Polyoxometalate-based Colloidal Crystal Thin Film

Fang Chai,[1,2] Xiaohong Wang,*[1,3] Rongxin Tan,[1] Fenghua Cao,[1] Fengying Zhai,[1]
Linlin Xu,[1] Changlu Shao,[3] and Yichun Liu*[3]
[1]*Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China*
[2]*Department of Chemistry, Harbin Normal University, Harbin 150500, P. R. China*
[3]*Center for Advanced Optoelectronic Functional Materials Research, Northeast Normal University, Changchun 130024, P. R. China*

(Received September 26, 2006; CL-061121; E-mail: Wangxh665@nenu.edu.cn)

An inverse opal structure three-dimensional array film of polyoxometalates (POMs) was constructed by using polystyrene (PS) colloidal crystals as templates. The thin film has exact inverse opal structure and the POMs remained Keggin stucture.

To fabricate films composed of functional molecules is crucial to both fundamental research and application. In recent years, POMs as inorganic functional clusters attract increasing attention due to their stability against oxidation and variety of physicochemical properties,[1] so precise construction of a thin film or three-dimensional (3D) array of POMs is desired for realizing POMs-based molecular devices. For POMs, the ordered property and porous media of resulting arrays are highly accessible, potentially exploitable for applications, such as catalysts,[2] magnetism,[3] and photochromism.[4]

Traditionally, thin films of POMs are typically made by dip coating,[5] the Langmuir–Blodgett technique,[6] electrodeposition,[7] or layer-by-layer (LBL) self-assembly technique.[8] However, there are only few reports about the preparation of 3D-ordered structure based on POMs, such as self-assemble method[9] or an ordered array of surfactant.[10]

Colloidal crystal template is another promising way for fabrication of thin film. This method offers a simple and inexpensive route to form 3D-ordered structure film. A promising prototype of 3D opal colloidal crystal is obtained by self-organization of monodispersion latex or silica spheres. And the inverse opal colloidal crystal replica can be produced by infiltration of nanometer-sized precursor,[11] and further remove the colloidal crystal template by chemical etching or calcinations, so the 3D-ordered structure film is built up. Many inverse opal structure colloidal crystals have been prepared such as metal oxide[12] (TiO_2, Fe_2O_3, ZnO, Mn_2O_3, MgO, NiO, Co_2O_3, and NiO), alloy,[13] and semiconductor,[12,14,15] salt.[15] Usually, the precursor may be nanoparticles,[16] sol–gel,[12,14,15] or solution.[17] Owing to the small diameter and the well solubility of POMs, it is difficult to fabricate POMs array thin film directly using POMs salt, so the sol–gel route seems to be the most appropriate way.

In this paper, we successfully fabricated POMs-based thin film using sol–gel process and polystyrene (PS) colloidal crystal as template. This offers a promising way to synthesize this new well-ordered POMs-based thin film colloidal crystal material and brings about the investigation of new properties and applications.

The 660-nm diameter polystyrene monodisperse spheres were synthesized according to the method of Stein,[12] and the PS colloidal crystal template was prepared by a convective self-assembly method[18] on the substrates (glass or silicon wafers). The POMs sol was prepared as follows: a 5-mL ethanol solution of 2-mL tetraethyl orthosilicate (TEOS) was dropped into a 10-mL aqueous solution of 2-g $H_3PW_{12}O_{40}$ (PW_{12}) with gentle stirring for about 60 min at room temperature to form PW_{12}/SiO_2 sol.

After forming PW_{12}/SiO_2 sol, the substrate with the PS colloidal crystal template was soaked in the PW_{12}/SiO_2 sol for about 2 h. During this process, PW_{12}/SiO_2 sol infiltrated into the PS colloidal crystal template, the voids of the PS template were filled with liquid sol by capillary force. The substrate was taken off from the PW_{12}/SiO_2 sol, stood at room temperature until dry. Most of the solvent vaporated and the PW_{12}/SiO_2 gel formed, which resulted in forming an intermediate composite structure of PW_{12}/SiO_2/PS. The PW_{12}/SiO_2 inverse opal structure colloidal crystal film was prepared by extracting the PS template using a solution of tetrahydrofuran (THF)/acetone (1:1) for about 24 h.

The concentration of $H_3PW_{12}O_{40}$ in film characterized by ICP-AES was W, 36.7%, P, 0.53%, respectively. The molar ratio of P:W is 1:12, indicating that the PW_{12} in the PW_{12}/SiO_2 film remained Keggin structure. The loading of PW_{12} on the film was about 47.9%.

The thin PW_{12}/SiO_2 film assembled on the silicon substrate was charactered by IR (4000–400 cm^{-1}, KBr) and UV–vis (756 CRT). In the spectrum of PW_{12}/SiO_2 film, four characteristic peaks at 1080, 987, 894, and 793 cm^{-1} can be attributed to ν as (P–Oa), ν as (W–Od), ν as (W–Ob–W), ν as (W–Oc–W), respectively. Compared to the IR spectra of its parent PW_{12} (1080, 983, 890–850, and 800–760 cm^{-1}), the shifts of W–Od and W–Ob–W contribute to interaction between PW_{12} and SiO_2, indicating that the interaction of POMs and SiO_2 is chemical force not simple physical absorption. In the UV–vis spectrum (Figure 1), the characteristic peaks of PW_{12}/SiO_2 films is located at 200 and 266 nm. The first peak is assigned to the Od $\rightarrow$ W charge-transfer and the second is attributed as the Ob/Oc $\rightarrow$ W charge-transfer band. So the UV–vis spectra indicates the

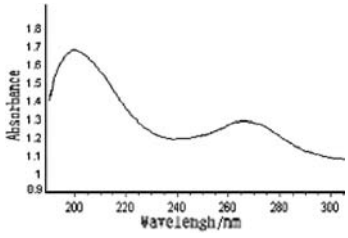

Figure 1. UV–vis spectra of PW_{12}/SiO_2 thin film.

existence of PW_{12} in the film.

In order to confirm the existence of POMs in the PW_{12}/SiO_2 thin film, the ^{31}P MAS NMR spectra (Varian Unity-400 NMR) was measured. The ^{31}P NMR spectra show two peaks present at -14.3 and -15.1 ppm, respectively, different from that of the pure PW_{12} having one peak at -15.1 ppm with a small line width, which is just the same as literature reported.[19] Therefore, it is confirmed that a strong chemical interaction, not simple physical adsorption, exists between the POM and the silica.[20] As the OH groups of silanol are protonated in the acidic medium of PW_{12}, it is supposed that one proton of PW_{12} will react with the OH of silanol and form a $SiOH^{2+}$ group which should act as a counterion for the polyanion. Thus, the reaction is an acid–base reaction between the silanol group (acting as the base) and the polyanion (acting as a Brønsted acid). This interaction results the distinction of ^{31}P NMR spectra between PW_{12}/SiO_2 and pure PW_{12}. So the silica-supported PW_{12} can be regard as a Brønsted acid, which has developed both in theory and application. Most of them acted as heterogenous catalyst to catalyze organic reaction,[21] decompose organic pollutants.[22]

The X-ray photoelectron spectra (XPS) (Escalab-MK II, Al Kα (1200 eV)) was used to examine the component of PW_{12}/SiO_2 thin film assembled on the glass substrate. The XPS spectra exhibited peaks assignable to O 1 s (binding energy (BE) = 532.2 eV), Si 2p (BE = 103.5), P 2p (BE = 135.3), W $4f_{5/2}$ (BE = 39.05), and W $4f_{7/2}$ (BE = 36.9). According to the XPS measurement, the presence of O, Si, P, and W atoms in the film was confirmed, and the expected molar ratio of 1:12 for P to W is also approximately established.

The scanning electron microscopy (SEM) (Hitachi H-800, 200 kV) image was measured to confirm the structure of the sample. Figure 2 shows the SEM images of PS colloidal crystal template and PW_{12}-based 3D thin film. It can be seen that the porous structure of film (Figure 2b) is the exact inverse replicas of the opal colloidal crystals (Figure 2a). The $POMs/SiO_2$ film (Figure 2b) shows inverse opal structure and the oriented pore framework is observed clearly. A regularly ordered hexagonal arrangement can be observed and the second layer can also be clearly seen.

Small angle X-ray diffraction (SARD) (Rigaku D/max 2500, Cu Kα, $\lambda = 1.5406$ nm) was measured to investigate the layer structure of the film. Figure 3 showed the SARD pattern of the thin film, which exhibited Bragg peaks similar to Fan reported in the literature.[23] From the SARD pattern, the POM-based film showed well-defined layered structure with regular periodicity. On the basis of the diffraction patterns, the layer distance (d spacing) of thin film calculated using Bragg's equation

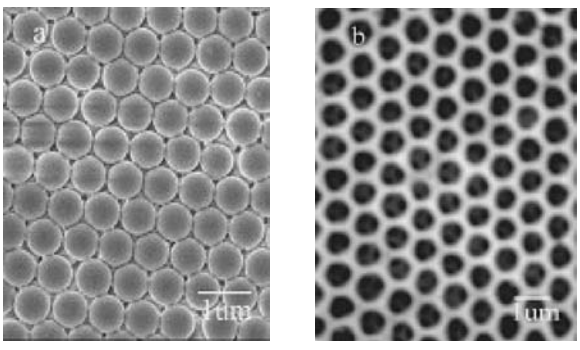

Figure 2. SEM of (a) PS template (b) PW_{12}/SiO_2 thin film.

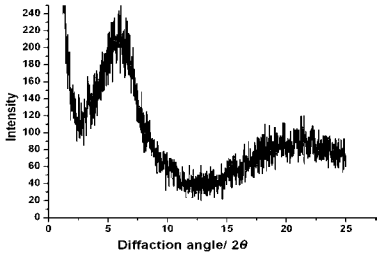

Figure 3. SXRD of the PW_{12}/SiO_2 thin film.

($n\lambda = 2d \sin\theta$) was about 3.29 nm.

We obtained the 3D-ordered PW_{12}/SiO_2 thin film by PW_{12} sol infiltrating into the PS colloidal crystal template. The inverse opal structure PW_{12}/SiO_2 film was successfully fabricated which showed 3D-ordered array sturcture and the POMs remained Keggin structure. The method we reported is an available way to fabricate POMs 3D-ordered array film. But there are still some interesting works need to be achieved, such as constructing different functional thin films by selecting of POMs molecules with appropriate size, structure, component, and charge for different application.

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