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Fabrication of polyoxometalate-based nano/micrometer composite films by electrophoretic deposition method

Yanyan Wang, Lin Xu *, Ning Jiang, Bingbing Xu, Guanggang Gao, Fei Li

Key Laboratory of Polyoxometalate Science of Ministry of Education Institute of Polyoxometalate, Chemistry Department of Chemistry Northeast Normal University, Changchun, Jilin 130024, PR China

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ABSTRACT

Keggin-type heteropolyanion $H_3PMo_{12}O_{40}$ encapsulated by a cationic surfactant dioctadecyldimethylammonium chloride (DODA·Cl) has been assembled on ITO substrates using an electrophoretic approach. The films were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), IR spectra, X-ray photoelectron spectra (XPS) and cyclic voltammetry. The AFM images exhibit a spherical assembly of surfactant-encapsulated complex (SEC) nanoparticles with uniform size. The SEM was also used to investigate the surface topography. It is the first report that the thin films of SEC are fabricated using this method, which provides a new route to explore the possibility of application to polyoxometalate-based hybrid inorganic–organic materials.

1. Introduction

The nanosized assembly at solid surfaces which can produces functionalized interfaces with well-defined composition, structure and thickness has been researched widely. Polyoxometalates (POMs) as a well-known class of metal oxide clusters attract increasing attention worldwide due to their intriguing structures and diverse properties, such as catalysis [1], molecular conduction [2], magnetism [3], medicine [4], luminescence as well as materials science [5,6]. POMs are generally considered as promising inorganic building blocks for their special structures [6–9] and to assemble POMs into defined structures can be effectively applied in many fields. The direct use of POM-containing amphiphiles to construct POM-based self-assembly has been reported widely in recent years [10–12]. The resulting surfactant-encapsulated complexes (SECs) formed through electrostatic interactions can be well dissolved in organic solvents, such as chloroform, toluene, tetrahydrofuran and dimethylformamide (DMF). A phase transition from gel to liquid-crystalline state during the heating process occurs for the assembly, of which the transition temperature relays on the solvent polarity [12–14].

Most SECs in organic solvents can be readily formed into thin films by LB technique or solvent-casting method [15–20]. The ordered microporous structures based on SECs are prepared [21–24] by casting a polymer solution under a moist airflow at ambient temperature. The experimental condition of the method must be controlled so strictly that no microporous structures can be formed if the relative humidity is too low. Although this method is quite effective for assembling SECs as three-dimensional arrays on solid substrates, the strict experimental condition and the low surface area of the films limit its use for further chemical modification.

Electrophoretic deposition (EPD) method was well used for preparation of inorganic film materials many years ago. Because of its simplicity and controllability, the electrophoretic method has become a favorable way to assemble various interesting nanometer materials. For example, using the EPD method, Chandrasekharan et al. [25] assembled gold nanoparticles as nanostructured films, Cao et al. [26] fabricated oxide nanorod arrays and Ouyang et al. [27] fabricated copper phthalocyanine-coated titania nanoarrays. To our knowledge, however, the EPD method has not been employed for the assembly of SEC composite films so far. The development of the EPD method to fabricate SEC nanometer composite films should thus become a challenging task.

Herein, we report a new route to fabricate POM-based nano/micrometer composite films by the EPD method, in which the SEC can be deposited on an ITO electrode from colloidal dispersion. The thus-prepared nano/micrometer composite films of $(DODA)_3PMo_{12}O_{40}$ were well characterized by the IR spectrum, X-ray photoelectron spectra (XPS) and cyclic voltammetry measurements, indicating the existence of $DODA^+$ and $PMo_{12}O_{40}^{3-}$ ions in the films. The surface topography of the films is investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively.

* Corresponding author. Fax: +86 431 85099668.
E-mail address: linxu@nenu.edu.cn (L. Xu).

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2. Materials and methods

2.1. Materials

DODA·Cl and $H_3PMo_{12}O_{40}$ were purchased as commercial products and used without further treatment. $(DODA)_3PMo_{12}O_{40}$ was prepared according to literature methods. [12] $H_3PMo_{12}O_{40}$ was dissolved in aqueous and then was stirred with chloroform solution of DODA·Cl. The initial molar ratio of DODA·Cl to $H_3PMo_{12}O_{40}$ was controlled at 3:1. The organic phase was separated, and $(DODA)_3PMo_{12}O_{40}$ was obtained by evaporating the chloroform to dryness. Then the sample was placed into a vacuum desiccator until the weight remained constant.

2.2. Preparation of the $(DODA)_3PMo_{12}O_{40}$ films

In preparation of the colloidal $(DODA)_3PMo_{12}O_{40}$ suspension, DMF solution of $(DODA)_3PMo_{12}O_{40}$ (5 min in a sonicator bath) was stirred strongly for 2 h in an ice bath. The concentrations of the SEC suspension in DMF were controlled at 0.2–0.4 mM. Indium tin oxide (ITO)-coated glass was used for the two electrodes. The surface of ITO-coated glass (1.0×4.0 cm^2) was cleaned in an $H_2O/H_2O_2/NH_4OH$ (1:1:1) bath for 20 min and then washed by ultrasonic bath with large quantity of deionized water, followed the preparation process of nanostructured films using electrophoretic approach. The two electrodes were immersed in a small glass cell containing the colloidal suspension. In the process of EPD, the small glass cell was immersed in an ice bath to keep the temperature of the colloidal suspension at about 2 °C. The distance between the two electrodes was maintained at 1.0–3.0 cm. A dc voltage 0–10.0 V was applied to initiate the EPD process. The time of EPD process was controlled at 10–30 min. The thin films were dried at ambient temperature and then washed by ultrasonic bath with deionized water for 20 min, followed were dried again in a vacuum desiccator at 60 °C.

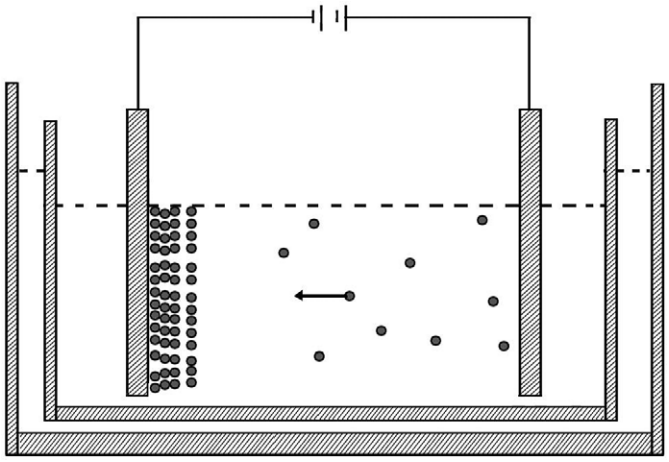
2.3. Measurements

The IR spectrum of the powder removed from ITO electrodes was measured with Perkin–Elmer 580B infrared spectrophotometer. XPS spectra of the thin films were done using an Escalab-MK II phtoelectronic spectrometer with ALK2 (1486.6 eV). CHI 660 electrochemical workstation at ambient temperature (25 °C) was applied for the cyclic voltammetric measurement. AFM images were taken using a Nanoscope IIIa instrument (Digital Instruments) operating in the tapping mode with silicon nitride tips. SEM images were collected on a JEOL model JSM-6700F scanning electron microscope.

3. Results and discussion

3.1. Electrophoretic preparation of the SEC films

In sol preparation, the colloidal suspension of $(DODA)_3PMo_{12}O_{40}$ is synthesized in an ice bath. The glass substrates with ITO coatings are used as electrodes in the electrophoretic device. During the deposition process, the positively charged SEC nanoparticles migrate and become deposited onto the cathode when we continue the application of dc field for an extended period (Scheme 1). The films exhibit bright iridescent colors when viewed with reflected light, indicating a periodic refractive index of variation through the film thickness [28,29]. It is possible to control the thickness of the film by controlling the applied voltage, the concentration of the colloidal suspension and the distance between the two electrodes. The size of the particles can also be controlled by changing the time of sonication bath and stir. The firm films



Scheme 1. Electrophoretic deposition of the SEC colloids on an ITO electrode in an ice bath. The SEC colloids were electrodeposited on ITO substrates using a dc field of 5.0 V. The distance between the two electrodes was kept at 3 cm and the time of the EPD process was for 30 min.

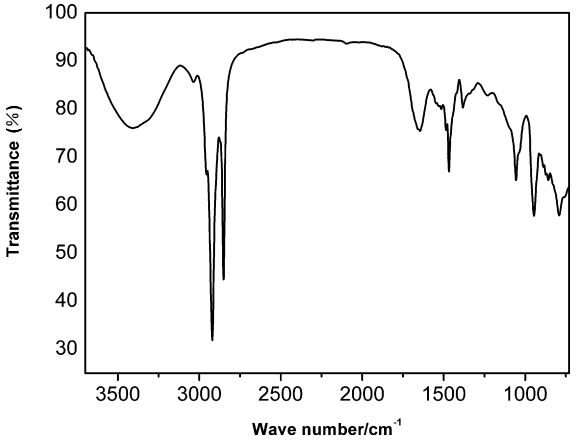


Fig. 1. IR spectrum of the powder obtained by scraping the SEC films off the ITO substrates.

are obtained from an optimized experimental condition: the concentration of the SEC suspension (0.2 mM), the distance between the two electrodes (3.0 cm), a dc voltage (5.0 V) and the time of the EPD process (30 min).

The assembly of nanoparticles shown in the AFM and SEM images is of fairly uniform size and the nanostructured film is highly porous, thus providing a large surface area. The nanoparticles strongly adhere onto the substrates and it is difficult to remove them even with a long time of washing by sonication in aqueous solutions. So the electrocatalytic functions of POM may be well performed in these films for their high surface area and strong electrode adhesion.

3.2. IR spectrum and X-ray photoelectron spectra

The powder used for the measurement of IR spectrum was obtained by scraping the SEC films off the ITO substrates. All the films were fabricated in an optimized experimental condition described above and the concentration of the colloidal suspension was maintained at 0.2 mM. Fig. 1 shows the IR spectrum of the powder. The arrangements of hydrocarbon chains in the nanocomposite films can be examined by IR spectrum. The $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ appeared at 2920 and 2850 cm^{-1}, respectively. In general, the $\nu_{as}(CH_2)$ at 2915–2920 cm^{-1} and the $\nu_s(CH_2)$ at 2846–2850 cm^{-1}, respectively, indicate that the hydrocarbon chains ag-