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

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A B S T R A C T
Keggin-type heteropolyanion H₃PMo₁₂O₄₀ 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 nanorays. 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 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)₃PMO₁₂O₄₀ were well characterized by the IR spectrum, X-ray photoelectron spectra (XPS) and cyclic voltammetry measurements, indicating the existence of DODA⁺ and PMO₁₂O₄₀⁻ ions in the films. The surface topography of the films is investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively.

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2. Materials and methods

2.1. Materials

DODA-Cl and H$_3$PMo$_{12}$O$_{40}$ were purchased as commercial products and used without further treatment. (DODA)$_3$PMo$_{12}$O$_{40}$ was prepared according to literature methods. [12] H$_3$PMo$_{12}$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$_3$PMo$_{12}$O$_{40}$ was controlled at 3:1. The organic phase was separated, and (DODA)$_3$PMo$_{12}$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)$_3$PMo$_{12}$O$_{40}$ films

In preparation of the colloidal (DODA)$_3$PMo$_{12}$O$_{40}$ suspension, DMF solution of (DODA)$_3$PMo$_{12}$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$_2$O/H$_2$O$_2$/NH$_4$OH (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 immered in a small glass cell containing the colloidal suspension. In the process of EPD, the small glass cell was immered 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 photoelectron 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)$_3$PMo$_{12}$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 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 $v_{as}$(CH$_2$) and $v_r$(CH$_2$) appeared at 2920 and 2850 cm$^{-1}$, respectively. In general, the $v_{as}$(CH$_2$) at 2915–2920 cm$^{-1}$ and the $v_r$(CH$_2$) at 2846–2850 cm$^{-1}$, respectively, indicate that the hydrocarbon chains ag-

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.
gregates are of the crystalline and highly ordered state [30–32]. Thus, the arrangement of hydrocarbon chains in the composite films is highly ordered and crystalline. The strong bands around 3300–3500 cm$^{-1}$ are assigned to the stretching modes of water in the composite films. The strong vibration bands at 1647 cm$^{-1}$ are associated to the stretching modes $\nu_{as}(\text{C}=\text{O})$. The bands at 2920, 2850, and 1468 cm$^{-1}$ are assigned to the stretching vibrations, asymmetrical bending vibrations and symmetrical bending vibrations modes of CH$_2$ and CH$_3$ groups in the DODA alkyl chains, respectively. The IR spectrum of the SEC films shows very strong bands below 1200 cm$^{-1}$, due to the POM. A slight blue shifts appear for the bands of Mo–O$_a$, P–O$_a$, Mo–O$_b$–Mo and Mo–O$_c$–Mo (1056, 946, 858 and 792 cm$^{-1}$), as compared to the values found in the literature (1065, 963, 869 and 793 cm$^{-1}$) [33]. The shift of the different peaks may be related to the organization and especially to the presence of positively charged DODA in the films [33–36].

We select (DODA)$_3$PMo$_{12}$O$_{40}$ as the object for investigation, as the DODA$^+$ and PMo$_{12}$O$_{40}^-$ are the classical surfactant and POM, respectively. The new method will probably be applied for assembly of many POM-based functional films.

To identify the elemental composition of the films, we measured the XPS of the SEC film on ITO substrates. Although the XPS measurement gives only semiquantitative elemental composition, the presence of C, N, Mo and P elements in the film are confirmed. The expected molar ratio of 1:12 for P to Mo is also approximately established. The XPS data suggest that we indeed incorporate DODA$^+$ and PMo$_{12}$O$_{40}^-$ into the films, in agreement with the IR spectrum results. The appearance of double N$_1s$ peaks at 401.9 and 398 eV in the XPS measurement (Fig. 2) shows two kinds of nitrogen atoms. One kind of nitrogen atom comes from DMO, corresponding to an N$_1s$ peak at 401.9 eV. The other kind is attributed to the nitrogen atom of the bond in (DODA)$_3$PMo$_{12}$O$_{40}^-$. The cyclic voltammogram of the thin film in KHSO$_4$ aqueous solution was studied. The thin film for the electrochemical measurement is prepared in the same way to that for the IR spectra. The cyclic voltammogram of the composite film shows three, reversible, two-electron waves in the potential range between 0.2 and 0.8 V (Fig. 3), which proves that the electrochemical characters of PMo$_{12}$O$_{40}^-$ are maintained in the film.
3.4. Atomic force microscopy

The AFM images were taken to provide detailed information about the surface morphology of the SEC films. The shape of the colloidal spheres can be maintained quite stably when free of solvent, as seen in Fig. 4. According to the AFM images, the diameter of SEC is approximately from 100 to 300 nm. The AFM images show a uniform distribution of the aggregate nanoparticles on ITO surface. This should be explained not only as a result of the colloidal stability but also as a lateral migration appears to result from an electrohydrodynamic mechanism [37].

3.5. Scanning electron microscopy

The surface morphology of the SEC films fabricated in different concentrations of the colloidal suspension is shown in Fig. 5. Obviously, a higher concentration of SEC colloids is not beneficial to the growth of SEC nanoparticles during EPD. It may be related to that the particles in a lower SEC concentration can remain separated without undergoing aggregation or inducing bulk film effects. When the concentration of the colloidal suspension is 0.4 mM, no spherical assemblies were formed (see Fig. 5e). Figs. 5a and 5b show the formation of separated and uniformly distributed spherical assemblies. A high magnification SEM image (Fig. 5b) shows the rough surface of the spherical assemblies. It may be associated...
to that the film is not kept under a moist airflow and the external solvent of the spherical assemblies is evaporated in drying process. Figs. 5c and 5d demonstrate that the surface of the thin film formed using the electrophoretic approach is very flat.

4. Conclusions

The film obtained by EPD is of a spherical assembly with uniform size exhibited by AFM and SEM images. The experiments completed in an ice bath can keep the suspension in a gel state. The nanostructured films may have potential applications in electrocatalysis for their high surface area and strong electrode adhesion. We believe that the simplicity of this assembly method makes the approach very attractive as a new route to economically manufacture nanostructured SECs films. In fact, the appropriate choice of POM should be helpful for fabricating functional ordered films having optical, magnetic, electrochromic and photochromic properties. The facile electrochemistry of the composite film will probably be used to prepare a sensitive conductometric catalytic electrode and to construct thin film molecular electronic devices based on POMs in future work.

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