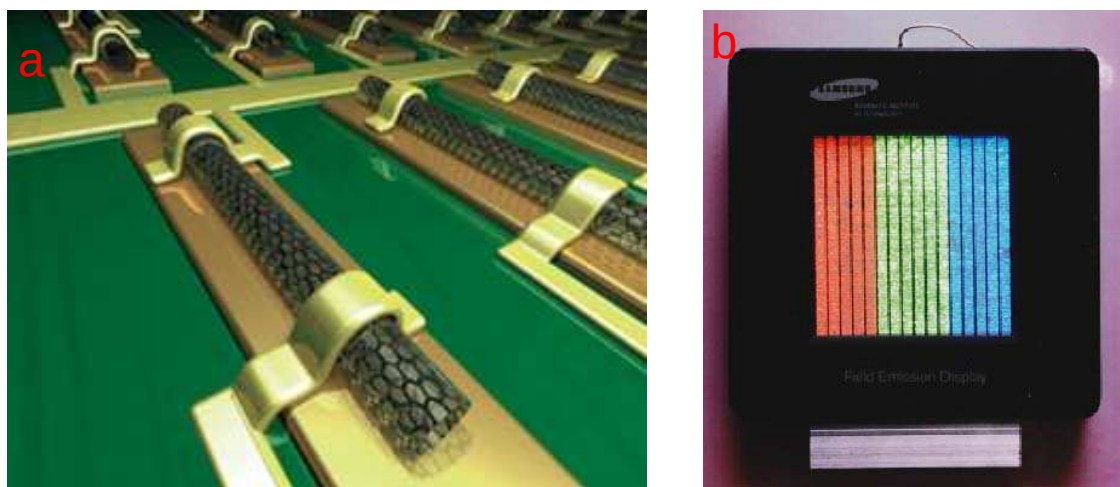


Figure 1.9 : (a) Nanotube based electronic circuit [92] and (b) field emission display [93]

Avouris and colleagues in 2001 described the fabrication of arrays of nanoscale field effect transistors (FETs), utilizing ropes of pure semiconducting SWCNTs [94]. To fabricate the arrays, the SWCNT ropes were deposited on an oxidized Si wafer, which also served as the back gate. An alternative approach to fabricating nanotube devices is self-assembly. The Israeli researchers [95] exploited the interaction of proteins and DNA to assemble nanotubes into a field effect transistor which operated at room temperature. Work on the field emission properties of carbon nanotubes began in about 1995 [96], which is now developed into a major field of research. This work has primarily been driven by the prospect of using arrays of field emitting nanotubes in flat screen displays as shown in Figure 1.9(b). Some of the first experiments on field emission from

nanotubes were carried out by Walt de Heer and colleagues [97]. They used MWCNTs prepared by arc-discharge method, which were purified and then deposited onto a plastic surface. It has been shown [98] that the optimum emitted current density would be achieved with an array of individual vertically aligned tubes spaced apart by twice their height.

In addition to the work on arrays of nanotubes, field emission experiments have also been carried out on individual CNTs. The earliest work arose in this area by Smalley's group [99] into the use of single nanotubes as probes in scanning tunneling or atomic force microscopy. The potential advantages of carbon nanotube tips are illustrated

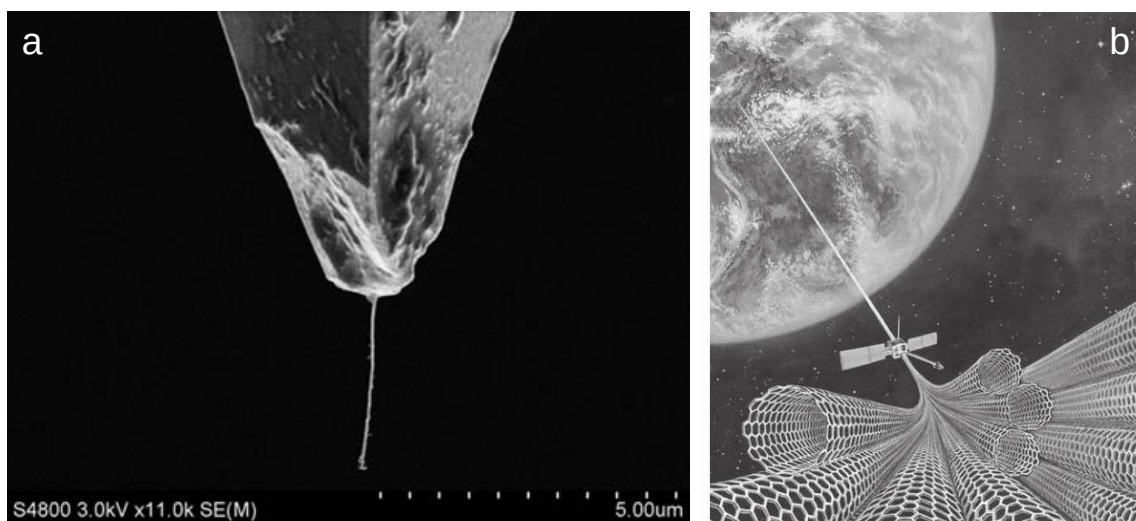


Figure 1.10 : (a) carbon nanotube attached to a conventional AFM tip [100] and (b) an illustration of a nanotube space elevator [101].

in Figure 1.10(a), from the work of A. Raman and colleagues [100], which shows a nanotube attached to a conventional microfabricated probe. There is also interest in

nanotube based light sources. In 2004, researchers from Lausanne [102] described a luminescent tube of 40 cm length based on carbon nanotube field emission. It was demonstrated that the device performed well in comparison to conventional fluorescent tubes. Gas sensing is another area where the properties of carbon nanotubes can be exploited. Alex Zettl's group [103] discovered that electronic properties of carbon nanotubes are highly sensitive to the presence of oxygen. This extreme oxygen sensitivity appeared to be not so good for the application of nanotubes in electronic devices but, on the positive note, it suggested that they might be very useful in gas sensors.

The second major area of carbon nanotube research has revolved around their mechanical properties. Again, theory came slightly ahead of experiment, but ingenious measurements using electron microscopy and scanning probe microscopy soon confirmed the theoretical predictions: carbon nanotubes are the stiffest and strongest fibres known. These properties, coupled with their low density, mean that carbon nanotubes are the only fibres suitable for producing a 'space elevator', an Earth-to-space cable first proposed by Arthur C. Clarke [104], as illustrated in Figure 1.10(b). On a more down-to-earth level, the outstanding mechanical properties of carbon nanotubes are beginning to find applications in a whole range of areas, from sports equipment to automobiles. In such applications it is almost always necessary to encapsulate the tubes in a matrix, and the production of carbon nanotube composites is becoming a major field in itself.

Some notable work has also been carried out on the production of nanotube containing polymer fibers. Following pioneering work by Poulin and co-workers [105], the Baughman group has produced SWCNT/PVA fibers with exceptional mechanical

properties [106]. Table 1 lists a few potential applications of chemically modified carbon nanotubes, in which our research is focused on fundamental aspects of utilizing CNTs for catalysts supports and mechanically reinforced composites.

(Potential) Application	Function of the covalently bonded moiety
Nanostructured electronic devices, e.g., nanodiodes	Local modification of the electronic band structure
(Bio-) chemical sensors	Selective recognition of analyte molecules
Catalyst supports	Anchoring of molecules or metal nanoparticles
Mechanically reinforced composites	Chemical coupling with a matrix
Chemically sensitive tips for scanning probe microscopy	Selective chemical interaction with surfaces
Field emission	Reduction of the work function for electrons at the tube ends
Nanofiltration	Control of the passage of molecules or ions through covalent cross-linking
Controlled drug release	Biocompatibility; recognition of biological fingerprints
Pharmacology	Enzyme inhibition or blocking of ionic channels in the cell membrane
Directed cell growth on surfaces	Specific interactions with cell surfaces

Table 1 : Potential applications of chemically modified carbon nanotubes [7].

Incorporating carbon nanotubes in polymers can also confer useful electrical properties. There has been much interest in using CNTs to improve the conductivity of low cost bulk polymers, for possible applications in the aircraft or automobile industry. Compared with the huge amount of research on CNT-polymer composites, there has been less work on incorporating nanotubes into other matrices, such as metals and ceramics.

Part of our research is concentrated in incorporating CNTs into metal matrices. As far as commercial applications of carbon nanotube composites are concerned, these have been relatively limited to date. One area where CNTs do seem to have had a significant commercial impact is in Li-ion batteries. Endo and colleagues have demonstrated considerable improvements to the performance of such batteries by the addition of catalytically-produced MWCNTs [107,108].

Spinning of MWCNT yarns can be achieved through post synthesis method and perhaps the most successful technique involves pulling yarns of nanotubes from arrays grown on flat substrates. This was first described by researchers from Tsinghua University [109]. They drew out a continuous yarn of nanotubes, a process they compared to drawing thread from a silk cocoon. A further advance on this process was described by Ray Baughman and colleagues [110].

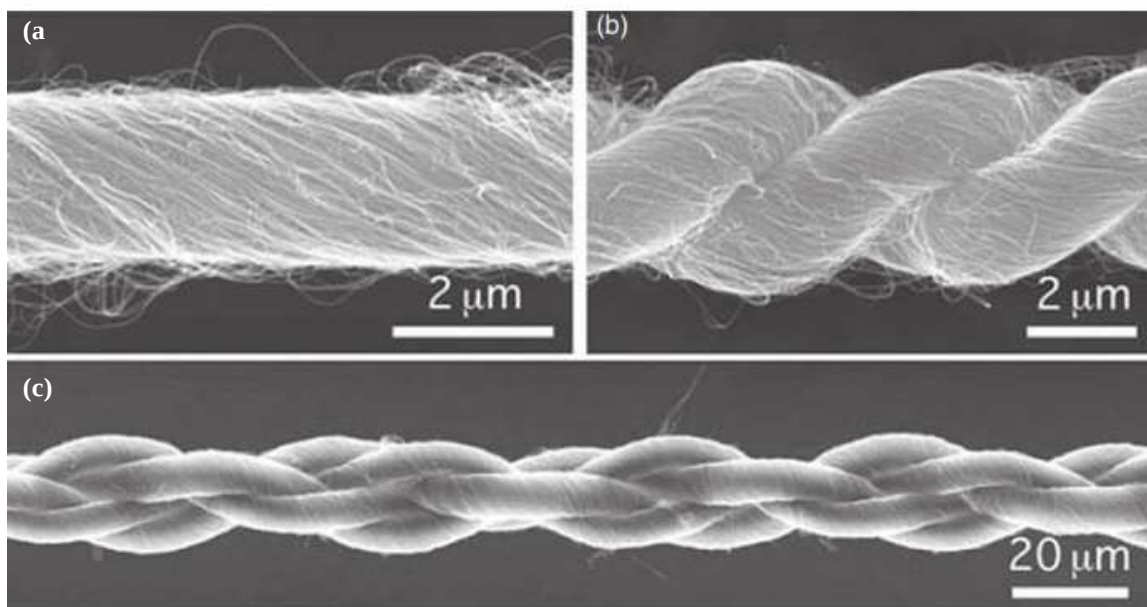


Figure 1.11 : SEM images of MWCNT yarns (a) single, (b) two-ply and (c) four-ply [110]

In this work a twist was introduced as the yarns were drawn, thus applying a technique that has been used in textile production since ancient times. The yarns could be further twisted into two and four-ply MWCNT threads, or formed into more complicated, knitted structures, as shown in Figure 1.11. They suggest that the MWCNT yarns could have a host of applications in areas such as structural composites, protective clothing, artificial muscles and electronic textiles. In another work the same group has also shown that MWCNT sheets can be drawn from catalytically grown nanotube forests [111]. The sheets were transparent, with highly anisotropic electronic properties and may have applications as electrodes or light-emitting diodes.

The unique properties of carbon nanotubes are useful for supporting metal nanoparticles in many potential applications, ranging from very sensitive electrochemical sensors to highly efficient fuel cells [112]. Functionalization of carbon nanotubes with metal nanoparticles has received increasing interest in recent years, and a few interesting routes have now been devised for either covalently or non-covalently attaching certain metal nanoparticles onto carbon nanotubes [113]. The size and shape of nanoparticles are responsible for interesting electronic properties [114]. A great deal of interest focuses on the modification of carbon nanotubes via the attachment of such nanoparticles. For example, the attachment of gold nanoparticles to carbon nanotube sidewalls shows particularly great promise towards novel, highly efficient photo electrochemical cells, fuel cells, or even sensor devices [113-115].

The use of CNT as a catalyst support induces peculiar activity and selectivity in several catalytic reactions involving hydrogen, such as the hydrogenation of nitrobenzene into aniline [116] or selective hydrogenation of the C=C bond in an unsaturated aldehyde

[117]. Planeix and colleagues [118] reported the activity of Ru/CNT catalyst for liquid-phase cinnamaldehyde hydrogenation. Their study reveals that carbon nanotubes could induce a metal-support interaction of a different kind to that existing for Ru supported on alumina or active carbon. For isopropanol dehydrogenation, Niesz et al [119] demonstrated that MWCNTs are a much better support for platinum than either graphite flakes or active carbon.

Carbon nanotubes have been used as biosensors in a variety of ways. Among the biomolecules that have been analyzed using nanotube containing electrodes are DNA [120], enzymes [121], proteins [122] and glucose [123]. The use of functionalized nanotubes in electrodes is also of interest. Many studies have now been carried out using CNT containing electrodes [120-127], and in few cases they have displayed characteristics that are equal or superior to that of conventional electrodes [128]. Various methods have been used to make the electrodes, including simply mixing the tubes with a binder [124,121,123] or drop coating onto a glassy carbon electrode [125,126]. Aligned nanotubes have also been used in electrodes, sometimes using self assembly [127,122] and some other times by direct growth [120].

Real-world applications of nanotubes require either large quantities of bulk materials or device integration in a scale-up fashion. Significant work has been carried out to tackle these issues. Nevertheless, many challenges remain in the nanotube growth area. The full potential of nanotubes for applications will not be realized until the growth of nanotubes can be further optimized and controlled. While some of the proposed applications remain still a far-off dream, others are close to technical realization. Recent advances in the development of reliable methods for the chemical functionalization of the

nanotubes provide an additional impetus towards extending the scope of their application spectrum. In particular, covalent modification schemes allow persistent alteration of the electronic properties of the tubes, as well as to chemically tailor their surface properties, whereby new functions can be implemented that cannot otherwise be acquired by pristine nanotubes.

1.2. Modification of carbon nanotube surfaces

Carbon nanotubes hold the promise of delivering exceptional mechanical properties and multifunctional characteristics. These properties could be enhanced by further modifying their surface by decorating them with metal/metal oxide nanocrystals. It is known that the methods of production of CNTs generate impurities such as byproduct carbonaceous species and residues from the transition metal catalysts used in preparing CNTs [12]. CNTs are also insoluble in most of the solvents due to strong van der Waals interactions that tightly hold them together, forming bundles. All of the above decrease the overall yield of usable material and interfere with the desired properties of the CNTs [11]. Consequently, an effective purification and functionalization of the nanotubes is required before their further processing.

1.2.1. Surface functionalization of carbon nanotubes

CNTs have high similarity in their chemical reactivity to graphite and other molecules of fullerene family like C_{60} . However, it is important to know that the

chemistry of the nanotubes is slightly different from the other polyaromatic carbonaceous materials because of their small size, unique shape and structure. Functionalized CNTs have been intensively studied in the last few years [129-135]. In general, based on the chemical reactivity of carbon nanotubes and interactions between the active molecules and carbon atoms on the CNTs the functionalization reactions can be classified into two main categories: (a) the covalent attachment of chemical groups, through reactions on the conjugated skeleton of CNTs, and (b) the non covalent supramolecular adsorption or wrapping of various functional molecules onto the tubes [136]. In this frame, CNTs enhance solubility in various solvents and produce novel hybrid materials potentially suitable for applications.

1.2.1.1. Covalent functionalization of carbon nanotubes

Among various surface functionalization techniques, covalent functionalization of CNTs is probably the most widely studied. It allows functional groups to be attached to tube ends and sidewalls. The sites of highest chemical reactivity in the CNT structure are the caps, which have a semifullerene-like structure. Chemical functionalization of CNT tips has been performed mainly on the basis of oxidative treatments. As a general rule, CNT oxidation yields opened tubes with oxygen-containing functional groups at both the sidewall and the tube endings. These groups can then be used as chemical anchors for further derivatization.

By comparison, functionalization of the sidewall comprising the regular graphene framework is more difficult to accomplish. In general, addition reactions to the partial

carbon–carbon double bonds cause the transformation of sp^2 into sp^3 hybridized carbon atoms, which is associated with a change from a trigonal-planar local bonding geometry to a tetrahedral geometry. This process is energetically more favorable at the caps due to their pronounced curvature in two dimensions, in marked contrast to the sidewall with its comparatively low curvature in only one dimension. On the other hand, the non-zero curvature makes the sidewall more reactive than a planar graphene sheet. Correspondingly, the binding energy of atoms or functional groups on the sidewall should increase with decreasing tube diameter. This tendency is supported by theoretical studies [137].

Another parameter that profoundly alters the chemical reactivity of CNT sidewalls is the presence of defects. Typically around 1–3% of the carbon atoms of a nanotube are located at a defect site [138].

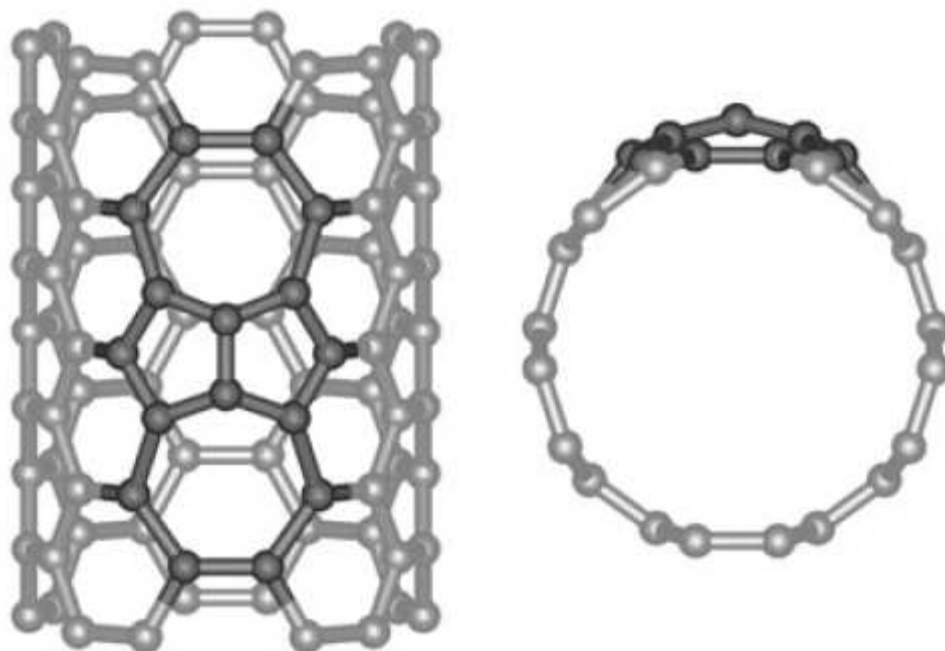


Figure 1.12 : Stone-Wales (or 7-5-5-7) defect on the sidewall of a nanotube [7].

A frequently encountered type of defect is the so-called Stone–Wales defect, which is composed of two pairs of five-membered and seven-membered rings, and is hence referred to as a 7-5-5-7 defect (Figure 1.12). A Stone–Wales defect leads to a local deformation of the graphitic sidewall and thereby introduces an increased curvature in this region. The strongest curvature exists at the interface between the two five-membered rings; as a result of this curvature, addition reactions are most favored at the carbon–carbon double bonds in these positions [139].

Covalent functionalization can be accomplished by either modification of surface-bound carboxylic acid groups on the nanotubes or by direct reagents to the side walls of nanotubes. Generally, functional groups such as --COOH or --OH or C=O are created on the CNTs during the oxidation by oxygen, air, concentrated sulfuric acid, nitric acid, aqueous hydrogen peroxide, and acid mixture [140-143]. The extent of the induced --COOH and --OH functionality also depends on the oxidation procedures and oxidizing agents [144]. The presence of carboxylic acid groups on the nanotube surface is more convenient than others because a variety of chemical reactions can be conducted with this group.

The presence of carboxylic groups leads to a reduction of van der Waals interactions between the CNTs, which strongly facilitates the separation of nanotube bundles into individual tubes. Additionally, the attachment of suitable groups renders the tubes soluble in aqueous or organic solvents, opening the possibility of further modifications through subsequent solution-based chemistry [145-147]. The CNTs functionalized in this way are soluble in many organic solvents because the hydrophobic nature of CNTs is changed to hydrophilic one due to the attachment of polar groups. The

chemically functionalized CNTs can produce strong interfacial bonds with many polymers, ceramics and metals, allowing CNT based nanocomposites to possess high mechanical and functional properties [148,149].

Carboxylated CNTs were extensively used as precursors for further covalent modification of CNTs, through esterification or amidation reactions. In most cases, carboxylic groups that bear on the sidewalls and tips of CNTs are converted to acyl chloride groups via reaction with thionyl or oxalyl chloride, followed by the addition of the appropriate alcohol or amine. In the seminal work of Liu et al [150], it was demonstrated that the groups generated by the acid treated nanotubes were carboxylates, which could be derivatized chemically by thiolalkylamines through amidation reaction. Carbon nanotube sidewalls have also been functionalized with amino groups. The amino-functionalized carbon nanotubes were further used for the covalent coupling of amino acids [151] and biologically active peptides [152] to their sidewalls. Bifunctional reagents have been used to modify the carbon nanotube sidewalls with different compounds. The carboxylic groups generated on CNTs have been used to covalently bind biomaterials such as sugar moieties [153], oligonucleotides [154], peptide nucleic acids [155] and proteins [156] via carbodiimide coupling of the respective amino-functionalized biomolecules or using hetero bifunctional coupling reagents. This approach provides an efficient method for attaching biomolecules to carbon nanotubes under ambient conditions.

In another significant work Lieber and co-workers [157] demonstrated that nanotube tips can be created by coupling basic or biomolecular probes to the carboxylic groups that are present at the open ends. These modified nanotubes were used as AFM

tips to titrate acids and bases, to image patterned samples. By analogous coupling reactions, various fluorescent probes were attached at the acid treated nanotubes for photophysical studies [158], whereas, solid catalysts have been fabricated by grafting of organic complexes of metal ions [159]. The groups of Castano [160] and Shaffer [161] independently described a method of silylating oxidized MWCNTs by reacting the carboxylic acids with the appropriate silanes. In a recent study, covalently linked CNTs by using methylenedianiline as diazonium salt precursor were spun in the form of microfibers and used as scaffolds for hydrogen storage [162].

The issue of controlled deposition and alignment of CNT on different types of surfaces has been studied by researchers. In principle, by attaching acidic moieties to the graphitic surface, one can guide the assembly on many substrates. Important progress concerning the controlled deposition of CNT on gold surfaces was achieved by the thiolization reaction of carboxyl terminated CNT [163,164]. Oxidized CNTs were treated with the appropriate thiol derivative and the resulting material was attached chemically to a gold substrate.

The electrochemical approach is a valuable method for the chemical alteration of nanotubes, as the extent of reaction can be directly adjusted by an applied potential. Kooi and co-workers [165] demonstrated that using SWCNTs as either the anode or cathode in an electrochemical cell enabled oxidation or reduction of small molecules to occur at the nanotube surface, forming radical species that could then attack the carbon lattice to form covalent bonds. Similarly, Collins and colleagues [166] performed electrochemistry studies to control and monitor covalent functionalization of SWCNTs.

There has been interest in covalently attaching polymers to nanotubes with the specific aim of improving bonding in nanotube-polymer composites. Ajayan and group [167] reported a method for preparing polystyrene grafted SWCNTs by firstly treating the tubes with sec-butyl lithium and using them as initiators for the anionic polymerization of styrene. In another similar study, Coleman and group [168] described a similar technique, this time with halogenated polymers. In another alternative method, oxidized SWCNTs and MWCNTs were functionalized with polystyrene copolymers under amidation or esterification reactions of the carboxylated CNTs [169].

1.2.1.2. Non-covalent functionalization of carbon nanotubes

On the other hand, a different approach to disperse the CNT bundles is the noncovalent functionalization. This type of functionalization mainly involves surfactants or biomacromolecules wrapping with polymers. In the search for non-destructive purification methods, nanotubes can be transferred to the aqueous phase in the presence of surfactants [170-172]. The non-covalent interaction is based on van der Waals forces or π - π stacking, and it is controlled by thermodynamics. When the hydrophilic part of the amphiphilic molecule contains an aromatic group, a strong interaction results, forming effective π - π stacking with the graphitic sidewalls of the CNT [173].

The ionic surfactant sodium dodecyl sulphate (SDS), employed in household products, was found to be of great value in solubilizing both MWCNTs and SWCNTs. Arjun and co-workers [174] showed that sodium dodecyl benzene sulphonate (SDBS) can be more effective than SDS in dispersing SWCNTs in water, because it contains a

benzyl ring. Non-ionic surfactants like triton X- 100 have also been used to solubilize nanotubes [175]. Apart from the surfactants, there are essentially two different approaches to the non-covalent functionalization of nanotubes. One employs relatively small molecules containing planar groups that irreversibly adsorb to the nanotube surfaces by π -stacking forces, while the other involves wrapping larger polymeric molecules around the tubes.

CNTs can interact with many biomolecules without forming a covalent bond. An important class of biomolecules having high affinity with the CNTs sidewalls is proteins. A number of studies were reported concerning the sonication assisted dispersion of CNT–protein hybrids in aqueous or polar media. These include proteins such as lysozyme [176], bovine serum albumin [177], cyclic peptides [178], porphyrinic peptides [179] and so on. Many groups have reported that DNA strands interact strongly with CNT to form stable hybrids that can be effectively dispersed in aqueous solutions [180,181].

Another example of biomolecules assembled onto the CNT sidewalls involves the polysaccharides. There are a few groups reported that chitosan derivatives interact strongly with CNTs, forming stable hybrids that can be effectively dispersed in aqueous solutions [182,183]. The integration of CNT-polysaccharide composites in biological applications was demonstrated by their successful utility as electrochemical sensors of glucose [184]. Using a different approach, Strano and co-workers [185] have fabricated an affinity sensor for glucose molecule based on SWCNT photoluminescence.

Although, non-covalent functionalization of CNT seems attractive as it offers the possibility of attaching chemical handles without affecting the electronic network of the tubes, it is not preferred in forming strong bonds with metals or metal oxide nanocrystals

and at times surfactants interfere with end results, posing difficulty in eliminating them from the surface.

1.2.2. Decoration of CNTs with metal and metal oxide nanocrystals

The external surface modification of CNTs and anchoring of metal or metal oxide nanoparticles on them can dramatically influence their physical, mechanical, thermal and electrical properties, which may lead to novel changes that are relevant to potential applications in diverse fields, such as catalysis, composites, chemical/biological sensing and optoelectronics [186-194]. It has been found that the binding energy between metals and pristine CNTs is rather small [195], resulting in poor metal-CNT adhesion. If the adhesion between the metal and the CNTs is not strong, the benefits of the high tensile strength of CNTs are lost.

One principle way to increase the surface reactivity of CNTs is by the inclusion of defects and functional groups on CNTs. The binding energies between CNT and transition metals are found to be significantly enhanced when vacancy defects are introduced into the CNTs [196]. CNTs are chemically inert owing to their properties such as insolubility in most of the solvents and low chemical reactivity, which hinders their manipulation and application in many potential fields. Attempts have been made in recent times to overcome these problems by surface functionalization of CNTs, which found broad applications, including composite materials, sensors and catalysis [197-200].

CNTs are considered as interesting support materials for catalytic properties because of their good water tolerance, unique hollow tubular structure, large surface area,

large adsorption capacity, high chemical, thermal and mechanical stability which favour the diffusion of reacting species [201,202]. In this regard, many studies have been focused on depositing metal or metal oxide nanoparticles on their outer surface. CNTs have been extensively used as supports for various nanoparticles such as TiO_2 , SiO_2 , Fe_3O_4 , CdS, Au, Pd, Pt, and Ag etc. [203-208]. Due to the turbostratic character of the hollow tubule nanostructures, it is possible for CNTs to function as supports for preparing nano-sized catalyst particles [209].

The aromatic ring system of the CNTs [210] can be disrupted by the application of oxidation reagents, such as HNO_3 or $\text{HNO}_3 / \text{H}_2\text{SO}_4$ mixture, and therefore the nanotubes can be functionalized with groups such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl (C=O) that are necessary to anchor metal ions to the tube [211-213]. This changes the reactivity of nanotubes and modifies the wetting characteristics, which would enrich their properties. It leads us to the issue of interfacial bonding between the metal atoms and defective and oxidized CNTs to ensure excellent mechanical performances for the CNT-reinforced metal-matrix composites. It is suggested that these stable CNT-metal systems could become promising engineering materials in many fields such as CNT devices for various spintronics applications and CNT metal-matrix composites [214-216].

1.3. Incorporation of carbon nanotubes into metal matrices

Carbon nanotubes possess extraordinarily high tensile strength, which outreaches that of a steel wire of corresponding thickness by around one order of magnitude. This attribute combined with their high length-to-diameter ratio and low density (one-sixth

that of steel) makes CNTs valuable components for mechanically reinforced composite materials [217-219]. The incorporation of CNTs into metal matrices is an important research area as the new reinforced materials generated possess unique properties and are potentially useful for nanotechnological applications. The surface modified CNTs performed in different techniques can be utilized to incorporate into metal matrices by electrogeneration to enhance their properties. This can be performed in both aqueous and ionic liquid. Ionic liquids are new kind of solvents which can be of great importance in the present study due to their good dispersion stability for CNTs.

1.3.1. Incorporation of carbon nanotubes from aqueous solutions

To date, most chemical reactions have been carried out in molecular solvents. For two millennia, most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. The electroplating industry, which dates back well over 100 years, is based solely on aqueous solutions due to the high solubility of electrolytes and metal salts resulting in highly conducting solutions. Electrodeposition of metals is essential for a variety of industries including electronics, optics, sensors, automotive and aerospace to name but a few. The main metals of interest include Cr, Ni, Cu, Au, Ag, Zn and Cd together with a number of copper and zinc-based alloys.

The potential for CNT-reinforced metal composites having extraordinary specific stiffness and strength represent tremendous opportunity for the development of new material systems [220,221]. The remarkable mechanical and physical properties

demonstrated by CNTs combined with their low density, offer scope for the development of high strength CNT-reinforced composite materials. Many of these outstanding properties of CNTs can be best exploited by incorporating them into host matrices. The preparation of CNT-reinforced composite materials is now a rapidly growing area of research interest. The focus of much of the research in CNT-based composites has been on polymer-matrix materials [222-224], however, there is a growing interest in incorporating nanotubes into ceramics, metals and other forms of carbon due to their potential properties [225,226].

A few groups have succeeded in preparing CNT composites with metals such as aluminium, titanium, copper, nickel etc [227-232]. Similarly, Ni/CNT composites have been studied by various researchers [233-243] due to its potential applications, but they could not give a promising result due to the difficulties associated with the processing of composites. CNTs are largely inert and do not disperse well in aqueous solutions, so uniform deposition of CNTs in the metal composites is a difficult task without the addition of surfactants or dispersants. The challenge is thus: how to incorporate individual CNTs, or at least relatively thin CNT bundles or disentangled CNTs, inside a matrix. In other words, dispersion of CNTs is not only a geometrical problem, dealing with the length and size of the CNTs, but also relates to a method on how to separate individual CNTs from CNT agglomerates and stabilize them in matrix to avoid secondary agglomeration. Therefore, it is important to explore possibilities of finding a compatible solvent which could, at the same time, show good dispersion stability for MWCNTs and conductivity. In this regard, ionic liquids are fast emerging as promising alternative solvents for electrochemistry purposes.

1.3.2. Incorporation of carbon nanotubes from ionic liquids

Recently, however, a new class of solvent called ionic liquids has emerged. These solvents are often fluid at room temperature, and consist entirely of ionic species [244]. In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point [245].

As ionic liquids have developed, the key advantages of the liquids have become: the wide potential windows, high solubility of metal salts, avoidance of water and metal/water chemistry and high conductivity compared to non-aqueous solvents [246-249]. Due to their low vapour pressures ionic liquids are well suited to perform electrodeposition at a range of temperatures. At elevated temperatures there is less concern about viscosity and conductivity and phenomena such as nucleation, surface diffusion and crystallization associated with metal deposition can be accelerated. The use of ionic liquids heralds not only the ability to electrodeposit metals that have hitherto been impossible to reduce in aqueous solutions but also the capability to engineer the redox chemistry and control metal nucleation characteristics. It is the latter area that is only now being addressed and will no doubt be the focus of research over the forthcoming decade [250].

DES is a new class of ionic liquid typically formed by mixing choline chloride (as quaternary ammonium salt) with hydrogen bond donors such as amides, acids and alcohols [251,252]. Abbott et al have shown that DES can be successfully employed in electropolishing, electroplating and electroless deposition [253-255]. Recently, they have also shown that choline chloride and either urea or ethylene glycol based DES can be

employed in the electrodeposition of zinc-tin alloys, copper composites and nickel [254,256,257].

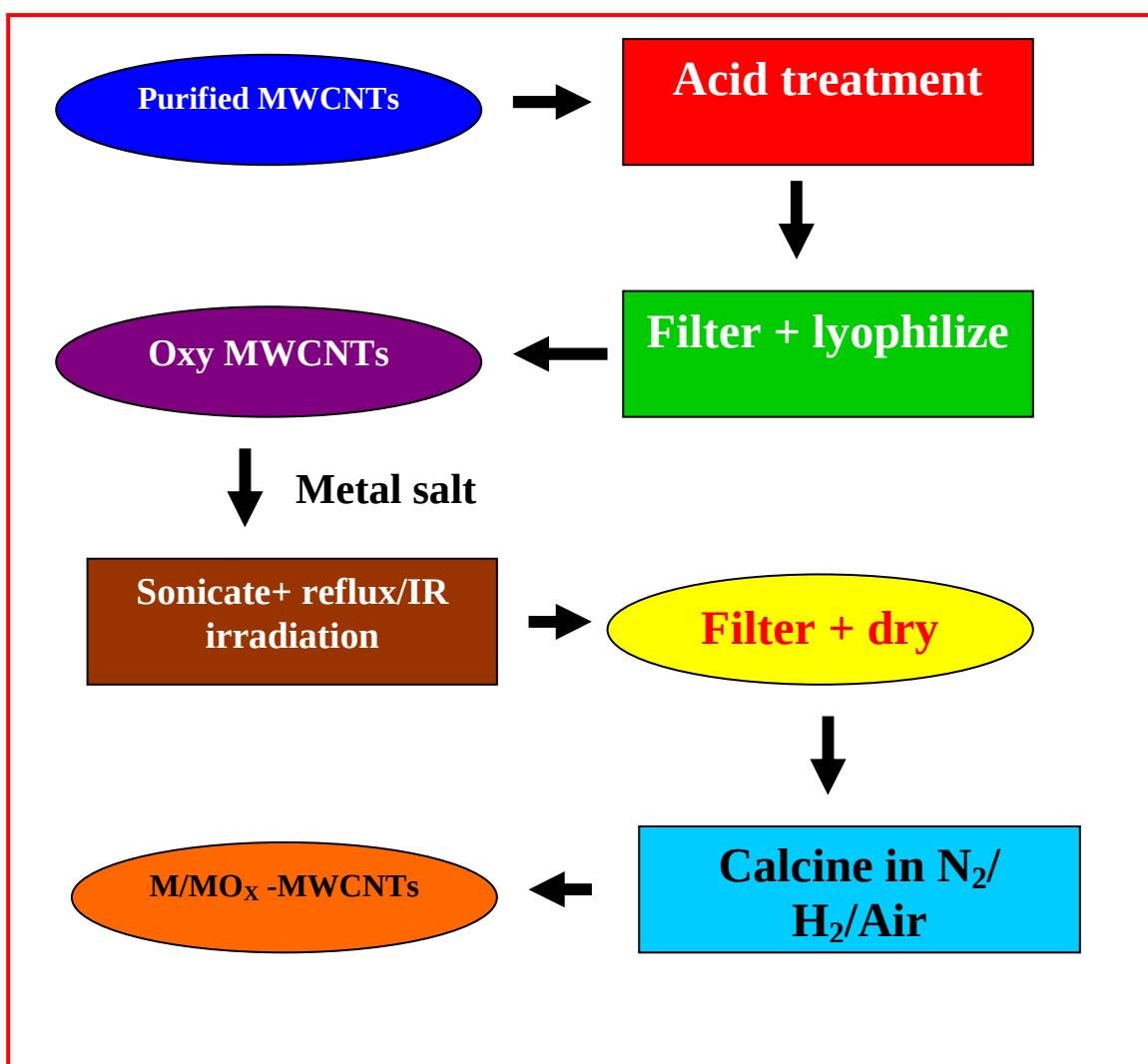
One of the first DES systems that were investigated, contained choline (2-hydroxyethyltrimethylammonium) chloride (ChCl) mixed with urea ($\text{NH}_2\text{CO.NH}_2$) [258]. Choline chloride is vitamin B4 and is produced on the Mtonne p.a. scale as an additive for chicken feed; urea is a common fertilizer. This is not only cheap and easy to make but it is non-toxic and even biodegradable. By themselves they have freezing points of $303\text{ }^\circ\text{C}$ and $135\text{ }^\circ\text{C}$, respectively. By combining these two compounds in a ratio of 1:2 (ChCl: urea), the product formed has a freezing point of $12\text{ }^\circ\text{C}$ [250]. The main reason behind ChCl being such a useful quaternary ammonium salt is to do with the fact it is an asymmetric quaternary ammonium salt with a polar functional group, but is also small. The asymmetric nature of this molecule reduces the freezing point of the ionic molecular liquid, as does the polar functional group.

Perhaps in terms of public perception of this being used as a part of a potential replacement for conventional solvents, the fact that choline chloride is essentially nontoxic is a large plus point for its use. These types of DES have been used very successfully for many purposes such as electrochemical applications. Liquids such as Maline 100 (ChCl : malonic acid) and Ethaline 200 (ChCl : 2 x 1,2-ethanediol) have generated a lot of industrial interest in their use for both polishing and plating of metals [259].

II. Proposed research strategies

II. Proposed research strategies

The first major part deals with surface functionalization of multi-walled carbon nanotubes and their decoration with metal and metal oxide nanocrystals. Metals chosen for our study are nickel and copper due to their low cost, easy accessibility and numerous potential applications with CNT reinforcements, such as enhanced hardness, excellent solid lubrication, corrosion resistance, catalytic performance etc.,



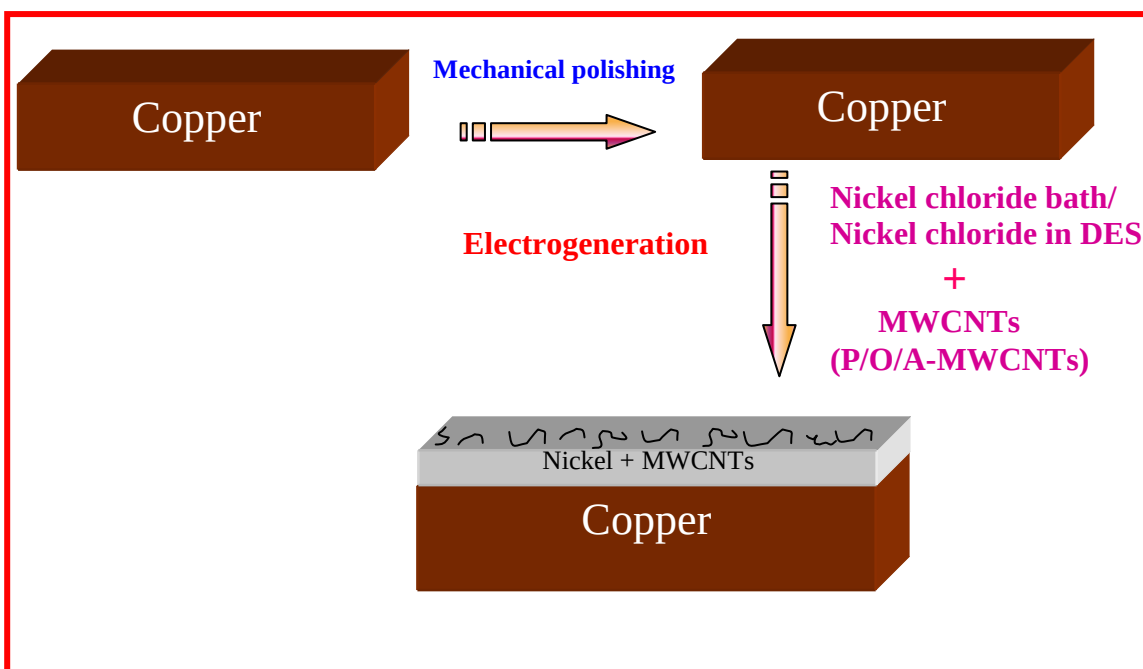
In this context, our objective has been to control the nature, diameter, concentration and homogeneous dispersion of metal and metal oxide nanocrystals on multi-walled carbon nanotubes. This first part is accordingly studied in Chapter 2 and 3, namely, decoration of copper and copper oxide nanocrystals on multi-walled carbon nanotubes and nickel and nickel oxide nanocrystals decoration on multi-walled carbon nanotubes, respectively. Proposed research strategy to decorate the MWCNTs with metal and metal oxide nanocrystals is explained using the flow chart.

The second major part of the work deals with the incorporation of surface modified multi-walled carbon nanotubes into metal matrices from aqueous solution and ionic liquid. That is, incorporation of surface modified multi-walled carbon nanotubes (obtained from the first part of the study) into metal matrices such as nickel. MWCNTs reinforced metal composites attract a lot of interest owing to their extraordinary specific stiffness and strength. Among the diverse synthesis processes, the electrodeposition method is preferred considering the advantages of high purity of deposits and simple procedure of deposition, apart from its convenience and economy.

In this context, the main objective of our study was to incorporate surface modified multi-walled carbon nanotubes into nickel and copper matrices and study their physicochemical, morphological and electrochemical properties. Our study is focused in two different media, namely, aqueous solution and ionic liquid. In aqueous solution we have explored the possibility of processing different types of surface functionalized MWCNTs reinforcing a nickel matrix by electrogeneration.

In this regard, pristine MWCNTs, amino-functionalized MWCNTs and oxygen-functionalized MWCNTs have been employed for the study. Since, MWCNTs are not

well dispersed in aqueous solutions, so uniform deposition of MWCNTs in the metal composites is a difficult task without the addition of surfactants or dispersants. Therefore, it is important to explore possibilities of finding a compatible solvent which could, at the same time, show good dispersion stability for MWCNTs and conductivity. This search for the compatible solvent has led us to ionic liquids. So in this part we focus our study on ionic liquids, where a new class of ionic liquid, namely, deep eutectic solvent has been employed for the study. This ionic liquid is prepared by mixing choline chloride (as quaternary ammonium salt) with hydrogen bond donors such as amides, acids and alcohols. Proposed research strategy to incorporate MWCNTs into metal matrices is explained using the flow chart.



Chapter 2: Decoration of multi-walled carbon nanotubes with copper and copper oxide nanocrystals

Chapter 2: Decoration of multi-walled carbon nanotubes with copper and copper oxide nanocrystals

2.1. Introduction

The properties of CNTs can be altered by modifying their surface so as to obtain the desired properties suitable for various applications. Many studies have been undertaken to decorate metal or metal oxide nanoparticles on their outer surface as we have mentioned in the introductory chapter. The aim of the present study has been to control the nature, diameter, concentration and homogeneous dispersion of the copper and copper oxide nanoparticles on the CNTs. In this context, Cu/CuO_x were chosen due to their relevance for photovoltaic nanodevices, solar energy applications, redox chemistry, extraordinary electrical, thermal, catalytic and sensing properties combined with its low cost and easy accessibility [260-268].

Thus far, many attempts have been made to decorate copper and copper oxide nanoparticles on CNTs with an outer diameter of CNTs ranging above 20 nm [269,270]. The use of Cu (I) phenylacetylide (CPA) as the precursor to deposit Cu₂O and Cu nanoparticles on thick MWCNTs having diameters ranging between 70 and 110 nm was recently reported [271]. In the present study, we report the use of CPA as a source of copper, to achieve uniform dispersion of Cu/CuO_x nanocrystals on thin MWCNTs having an average diameter of 10 nm. Even though, deposition of copper and copper oxide nanoparticles on CNTs in the literature is reported [272-277], the processes are either lengthy or tedious and in other cases surfactants and reducing agents have been used to control the size of the particles.

Due to the efficient photo-absorption and photothermal conversion properties of CNTs in near infrared (IR) region, they have been used as near IR functional materials [278]. CNTs can absorb near IR radiation rapidly transferring electronic excitations into molecular vibration energies which induce heat [279]. This remarkable photo-absorption and photothermal property of CNTs has been made use for remote thermal reactions [280], phase transitions of polymer gel hybrids [281], cancer therapies [282], and so forth. In the present study, this photothermal property is used to impregnate CPA on MWCNTs and then to decorate Cu/CuO_x nanocrystals on MWCNTs.

Our study focuses on two different methods of impregnating CNTs with metal containing nanoparticles. The later part to obtain the required nanocrystals by calcination remains the same for both those methods. In the first method of impregnation we reflux the mixture of metal salt and CNTs suspension and in the second method we irradiate the mixture of metal salt and CNTs suspension in the presence of infrared radiation. In both cases, CPA was used as a source of copper. In this work, we briefly explain the first method of impregnation and then move on to the second method along with the results and discussion as it is a simple and effective method and gives rise to desired results in a shorter time.

2.2. Preparation of Cu/CuO_x nanocrystals decorated MWCNTs

It is essential to generate the oxygen functionalities on the surface of MWCNTs in order to anchor metal or metal oxide nanoparticles on them. As a first step of preparation of Cu/CuO_x nanocrystals on MWCNTs, we functionalize the surface of

MWCNTs. The oxygen functionalities were generated on surface of MWCNTs by treating them with the mixture of concentrated H_2SO_4 and HNO_3 with a molar ratio of 3:1 following the method reported in the literature [141,142]. In a typical experiment, 75 ml of conc. H_2SO_4 (97 %) and 25 ml of conc. HNO_3 (65 %) were carefully mixed together and added to 1 g of MWCNTs in a round bottomed flask. The above suspension was then heated under constant agitation at $50\text{ }^\circ\text{C}$ for 8 hours. Afterwards the mixture was allowed to cool down to room temperature, added to equal quantity of deionized water, filtered and the residue was washed several times with deionised water until neutral pH was attained. The residue was then filtered and freeze-dried. The oxidized MWCNTs thus obtained are designated as O-MWCNTs. This is schematically represented in Figure 2.

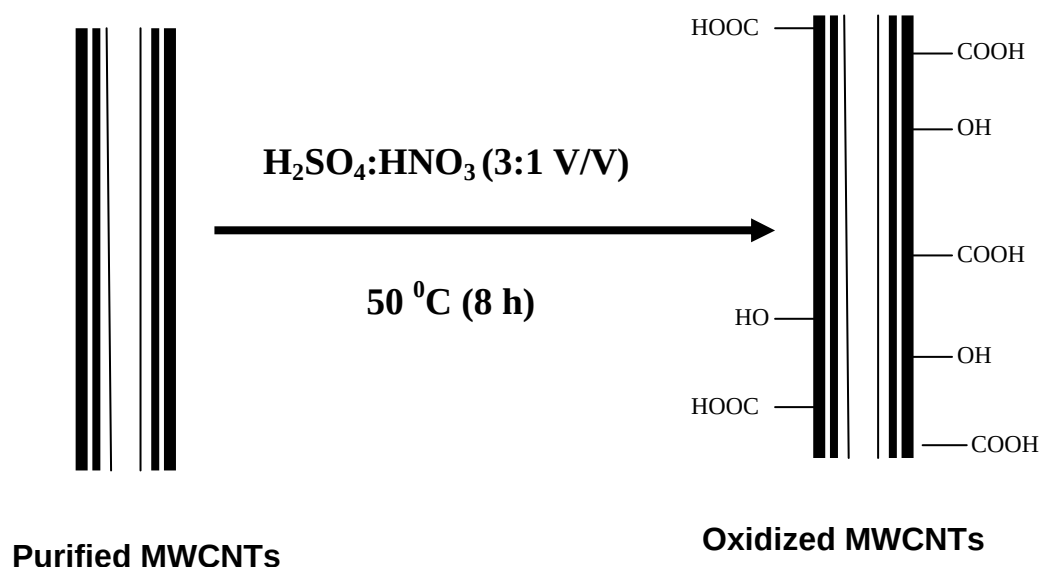


Figure 2 : Surface functionalization of purified MWCNTs

2.2.1. Impregnation of CPA on MWCNTs by reflux method

The O-MWCNTs were then used to impregnate CPA by reflux method. A 100 mg of oxygen-functionalized MWCNTs was sonicated in 50 ml of xylene for an hour to form a good suspension. Similarly, 45.7 mg of CPA (15 wt % of Cu) in 30ml of xylene was also sonicated for the same amount of time. While the suspensions were still under ultrasonication, CPA in xylene was added to the MWCNTs in xylene suspension.



Figure 2.1 : Experimental setup for reflux method.

When both the suspensions were mixed together green colour was imparted to the black suspension due to the change of the color of CPA suspension from yellow to green. The mixture was further sonicated for a few minutes and then refluxed for 12 hours under magnetic stirring until the green color of CPA suspension totally disappeared indicating the completion of the impregnation process. The experimental setup for reflux method is depicted in Figure 2.1. The mixture was cooled to room temperature, filtered and the residue was washed three times with acetone. The copper-treated MWCNTs thus obtained were finally dried under vacuum at room temperature.

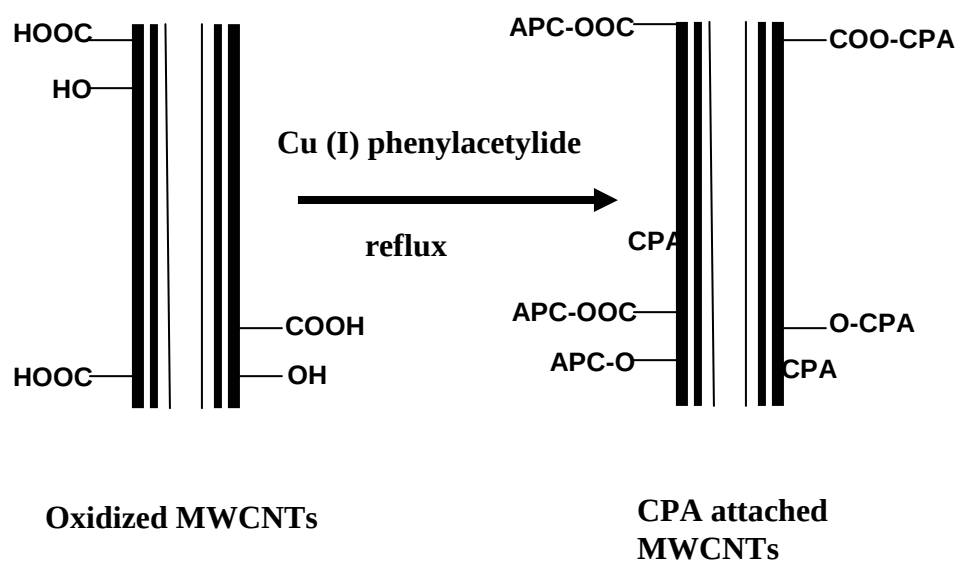


Figure 2.2 : CPA attached MWCNTs by reflux method.

The CPA impregnated MWCNTs thus obtained were referred to as CPA-MWCNTs. This is schematically represented in Figure 2.2.

2.2.2. Impregnation of CPA on MWCNTs by infrared (IR) irradiation

We have also designed a simpler impregnation method to attach CPA on O-MWCNTs that is by IR irradiation. In a typical experiment, 100 mg of O-MWCNTs was sonicated in 50 ml of xylene until (~ 5 min) a well dispersed black suspension was obtained. Similarly yellow suspension of CPA in xylene was obtained by sonicating 45.7 mg of CPA (15 wt % of Cu) in 30 ml of xylene for the same amount of time. While the suspensions were still under ultrasonication, CPA in xylene was added to the O-MWCNTs in xylene suspension. The mixture was further sonicated for a few minutes. When both the suspensions were mixed together a green tinge was imparted to the black suspension due to the change of the color of CPA suspension from yellow to green. The mixture was then IR irradiated under magnetic stirring until the green color of CPA suspension totally disappeared (two and a half hours) indicating the completion of the impregnation process. This time duration is considered the optimum under the current experimental conditions for the uniform distribution of CPA on MWCNTs. The experimental setup for IR irradiation method is demonstrated in Figure 2.3. The mixture was cooled to room temperature, filtered and the residue was washed three times with acetone. The CPA impregnated MWCNTs thus obtained, referred to as CPA-MWCNTs hereafter, were finally dried at room temperature. The schematic presentation is shown in Figure 2.4.



Figure 2.3 : Experimental setup for IR irradiation method.

Compared to the first method of refluxing the mixture of CPA and CNTs suspension, second method has advantage of time duration, easier handling and simpler manipulation considering the requirement of high temperature in reflux method. Both these dried samples in room temperature were calcined in a similar manner to obtain the respective copper and copper oxide nanocrystals on MWCNTs.

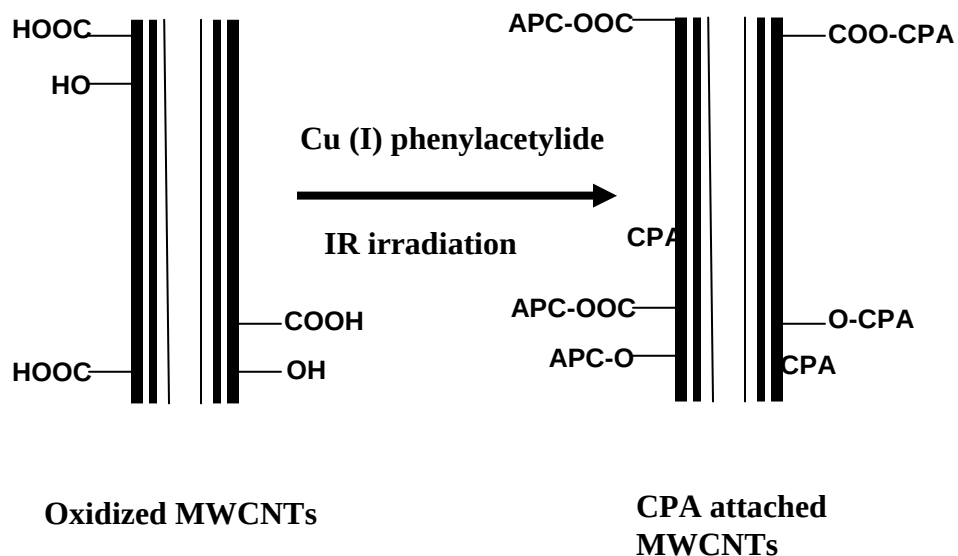


Figure 2.4 : CPA attached MWCNTs by IR irradiation.

2.2.3. Calcination of CPA-MWCNTs

The CPA-MWCNTs were then calcined in a tubular furnace equipped with a quartz tube pre-heated to a desired temperature under the continuous flow of either air/nitrogen/ hydrogen at a flow rate of 300 μL per min. In a typical experiment, 20 mg of CPA-MWCNTs were calcined at desired temperatures (150-300 $^{\circ}\text{C}$) for 1 hour under continuous flow of air/nitrogen/hydrogen. Copper and copper oxide nanocrystals decorated on MWCNTs are schematically illustrated in Figure 2.5.

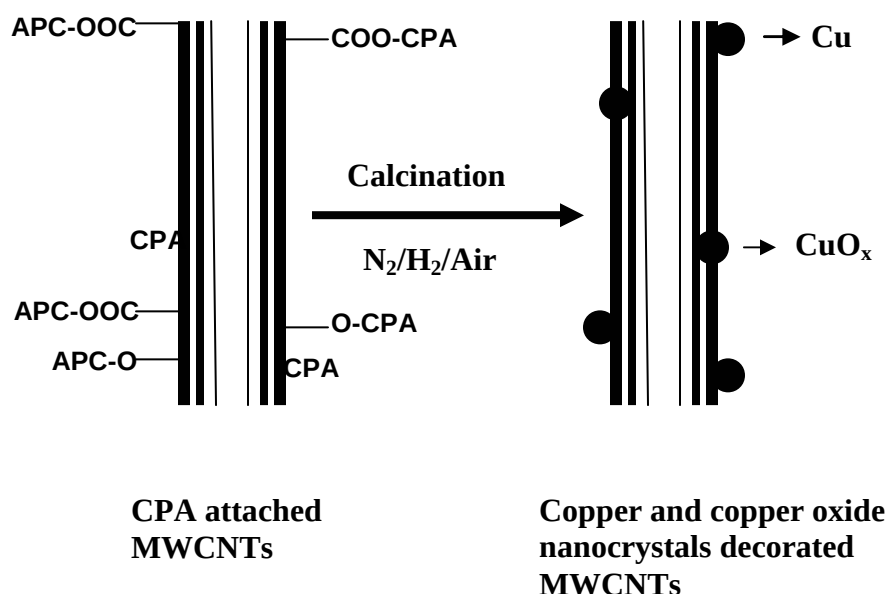


Figure 2.5 : Copper and copper oxide nanocrystals decorated MWCNTs

2.3. Results and discussion

As a first approach to understand the extent of oxidation of MWCNTs we have characterized the P-MWCNTs and O-MWCNTs by fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The FTIR spectrum of MWCNTs is compared with that of O-MWCNTs in Figure 2.6. The broad peak observed around 3433 cm^{-1} in the spectrum of MWCNTs (Figure 2.6a) is attributed to O-H stretching frequency, originating from the adsorbed water molecules on the amorphous carbon present in the MWCNTs [283]. The two peaks at 1622 and 1381 cm^{-1} are assigned to C=C stretching frequency, which are due to the inherent structure of CNTs. In the FTIR spectrum of O-MWCNTs (Figure 2.6b), there is an additional peak observed at

1719 cm^{-1} due to the C=O stretching frequency, indicating the presence of carboxylic groups created during the oxidation of MWCNTs. The presence of acidic groups such as

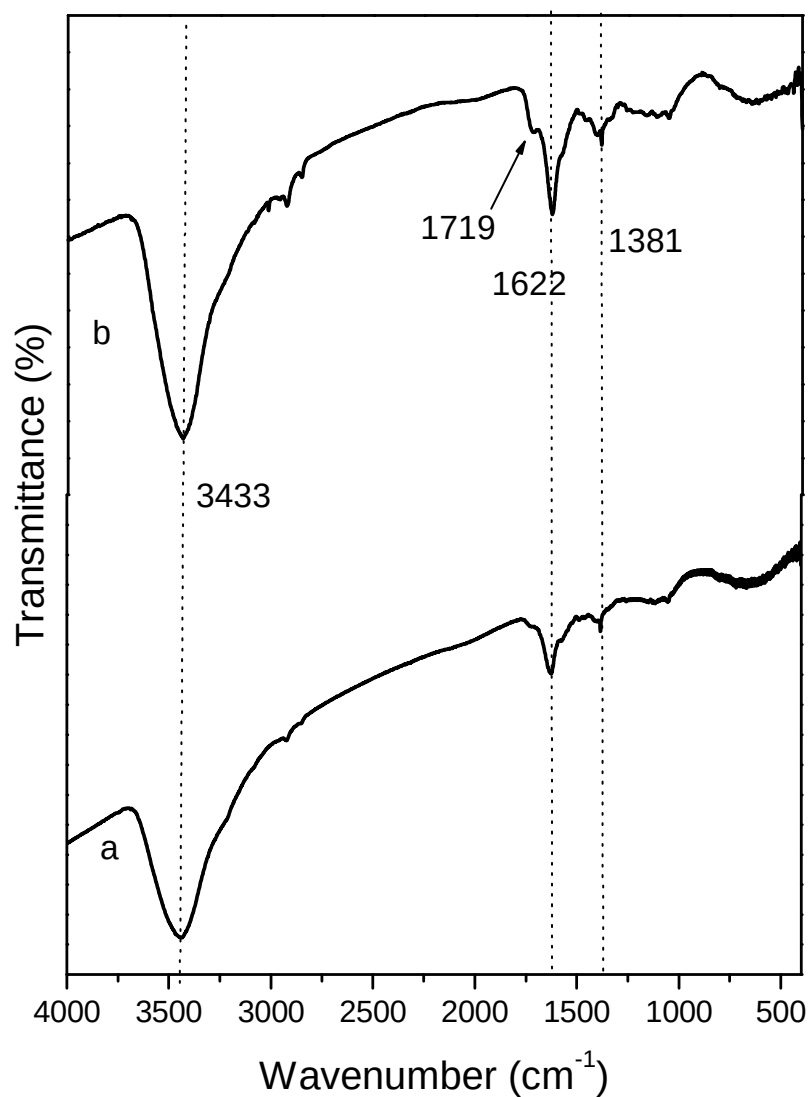


Figure 2.6 : FTIR spectra of (a) MWCNTs and (b) O-MWCNTs.

carboxylic and hydroxylic groups on CNTs is further confirmed by the slight increase in the intensity of the peak around 3433 cm^{-1} (Figure 2.6b) due to O-H stretching frequency.

To further understand the extent of oxidation of MWCNTs and the composition of the final products, XPS analysis was performed. Figure 2.7 shows the XPS general survey spectra of MWCNTs, O-MWCNTs and CPA-MWCNTs. The oxidation of CNTs and the impregnation of CPA on the walls of the oxygenated CNTs are confirmed by the presence of O 1s and Cu 2p peaks, respectively. It was calculated from the XPS

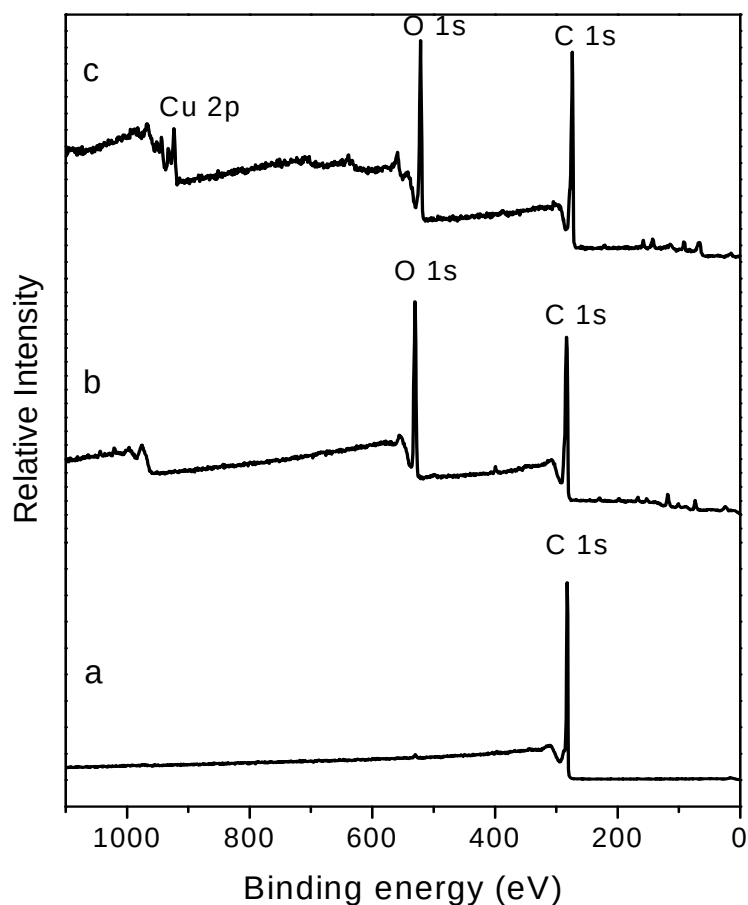


Figure 2.7 : XPS spectra of (a) MWCNTs, (b) O-MWCNTs, (c) CPA-MWCNTs.

spectrum, for O-MWCNTs (Figure 2.7b), and found that there was about 18 % of oxygen content in comparison to 82 % carbon on the surface of O-MWCNTs. These results corroborate the FTIR investigations done on O-MWCNTs, previously.

Figure 2.7c shows the XPS general survey spectrum of calcined CPA-MWCNTs for both reflux method and IR irradiation of CPA impregnated MWCNTs and it clearly shows the characteristic peak Cu 2p for copper, besides O 1s and C 1s peaks. In both the cases we succeed in obtaining the copper and copper oxide nanocrystals from calcined CPA-MWCNTs at different temperatures and in different atmospheres. At this part of the study to be precise we have shown the results of only the CPA impregnated MWCNTs from IR irradiation. CuO nanocrystals decorated MWCNTs (CuO-MWCNTs) were obtained when CPA-MWCNTs were calcined in air at 300 °C, while Cu₂O nanocrystals decorated MWCNTs (Cu₂O-MWCNTs) were observed in nitrogen at 250 °C. In the presence of hydrogen gas Cu nanocrystals decorated MWCNTs (Cu-MWCNTs) were obtained at 150 °C.

The high resolution XPS spectra for Cu 2p core level for all the calcined products recorded in the range of 925 to 970 eV are shown in Figure 2.8. For CuO-MWCNTs, the presence of most intense peak at 934.8 eV, corresponding to the binding energy of Cu 2p_{3/2} along with few satellite peaks in Figure 2.8a is due to the presence of CuO in the composite which agrees well with the literature report [284]. In case of Cu₂O-MWCNTs (Figure 2.8b) the peak at 932.3 eV, corresponding to the binding energy of Cu 2p_{3/2} confirms that the peak is due to the presence of Cu₂O phase [276,284] in the composite. Similarly, in case of Cu-MWCNTs (Figure 2.8c) the peak at 932.8 eV corresponding to the binding energy of Cu 2p_{3/2} is due to Cu phase from the composite [263,285]. The

presence of CuO related peaks in both Figure 2.8b and 2.8c is due to the presence of thin CuO layer on the surface of Cu₂O/Cu in the composites, which is usually observed due to surface passivation [276,284,285].

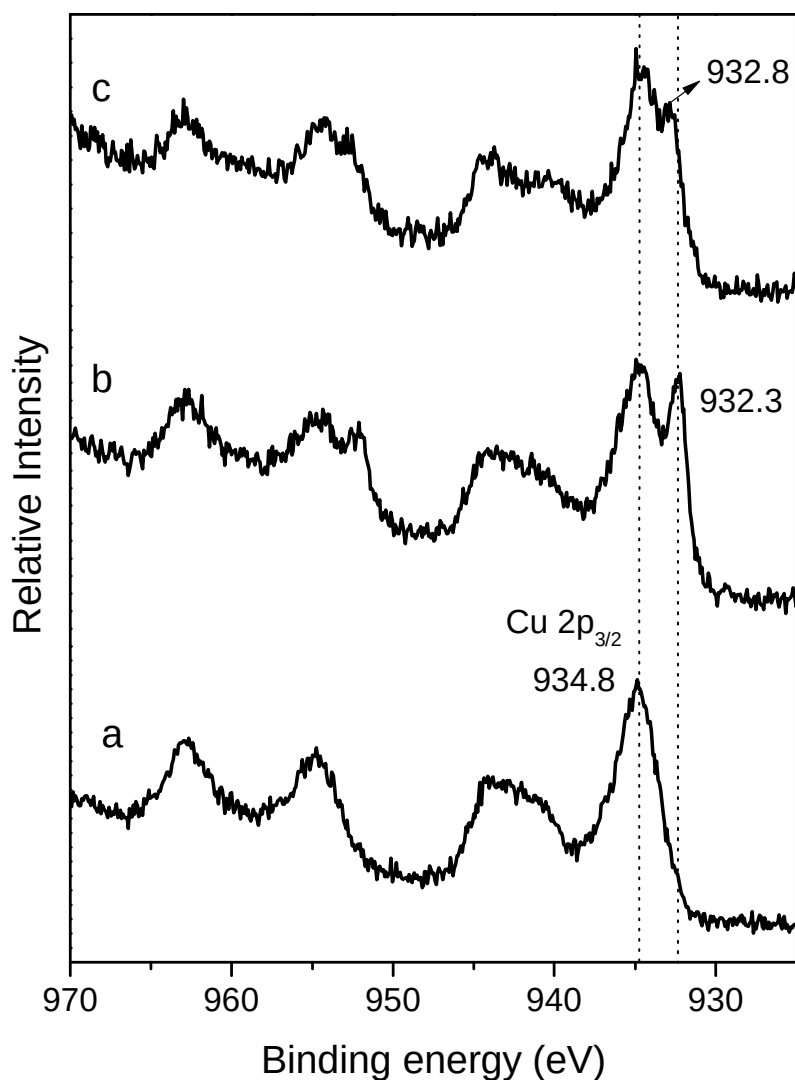


Figure 2.8 : High resolution XPS spectra of core Cu 2p of the calcined products (a) CuO-MWCNTs, (b) Cu₂O-MWCNTs and (c) Cu-MWCNTs.

Since the formation of CuO layer is very thin, it is not detected in the powder X-ray diffraction (PXRD) pattern of both Cu₂O-MWCNT (Figure 2.9d) and Cu-MWCNT (Figure 2.9e) composites. The appearance of the peaks due to Cu₂O (Figure 2.8b) and Cu (Figure 2.8c) in their corresponding composites with such close proximity makes it difficult to distinguish between these two phases. However based on both XPS and PXRD analysis we conclude that the peaks in Figure 2.8b and 2.8c are due to Cu₂O and Cu phases, respectively.

The PXRD patterns of O-MWCNTs and CPA-MWCNTs along with Cu/CuO_x decorated MWCNTs are shown in Figure 2.9. In all the cases, the diffraction peaks at $2\theta = 25.3^\circ$ and 43.1° are due to (002) and (100) *hkl* reflections of the graphitic structure of CNTs. The PXRD pattern of CPA-MWCNTs (Figure 2.9b) is similar to that of O-MWCNTs, even though CPA is impregnated on the MWCNTs. This may be because the impregnated particles of the composites are usually amorphous before calcination [286]. In case of CuO-MWCNTs (Figure 2.9c), Cu₂O-MWCNTs (Figure 2.9d) and Cu-MWCNTs (Figure 2.9e) the PXRD patterns are similar to the literature reports of corresponding phases [287,260,277], indicating that the phases obtained are pure and no impurities or mixed phases are formed. The CuO-MWCNTs (Figure 2.9c) display two diffraction peaks at $2\theta = 35.1^\circ$ and 38.2° with *hkl* reflections (-111) and (111), respectively, corresponding to the monoclinic CuO phase. The three diffraction peaks at 36.1° , 42.2° and 61.1° with *hkl* reflections (111), (200) and (220), respectively, as shown in Figure 2.9d correspond to the cubic phase of Cu₂O nanocrystals in Cu₂O-MWCNTs.

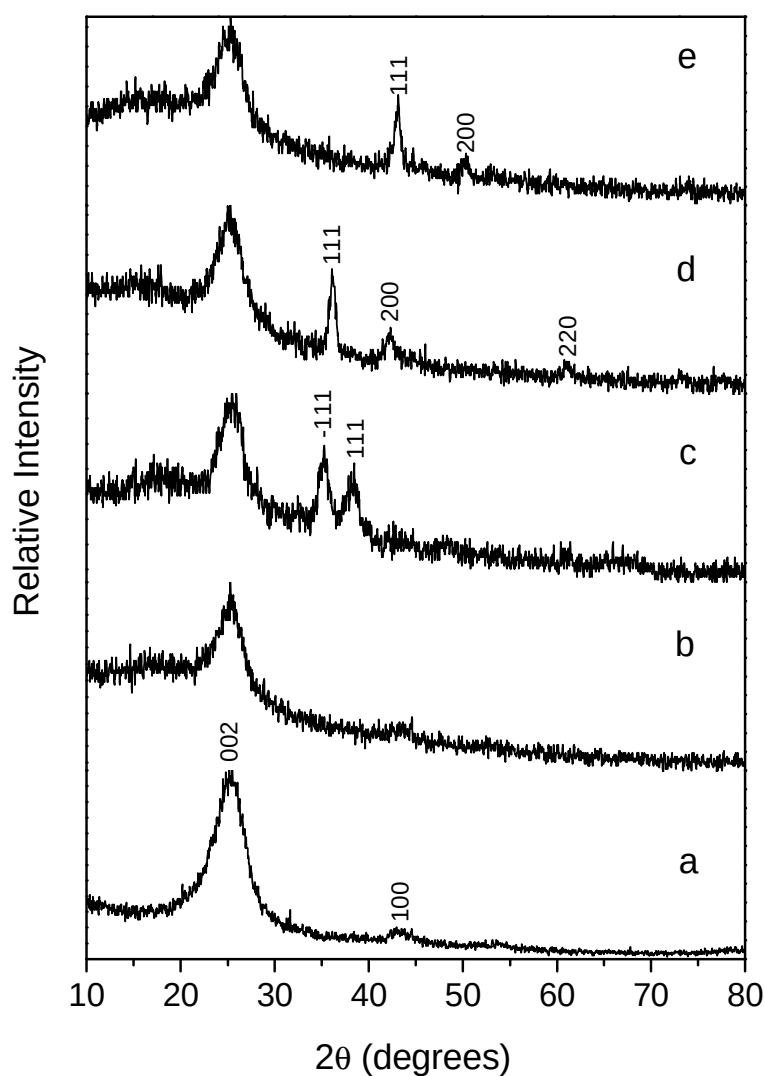


Figure 2.9 : PXRD patterns of (a) O-MWCNTs, (b) CPA-MWCNTs, (c) CuO-MWCNTs, (d) Cu₂O –MWCNTs and (e) Cu-MWCNTs.

The Cu-MWCNTs (Figure 2.9e) show two diffractions peaks at 43.1° and 50.2° with hkl reflections (111) and (200), respectively, corresponding to the cubic phase of Cu. In all the calcined products the reflections due to the CNTs are unchanged indicating that graphitic structure of the CNTs are intact in spite of treating them at different

temperatures in presence of nanocrystals. The particle sizes of CuO-MWCNTs, Cu₂O-MWCNTs and Cu-MWCNTs calculated using Scherrer formula from the most intense peaks of their corresponding PXRD patterns are found to be around 7-8 nm, 11 nm and 14-15 nm, respectively.

To understand the surface morphology of all the calcined products field emission scanning electrosopy (FE-SEM) has been performed. The FE-SEM images of CuO-MWCNTs (Figure 2.10a), Cu₂O-MWCNTs (Figure 2.10b) and Cu-MWCNTs (Figure 2.10c) show the presence of uniformly sized nanoparticles well dispersed on the walls of CNTs, indicating the efficiency of the rather simple route employed for their preparation. The observed size of Cu particles (Figure 2.10c) is found to be bigger than that of other calcined products. The energy dispersive X-ray (EDX) spectral analysis of CPA-MWCNTs and all the calcined samples are shown in Figure 2.11, which indicate that the mass percentage of copper on MWCNTs is around 15 % indicating almost all of the copper loaded initially is decorated on the surface of MWCNTs.

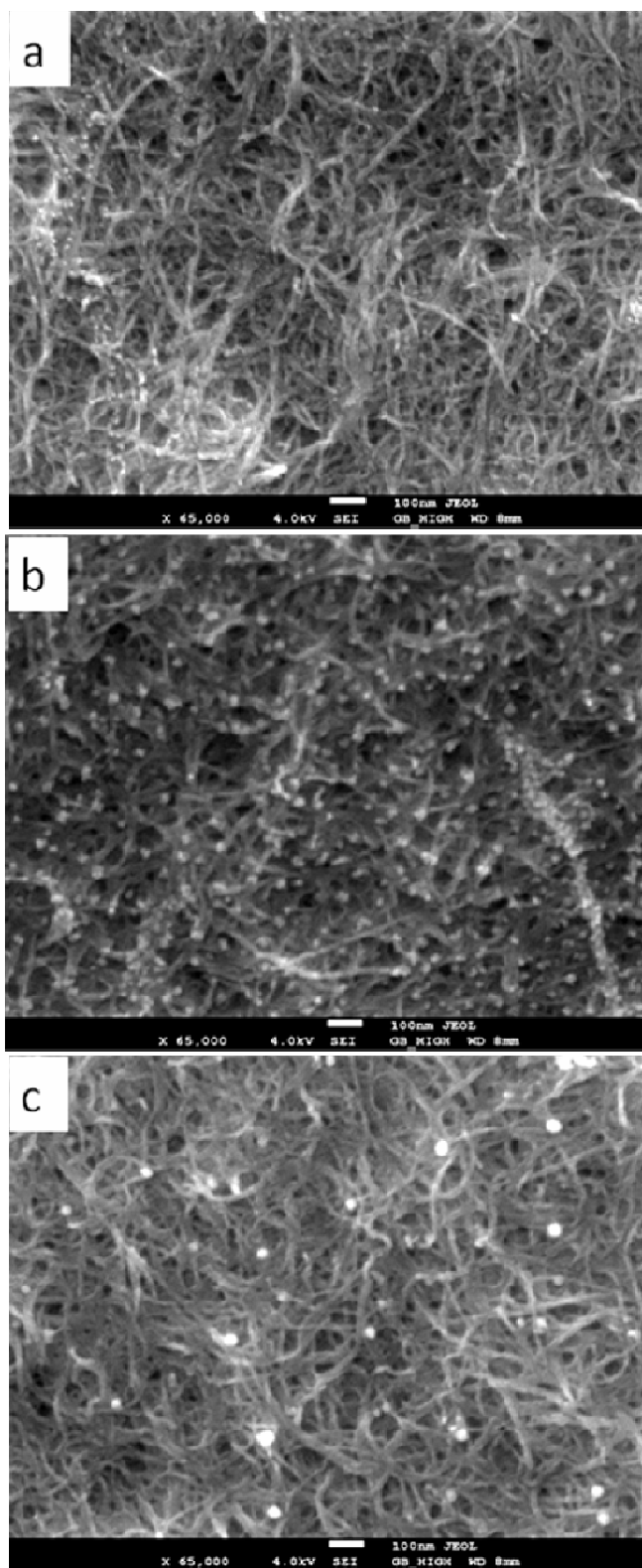


Figure 2.10 : FE-SEM images of (a) CuO-MWCNTs (b) Cu₂O-MWCNTs and (c) Cu-MWCNTs. The scale bar corresponds to 100 nm.

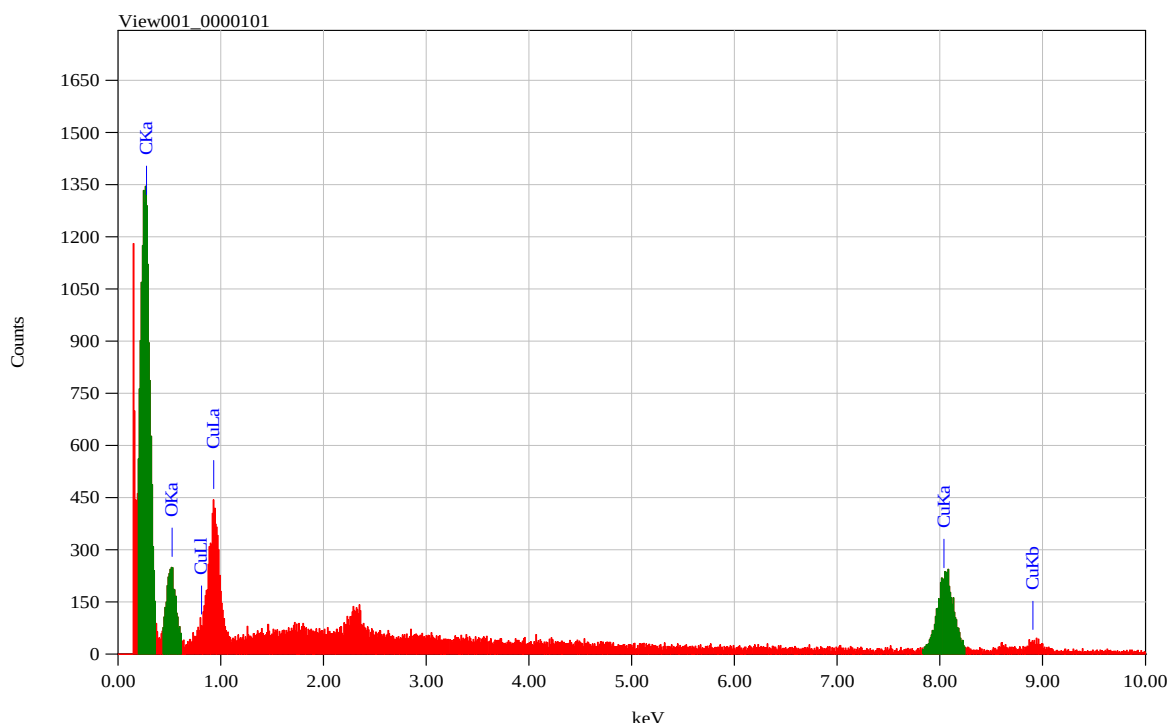


Figure 2.11 : EDX spectrum of CPA-MWCNTs.

The particle sizes of the Cu/CuO_x on the MWCNTs have been investigated using transmission electron microscopy (TEM) as shown in Figure 2.12. Uniformly distributed copper containing nanoparticles on the surface of MWCNTs in CPA-MWCNTs are clearly seen in Figure 2.12a and the estimated sizes of the nanoparticles are in the range of 8-12 nm. The TEM image of CuO-MWCNTs (Figure 2.12b) shows the formation of CuO nanoparticles on the surface of MWCNTs which are indicated by arrows. The particle size is found to be less than 10 nm, which is in agreement with the PXRD data (Figure 2.9c).

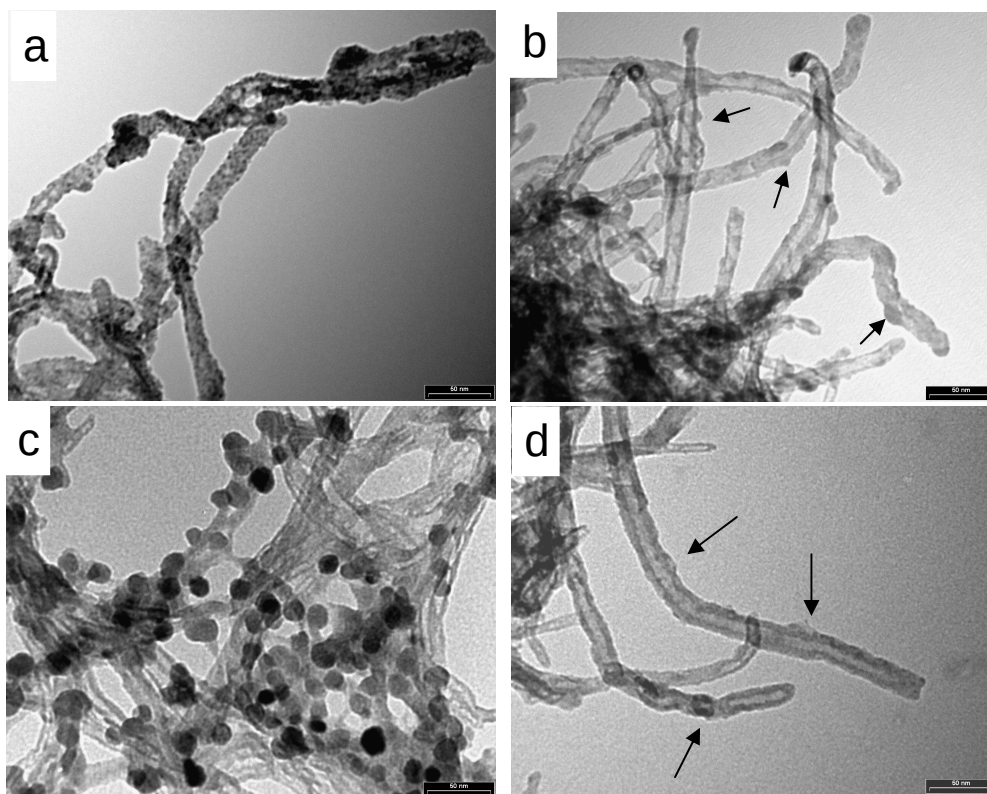


Figure 2.12 : TEM images of (a) CPA-MWCNTs, (b) CuO-MWCNTs, (c) Cu₂O-MWCNTs and (d) Cu-MWCNTs. The scale bar corresponds to 50 nm.

This means that the CPA-MWCNTs are not coalesced while calcining them at 300 °C in air to obtain CuO-MWCNTs and this is considered the optimal calcination temperature to obtain the homogeneous CuO nanocrystals decorated on MWCNTs. Indeed, when CPA-MWCNTs were heated at higher temperatures than the mentioned above, they tend to coalesce and grow to become larger particles. Spherical Cu₂O nanoparticles with uniform size and distribution (in the range of 10 to 15 nm) are observed on the surface of MWCNTs as shown in Figure 2.12c for the Cu₂O-MWCNTs. These particles are seen to be well resolved and this is in good accordance with PXRD

data. In case of Cu-MWCNTs (Figure 2.12d) isolated Cu nanoparticles are seen with the particle sizes of 10 to 15 nm. These results fully corroborate the investigations made using FE-SEM.

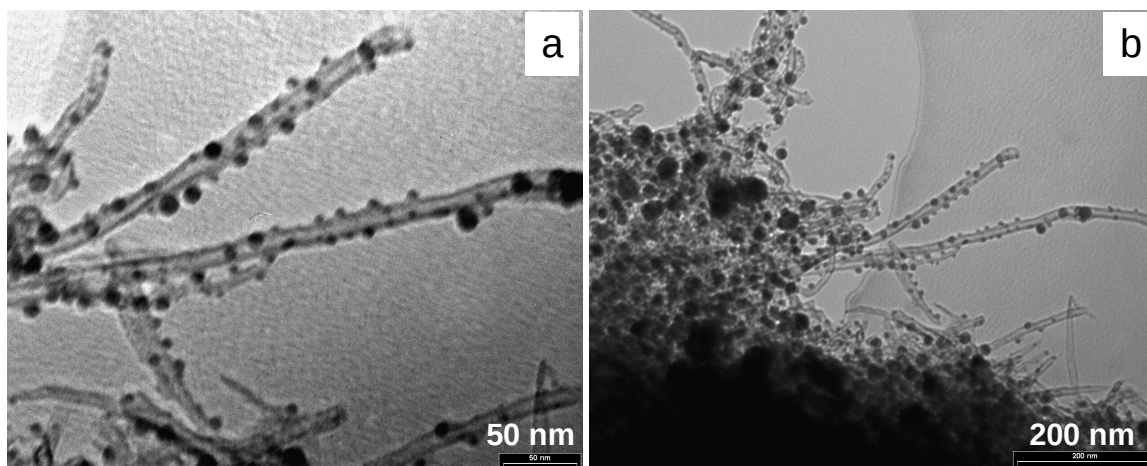


Figure 2.13 : TEM images of CPA-MWCNTs by reflux method.

Figure 2.13 depicts the TEM images of CPA impregnated MWCNTs by reflux method for 12 hours. It can be clearly seen that CPA-MWCNTs having small size particles are well decorated on the outer surface of the tubes as shown in Figures 2.13a and 2.13b. However, some particles are quite large and isolated. There is a high degree of spheroid particles observed, despite the difference in their sizes.

The thermal decomposition patterns of MWCNTs, O-MWCNTs, CPA and CPA-MWCNTs recorded in nitrogen by thermogravimetric analysis (TGA) are shown in Figure 2.14. In case of MWCNTs (Figure 2.14a) it is clearly seen that the CNTs slowly start degrading at a temperature around 650 °C and the decomposition is incomplete in the temperature range studied. In the case of O- MWCNTs (Figure 2.14b), the weight

loss was observed in several steps till 750 °C and further, with the total weight loss of about 30 %. First stage of weight loss observed upto a temperature of 150 °C corresponds to the removal of the adsorbed water.

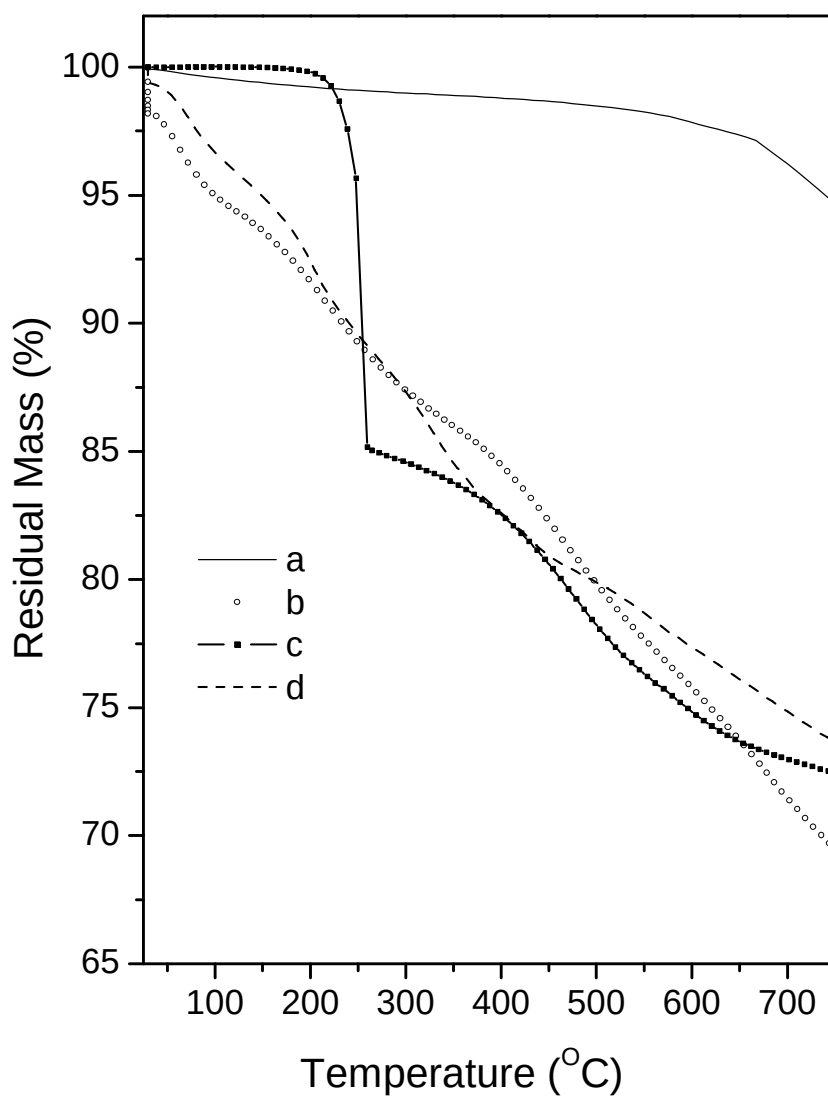


Figure 2.14 : TGA of (a) MWCNTs, (b) O-MWCNTs, (c) CPA and (d) CPA-MWCNTs in nitrogen.

The second stage weight loss observed in the range of 150 to 350 °C can be ascribed to the decarboxylation due to the carboxylic groups present on the walls of MWCNTs. The weight loss in the range between 350 °C and 500 °C can be attributed to the elimination of hydroxyl functionalities present on the surface of MWCNTs. At temperatures higher than 500 °C the thermal degradation correspond to the thermal oxidation of the remaining amorphous carbon [211]. The thermogram of CPA (Figure 2.14c) shows two stages of weight loss, one at around 230 °C having 15 % weight loss, may correspond to the loss of the acetylene moiety, and the second slow decomposition stage above 405 °C with 10 % weight loss. The TGA of CPA-MWCNTs (Figure 2.14d) shows the combined properties of those of both CPA and O-MWCNTs. In general CPA-MWCNTs shows a multi stage weight loss similar to O-MWCNTs, however the total weight loss % is less due to the presence of organic moiety. The fact that major weight loss was observed at around 230 °C in case of CPA (Figure 2.14c) and the corresponding weight loss in CPA-MWCNTs composite (Figure 2.14d) at around 250 °C, shows that the CPA moiety in the composite is decomposed to form Cu₂O nanocrystals on the surface of MWCNTs (Figure 2.9d), which is in line with the PXRD analysis discussed earlier.

Figure 2.15 shows the thermal decomposition patterns of MWCNTs, O-MWCNTs, CPA and CPA-MWCNTs recorded in air. In general, it is evident that the thermogravimetric patterns of the samples recorded in air (Figure 2.15) are much different compared to the ones recorded in nitrogen (Figure 2.14). In case of MWCNTs (Figure 2.15a) the degradation of CNTs starts at around 450 °C which is followed by a rapid decomposition stage. At around 650 °C most of the decomposition is complete with about 81 % weight loss. The decomposition of O-MWCNTs (Figure 2.14b) follows

a multistage pattern similar to the one seen previously in nitrogen atmosphere. The initial weight loss till 150 °C is due to the adsorbed water.

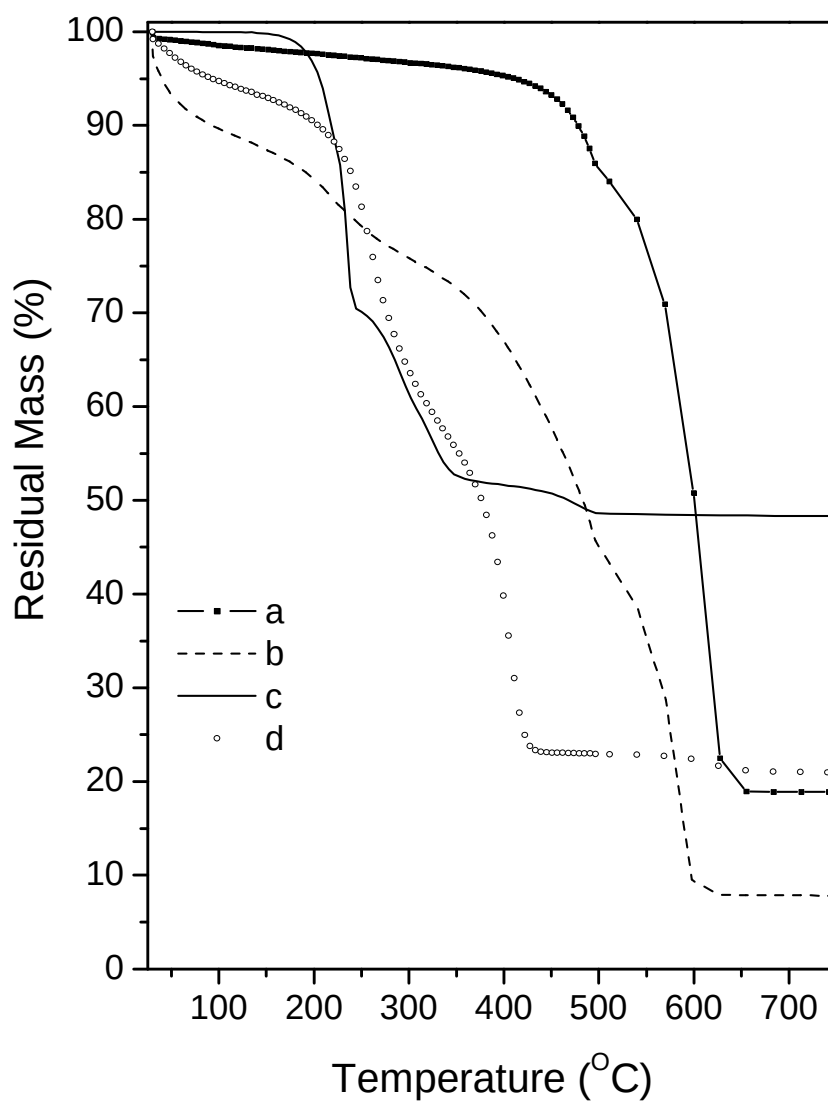


Figure 2.15 : TGA of (a) MWCNTs, (b) O-MWCNTs, (c) CPA and (d) CPA-MWCNTs in air.

The decarboxylation of the carboxylic groups from the surface of the MWCNTs proceeds till 350 °C, followed by the dehydroxylation step till 530 °C. The decomposition

almost completes at around 630 °C with the oxidation of remaining amorphous carbon [211] with a total weight loss of 92 %. The decomposition pattern of CPA (Figure 2.15c) in air is similar to the one recorded in nitrogen (Figure 2.14c) except that the decomposition completes around 500 °C with total weight loss around 50 %. In case of CPA-MWCNTs (Figure 2.15d), unlike in nitrogen atmosphere, the decomposition in air is almost completed at around 650 °C with the total weight loss of 79 %. The TGA further corroborates with PXRD data for the formation of CuO nanocrystals on the surface of MWCNTs (Figure 2.9c).

The simple procedure employed without the addition of any external agents to prepare such materials indicates the effectiveness of this method. Though it is difficult to clearly understand the mechanism for the controlled decoration of Cu/CuO_x nanocrystals on MWCNTs, we can largely illustrate the reasons for the same. The surface modification of MWCNTs by chemical functionalization via acid treatment created sufficient anchoring sites for the impregnation of CPA on MWCNTs. The change in color of CPA from yellow to green observed during their addition to O-MWCNTs, could possibly due to the redox reaction taking place at the interface of CPA and O-MWCNTs. In general, IR irradiation raises the temperature of the MWCNTs in solution facilitated by the photothermal conversion of the radiation by CNTs. Only when the suspension was IR irradiated the impregnation of CPA on MWCNTs reaches completion, leaving behind the colorless supernatant liquid while the black residue was settled down. The complete disappearance of the green color in the supernatant was taken as the indication for the completion of the impregnation process. It can be said that the elevation of temperature generated by IR irradiation on MWCNTs gave impetus to cross the activation energy

barrier leading to the effective formation of CPA-MWCNTs. Our attempts to carry out the experiment in the absence of IR irradiation did not result in complete removal of the green color from the supernatant even after prolonged stirring indicating that the impregnation process was not complete. The impregnation in the presence of IR irradiation seems to be the key step for the homogeneous decoration of CPA on MWCNTs.

2.4. Conclusion

Copper, cuprous oxide and cupric oxide nanocrystals were uniformly decorated on oxygen-functionalized multi-walled carbon nanotubes and their structure and morphology were investigated by different techniques. Two different impregnation methods, namely, reflux method and IR irradiation method were employed to impregnate CPA on MWCNTs. IR irradiation method was found to be more simple and efficient to impregnate copper containing nanoparticles on the MWCNTs. Photo-absorption and photothermal properties of CNTs in IR region played an important role on the homogeneous impregnation of CPA on MWCNTs. The calcination of the products at different atmospheres and suitable temperatures resulted in homogeneous decoration of Cu/CuO_x nanocrystals on the surface of MWCNTs. The as decorated Cu/CuO_x nanoparticles could be used in various potential applications such as catalysis and nanodevices.

Chapter 3: Decoration of multi-walled carbon nanotubes with nickel and nickel oxide nanocrystals

Chapter 3: Decoration of multi-walled carbon nanotubes with nickel and nickel oxide nanocrystals

3.1. Introduction

Owing to their large chemically active surface and stability at high temperatures carbon nanotubes have been used as a support material for the dispersion and stabilization of metal and metal oxide nanocrystals [288]. Nanomaterials and especially metal nanoparticles [289] have emerged as a new class of compounds that are particularly interesting for materials science due to their unique electronic, optical, magnetic and catalytic properties. Importantly, these features differ from those of the bulk materials [290] and depend on the size and shape of the nanoparticles. Fabrication of CNT-nanocrystal heterostructures with desired size, shape, morphology, crystallinity and chemical composition remains an active area of study. In this regard, our interest has been on decorating transition metals such as nickel on MWCNTs, as they have been considered for use in many applications such as fuel cells, catalysis, rechargeable batteries, super capacitors, and hydrogen production [291-294].

Many researchers have attempted to produce CNT-Ni/NiO nanoparticle heterostructures. However, the difficulty of obtaining a uniform coating on CNTs imposes limitations. Sometimes prior to the decoration of these nanoparticles, the CNTs are modified with polymer to facilitate the process [295,296]. For example, Tang et al [295] reports the distribution of Ni nanoparticles on poly (acrylic acid) modified MWCNTs for hydrogenation of α , β -unsaturated aldehyde. Similarly, homogeneous electrodeposition of Ni nanoparticles on 4-nitroaniline radical monolayer grafted on MWCNT was reported by Jin et al [296]. There have been reports of employing stringent conditions such as microwave irradiation

[297], hydrothermal [298], solvothermal [299], chemical vapor deposition [300], electrophoretic deposition [301] etc for the uniform distribution of Ni/NiO on CNTs.

Keeping in mind the potential applications of the CNT based composites with metal/metal oxides such as Ni/NiO and the complexity involved in achieving their uniform distribution we report a simple and convenient method for the preparation of nickel and nickel oxide nanoparticles well dispersed on MWCNTs. Our purpose is to establish a novel and a low cost alternative route for coating the external surface of MWCNTs with nano-size metal and metal oxide nanoparticles of nickel for potential applications. In this context, nickel acetylacetonate (NAA) was used, for the first time, as the precursor to decorate on MWCNTs. The weight percentage ratio of NAA to CNTs, impregnation time, reaction temperature and atmosphere are selectively controlled to obtain the amount, particle size and homogeneous distribution of nickel/nickel oxide particles on CNTs.

3.2. Preparation of NAA on MWCNTs

As we have seen in the previous chapters, before impregnating the MWCNTs, one has to oxidize their surface to create active sites. As a first step, we have used the same method as used in Chapter 2 to oxidize the MWCNTs and then employed them for the impregnation of NAA on MWCNTs.

3.2.1. Impregnation of NAA on MWCNTs

The O-MWCNTs were then impregnated by a modified reflux method than it was done in the earlier case with copper in Chapter 2. 100 mg of O-MWCNTs was sonicated in 50 ml of xylene until (~ 5 min) a good suspension is obtained. Similarly suspension of NAA in xylene was obtained by sonicating 77.2 mg of NAA (15 wt % of Ni) in 30 ml of xylene for the same amount of time. While the suspensions were still under ultrasonication, NAA in xylene was added to the O-MWCNTs in xylene suspension. The mixture was further

sonicated for a few minutes. The mixture was then refluxed under magnetic stirring for 4 hours and cooled to room temperature, filtered and the residue was washed three times with acetone. The NAA impregnated MWCNTs thus obtained, designated as NAA-MWCNTs hereafter, were finally dried at room temperature under vacuum. The experimental setup is similar to the one shown in Figure 2.1 in Chapter 2. The schematic presentation of the impregnation of NAA on O-MWCNTs is shown in Figure 3.

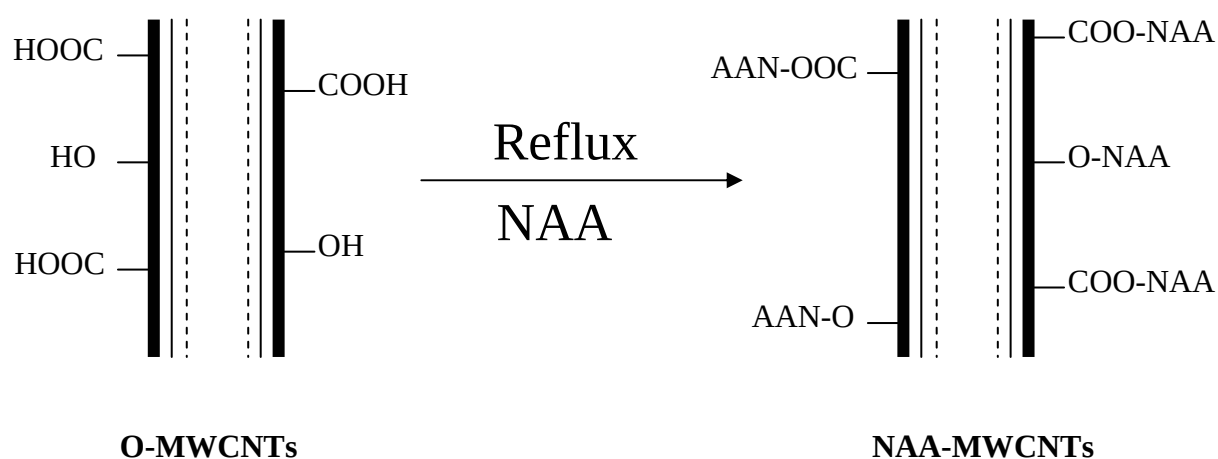


Figure 3 : Schematic diagram of NAA-MWCNTs

3.2.2. Calcination of NAA-MWCNTs

The NAA-MWCNTs was then calcined in a tubular furnace equipped with quartz tube pre- heated to a desired temperature under the continuous flow of either nitrogen/ hydrogen at a flow rate of 300 μL per min. In a typical experiment, 20 mg of NAA-MWCNTs was calcined at 400 $^{\circ}\text{C}$ temperature for 1 hr under continuous flow of hydrogen and 3 hrs in nitrogen, respectively. The schematic diagram of calcination of NAA-MWCNTs to obtain Ni and NiO nanocrystals on MWCNTs is shown in Figure 3.1.

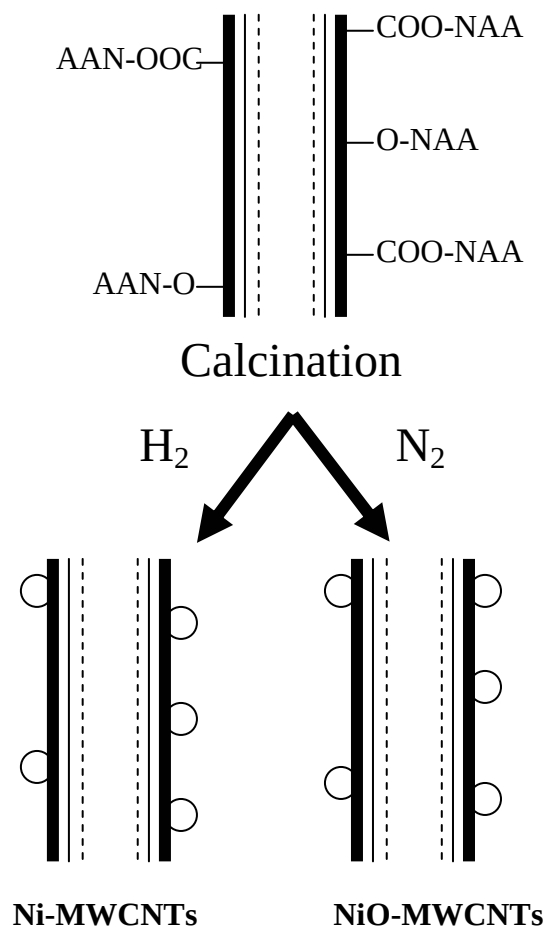


Figure 3.1 : Schematic representation of production of Ni-MWCNTs and NiO-MWCNTs

3.3. Results and discussion

The thin MWCNTs were oxidized to create active sites to anchor nanoparticles on their walls and were investigated by FTIR. The FTIR characterization was discussed in the previous chapter in detail and hence will not be discussed here. The sample was then further characterized by PXRD to understand the crystalline phase purity of the material. The PXRD patterns of the O-MWCNTs, NAA-MWCNTs along with the calcined products of NAA-MWCNTs in hydrogen and nitrogen atmosphere are shown in Figure 3.2.

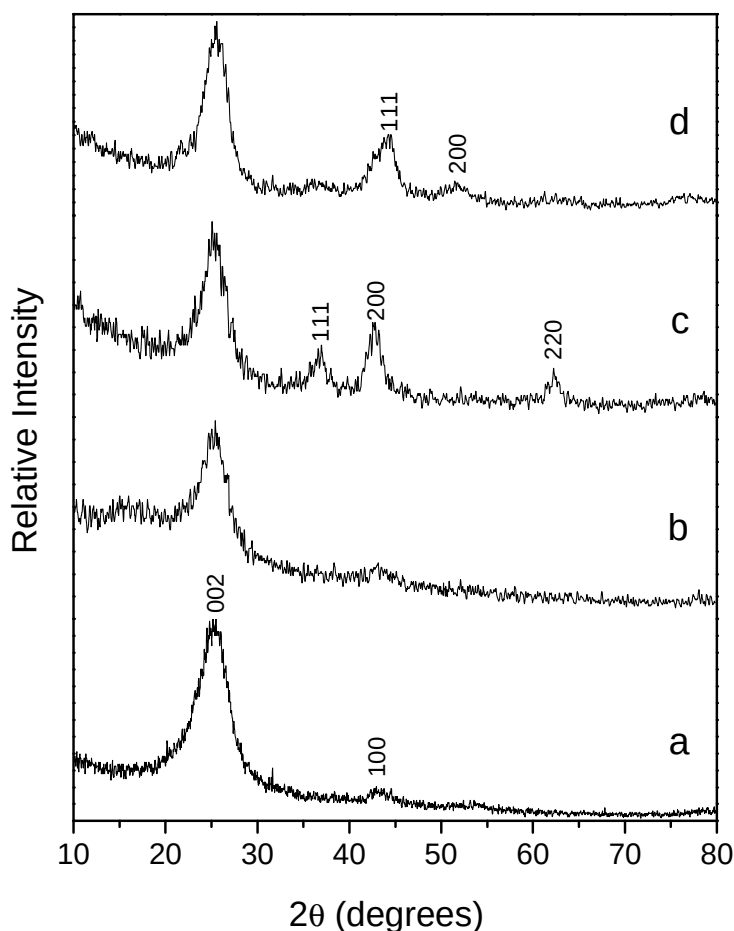


Figure 3.2 : PXRD patterns of (a) O-MWCNTs, (b) NAA-MWCNTs, (c) NiO-MWCNTs and (d) Ni-MWCNTs.

The O-MWCNTs (Figure 3.2a) display two distinct diffraction peaks for graphitic structure at $2\theta = 26^\circ$ and 43° corresponding to the hkl reflections (002) and (100), respectively. They are the characteristic peaks for the CNTs, which indicate that even after the vigorous treatment of CNTs in concentrated acids the graphitic structure remained mainly intact. PXRD pattern of the NAA impregnated MWCNTs (Figure 3.2b) is similar to that of the O-MWCNTs. This may be due to the amorphous nature of the impregnated NAA before calcinations [286]. Figure 3.2c reveals the formation of the phase pure NiO nanocrystals, having three distinct diffraction peaks at $2\theta = 36.9^\circ$, 42.8° and 62.3° corresponding to the hkl

reflections (111), (200) and (220), on the surface of MWCNTs in the NiO-MWCNT composites [296]. It was obtained in the presence of nitrogen atmosphere at 400 °C. In the presence of hydrogen atmosphere at 400 °C, the two distinct diffraction peaks were obtained at $2\theta = 44.2^\circ$ and 51.7° (Figure 3.2d) corresponding to the *hkl* reflections (111) and (200), respectively, indicate the formation of phase pure Ni nanocrystals in the Ni-MWCNT composites [296]. Both the composites show MWCNT peaks in spite of them being treated at high temperatures in the presence of metal/metal oxide nanocrystals, which show that CNT structure is kept intact. In all the cases, no other peaks than nickel and nickel oxide are seen, indicating that there are no impurities formed during the composite formation.

To further understand the extent of oxidation of MWCNTs and the composition of the final products, XPS was performed. Figure 3.3 shows the XPS general survey spectra of purified MWCNTs, O-MWCNTs and NAA-MWCNTs. The oxidation of CNTs and the impregnation of NAA on the walls of the oxygenated CNTs are confirmed by the presence of the O 1s (Figure 3.3b) and Ni 2p peaks (Figure 3.3c). It was calculated from the XPS spectrum, for O-MWCNTs (Figure 3.3b), and found that there was about 18 % of oxygen in comparison to 82 % carbon on the surface of O-MWCNTs. These results corroborate the FTIR investigations done on O-MWCNTs, previously. The high resolution XPS spectra for Ni 2p core level for the calcined products recorded in the range of 840 to 890 eV are shown in Figure 3.4. For NiO-MWCNTs (Figure 3.4a), the presence of most intense peak at 856 eV, corresponding to the binding energy of Ni 2p_{3/2} along with a intense satellite peaks at the higher binding energy side of the main peaks is due to the presence of NiO in the composite which agrees well with the literature report [302,303].

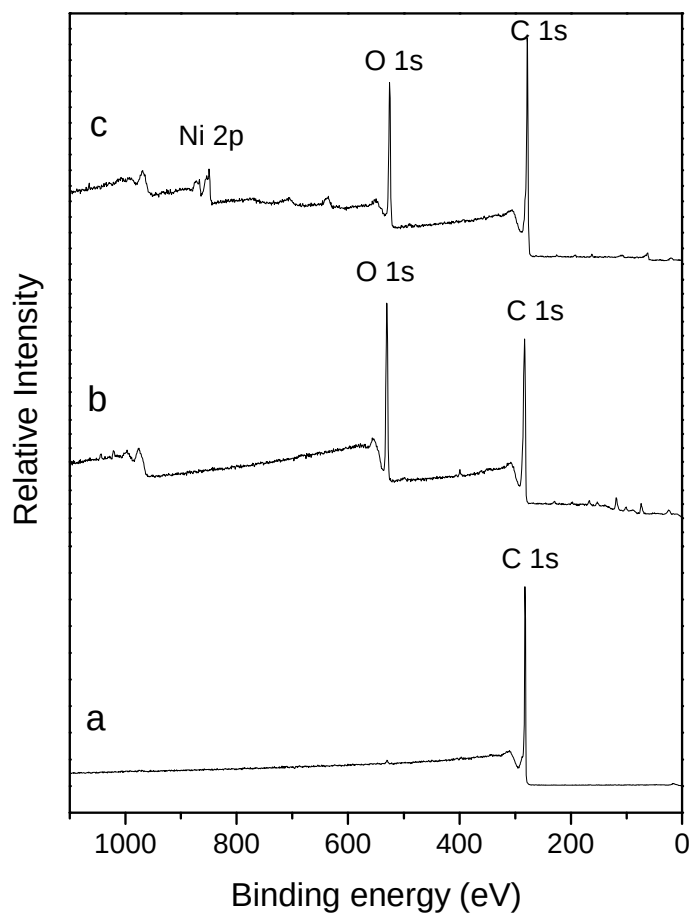


Figure 3.3 : XPS spectra of (a) Pristine MWCNTs, (b) O-MWCNTs and (c) NAA-MWCNTs.

The presence of NiO related peaks in Figure 3.4b is due to the presence of thin NiO layer on the surface of Ni in the composites, which is usually observed due to surface passivation [304]. Since the formation of NiO layer is very thin, it is not detected in the PXRD pattern of Ni-MWCNT (Figure 3.2d) composite.

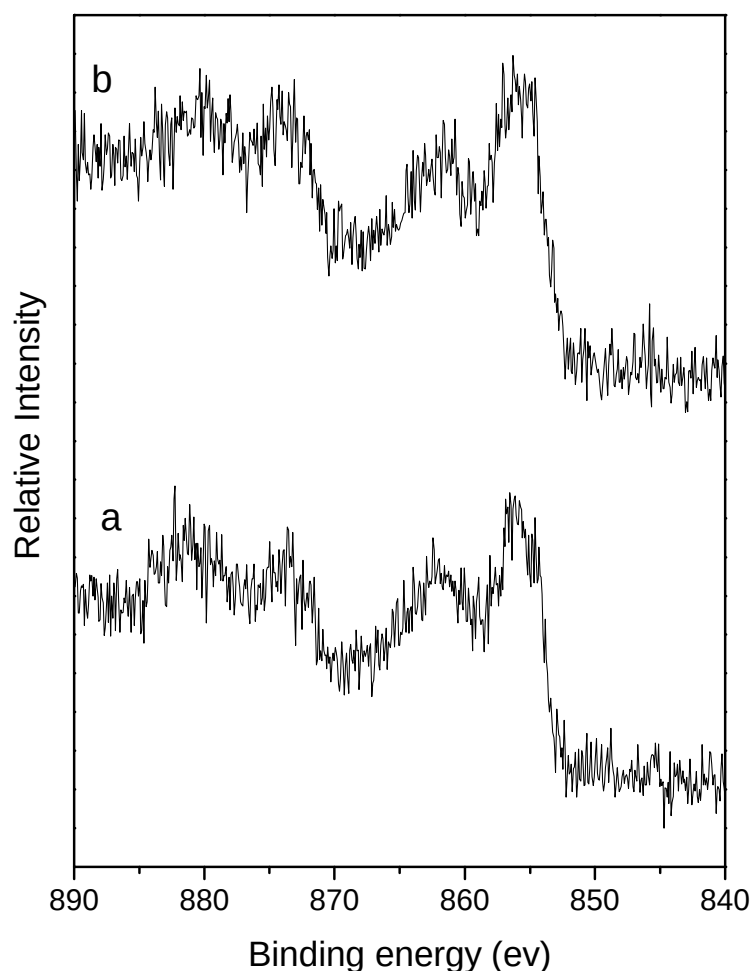


Figure 3.4 : High resolution XPS spectra of core Ni 2p of the calcined products (a) NiO-MWCNTs and (b) Ni-MWCNTs.

The morphology of the composites was investigated by FE-SEM and TEM analysis as shown in Figure 3.5. Figures 3.5a, 3.5b and 3.5c are the FE-SEM images of NAA-MWCNTs, Ni-MWCNTs and NiO-MWCNTs, respectively, which reveal the undamaged structure of MWCNTs in the composites. In both FE-SEM and TEM images of NAA-MWCNTs (Figures 3.5a and a1) the impregnated NAA species are not well-formed. The distinct and uniformly spread nickel nanocrystals on the external surface of MWCNTs in Figure 3.5b demonstrate the effectiveness of the new approach of calcining the NAA-MWCNTs at 400 °C in the

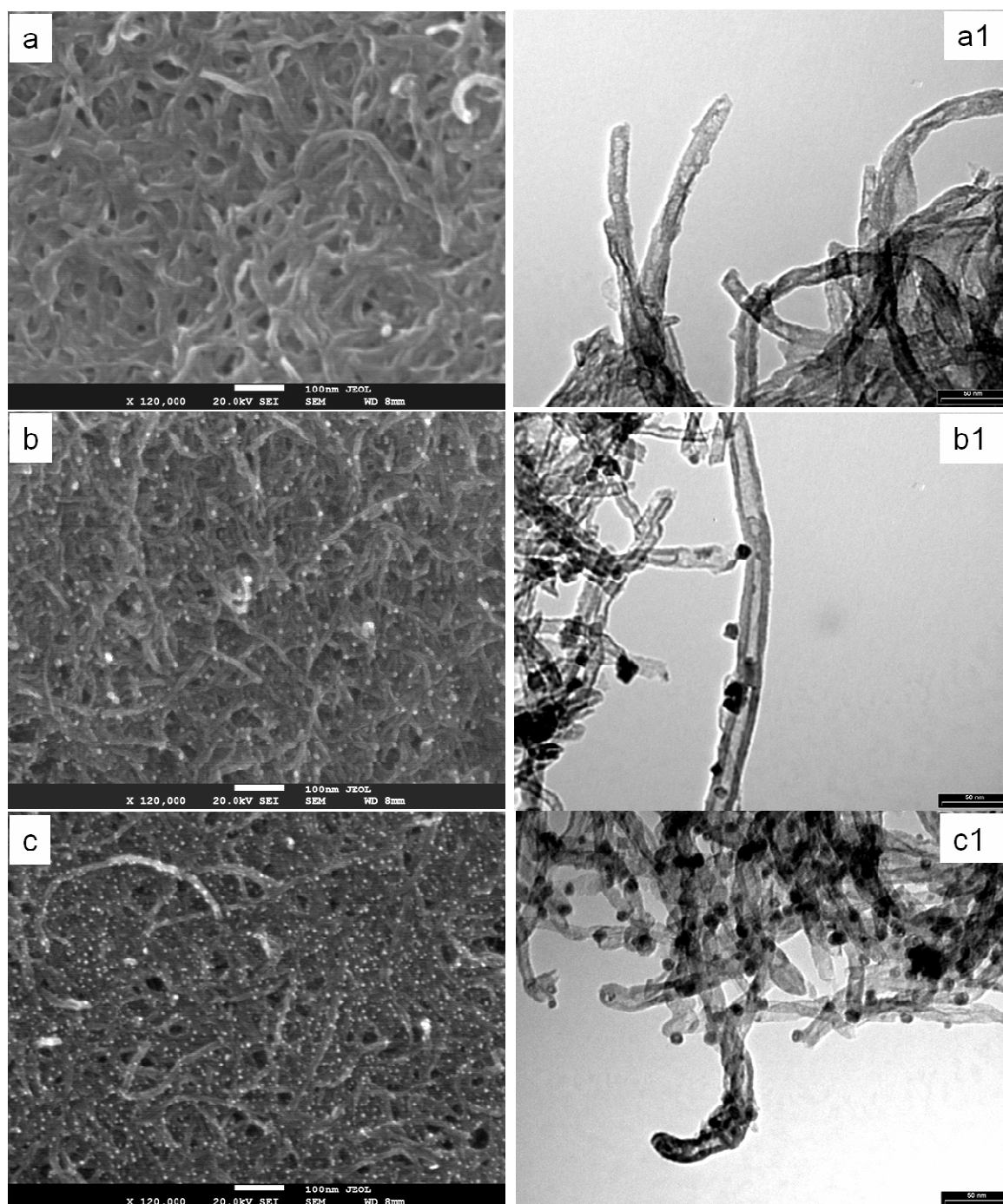


Figure 3.5 : FE-SEM images of (a) NAA-MWCNTs (b) Ni-MWCNTs and (c) NiO-MWCNTs. TEM images of (a1) NAA-MWCNTs, (b) Ni-MWCNTs and (c) NiO-MWCNTs.

presence of hydrogen to form Ni-MWCNTs. In case of NiO-MWCNTs (Figure 3.5c), although the size of the particles is similar, the particle distribution is more dense compared to Ni-MWCNTs (Figure 3.5b). TEM images of NAA-MWCNTs, Ni-MWCNTs and NiO-

MWCNTs are shown in Figure 3.5a1, b1 and c1, respectively. The particle sizes of nickel in Ni-MWCNTs as seen in Figure 3.5b1 are in the range of 13-15 nm, while in the case of NiO-MWCNTs the nickel oxide particles are in the range of 8-10 nm. The presence of the nanoparticles only on the surface of the nanotubes indicates that the nanoparticles are strongly anchored onto their surface. The compositional purity of the impregnated and the calcined composites were investigated by EDX (Figure 3.6) and found that only nickel is present apart from carbon and oxygen, which shows that there are no impurities in the product. In all the cases average nickel mass percentage was in the range of 10-12 % indicating that most of the NAA utilized for the impregnation process is incorporated in the final products.

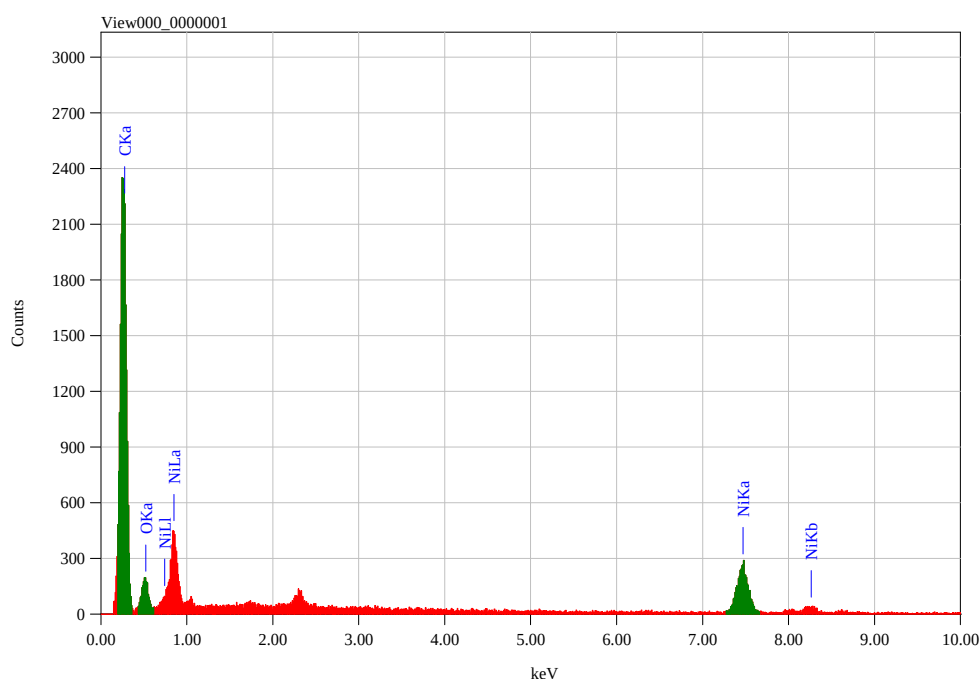


Figure 3.6 : EDX spectrum of NAA-MWCNTs.

The thermal decomposition behavior of all the samples was investigated by TGA in a flowing nitrogen atmosphere is shown in Figure 3.7. Figures 3.7a and b present the TGA patterns of pristine and O-MWCNTs, respectively. In the case of pristine MWCNTs it is clearly seen that the CNTs slowly start degrading at a temperature around 650 °C. Whereas, in

the case of O-MWCNTs, the weight loss was observed in several steps starting from 100 °C up to 750 °C and further. The total weight loss observed was about 30% for O-MWCNTs. First stage of weight loss was observed up to a temperature of 150 °C, corresponding to the evaporation of the adsorbed water. The second stage from 150 to 350 °C is ascribed to the decarboxylation due to the carboxylic groups present on the walls of CNT. The weight loss in the range between 350 °C and 500 °C can be explained by the elimination of hydroxyl functionalities present on the surface of MWCNTs.

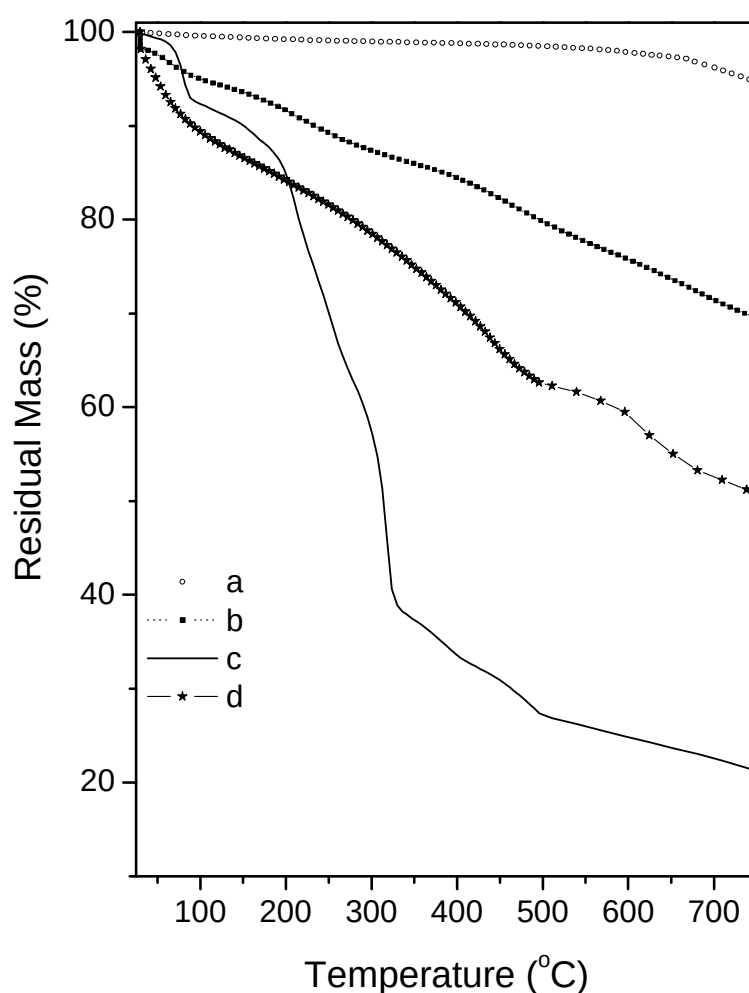


Figure 3.7 : TGA curves of (a) Pristine MWCNTs, (b) O-MWCNTs and (c) NAA (d) NAA-MWCNTs in nitrogen.

For the temperatures higher than 500 °C the thermal degradation corresponds to the thermal oxidation of the remaining disordered carbon [211]. Figure 3.7c represents the thermograms of pure NAA, which exhibits mainly two stages of degradation on weight loss with a minimum at 289 °C having 40% weight loss and the other at 420 °C having 28% weight loss [305]. Small degradation on weight loss observed at 179 °C.

Since, major weight loss was observed around 420 °C, possibly the NAA is decomposed to form NiO at this stage. Hence NAA-MWCNTs were calcined around 400 °C in nitrogen atmosphere which gave rise to NiO-MWCNT composites as evidenced by PXRD pattern shown above (Figure 3.2c). However, as shown in Figure 3.7d, a slight difference in weight loss pattern was observed for the TGA of NAA-MWCNTs compared to the O-MWCNTs. Here too we see that the decomposition pattern of NAA-MWCNTs is similar to that of NAA except that the weight loss percentage is different due to the presence of CNTs in the composites.

Possible formation mechanism of nickel and nickel oxide decorated CNTs can be explained as represented in Figure 3.8. This work demonstrates the feasibility of decorating CNTs with nickel and nickel oxide nanocrystals via the calcination of impregnated NAA precursors in xylene solvent in hydrogen and nitrogen atmospheres, respectively. The CNT-coating mechanism, as schematically illustrated, may be closely associated with the wetting of oxygen-functionalized CNT surfaces with the precursor NAA. We believe that refluxing of NAA in xylene played a pivotal role in decorating CNTs with NAA as elevated temperature may have given impetus for the NAA to anchor on the defect sites created during the acid treatment of MWCNTs.

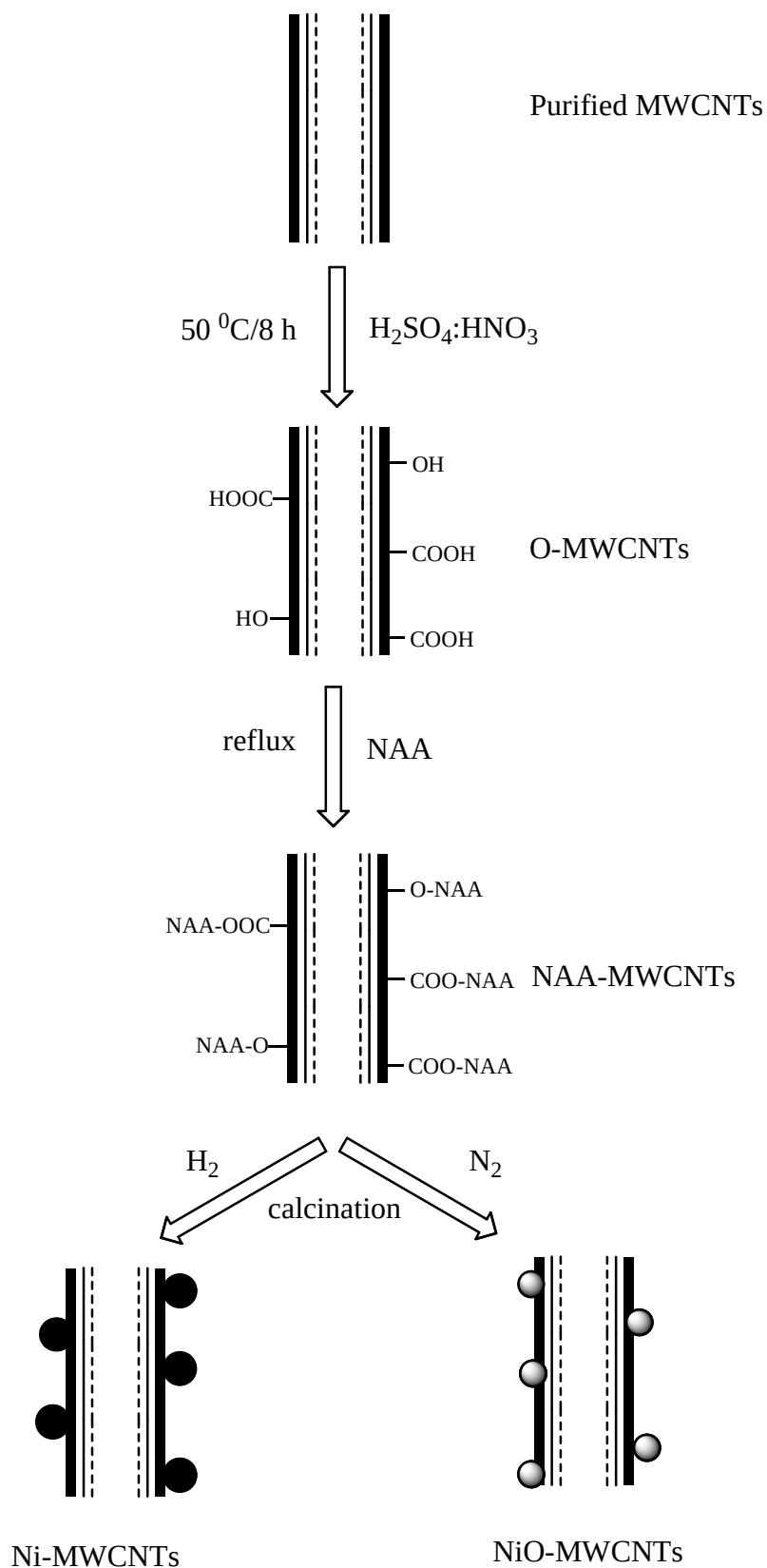


Figure 3.8 : Schematic illustration of the various steps involved to obtain the final products.

It is well known that chemical oxidation using sulfuric and nitric acid mixture can create various functional groups, such as $-\text{COOH}$, $-\text{OH}$ and $-\text{C}=\text{O}$ at the defective sites on the nanotubes wall. They act as active sites for metal cations to attach during the impregnation process. When, the as obtained NAA-MWCNTs were calcined at certain temperatures in suitable atmospheres such as hydrogen and nitrogen led to the decomposition of the NAA trapped on the surfaces of CNTs and the formation of respective metal and metal oxide nanocrystals. As a consequence, CNTs were readily decorated with uniform nickel and nickel oxide nanocrystals under suitable conditions. The final products were confirmed by different techniques used for the characterization.

3.4. Conclusion

A facile and alternative method for the synthesis of nickel and nickel oxide nanoparticles decorated on MWCNTs was described using NAA for the first time. The metal-carbon nanotube composites were synthesized by impregnation of carbon nanotubes with NAA metal precursor followed by calcination at suitable temperatures and atmospheres. A chemical impregnation led to the homogeneously dispersed nickel and nickel oxide nanocrystals onto to the surface of MWCNTs, and the particles were found to possess an average size of 8-15 nm, which can be controlled by adjusting preparation parameters. This process implied a simple route to prepare Ni and NiO nanocrystals support on CNTs through tuning the experimental conditions. Both the decorated nanocrystals on CNTs have potential applications in heterogeneous catalysis and semiconductor industries.

Chapter 4: Incorporation of multi-walled carbon nanotubes into nickel matrices

Chapter 4: Incorporation of multi-walled carbon nanotubes into nickel matrices

4.1. Introduction

The development of advanced technologies in the aeronautics, space and energy sectors requires high performance materials with excellent mechanical properties, high thermal conductivity and good wear resistance. The combination of high strength, stiffness, aspect ratio and flexibility make CNTs ideal reinforcement materials for metals and alloys. Moreover, the excellent thermal and electrical conductivities of CNTs facilitate development of novel functional composites for advanced engineering applications. It is also expected that carbon nanotubes with superior flexibility can overcome the difficulties encountered by ceramic fillers and carbon fibers. Thus, multifunctional composites with improved mechanical, electrical and thermal properties can be prepared by adding low level content of carbon nanotubes.

The preparation of CNT-metal reinforced composite materials is now a rapidly growing area of research interest. Electrodeposited Ni coatings with nanograins generally exhibit much higher tensile strength and stiffness but poorer tensile ductility compared with their micrograin counterparts [306]. It is considered that CNTs with superior tensile strength, stiffness and fracture strain can further enhance the mechanical performances of Ni coatings. Moreover, nickel exhibits good wettability for graphite powders [307]. Even though, Ni/CNT composites have been studied by many researchers for various applications [233-243], they could not give promising results due

to the difficulties associated with the processing of composites. Uniform dispersion of CNTs in the bath, which affects their uniform distribution in the metal matrix, is a major challenge demanding the addition of some dispersive agents. This results in poor interfacial adhesion between nanotubes and metals.

In the present research work, we have sought two ways of tackling this problem. In the first part of the study, we have taken three different kinds of MWCNTs to understand their incorporation into nickel matrix from aqueous solution and then study their physicochemical, morphological and electrochemical properties. The impact of surface functionalization of MWCNTs on their dispersion stability and their interfacial adhesion reinforcing the composite coatings is studied and discussed in detail. Pristine MWCNTs (P-MWCNTs), amino-functionalized MWCNTs (A-MWCNTs) and oxygen-functionalized MWCNTs (O-MWCNTs) are employed for the study.

In the second part of the study, we have explored the possibility of alternative solvent, which could show good dispersion stability for MWCNTs and at the same time be conductive. Ionic liquids seem to be proper alternative solvents, which can fulfill the aforementioned properties. Moreover, they are fast emerging as promising alternative solvents for electrochemistry purposes [247,248]. DES is a new class of ionic liquid typically formed by mixing choline chloride (as quaternary ammonium salt) with hydrogen bond donors such as amides, acids and alcohols. In the current study, for the first time, we make an attempt to study the feasibility of DES to electrodeposit Ni/MWCNT composites. Firstly, dispersion stability of both pristine MWCNTs (P-MWCNTs) and oxidized MWCNTs (O-MWCNTs) was studied in DES in comparison to aqueous media. We have mainly employed P-MWCNTs and O-MWCNTs as they

showed better incorporation into nickel matrices compared to A-MWCNTs. Then electrodeposited Ni/MWCNT composites were investigated in relation to their stability, morphology and electrochemistry.

4.2. Preparation of Ni/ MWCNT composite coatings

Thus far, Ni/MWCNT composites have been produced by various methods such as pyrolysis, electroless deposition, laser-deposition and electrodeposition [308-311]. Among these diverse synthesis processes, electrodeposition is a simple and cost effective method to prepare high purity of deposits. In this sub-section we explain the preparation of Ni/MWCNT composites in both aqueous solution and in ionic liquid. As we have mentioned earlier, we have taken three kinds of MWCNTs. The P-MWCNTs were treated with a conc. H_2SO_4 : conc. HNO_3 (3:1 v/v) solution at 50 °C for 8 h to generate oxygen functionalities on the surface to get O-MWCNTs. The detailed procedure is given in Chapter 2. The percentage of oxygen content was found to be 18 % in relation to the 82 % carbon content. A-MWCNTs (NC3152) were procured from Nanocyl S.A. A-MWCNTs have an average outer diameter of about 15 nm and a length of several micrometers. Amino-functionalization was achieved by ball-milling purified MWCNTs in ammonia. The percentage of nitrogen content is about 1 % in relation to the carbon content as specified by the manufacturer.

4.2.1. Preparation of Ni/MWCNT composite coatings from aqueous solution

The nickel chloride plating bath consisting of $300 \text{ g L}^{-1} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $30 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$ was prepared from reagent grade chemicals (purity >98%),

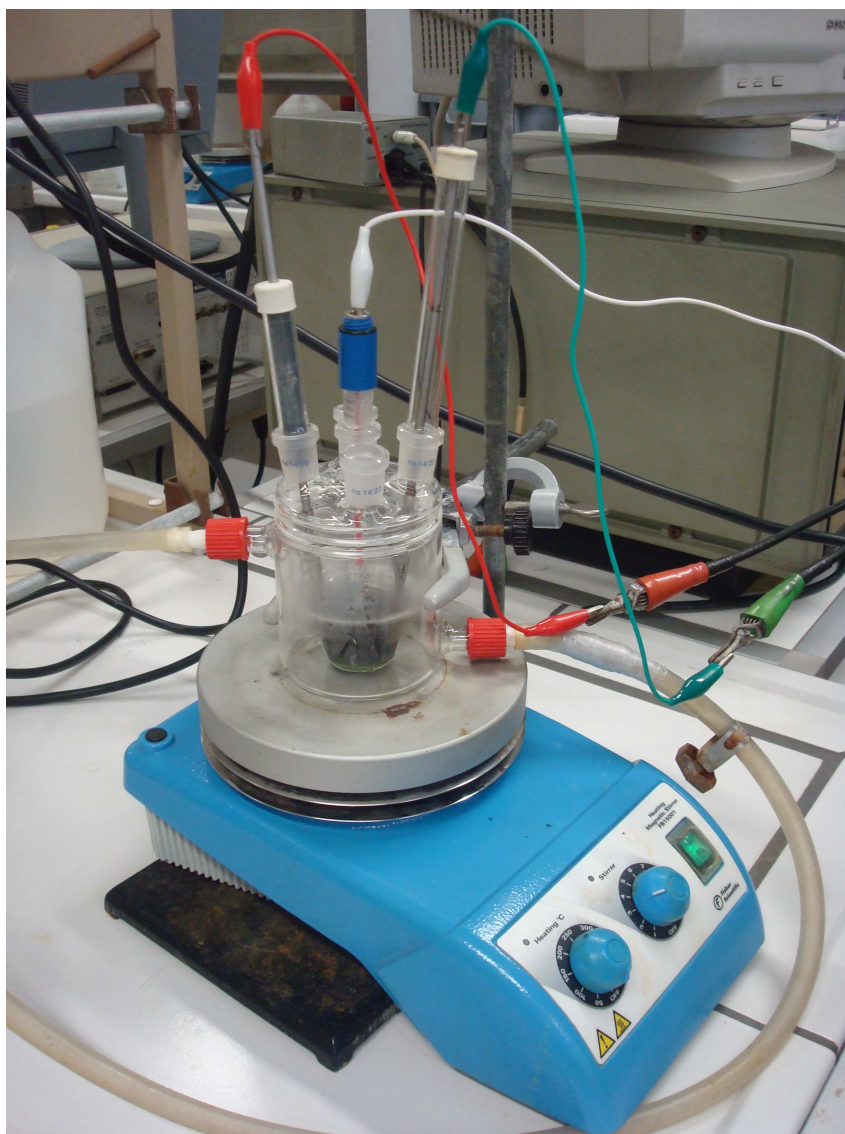


Figure 4 : Experimental setup for electrodeposition from aqueous solution (SCE as reference electrode).

The amount of P-MWCNTs, A-MWCNTs or O-MWCNTs in the bath was maintained to 0.3 g L^{-1} in each case. After these different types of surface functionalized MWCNTs were added to the bath each separately, the suspension was ultrasonicated for 10 min for a good dispersion. The pH value of the bath was maintained at 3 ± 1 . The suspensions were kept mechanically dispersed by constantly agitating them during the electrodeposition process. The experimental setup for the electrodeposition process is shown in Figure 4 with saturated calomel electrode as reference electrode. All the operating conditions performed during the electrodeposition process are given in Table 1. The plated specimens were washed copiously in ultra-pure water ($18 \text{ M}\Omega \text{ cm}$) and then subjected to various tests.

Current mode	Direct current
Current density	-5 A dm^{-2}
Bath temperature	$30 \pm 0.5 \text{ }^{\circ}\text{C}$
Deposition Time	20 min
Working electrode	Copper plate polished
Counter electrode	Nickel wire
Bath	Nickel chloride bath
pH	3 ± 1

Table 1 : Electrodeposition operating conditions.

4.2.2. Preparation of Ni/MWCNT composite coatings from ionic liquid

The plating bath was prepared from reagent grade chemicals (purity >98 %) and were used as such. The choline chloride/urea based DES was prepared from a previous report [144]. Nickel solution (0.3 M) in DES was prepared from anhydrous NiCl_2 .

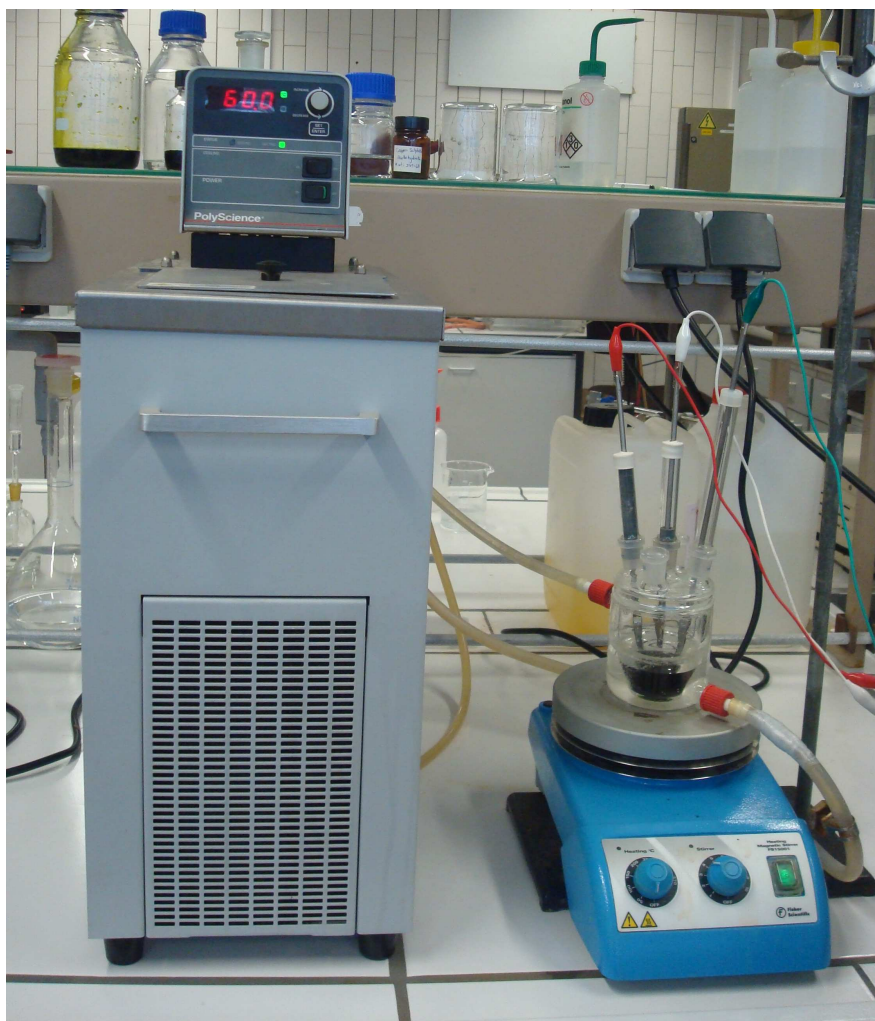


Figure 4.1 : Experimental setup for electrodeposition from ionic liquid (quasi-silver as reference electrode).

The amount of MWCNTs in the nickel solution was 0.1 g L^{-1} . The suspension of MWCNTs in the NiCl_2 solution was ultrasonicated for 10 min to get a stable dispersion. Before electrodeposition, the copper electrode surface was activated by immersing into a 10 % sulfuric acid solution for 30 sec. All electrodeposition experiments were performed galvanostatically in a conventional three electrode electrochemical cell (nickel-counter electrode, silver - quasi-reference electrode and copper-working electrode) with constant agitation using a magnetic stirrer (900 rpm). The experimental setup is demonstrated in Figure 4.1 with quasi silver electrode as reference electrode. All the operating conditions performed during the electrodeposition process are given in Table 2. The temperature was kept at 60°C during electrodeposition. The plated specimens were washed copiously with ultra pure water and dried with nitrogen gas before subjected to various tests.

Current mode	Direct current
Current density	-2 mA cm^{-2}
Bath temperature	$60 \pm 0.5^\circ\text{C}$
Deposition Time	30 min
Working electrode	Copper plate polished
Counter electrode	Nickel wire
Bath	Nickel chloride bath

Table 2 : Electrodeposition operating conditions.

4.3. Results and discussion of composites from aqueous solution

The key determining factor for the MWCNTs insertion into the nickel matrix during the electrodeposition process is their dispersion in the nickel chloride aqueous solution. The employment of three kinds of MWCNTs, differing in outer functionalities, is aimed at improving their dispersion in the nickel chloride bath and consequently their insertion into the nickel matrix. As a first step, the characterization of the MWCNTs is performed using the XPS. As displayed general survey spectra of the P-MWCNTs (Figure 4.2a), O- MWCNTs (Figure 4.2b) and A-MWCNTs (Figure 4.2c) show a main

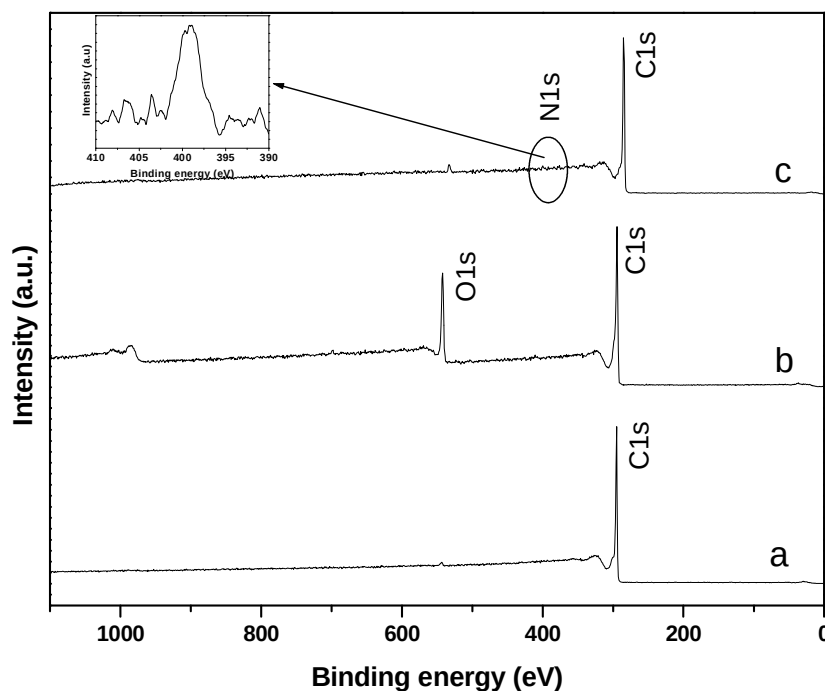


Figure 4.2 : XPS survey spectra of (a) P- MWCNTs (b) O-MWCNTs and (c) A-MWCNTs

peak at 284.6 eV, which is attributed to “sp²-hybridized” carbon in the graphitic layers of the CNTs. For O-MWCNTs (Figure 4.2b), in addition to C 1s there is an intense O 1s peak observed due to the formation of various oxygen containing functional groups such as carboxylic and phenolic, because of the surface functionalization of MWCNTs [212]. The relative concentration of oxygen from the survey spectra is found to be 18 % in comparison to 82 % for carbon. Consistent with the data provided by the manufacturer

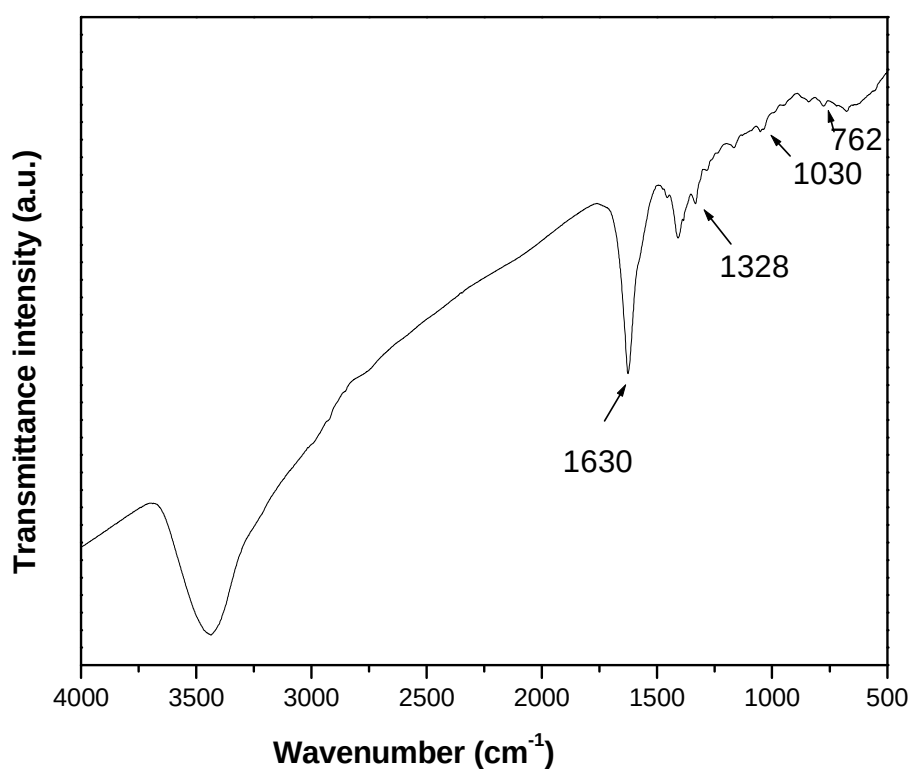


Figure 4.3 : FTIR spectrum of A- MWCNTs.

For A-MWCNTs, Figure 4.2c shows the presence of nitrogen (N 1s core-level is shown inset) with a relative concentration of about 1 % in addition to 97 % of carbon and 2 % of oxygen. The various surface functionalized multi-walled carbon nanotubes were

further investigated by FTIR. The FTIR characterization of P-MWCNTs and O-MWCNTs are discussed in details in Chapter 2.

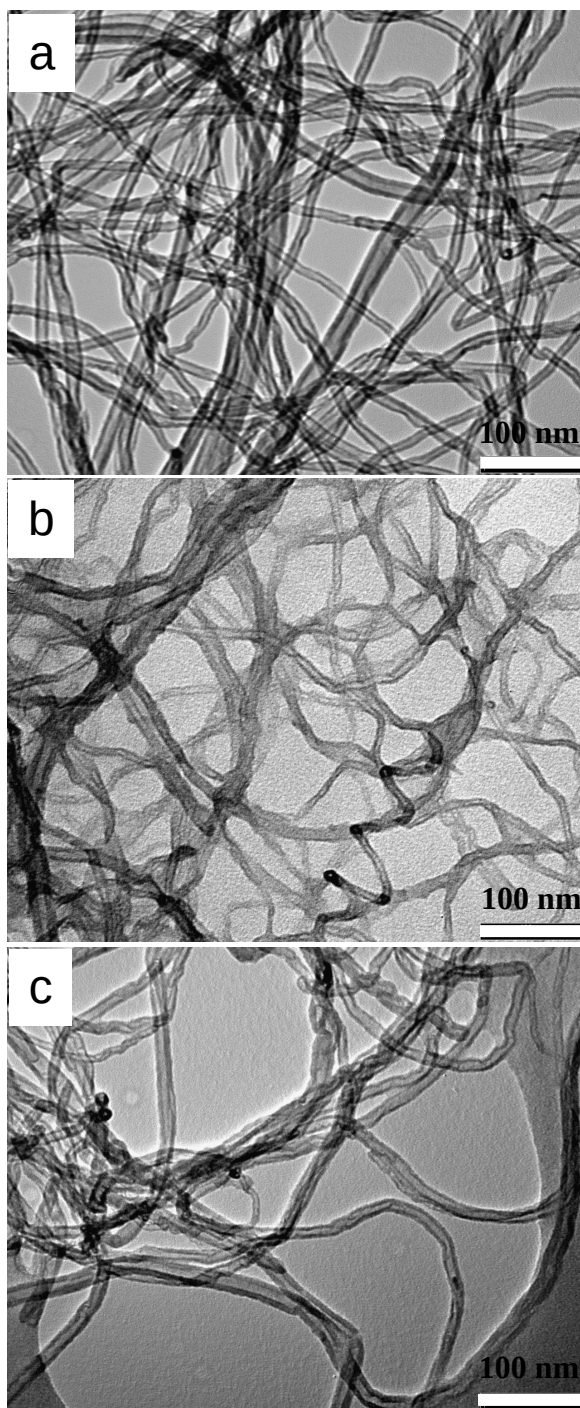


Figure 4.4 : TEM images of (a) P- MWCNTs (b) O-MWCNTs and (c) A-MWCNTs

In Figure 4.3, the peak at 1630 cm^{-1} can be attributed to the NH_2 scissoring in plane bending mode and also the vibration of carbon skeleton of CNTs [312]. The peaks at 1328 cm^{-1} and 1030 cm^{-1} are ascribed to C-N bond stretching vibrations and the peak at 762 cm^{-1} is due to the out of plane NH_2 bending mode [313, 314]. The characteristic peak within $3300\text{--}3600\text{ cm}^{-1}$ is due to the NH_2 stretch of the amine group overlapped with O-H stretching vibration [313]. These results corroborate the observations made using XPS earlier.

Figure 4.4 shows the TEM images of P-MWCNTs, O-MWCNTs and A-MWCNTs, evidencing that O-MWCNTs (Figure 4.4b) and A-MWCNTs (Figure 4.4c) remain quite stable even after the vigorous treatment being performed on the P-MWCNTs (Figure 4.4a) to introduce oxygen-functionalities (carboxylic and phenolic) and amino-functionalities. Thus, it is clear from the TEM images that up to a certain degree of surface functionalization does not affect the morphology of the MWCNTs.

The influence of functionalization of MWCNTs in the nickel chloride bath on the electrodeposition process to form Ni/MWCNT composites on a copper substrate was studied from the chronopotentiometric curves (Figure 4.5). These curves show different behaviour for nickel (Figure 4.5a), Ni/P-MWCNTs (Figure 4.5b), Ni/A-MWCNTs (Figure 4.5c) and Ni/O-MWCNTs (Figure 4.5d) in the plating bath. The curve displayed for the bare nickel electrodeposition from the aqueous nickel chloride bath indicates that it immediately attains a constant potential value (-0.77 V). The curves displayed for Ni/P-MWCNTs and Ni/O-MWCNTs composite electrodeposition from the aqueous nickel chloride bath containing their respective MWCNTs show clear deposition peak

during the initial 100 s. Furthermore, the steady electrodeposition potential is more anodic (-0.75 V) for both Ni/P-MWCNTs and Ni/O-MWCNTs compared to bare nickel.

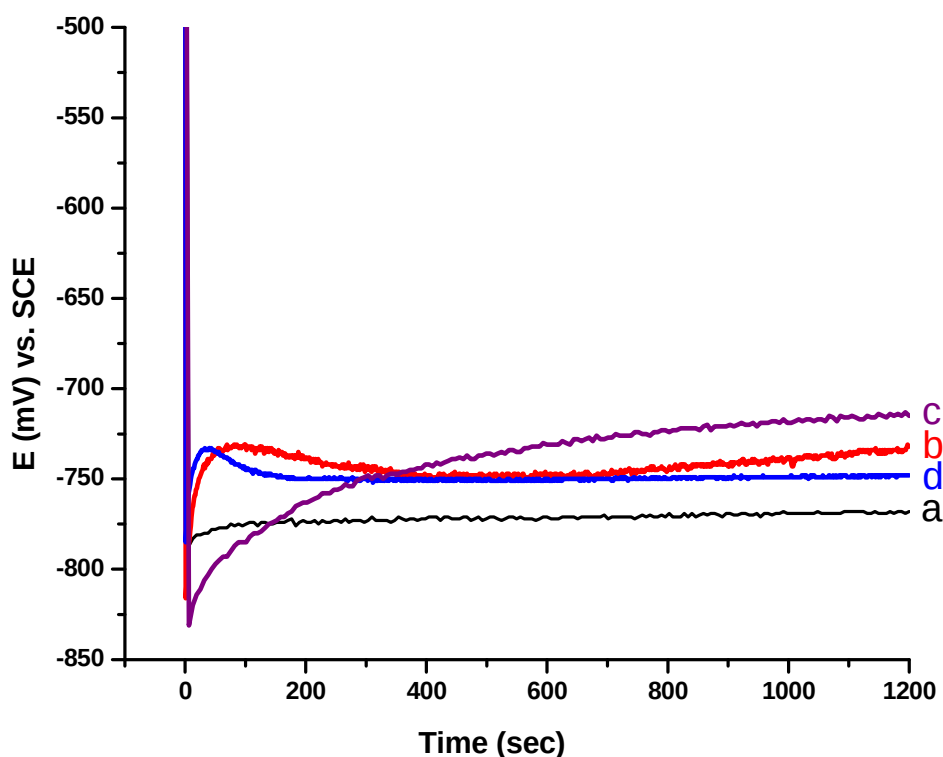


Figure 4.5 : Chronopotentiometric curves recorded for the electrodeposition of (a) bare nickel (b) Ni/P-MWCNTs (c) Ni/A-MWCNTs (d) Ni/O-MWCNTs for 1200 s.

However, Ni/P-MWCNTs show a slight increase in anodic shift in the potential (-0.73 V) after 600 s of electrodeposition process, while Ni/O-MWCNTs exhibit stable potential after the initial nucleation process. On the other hand, the curve displayed for

Ni/A-MWCNTs composite electrodeposition from the A-MWCNTs containing aqueous nickel chloride bath illustrates different behaviour, in terms of its initial peak potential and nucleation, showing a gradual anodic increment in electrodeposition potential from -0.81 to -0.71 V.

In order to understand the initial stages of nucleation, the electrodeposition process was carried out for a shorter time of 100 s and the corresponding chronopotentiograms are shown in Figure 4.6. These observed curves show similar behaviour as before (Figure 4.5).

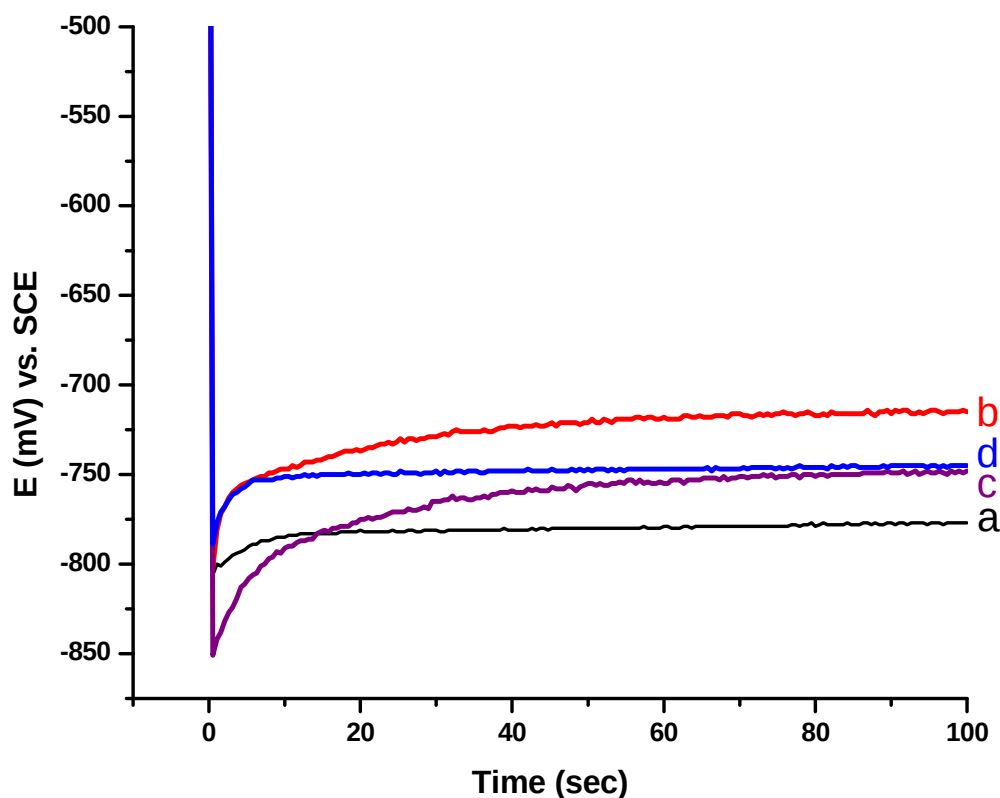


Figure 4.6 : Chronopotentiometric curves recorded for the electrodeposition of (a) bare nickel (b) Ni/P-MWCNTs (c) Ni/A-MWCNTs (d) Ni/O-MWCNTs for 100 s.

This throws some light on the effect of the dispersion stability of different kinds of MWCNTs in the nickel chloride bath, in turn influencing their electrodeposition process leading to the formation of their respective composite coatings. It was observed that P-MWCNTs and A-MWCNTs show comparatively lower dispersion in the plating bath than O-MWCNTs. The good dispersion of O-MWCNTs and their incorporation into nickel matrix during electrodeposition process may be the reason for the observed stable potential during Ni/O-MWCNT electroplating.

The morphology of the Ni/MWCNT composite coatings was studied by FE-SEM for both 100 s and 1200 s (Figure 4.7 and 4.8). Figure 4.7 (a-d) displays the images of the bare nickel, Ni/P-MWCNTs, Ni/A-MWCNTs and Ni/O-MWCNTs electrogenerated for 100 s. Figure 4.7 (a₁-d₁) presents the high magnification FE-SEM images for the same. As is evident from the images, bare nickel crystals are well formed on a copper substrate in as early as 100 s. Whereas, in the case of Ni/P-MWCNTs and Ni/A-MWCNTs, we can see a mass of protruding structures probably due to the incorporation of MWCNTs into the nickel matrix. Although, Ni/O-MWCNTs show similar behaviour in terms of protruding structures, the as-formed nickel crystals are seen with sharp edges similar to the ones observed on the bare nickel. These morphological differences corroborate the previous observations made for their dispersion in the bath leading to their composite formation. Figure 4.8 (a-d) presents the FE-SEM images of bare nickel, Ni/P-MWCNTs, Ni/A-MWCNTs and Ni/O-MWCNTs for 1200 s of the electrodeposition process. Figure 4.8a displays the FE-SEM images of sharp edged nickel crystals on the copper substrate, which is similar to the ones shown in Figure 4.7a for a shorter deposition time.

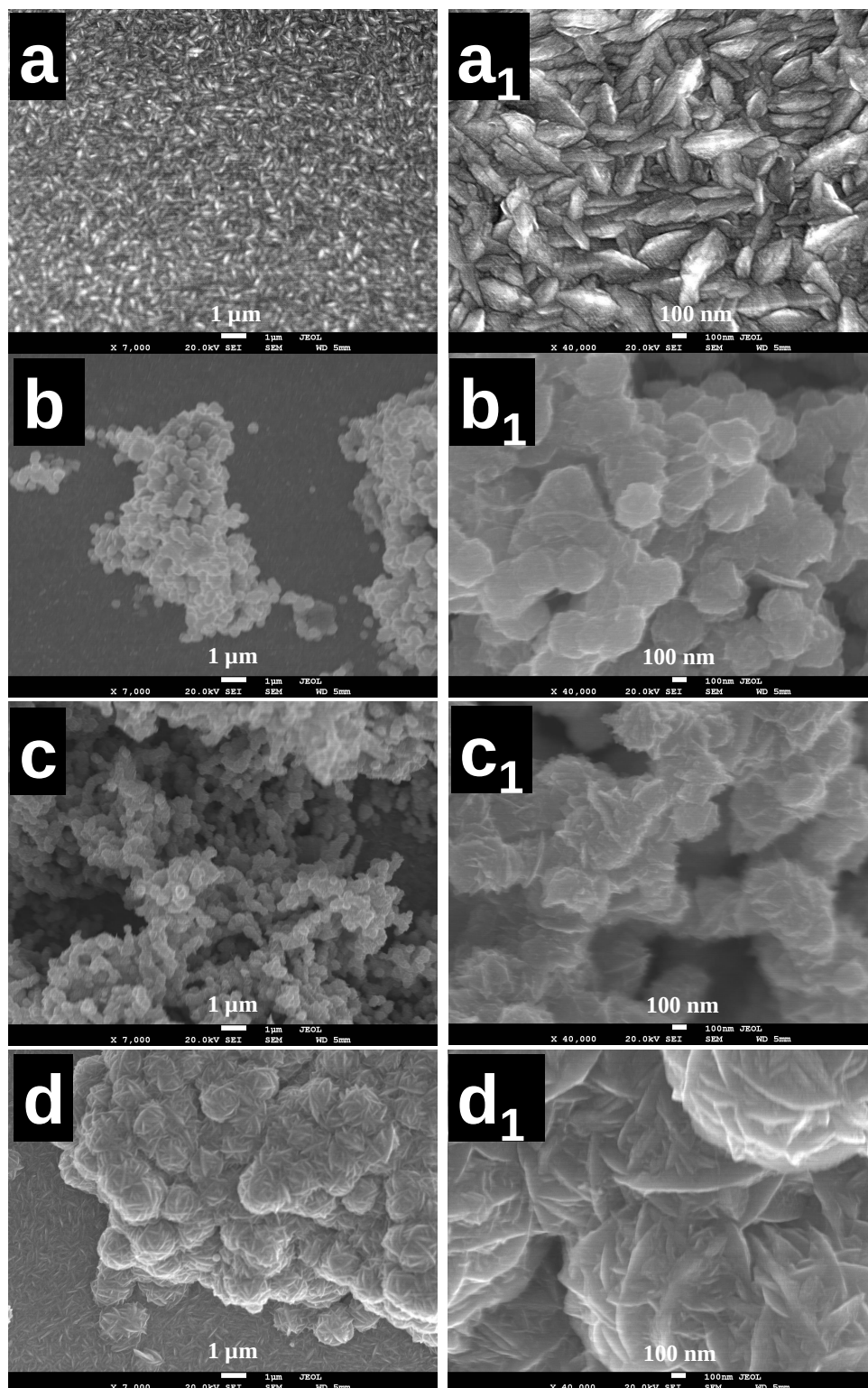


Figure 4.7 : FE-SEM low magnification images of (a) bare nickel (b) Ni/P-MWCNTs (c) Ni/A-MWCNTs (d) Ni/O-MWCNTs. FE-SEM high magnification images of (a₁) bare nickel ((b₁) Ni/P-MWCNTs ((c₁) Ni/A-MWCNTs ((d₁) Ni/O-MWCNTs (Time duration of plating – 100 s).

The bare nickel FE-SEM results corroborate the chronopotentiograms recorded in Figures 4.5 and 4.6 for the same, showing no change in kinetics during the electrodeposition process. Whereas, FE-SEM images in Figure 4.8b, 4.8c and 4.8d display different morphologies that may be due to the incorporation of differently functionalized MWCNTs into the nickel matrix. Since different kinds of surface functionalized MWCNTs (oxygen and amino) are employed, probably different morphologies have been seen upon their incorporation into the matrix.

In the case of Ni/P-MWCNTs, though nickel crystals are seen, they are formed in a cauliflower shape having small protruding structures. However, Ni/A-MWCNT coatings exhibit different morphology, having large protruding structures with nickel crystals, while Ni/O-MWCNTs coatings having protruding structures consist of sharp edged nickel crystals, which resemble nickel crystals observed on the bare nickel surface. This result again confirms the kinetics of electrodeposition process observed previously, influenced by their better dispersion stability compared to P-MWCNTs and A-MWCNTs. In addition, EDX analyses indicate that Ni/O-MWCNTs composite coatings have the nickel average mass of 94.5 % which is almost same for bare nickel coatings (96 %). Whereas, nickel average mass is low for Ni/P-MWCNTs (88 %) and Ni/A-MWCNTs (86 %), compared to Ni/O-MWCNTs. These results point out that O-MWCNTs do not hinder the deposition of nickel in the composite formation, which is attributed to their good dispersion in the nickel bath.

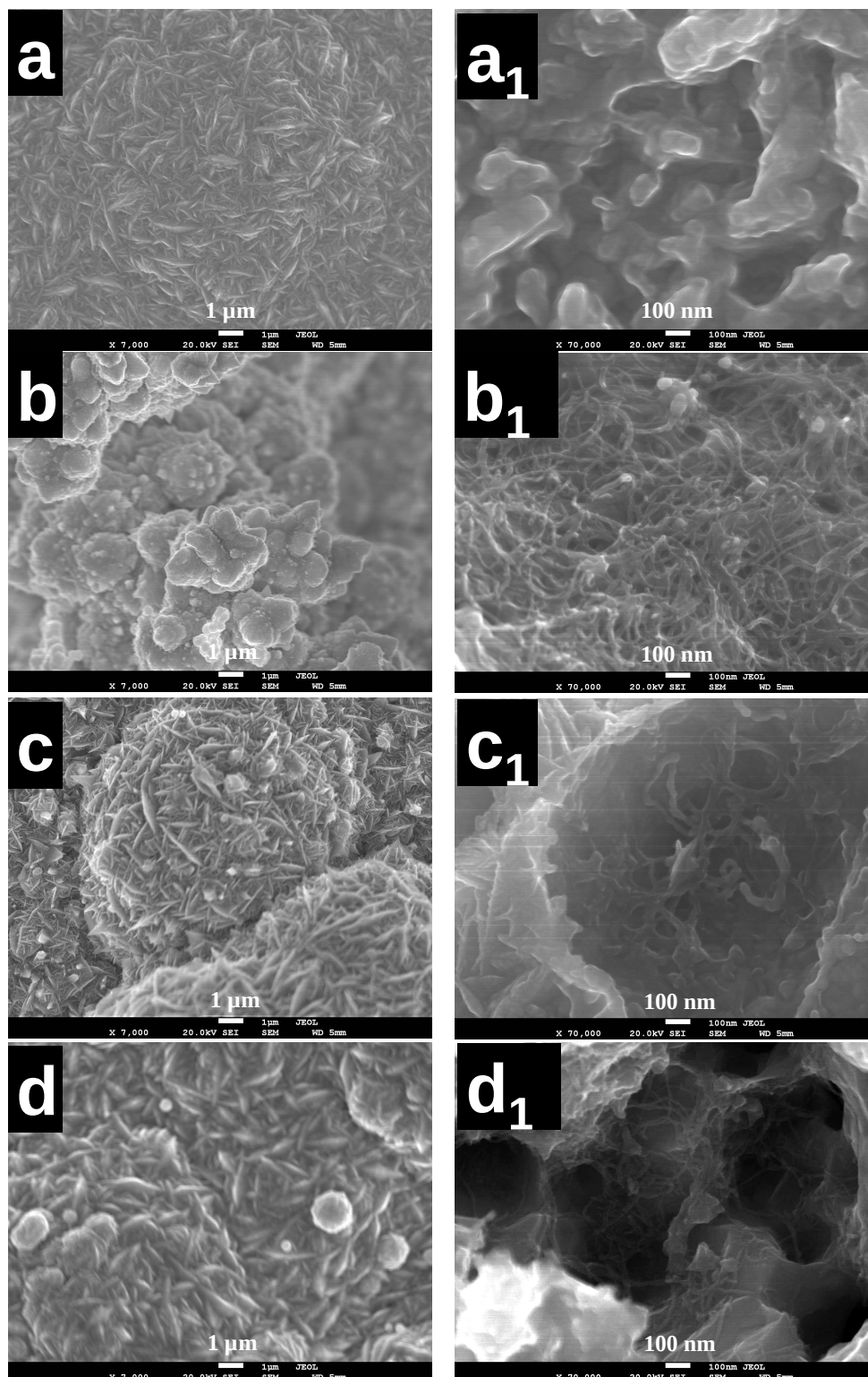


Figure 4.8 : FE-SEM images of (a) bare nickel (b) Ni/P-MWCNTs (c) Ni/A-MWCNTs (d) Ni/O-MWCNTs. FE-SEM images of etched surface of (a₁) bare nickel ((b₁) Ni/P-MWCNTs ((c₁) Ni/A-MWCNTs ((d₁) Ni/O-MWCNTs (Time duration of plating – 1200 s).

A soft electrochemical etching of the coatings was performed to study the internal morphology of the Ni/MWCNT composites. For the sake of comparison, the bare nickel etched surface is shown in Figure 4.8a₁. Figure 4.8(b₁-d₁) shows the electrochemically etched surface of Ni/P-MWCNTs, Ni/A-MWCNTs and Ni/O-MWCNTs, respectively. In all the etched composites CNTs are observed inside the protruding structures, as it was previously assumed. From these results, we can derive that the CNTs are well incorporated into the nickel matrix.

Thickness and roughness values for the bare nickel, Ni/P-MWCNTs, Ni/A-MWCNTs and Ni/O-MWCNT coatings for 100 s and 1200 s of electrodeposition duration are given in Table 3. Thickness as well as roughness values show same trend for both the electrodeposition durations (100 s and 1200 s). Although, the bare nickel and Ni/O-MWCNT composite coatings show almost the same average thickness, their average roughness values differ, that is 177 nm and 764 nm, respectively. However, roughness of Ni/O-MWCNTs (764 nm) is appreciably lower than that of Ni/P-MWCNTs (8663 nm) and Ni/A-MWCNTs (6688 nm). Similarly, thickness of Ni/P-MWCNTs (4.6 μm) and Ni/A-MWCNTs (6.4 μm) is also lower than that of bare nickel (21 μm) and Ni/O-MWCNTs (19 μm).

From these results, we may deduce that the negative surface charges on the O-MWCNTs probably facilitate the deposition of nickel in their composite formation. Whereas, the presence of P-MWCNTs and A-MWCNTs in the nickel bath hinders the uniform growth of their composites, may be due to the presence of electrically neutral P-MWCNTs and positively charged A-MWCNTs. These results corroborate the

morphological differences observed on the FE-SEM studies (Figure 4.7 and Figure 4.8) before the soft electrochemical etching was performed.

Electrodes	Deposition (100 sec)		Deposition (1200 sec)	
	Average thickness (μm)	Average roughness (nm)	Average thickness (μm)	Average roughness (nm)
Nickel	1.3	32.2	21	177
Ni/P-MWCNTs	0.6	2780	4.6	8663
Ni/A-MWCNTs	0.5	1828	6.4	6688
Ni/O-MWCNTs	1.5	407	19.5	764

Table 3 : Thickness and roughness values for composites determined at different time intervals.

The electrochemical behaviour of these coatings was studied in 2 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ ($\text{Fec}^{4-}/\text{Fec}^{3-}$) dissolved in 0.05 M NaOH solution. The potential window (-0.05 to +0.65 V) has been chosen to investigate the electrochemical activity of $\text{Fec}^{4-}/\text{Fec}^{3-}$ redox couple and, at the same time, the passivation behaviour of the composite surface. Figure 4.9 represents cyclic voltammograms (CVs) recorded for all the coatings at a scan rate of 0.01 V s^{-1} . Anodic and cathodic peak potentials for $\text{Fec}^{4-}/\text{Fec}^{3-}$ redox system were observed at 0.228 and 0.106 V, respectively, and found to be identical for all the coatings.

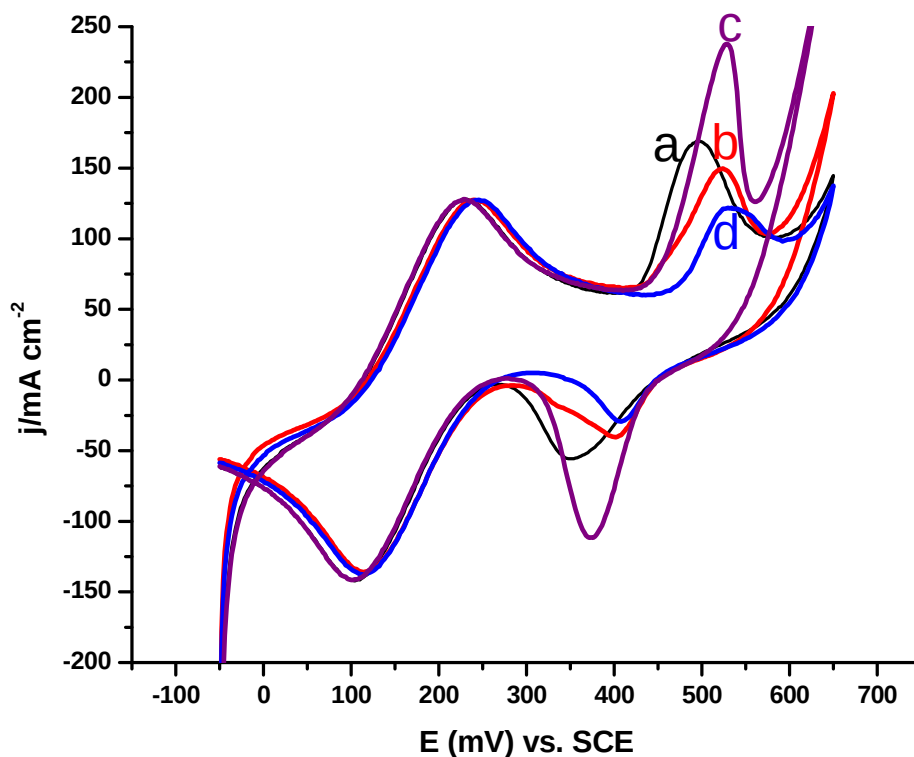


Figure 4.9 : Cyclic voltammograms recorded for (a) bare nickel (b) Ni/P-MWCNTs (c) Ni/A-MWCNTs (d) Ni/O-MWCNTs in 2 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ dissolved 0.05 M NaOH solution.

The identical CVs show that the electrochemical active surface area is the same for all the electrodes irrespective of their increased roughness. The observed second anodic peaks are due to the oxidation of nickel and its passivation in NaOH solution [315]. The anodic peak potentials and the corresponding anodic peak charges are given in Table 4. The positive shift in anodic peak potential (536 mV) and low anodic charge

(0.295 mC cm⁻²) for Ni/O-MWCNTs indicate that they are more stable. This enhanced stability may be due to the strong affinity of nickel to oxygen and hence oxygen-functionalized MWCNTs binding strongly to the nickel matrix.

Electrodes	Anodic charge (mC cm ⁻²)	Anodic peak potential (mV)	E _{corr} (mV)	i _{corr} (μA cm ⁻²)
Nickel	0.579	494	-291	4.2
Ni/P-MWCNTs	0.387	525	-275	2.3
Ni/A-MWCNTs	0.760	526	-280	6.8
Ni/O-MWCNTs	0.295	536	-264	1.5

Table 4: The anodic charge and anodic peak potential obtained from the second oxidation peak in Figure 4.7 and E_{corr} and i_{corr} values obtained from the polarization studies in Figure 4.8 .

The corrosion resistance of the coatings was investigated by polarization studies in 0.5 M NaCl solution (Figure 4.10). The corrosion current density (i_{corr}) and corrosion potential (E_{corr}) values for all the coatings are given in Table 4. The bare nickel coating shows a clear passive region during the anodic polarization, however, this passivation behaviour became less significant for the composite coatings. Among the composite coatings the anodic polarization was the lowest for Ni/O-MWCNT composite coatings and the highest for Ni/A-MWCNT coatings. This observation indicates the higher

corrosion resistance of Ni/O-MWCNT and the least corrosion resistance of Ni/A-MWCNTs. The i_{corr} values given in Table 4 also confirm this observation.

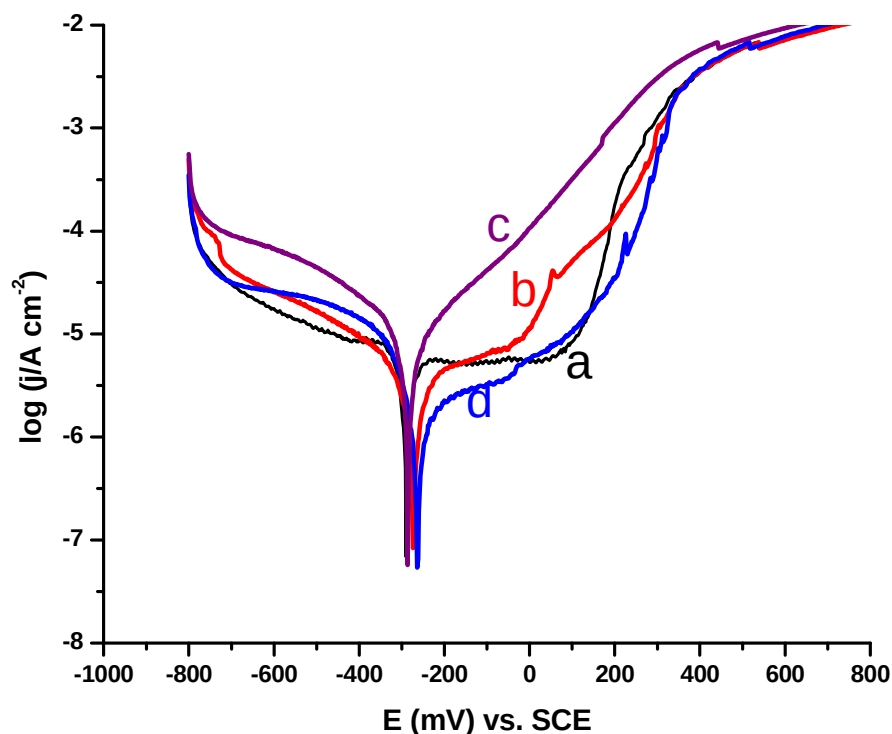


Figure 4.10 : Polarization curves recorded for (a) bare nickel (b) Ni/P-MWCNTs (c) Ni/A-MWCNTs (d) Ni/O-MWCNTs in 0.5 M NaCl solution.

The least i_{corr} ($1.5 \mu\text{A cm}^{-2}$) and the high positive E_{corr} (-264 mV) values were observed for Ni/O-MWCNTs, whereas the highest i_{corr} ($6.8 \mu\text{A cm}^{-2}$) and the least positive E_{corr} (-280 mV) values were observed for Ni/A-MWCNTs. Thus Ni/O-MWCNT composites coatings exhibited higher corrosion resistance and were strongly adhered within the matrix compared to that of Ni/P-MWCNTs and Ni/A-MWCNTs.

4.4. Results and discussion of composites from ionic liquid

From the results obtained in aqueous solution we understood that for a better dispersion of MWCNTs in a metal solution we need to look for an alternative solvent. We succeeded to find an ionic liquid which showed better dispersion stability for MWCNTs in nickel bath. The preparation procedure for the Ni/MWCNT composite in DES is given in the beginning of this chapter. Here we discuss the results obtained from the composite formation.

The homogeneous dispersion of MWCNTs in an electrolyte is a key factor to achieve their incorporation in the metal matrix during electrodeposition process leading to the formation of composites. As a first step, the dispersion of both P-MWCNTs and O-MWCNTs, in water has been studied. As it is already known, P-MWCNTs settle down immediately after sonication, however O-MWCNTs were found to be well dispersed and stable for a long time (more than one year). This is due to the oxidized groups, grafted on the surface of the CNTs during oxidation process [Figure 4.11B], making them compatible with water. On adding P-MWCNTs to the aqueous nickel chloride bath, the stability of P-MWCNTs is lost as expected (Figure 4.11C). However, when O-MWCNTs were added to the aqueous nickel chloride bath, the stability of O-MWCNTs is also lost after a while, resulting in sedimentation (Figure 4.11D). This is due to the major sorption mechanism, mainly attributable to chemical interaction between the metal ions and the surface functional groups on MWCNTs.

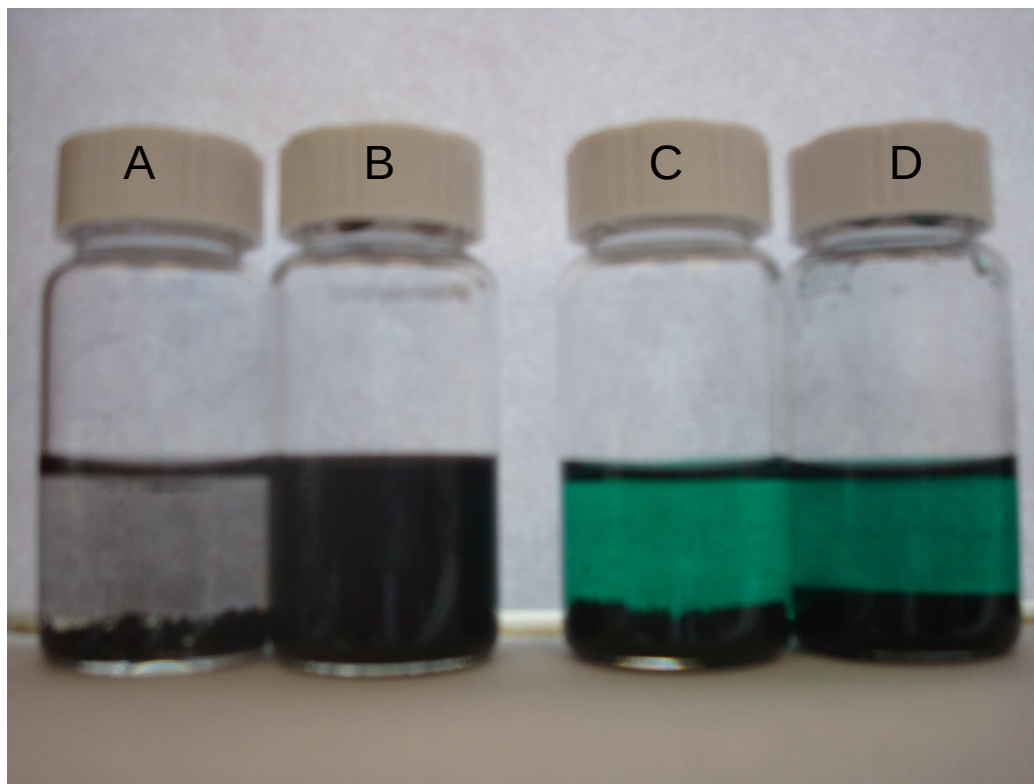


Figure 4.11 : Dispersion of P-MWCNTs (A) and O-MWCNTs (B) in water, and dispersion of P-MWCNTs (C) and O-MWCNTs (D) in aqueous 0.3 M NiCl_2 solution.

This happens when the protons in the carboxylic and phenolic groups of O-MWCNTs exchange with the metal ions in the aqueous phase [316,317]. The mechanism by which the metal ions are sorbed onto O-MWCNTs are very complicated and appear attributable to electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and the surface functional groups of O-MWCNTs. To elaborate the Ni/MWCNTs composites, one has to look for an alternative solvent which has to be, at the same time, appropriate for electrochemistry and for MWCNTs dispersion in the presence of nickel cations. As mentioned in the introduction, DES is a suitable medium for several electrochemical purposes including nickel electrodeposition [254].

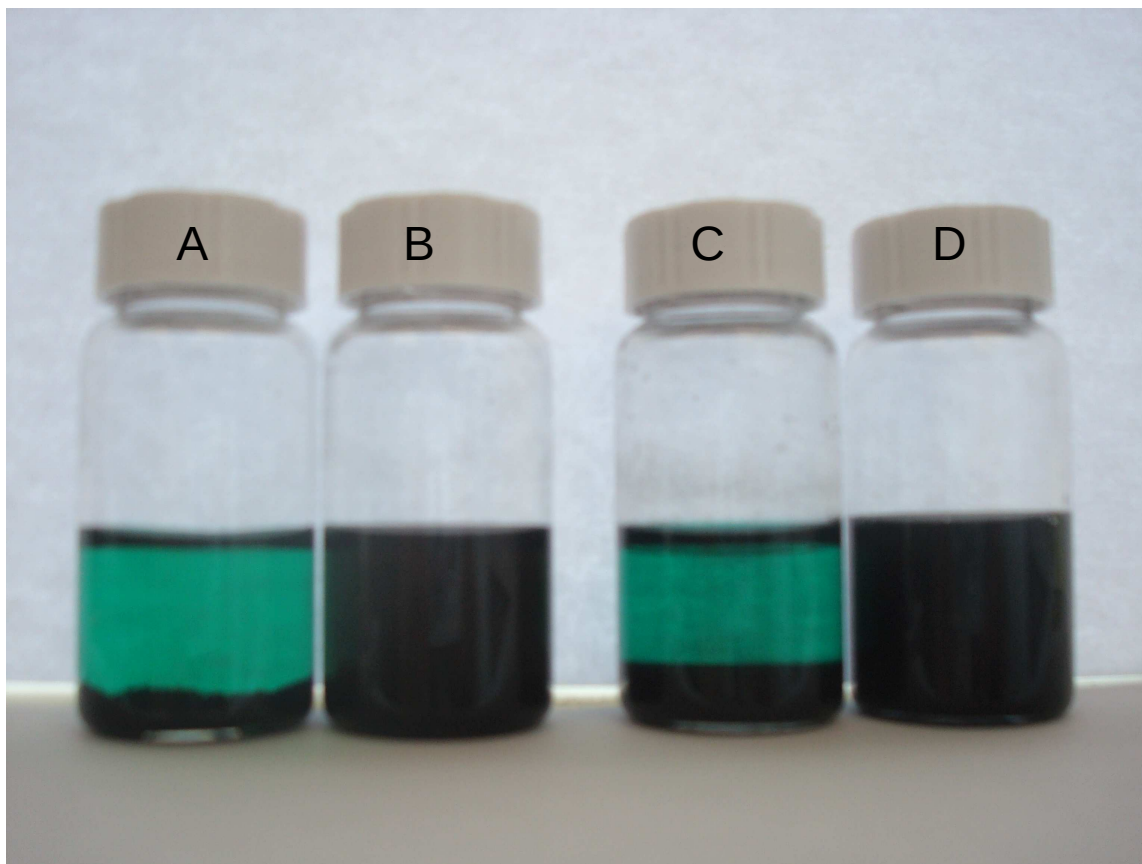


Figure 4.12 : Dispersion in aqueous + 0.3 M NiCl_2 and DES + 0.3 M NiCl_2 solutions of O-MWCNTs (A and B) and P-MWCNTs (C and D).

As discussed before for water, dispersion experiments were carried out for P-MWCNTs as well as O-MWCNTs in DES and in NiCl_2 dissolved DES (DNiCl_2). In all cases the dispersion was found to be excellent. The stability in DES is unaltered for a long time (at least 6 months), however, the addition of NiCl_2 decreases the time stability but remains unaffected for 30 days (Figure 4.12B and Figure 4.12D). This duration is largely sufficient for an electrodeposition process. This positive effect of DES for dispersion of MWCNTs in DNiCl_2 may be due to a combination of its higher viscosity (ca. 1100 cP at 20 $^\circ\text{C}$) [251] than that of water which effects in its kinetic stability and the

coulombic screening of surface charge of the MWCNTs by the DNiCl_2 . Similar observation was made by Abbott et al [256] in the case of dispersion of various particulate materials like Al_2O_3 and SiC in DES.

These stable dispersions of MWCNTs in DNiCl_2 were used for electrodeposition of Ni/MWCNT composites. Figure 4.13 shows the cyclic voltammograms recorded between 0.00 and -1.60 V (vs. Ag quasi-reference) for copper working electrode in DNiCl_2 , DNiCl_2 +P-MWCNTs and DNiCl_2 +O-MWCNTs solutions. In all cases, plating process starts at -0.65 V and reaches the maximum peak potential at -1.0 V. A typical crossing of curve (loop) is observed in the reverse scan which is characteristic of the electrodeposition process.

The maximum current density (i_{p_c}) is obtained for the electrodeposition in DNiCl_2 +P-MWCNTs (-5.85 mA cm^{-2}) followed by DNiCl_2 +O-MWCNTs (-4.93 mA cm^{-2}). The i_{p_c} values in both DNiCl_2 +P-MWCNTs and DNiCl_2 +O-MWCNTs solutions were found more negative than that in DNiCl_2 (-4.28 mA cm^{-2}) probably because MWCNTs act as effective preferential nucleation sites facilitating the electrodeposition process. Compared to O-MWCNTs, the more negative i_{p_c} is obtained for P-MWCNTs because they are less defective and consequently more conductive. There is a synergetic effect of an increase of nucleation sites due to the presence of MWCNTs and, at the same time, their surface composition which influences their conductivity and their interactions with the medium.

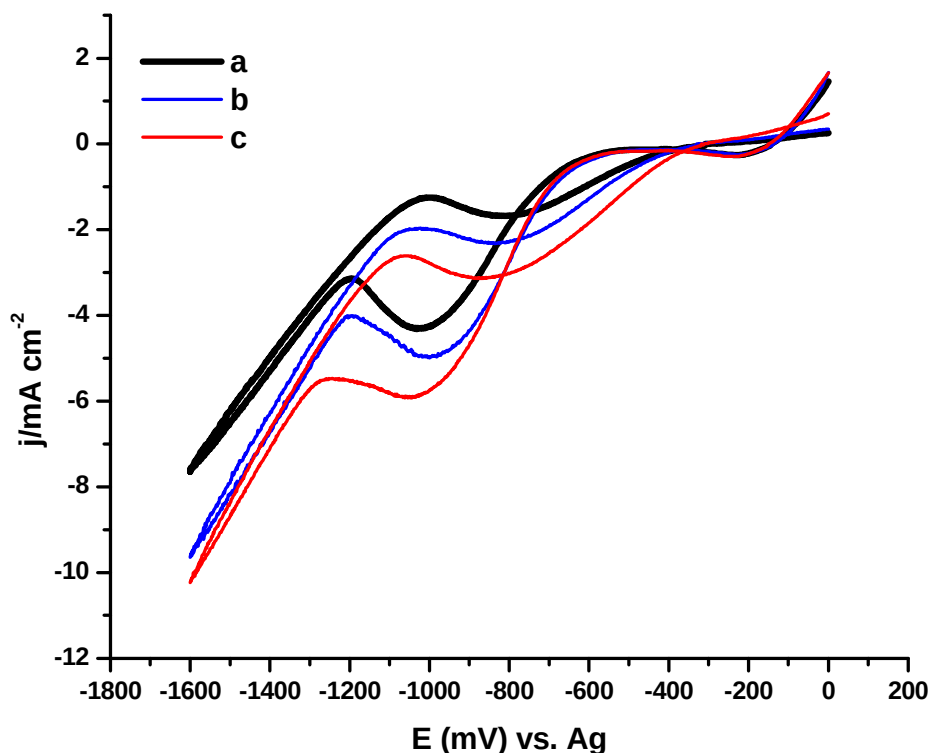


Figure 4.13 : Cyclic voltammograms for a copper electrode (a) DES + 0.3M NiCl₂, (b) O-MWCNT+ 0.3 M NiCl₂ and (c) P-MWCNT in DES + 0.3 M NiCl₂. SR= 0.02 V/s.

Figure 4.14 displays the curves ($E=f(t)$) recorded during the electrodeposition process at a constant current density of -2 mA cm^{-2} . The more positive potential (-0.61 V) indicating a more facile electrodeposition, is seen when P-MWCNTs are dispersed in the solution. The electrodeposition from solution containing O-MWCNTs gives an intermediate potential value (-0.65 V) which is in between P-MWCNTs and the MWCNTs-free solutions (-0.70 V).

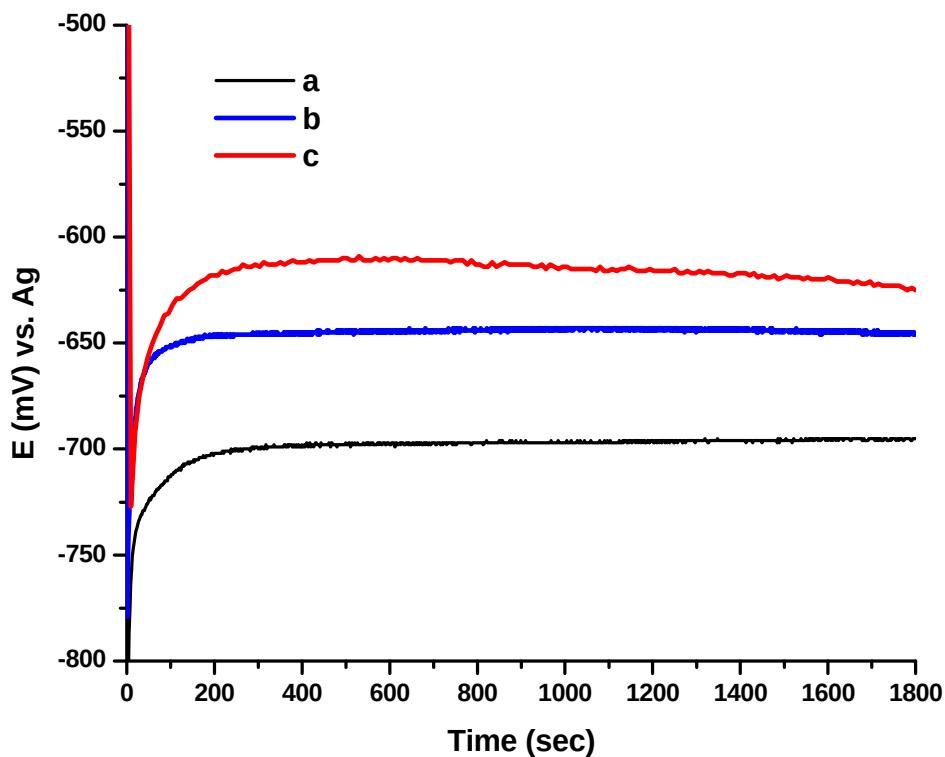


Figure 4.14 : Chronopotentiograms recorded for (a) DES + 0.3M NiCl₂, (b) O-MWCNT+ 0.3 M NiCl₂ and (c) P-MWCNT in DES + 0.3 M NiCl₂. $j = -2 \text{ mA cm}^{-2}$.

The thickness of Ni, Ni/P-MWCNTs and Ni/O-MWCNTs coatings is 1.8, 1.8 and 1.9 μm , respectively. The morphology of nickel and composite films was evaluated by means of FE-SEM. Figure 4.15a presents the morphology of bare nickel which exhibits highly crystalline sharp edged grains having definite boundaries. Ni/O-MWCNTs coating shows protruding structures probably due to the incorporation of O-MWCNTs in the nickel matrix. These structures are covered with sharp nickel crystalline grains (Figure 4.15b). The incorporation of P-MWCNTs (Figure 4.15c) gives a different morphology compared to the previous Ni/O-MWCNT composite. There are also protruding structures but with smaller sizes as seen in Figure 4.15c. In addition, nickel particles covering these structures are non-crystalline.

Besides morphological differences, EDX analyses indicate that bare nickel coating composition has higher nickel average mass (90 %) compared to the composites (75 %). A significant distinction, which is in correlation with the observed morphology, is also evident in surface roughness (38.1 nm for Ni, 112.6 nm for Ni/O-MWCNTs and 290 nm for Ni/P-MWCNTs).

A soft electrochemical etching at a current density of 5 mA cm^{-2} was performed in 0.1 M HCl for 3 min in order to study the internal morphology of composite coatings and to evidence the presence of CNTs inside the nickel matrix. This process favors the selective dissolution of nickel and makes the MWCNTs visible when the etched coatings are characterized by FE-SEM. For the sake of comparison, bare nickel coating was also etched in a similar way. Figures 4.15 (a₁, b₁, c₁) display the FE-SEM images of Ni, Ni/O-MWCNTs and Ni/P-MWCNTs coatings after etching. The figures clearly reveal the presence of homogeneously distributed O-MWCNTs and P-MWCNTs in the nickel matrix forming a compact coating. This homogeneous incorporation of the MWCNTs inside the matrix is certainly in close relation to their high dispersion stability in DES. The morphological and roughness differences observed between Ni/O-MWCNTs and Ni/P-MWCNTs composites highlight the importance of surface composition of the MWCNTs during the electroreduction of Ni^{2+} and the incorporation of MWCNTs. At an appropriate negative current density cathodically polarized electrode induces the reduction of nickel cations allowing the formation of nucleus and fine grained thin metal films.

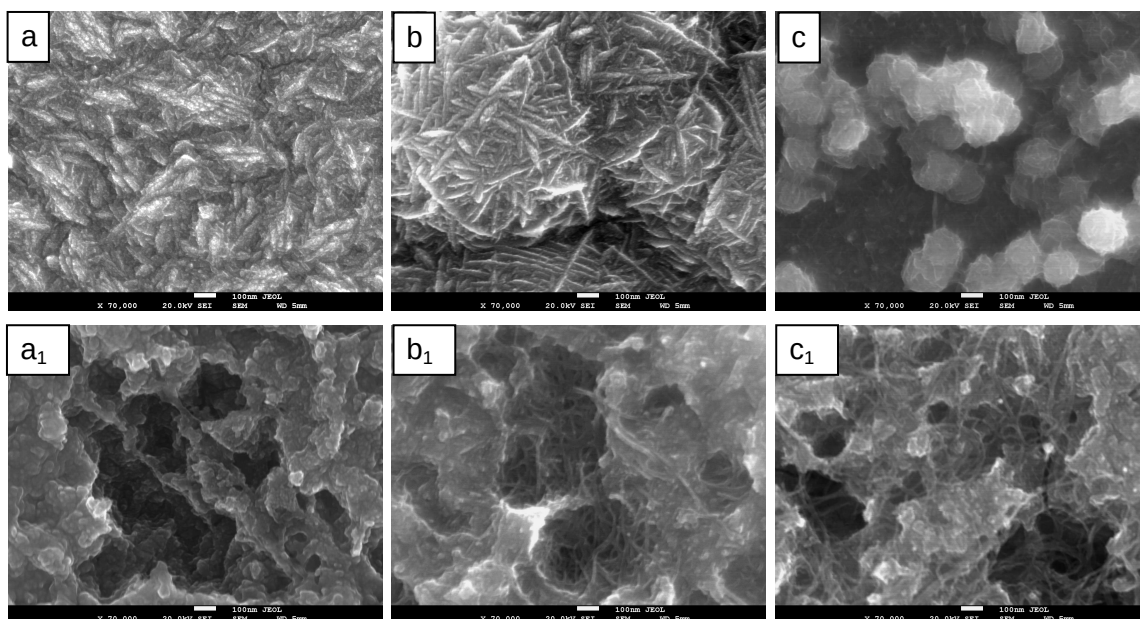


Figure 4.15 : FE-SEM images of bare nickel, Ni/O-MWCNTs and Ni/P-MWCNTs, respectively, before (a, b and c.) and after electrochemical etching (a₁, b₁ and c₁) in 0.1 M HCl, $t = 3$ min.

The well dispersed MWCNTs in DNiCl_2 in close vicinity to the cathode are deposited on it alongside and are entrapped as individual nanotubes or aggregates. Further nickel electrodeposition occurs on nickel sites and also on the incorporated MWCNTs as they are conductive. As the time duration increases, more amounts of MWCNTs deposit along with nickel and progressively link together to form the Ni/MWCNT composites.

The electrochemical behavior of these coatings was studied in 2 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ ($\text{Fec}^{4-}/\text{Fec}^{3-}$) dissolved in 0.05 M NaOH solution. The potential window (-0.05 to +0.65 V) has been chosen to investigate the electroactivity of $\text{Fec}^{4-}/\text{Fec}^{3-}$ redox couple and, at the same time, the nickel surface.

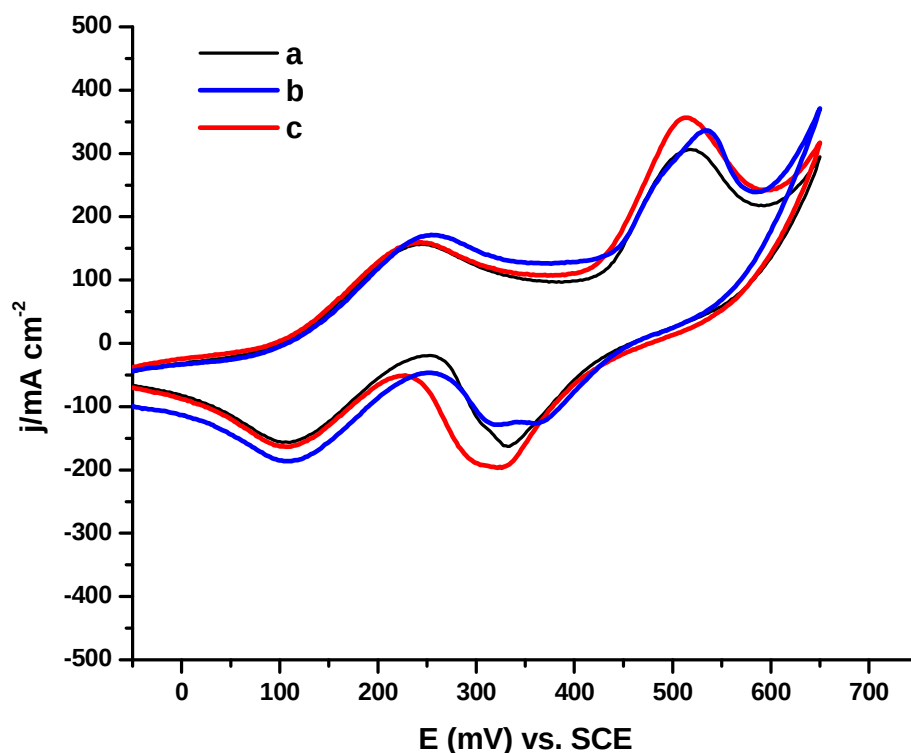


Figure 4.16 : Cyclic voltammograms for (a) bare nickel, (b) Ni/O-MWCNTs and (c) Ni/P-MWCNTs. 2 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ dissolved in 0.05 M NaOH solution.

Figure 4.16 presents the CVs recorded for all coatings at a scan rate of 0.01 V/s. Anodic and cathodic peak potentials were observed at 0.24 and 0.11 V, respectively, and the $\text{Fe}^{4-}/\text{Fe}^{3-}$ redox peaks were identical for all coatings. The identical CVs show that the electrochemical active surface area is same for all electrodes in spite of increased roughness of the composite coatings. The observed second anodic peaks are due to the oxidation of nickel and its passivation in NaOH solution [315]. The peak potential appears at 0.51 V for both Ni and Ni/P-MWCNTs coatings, whereas, it emerges at slightly higher positive value (0.54 V) for Ni/O-MWCNTs. The anodic charge for Ni/O-

MWCNT (0.83 mC) is also low compared to the other coatings (Ni - 1.35 mC and Ni/P-MWCNTs - 1.67 mC). This difference, which is highly reproducible, indicates a higher stability of Ni/O-MWCNTs composite that may be due to the interface between nickel atoms and O-MWCNTs. The strong affinity of nickel to oxygen makes a strong bonding of nickel to the oxygen-functionalized MWCNTs.

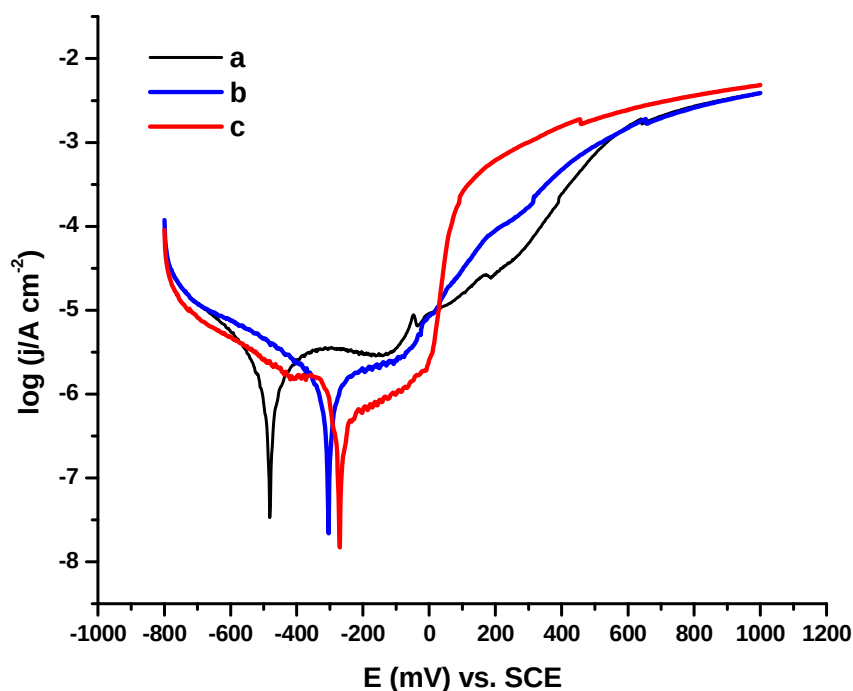


Figure 4.17 : Polarization curves recorded for (a) bare nickel (b) Ni/O-MWCNTs (c) Ni/P-MWCNTs in 0.5 M NaCl solution.

The corrosion studies performed in 0.5 M NaCl solution (Figure 4.17) also confirm these differences. Corrosion current density (i_{corr}) values for Ni, Ni/O-MWCNTs and Ni/P-MWCNTs coatings are 4.6, 2.8 and 1.8 $\mu\text{A cm}^{-2}$, respectively. Even if the differences are not huge, they are reproducible and go along with the distinctions

highlighted above. Similarly, corrosion potential (E_{corr}) values, respectively, -0.48, -0.30 and -0.26 V also point out an influence on the anodic dissolution of nickel. Even though, Ni/P-MWCNTs coating shows the least i_{corr} value, it undergoes sudden pitting corrosion. Whereas, Ni/O-MWCNTs does not show enhancement of pitting corrosion compared to bare nickel. Therefore, Ni/O-MWCNTs composite seems to have more stable adhesive coating than Ni/P-MWCNTs.

Based on the above results DES appears to be an excellent solvent for dispersion of MWCNTs, pristine or oxidized ones. In both cases, incorporation inside the electrochemically generated nickel matrix was successfully achieved. However, the morphology, roughness and electrochemical stability differences between the two composites (Ni/P-MWCNTs and Ni/O-MWCNTs) indicate that surface functionalization of MWCNTs has a significant effect on the film properties. This may be due to two parameters. The first can be the influence of the chemical composition of the MWCNTs surface in the beginning stages of nickel nucleation on MWCNTs. The second may be the interaction of the MWCNTs between each other which is highly dependent on the nature of the chemical groups on their surfaces.

4.5. Conclusions

We have demonstrated successful incorporation of MWCNTs into nickel matrices from aqueous solution and ionic liquids. In the first part, the different kinds of surface functionalized MWCNTs were incorporated into the nickel matrix to form MWCNT-reinforced nickel composite coatings from aqueous solution. The investigation on the

electrogenerated Ni/MWCNT composite coatings indicated that Ni/P-MWCNTs, Ni/A-MWCNTs and Ni/O-MWCNTs exhibited different physicochemical, morphological and electrochemical properties. The Ni/O-MWCNT composite coatings displayed more electrochemical stability and high corrosion resistance compared to Ni/P-MWCNTs and Ni/A-MWCNTs.

In the second part, for the first time, we have shown that the incorporation of MWCNTs into the nickel matrix from ionic liquid to form Ni/MWCNT composite coating is achievable. A highly stable dispersion of pristine as well as oxidized MWCNTs in DNiCl_2 resulted in a stable homogeneous incorporation of MWCNTs in nickel matrix. Morphology, crystallinity, roughness as well as electrochemical stability of the coatings are strongly dependent on the presence of MWCNTs as they act as composite reinforcement in the nickel matrix. These properties are a direct consequence of MWCNTs dispersion in the solution which influences the electrodeposition process.

III. Conclusions and perspectives

III. Conclusions and perspectives

Conclusions

Fundamentally, the importance of generating a true nanoscale heterostructures with properties that transcend the isolated properties of its constituent components is one major motivation for continuing this line of scientific pursuit. That is, the properties of carbon nanotube-nanocrystal heterostructures are not merely the simple sum of their parts; rather creating synergistic effects like the potential enhancement in favorable properties in these discrete systems could impact a wide range of areas including catalysis, sensing, optoelectronic devices, nanocomposites and nanobiotechnology. We also believe that this will be a key architecture in the ongoing struggle to develop improved energy storage devices as well as alternative power sources such as efficient solar cells.

In this research work, we have described a few approaches and strategies for the homogeneous decoration of multi-walled carbon nanotubes with copper and copper oxide nanocrystals and nickel and nickel oxide nanocrystals. We have largely succeeded in controlling the size, dispersion and concentration of these nanocrystals on MWCNTs. At the same time, we have attempted to homogeneously incorporate multi-walled carbon nanotubes into nickel matrices from both aqueous solution and ionic liquid. We discovered, for the first time, that the ionic liquid has better dispersion stability for CNTs

than aqueous solution and therefore succeeded in achieving the homogeneous incorporation of MWCNTs into nickel matrices from the DES based ionic liquid.

In the introductory chapter, apart from describing the structure, synthesis and properties of CNTs, we have highlighted the importance of covalent functionalization of MWCNTs for the efficient decoration of metal and metal oxide nanocrystals on them as they create anchoring sites for the metals. In this study, we have designed a simple and efficient method to decorate MWCNTs with metal and metal oxide nanocrystals and optimized the conditions to achieve their homogeneous decoration on MWCNTs. We have also highlighted the importance of the dispersion stability of MWCNTs in aqueous solution and in ionic liquid in the formation of stable composites and found that DES based ionic liquid has a better dispersion stability.

In the first part of the research, we devoted our time and energy on efficiently decorating copper and nickel nanocrystals and their oxides on MWCNTs. In both cases, we succeeded in uniformly decorating the metal and metal oxide nanocrystals on MWCNTs by designing simple and efficient impregnation methods and optimized condition to achieve the controlled size, dispersion and concentration of nanocrystals on MWCNTs. The as prepared products were characterized by different techniques such as XRD, FTIR, XPS, TGA, TEM, FE-SEM, EDX to investigate their structure and morphology. In both cases, we have used organic metal precursors to impregnate on the surface of MWCNTs, as they proved to be better than inorganic metal salts. It could be noted that organic metal precursors play an important role in linking the metals to the O-MWCNTs during the impregnation step through synergistic effects of both covalent

bonds and weak intermolecular interactions such as π - π stacking or electrostatic attractions.

Two different impregnation methods, namely, reflux method and IR irradiation method were employed to impregnate cuprous phenylacetylide (CPA) on MWCNTs. IR irradiation method was found to be more simple and efficient to impregnate CPA on MWCNTs. Photo-absorption and photothermal properties of CNTs in IR region played an important role on the homogeneous impregnation of CPA on MWCNTs. Further, the calcination of the products at appropriate atmospheres and suitable temperatures resulted in homogeneous decoration of Cu/CuO_x nanocrystals on the surface of MWCNTs. In case of nickel and nickel oxide decorated MWCNTs, we have, for the first time, demonstrated that nickel acetylacetonate (NAA), as metal precursor is efficient in impregnating on oxidized MWCNTs. Further, the carbon nanotube-nickel nanocrystals were synthesized by impregnation of NAA by a modified reflux method on MWCNTs, followed by calcination at suitable temperatures and appropriate atmospheres.

In the second part of the research, we concentrated on efficiently incorporating MWCNTs into nickel matrices from aqueous solution and from ionic liquid. We have used several techniques such as cyclic voltammetry, chronopotentiometry, FE-SEM, EDX, DEKTAK profilometer, soft electrochemical etching and polarization curves to demonstrate the incorporation of MWCNTs into nickel matrices from aqueous solution and ionic liquid. As a first approach, different kinds of surface functionalized MWCNTs were attempted to incorporate into nickel matrices to form MWCNT-reinforced nickel composite coatings from aqueous solution. The investigation on the electrogenerated Ni/MWCNT composite coatings indicated that Ni/P-MWCNTs, Ni/A-MWCNTs and

Ni/O-MWCNTs exhibited different physicochemical, morphological and electrochemical properties. In this study, we learnt the impact of surface functionalization of MWCNTs on their dispersion stability in aqueous solution to uniformly incorporate them into nickel matrices.

As a second approach, for the first time, we have shown that the incorporation of MWCNTs into nickel matrices from ionic liquid to form Ni/MWCNT composite coating is achievable. A highly stable dispersion of pristine as well as oxidized MWCNTs in nickel chloride dissolved DES based ionic liquid, resulted in a stable homogeneous incorporation of MWCNTs in the matrix. We found that the morphology, crystallinity, roughness as well as electrochemical stability of the coatings were strongly dependent on the presence of MWCNTs as they act as composite reinforcement in the nickel matrix. These properties are a direct consequence of MWCNTs dispersion in the solution, which influences the electrodeposition process. In both aqueous and ionic liquid oxygen functionalized MWCNTs exhibited improved electrochemical stability and higher corrosion resistance compared to pristine and the amino functionalized MWCNTs.

Perspectives

The area of carbon nanotube-metal nanocrystals and carbon nanotube-metal composites has evolved from merely being a subject of esoteric scientific curiosity to one that has gained broad applicability, acceptance, and serious interest in recent years. In our research work, we have succeeded in designing a simple and efficient method for the decoration of metal and metal oxide nanocrystals, starting from an organic metal precursor for both copper and nickel. This method could be employed to extend the work

in case of other transition metals to achieve the results. Similarly, one can exploit the potential benefits of IR irradiation method in decorating other metal nanocrystals on MWCNTs and on SWCNTs.

In our studies, we explored DES based ionic liquid in achieving good dispersion for MWCNTs and to homogeneously incorporate MWCNTs into nickel matrices. This work opens new possibilities for investigation of appropriate ionic liquids as a medium for dispersion of pristine or specifically modified CNTs and electrodeposition of their composites based on other matrices like tantalum, titanium etc.

Apart from aforementioned aspects, there are many aspects which are closely related to the main area of this work and could not be devoted enough time. This work can be very well extended to find suitable applications in the area of heterogeneous catalysis, electrocatalysis, sensors, photovoltaic nanodevices, solar cells, reinforcement composites and so forth.

Since their discovery in 1991, carbon nanotubes have come a long way. There have been great improvements in synthesis techniques, which can now produce reasonably pure nanotubes in gram quantities. However, there is still a need to develop and optimize processing methods to make well-defined (in terms of structure and dimensions) and well-organized nanotubes, since this will have real impact on applications. It is conceivable that nanotubes will be important players in future technology, especially as part of the ongoing revolution based on nanotechnology and nanostructures. To conclude, even if this work is quite fundamental and preliminary, there is no doubt that our thesis will pave the way to other studies which will aim at further expanding the field of nanoscience and nanotechnology.

IV. References

IV. References

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V. Annexes

V. Annexes

V.1. Materials and methods

All the chemicals used for all the experiments were of analytical grade and used without further purification. List of all the chemicals used are given below. Copper (I) phenylacetylide (97 %, Strem Chemicals, USA), Nickel acetylacetonate (96 %, Acros Organics), NaCl (99.5 %, Acros Organics), Xylenes (98 %, Acros Organics), Choline Chloride (99 %, Acros Organics), Urea (99 %, Sigma-Aldrich), Nickel (II) Chloride Hexahydrate (98 %, Sigma-Aldrich), Nickel (II) Chloride (98 %, Sigma-Aldrich), NaOH (98.5 %, Acros Organics), Boric acid (99 %, Sigma-Aldrich), Acetone (99.9 %, Fisher Scientific), Absolute Ethanol (99.9 %, Analar Normapur), Potassium ferrocyanide (II) trihydrate (99 %, Acros Organics), Potassium ferricyanide (III) (99 %, Acros Organics), Nitric acid (65 %, Chem Lab), Sulfuric acid (95-97 %, Chem Lab), Petra IR 11 Infrared lamp (capacity: 150 W, voltage: 230 V, 50/60 Hz) was used for the irradiation of the samples during impregnation step.

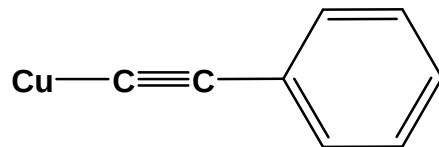
The thin MWCNTs (NC-3100) obtained from Nanocyl S.A., Belgium, were synthesized by decomposition of ethylene using the CCVD method. The MWCNTs have an average diameter of 10 nm and length of several (0.1-10) micrometers. The purity of the MWCNTs was more than 95 %. The P-MWCNTs were treated with a conc. H_2SO_4 : conc. HNO_3 (3:1 v/v) solution at 50 °C for 8 h to generate oxygen functionalities on the surface to get O-MWCNTs. The percentage of oxygen content was found to be 18 % in

relation to the 82 % carbon content. A-MWCNTs (NC3152) were also procured from Nanocyl S. A. These A-MWCNTs have an average outer diameter of about 15 nm and a length of several micro-meters. Amino-functionalization was achieved by ball-milling purified MWCNTs in ammonia. The percentage of nitrogen content is about 1 % in relation to the carbon content as specified by the manufacturer.

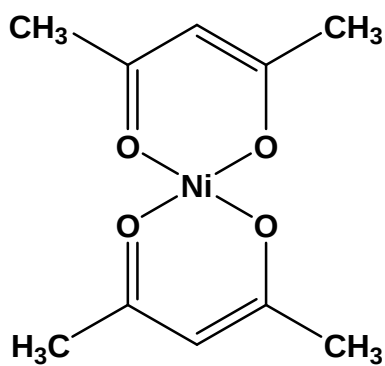
Copper plate (99.99 %, GOODFELLOW) was used as substrate for all the electrodeposition experiments. The copper plate with 1cm² working surface area was first polished (Buehler-Phoenix 4000) with silicon carbide papers (P 1200–Struers), then with 9, 3 and 1µm diamond powders, respectively, to get a mirror finish. Copper plate was then subjected to ultrasonication in acetone for 15 min. After this process, rinsing it in ultra-pure (18 MΩ cm) water and drying it immediately with high purity nitrogen stream completes the preparation. Just before the electrodeposition, the copper working electrode was immersed in a 10 % sulfuric acid solution for 30 s and then rinsed with ultra-pure water. Nickel wire (99.98 %, Advent Research Materials Ltd.) was used as working electrode for all the electrodeposition experiments.

Deep eutectic solvent based ionic liquid was prepared by mixing the two components, namely, choline chloride (2-hydroxyethyl-trimethylammonium chloride) and urea in a 1:2 molar ratio, respectively, at 75 °C with constant stirring until a homogeneous, colourless liquid was formed.

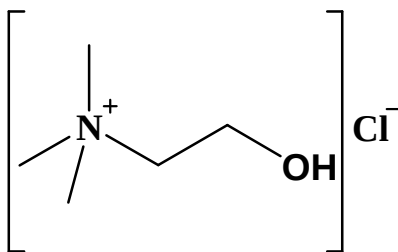
The structures of Cu (I) phenylacetylide, nickel acetylacetonate and choline chloride are depicted below.



Structure of Cu (I) phenylacetylide



Structure of nickel acetylacetonate



Structure of choline chloride (2-hydroxyethyl-trimethylammonium chloride)

V.2. Characterization techniques

Various techniques were used to characterize the samples before and after the experiments were performed. The detailed procedure of each of the characterization techniques used is illustrated below. All the electrochemical analyses were carried out using a potentiostat/galvanostat (model 273 purchased from EG&G Princeton Applied Research) connected to a computer with ECHEM software. A conventional three-electrode cell with a platinum plate or a nickel wire as the counter electrode, a saturated calomel electrode or quasi silver electrode as the reference electrode and the copper substrate as the working electrode was used for all the electrochemical analyses. All electrochemical characterizations on composite coatings were carried out in a spot cell using a potentiostat/galvanostat (EG&G Princeton Applied Research, model 273) with ECHEM software. Platinum plate was used as the counter electrode and saturated calomel electrode was used as the reference electrode.

1. X-ray Powder Diffraction (XRD)

X-ray powder diffraction is a non-destructive analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The technique is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction [1]. In our case, the phase purity of the materials were determined by powder X-ray powder

diffraction (PXRD) analysis using PHILIPS-7602EA diffractometer operating with 40 kV of voltage and 30 mA of tube current with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of 10 to 80°.

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law : $n\lambda = 2d \sin \theta$, where λ is the wavelength, d is the distance between crystal planes, θ is the angle of the diffracted wave and n is an integer known as the order of the diffracted beam [1]. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Figure A1 shows the reflection of X-rays from two planes of atoms in a solid.

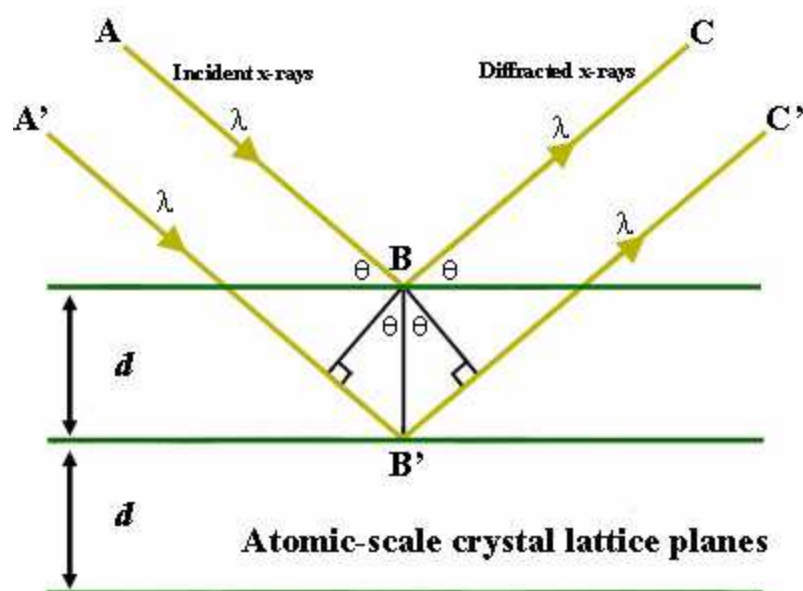


Figure A1: Reflection of X-rays from two planes of atoms in a solid.

Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction as is explained by the Scherrer Equation.

A shape factor is used in X-ray diffraction and crystallography to correlate the size of sub-micrometer particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. In the Scherrer equation, $\tau = K\lambda / \beta \cos\theta$, where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle; τ is the mean size of the ordered

(crystalline) domains, which may be smaller or equal to the grain size [1,2]. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 μm .

2. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy also known as electron spectroscopy for chemical analysis (ESCA) is a quantitative technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed.

XPS was developed in the mid 1960s by K. Siegbahn and his research group. K. Siegbahn was awarded the Nobel Prize for Physics in 1981 for his work in XPS. The phenomenon is based on the photoelectric effect outlined by Einstein in 1905 where the concept of the photon was used to describe the ejection of electrons from a surface when photons impinge upon it [3]. For XPS analysis, Al $K\alpha$ (1486.6eV) or Mg $K\alpha$ (1253.6eV) is often the photon energies of choice. The energy diagram of the phenomenon is represented in Figure A2.

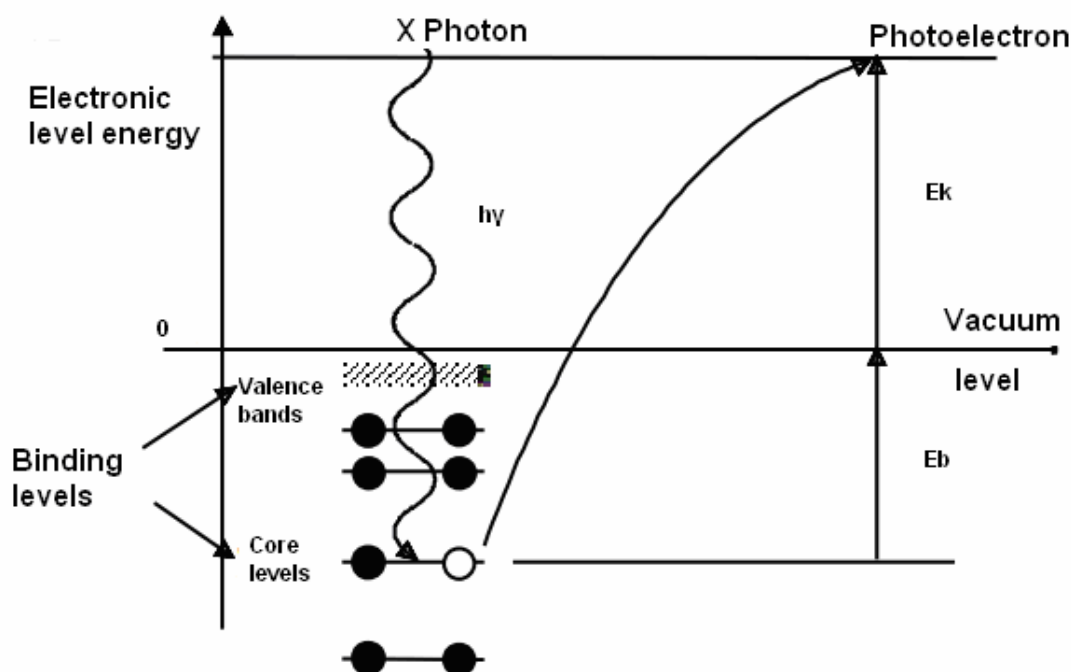


Figure A2 : Energy diagram of the photo emission process [5].

XPS is among the most frequently used surface chemical characterization techniques. XPS is based on the photoelectric effect: an atom absorbs a photon of energy $h\nu$ from an X-ray source; next, a core or valence electron with binding energy E_b is ejected. The photoelectron has a kinetic energy $E_k = h\nu - E_b - \phi$, where, E_k is the kinetic energy of the photoelectron, h is Planck's constant, ν is the frequency of the exciting radiation, E_b is the binding energy of the photoelectron with respect to the Fermi level of the sample, ϕ is the work function of the spectrometer [4].

Because the energy of a particular X-ray wavelength is known, the electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914): $E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$, where E_{binding} is the binding energy (BE) of the electron, E_{photon} is the energy of the X-ray

photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument and ϕ is the work function of the spectrometer [4,5]. XPS detects all elements with an atomic number (Z) of 3 (lithium) and above. It cannot detect hydrogen ($Z = 1$) or helium ($Z = 2$) because the diameter of these orbitals is so small, reducing the catch probability to almost zero. All the XPS measurements were carried out, in our case, in SSX-100 spectrometer using monochromatized Al $K\alpha$ radiation (1486.6 eV) and at 35° take-off angle (relative to the surface normal). The analyzed core-level lines were calibrated with respect to the component C 1s of binding energy set at 284.6 eV and relative percentage of different elements were calculated from the general survey spectrum in relation to carbon by CasaXPS software version 2.0.

3. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a fourier transform infrared spectrometer. FTIR is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint" [6]. In our case, FTIR spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR Spectrometer. Trace amount of the sample was added to prepare the KBr pellets, which was then employed for the characterization.

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify functional groups and compounds [7]. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material.

4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a thermal analysis technique which measures the weight change in a material as a function of temperature and time, in a controlled environment. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000 °C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration [8]. This can be very useful to investigate the thermal stability of a material, or to investigate its behavior in different atmospheres (e.g. inert or oxidizing). TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures,

absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.

TGA is considered to be one of the five basic thermal analysis techniques. It involves the measurement of change of sample mass with change of temperature. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting, do not. The latter may be studied by differential thermal analysis (DTA) or differential scanning calorimetry (DSC), both of which measure the variation of heat flux in a sample with variation of temperature. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss (e.g., melting and crystallization) and those that involve a weight loss (e.g., degradation). TGA measurements, in our case, were performed on a METTLER TOLEDO TGA/SDTA 851e. The samples were heated from 30 to 800 °C at a heating rate of 10 °C per minute in nitrogen and air. The residual mass loss was recorded as a function of temperature.

5. Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted

through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD (charge-coupled device) camera. The image detected by the CCD may be displayed on a monitor or computer [9]. This is diagrammatically represented in Figure A3. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200 kV electrons have a wavelength of $0.025\text{\AA}$. However, whereas the resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about $1\text{-}2\text{\AA}$.

TEM is capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939 [9]. TEM studies, in our case, were carried out using a TECNAI 10 PHILIPS microscope. Prior to the analysis, the samples were dispersed in ethanol and a drop of the suspension was deposited on a holey carbon-coated copper grid.

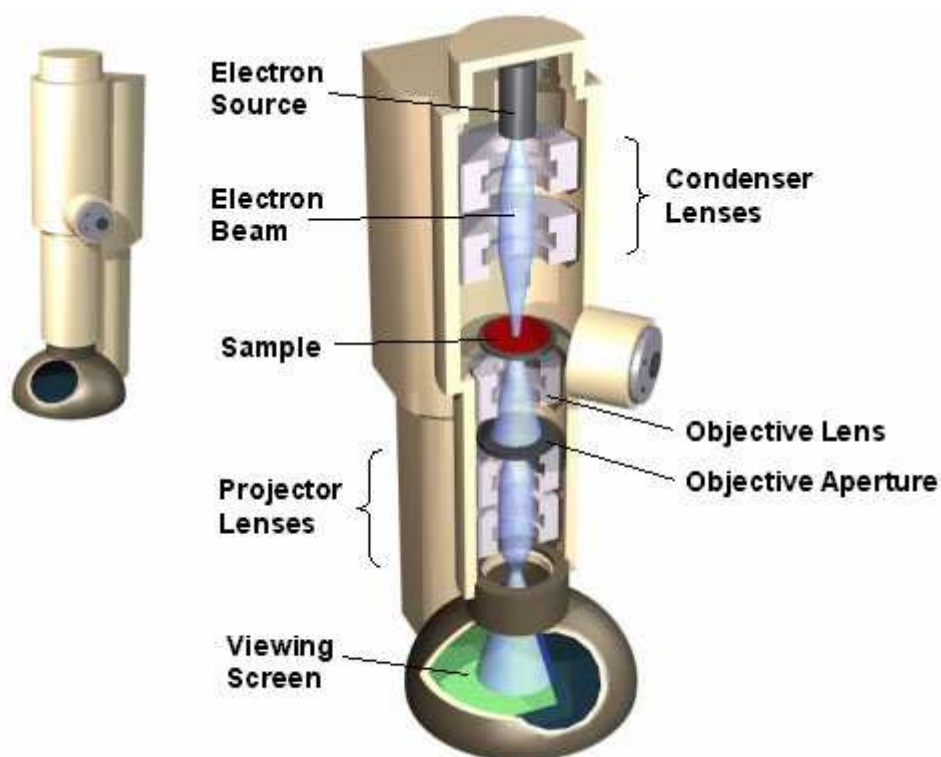


Figure A3 : Diagrammatical representation of a TEM [10].

TEM uses a high voltage electron beam to create an image. The electrons are emitted by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at +100 keV (40 to 400 keV) with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the specimen that is in part transparent to electrons and in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope [9].

6. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

Field emission scanning electron microscopy is a high-resolution imaging technique providing topographical and structural information. Often used in conjunction with SEM, energy dispersive X-ray spectroscopy is used to qualitatively and quantitatively analyze the elements present in a selected area of the SEM image. Together FE-SEM and EDX capabilities allow the irradiation by a focused electron beam, imaging secondary or backscattered electrons and energy analysis of X-rays. The types of signals produced by an SEM include secondary electrons, back-scattered electrons, characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample [11]. A diagrammatical representation of FE-SEM is depicted in Figure A4.

In the most common or standard detection mode, secondary electron imaging (SEI), the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

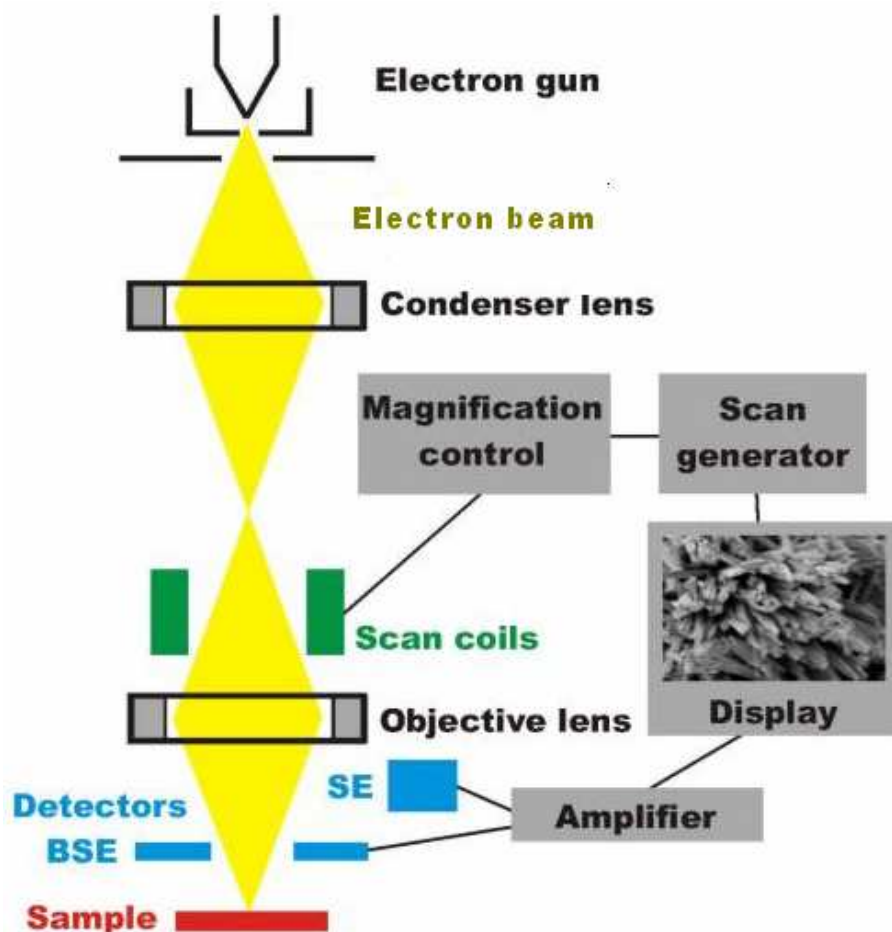


Figure A4 : Diagrammatical representation of a FE-SEM [12].

The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface [11]. The surface morphology of the materials, in our case, were studied by FE-SEM using JEOL JSM-7500F microscope operating at 20 kV at a working distance of 8 mm equipped with

energy dispersive X-ray (EDX) analysis facility. EDX was used to find out the elemental composition in the given material.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube.

7. DekTak Profilometer

DekTak profilometer is used to measure the surface topology of a material and to get a profile of the surface details. The Veeco DekTak 8 profilometer scans the surface of a material and outputs a single line graph of the surface vertical topology. The purpose of the DekTak is to give a quantifiable measurement of the surface profile of a material. This can be used to measure the height or width of the surface, such as an etch, a metal deposit, or resist thickness. The profile can provide information of the roughness of the surface of a material [13].

The profilometer operates by lightly dragging a sharp stylus over the surface of the substrate and recording the vertical profile of the surface. The profile of the surface of a specimen is useful to either characterize it being measured, or a machine that was used on it. The profilometer could be used to find the depth of an etch. A more precise measurement of the thickness of metal film can be achieved with the profilometer, as well as a characterization of the roughness of that film. The thickness and roughness of the composites were measured by Veeco DekTak 8 profilometer. It was measured using a stylus, placing in contact with, and then gently dragging along the surface of the substrate. The vertical deflection measures the change in step height.

8. Cyclic voltammetry (CV)

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process [14].

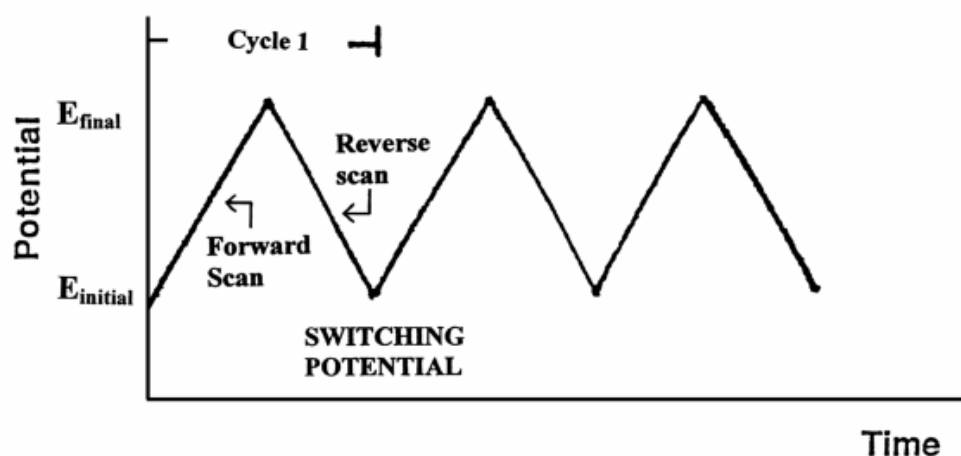


Figure A5 : Potential-time excitation signal in cyclic voltammetric experiment.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode using a triangular potential waveform. Depending on the information sought, single or multiple cycles can be used as shown in Figure A5. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current versus potential is termed a cyclic voltammogram. The cyclic voltammogram is a complicated, time-dependent function of a large number of physical and chemical parameters [15].

Figure A6 illustrates the expected response of a reversible redox couple during a single potential cycle. It is assumed that only the oxidized form O is present initially. Thus, a negative-going potential scan is chosen for the first half-cycle, starting from a value where no reduction occurs. As the applied potential approaches the characteristic E for the redox process, a cathodic current begins to increase, until a peak is reached.

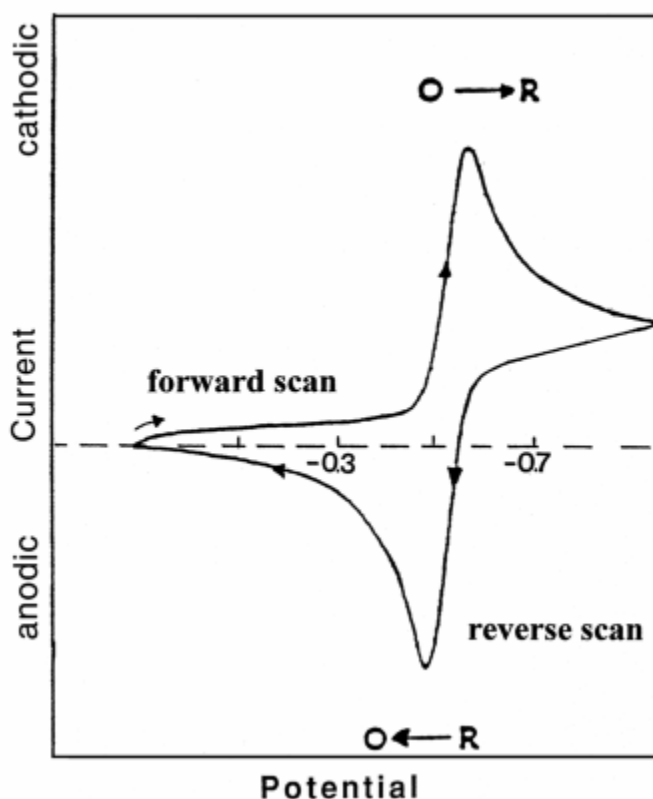


Figure A6 : Typical cyclic voltammogram for a reversible $O + ne^- \leftrightarrow R$ redox process.

After traversing the potential region in which the reduction process takes place, the direction of the potential sweep is reversed. During the reverse scan, R molecules (generated in the forward half cycle, and accumulated near the surface) are reoxidized back to O and an anodic peak results [15].

9. Chronopotentiometry

This is a galvanostatic method in which the current at the working electrode is held at a constant level for a given period of time. The working electrode potential and

current are recorded as a function of time. The galvanostat uses a three electrode configuration, in which a current is applied between the auxiliary and working electrodes, and the potential of the working electrode (measured with respect to the reference electrode) is monitored. The basis of controlled current experiments is that a redox (electron transfer) reaction must occur at the surface of the working electrode in order to support the applied current [14].

Common applications of the galvanostat include constant current stripping potentiometry and constant current electrolysis (including applications where a constant rate of electrolysis is important, such as electrodeposition and battery studies). One advantage of all constant current techniques is that the ohmic drop due to solution resistance is also constant, as it is equal to the product of the current and the solution resistance. The ohmic distortion can therefore be simply corrected by a constant potential offset [15].

10. Potentiodynamic polarization curve

Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often O_2 or H^+) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs.

The two reactions can take place on one metal or on two dissimilar metals (or metal sites) that are electrically connected. The vertical axis is potential and the horizontal axis is the logarithm of absolute current. The theoretical current for the anodic and cathodic reactions are shown as straight lines as in Figure A7. The curved line is the total current - the sum of the anodic and cathodic currents. This is the current that is measured when sweeping the potential of the metal with the potentiostat. The sharp point in the curve is actually the point where the current changes signs as the reaction changes from anodic to cathodic, or vice versa [15]. The sharp point is due to the use of a logarithmic axis. The use of a log axis is necessary because of the wide range of current values that must be displayed during a corrosion experiment.

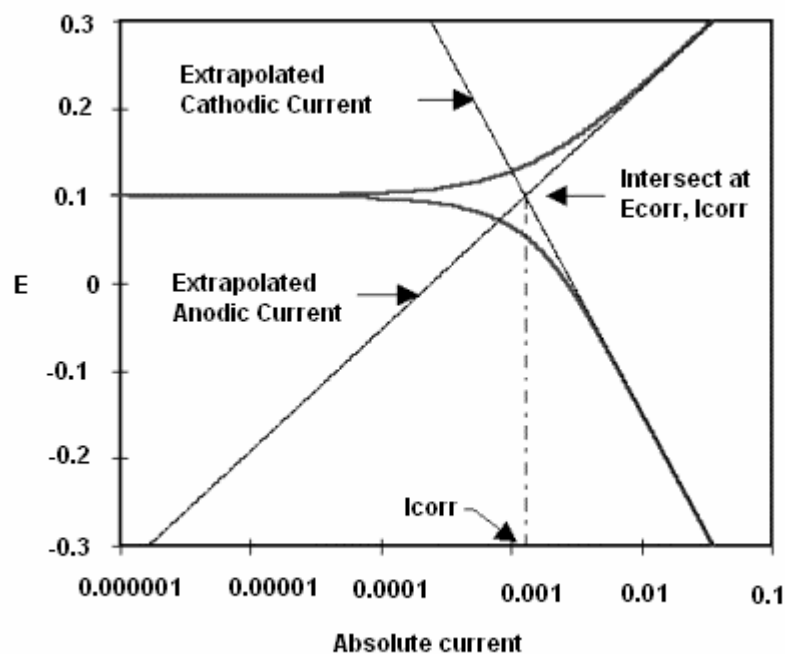


Figure A7 : A typical potentiodynamic polarization curve for Tafel analysis.

The model used for the corrosion process assumes that the rates of both the anodic and cathodic processes are controlled by the kinetics of the electron transfer reaction at the metal surface. This is generally the case for corrosion reactions. An electrochemical reaction under kinetic control obeys Equation 1 in the Tafel Equation.

$$I = I_0 e^{(2.3(E-E^0)/\beta)} \quad \text{Equation 1.}$$

In this equation, I is the current resulting from the reaction, I_0 is a reaction dependent constant called the exchange current, E is the electrode potential, E^0 is the equilibrium potential (constant for a given reaction), β is the reaction's Tafel Constant (constant for a given reaction). Beta has units of volts/decade [16].

The Tafel equation describes the behavior of one isolated reaction. In a corrosion system, we have two opposing reactions – anodic and cathodic. The Tafel equations for both the anodic and cathodic reactions in a corrosion system can be combined to generate the Butler-Volmer Equation (Equation 2).

$$I = I_a + I_c = I_{\text{corr}}(e^{(2.3(E-E_{\text{oc}})/\beta_a)} - e^{(-2.3(E-E_{\text{oc}})/\beta_c)}) \quad \text{Equation 2.}$$

Where I is the measured cell current in amps, I_{corr} is the corrosion current in amps, E is the electrode potential, E_{oc} is the corrosion potential in volts, β_a is the anodic Beta Tafel Constant in volts/decade, β_c is the cathodic Beta Tafel Constant in volts/decade. At E_{oc} , each exponential term equals one. The cell current is therefore zero, as one would expect. Near E_{oc} both exponential terms contribute to the overall current. Finally, as the potential is driven far from E_{oc} by the potentiostat, one exponential term predominates and the other term can be ignored [16]. When this occurs, a plot of log current versus potential becomes a straight line.

A log I versus E plot is called a Tafel Plot. The Tafel Plot in Figure A7 was generated directly from the Butler-Volmer equation. In practice, many corrosion systems are kinetically controlled and thus obey Equation 2. A log current versus potential curve that is linear on both sides of E_{corr} is indicative of kinetic control for the system being studied.

V.3. Ionic liquids

Ionic liquids are often fluid at room temperature, and consist entirely of ionic species. The salts are characterized by weak interactions, owing to the combination of a large cation and a charge-delocalized anion. This results in a low tendency to crystallize due to flexibility (anion) and dissymmetry (cation). In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point. From these studies the arbitrary definition arose of an ionic liquid being an ionic material with a melting point below 100 °C. The first room-temperature ionic liquid triethylammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ (m.pt. 12 °C) was discovered in 1914, but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum(III) chloride and *N*-alkylpyridinium or 1,3-dialkylimidazolium chloride [17,18].

Ionic liquids can be divided into two major classes; those based on discrete anions and those with anionic complexes [19]. These two classes of compounds have quite different characteristics, which will lead to different applications. Both types of liquid are tunable and the variables are largely common to both systems. It is an interesting

observation that despite their short history there are more ionic solvents that have been reported and characterized than molecular ones. The large range of anion–cation combinations possible means that the physical and chemical properties can be tailored to the specific application and this is the subject of a corresponding review by Endres [20]. Anions such as BF_4^- and PF_6^- were initially used quite extensively because of their wide potential window, however, slow hydrolysis by water, yielding HF, has led to an increase in the use of water stable anions such as $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. These have even larger potential windows and have higher conductivities and lower viscosities than the corresponding BF_4^- and PF_6^- salts.

Anionic complexes such as eutectic based ionic liquids can be expressed in terms of the following general formula $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+ \text{X}^- \cdot z \text{Y}$ [19]. The ionic liquids described can be subdivided into three types where $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+$ is for example a choline-like cation such as $\text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3$, X is generally a halide anion (usually Cl^-). They are based on equilibria set up between X^- and a Lewis or Brønsted acid Y, z refers to the number of Y molecules which complex X^- .

e.g. $3\text{AlCl}_3 + 2\text{Cl}^- \rightleftharpoons 2\text{AlCl}_4^- + \text{Al}_2\text{Cl}_7^-$ or $\text{Cl}^- + 2\text{urea} \rightleftharpoons 2\text{Cl}^- \cdot 2\text{urea}$.

Eutectic Type 1 $\text{Y}=\text{MCl}_x$, $\text{M}=\text{Zn}, \text{Sn}, \text{Fe}, \text{Al}, \text{Ga}$

Eutectic Type 2 $\text{Y}=\text{MCl}_x \cdot y\text{H}_2\text{O}$, $\text{M}=\text{Cr}, \text{Co}, \text{Cu}, \text{Ni}, \text{Fe}$

Eutectic Type 3 $\text{Y} = \text{RZ}$, $\text{Z} = \text{CONH}_2, \text{COOH}, \text{OH}$

The relative proportions of anionic species depend on the ionic liquid composition. The ability to vary the composition of Lewis or Brønsted acid adds an additional dimension to the tenability of the eutectic-based ionic liquids. They are also clearly useful for electroplating if the metal of interest falls in the category defined above

under Type I or Type II as the metal ion concentration can be as high as 10 mol dm^{-3} . There is some controversy over the classification of complex anions as ionic liquids. It could, however, be argued that discrete anions are just a subset of complex anions where the Lewis acid and Lewis base are present in equimolar amounts and the equilibrium constant lies considerably over to the right. e.g. $\text{R}_4\text{N}^+ \text{F}^- + \text{BF}_3 \rightleftharpoons \text{R}_4\text{N}^+ \text{BF}_4^-$

Deep eutectic solvents as new class of ionic liquids

While the number of ionic liquids has expanded almost exponentially over the past 20 years it is evident that new classes of salts will be developed in the coming years. Another alternative approach to making ionic liquid analogues is to take a simple organic halide salt and complex the anion with something that will form a hydrogen bond. The complexing agent will decrease the interaction between the anion and the cation and decrease the freezing point of the mixture.

To differentiate these liquids from the more commonly studied imidazolium salts the term Deep Eutectic Solvents has been coined by Abbott et al [21]. This approach is not only cheaper and easier to make, but many of the formulations are non-toxic and even biodegradable. A wide variety of salts can be used with an even wider range of hydrogen bond donors. The Abbott group has been the first to pioneer this new technology and there has been a large amount of work in the area of new class of ionic liquids.

Deep eutectic solvents made from hydrogen bond donor and quaternary ammonium salt mixtures

One of the biggest areas in the DES field is the use of a quaternary ammonium salt and complexing it with a hydrogen bond donor. The various hydrogen bond donors

that have been looked at involve polycarboxylic acids, polyamides, polyalcohols. These liquids are easy to prepare in a pure state, they are non-reactive with water and many of them are bio-degradable. These systems contain a cation and an anion and more importantly there is a hydrogen bond donating species there as well.

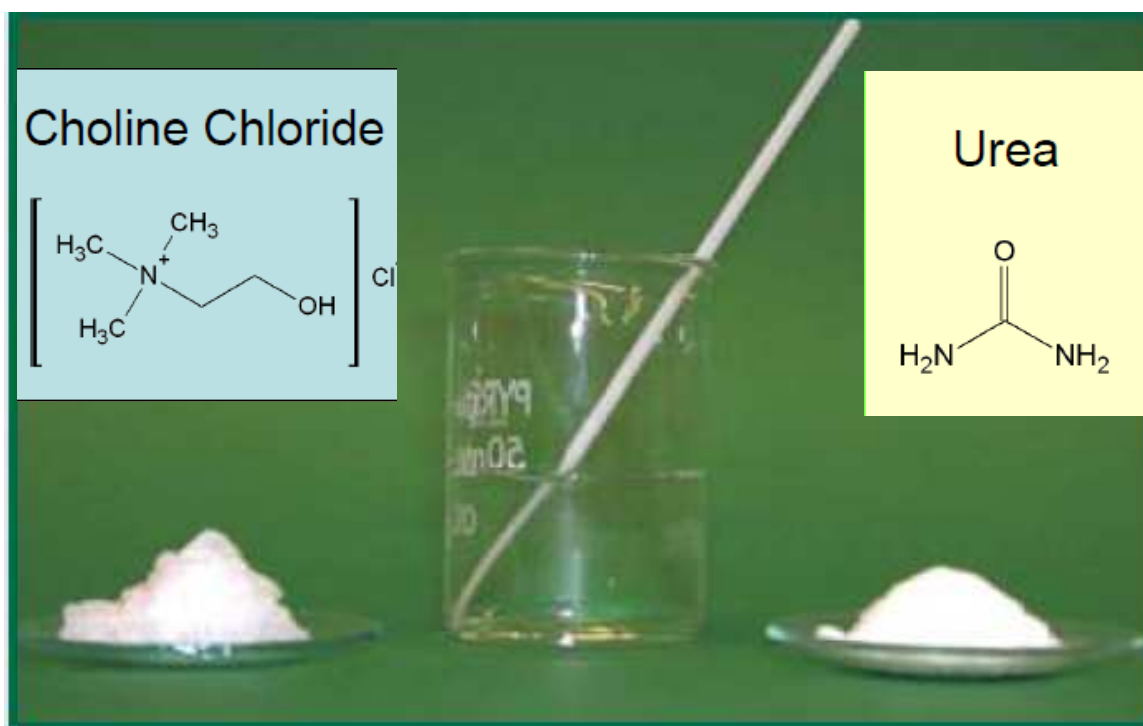


Figure A8 : Picture representation of choline chloride (left side powder) and urea (right side powder) mixture turns liquid at certain conditions (shown in beaker).

The end result is similar to conventionally known ionic liquids, however, a liquid that is made up a cation and anion is formed, but its route to the reduction of lattice energy of the system is different. This occurs through the hydrogen bond donor complexing to the anion and withdrawing the electron density of the anion from the

cation. This separation results in a weaker anion/cation interaction, which is the way ionic liquids achieve their low melting temperatures. The mixture of two components is pictorially represented in Figure A8 and diagrammatic representation is shown in Figure A9.

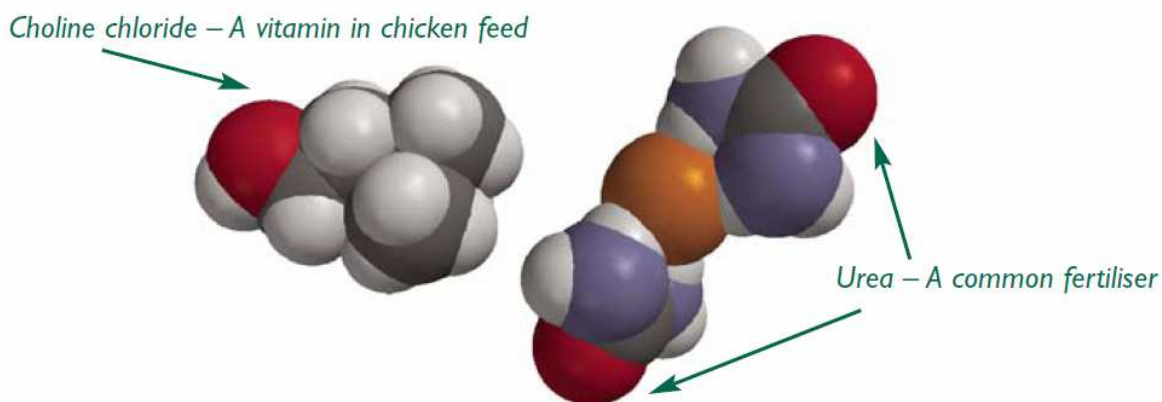


Figure A9 : Diagrammatic representation of choline chloride and urea.

One of the first DES systems that was investigated, contained choline (2-hydroxyethyltrimethylammonium) chloride (ChCl) mixed with urea ($\text{NH}_2\text{CO.NH}_2$). Choline chloride is vitamin B4 and is produced on the Mtonne p.a. scale as an additive for chicken feed; urea is a common fertilizer. This is not only cheap and easy to make but it is non-toxic and even biodegradable. By themselves they have freezing points of 303 °C and 135 °C respectively. It also showed lower viscosities than in a ratio of 1:2 respectively. The main reason behind ChCl being such a useful quaternary ammonium salt is to do with the fact it is an asymmetric quaternary ammonium salt with a polar functional group, but is also small. The asymmetric nature of this molecule reduces the

freezing point of the ionic molecular liquid, as does the polar functional group. By combining these two compounds in a ratio of 1:2 (ChCl: urea), the product formed has a freezing point of 12 °C.

V.4. References

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V.5. Publications and conferences

Research Papers

1. P. Martis, A. Fonseca, Z. Mekhalif, J. Delhalle, Optimization of cuprous oxide nanocrystals deposition on multiwalled carbon nanotubes, *Journal of Nanoparticle Research*, 2010, 12, 439.
2. P. Martis, V.S. Dilimon, J. Delhalle, Z. Mekhalif, Electrogenation of nickel/carbon nanotube composites in ionic liquid, *Electrochimica Acta*, 2010, 55, 5407.
3. P. Martis, V.S. Dilimon, J. Delhalle, Z. Mekhalif, Impact of surface functionalization of MWCNTs on electrogenerated Ni/MWCNT composites from aqueous solutions, *Materials Chemistry and Physics*, accepted for publication.
4. P. Martis, B.R. Venugopal, J. Delhalle, Z. Mekhalif, Selective decoration of nickel and nickel oxide nanocrystals on multiwalled carbon nanotubes, communicated for publication.
5. P. Martis, B.R. Venugopal, J. Delhalle, Z. Mekhalif, Infrared irradiated controlled decoration of multiwalled carbon nanotubes with Cu/CuO_x nanocrystals, communicated for publication.

Conferences, posters and oral presentations

1. Ninth international conference on the science and application of Nanotubes (NT08) held in Le Corum Montpellier, France from June 29-July 4, 2008, presented a poster.
2. MRS 2008 Fall meeting held in Boston, USA from December 1-5, 2008, participated.

3. CARBON conference 2009 held in Biarritz, France from June 14 – 19, 2009, presented a poster.
4. Outstanding PhD formation day held at ULB, Brussels, Belgium on January 20, 2009, presented a poster.
5. Journée de l'Ecole Doctorale Thématique CHIM, held at FUNDP, Namur, Belgium from January 21-22, 2009, participated.
6. Journée de l'Ecole Doctorale Thématique CHIM, held at FUNDP, Namur, Belgium on April 24, 2009, participated.
7. Colloque NANOFAC held at FUNDP, Namur, Belgium on October 1, 2009, participated.
8. Symposium sur la toxicite des nanomateriaux held at FUNDP, Namur, Belgium on October 2, 2009, participated.
9. Certificat de participation aux lecons de la Chaire Francqui 2007-2008 held at FUNDP, Namur, Belgium from 28 February – 20 March 2008, participated.
10. Certificat de participation a l'ecole de formation interdisciplinaire pour doctorants held at FUNDP, Namur, Belgium from January 18-22, 2010, participated.
11. Leuven summer school at Leuven University, Leuven, Belgium from August 22-27, 2010, presented a poster.
12. Nano EEB International workshop on Nanotechnology held at St. Aloysius College, Mangalore, India from December 14-16, 2010, given an oral presentation.