Chinese Chemical Letters Vol. 12, No. 12, pp 1127 – 1130, 2001
http://www.imm.ac.cn/journal/ccl.html

Ultrathin Multilayer Films Incorporating Keggin-type Heteropolyanion Clusters

Lin XU[1], En Bo WANG[1]*, Zhuang LI[2], Hong Yu ZHANG[1], Chao QIN[1]

[1]Department of Chemistry, Northeast Normal University, Changchun 130024
[2]Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022

Abstrac: Two new ultrathin multiplayer films have been successfully prepared from Keggin-type heteropoly acids $H_4[SiW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ with polyelectrolytes PEI, PSS, and PAH, using the electrostatic layer-by-layer self-assembly technique. The XR results reveal their film thickness at nanoscale (~ 20 nm). According to the AFM images, it is believed that the surface roughness (rough degree of film surface) of the polyelectrolyte-polyoxometalate film greatly depends on the kind of polyoxometalates.

Keywords: Materials, multiplayer, polyelectrolyte-polyoxometalate, layer-by-layer.

In recent years, there has been considerable interest in the fabrication of self-assembled ultrathin multilayer films, because of their availability to form nanostructured materials with tailored architecture and properties[1]. The layer-by-layer (LBL) self-assembly, initially developed for pairs of oppositely charged polyelectrolytes[2], is an unusually simple and versatile technique to built up of ultrathin multilayer films. A special feature of the multilayer films is that the composition, thickness, and orientation of each layer can be manipulated at the molecular level. This manipulation offers many potential advantages in device applications, such as active components in nonlinear optical devices, chemical sensor, and light-emitting diodes, *etc.*[3,4].

Since polyoxometalate (POM) is an extremely versatile inorganic building blocks for the construction of functionally active solid materials[5,6], their potential applications in electrocatalytic, molecular electronic, and electrooptical devices have required the successful fabrication of thin solid films containing POMs. Keggin-type heteropoly compounds are a main class of POMs that plays an important role in catalytic and electrochemical applications. The successful incorporation of Keggin-type heteropoly anions into ultrathin multilayer films is of critical importance for developing a new-type functional film materials. Here we report the first example of two ultrathin multiplayer films prepared from Keggin-type heteropoly acids $H_4[SiW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ with polyelectrolyte PAH.

---

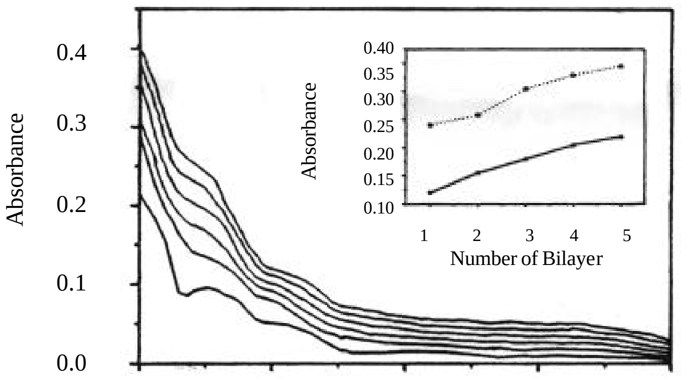
* E-mail: linxu@nenu.edu.cn

Experimental

Heteropoly acids of $H_4SiW_{12}O_{40}$ó 12H_2O (SiW_{12}) and $H_3PMo_{12}O_{40}$ó 6H_2O (PMo_{12}) were purchased from Beijing Chem. Corp. and used without further purification. Poly (allylamine hydrochloride) (PAH; MW 70,000; Aldrich), sodium poly (styrenesulfonate) (PSS; MW 70,000; Aldrich), and poly(ethylenimine) (PEI; MW 50,000; Aldrich) were used without further purification. The pH value of the PAH solution was adjusted by adding aqueous HCl.

The cleaned substrates were immersed in a 0.05 mol/L PEI solution (based on the molecular weight of the monomer unit) for 20 min, rinsed with water, and dried under a nitrogen stream. The PEI-coated substrates were then exposed to a 0.05 mol/L PSS solution for 20 min, followed by alternating 20 min immersions in PAH (0.05 mol/L) containing 1 mol/L NaCl; pH~2.5-3.0) and SiW_{12} or PMo_{12} (1×10^{-3} mol/L, pH~2-3) solutions. Water rinses and nitrogen drying steps were performed after each adsorption step. UV-vis spectra were measured on a Beckman-DU8B spectrophotometer. XPS spectra were recorded on an Escalab-MKII photoelectronic spectrometer with ALKá (1486.6 eV) as excitation source. X-ray reflectance experiment was performed with a Philips X' Pert instrument using copper $K_á$ radiation (ë = 1.5405Å). AFM images were taken using a Nanoscope III a instrument (Digital Instruments) operating in the tapping mode with silicon nitride tips.

Figure 1 UV-vis spectra of $(PMo_{12}/PAH)_n$ multilayer films with n=0-5 on PEI/PSS/PAH-modified quartz substrates (both sides)[a]



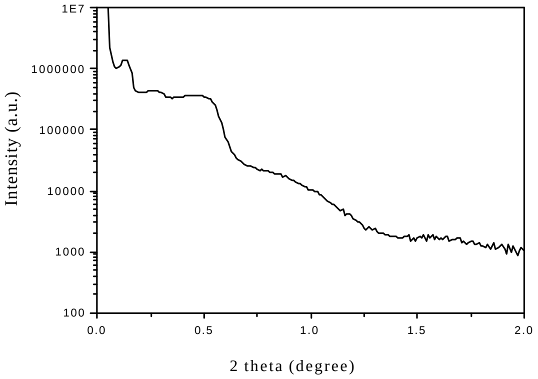
[a] These curves, from bottom to top, correspond to n=0, 1, 2, 3, 4 and 5, respectively. The inset shows the plot of absorbance (at 200 nm) corresponding to pH=5 (solid line) and pH=2.5 (dotted line) for aqueous PAH solutions, respectively, *versus* the number of PMo_{12}/PAH bilayer in the adsorption cycles.

Results and Discussion

UV-vis spectra were used for monitoring the layer-by-layer adsorption process (**Figure 1**). The absorption band at 225 nm of the precursor PEI/PSS/PAH film (n = 0) in the UV-vis spectrum arises from the aromatic group present in the PSS polyanion. Under the same experimental condition the anionic cluster SiW_{12} can be absorbed more than PMo_{12}. The difference may result from the higher negative charge for the former. With increasing the number of {SiW_{12}/PAH} bilayer, the characteristic absorption band at 262 nm for SiW_{12} become observable. The research results reveal that the adsorption amount of SiW_{12} or PMo_{12} on the PAH layer remarkably depends on the pH value of the PAH solution and the lower pH value of the PAH solution is favorable condition for the deposition (see the inset in **Figure 1**). Consequently, we chose the optimal experimental conditions in which the pH value of the PAH solution was 2.5. The plots of absorbance at 200 nm *versus* the number of {PMo_{12}/PAH} layers result in nearly straight line, such case also occurs in {SiW_{12}/PAH} films; these confirm that the constant increases in the total amount of PMo_{12} deposited on the multilayer films.

Although the XPS measurement gives only semi-quantitative element composition for the multilayer films, the presence of the expected elements in the films can be confirmed by their contents, and the expected molar ratio 1:12 for Si to W (or for P to Mo) can be approximately established. The XPS results confirm that we have indeed incorporated SiW_{12} or PMo_{12} anions into the multilayer film. It is in agreement with the UV-vis result. The existence of two N_{1s} sub-peaks, at 401.1 and 399.1 eV for PMo_{12}/PAH, and at 401.5 and 399.8 eV for SiW_{12}/PAH in XPS measurement, indicates the presence of two types of nitrogen atoms in the films. From the XPS results, we infer that the charge-transfer interaction may partially occur between the PAH molecules and the SiW_{12} (or PMo_{12}) anions, because the Keggin-type polyoxometalate anion generally behaves as the strong electron acceptor.

Figure 2 X-ray reflectance spectra of the {$(PEI/PSS/PAH)(PMo_{12}/PAH)_6$} multilayer film on silicon substrate



Small-angle X-ray reflectance (XR) was also used to investigate the film structure. For the [PEI/PSS/PAH(PMo_{12}/PAH)$_6$] film, the XR curve (**Figure 2**) exhibits Kiessig fringes in the region of small angle, suggesting that the film thickness was uniform. Because the best-fit results were not achieved, the total film thickness has to be estimated from the spacing of the Kissig fringes[7]. We found that Q_z (the distance between the positions of Kiessig maxima, Q_z = 4ðsinè/ë) is *ca*. 0.036 Å^{-1} for the SiW_{12} film, indicating that a total film thickness of d_{total} = [2ð/ Q_z] is *ca*. 174 Å The total film thickness for the PMo_{12} film was *ca*. 158 Å With the same number of layers and under the same experimental condition, the total film thickness of the SiW_{12} film is larger than that of the PMo_{12} film. It is agreed with the results of UV-vis spectra. This is understandable that the anion volume for SiW_{12} is larger than that for PMo_{12}.

AFM images provided further information involving the surface morphology and the homogeneity of the deposited films at the nanometer scale. From the AFM images, the roughness (rough degree of film surface) values of these films can be obtained. Before Keggin-type anions are adsorbed, the outer PAH surface layer of the three-layers precursor is observed to be uniform and smooth, with mean roughness of 0.469 nm. After adsorption of PMo_{12} to the PAH surface, the mean roughness of the PMo_{12} layer becomes 1.153 nm. After the PMo_{12} layer adsorbed a new outer PAH surface layer, the roughness of outer PAH surface increased to 2.865 nm, and the AFM image of the new outer PAH surface shows almost uniform distribution of nanosized aggregates. In the case of SiW_{12}, its outer PAH layer exhibits more smooth surface than that of PMo_{12}, with mean roughness of 0.883 nm. The difference of surface roughness between SiW_{12} and PMo_{12} film results from the relatively large adsorption amount of SiW_{12} than that of PMo_{12}.

Acknowledgments

This project was financially supported by the National Natural Science Foundation of China (Grant No. 29971006).

References

1. Ulman, Introduction to Thin Films: From Langmuir-Blodgett to self-Assembly, Academic, Boston, **1991**, p.26.
2. G. Decher, Science, **1997**, 277, 1232.
3. D. Piscevic, W. Knoll, M. J. Tarlov, *Supramolecular Sci.*, **1995**, *2*, 99.
4. C. Fou, O. Onisuka, M. Ferreira, M. F. Rubner, *J. Appl. Phys.*, **1996**, *79*, 7501.
5. M. T. Pope, A. Müller, *Polyoxometalates: From Platonic Solid to Anti-Retroviral Activity*, Kluwer Dordrecht, **1994**, p.233.
6. L. Hill, *Chem. Rev.*, **1998**, *98*, 1.
7. J. Schmitt, T. Grunewald, G. Decher, P. S. Pershan, K. Kjaer, M. Losche, *Macromolecules*, **1993**, *26*, 7058.

Received 2 April, 2001