

Rapid communication

Preparation of hollow layered MoO₃ microspheres through a resin template approach

Wen-Zhuo Li, Cheng-Gang Qin, Wen-Ming Xiao, Jie-Sheng Chen*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

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Abstract

Hollow layered MoO₃ microspheres were obtained by the adsorption of 12-molybdodiphosphate onto the surface of a spherical anion exchange resin followed by calcination of the resulting 12-molybdodiphosphate-resin composite. The conductivity of the sphere shell can be improved by intercalating polyaniline between layers of MoO₃ particles in the sphere shell.

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1. Introduction

Hollow spheres are an important class of materials [1,2] that are widely used as fillers, coatings, catalysts, controlled release capsules for drugs, protectors of electronics and sensitive agents such as enzymes and proteins [3]. A variety of hollow spheres [4], from nanometer-sized Fe₃O₄ and TiO₂ [5] to micrometer-sized clay [6] and silica [7], have been prepared in recent years. It is obvious that the physical and chemical properties of hollow spheres depend on the components of the sphere shell. Inorganic layered compounds [8,9] are excellent host materials between sheets of which guest species can be intercalated and novel composites with many functions can be obtained through intercalation [10,11]. However, very few inorganic layered materials have been used to prepare hollow spheres [7,12]. MoO₃, which is known as a layered compound consisting of two-dimensional metal oxide sheets separated by a van der Waals gap [13], has attracted much attention because of its electrical, optic and catalytic properties [14,15]. If MoO₃ is reduced, the metal oxide sheets in it will have negative charges, and as a result, cations such as H⁺, Na⁺ and K⁺ can be

intercalated between the metal oxide sheets [16–18]. Liu et al. reported a special micrometer MoO₃ crystal with a simple cubic structure prepared through triblock copolymer micelles [19]. The basic units of this MoO₃ crystal were hollow nanospheres with a diameter of 5 nm. But the individual nanosphere in this MoO₃ crystal cannot move randomly because the nanospheres packed together tightly. Also, because each sphere shell is composed of a single metal oxide layer, there is no space in the sphere shell for guest molecules to be intercalated. Our purpose is to prepare hollow MoO₃ spheres whose sphere shells can be modified. We employed the core-shell technique in which hollow spheres were prepared by a controlled adsorption, involving precipitation reaction, sol-gel condensation and layer-by-layer deposition of the desirable material onto the surface of an appropriately modified colloidal template (usually a polymer), and subsequent removal of the template through thermal and/or chemical treatments [20,21].

2. Experimental

Anion exchange resin spheres (Dowex 2, × 8 100/200 mesh) were purchased from Sigma company; NaCO₃,

*Corresponding author. Fax: +86 431 5168624.

E-mail address: chemcj@mail.jlu.edu.cn (J.-S. Chen).

12-molybdodiphosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$ or $\text{H}_3\text{PMo}_{12}$) and aniline (PhNH_2) were used as received without further purification.

At first, the resin spheres were treated with 1 M NaCO_3 aqueous solution to obtain their carbonated forms which were subsequently stirred in a 1 M 12-molybdodiphosphoric acid ($\text{H}_3\text{PMo}_{12}$) solution at $\text{pH}=3$ and 60°C for 30 min. During the reaction, CO_2 gas was released, indicating that PMo_{12} with negative charges substitute for CO_3^{2-} on the positively charged resin surface. The reaction mixture was centrifuged (5000 rpm/min), washed twice with deionized water and then dried at room temperature. The resulting PMo_{12} -resin composite was yellow-green in color. After calcination in air at 350°C for 20 h, the PMo_{12} -resin became dark because the resin was carbonized. Finally these dark spheres were calcined in air at 500°C for 20 h and deep blue hollow spheres formed.

Hollow spheres (0.5 g) obtained above were mixed with 1 mL PhNH_2 liquid at 50°C for 8 h and the resulting MoO_3 - PhNH_2 product was washed by ethanol for three times to remove the PhNH_2 molecules physically adsorbed on the external surface of the MoO_3 . The MoO_3 - PhNH_2 product was treated by 0.4 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution, which can cause the polymerization of the PhNH_2 as a catalyst, at room temperature for 2 h, washed with deionized water and then dried in air. Under an optical microscope, the final product was still spherical in shape.

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The infrared (IR) spectra were recorded on a Nicolet Impact-410 FTIR spectrophotometer using KBr pellets. The scanning electron microscopic (SEM) images were taken on a JEOL JSM-840 microscope operating at 20 kV. The ionic

conductivity measurements of the samples were performed on a Solartron 1260A impedance/gain-phase analyzer; the hollow spheres were ground into powder and then pressed into a compact disk before conductivity measurements.

3. Results

3.1. The optical microscopic images

The optical microscopic images of the PMo_{12} -resin and the hollow spheres are shown in Fig. 1. The PMo_{12} -resins are transparent, similar to the parent resin while the hollow spheres are not transparent because the PMo_{12} on the surface of PMo_{12} -resin spheres converts to MoO_3 after thermal treatment. From the images, we can see that the hollow spheres retain the spherical shape of the resin template.

3.2. The scanning electron micrographs

The scanning electron micrographs (Fig. 2) show some hollow spheres whose diameter ranges from 60 to $120 \mu\text{m}$. From several broken spheres, it is seen that these spheres are hollow inside. Fig. 2(b) displays an entire sphere with a diameter of $80 \mu\text{m}$. The surface of the sphere is not even. Fig. 2(c) shows the cross-section of a broken semi-sphere, which indicates that the wall thickness of the spherical shell is about $7 \mu\text{m}$. Moreover, the sphere shell is composed of plenty of hexagonal crystal particles. The size of the particles ranges from 2 to $4 \mu\text{m}$ and these particles are stacked irregularly.

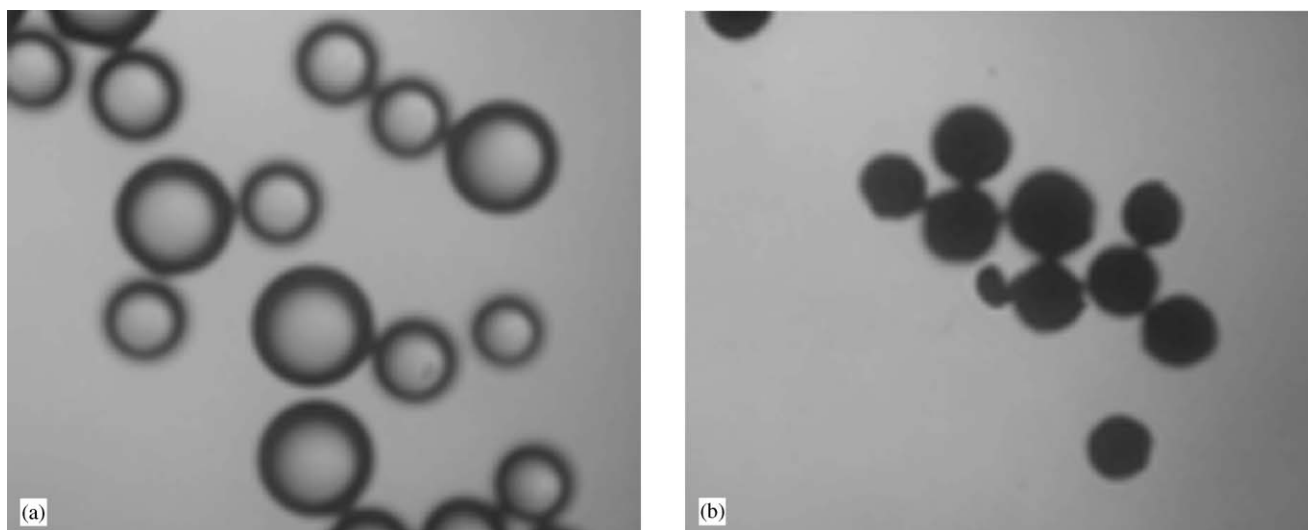


Fig. 1. Optical microscopic images of: (a) PMo_{12} -resin spheres and (b) MoO_3 hollow spheres.

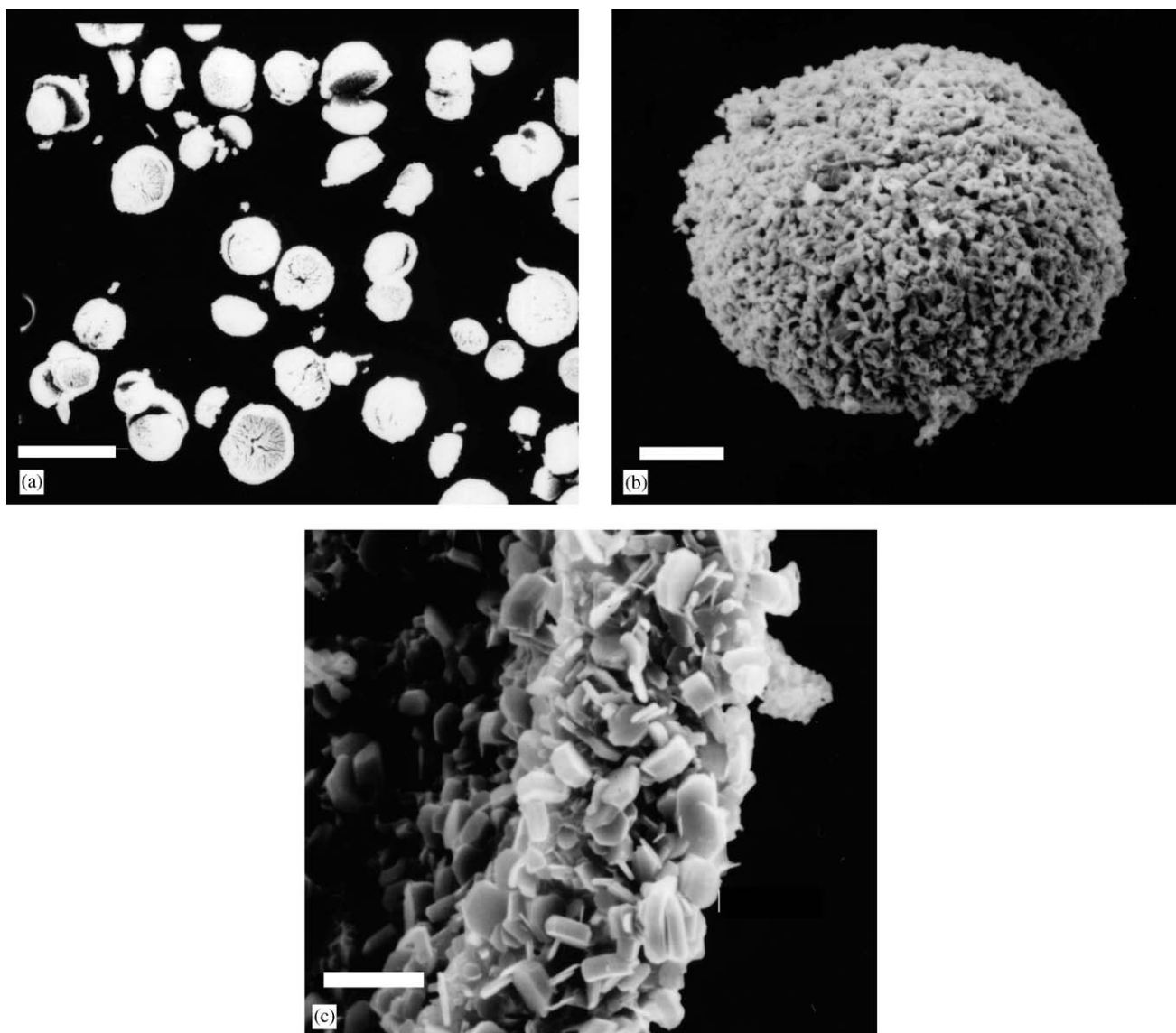


Fig. 2. Scanning electron micrographs of MoO_3 hollow spheres after calcination. (a) Broken MoO_3 hollow spheres, clearly showing the hollow interior, scale bar = $150\ \mu\text{m}$; (b) the surface of an individual MoO_3 hollow sphere, scale bar = $15\ \mu\text{m}$; (c) the cross-section of a broken semi-sphere showing that the wall thickness of the spherical shell is about $7\ \mu\text{m}$, scale bar = $3.75\ \mu\text{m}$.

3.3. Powder X-ray diffraction

The powder XRD patterns of the hollow spheres are shown in Fig. 3(a). By comparison of the pattern with the XRD data for $\text{H}_{0.34}\text{MoO}_3$ reported in the literature [22], it is clear that the predominant component of the hollow spheres is $\text{H}_{0.34}\text{MoO}_3$. The first reflection peak of the hollow spheres is located at 12.58° (2θ), corresponding to the layer distance of MoO_3 ($d_{001} = 7.01\ \text{\AA}$) in the sphere shell.

To check whether the shell of the MoO_3 hollow spheres can be modified, we soaked the hollow spheres into PhNH_2 liquid followed by addition of a $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution to intercalate polyaniline into the MoO_3 sphere layers. From the X-ray diffraction pattern

(Fig. 3b) of the hollow spheres after treatment of PhNH_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, a new peak at 5.6° (2θ) is clearly seen, indicating that the layer distance of the MoO_3 particles in the shells of the hollow spheres is increased from 7.01 to $15.75\ \text{\AA}$ due to the insertion of polyaniline into the gallery space of the layered MoO_3 .

3.4. Conductivity of MoO_3 hollow spheres and the polyaniline– MoO_3 hollow spheres

The room temperature conductivity of the polyaniline– MoO_3 hollow spheres is $8.3 \times 10^{-4}\ \text{S cm}^{-1}$, distinctly higher than that ($1.6 \times 10^{-11}\ \text{S cm}^{-1}$) of the parent MoO_3 hollow spheres. Obviously, the intercalation of

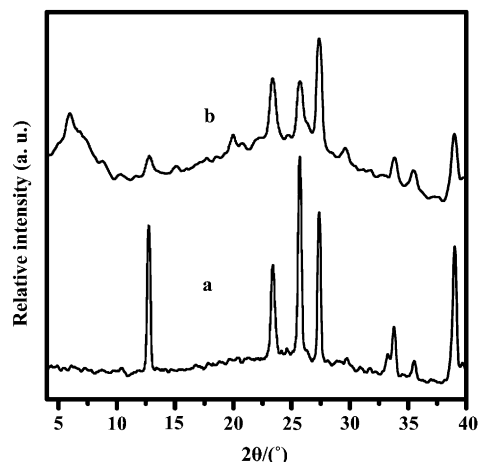


Fig. 3. Powder X-ray diffraction patterns for: (a) MoO_3 hollow spheres and (b) polyaniline- MoO_3 hollow spheres.

polyaniline in between the MoO_3 sheets improves the conductivity to a considerable extent.

4. Discussion

It has been reported that anionic resin spheres were successfully used as cores in the preparation of hollow clay spheres [8]. At first, clay particles with a proper size were selected through gravitation and ion-exchanged to obtain their sodium-saturated form; and the resulting particles with negative charges on the metal oxide layers were adsorbed on anionic resin spheres through mixing of the clay particles with the resin spheres in an aqueous medium. Finally the clay-resin spheres were calcined at 600°C , and as a result, the resin spheres were removed but the clay shells were retained. Apparently, our approach to obtain hollow MoO_3 spheres was different from that described in the literature for preparation of hollow clay spheres. In our experiment, what we chose was an anionic exchange resin with a quaternary ammonium head and chloride ions as the charge-balancing species. In the meantime, 12-molybdodiphosphoric acid ($\text{H}_3\text{PMo}_{12}$) was used to coat the surface of the resin spheres through ion-exchange reactions. 12-molybdodiphosphoric acid is a heteropoly anionic compound and soluble in water. Therefore, the procedure for preparation of PMo_{12} -resin spheres is simpler than that for clay-resin composite because no particles selection is needed in the preparation of PMo_{12} -resin spheres and the dispersion of $[\text{PMo}_{12}\text{O}_{40}]^{n-}$ anions in aqueous medium is more homogeneous than that of clay particles. When the PMo_{12} -resin composite is heated in air, the resin is burned off and the remaining $[\text{PMo}_{12}\text{O}_{40}]^{n-}$ species (with charge-balancing protons) decompose to form MoO_3 and P_2O_5 so that sphere shells consisting of MoO_3 sheets are formed during the calcination of the PMo_{12} -resin spheres, while sphere

shells with clay particles are formed before the calcination of the clay-resin composite in the preparation of hollow clay spheres. Fig. 4 schematically shows the formation process of MoO_3 hollow spheres.

12-Molybdodiphosphoric acid is easy to be reduced in air without the change of its structure. The formula of reduced 12-molybdodiphosphoric acid is $\text{H}_n\text{PMo}_{12}\text{O}_{40}$ ($n > 3$) because the oxidation state of some Mo atoms decreases from 6 to 4 [23]. As the 12-molybdodiphosphoric acid used in our experiment was not oxidized before using, it should be in a reduced form and its formula should be $\text{H}_n\text{PMo}_{12}\text{O}_{40}$ ($n > 3$). When the $\text{H}_n\text{PMo}_{12}\text{O}_{40}$ is dissolved in water, the resulting PMo_{12}^{n-} anions with negative charges can be adsorbed on the surface of the anionic exchange resin through static electrical interactions. Our experiment has proved that it is essential to prepare carbonated forms of resin at the beginning in order to obtain high quality hollow spheres. The reason is that use of resin treated by Na_2CO_3 could make more PMo_{12}^{n-} anions to be adsorbed on the surface of the resin. There is no IR absorptions characteristic of organic species in the IR spectrum of the final sample, indicating that the organic resin has been completely removed after the thermal treatment. No IR absorptions corresponding to P–O bonds in the IR spectrum has been observed either because the phosphorus has escaped into the air as P_2O_5 at above 300°C [24]. In fact, the choosing of appropriate parent material as coating on the surface of resin spheres is important to obtain hollow spheres. When Na_2MoO_4 was used as the parent material, no hollow sphere but white powder was observed. Additionally, the heating temperature should not be raised too rapidly, otherwise the gas resulting from the organic resin decomposition and oxidation forms pressure which breaks the sphere shells. Temperature also plays a critical role in the maintenance of the hollow spheres. If the temperature is increased to above 650°C , no hollow spheres but white needle crystals form. Because the hollow spheres were

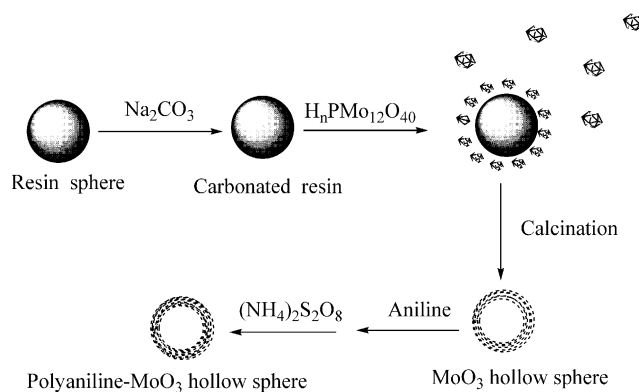


Fig. 4. Schematic illustration of the procedure used to prepare MoO_3 hollow spheres and polyaniline- MoO_3 hollow spheres.

prepared by calcination at 500 °C, the spheres should have a high thermal stability.

From the XRD data of MoO₃ hollow spheres in combination with those reported previously [22], it appears that the MoO₃ sphere shell mainly consists of H_{0.34}MoO₃. The oxidation state of some Mo atoms in H_{0.34}MoO₃ is not +6 so that the MoO₃ sheets are negatively charged with the charges being balanced by the protons located between the sheets. Because of the presence of protons, it is facile to intercalate basic guest species between the sheets of H_{0.34}MoO₃. Aniline (PhNH₂) is basic, and it can be intercalated in between the H_{0.34}MoO₃ sheets easily. Upon addition of the initializer (NH₄)₂S₂O₈ into the MoO₃–PhNH₂ intercalation composite, the PhNH₂ molecules get polymerized and polyaniline is formed between the MoO₃ sheets of the sphere shells, as evidenced by the appearance of the 5.6° (2θ) reflection peak in the XRD pattern of the resulting intercalated compound. However, after the polymerization treatment, diffraction peaks of MoO₃ still exist in Fig. 3(b) because some MoO₃ particles without intercalated polyaniline still remain in the shell. Under an optical microscope, the resulting products after PhNH₂ interaction and the following polymerization treatments retain the spherical shape, indicating that the hollow MoO₃ spheres is stable towards intercalation. It is interesting to note that in contrast to that of the parent MoO₃ spheres which are almost insulating, the room temperature conductivity of the polyaniline–MoO₃ hollow spheres is in the range of semiconducting materials. It has been proved that the encapsulated polymer plays a role more important than (MoO₃)^{X-} layers in charge transport of polyaniline–MoO₃ compound [18]. Therefore, the semiconducting properties of our polyaniline–MoO₃ hollow spheres are mainly originated from the intercalated polyaniline species. Conductive shell materials and hollow conductive polymer capsules [25] have recently been studied owing to their applications in, for example, high performance electrochromatography [26] and immunodiagnosics [27,28]. The hollow spheres we prepared may act as a new type of hosts for encapsulating interesting guest species.

Acknowledgments

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