

Room Temperature Synthesis of Hollow CdMoO₄ Microspheres by a Surfactant-Free Aqueous Solution Route

Wen-Shou Wang, Liang Zhen,* Cheng-Yan Xu, Bao-You Zhang, and Wen-Zhu Shao

School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

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Hollow cadmium molybdate microspheres have been successfully prepared via a template-free aqueous solution method with the assistance of NaCl at room temperature. The structure and morphology of the CdMoO₄ hollow microspheres were characterized by X-ray diffraction, field-emission scanning electron microscopy, and transmission electron microscopy. The microspheres have diameters of 3–6 μm and hollow interiors of 2–3 μm . The shell is composed of numerous single-crystalline nanorods with diameters of 30–120 nm and lengths of 1–2 μm which are radially oriented to the center. A certain concentration of NaCl plays a key important role in the formation process of hollow microspheres, which might provide a suitable chemical environment to favor the formation of hollow CdMoO₄ microspheres. A possible NaCl-induced Ostwald ripening process is proposed for the formation of hollow CdMoO₄ microspheres on the basis of scanning electron microscopy observation of intermediate products at different precipitation stages.

Introduction

Among the many inorganic materials with distinct structural and geometrical features, hollow nano/microspheres currently represent one of the fastest growing areas of materials research.¹ The fabrication of hollow microspheres or nanospheres with varying sizes and shapes has attracted fascinating interest, due to their distinct low effective density, high specific surface area, and potential scale-dependent applications in photonic devices, drug delivery, light-weight fillers, active material encapsulation, ionic intercalation, acoustic insulation, surface functionalization, robust catalysts/carriers, and size-selective reactions.² Until now, numerous efforts have been devoted to the exploration of different approaches to the synthesis of hollow structures, most of which focus on the inorganic precipitation process against a variety of sacrificial templates, including polystyrene latex spheres,³ spherical silica,⁴ carbon spheres,⁵ liquid droplets,⁶ vesicles,⁷ microemulsions,⁸ polymer or macromolecule micelles,⁹ etc. Generally, for the template-directed processes, the template particles were first treated by specific functional groups, followed by coating with desired materials through surface reaction on the core to obtain core–shell structures. The template particles were subsequently removed by calcinations at elevated temperatures or wet chemical etching in an appropriate solvent to create hollow structures. For example, CdS hollow spheres were synthesized in the presence of Pluronic amphiphilic triblock copolymer^{10a} or by using silica^{10b} and polystyrene spheres^{10c} as the sacrificial templates. Xia et al.¹¹ prepared hollow titania mesoscale spheres utilizing polystyrene spheres as the sacrificial template via a sol–gel approach. Cheng et al.¹² fabricated monodispersed hollow titania by using polystyrene spheres as the sacrificial template, which was dissolved simultaneously in the precursor during the formation of titania. Yan et al.¹³ reported the fabrication of hollow ZnS and ZnO architectures by employing Zn₅(CO₃)₂(OH)₆ microspheres as the sacrificial template through a spontaneous ion replacement reaction. In addition, sacrificial metal templates

have also been introduced to prepare metal nanoshells through redox electrochemical reactions, where metal templates vanished through surface defects.¹⁴ Although these methods are straightforward to perform and have already been demonstrated as an effective route to hollow structures, the preparation strategies seem to be inconvenient because complete template removal is needed, which means a much more complicated process involving the selection of an appropriate solvent or calcinations at elevated temperatures. In some cases, the yield of hollow spheres through template-directed processes is relatively low and the shell has a poor mechanical strength, which are disadvantageous for potential applications. Recently, the utilization of some physical phenomenon, such as the Kirkendall effect,^{15a} Ostwald ripening,^{15b} and the oriented attachment process,^{15c} to fabricate hollow structures provides new alternative opportunities for the template-free fabrication of hollow structures. However, there has been only little progress in the template-free synthesis of hollow structures compared with the template-directed process. Thus, the search for template-free, simple, mild, high-yield, and environmentally benign methods to synthesize microspheres or nanospheres with hollow interiors is still an ongoing process and represents a major challenge.

Cadmium molybdate has excellent optical, chemical, and electronic structural properties from several points of review.¹⁶ During the past few decades, CdMoO₄ has received increasing attention due to its electronic excitation with VUV synchrotron radiation^{17a} and pressure-induced phase transformations.^{17b} Recently, using SrCl₂ and Na₂CrO₄ aqueous solutions as precursors, we were able to prepare SrCrO₄ nanowires and PbCrO₄ nanorods on a large scale at room temperature without using templates or surfactants.¹⁸ Herein, we further demonstrate the preparation of hollow CdMoO₄ microspheres on a large scale by a similar approach, except that NaCl was introduced into the reaction system. A certain concentration of NaCl was found to be necessary for the formation of hollow microspheres. The growth mechanism of the hollow microspheres is suggested to be a NaCl-induced Ostwald ripening process on the basis of scanning electron microscopy (SEM) observation of intermediate

* To whom correspondence should be addressed. E-mail: zhenl@hit.edu.cn.

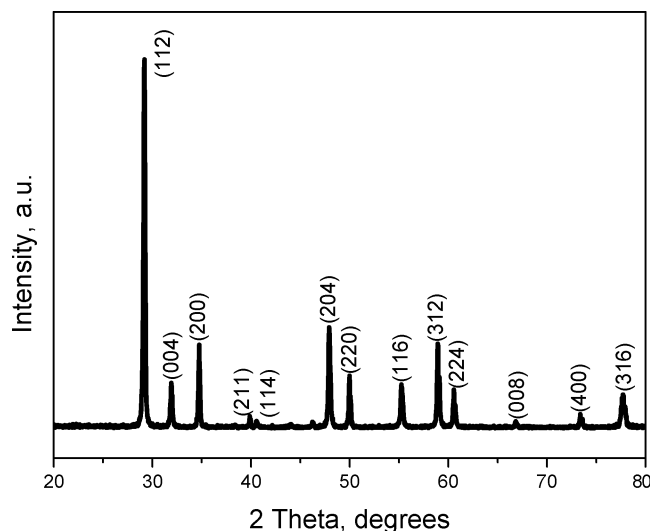


Figure 1. XRD pattern of the as-synthesized hollow CdMoO₄ microspheres.

products at different precipitation stages. The result may represent a new example of the Ostwald-ripening-based formation of inorganic hollow structures in a surfactant or template-free aqueous solution at room temperature. To the best of our knowledge, it is the first time hollow CdMoO₄ microspheres on a large scale have been synthesized by this facile method.

Experimental Section

All chemicals were analytical grade and used as received without further purification. In a typical synthesis process, 5 mmol of Na₂MoO₄ was first dissolved in 25 mL of distilled water to form a homogeneous aqueous solution in a 100 mL glass beaker, then 10 mmol of NaCl was added to the Na₂MoO₄ aqueous solution, and the resulting mixture was stirred until the NaCl was completely dissolved in the Na₂MoO₄ aqueous solution. A 25 mL portion of a CdCl₂ aqueous solution (0.2 M) was added in the mixed aqueous solution of Na₂MoO₄ and NaCl drop by drop under strong magnetic stirring at room temperature. After 10 min of magnetic stirring, the resulting suspension was stored at room temperature for 5 days without stirring or shaking. The resulting white products were collected by centrifugation, washed several times with distilled water and absolute ethanol, and finally dried in air at 60 °C for 60 min.

The products were characterized by X-ray diffraction (XRD) recorded on a Rigaku D/max-rA diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). Field-emission scanning electron microscopy (FESEM) images of the products and energy-dispersive X-ray analysis spectra were taken on a Hitachi S-4700 scanning electron microscope. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were carried out with a Phillips Tecnai 20 microscope operated at an accelerating voltage of 200 kV. The as-synthesized powders were first dispersed in ethanol by ultrasonic treatment. A small drop of the dispersions was transferred to a holey carbon film supported on a copper grid for TEM observation.

Results and Discussion

Figure 1 shows the XRD pattern of the as-synthesized CdMoO₄ hollow microspheres. The strong and sharp diffraction peaks indicate the good crystallization of the sample. All diffraction peaks can be perfectly indexed to the tetragonal phase of CdMoO₄ (JCPDS 07-0209), with lattice parameters of $a = 5.155$ Å and $c = 11.194$ Å. Only diffraction peaks belonging

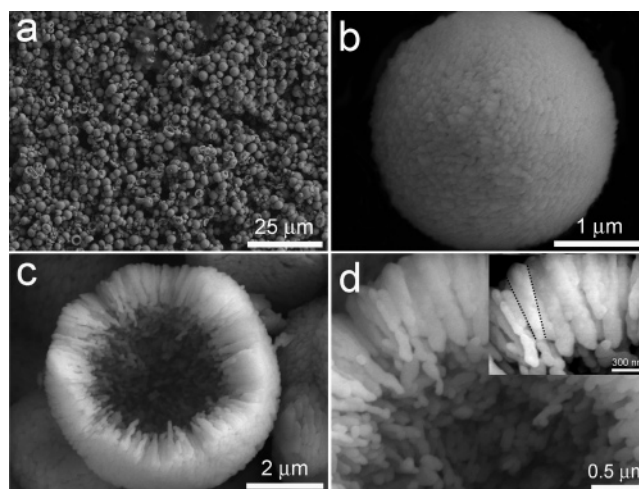


Figure 2. FESEM images of hollow CdMoO₄ microspheres: (a) overall product morphology, (b, c) two individual microspheres. (d) is a high-magnification FESEM image of the shell wall of the individual hollow CdMoO₄ microsphere corresponding to (c). Inset: magnified FESEM image of the shell wall of the hollow microsphere.

to CdMoO₄ can be detected in the XRD pattern, which implies the high purity of the final products.

Figure 2 shows the representative FESEM images of the as-synthesized CdMoO₄ microspheres. The low-magnification FESEM image (Figure 2a) indicates that the product consists of a wealth of microspheres with diameters ranging from 3 to 6 μ m. Under the reported conditions, the CdMoO₄ products are all in this morphology, implying that almost a 100% yield can be achieved by this facile method. Figure 2b shows an individual microsphere with a diameter of 3.5 μ m. The peripheral surface of the microsphere is not smooth. It seems that the microsphere is composed of numerous nanoparticles 50 nm in diameter, but in fact, they are not individual “nanoparticles”, but tips of CdMoO₄ nanorods (to be discussed below). Further FESEM observation indicates that the obtained CdMoO₄ microspheres have hollow interiors. Figure 2c shows a typical FESEM image of an individual hollow hemisphere with a diameter of about 5 μ m and shell thickness of 1.5 μ m. The high-magnification FESEM image (Figure 2d) on the interior shows that the inner surface is not smooth, which is similar to the peripheral surface. The magnified FESEM image on the shell wall of the hollow hemisphere (inset in Figure 2d) shows that the shell is composed of numerous packed nanorods. The diameter of the nanorod is not consistent along its length, as marked by dashed lines in the inset. The average diameters of the two tips of the nanorods are about 60 and 100 nm. All the nanorods are radially oriented to the interior center, and both the peripheral surface and the inner surface are not smooth. The chemical compositions of the sample are characterized using energy-dispersive X-ray spectroscopy (EDS). Only Cd, Mo, and O peaks are observed in the spectrum for the as-synthesized CdMoO₄ microspheres, together with the Pt peaks generated by coating Pt on the sample and the normal C peak (see the Supporting Information, Figure S1). Quantitative analysis shows that the molar ratio of Cd to Mo to O is about 1:1:4, which is in agreement with the nominal composition of CdMoO₄.

The morphology and structure have further been characterized using TEM and SAED. Figure 3a shows the TEM image of one individual shell of the hollow CdMoO₄ microspheres. It is clear that the shell is composed of nanorods with diameters of 30–120 nm and lengths of 1–2 μ m. All the nanorods are radially oriented to the center, which is in agreement with the

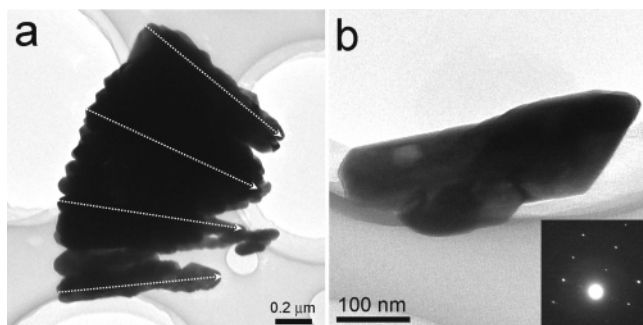


Figure 3. TEM images of (a) a shell of hollow CdMoO_4 microspheres and (b) an individual nanorod broken from the hollow CdMoO_4 microspheres. Inset: corresponding SAED pattern taken on the selected nanorod (shown in (b)).

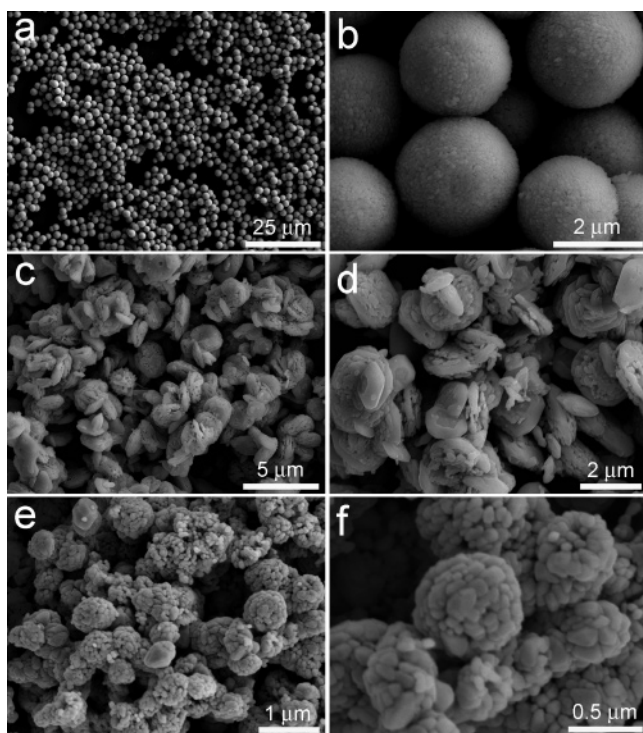


Figure 4. FESEM images of the CdMoO_4 products prepared in the presence of different concentrations of NaCl: (a, b) 6 mol/L, (c, d) 50 mol/L, (e, f) 0 mol/L (in the absence of NaCl).

SEM observation. Figure 3b shows the TEM image of an individual CdMoO_4 nanorod broken from the hollow CdMoO_4 microspheres. The nanorod is not straight along its length, and the surface is not smooth. The selected nanorod has a diameter of about 100 nm and length of 400 nm. The SAED pattern taken from the selected nanorod (inset in Figure 3b) clearly demonstrates that the nanorod is single-crystalline.

To investigate the influence of NaCl on the formation process of the hollow CdMoO_4 microspheres composed of nanorods, a series of controlled experiments are carried out under different conditions, and it is found that the appearance of hollow CdMoO_4 microspheres is dependent on some experimental factors. It is revealed that only an appropriate concentration of NaCl in the range of ~ 10 – 30 mol/L is indispensable for the surfactant-free, room temperature formation of hollow CdMoO_4 microspheres. A reduction in concentration of NaCl (e.g., 6 mol/L) could result in monodisperse solid CdMoO_4 microspheres (Figure 4a,b) while the other reaction conditions are kept the same. The microspheres obtained have a rough surface and range from 2 to 3 μm in diameter. In contrast to the sample obtained

at a NaCl concentration of 10 mol/L, no hollow interiors can be observed in the microspheres on the basis of the FESEM images. When the reaction is carried out at a relatively higher concentration of NaCl (e.g., 50 mol/L), floret-shaped particles with a size of around 2 μm are produced (Figure 4c,d) while the other reaction conditions are kept the same. Furthermore, when the experiment is carried out in the absence of NaCl and the other reaction conditions are kept the same, only near-spherical CdMoO_4 aggregates are obtained. A low-magnification FESEM image (Figure 4e) shows that irregular near-spherical CdMoO_4 aggregates with diameters of 300 nm to 1 μm are formed along with a few polyhedrons. The aggregates are composed of nanoparticles with an average diameter of 50 nm (Figure 4f). These results demonstrate that the surfactant-free, room temperature synthesis of hollow CdMoO_4 microspheres in the absence of organic agents and/or hard templates can be realized only if a suitable NaCl concentration is selected to accurately control the nucleation and growth process of hollow CdMoO_4 microspheres. Although the synthetic procedure is very simple, the effect of a certain range of concentration of NaCl on the formation of hollow CdMoO_4 microspheres seems to be quite complex. Our controlled experiments also indicate that the cooperation of Na^+ and Cl^- ions plays a crucial role in the formation of hollow CdMoO_4 microspheres. No hollow CdMoO_4 microspheres will be obtained if NaCl is substituted with NaNO_3 or KCl while the other reaction conditions are kept the same. Typically, in the substitution of NaCl with NaNO_3 , irregular particle aggregates are prepared (see the Supporting Information, Figure S2a,b), while CdMoO_4 nanorod bundles with hierarchical structures are obtained (see the Supporting Information, Figure S2c,d) when KCl is used instead of NaCl. On the basis of the above results, it appears to be the synergy of Na^+ and Cl^- ions that directs the growth of hollow CdMoO_4 microspheres.

It is well-known that the salt NaCl does not react with any compound in our reaction system, which is usually called a “spectator”. Previous literature demonstrates that the inorganic soluble salts can act as complexing agents in solution to affect the deposition rate of crystals.¹⁹ The deposition rate of CdMoO_4 could be reasonably adjusted in a certain range of the NaCl concentration because of the strong coordination of the most electronegative Cl^- anions to Cd^{2+} cations, which would be accompanied by heterogeneous nucleation, and thus, hollow CdMoO_4 microspheres are preferred.^{19,20} Several groups have investigated the effect of various inorganic soluble salts on the crystallization process of inorganic crystals. These studies demonstrate that the ionic strength, ζ potential of chemical species, chemical potential, viscosity of the solution, etc. can be significantly changed using these inorganic soluble salts, which would provide a suitable chemical environment for the growth of the desired crystals.^{19–21} Therefore, an appropriate concentration of NaCl may provide a suitable chemical environment to direct the specific nucleation and growth of hollow CdMoO_4 microspheres in the present reaction system, which will also be discussed below.

To further investigate the formation process of CdMoO_4 microspheres with hollow interiors, the intermediate products with different precipitation durations were studied in detail by FESEM observation. Figure 5 shows a series of typical intermediate morphologies corresponding to the growth process evolution of hollow CdMoO_4 microspheres. Figure 5a shows the FESEM image of CdMoO_4 microspheres produced by the reaction between Cd^{2+} and MoO_4^{2-} for 10 min under magnetic stirring without further placement. The obtained precipitation

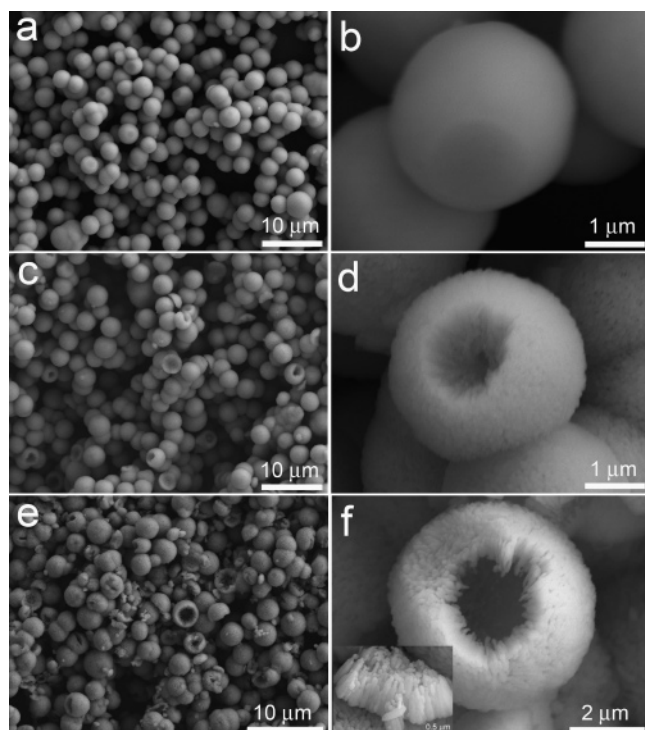


Figure 5. FESEM images showing the evolution process of CdMoO₄ microspheres obtained at different reaction periods: after 10 min (a, b), 12 h (c, d), and 72 h (e, f). Inset: a broken shell of CdMoO₄ microspheres.

is composed of large-scale, uniform microspheres with diameters of 3–5 μm . A high-magnification FESEM image (Figure 5b) exhibits that the microsphere is very round and perfectly smooth. When the reaction time reaches 12 h, the FESEM observation reveals that a number of hollow microspheres are found from the microspheres with an “open mouth” (Figure 5c). A high-magnification FESEM image (Figure 5d) shows that the peripheral surface becomes a little rough, which indicates that the constructed nanorods begin to form during this process. However, the interior is not completely hollow from the “open mouth” on the surface of the microsphere. When the reaction time increases to 72 h, almost all the obtained CdMoO₄ microspheres have hollow interiors and a puffy appearance composed of nanorods, as shown in Figure 5e. The hollow structure is completely formed, and the peripheral surface becomes quite rough (Figure 5f). The inset in Figure 4f shows a broken shell of CdMoO₄ microspheres 1 μm thick which is composed of orderly oriented nanorods. Meanwhile, from the XRD patterns of these samples (see the Supporting Information, Figure S3) corresponding to Figure 5, all diffraction peaks can be perfectly indexed to the tetragonal phase of CdMoO₄ (JCPDS 07-0209), which indicates that only phase-pure CdMoO₄ microspheres are prepared. The inset in Figure S3 is the (112) diffraction peak of the corresponding samples. It can be seen that the width of the diffraction peaks is gradually weakened with increasing reaction time, which suggests that the crystallinity is enhanced with increasing reaction time. On the basis of our results, it is clear that the continuous extension of reaction

time results in hollow microspheres with good crystallization composed of radially oriented nanorods.

For the formation mechanism of the hollow CdMoO₄ microspheres, it is clear that the growth process is neither surfactant-assisted nor template-directed, because no surfactants or templates were employed in the reaction system. Recently, Yang and Zeng^{1c,15b,22a} proposed the Ostwald ripening process model for the formation of hollow TiO₂ nanospheres, which was further verified in the formation of hollow Cu₂O and ZnS nanospheres.^{22b,c} Since a certain concentration of NaCl is indispensable for the formation of hollow CdMoO₄ microspheres, we presume that the formation mechanism of hollow CdMoO₄ microspheres might also be controlled by a NaCl-induced Ostwald ripening process. The possible formation mechanism of hollow spheres is shown by the schematic diagram in Figure 6. At the first stage, CdMoO₄ nuclei are initially formed via the reaction between Ca²⁺ and MoO₄²⁻ ions in the aqueous solution system (step 1). In the following process, the presence of suitable NaCl can behave as an electrolyte and thus modify the ζ potential of spherical CdMoO₄ species generated at the initial stage of the reaction (step 2).^{21b,23} The core–shell microspheres may therefore be created due to the subsequent precipitation of CdMoO₄ onto the NaCl-stabilized spherical CdMoO₄ (step 3), which is similar to core–shell TiO₂ structures with hollow interiors obtained with the assistance of (NH₄)₂-SO₄.^{21b} The core–shell structure of the microspheres is formed in this period, which could be demonstrated by FESEM observation of the morphology of a few intermediates of core–shell CdMoO₄ structures obtained at the reaction period of 72 h, as shown in Figure 7. The core is clearly observed (Figure 7a), and its surface is not smooth (Figure 7b). During this process, the particles of the inner core can be visualized as smaller spheres with higher curvature compared to the outer particles for a whole sphere. Owing to the higher surface energy, the core was easily dissolved and merged into particles in the outer surface with enough ripening time, resulting in the formation of a hollow microsphere structure, controlled by the Ostwald ripening mechanism (steps 4 and 5). On the basis of our results, a reduction or increase in concentration of NaCl or using other salts (NaNO₃ and KCl) might not give suitable inorganic salt-stabilized spherical CdMoO₄ structures, which would not result in a core–shell structure of CdMoO₄ microspheres (step 2), leading to nonhollow CdMoO₄ microspheres (step 2), leading to nonhollow CdMoO₄ microspheres. However, further investigation is needed to better understand the exact effect of NaCl and formation mechanism of hollow CdMoO₄ microspheres obtained only in a certain range of NaCl concentration.

Conclusions

In conclusion, we have developed a novel and convenient solution approach to hollow CdMoO₄ microspheres composed of radially oriented nanorods at room temperature. A certain concentration of NaCl plays a key role in the formation process of hollow microspheres, which might provide a suitable chemical environment to favor the formation of hollow CdMoO₄ microspheres. The formation of the hollow microspheres might be a NaCl-induced Ostwald ripening process. The CdMoO₄

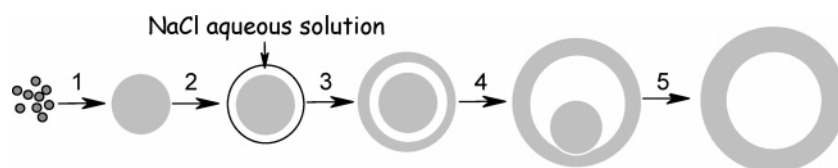


Figure 6. Scheme showing the formation process of CdMoO₄ hollow microspheres controlled by a NaCl-induced Ostwald ripening process.

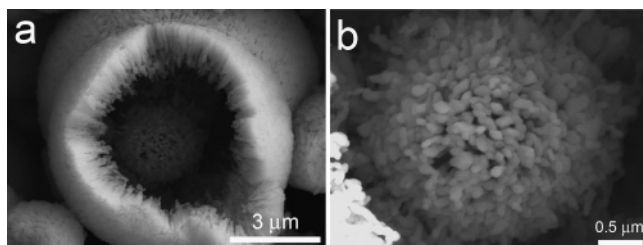


Figure 7. (a) Low-magnification FESEM images of the CdMoO₄ core-shell microspheres. (b) High-magnification FESEM image of the core. The sample was obtained at a reaction period of 72 h.

microspheres prepared using this method may find potential applications in the fabrication of optical devices and as material encapsulators or carriers. This method is very simple, mild, environmentally safe, and economical, and it may be general for other molybdate micro- or nanospheres with a hollow interior.

Supporting Information Available: EDS spectrum of hollow CdMoO₄ microspheres, SEM images of CdMoO₄ prepared using NaNO₃ and KCl instead of NaCl, and XRD patterns of CdMoO₄ obtained at different reaction periods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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