

General Sacrificial Template Method for the Synthesis of Cadmium Chalcogenide Hollow Structures

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Semiconductor CdX (X = Te, Se, S) hollow structures have been successfully prepared by using Cd(OH)Cl precursors as a sacrificial template. The hollow structures can be hollow spheres or tubes by controlling the shape of the sacrificial template. The products were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and energy-dispersive spectrometry. The obtained results showed that the hollow structures had complementary shapes and sizes of the original sacrificial templates. This is a general method for the synthesis of cadmium chalcogenide hollow structures, and the method is simpler and more practical than direct synthesis of certain hollow structures, which further widens the avenue to using those materials that have been synthesized with various shapes to fabricate specific hollow structures.

1. Introduction

In recent years, there has been growing interest in the fabrication of hollow structured nanomaterials, especially hollow spheres and nanotubes, owing to their important applications in catalysis, sensors, controlled release, and electronic and optic devices.^{1–3} In addition to the commonly used hard template method,^{4–7} many techniques such as interface assembly,⁸ the Ostwald ripening process,⁹ and sonochemical methods¹⁰ are being developed to prepare

different kinds of hollow structures. In the case of nanotubes, nanotubes of many compounds, such as polymers, metals, nonmetals, oxides, and sulfides, have been synthesized with various methods.^{11–15} The vapor deposition method is generally used to prepare carbon nanotubes. The template method provides a straightforward synthesis route, and materials with channel structures, such as mesoporous silica,¹⁶ a porous polymer film,¹⁷ and an anodic aluminum oxide membrane,¹⁸ can serve as the templates. The size and morphology of nanotubes can be controlled by changing the channel structures of templates. Nontemplate methods, such as the hydrothermal method,¹⁴ thermal decomposition,¹⁵ sol–gel methods,¹⁹ are also used in the fabrication of nanotubes and show great promise in the large-scale synthesis of nanotubes.

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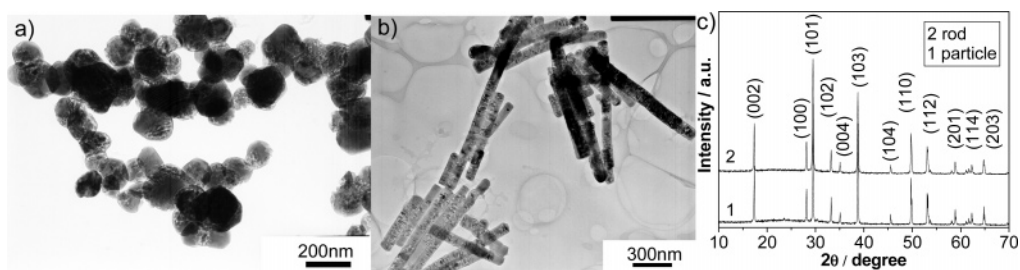
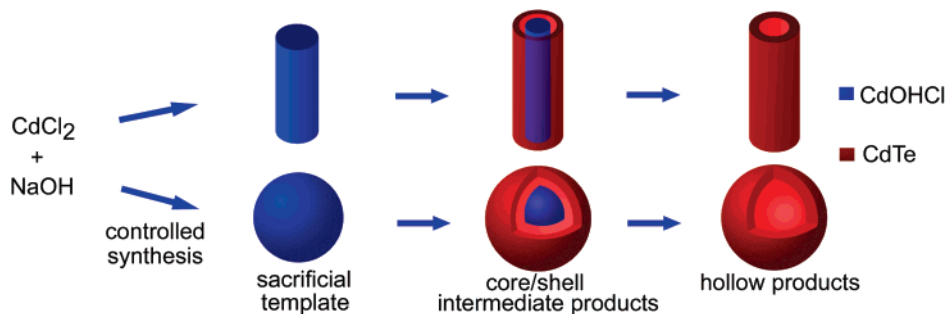


Figure 1. TEM images (a and b) and the XRD pattern (c) of the as-prepared Cd(OH)Cl nanoparticles and nanorods.

Scheme 1. Fabrication of the CdTe Nanotubes and Hollow Spheres via a Sacrificial Template Method



Among all of the methods mentioned above, a promising sacrificial template method interested us very much.^{20–23} During the reaction, the resultant shell forms around the surface of the sacrificial template and takes the shape of the template. At the same time, the sacrificial template is gradually consumed to form the hollow interior. Such a process endues the method with many advantages. First, template removal can be avoided, which can prevent possible damage to the produced shell. Second, the method is very simple, usually carried out in a stirring aqueous solution or a hydrothermal system and shows good generality. A series of noble metal and semiconductor nanotubes and hollow spheres were prepared by using this method.

In the present work, we further developed the sacrificial template method. Taking advantage of the fact that the products take the shapes of the templates, we can get final hollow structures with desired shapes by controlling the shapes of the templates, which is simpler and more practical than directly synthesizing the hollow structures. Cadmium chalcogenides (CdE; E = S, Se, Te) are one of the most important semiconductors with excellent tunable optical properties. They have been extensively studied in the fields of solar cells, photoelectronic devices, catalysis, and sensors.²⁴ So, we tried to synthesize cadmium chalcogenide hollow structures. We successfully synthesized CdTe hollow spheres and nanotubes by controlling the sacrificial template shape. The synthesis procedure is shown in Scheme 1. Like CdTe hollow structures, CdS and CdSe hollow spheres and nanotubes were also prepared with the same procedures. This

general method may be further used to fabricate other specific hollow structures.

2. Experimental Section

2.1. Materials. All of the reagents were of analytical purity and were used without further purification. CdCl₂·2.5H₂O, NaOH, Na₂SO₃ gelatin, and thioacetamide (TAA) were purchased from Shanghai Chemical Reagent Factory (China). NaBH₄ was purchased from Tianjin Chemical Reagent Factory. Poly(vinylpyrrolidone) (PVP) was purchased from HuaKang Chemical Reagent Factory. A Na₂SeSO₃ solution used as the selenium resource was synthesized by refluxing selenium powders (from Aldrich) in a sodium sulfite solution. A NaHTe solution used as the tellurium resource was synthesized by reacting tellurium powders (from Aldrich) in a sodium borohydride solution.

2.2. Synthesis of Cd(OH)Cl Precursors and CdX (X = S, Se, Te) Hollow Structures. For the synthesis of Cd(OH)Cl precursors, NaOH (1 g, 0.25 mol) and CdCl₂·2.5H₂O (5.7 g, 0.25 mol) were added into 3% gelatin or a PVP aqueous solution (30 mL), respectively. Then the NaOH solution was added into the CdCl₂ solution dropwise under stirring. The obtained white precipitation was aged at 90 °C overnight, filtered, washed with distilled water, and dried in a vacuum.

For the synthesis of CdTe hollow structures, the as-prepared Cd(OH)Cl precursors (0.5 g) were added into a 0.1 M NaHTe solution (30 mL) in a round-bottomed flask, and the reaction was carried out for 15 min in dinitrogen gas protection under sonication. After the reaction was finished, dark-brown precipitates were obtained. The precipitates were centrifuged, washed sequentially with distilled water and acetone, and then dried in air. For the synthesis of CdS and CdSe hollow structures, 0.1M TAA and Na₂SeSO₃ were used in the reaction in place of NaHTe, while other conditions were the same as those in the preparation of the CdTe hollow structures.

2.3. Characterization. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3 X-ray diffractometer (Cu K α radiation, $\lambda = 0.15418$ nm). The transmission electron microscopy (TEM) measurements were carried out on a JEOL JEM-200CX transmission electron microscope using an accelerating voltage of

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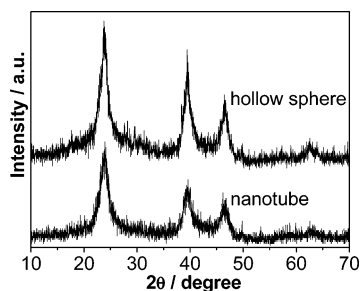


Figure 2. XRD patterns of the as-prepared CdTe products.

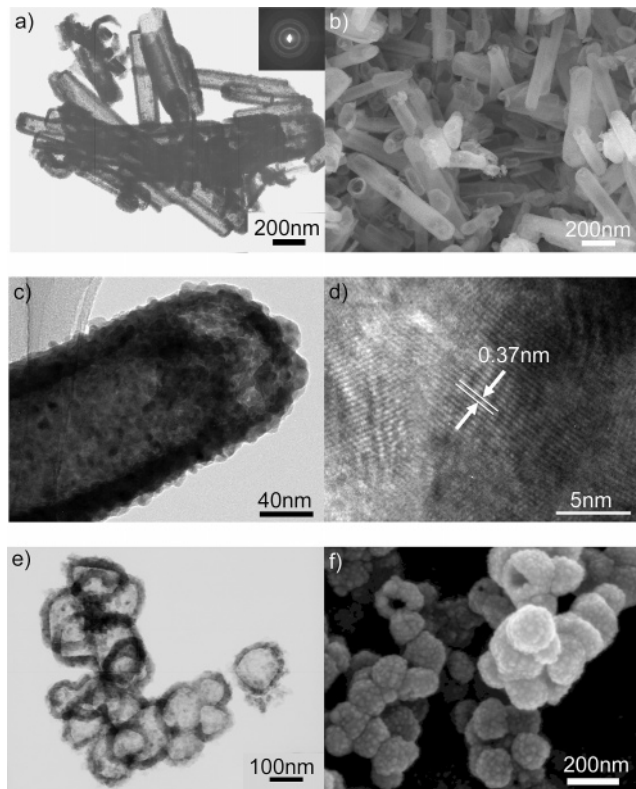


Figure 3. TEM and SEM images of the CdTe nanotubes (a and b) and hollow spheres (e and f) and HRTEM images (c and d) of a single CdTe nanotube.

200 kV. The samples used for TEM were prepared by dispersing the products in ethanol and then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. High-resolution transmission electron microscopy (HRTEM) micrographs were obtained by employing a JEOL-2010 high-resolution transmission electron microscope with a 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were taken on a LEO-1530VP scanning electron microscope.

3. Results and Discussion

3.1. Cd(OH)Cl Sacrificial Templates. Figure 1 shows the Cd(OH)Cl sacrificial templates with different morphologies. When gelatin was used as a soft template, Cd(OH)Cl nanospheres (Figure 1a) were formed. The particles have quasi-spherical structures with an average diameter of about 100 nm. However, when PVP was selected as a soft template, the as-prepared Cd(OH)Cl showed a rodlike structure, as shown in Figure 1b, with a uniform diameter of about 90 nm and lengths from 500 to 1500 nm. XRD patterns (Figure 1c) indicated that both of the products were pure hexagonal-

Ele.	Wt. %	At. %
C K	4.71	33.05
Cd L	44.55	33.42
Te L	50.74	33.53

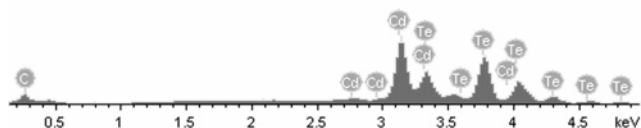


Figure 4. EDS analysis of CdTe nanotubes.

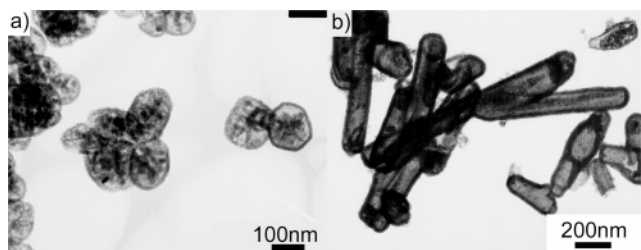


Figure 5. TEM image of typical intermediate products of CdTe hollow spheres (a) and nanotubes (b).

phase Cd(OH)Cl (JCPDS 74-1047). Recently, a soft template has been widely used in the controlled synthesis of various nanomaterials. PVP is an often-used template-directing agent. It has excellent effects on anisotropic growth and has been used in the preparation of one-dimensional nanostructures such as tellurium and selenium nanorods and silver, gold, and lead nanowires.²⁵ We have prepared the Cd(OH)Cl nanorods with a diameter of about 110 nm without any soft template in previous work.²⁶ However, when PVP was used, the diameter of the obtained nanorods decreased to about 90 nm and more uniform products were obtained. Different from the template-directing effect of PVP, gelatin is known for its good adsorption properties on various surfaces.^{27–30} It is an amphoteric polyelectrolyte consisting of amino acid groups. The abundant amino and carboxyl groups would strongly adsorb on the nascent Cd(OH)Cl particles, which prevented their anisotropic growth; as a result, only quasi-spherical nanostructures could be observed.

3.2. CdTe Hollow Structures. The CdTe hollow structures were prepared by reacting the Cd(OH)Cl template with the tellurium source. Figure 2 shows the XRD patterns of the as-prepared CdTe products. All of the diffraction peaks match well with the cubic-phase CdTe (JCPDS 75-2086). No Cd(OH)Cl diffraction peaks were detected in the pattern, indicating that the Cd(OH)Cl precursors had been completely converted into CdTe. The apparently broadening peaks indicated that both of the products were composed of small crystalline particles. The average crystal sizes are estimated to be about 4.6 nm according to the Debye–Scherrer formula.³¹

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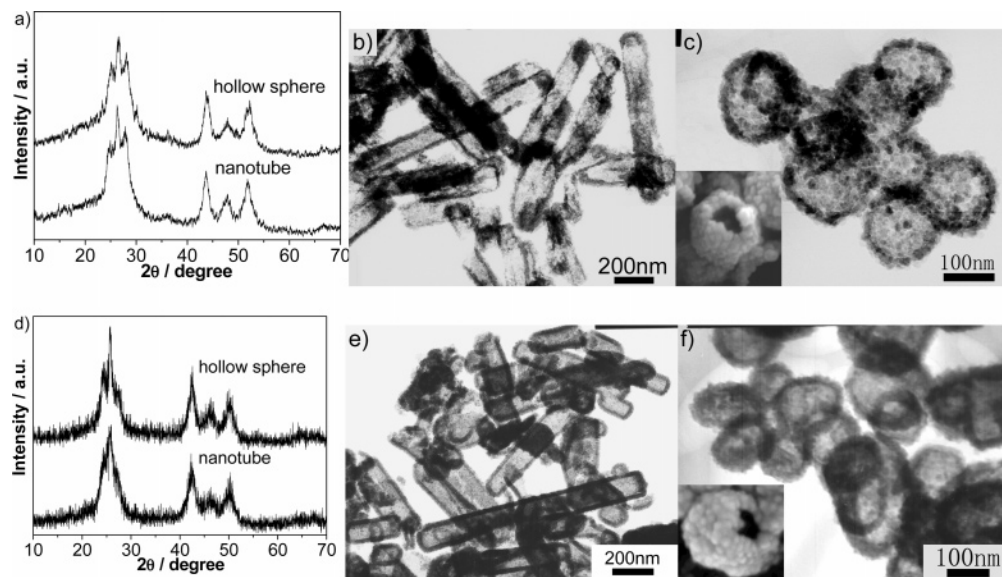


Figure 6. XRD pattern and TEM images of hollow products of CdS (a–c) and CdSe (d–f).

The morphologies of the as-prepared CdTe converted from the Cd(OH)Cl template are shown in Figure 3. Figure 3a is a TEM image of the CdTe nanotubes with external diameters of about 130 nm. The lengths of the nanotubes are in the range of 400–1000 nm, which is similar to those of the Cd(OH)Cl nanorods. A selected area electron diffraction (SAED) image of a nanotube (inset in Figure 3a) shows a set of diffraction rings, which correspond to the cubic phase of CdTe with polycrystalline nature. The SEM image (Figure 3b) shows a three-dimensional image of the nanotubes. It also shows that the products are almost tubes with both ends closed, and open ends of some broken tubes caused by sonication can be clearly observed. An energy-dispersive spectrometry (EDS) analysis was performed for the CdTe nanotubes, as is shown in Figure 4. Only cadmium and tellurium elements were detected (carbon comes from the electric conductive adhesive used to immobilize the sample powder), and their atom ratio was 1:1, which is in agreement with the chemical composition of CdTe. The HRTEM investigation (Figure 3c) provides further information about the microstructure of the nanotubes. As can be clearly seen, the wall is composed of very small particles with sizes of 4–6 nm, which is consistent with XRD and SAED results. The wall thickness is about 20 nm, and the internal diameter is about 90 nm, which is in accordance with the diameters of the Cd(OH)Cl nanorods. A higher resolution image (Figure 3d) shows that the tube wall is well crystallized and exhibits a clear lattice fringe with a d spacing of 0.37 nm, corresponding to the (111) reflection of the cubic CdTe structure.

When the Cd(OH)Cl quasi-spherical structures were used as a sacrificial template, CdTe hollow spheres were obtained, as shown in Figure 3e. The average diameters of the spheres are about 140 nm. SEM images (Figure 3f) show that the hollow spheres are also quasi-spherical, much like the shape of the Cd(OH)Cl nanoparticles, and it can be clearly seen that the shells are also composed of numerous small particles.

Some intermediate products with reaction times of 1 min could be obtained so as to study the formation process of the hollow structures. Figure 5 shows the typical intermediate products of the CdTe hollow spheres and the nanotubes. XRD results indicated that they still contained unreacted Cd(OH)Cl. The TEM image (Figure 5a) shows that a shell is formed around each Cd(OH)Cl nanoparticle. Hollow interiors (the low-contrast part) can be observed between the shell and the inner part, just like the core/shell intermediate structure in Scheme 1. In Figure 5b, such a core/shell structure is much clearer. The unreacted Cd(OH)Cl wires can be observed in the center of the CdTe tubes. These intermediate structures and the complementary shapes and sizes of the CdTe hollow structures with the corresponding Cd(OH)Cl precursors effectively proved that all of the hollow spheres and nanotubes are fabricated following the procedure shown in Scheme 1. The detailed formation procedure may be described as follows: when the tellurium source (NaHTe) was added into the solution, Te^{2-} ions were released. The Te^{2-} ions reacted with Cd(OH)Cl on the surface of the template to form CdTe nuclei because CdTe had a smaller K_{sp} value than Cd(OH)Cl.³² As the reaction continued, Cd(OH)Cl was consumed gradually and the formed CdTe nuclei grew into CdTe nanoparticles. The CdTe nanoparticles further aggregated to form CdTe shells. Finally, when the Cd(OH)Cl templates were completely consumed, CdTe hollow structures (nanotubes or hollow spheres) were obtained.

3.3. Synthesis of CdS and CdSe Hollow Structures.

Following similar procedures, the CdS and CdSe nanotubes and hollow spheres were also successfully prepared. XRD patterns shown in parts a and d of Figure 6 indicate that all diffraction peaks match well with the hexagonal-phase CdS and CdSe, respectively. The peaks are all broadened,

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indicating that the shells of the tubes and spheres are all composed of small particles. TEM and SEM images shown in parts b, c, e, and f of Figure 6 indicate that the nanotubes and hollow spheres of CdS and CdSe have the same sizes and morphologies as those of CdTe because of the same precursors used in the experiments.

In summary, a general sacrificial template method has been proposed to fabricate cadmium chalcogenide hollow structures. With this method, the CdTe, CdSe, and CdS hollow spheres and nanotubes have been successfully synthesized from Cd(OH)Cl precursors with corresponding morphologies.

This general method might have further applications in the synthesis of other hollow structures.

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