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Facile Preparation of Strontium Tungstate and Tungsten Trioxide Hollow Spheres

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A simple and low-cost technique was developed to produce unique $SrWO_4$ and WO_3 hollow spheres. The $SrWO_4$ hollow spheres were prepared via a precipitation reaction between $SrCl_2$ and Na_2WO_4 in the presence of polymethacrylic acid, and the synthesis of WO_3 spheres used the as-prepared $SrWO_4$ hollow spheres as both precursors and templates. After soaking in HNO_3 and calcinations, the $SrWO_4$ were completely transformed into WO_3 while the hollow structures were perfectly retained. The "polymer-cation template" model was proposed to describe the formation of the $SrWO_4$ hollow spheres. This technique is feasible in fabricating other inorganic hollow-structured materials.

I. Introduction

Micrometer-sized and nanometer-sized inorganic hollow spheres, with unique microstructures and large specific areas, have a wide range of applications in medicine release, catalysis, sensing, filtering, chromatograph separation, optical, and electronic devices.[1–5] Techniques for preparing inorganic hollow spheres are becoming subjects of intense research. Numerous physical and chemical methods based on templating processes had been developed to fabricate various inorganic hollow spheres in glass, ceramic, semi-conducting and magnetic materials, and biominerals.[6–10] Among these, a technique using mixed polymer-surfactant to produce soft micelles templates was particularly remarkable.[9,10] Both inorganic $CaCO_3$ and Ag hollow spheres were successfully prepared. In this approach, a so-called double hydrophilic block copolymer polyethylene oxide-*block*-poly methacrylic acid (PEO-*b*-PMAA) and a surfactant sodium dodecylsulfate were used. More recently, $CaCO_3$ hollow spheres were also synthesized by using another mixed polymer-surfactant system, which was composed of polystyrene-*alt*-maleic acid (PSMA) and cetyltrimethyl ammonium bromide.[11] However, the relatively high costs of PEO-*b*-PMAA and PSMA, and the needs of compatible surfactants, had limited this technique to producing hollow structures on a small scale. Thus, there is still a pressing need for exploring other facile, general, and low-cost routes.

We had studied an early report on ionic elastomers.[12] It was suggested that ionic cross-links could be formed by the neutralization of polymeric chains in the copolymer of butadiene, acrylonitrile, or acrylic acid with a certain type of cations (M). This idea had inspired us to develop an alternative route for preparing inorganic materials with hollow structures. If the M on the surface of the *in situ* formed cross-links were able to react with free anion species (X) in the reaction solution, it was possible that these cross-links could be used as the so-called "polymer-cation templates" for the growth of inorganic MX hollow structures.

Inexpensive commercially available PMAA is highly soluble in water, because its helical chain buries the hydrophobic backbone and shows only the hydrophilic –COOH ions on the outer rim of its chain.[13] It is therefore possible for the PMAA macromolecules to form cross-links with the co-existing M in the solution. In this work, PMAA was chosen to generate the "polymer-cation template" with the divalent Sr^{2+}, and the polymer-cation templating technique was demonstrated by synthesizing hollow-structured $SrWO_4$.

The potential applications of $SrWO_4$ and tungsten trioxide (WO_3) have attracted our attention. Scheelite-type $SrWO_4$ has been widely used in the optoelectronic industry and the solid-state laser system due to its luminescence behavior and stimulating Raman scattering property.[14] There is no report on the fabrication of $SrWO_4$ hollow spheres so far, although the structural properties and optical characteristics of $SrWO_4$ crystals have been extensively investigated.[15–18] WO_3 is an electrochromic, optochromic, and gaschromic material, which is widely used and found in electrochromic windows, infrared switching devices, photo-catalysis, writing–reading erasing optical devices, and gas sensors for detecting NO_2, H_2S, NH_3, H_2, O_3, and H_2O.[19,20] Li *et al.*[21] had synthesized WO_3 nanometer-sized hollow spheres via the hydrolysis of WCl_6 using pre-synthesized carbon micro-spheres as templates. However, considering the instability and toxicity of WCl_6 and the high production cost, extensive studies in exploring new routes for preparing WO_3 hollow spheres remain a challenge. In this article, we report the preparation of micrometer-sized $SrWO_4$ hollow spheres based on the "polymer-cation" templating technique. In addition, a novel route for the preparation of WO_3 hollow spheres using the as-prepared $SrWO_4$ hollow spheres as precursors and templates is also presented.

II. Experimental Procedure

Analytical-grade $SrCl_2 \cdot 6H_2O$ (Beijing Chemical Industrial Company, Beijing, China), $Na_2WO_4 \cdot 2H_2O$ (International Laboratory, Las Vegas, NV), and PMAA (Sigma Aldrich, St. Louis, MO, 30% aqueous solution, M_w 6500) were used in this work. In a typical procedure for preparing $SrWO_4$ hollow spheres, 10 mL $SrCl_2$ solution (0.1 mol/L), 0.5 mL PMAA solution (10 g/L), and 29.5 mL distilled water were mixed in a

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beaker under magnetic stirring for 5 min. Then, 10 mL Na_2WO_4 solution (0.1 mol/L) was slowly added under vigorous stirring, giving final concentrations of 0.02 mol/L for both Sr^{2+} and WO_4^{2-}, and 0.1 g/L for PMMA. The starting pH value of the mixture was adjusted to 12 using 2 mol/L NaOH and HCl solutions. After continuous vigorous stirring for 5 min, the mixture was sealed and incubated for 12 h at room temperature. Thereafter, the resulting white precipitate was collected, washed with distilled water and ethanol, and dried in air. To prepare WO_3 hollow spheres, the as-synthesized $SrWO_4$ was soaked in HNO_3 (8 mol/L) for 12 h at room temperature, followed by calcination at 500°C for 2 h, resulting in a yellow powder.

X-ray diffractometry (XRD) was performed using a Rigaku RU-300 X-ray diffractometer (Spring, TX) with monochromatic Cu*K*α radiation ($\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS) were performed with a LEO1450 VP scanning electron microscope equipped with an EDS spectrometer. The Raman spectra of the samples were obtained by a Renishaw RM 1000B spectrometer with a radiation of 514.5 nm from an argon ion laser.

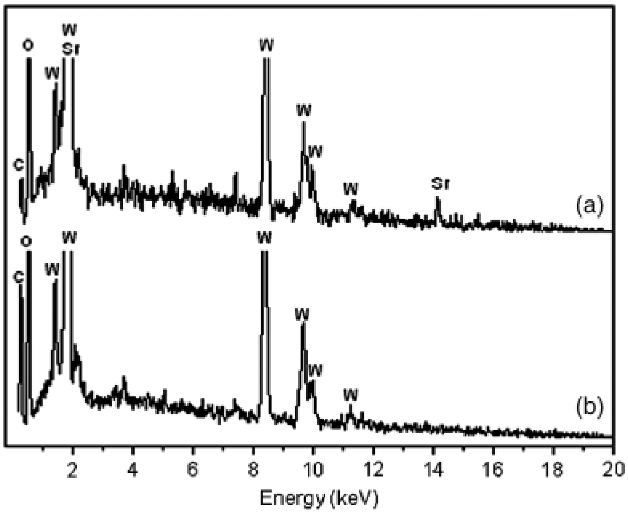

Fig. 2. Energy-dispersive X-ray spectrometry spectra of the as-prepared (a) $SrWO_4$, and (b) WO_3.

III. Results and Discussion

The $SrWO_4$ samples were produced via a precipitation reaction between $SrCl_2$ (0.02 mol/L) and Na_2WO_4 (0.02 mol/L) solutions in the presence of PMAA (0.1 g/L) at room temperature. Figure 1(a) shows an XRD pattern of the $SrWO_4$ product. All the peaks were indexed, and it was confirmed that a pure tetragonal scheelite-type structured $SrWO_4$ was produced. (JCPDS card no. 08-0490, $a = 5.4168$ Å, and $c = 11.951$ Å). EDS was used to determine the composition of the prepared $SrWO_4$ product. The EDS result shown in Fig. 2(a) indicates that the product was composed of Sr, W, and O with an atomic ratio of 1:1.10:3.88 for Sr, W, and O, which was close to the stiochiometric ratio of $SrWO_4$.

The SEM micrograph in Fig. 3(a) shows that the product consisted of well-defined $SrWO_4$ spheres, with size ranging from 2 to 3 μm. A high-magnification SEM image in Fig. 3(b) shows an open $SrWO_4$ sphere, revealing its hollow nature. The rugged surface suggested that the hollow spheres were composed of smaller crystallites. This observation was in agreement with the grain size calculation based on the width of the (112) reflection peak from the XRD pattern (Fig. 1(a)), which determined that the size of the crystallites was about 15 nm. In Fig. 3(a), only a few open $SrWO_4$ spheres (about 0.5%) can be observed. Attempts had been made to produce more $SrWO_4$ open spheres by sonication of the as-prepared precipitate, but it was not successful. Although the hollow nature of the open spheres had been observed by SEM, there was no solid evidence to verify that the close spheres of $SrWO_4$ spheres were also hollow. As an alternative to show that the as-prepared $SrWO_4$ spheres were hollow, we had produced WO_3 hollow spheres by using these $SrWO_4$ spheres as precursors (to be shown later). This could provide extra evidence that the $SrWO_4$ product was hollow.

We propose the "polymer-cation template" model to describe the mechanism in the formation of these $SrWO_4$ hollow spheres. In this model, the PMAA macromolecules were cross-linked via the electrostatic interaction between the ionized carboxylic acid groups (COO^-) and the Sr^{2+} cations in the reaction solution, resulting in the formation of spherical "PMAA–Sr^{2+}" cross-link micron-sized lumps. On the surface of these lumps, the Sr^{2+} ions readily reacted with the free-floating WO_4^{2-} ions in the reaction solution and formed $SrWO_4$ crystals. As a result, nucleation and growth of $SrWO_4$ crystallites occurred on the surface of the spherical templates, and eventually, $SrWO_4$ engulfed the entire cross-link lump and formed a closed shell. This proposal was supported by the observed fact that the PMAA solution became turbid immediately after the addition of $SrCl_2$, implying a strong interaction between Sr^{2+} and PMAA. In contrast, white precipitates could only be observed approximately 10 min after the addition of Na_2WO_4 solution. It has to be mentioned that the rest of the free-floating PMAA in the reaction solution acted as an inhibitor. It functioned to halt the further growth of the $SrWO_4$ once they were formed, and prevented them from aggregation. As can be seen in the SEM images of these samples,

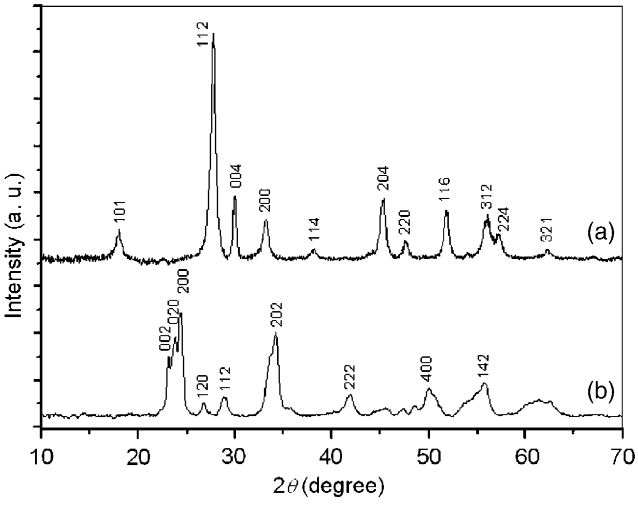

Fig. 1. X-ray diffraction patterns of the as-prepared (a) $SrWO_4$, and (b) WO_3 samples.

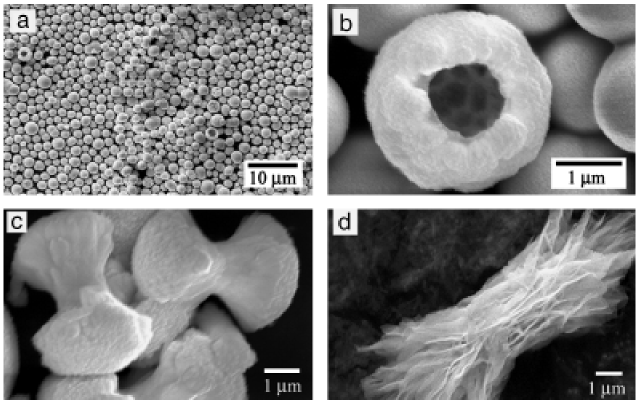

Fig. 3. Scanning electron microscopy images of (a) the typical as-prepared $SrWO_4$ product, (b) magnified image of a hollow sphere; products obtained from controlled experiments, (c) when polymethacrylic acid (PMAA) was not present, and (d) when the pH value was 4 in the presence of PMAA.

the range of the size of the spheres was relatively narrow, and no aggregation was observed in the $SrWO_4$ precipitate.

Some controlled experiments were performed to verify whether both PMAA and a suitable pH value were vital to the formation of the $SrWO_4$ hollow spheres. When PMAA was not present, the $SrWO_4$ product did not appear spherical as shown in Fig. 3(c). It was because no "polymer-cation templates" could be formed. Moreover, when the pH value was adjusted from 12 to 4, no $SrWO_4$ hollow spheres were formed as shown in Fig. 3(d). It was evident that the formation of those "polymer-cation templates" required a high degree of ionization (i.e., high concentration of COO^-). Reducing the pH value of the system would reduce the degree of ionization in PMAA. Thus, the electrostatic interaction between PMAA and Sr^{2+} was weakened, and the formation of the "polymer-cation templates" became difficult.

In the fabrication of the WO_3 hollow spheres, the as-prepared $SrWO_4$ spheres were used as the precursors. The $SrWO_4$ sample was bathed in HNO_3 (8 mol/L), followed by calcination at 500°C. Figure 1(b) shows the XRD pattern of the product. The reflection peaks were indexed to a pure monoclinic WO_3 (JCPDS card no. 83-0951, $a = 7.301$ Å, $b = 7.539$ Å, $c = 7.689$ Å, and $\beta = 90.893°$). The EDS spectrum shown in Fig. 2(b) further confirmed that the product was WO_3. The quantitative analysis indicated that the elemental ratio of W to O was 1:2.9. Thus, $SrWO_4$ had been successfully transformed to WO_3 after the nitric acid treatment and calcination.

The SEM image in Fig. 4(a) shows the as-prepared WO_3 hollow spheres with size ranging from 2 to 3 μm, which is similar to that of the $SrWO_4$ precursors. A closeup view of the outer surface of a WO_3 hollow sphere is shown in Fig. 4(b). It reveals that each shell was composed of a large number of flake-like nano-crystallites with a thickness of about 45 nm. From another micrograph shown in Fig. 4(c), the thickness of the shell was determined to be about 500 nm.

The $SrWO_4$ was completely transformed into WO_3. During the nitric acid treatment, the Sr^{2+} was removed from $SrWO_4$, while the original hollow structures were retained. At the same time, the calcination process removed the water content and promoted the crystallization of WO_3 to form stable shells. The reactions are decribed as follows:

$$SrWO_4\,(\textit{hollow sphere}) + 2H^+ + (n-1)\,H_2O \rightarrow WO_3\cdot nH_2O\,(\textit{hollow sphere}) + Sr^{2+} \qquad (1)$$

$$WO_3\cdot nH_2O\,(\textit{hollow sphere}) \xrightarrow{\text{Calcination}} WO_3\,(\textit{hollow sphere}) + nH_2O \qquad (2)$$

The as-synthesized $SrWO_4$ hollow spheres had not only acted as precursors but also as "hard templates" for the formation of WO_3 hollow spheres. As the WO_3 spheres were proven to be hollow, the hollow nature of the $SrWO_4$ spheres was confirmed. However, it was possible that some PMAA cross-links would have been enclosed inside the closed $SrWO_4$ spheres. After the HNO_3 treatment and calcinations, all the polymer cross-links inside the spheres should have been removed.

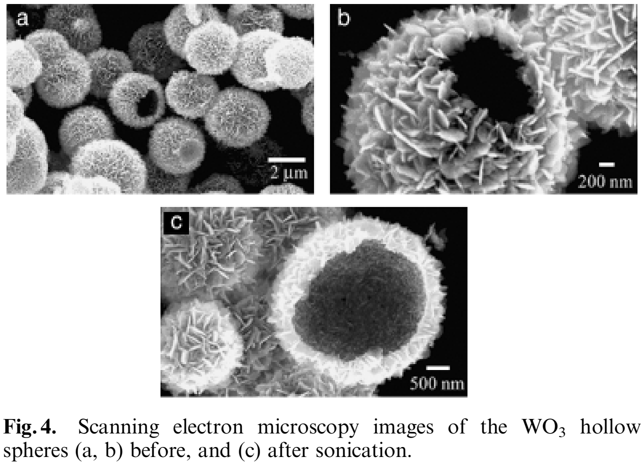

Fig. 4. Scanning electron microscopy images of the WO_3 hollow spheres (a, b) before, and (c) after sonication.

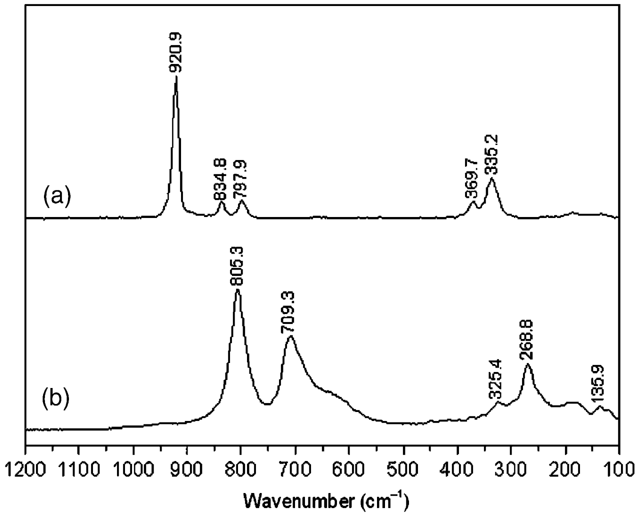

Fig. 5. Raman spectra of (a) $SrWO_4$, and (b) WO_3 hollow spheres.

Raman spectroscopy was conducted on the as-prepared $SrWO_4$ and the WO_3 hollow spheres. The scheelite-type structured tungstates such as $CaWO_4$, $SrWO_4$, $PbWO_4$, $SrMoO_4$, and $CaMoO_4$ are known to have strongly bonded $XO_4^{=}$ groups (X = W or Mo), but these groups were loosely bonded to the cations. Thus, many of the internal vibration modes in these tungstates were rather similar.[22] The Raman spectrum of the $SrWO_4$ hollow spheres is shown in Fig. 5(a). The bands located at 920.9, 834.8, 797.9, 369.7, and 335.2 cm^{-1} corresponded to the vibration modes $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(B_g)$, and $\nu_2(A_g)$ of the WO_4^{2-} groups in the $SrWO_4$ crystal lattice, and these values were close to those of an early report in bulk samples.[22] Notably, the almost identical intensities of bands at 834.8 and 797.9 cm^{-1} suggested that identical growth had occurred along the a and b axes of the nano-crystallites in the $SrWO_4$ hollow spheres.[23] Figure 5(b) shows the Raman spectrum of the WO_3 hollow spheres. The bands located at 805.3 and 709.3 cm^{-1} were related to the O–W–O stretching modes of the bridging oxygens, and the bands at 325.4 and 268.8 cm^{-1} corresponded to the O–W–O bending modes.[24] The weak band at 135.9 cm^{-1} was attributed to the O–O deformation.[25] The terminal W = O stretching mode at around 950 cm^{-1} was not observed, and this mode was associated with $WO_3\cdot H_2O$.[24] This result was consistent with that of the XRD (Fig. 1(b)) in which no $WO_3\cdot H_2O$ phase was detected.

IV. Conclusions

A foremost fabrication method to produce micrometer-sized $SrWO_4$ and WO_3 hollow spheres has been developed. $SrWO_4$ hollow spheres were formed via a simple precipitation reaction between $SrCl_2$ and Na_2WO_4 solutions in the presence of PMAA. A "polymer-cation template" model was established to describe the formation mechanisms. WO_3 hollow spheres with flake-like nano-crystallites growing perpendicularly to its surface were produced by subsequent HNO_3 treatment and calcination. This study is of practical importance due to the commercial availability and relatively low cost of PMAA, and the simplicity of the method wherein no surfactant is required. It is expected that this approach can be applied as a general and facile method for large-scale production of other inorganic hollow-structured materials. Furthermore, unusual WO_3 hollow spheres have been facilely prepared by using pre-synthesized $SrWO_4$ hollow spheres as precursors and templates. This approach is novel because the templates can be completely transformed into the final hollow product.

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