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Oriented polyoxometalate–polycation multilayers on a carbon substrate

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In this paper, a new method of fabricating multilayers on a carbon substrate is presented. First, a uniformly charged carbon surface was prepared through molecular design. Then an ultrathin film consisting of layer-pairs of oppositely charged polymeric cationic poly(diallyldimethylammonium chloride) (PDDA) and silicotungstate, $SiW_{12}O_{40}^{4-}$ (SiW_{12}), was grown layer-by-layer onto the grafted carbon substrate using a molecular self-assembly technique and an electrochemical method. The technique allows one to prepare highly adherent, dense and smooth films of polyoxometalates with special properties. By combining cyclic voltammetry (CV) and X-ray (XR) reflectometry, it was determined that the average surface density of SiW_{12} was 2.10×10^{-10} mol cm^{-2}, and the thickness increase per adsorption of PDDA–SiW_{12} was 1.7 ± 0.2 nm, indicating that the amount of SiW_{12} anion per one layer adsorption corresponded to a monolayer coverage. Atomic force microscopy (AFM) was also used to examine the surface morphology and determine the grain size distribution and roughness for multilayer films. An increase in root-mean-square (RMS) surface roughness from 7 to 9 Å was observed as the number of layer-pairs in the film increased from 2 to 6. FTIR results showed that the good stability of the multilayer films was due to Coulomb interactions between the SiW_{12} anion and the polymeric cations PDDA. Moreover, the multilayer films, in acidic aqueous solution, showed good electrocatalytic activity toward the reduction of NO_2^-, and the catalytic currents increased with increasing the layer numbers of SiW_{12} adsorption. These characteristics of the multilayer films might find potential applications in the field of sensors and microelectronics devices.

1. Introduction

The design of molecule-based materials with useful physical properties, in particular electrical, magnetic, and optical properties, is at the centre of active interest in materials chemistry research. One reason for this interest has been the realization that these materials can exhibit cooperative properties typically associated with solid state materials. One of the outstanding challenges in this area is the search for materials that will be useful for the next generation of thin films. Polyoxometalates (POMs), owing to their chemical, structural and electronic versatility, are very versatile inorganic building blocks for the construction of functional thin films.[1–5] In this field various strategies[6–19] are being used with a common aim: to control the molecular assembly as far as possible, as it very often determines the solid state properties of the material. Faulkner's[6,7] and Anson's groups[8] first described the adsorption of multiple layers of POMs on various electrodes by co-adsorbing large mono-, multi- and poly-valent cations due to the fact that the heteropolyanions interact strongly with these cations, but the rate and extent of the adsorption of POMs were controlled by the identity and nature of the electrode surface. The old but elegant Langmuir–Blodgett (LB) technique is clearly one of the most attractive for arranging POMs into organized assemblies. By taking advantage of the adsorption properties of POMs along a positively charged monolayer spread in water, Clemente-Leon *et al.*[9–11] and our group[12] were able to obtain organic–inorganic LB films of POMs. Sun *et al.*[17] have extended the technique of self-assembled monolayers of alkanethiols on gold to the development of POM multilayer systems, unfortunately, these multilayer films are not stable under typical hydrothermal conditions (high pH, high temperature). In this article we discuss the possibilities for constructing POM organized molecular assemblies experimentally with precise control of layer composition and thickness, which can maintain its integrity under exposure to harsh environments.

Recently, Decher and co-workers[20,21] have developed a molecular self-assembly process in which multiple layers can be grown layer-by-layer onto an oxide substrate. This molecular self-assembly method relies on the electrostatic attraction between alternately deposited charged materials to produce multilayer films. This method has been widely employed for the formation of multilayer films of a wide range of materials such as proteins, colloids, enzymes, inorganic species *etc.*[13–16,22–24] There are also some undesired disadvantages such as condensation and unsaturation appearing in the multilayer preparation, which can result in inhomogeneity of the multilayer structure. An important cause of this is the inhomogeneity of charge on the substrate surface.

In this paper, we explore the use of this method and an electrochemical method for making oriented POM–polycation multilayers on a carbon substrate. Before fabricating a multilayer, a uniform charged surface of carbon substrate was prepared through molecular design. The reason for choosing carbon as the substrate is this material has good conductivity and resistance to environmental and chemical attack. The carbon surface has been extensively used as a support substrate, especially as electrodes with a wide potential window in electrochemistry. The CV, XR reflectometry and AFM results demonstrate that the prepared multilayer films are uniform, dense and highly adherent to the grafted carbon substrate.

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2. Experimental

2.1 Chemicals

4-Nitrophenyl diazonium fluoroborate (Aldrich), tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) (Fluka) and poly (diallyldimethylammonium chloride) (abbreviated as PDDA, 20 wt% aqueous solution, Aldrich) were used as received. Acetonitrile (MeCN) was distilled prior to use. Silicotungstate, $H_4SiW_{12}O_{40}$, was of analytical grade and home made. All other chemicals were of reagent grade and used as received. Solutions were prepared using a Millipore Milli-Q water purification system and deaerated with argon prior to use.

2.2 Preparation of ultrathin POM–PDDA multilayer films

Preparation of ultrathin SiW_{12}–PDDA multilayer films was as follows: the carbon electrode was first immersed in a MeCN + 0.1 M n-Bu_4NBF_4 solution containing 5 mM 4-nitrophenyl diazonium fluoroborate and modified by the 4-nitrophenyl radicals generated through electrolysis at −1.0 V *vs.* Ag|Ag$^+$ (0.01 M $AgNO_3$ in MeCN). After rinsing and ultrasonically washing with water, the 4-nitrophenyl derivatized electrode was transferred to the protonic solution (90 : 10 H_2O–EtOH + 0.1 M KCl), and reduction of the NO_2 group to an NH_2 group on the electrode surface was carried out by applying a potential of −1.2 V over 600 s.[25,26] The electrode was then immersed in an aqueous solution containing 5 mM SiW_{12} and cyclic scanning between −0.7 V and 0.1 V at 100 mV s^{-1}.[27,28] The surface coverage of SiW_{12} was controlled by the number of potential scans. Multilayers were prepared by alternate immersion in PDDA solution (10 mM based on the molecular weight of the monomer unit, pH ~ 3.0) for 5 min and in 5 mM SiW_{12} solutions (pH ~ 3.0) for 5 min. Washing with dilute aqueous HCl solution (pH 3.0) and argon drying steps were performed after each adsorption step for multilayer construction. The process is shown schematically in Fig. 1.

2.3 Instrumentation and measurements

Electrochemistry. Electrochemical experiments were carried out on a Model 600 Voltammetric Analyzer (CH Instruments, USA) in a conventional one-compartment cell with a glassy carbon electrode (GCE, Crystal Research Institute, Beijing) or GC plate or a highly oriented pyrolytic graphite (HOPG) plate as working electrode, a Ag|AgCl|sat. KCl or Ag|Ag$^+$ (0.01 M $AgNO_3$ in MeCN) electrode as reference electrode, and a Pt electrode as counter electrode.

Prior to modification, GCE was successively polished with 1.0 and 0.3 μm α-Al_2O_3 and ultrasonically washed with acetone and water between each experiment. Fresh surfaces of HOPG were obtained by pealing off the top layers before use.

X-Ray (XR) reflectometry measurements. Thin film XR reflectometry experiments were performed on a commercial $\theta/2\theta$ instrument (STOE & CIE GmbH, Darmstadt, Germany) using Cu-Kα radiation (wavelength 1.54 Å). The divergence of the incoming beam was 0.1°. The lower angle part of the diffraction patterns (Kiessig fringe) were obtained after optimizing the alignment of the incident and reflected beams. XR Reflectometry results obtained for multilayer films assembled on GC plates were similar to those obtained for multilayer films on HOPG plates.

Atomic force microscopy (AFM) measurements. AFM was performed with a Digital NanoScope IIIa system (Santa Barbara, CA). All AFM images were collected in the tapping mode in air,[29] resonating the tip just below the oscillation frequency of the silicon cantilever unit (nanoprobe, typically 307–375 kHz). The scanning frequency was 1 Hz. A drive amplitude of 20 to 50 mV was used. Surface height images were used for calculation. RMS surface roughness was calculated with the software supplied by the instrument manufacturer.

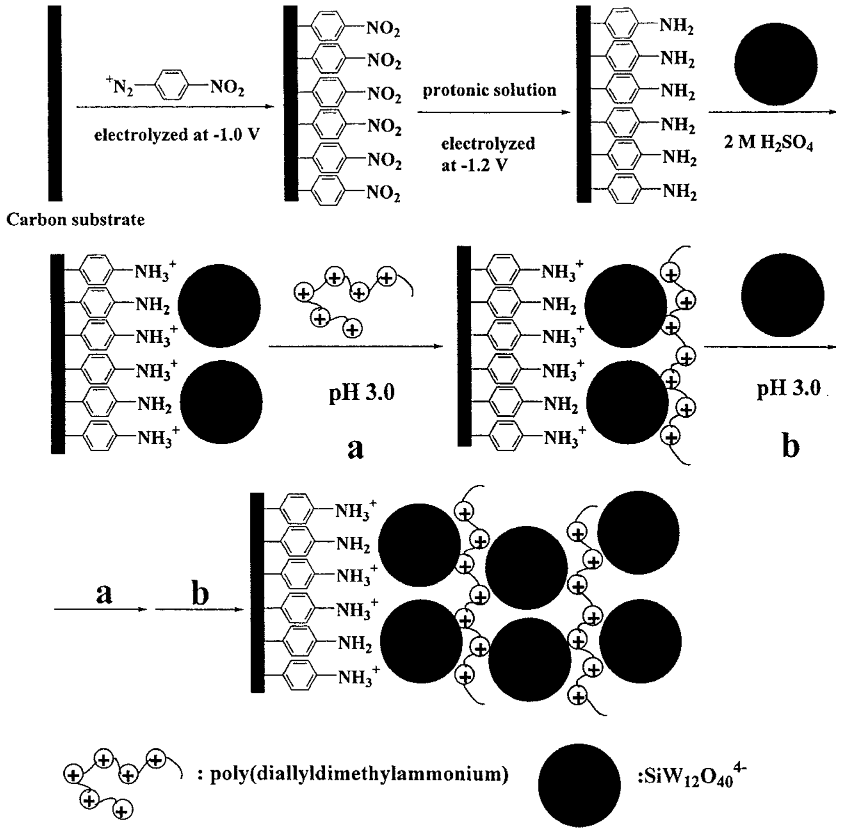

Fig. 1 Schematic for the preparation of ultrathin silicotungstic heteropolyanion–PDDA multilayer films.

FTIR Reflection spectroscopy. FTIR measurements were conducted using a Nicolet 520 SX FTIR spectrometer with a DTGS detector. The external reflectance system was constructed from a variable angle specular reflectance attachment (Spectra Tech, Inc.). All the spectra were obtained with an average of 100 scans with 4 cm^{-1} resolution. The sample chamber was purged with dry N_2 to eliminate spectral interference from water vapor in the air. The HOPG samples were prepared following the above procedure. FTIR results obtained for multilayer films assembled on GC plates were similar to those obtained for multilayer films on HOPG plates.

3. Results and discussion

3.1 Preparation and characterization of PDDA–SiW$_{12}$ ultrathin multilayer film modified carbon substrate

The PDDA–SiW$_{12}$ ultrathin multilayer films were prepared by the sequential adsorption scheme outlined in Fig. 1. The 4-aminophenyl–SiW$_{12}$ composite film grafted on various carbon substrates (including GCE, carbon fibre and HOPG) can attract positively charged polycationic PDDA resulting in a monolayer of PDDA molecules on the surface. The positive charges that are not equilibrated are then able to attract SiW$_{12}$ anions. Multilayers of PDDA and SiW$_{12}$ can be obtained by repeating these steps. Special care must be taken when performing these experiments, because the concentration of SiW$_{12}$ and the immersion time have obvious effects on the multilayer film formation. In general, multilayer films can not be obtained in the aqueous solution containing a lower concentration of SiW$_{12}$. In addition, immersion time also affects the coverage of SiW$_{12}$, and 5 min was found to be sufficient for the adsorption of one layer of PDDA and one layer SiW$_{12}$, respectively. Therefore, in order to obtain a uniform multilayer film, 5 mM SiW$_{12}$ and 5 min immersion time were used. The stepwise growth of multilayer films was monitored by cyclic voltammetry and low-angle XR reflectometry, and AFM was used to examine the morphology of the films. HOPG was found to allow a more complete characterization of the ultrathin films and estimation of the resulting film thickness because of its well-defined structure with large crystallites and atomic flatness. Therefore all results presented in this study were obtained on HOPG.

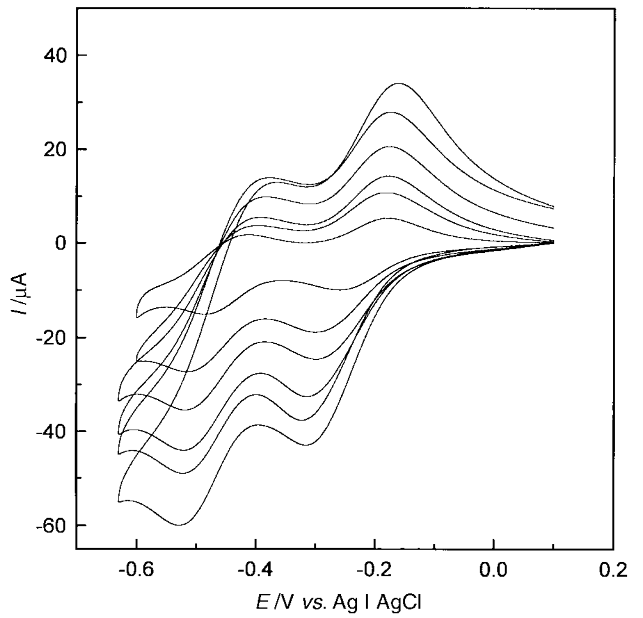

Fig. 2 Cyclic voltammograms of the silicotungstic heteropolyanion–PDDA multilayer film-modified HOPG electrode with increasing m in aqueous 0.1 M HCl. m in HOPG–4-aminophenyl–SiW$_{12}$–(PDDA–SiW$_{12}$)$_m$ = 0, 1, 3, 5, 7, 9 and 11 (from inside to outside). Scan rate: 100 mV s^{-1}.

Cyclic voltammetry. Fig. 2 displays cyclic voltammograms of (PDDA–SiW$_{12}$)$_m$ multilayers (with $m = 0, 1, 3, 5, 7, 9, 11$) assembled on the 4-aminophenyl–SiW$_{12}$ composite film with HOPG as substrate. As shown in Fig. 2, the voltammogram of the 4-aminophenyl–SiW$_{12}$ composite film on an HOPG electrode in 0.1 M HCl presents the same features described in our previous study,[27,28] and displays two redox waves with the surface potentials E'_{sur}s[$E'_{\mathrm{sur}} = (E_{\mathrm{pc}} + E_{\mathrm{pa}})/2$] of −0.223 and −0.456 V, and the peak-to-peak separations ΔE_{p} of 64 and 60 mV, respectively. These cyclic voltammograms do not change upon cycling. It is noteworthy that the $\Delta E'_{\mathrm{sur}}$ values for the two redox couples were near the formal potentials for the solution of SiW$_{12}$ on bare GCE.[30–33] Therefore, these two redox waves are attributed to one- and one-electron processes of the SiW$_{12}$ anion. PDDA is not electroactive, and therefore its presence is not reflected in the cyclic voltammograms. As can be observed, with each additional deposition of PDDA–SiW$_{12}$, the peak currents for the first and second redox waves

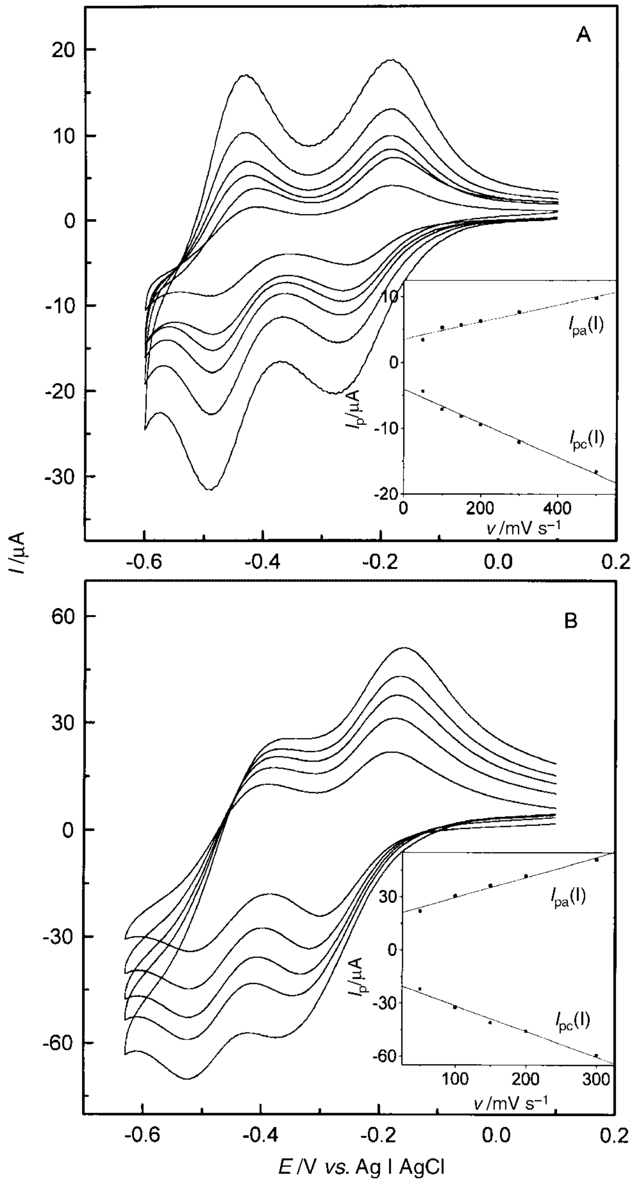

Fig. 3 Cyclic voltammograms of the silicotungstic heteropolyanion–PDDA multilayer film-modified HOPG electrode with different values of m in aqueous 0.1 M HCl at different scan rates. m in HOPG–4-aminophenyl–SiW$_{12}$–(PDDA–SiW$_{12}$)$_m$: (A) $m = 1$; (B) $m = 9$. Scan rate: 50, 100, 150, 200 and 300 mV s^{-1} (from inside to outside).

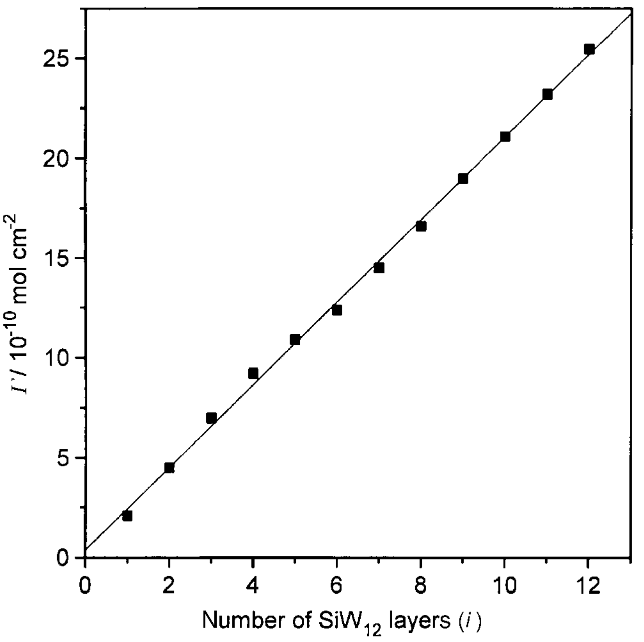

Fig. 4 Dependence of the total surface coverage Γ_i on the number of SiW_{12} layers i.

increase regularly, which reveals a constant increase in the total amount of SiW_{12} anion remaining in the film. Moreover, each additional deposition of PDDA–SiW_{12} still results in the reduction peak potentials for the first and second redox waves shifting to more negative values while the corresponding oxidation peak potentials shift to more positive values. For the (PDDA–$SiW_{12})_m$ multilayers with $m<12$, a good linearity in the plot of peak current *versus* scan rate up to 500 mV s^{-1} can be obtained, as shown in Figs. 3A and 3B, revealing that the electrochemical behavior of SiW_{12} in multilayer films shows a non-diffusion-controlled electron transfer process. Therefore, the total surface coverage of SiW_{12} can be calculated using:

$$Q = nFA\Gamma_i \qquad (1)$$

where Q, A, Γ_i and i represent the adsorbed charge (C), electrode area (cm^2), total surface coverage of SiW_{12} (mol cm^{-2}) and the number of SiW_{12} layers ($i=m+1$), respectively, and all the other terms have their usual significance. Quantitative determination of the adsorbed charge, Q, is obtained by integration of the first reduction peak of the cyclic voltammograms. The background corrected Q of the first reduction peak is invariant with the inverse square root of the scan rate, indicating that mechanisms involving immobilized film with a smaller diffusional charge transport constant[34] are not present. Thus the background corrected Q of the first reduction peaks obtained at any v corresponds to the total charge of the reducible species in the corresponding potential range. The total surface coverage of SiW_{12} in multilayer films calculated according to the above equation is plotted as a function of the number of SiW_{12} layers in Fig. 4. For the (PDDA–$SiW_{12})_m$ multilayers with $m<12$, the total surface coverage of SiW_{12} in multilayer films increases linearly with increasing number of SiW_{12} layers. This plot confirms the fact that the films grow in a stepwise manner, and that each sequentially adsorbed layer adds about the same amount of material to the surface. Moreover, it is noteworthy that the linear regression curve passes through the origin, demonstrating that the SiW_{12} anion does not penetrate the polyelectrolyte layers.

The average surface density, Γ_A, of SiW_{12} in multilayer films can be calculated as follows

$$\Gamma_A = \Gamma_i / i \qquad (2)$$

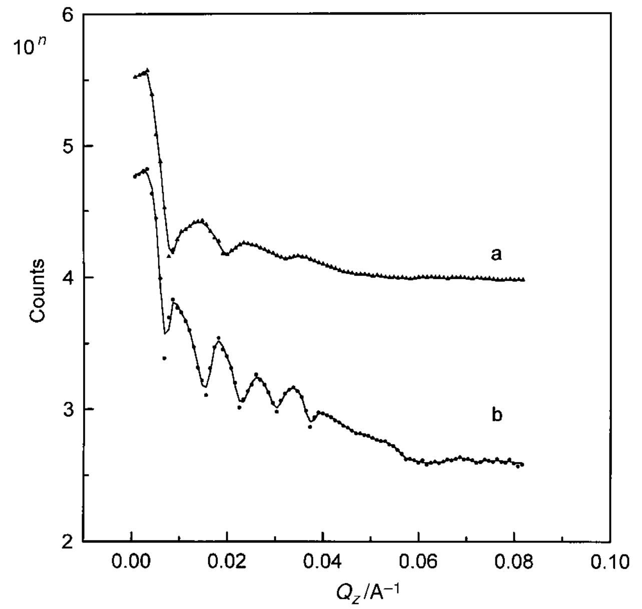

Fig. 5 X-Ray reflectivity curves of a silicotungstic heteropolyanion–PDDA multilayer film-modified HOPG electrode with varying m. m in HOPG–4-aminophenyl–SiW_{12}–(PDDA–$SiW_{12})_m$: (a) $m=2$; (b) $m=5$.

where Γ_A, Γ_i and i represent the average surface density (mol cm^{-2}), the total surface coverage (mol cm^{-2}) and the number of SiW_{12} layers. Using the total surface coverage in Fig. 4, an average SiW_{12} surface density of $2.08 \pm 0.2 \times 10^{-10}$ mol cm^{-2} is obtained for the (PDDA–$SiW_{12})_m$ multilayer films with $m \geqslant 1$. This value is very close to the closest-packing concentration of SiW_{12} monolayers, 2.15×10^{-10} mol cm^{-2}, assuming a single SiW_{12} anion occupies an area of approximately 85 Å^2,[35] suggesting that the amount of SiW_{12} per adsorption process is a monolayer. The above results suggest that condensation of POMs can be ruled out in our experiments.

XR Reflectometry measurements. The assembly of the (PDDA–$SiW_{12})_m$ multilayer film was further confirmed by XR experiments. Fig. 5 shows the reflectivity profiles of 2- and 5-layer multilayer films grown on HOPG substrate, which has been primed with the 4-aminophenyl–SiW_{12} composite film. The pattern consists of a set of low angle Kiessig fringes, which corresponds to reflections from the entire film, and which give a thickness of 8.0 and 13.3 nm. Therefore, the average thickness of a layer-pair PDDA and SiW_{12} can be calculated to be 1.7 ± 0.2 nm. We note that the XR reflectometry results give an average thickness of a layer-pair PDDA and SiW_{12} that is approximately 10 times smaller than that reported for the $Mo_8O_{26}^{4-}$–PAH layer-pair (~20 nm)[16] which corresponds to *ca.* 20 layers of $Mo_8O_{26}^{4-}$ units. This suggests that condensation of POMs can be ruled out in our experiments. This point is important when one tries to integrate POMs with a small size into organized thin films. One of the explanations is that the first layer that attaches to the substrate derivatized by 4-aminophenyl groups is the two-dimensional ordered SiW_{12} monolayer (which has been confirmed in ref. 27). This monolayer provides a uniform surface with negatively charged sites, which serve as a bridge for binding PDDA. These multiple charge attractions are able to generate a good surface adhesion between the film and substrate, and prevent the condensation of POMs. Indeed, FTIR and AFM data have strongly supported this explanation. Another explanation is that PDDA is a hard polycation.[36]

AFM. Electrochemistry and XR reflectometry all confirm the feasibility of preparing orientated PDDA–SiW_{12} multilayer

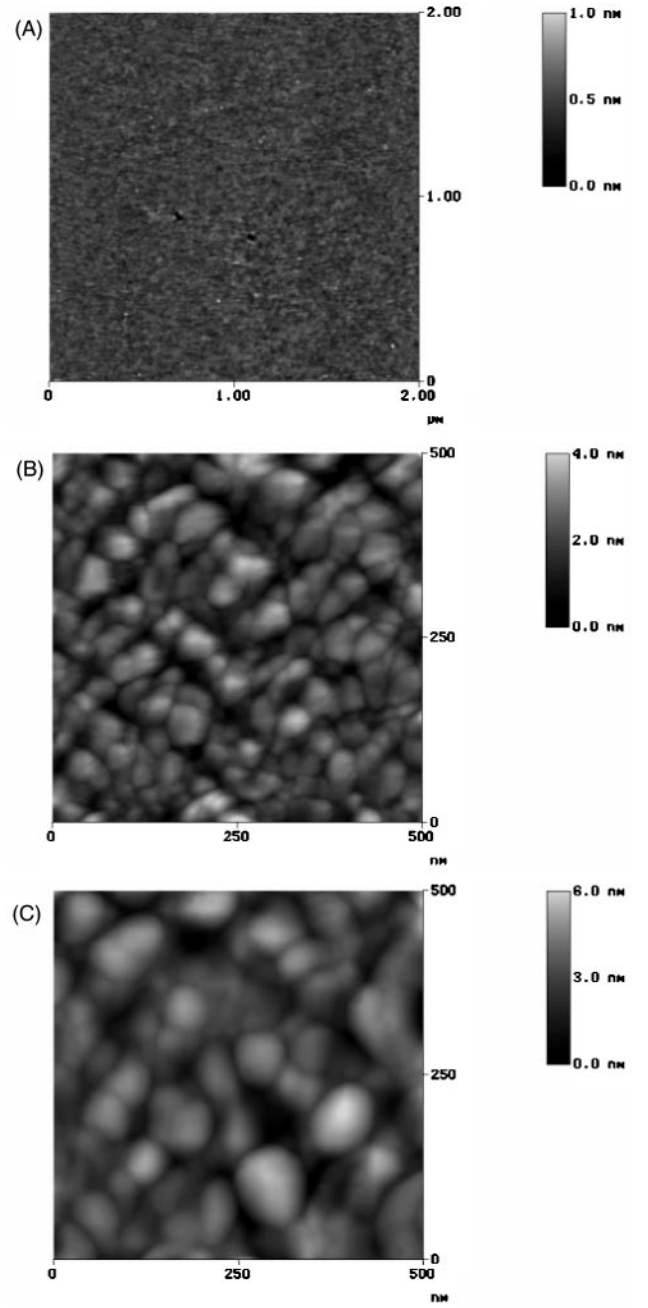

Fig. 6 Tapping-AFM images of the silicotungstic heteropolyanion–PDDA multilayer film-modified HOPG electrode with varying *m*. *m* in HOPG–4-aminophenyl–SiW_{12}–$(PDDA–SiW_{12})_m$: (A) $m=0$; (B) $m=2$; (C) $m=5$.

assemblies on a grafted HOPG surface by electrostatic layer-by-layer deposition. However the above methods only reflect the average and macroscopic information of the multilayer assemblies. Atomic Force Microscopy (AFM) can provide further detailed information involving the surface morphology and structure of the multilayer films down to the nanometer scale. Fig. 6 shows typical tapping-AFM images of the SiW_{12} monolayer (Fig. 6A), the 4-aminophenyl–SiW_{12}–$(PDDA–SiW_{12})_2$ multilayer with SiW_{12} as the outermost layer (Fig. 6B), and SiW_{12}–$(PDDA–SiW_{12})_5$ multilayer with SiW_{12} as the outermost layer (Fig. 6C). These images were obtained using tapping mode AFM as opposed to contact AFM to avoid the strong probe-sample forces which may result in substantial damage and displacement of the sample.[37] In Fig. 6A, the surface of the SiW_{12} monolayer on the grafted HOPG surface is observed to be extremely smooth with a small RMS value of 0.1 nm, which is consistent with our previous STM measurements.[27] The absence of aggregates or multilayers in the TMAFM image shows that the composite structure of 4-aminophenyl–SiW_{12} is homogeneous and can provide a uniform charged surface to anchor follow-up PDDA–SiW_{12} multilayers. When the first two layer-pairs of PDDA and SiW_{12} are adsorbed on the SiW_{12} monolayer, many domains appear on the sample surface (Fig. 6B). The analysis of Fig. 6B shows that the RMS roughness of the film is only about 0.7 nm and the maximum height variation between the domains is also below 4 nm. After adsorption of five layer-pairs on the SiW_{12} monolayer (Fig. 6C), domains still exist but they are only slightly larger than those of the two layer-pairs on the SiW_{12} monolayer. The RMS roughness and the maximum height variation are determined to be only around 0.9 and 6 nm, respectively. It is noticed that the RMS roughness and the maximum height variation obtained for the PDDA–SiW_{12} multilayer are much less than that obtained for $W_{10}O_{32}^{4-}$–PDDA assemblies on mica.[14] The AFM results are also in agreement with the electrochemical measurements that the SiW_{12} anions in the same layer are arranged in a close-packed monolayer manner with a small surface undulation. The small RMS values and height variations demonstrate that the new kind of substrate surface with uniform charge can effectively prevent the condensation or unsaturation phenomena in the multilayer structures, which is in favor of the formation of an oriented multilayer.

FTIR Reflection spectroscopy. One of the advantages of this method is that the $(PDDA–SiW_{12})_m$ multilayers have good stability. For example, after potential cycling between 0.1 and −0.63 V at 100 mV s^{-1} in 0.1 M HCl for 100 cycles, a decrease in the cathodic current of about 10% was observed for the $(PDDA–SiW_{12})_9$ ultrathin multilayer film modified HOPG substrate. To illustrate this point, we used FTIR reflection spectroscopy to study the multilayer films. In Fig. 7 IR spectra of the 4-aminophenyl–SiW_{12}–$(PDDA–SiW_{12})_5$ ultrathin multilayer film (Fig. 7C) is presented and compared with those of the PDDA (Fig. 7A) and the crystalline heteropolyacid (Fig. 7B). Note that besides the bands at 1096 and 753 cm^{-1} associated with the PDDA, the IR spectrum of the 4-aminophenyl–SiW_{12}–$(PDDA–SiW_{12})_m$ ultrathin multilayer film reveals six clear peaks: 1012, 964, 937, 906, 879 and 824 cm^{-1}, which are attributed to the stretching modes of Si–O, W–O_d, Si–O–$C(C_6H_5)$, Si–O, W–O_b–W and W–O_c–W, respectively[38] (Fig. 7(C)). Clearly, the bands in the composite film associated with the anions are narrower and generally slightly shifted

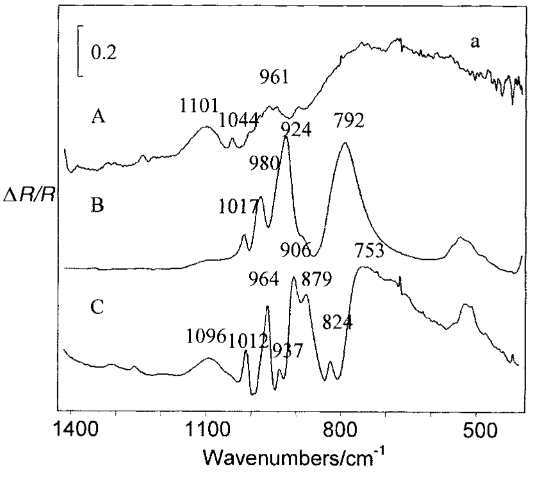

Fig. 7 FTIR spectra of PDDA cast film in a KBr pellet (A), $H_4SiW_{12}O_{40}$ in KBr pellet (B), and HOPG–4-aminophenyl–SiW_{12}–$(PDDA–SiW_{12})_5$ ultrathin multilayer film (C).

when compared to the spectrum of SiW_{12} in the KBr pellet. The shift of different peaks observed is probably related to the organization and in particular to the presence of positively charged PDDA in the multilayer film.

Indeed, Rocchiccioli-Deltcheff *et al.*[39] observed a shift of the Keggin infrared bands depending on the size of the tetraalkylammonium cations used as a counterion in the solid state. The values reported for the larger cations used by these authors are in close agreement with those measured for SiW_{12} in the multilayer film. Hasik *et al.*[40] also observed that a shift in the Mo–O_c–Mo vibration of $PMo_{12}O_{40}{}^{3-}$ incorporated into the polyaniline was induced by the Coulombic interactions between heteropolyanions and the protonated polymeric support. Clemente-Leon *et al.*[9–11] also reported the shift in M–O_c–M vibration of POMs induced by Coulombic interactions between the POMs and amphiphilic cations in the multilayer film. Based on the results obtained and on studies reported in the literature, we propose that the shift of the SiW_{12} infrared bands is attributed to the formation of an ionic bond between SiW_{12} and cationic PDDA. This multiple Coulombic interaction between SiW_{12} and the PDDA polycation generates a good surface adhesion between the film and substrate.

3.2 Electrocatalytical behavior of the 4-aminophenyl–SiW_{12}–(PDDA–SiW_{12})$_m$ ultrathin multilayer film modified HOPG toward nitrite

The direct reduction of nitrite at carbon electrodes is thermodynamically favorable but the charge-transfer kinetics associated with the reaction are slow,[41] and consequently the reduction potential of nitrite is extremely negative,[42,43] and it is difficult to detect nitrite directly using its reduction behavior.[36] However, electrocatalytic nitrite reduction has been demonstrated for POMs.[44]

In our study, we found that the 4-aminophenyl–SiW_{12}–(PDDA–SiW_{12})$_m$ ultrathin multilayer film modified carbon electrode may act as an efficient catalyst for the reduction of nitrite. Fig. 8 shows cyclic voltammograms of the modified HOPG electrode before and after the addition of nitrite. A typical cyclic voltammogram of the 4-aminophenyl–SiW_{12}–(PDDA–SiW_{12})$_m$ ultrathin multilayer film-modified HOPG electrode displays two redox waves in 0.5 M H_2SO_4 (Fig. 8a). The presence of nitrite in the bulk solution (Fig. 8b–d) dramatically changes the current response of electrode. The peak current associated with the first reduction peak is enhanced greatly while the peak current of the second reduction peak remains almost constant, indicating that the electrocatalytic reduction of nitrite occurs at the first reduction peak. Note that increasing the number of SiW_{12} layers results in an obvious rise in the catalytic current, but the catalytic current is linear with the square root of *i* but does not increase linearly with the increase of *i* (see inset to Fig. 8). This result demonstrates that the transport of ions in the multilayer films may be suppressed, that is to say, the multilayer film is relatively dense.

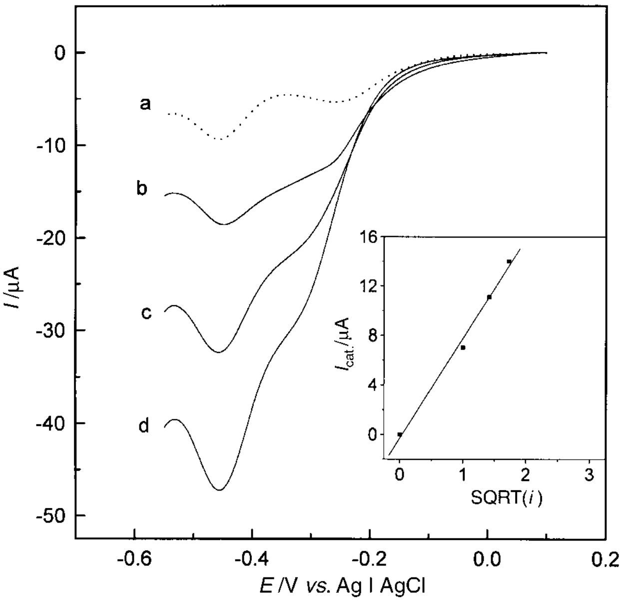

Fig. 8 Cyclic voltammograms of the silicotungstic heteropolyanion–PDDA multilayer film-modified HOPG electrode with varying *m* in aqueous 0.1 M HCl in the absence (dashed line) or presence (solid line) of 0.5 mM NO_2^-. *m* in HOPG–4-aminophenyl–SiW_{12}–(PDDA–SiW_{12})$_m$: (a, b) $m = 0$; (c) $m = 1$; (d) $m = 2$. Scan rate: 100 mV s^{-1}.

4. Conclusion

In previous studies,[27,28] we reported a two-dimensional ordered POM monolayer on a carbon substrate derivatized by 4-aminophenyl groups. This POM monolayer can serve as an anchor to attach subsequent layers to the carbon surface. In the present study, a very simple scheme which combines an electrochemical method and a self-assembly technique, comparable to the Langmuir–Blodgett technique, was proposed for the fabrication of multilayer films consisting of layer-pairs with oppositely charged SiW_{12} and PDDA macromolecules on a carbon surface through the anchoring of the POM monolayer. Electrochemistry, XR, FTIR reflection spectroscopy and AFM reveal that PDDA and SiW_{12} multilayer films are constructed with regularly ordered layers. The average thickness of the PDDA and SiW_{12} layer-pairs was measured to be ~17 Å with a small RMS surface roughness, and the average surface density of SiW_{12} was determined to be $\sim 2.10 \times 10^{-10}$ mol cm^{-2}, which was close to the closest-packing concentration of the SiW_{12} monolayer. These results showed that condensation or unsaturation of SiW_{12} in polyelectrolyte multilayer films can be ruled out. Moreover, we found that the multilayer films showed good electrocatalytic activity toward the reduction of nitrite, and the catalytic current increased with increasing number of SiW_{12} layers, although it was not proportional to the number of SiW_{12} layers which may be due to the presence of PDDA polymeric cations . By combining the above results, one can conclude that (PDDA–SiW_{12})$_m$ multilayer films prepared on carbon substrate by this method are highly dense, uniform and adherent to the carbon substrate. These characteristics might lead to potential applications of multilayer films in the field of sensors and microelectronic devices.

Acknowledgements

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