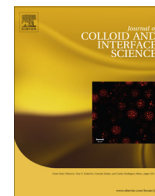




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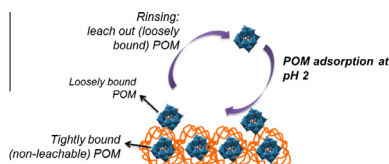


In situ quartz crystal microbalance monitoring of the adsorption of polyoxometalate on a polyampholyte polymer matrix

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GRAPHICAL ABSTRACT



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ABSTRACT

Hybridization of polyoxometalates (POMs) via an organic–inorganic association constitutes a new route to develop heterogeneous POM catalysts with tunable supramolecular architecture. As the structural stability of POMs is strongly influenced by the pH conditions, a quantitative understanding of the POMs–polymer association is important in practical applications. Herein, we use Quartz Crystal Microbalance (QCM) to systematically investigate the interactions of Keggin phosphotungstic acid POM with a polyampholyte polymer-coated QCM sensor as a function of pH. The mass of adsorbed POMs increases when pH decreases from 5.6 to 2, indicating that electrostatic forces play a major role in the formation of POM–polymer hybrids. This finding is complemented by AFM images that show an increase in the size of the hybrid entities from 5 to 12 nm as the pH decreases from 5.6 to 2. The POM adsorbed amount at a particular pH value reaches an equilibrium level with time. The hybrids further gain in adsorbed mass only when lowering the pH value of the POM solution. The hybrid structure formed above pH 2 shows resistance to leaching as indicated by the steady level of the adsorbed mass during a rinsing step with water. However, at pH 2, the rinsing step causes desorption of some weakly adsorbed POMs. It is shown that leached POMs can be re-adsorbed back into the polymer matrix during a second contact with a POM solution at pH 2. This adsorption–desorption cycles of POMs were successfully repeated. Our experiments shed light into the coexistence of tightly as well as loosely bound POMs in hybrid catalyst formed at pH 2. The loosely bound POMs can potentially act as homogeneous catalysts when desorbed. However, these leached POMs can be re-adsorbed back into the matrix, preserving the heterogeneous state of the catalyst. Our results show that QCM is a powerful technique to study in situ the dynamics of the adsorption of POMs on a polymer matrix under different pH conditions.

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1. Introduction

Polyoxometalates (POM) are oxoanionic clusters of early transition metals with well-defined molecular structure and properties. They have attracted growing interest in developing advanced functional materials owing to their plethora of tunable properties, as well as their ability to combine with organic moieties to form hybrid materials. These have opened up new avenues not only in

the field of supramolecular chemistry, but also in new materials technology [1,2]. Their tunable molecular architecture, charge density, strong redox capability, and electro- and photochemical properties, make that these molecular metal-oxide nano-clusters find emerging applications in diverse fields, such as magnetism [3–5], electronics [6], electro- and photochromic systems [7,8], medicine [9], molecular batteries [10] and catalysis [11–15].

POM anions are often hybridized in an organic matrix in order to improve their processability in device fabrication. The hybridization strategy essentially involves the association of POM anions with an organic matrix through either covalent [16] or non-covalent bonds [17]. The later approach may be applied with charged polymer matrices. The electrostatic interactions between POM and such polymers lead to a fast hybridization and, provided that the polymers have a supramolecular structure, allow a well-controlled assembly of POM with multifunctional properties e.g. thermo- and photoresponsive properties [18], dielectric property [16], and catalytic activity [15]. In catalysis, hybridization offers a means to synthesize heterogeneous POM-based catalysts with useful properties such as enhanced processability, recoverability, and reusability [15]. As the charges and structure of both POM and weak polyelectrolytes are highly dependent on the pH conditions [19], a fundamental understanding of the POM-polymer association under different pH conditions is necessary to optimize their properties for practical applications e.g. heterogeneous catalysis.

Quartz Crystal Microbalance (QCM) has emerged as a powerful technique to study the dynamics of adsorption processes on soft and solvated interfaces between solid surfaces and bulk liquids, with mass resolution of a few ng/cm² [20,21]. The technique is operational under liquid media, and is highly useful to quantitatively monitor the growth of soft layers of e.g. adsorbed proteins on solid substrates [22]. In another application of the technique, QCM was recently used to monitor the growth of organic–inorganic hybrid films. The high sensitivity of QCM allows the growth process of the hybrid material to be monitored either in situ, by the sequential deposition of molecular layers of the organic and inorganic species [23–26], or ex situ, after deposition of organic–inorganic hybrid directly on a substrate e.g. silica or alumina [27]. In all cases, the film growth was monitored by recording the frequency decrease of the quartz crystal during each adsorption cycle. With the advent of additional modules, such as flow- and temperature-controlled cells, QCM allows the temperature-dependent growth of hybrid films to be examined. For example, hybrid materials based on trimethylaluminum and ethylene glycol showed lower growth rates at higher temperatures [23,24]. Polyoxometalates, however, exhibit a structural stability largely dependent on the pH conditions. Flow cells equipping QCM offer means to investigate the POMs-polymer electrostatic association under liquid medium and in dynamic conditions. In such a way, it is thus possible to mimic with much realism the working environments used in applications involving POMs as heterogeneous catalysts.

The aim of this paper is to systematically investigate the adsorption of Keggin phosphotungstic acid (H₃PW₁₂O₄₀) POM on a polyampholyte copolymer (poly N,N-diallyl-N-hexylamine-alt-maleic acid) as a function of pH. The copolymer was coated on a QCM sensor and POM adsorption was then monitored as a function of time and in different pH conditions. The morphology of the sensor surface was also analysed using Atomic Force Microscopy (AFM) before and after POM adsorption.

2. Materials and methods

2.1. Polyampholyte polymer

The polyampholyte polymer used in this study is an alternating copolymer, poly(N,N-diallyl-N-hexylamine-alt-maleic acid) (from

now on called “copolymer C6”), having repeating units consisting of a diallylhexylamine group linked to a maleic acid group. The structure of the copolymer C6 is shown in Scheme 1. Copolymer C6 was synthesized according to a procedure reported elsewhere [28]. Depending on pH, the amine (pK_a = 8–9) and carboxylic acid groups (pK_{a1} = 2–3; pK_{a2} = 4–5) may be positively and negatively charged, respectively.

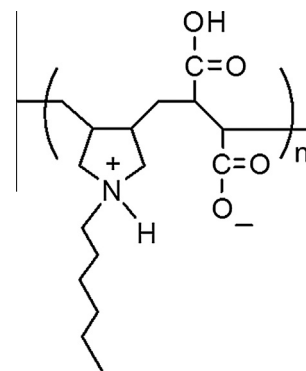
2.2. Preparation of copolymer C6-coated QCM crystals

Standard SiO₂-coated crystals (Q5X 303 from Q-sense, coating thickness ~ 50 nm) were used for QCM experiments. The crystals were initially rinsed with ultrapure water (Elgastat Maxima system, resistance: 18.2 MΩ) and subsequently immersed in absolute ethanol under ultrasonic bath for 20 min. The crystals were then dried under dry N₂ and treated in an UV–O₃ chamber (Jelight USA) for 20 min. A drop (10 μL) of copolymer C6 solution (0.2 g/L in water) stabilized at pH 7 was deposited on the freshly cleaned crystals. The crystals were allowed to dry under ambient conditions for at least 48 h.

2.3. QCM measurements

The adsorption of phosphotungstic acid POM (H₃PW₁₂O₄₀, purchased from Sigma Aldrich) under different pH conditions on the copolymer C6 coating was monitored in situ using QCM. The system used was a Q-Sense E4 (Biolin Scientific, Sweden) equipped with four QFM 401 flow modules. The flow was maintained at 50 μL/min using a peristaltic pump (Ismatec, Germany) at constant temperature of 22 °C. The pH value of POM solutions (0.1 g/L in water, initial pH 3.5) was set at 2, 3, 4, and 5.6 using 0.1 N HCl and 0.1 N aq. ammonia to reach more acidic and more basic pH, respectively. In order to check the reproducibility of the measurements, each experiment was repeated on two independent flow cells. The frequency and dissipation shifts (Δf and ΔD, respectively) were monitored as a function of time. Different experiments were designed as described in Table 1, with the aim to (i) study the effect of pH on POM adsorbed amount (program 1), (ii) investigate the sequential adsorption of POM at different pH values (programs 2 and 3), (iii) address the question of the saturation of the interface by POM at a given pH (program 3), and (iv) show the reversibility of POM adsorption/desorption processes depending on pH (program 3).

The mass adsorbed on the copolymer C6-coated crystal surface after the POM deposition step was calculated based on the shift of frequency (Δf) recorded between the baselines established during



Scheme 1. Molecular structure of the zwitterionic polyampholyte polymer, poly(N,N-diallyl-N-hexylamine-alt-maleic acid). The amine and the two carboxylic functions may be charged or not depending on the pH conditions. For example, the scheme here (with the protonated amine and one of the carboxylic moiety deprotonated) corresponds to the situation likely obtained at pH 5.

Table 1

Steps of the different QCM experiments. The QCM crystal was coated with copolymer C6 before the experiments.

Program 1: POM adsorption at different pH (Fig. 1)	Program 2: POM sequential adsorption (Fig. 6)	Program 3: POM saturation and adsorption/desorption (Fig. 7)
Rinse H ₂ O	Rinse H ₂ O	Rinse H ₂ O
POM solutions (pH 2, 3, 4 or 5.6)	POM pH 5.6	Rinse pH4
Rinse H ₂ O	Rinse pH 5.6	POM pH4
	Rinse H ₂ O	Rinse pH4
	POM pH 3	Rinse H ₂ O
	Rinse pH3	POM pH4
	Rinse H ₂ O	Rinse H ₂ O
		POM pH2
		Rinse pH2
		Rinse H ₂ O
		POM pH2
		Rinse H ₂ O
		} repeated twice

the rinsing step with H₂O, before and after the POM adsorption steps. This corresponds to the mass of POMs left adsorbed on the polymer matrix after rinsing. In such a way, effects related to the density and viscosity of the different liquid media were avoided. Δf was converted to an increment of adsorbed mass (Δm) using the Sauerbrey equation:

$$\Delta m = -C \cdot \Delta f / n \quad (1)$$

where C is the mass sensitivity constant, related to the quartz crystal (here, $C = 17.7 \text{ ng cm}^{-2} \text{ Hz}^{-1}$), and n is the overtone used for the measurement. It must be noted that Sauerbrey equation only holds if the characteristics of the adsorbed layer are identical to the one of the quartz crystal, i.e. if the layer is rigid and homogeneous. In our experiments, the dissipation shifts recorded upon POM adsorption were always lower than 2×10^{-6} , and the $\Delta D/\Delta f$ ratio was in the range of 4×10^{-8} or lower. In such conditions, it is considered that the Sauerbrey equation gives a good estimation of the adsorbed mass [20]. Dissipation values will therefore not be further exploited. Normalized $\Delta f/n$ values are reported for the 5th overtone ($n = 5$).

2.4. Atomic force microscopy

AFM experiments were performed using a Nanoscope VIII multimode AFM (Nano Surfaces Business, Bruker Corporation, Santa Barbara, CA) in Tapping Mode™ under ambient conditions (23 °C, 56%RH). After QCM experiments the sensors were taken out from the flow module and flushed with dry nitrogen. The sensors were further dried under ambient conditions for 48 h before AFM analysis. Dried QCM sensors were glued on a magnetic stainless steel disc using a small piece of double sided adhesive tape, and mounted on the J type piezoelectric scanner. Etched Si tapping mode cantilever (TESP type, Bruker AFM probes), having a nominal tip radius of curvature of 8 nm, were used for imaging at a scan speed of 0.5 $\mu\text{m/s}$. The images were acquired under light tapping conditions in order to minimize sample deformation during imaging. The captured images were analyzed using the Nanoscope scan analysis software (Bruker) and flattened to the zeroth order to remove any underlying surface curvature.

3. Results and discussion

The changes in the normalized Δf of the copolymer C6-coated QCM sensors during the adsorption of H₃PW₁₂O₄₀ POM were monitored under different pH conditions (Table 1, Program 1). The results are reported in Fig. 1. An increment in the frequency was

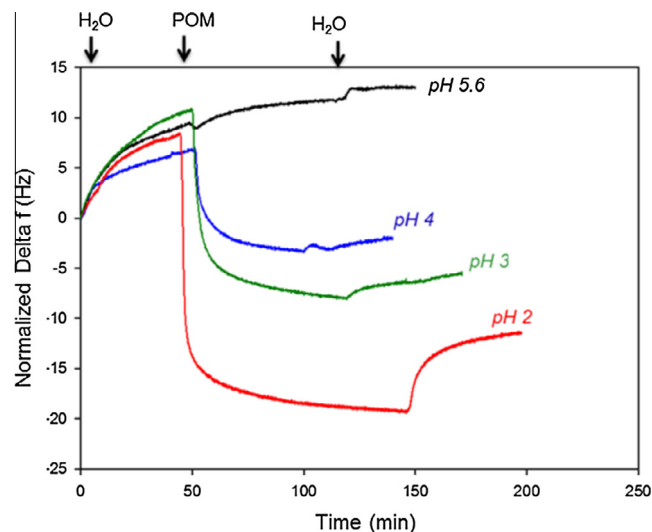


Fig. 1. Normalized Δf vs. time of the copolymer C6-coated QCM sensor during the adsorption of POM solutions at different pH values.

observed during the initial rinsing step with water (0–45 min). This positive Δf could be attributed to partial leaching of the water-soluble and not well anchored copolymer C6 from the sensor surface. Subsequent contact of POM solutions with the sensor results in the decrease of the frequency. A maximum frequency decrease ($\Delta f = -19.8 \text{ Hz}$) occurs under the most acidic conditions (pH 2). However, when the pH of the flowed POM solution is higher (from pH 3 to 5.6), the Δf is correspondingly lower (from -16.4 to 3.8 Hz).

The adsorbed mass of POMs (calculated from Eq. (1)) as a function of pH is plotted in Fig. 2. The maximum adsorbed mass of POM (355–404 ng/cm^2) was recorded under the most acidic conditions (pH 2). As the pH of the POM solution increased from 3 to 4, the adsorbed quantity of POM decreased significantly from ~ 300 to $\sim 150 \text{ ng/cm}^2$ respectively. At pH 5.6, no POM adsorption could be detected. The increase in the adsorbed quantity of POM at more acidic pH values is a clear indication that POM-polymer interactions are largely electrostatic in nature. The pK values of the carboxylic acid groups in the repeating unit of the copolymer C6 are

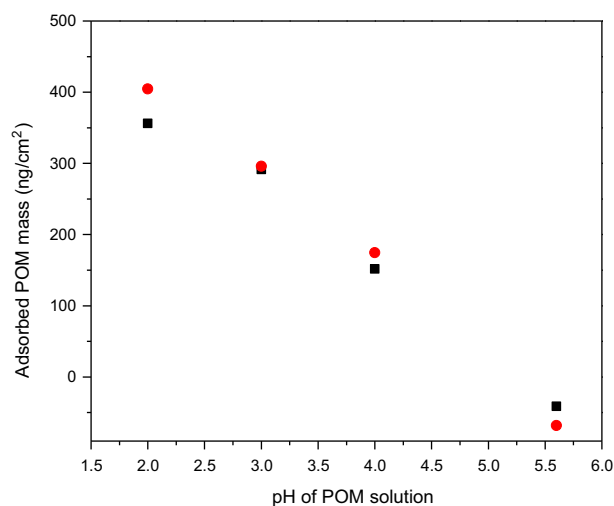


Fig. 2. Adsorbed POM mass (ng/cm^2) on the copolymer C6-coated QCM sensor after adsorption from POM solutions at different pH values. Results are given for duplicate experiments at each pH value.

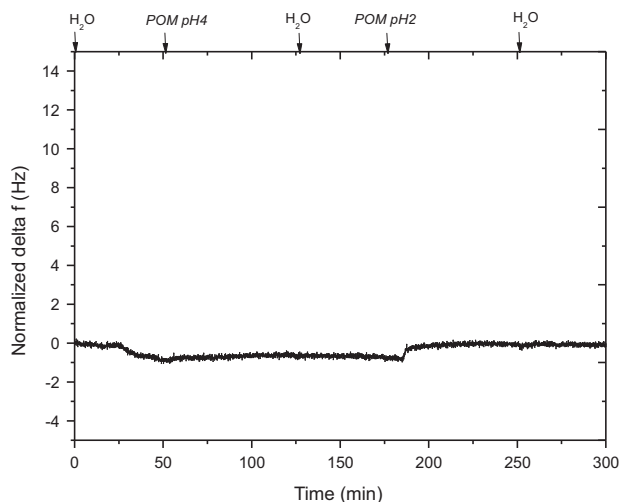


Fig. 3. Control experiment: Frequency decrease was not observed upon contact with POM solutions at different pH on bare SiO_2 QCM sensor. Bare sensor was initially rinsed with water before passing POM (pH 4) solution. Next, a rinsing step with water was applied before flowing a POM solution at pH 2 on the sensor surface, and rinsing again with water.

in the range of $\text{pK}_{\text{a}1} = 2\text{--}3$ and $\text{pK}_{\text{a}2} = 4\text{--}5$, and for amine group, $\text{pK}_{\text{a}} = 8\text{--}9$ [29]. Thus at pH 5.6 ($>\text{pK}_{\text{a}2}$, $<\text{pK}_{\text{a}}$), the least adsorption of POMs is due to the presence of many negative charges on the carboxylic group of the copolymer, which outweigh the effect of positively charged amines. This results in an electrostatic repulsion between the POM anions and the copolymer. Conversely, at pH 2 ($<\text{pK}_{\text{a}2}$, $\approx \text{pK}_{\text{a}1}$, $<\text{pK}_{\text{a}}$) most carboxylic groups are protonated, which results in an electrostatic attraction between positively-charged amines and POM anions leading to a mass gain of the copolymer C6-coated sensor in QCM experiments.

Control experiments performed on bare SiO_2 sensors do not show frequency decrease upon exposing the sensor surface to POM solutions (Fig. 3). This confirms that POM adsorption only

takes place in the presence of the copolymer C6 coating on the sensor surface, and thus that copolymer C6 is not completely leached from the sensor surface during initial rinsing step.

Fig. 4a and b shows the AFM images of bare and copolymer C6-coated QCM sensors respectively. When compared to the bare sensor surface, which has a rough morphology (root-mean-square roughness (R_{rms}) = 1.2 ± 0.06 nm), the copolymer C6 deposition results in the formation of a smoother (R_{rms} = 0.5 ± 0.08 nm) and more homogeneous film on the sensor surface. After the initial rinsing step with water performed in the QCM flow cell, the sensor surface shows rough features (R_{rms} = 2.0 ± 0.07 nm) with size and shape different to that of bare sensor surface, while the topography of the bare sensor is again visible in the background (Fig. 4c). The observed features indicate the presence of adsorbed copolymer C6 after rinsing, in line with the results of the control experiment performed by QCM (see Fig. 3). It should be noted that the observed heterogeneity of the copolymer C6 coating may be attributed to aggregation occurring during the drying step after opening the flow cell.

Fig. 5 shows AFM topographic images of the copolymer C6-coated QCM sensors after the adsorption of POMs under different pH conditions. When compared to the polymer entities (R_{rms} 2.0 ± 0.07 nm, 4–6 nm high) observed on the copolymer C6-coated sensor after rinsing (Fig. 4c), the hybrid particles formed at pH 2 are more rough (R_{rms} 4.2 ± 0.1 nm) and ~ 12 nm high (Fig. 5a). It is interesting to note that the height of these hybrid entities is in good agreement with the reported size of the same hybrid material (~ 12 nm high) deposited on a smooth mica surface [30]. At pH 3 and 4, the height and rms roughness of the hybrid material were smaller when compared to the hybrid material formed at pH 2 i.e., R_{rms} 2.5 ± 0.03 nm and 2.9 ± 0.02 nm respectively (Fig. 5b and c). The lowest roughness R_{rms} was measured for the POM adsorbed at pH 5.6 (Fig. 5d). In the latter case, R_{rms} was close to that of bare sensor surface, indicating no or very weak POM adsorption. This is in line with the QCM results that also show low adsorption of POM at the most basic pH explored.

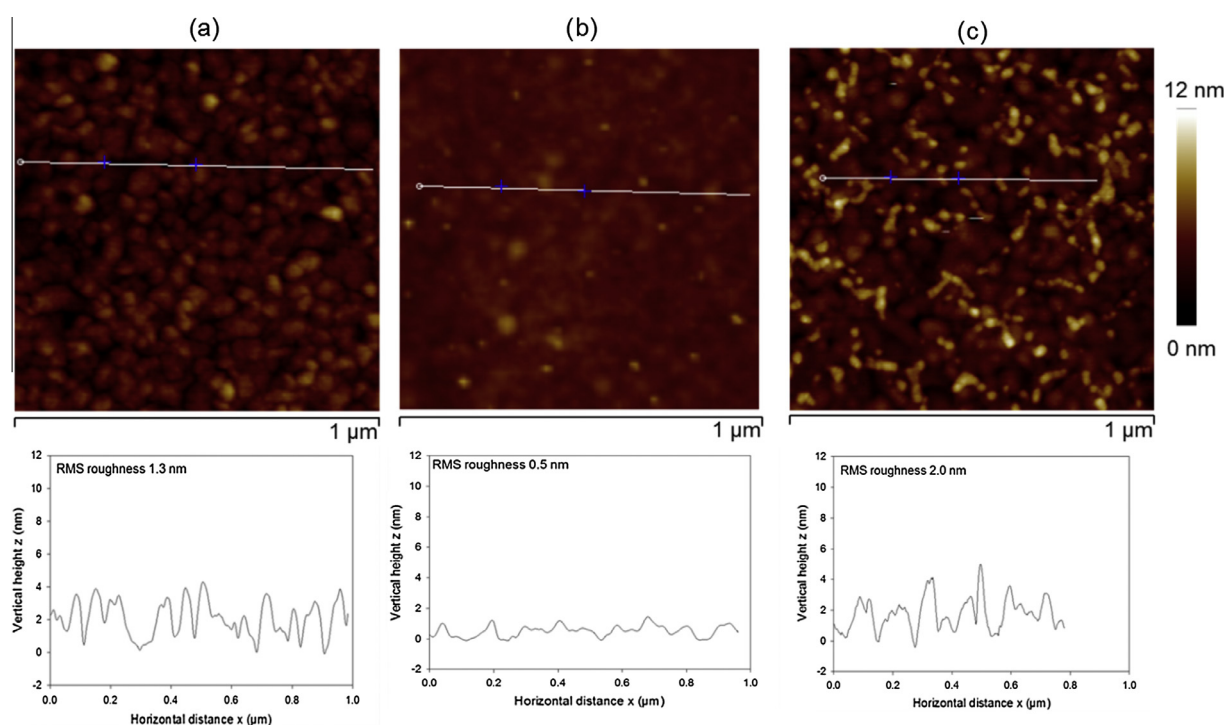


Fig. 4. AFM images of (a) bare SiO_2 QCM sensor, (b) copolymer C6-coated QCM sensor, and (c) copolymer-coated QCM sensor after the initial rinsing step with water. Corresponding cross-sections taken along the white line are shown below each image.

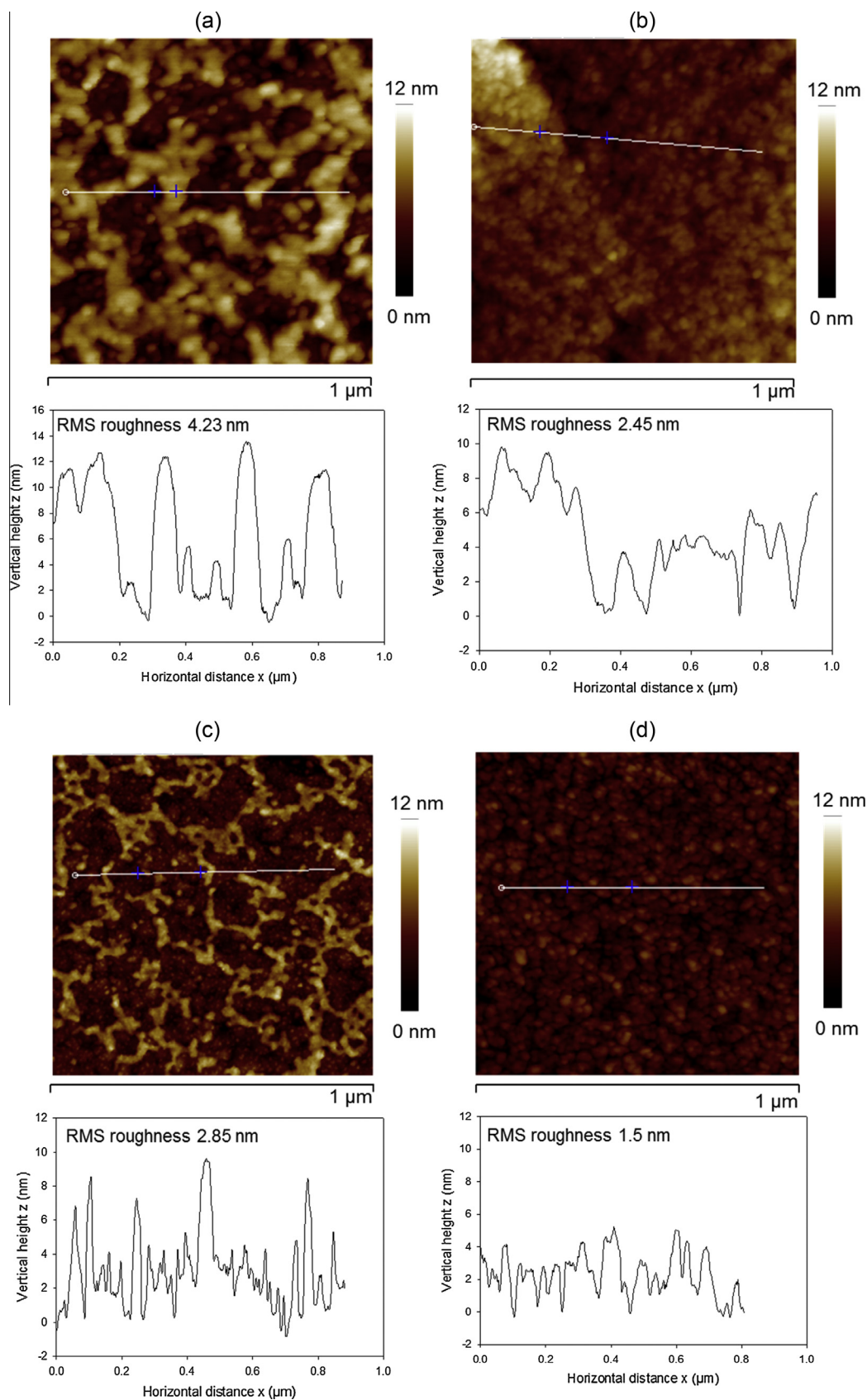


Fig. 5. AFM images of the copolymer C6-coated QCM sensor after the adsorption of POM solutions under different pH conditions. (a) pH 2, (b) pH 3, (c) pH 4, and (d) pH 5.6. Corresponding cross-sections taken along the white line are shown below each image.

3.1. Sequential adsorption of POMs

In a further experiment, we studied adsorption on a given sensor surface upon progressively lowering the pH of the POM solution (Table 1, Program 2). Fig. 6 shows the sequential adsorption of POM, initially at pH 5.6 and then at pH 3. As already shown in Fig. 1, POM adsorption does not occur at pH 5.6. However, at pH 3, a strong adsorption of POM is observed on the copolymer film. This unambiguously indicates that pH of the POM solution determines the degree of adsorption of POMs onto the copolymer C6 matrix. Further, it is interesting to note here that the Δf (−17.5 Hz) at pH 3 is very close to that observed in Fig. 1. This clearly indicates the reproducibility of our sample preparation, experimental set-up and measurements. A similar observation is made when adsorbing POM at pH 2 after a first adsorption step at pH 4 (Table 1, program 3), as shown in Fig. 7.

Ichinose et al. [26] have monitored the layer-by-layer growth of $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]$ POM and poly(allylamine hydrochloride) (PAH), by measuring the frequency change of a quartz sensor crystal dipped in $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]$ (pH 3.5) and polymer solutions (pH 2.5–3) in alternate cycles. Assembly of $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]$ and PAH was remarkably dependent on the pH of the PAH solution. The layer-by-layer assembly did not proceed with PAH solution at pH 5–6. It is interesting to note that in our experiments, adsorption of POM did not take place when the pH of the POM solution was 5.6, that is to say when the pH was above the $\text{pK}_{\text{a}2}$ value of the host copolymer C6 matrix.

3.2. POMs saturation and reversible POM adsorption/desorption

The objective here was to verify if the initial quantity of POM adsorbed onto the copolymer C6 reaches a saturation level at a particular pH condition, and if POM adsorption/desorption cycles could be performed. Fig. 7 shows the adsorption of POMs, initially achieved at pH 4 ($\Delta f = -15$ Hz). The adsorption was followed by rinsing steps, first with an aqueous solution (HCl) at pH 4 and then with ultrapure water (Program 3, Table 1). It is interesting to note here that even after rinsing with water, desorption of POM from the films does not occur, indicating that the POM-polymer hybrid formed at pH 4 clearly resists to leaching of POMs by the water solvent. This could be an indication that the hybrid material is formed by the POM species encapsulated in the polymer matrix thus preventing its direct contact with water. This finding has implications in heterogeneous catalyst design, where one of the major objectives of organic–inorganic hybridization is to impart useful

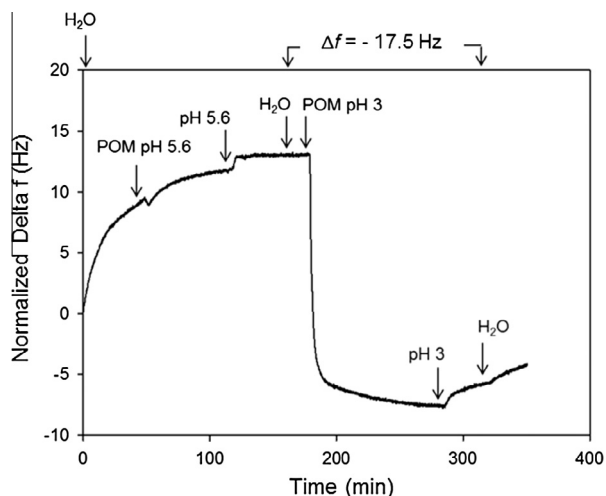


Fig. 6. Normalized frequency shift (Δf) of the copolymer C6-coated QCM sensor under sequential adsorption of POM solutions at pH 5.6, and then at pH 3.

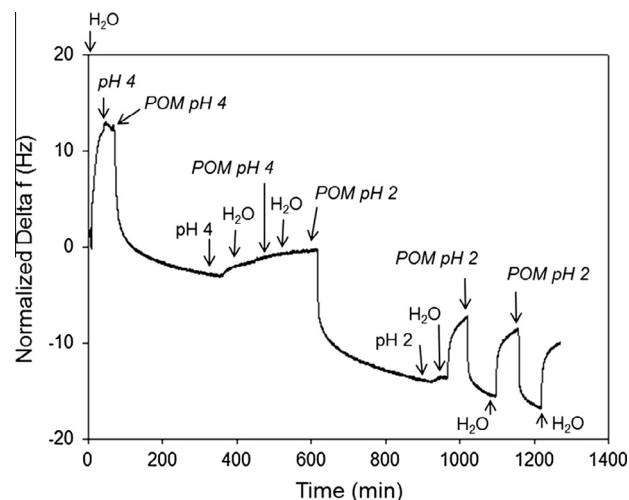
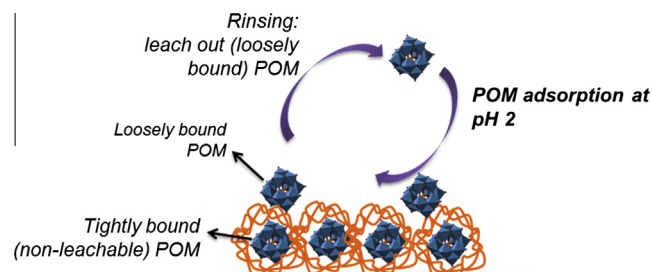


Fig. 7. Normalized frequency shifts (Δf) of the copolymer C6-coated QCM sensor under sequential adsorption of POM solutions first under pH 4, and then under pH 2.

properties, such as resistance to leaching, to the active POM species. QCM experiments provide here valuable quantitative evidence to measure such useful properties of the hybrid catalyst.

The adsorption of POM at pH 4 reaches a saturation level as evidenced by the steady level of Δf recorded after a second contact of the sensor surface with POM solution. This could be attributed to POM adsorption reaching an equilibrium state where net charge on the surface could be close to zero. Further adsorption of POM occurred only when more acidic conditions were applied, as shown by a frequency decrease ($\Delta f = -15$ Hz) when POM solution at pH 2 is introduced. Here, less negative charged sites are present on the copolymer C6 due to protonation of more carboxylic groups, and POM adsorbs in higher amount. A rinsing step with water was later applied, and slight increase in frequency was recorded ($\Delta f = 8$ Hz). This Δf could be related to a bulk effect (change of liquid properties) or to a mass loss. From Fig. 2, we can tell that no large bulk effect occurs for POM solution at pH 2 compared to water. The positive Δf recorded upon rinsing is thus attributed to a mass loss. However the mass lost (143 ng/cm^2) during rinsing is lower than the mass adsorbed (268 ng/cm^2). This suggests that the decrease in mass is due to desorption of some POM species that are weakly adsorbed on the surface. These POM species are more prone to leach as they are not interacting strongly with the polymer matrix and come into contact with water molecules during the rinsing step. However, a subsequent passage of POM solution (at pH 2) records a mass gain, which corresponds to the mass lost during the previous rinsing step. A quantity of POMs which corresponds to the leached amount is adsorbed back into the matrix. This indicates that POM adsorption and desorption are indeed controlled by the number of charged sites present on the zwitterionic copolymer C6 under given pH conditions. Scheme 2 illustrates this cycle of



Scheme 2. Illustration of the adsorption and leaching of weakly bound POM species on the POM-polymer hybrid formed at pH 2.

POM adsorption and desorption that occurs in a repetitive manner leading to 'saw-tooth' patterns in the frequency curve (Fig. 7).

A practical implication of these results is that when the hybrid material is prepared under highly acidic conditions, some weakly adsorbed (non-encapsulated) POM species can leach out to the solution, showing a homogeneous character, while other POMs remain within the polymer matrix, showing a heterogeneous character. The coexistence of both homogeneous and heterogeneous characteristics may be advantageous for some catalytic transformations.

4. Conclusions

QCM was used to in situ monitor the formation of an organic–inorganic hybrid by the association of Keggin phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) POM on a polyampholyte copolymer (poly N,N-diallyl-N-hexylamine-alt-maleic acid) film. The adsorption of POMs onto the copolymer-coated QCM sensor was monitored as a function of time under different pH conditions. The POM adsorbed amount was found to be strongly dependent on the pH of the POM solution, indicating that electrostatic forces play a major role in the formation of the organic–inorganic hybrid material. Maximum quantity of POMs was adsorbed under the most acidic conditions (pH 2) while, toward more basic pH, the adsorbed quantity of POMs decreased with negligible adsorption recorded at pH 5.6, that is to say above the pK_a value of the host polymer. The low adsorption of POM at pH 5.6 is in good agreement with previous reports, for example on the growth of multilayer films formed ex situ on a QCM sensor from octamolybdate POM and a linear cationic polymer [26]. Flow cells equipping QCM used in this study, however, offers means to investigate the adsorption of POMs in liquid medium and under dynamic conditions. This, for example, allows to understand different processes such as the sequential adsorption of POMs at different pH values; to address the question of the saturation of the interface by POM at a given pH; and to show the reversibility of POM adsorption/desorption depending on pH. The POM adsorption reaches almost a saturation level at a given value of pH (e.g. at pH 4) and further adsorption takes place only when lowering the pH (e.g. at pH 2). The POMs in the hybrid material formed at pH 4 exhibit a clear resistance to leaching by the water solvent, indicating that POM species are encapsulated in the polymer matrix thus preventing its direct contact with water. However, when more acidic conditions are applied (pH 2), some weakly bound POM species are also associated with the hybrid material. These species leached out to the rinsing solution, showing the characteristics of a homogeneous catalyst. However, the leached POMs could be adsorbed back into the polymer matrix during a second contact with a POM solution at pH 2, hence preserving its heterogeneous state. Our experiments shed light to the existence of both tightly and loosely bound POMs in the hybrid material, which may provide mixed properties typical of heterogeneous and homogeneous catalysts, respectively, that could be valuable in some chemical transformations. The ability of QCM to operate under liquid medium is here demonstrated to be highly useful to optimize the conditions, as well as to study the dynamics

of the adsorption and desorption of POMs in the working environment of an organic–inorganic heterogeneous hybrid catalyst. In the future, the developed strategy could help understanding better the adsorption phenomena of various types of inorganic species, e.g. POMs with more complex molecular architectures, on a variety of organic matrices.

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