

Sacrificial template growth of CdS nanotubes from Cd(OH)₂ nanowires

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Abstract

A diffusion-controlled process was proposed for the preparation of inorganic nanotubes from nanowires. The preformed Cd(OH)₂ nanowires were used as the sacrificial templates to generate CdS nanotubes with different wall thickness. The axle-sleeve transition state found in-between the precursor and the formation of products proves the diffusion-controlled mechanism. CdS nanotubes can be prepared via this method at different temperature and with various sulfide sources. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) results showed that all obtained CdS nanotubes consist conglomerated crystallites, and the crystallinity can be altered by changing the temperature of the growth process. The wall thickness of the produced CdS nanotubes can be controlled by changing the concentration of the sulfide source and stopping the reaction at different stages.

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1. Introduction

Inorganic nanostructures with hollow interiors have attracted much attention because of their superior physical properties and potential applications in the fields of catalysis, drug delivery, sensor, lubricants, fuel cell, electronics and photonics [1–8]. Nanoparticle nanotubes is one type of nanotubes, whose tube walls are composed of nanoparticles. These nanomaterials possess high surface area and have many applications, especially in catalysis, sensor and nanodevices [7,8]. In this work, we present the synthesis of CdS nanoparticle nanotubes using a template method. We have been able to obtain CdS nanotubes of different diameter and different wall thickness.

Template method is an effective and simple strategy to obtain nanostructures of various morphologies. The templates used involve soft templates [9–14], which generally refer to surfactant assemblies, and hard ones [15–20], which are normally solid materials with designed morphologies. Most of the hard-template approaches of nanostructures with hollow interiors include two steps.

First, nanostructures made of the desired materials or precursors grow or/and assemble on or around the surface of a template via chemical or physical adherence to form transitional composites. And then, the templates are selectively removed from the composite structures. If the template is converted entirely to the desired materials, the method is called sacrificial template method [21–24]. Up to now, only a few nanomaterials with hollow interiors have been synthesized via sacrificial template method. Zhu et al. have obtained hollow spherical structure of CdSe sonchemically via an in-situ templated route from amorphous Cd(OH)₂, in which it was ultrasonic irradiation that makes the CdSe at Cd(OH)₂ balls change to hollow sphere [25]. However, most of the formation processes are considered as diffusion-controlled mode. Tenne and co-workers have prepared hollow WS₂ nanoparticles using WO₃ nanoparticles and the formation process is diffusion-controlled, in which sulfur diffuses in and oxygen diffuses out of the cores of the WO₃ nanoparticles [26]. Sun et al. have demonstrated a galvanic replacement reaction to prepare nanostructured gold with pinholes in the walls by using preformed silver nanostructures as the templates, where diffusion plays an essential role [21,27–29]. Very recently, Yin et al. have synthesized hollow nanocrystals through a

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mechanism analogous to the Kirkendall effect, in which pores form because of the difference in diffusion rates between two components in a diffusion couple [30]. They also pointed out that spherical symmetry is not required for obtaining shells of regular thickness. Most of the reported processes are focused on nanospheres with hollow interior, and till now, except noble metals (e.g. gold) [21,27–29], little research is about the formation of other morphologies such as tubes by diffusion process.

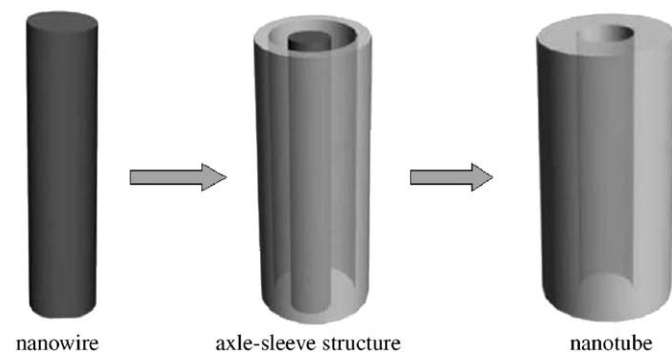
Nanomaterials of II–VI group semiconductors are of particular interest for their important optical, optoelectronic and catalytic properties. Hollow structures, such as tubular materials, are favorable for enhancing the properties. The idea of preparing semiconductor nanotubes by nanowires as sacrificial templates in solution via a diffusion process is illustrated in Scheme 1. We chose CdS as a very convenient example to test this idea because CdS is very competent for this role because the morphology-controlled synthesis of CdS nanomaterials has been intensively studied, [11,31–46] yet none of them was via diffusion-controlled templated route.

2. Experimental

Cadmium acetate hydrate (>99.5%, AR), thioacetamide (TAA) (>98%, AR), and other chemicals are of analytical grade and were used without additional purification. All chemicals are from Beijing Chemical Corp.

Cd(OH)₂ nanowires were obtained by hydrolysis of cadmium acetate hydrate. A typical synthesis was carried out as follows. Cadmium acetate hydrate (1.80 g) was added to the mixed solvent of 24 mL distilled water and 16 mL ethanol and then poured into a stainless Teflon-lined 50-mL-capacity autoclave while passing a stream of Nitrogen gas through the mixture. The autoclave was maintained at 150 °C for 27 h, and air cooled to room temperature. The products were collected and washed with distilled water and ethanol, then dried in N₂.

The CdS nanotubes were synthesized using as-prepared Cd(OH)₂ nanowires as the precursor materials. Several methods were used to synthesize CdS nanotubes. The typical reaction conditions were listed below.



Scheme 1. Schematic illustration of nanotube formation via nanowire.

2.1. Normal solution method

As-prepared Cd(OH)₂ nanowires were washed with distilled water and ethanol, then re-dispersed in ethanol. Excessive TAA was added into the mixture and the solution was kept for 5 h at room temperature or for 24 h at 5 °C. The products were collected and washed with distilled water and ethanol.

2.2. Solvothermal method

As-prepared Cd(OH)₂ nanowires were washed with distilled water and ethanol, then re-dispersed in ethanol. Excessive TAA was added into the mixture and the solution was poured into a Teflon-lined stainless autoclave. The autoclave was maintained at 150 °C for 5 h, and air cooled to room temperature.

2.3. Two-phase solvothermal method

As-prepared Cd(OH)₂ nanowires were washed with distilled water and ethanol, and re-dispersed in ethanol. Then CS₂ (the molar ratio of CS₂ and Cd(OH)₂ is approximately 1:10) dissolved in cyclohexane was added. The reaction mixture was first kept at 65 °C for 5 h, then poured into a stainless Teflon-lined autoclave and maintained at 150 °C for 4 h. After that, air cooled to room temperature. The products were washed with acetic acid, distilled water and ethanol, respectively.

The X-ray diffraction (XRD) analysis was performed using a Rigaku D/max Diffractometer with CuK α irradiation ($\lambda = 0.15418$ nm). The XRD patterns with diffraction intensity versus 2θ were recorded from 10° to 80° at a scanning rate of 8° min⁻¹. X-ray tube voltage and current were set at 40 kV and 100 mA, respectively. The transmission electron microscopy (TEM) images were obtained by a JEOL 200-CX Electron Microscope operated at 120 kV. The high-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns were taken using a Hitachi-9000 Electron Microscope operated at 100 kV. The specimen for TEM imaging was prepared by suspending the powder sample in ethanol and sonicating for 2 min then drop-dry on the copper grids. Luminescence experiments were carried out at room temperature on a Hitachi F-4500 fluorescence spectrometer with a Xe lamp.

3. Results and discussion

3.1. The preparation of Cd(OH)₂ nanowires

Cd(OH)₂ nanowires were obtained through a hydrolysis process. The TEM (Fig. 1a) image shows that the Cd(OH)₂ nanowires have diameters of 30–100 nm. All of the diffraction peaks of the XRD pattern (Fig. 1b) can be readily indexed to hexagonal Cd(OH)₂ (JCPDS 31-0228). The abnormal high intensity of the (001) peak (as compared to the standard file)

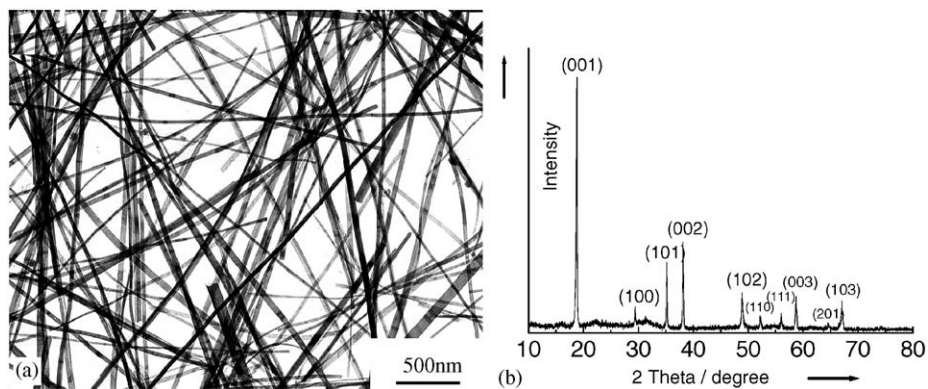


Fig. 1. Typical TEM image of the as-prepared $\text{Cd}(\text{OH})_2$ nanowires (a) and the corresponding XRD pattern (b).

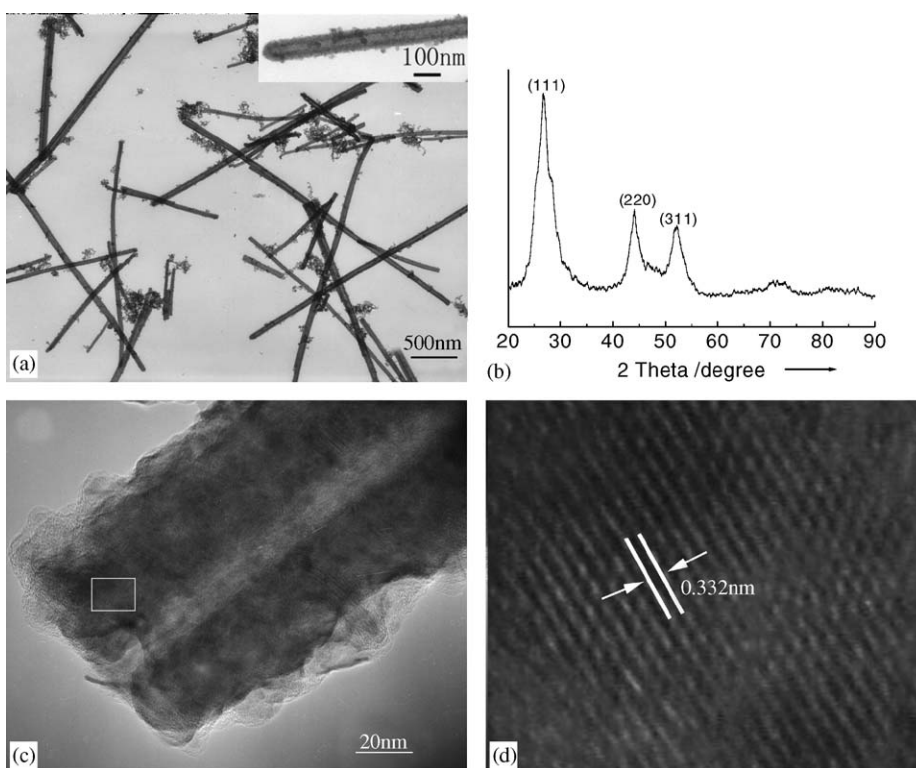
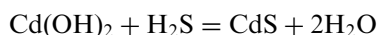


Fig. 2. TEM image (a), XRD pattern (b) and HRTEM image (c) and (d), (d) is a magnified image of the area marked in (c) of CdS nanotubes obtained via $\text{Cd}(\text{OH})_2$ nanowires at room temperature by thioacetamide. The tubes are with the outer diameters of 50–120 nm and inner diameters of 10–40 nm.

indicates that these $\text{Cd}(\text{OH})_2$ nanowires grow preferentially along the c -axis, i.e. the [001] direction.

3.2. Preparation of CdS nanotubes under ambient condition

Using the as-prepared $\text{Cd}(\text{OH})_2$ nanowires as templates, we synthesized CdS nanotubes at room temperature. In this reaction, TAA was used as the source of S^{2-} . The chemical reactions taking place are as follows:



A typical TEM image (Fig. 2a) of the CdS nanotubes shows that the nanotubes are composed of nanoparticles and the outer diameters of the tubes are 30–120 nm, inner diameters are 10–40 nm, and the lengths are smaller than those of the $\text{Cd}(\text{OH})_2$ nanowire precursors. It is also found that the outer diameter of CdS nanotubes are larger than the diameter of $\text{Cd}(\text{OH})_2$ nanowires. The measured cross-sectional area of $\text{Cd}(\text{OH})_2$ nanowires is $1.2\text{--}7.8 \times 10^3 \text{ nm}^2$ and those of the CdS nanotubes are $0.9\text{--}5.6 \times 10^3 \text{ nm}^2$. If we assumed that every $\text{Cd}(\text{OH})_2$ nanowire was transformed thoroughly into a CdS nanotube of the same length, the calculated cross-sectional area of the nanotube should be

$1.2\text{--}7.6 \times 10^3 \text{ nm}^2$, which is a little larger than the measured result. Considering the consumption during the reaction process, this result is reasonable if the $\text{Cd}(\text{OH})_2$ nanowires acted as the sacrificial templates for the formation of the CdS nanotubes.

All of the peaks in the XRD pattern of the CdS nanotubes (Fig. 2b) can be readily indexed to cubic CdS (JCPDS 80-0019). Although some intense peaks of the hexagonal phase may present at the same d values, no unique peaks of hexagonal phase, such as (100) at $2\theta = 26.9^\circ$ ($d = 3.57 \text{ \AA}$) and (101) at $2\theta = 28.33^\circ$ ($d = 3.15 \text{ \AA}$), are found in the CdS diffraction pattern, indicating the absence of hexagonal phase. The high-HRTEM images show that the CdS nanotubes are composed of nanoparticles (Fig. 2c), and the fringe spacing in Fig. 2d is 0.33 nm , which is very close to the (111) lattice spacing of cubic CdS.

The structural and morphological changes involved in the sacrificial template reaction of $\text{Cd}(\text{OH})_2$ are further illustrated by TEM images taken at different stages during the reaction (Fig. 3). First, Cd^{2+} dissociated from $\text{Cd}(\text{OH})_2$ reacts with S^{2-} released from TAA and form $\text{Cd}(\text{OH})_2$ at CdS axle-sleeve (of a bearing) structures, and then CdS nanotubes are obtained when all $\text{Cd}(\text{OH})_2$ is converted into CdS. The XRD patterns of the sample at the intermediate stage shown in Fig. 3 proved the coexistence of CdS and $\text{Cd}(\text{OH})_2$. This experimental result is well consistent with the mechanism shown in Scheme 1.

3.3. Preparation of CdS nanotubes at diverse temperatures

Temperature should be a very delicate parameter in the process. The decomposition of TAA to give off H_2S [8g] and ulteriorly S^{2-} , the solubility of $\text{Cd}(\text{OH})_2$, the diffusion of Cd^{2+} and eventually the formation of CdS are all temperature dependent. Therefore, temperature will greatly influence the morphology of the final products. When we performed the above templated synthesis at a lower temperature of 5°C , CdS nanotubes with continuous tube walls were obtained as shown in Fig. 4. The SAED patterns are in good agreement with the (111), (220) and (311) planes of cubic CdS.

When we performed the synthesis at 150°C under a solvothermal condition, nanotubes and nanoparticles were obtained as shown in Fig. 5a. It seems that the tube walls are composed of nanoparticles. All of the XRD peaks of the products (Fig. 5b) can be indexed to cubic and hexagonal CdS (JCPDS 80-0019 and 80-0006). Some intense peaks of the hexagonal phase such as (100) at $2\theta = 26.9^\circ$ ($d = 3.57 \text{ \AA}$) and (101) at $2\theta = 28.33^\circ$ ($d = 3.15 \text{ \AA}$), and some characteristic peak of cubic phase, such as (220) at $2\theta = 30.75^\circ$ ($d = 2.90 \text{ \AA}$), were found, indicating the coexistence of hexagonal and cubic phase of CdS in the products.

We also tried the synthesis at moderately high temperatures, such as 70°C , but no tubes can be obtained. These results show that temperature is a very important factor for the formation of tubular structure.

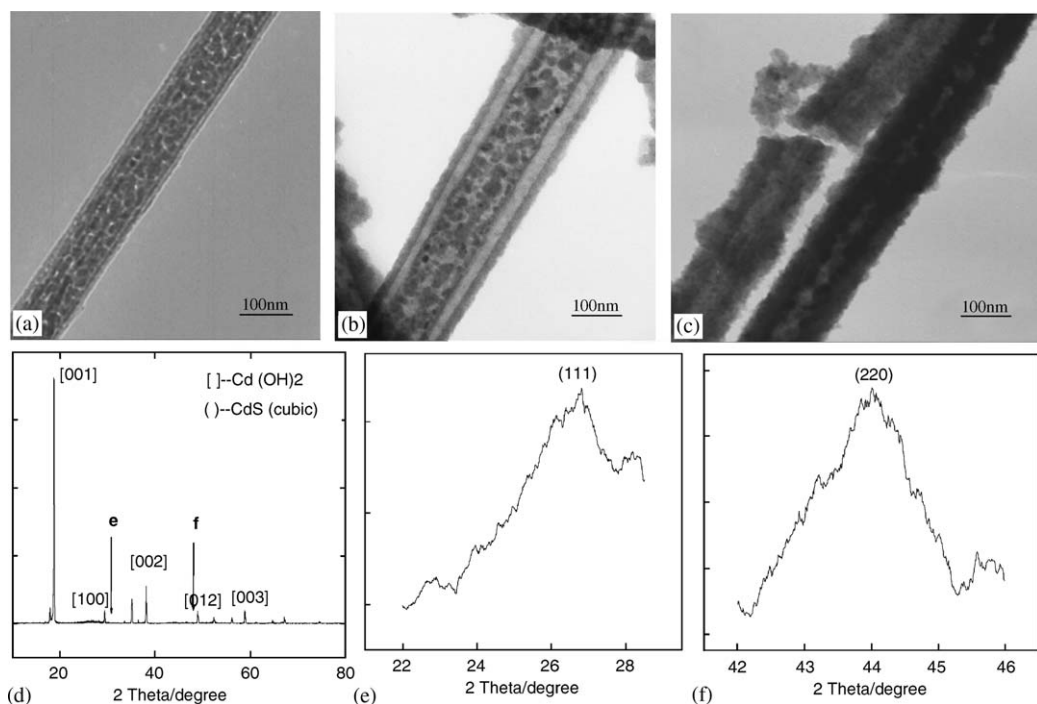


Fig. 3. TEM images at different stages during the formation of CdS nanotubes at room temperature and the XRD patterns of the intermediate CdS at $\text{Cd}(\text{OH})_2$. (a–c) are the TEM images of as-prepared $\text{Cd}(\text{OH})_2$ nanowires, intermediate CdS at $\text{Cd}(\text{OH})_2$ axle-sleeve structures and the CdS nanotube products, respectively; (d) is the XRD pattern of the intermediate species, and the corresponding magnified parts are shown in (e and f).

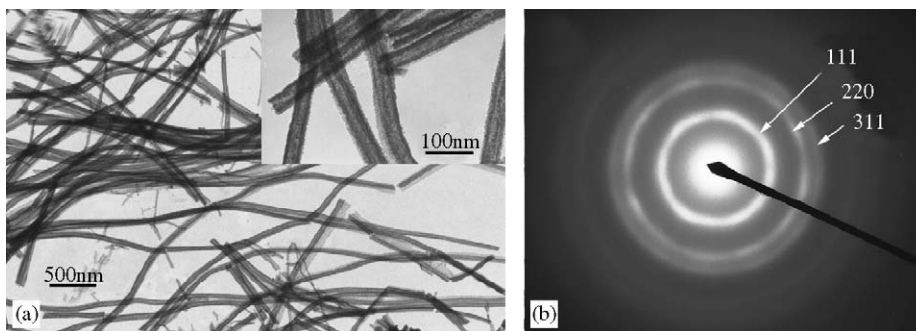


Fig. 4. TEM image (a), ED pattern (b) of CdS nanotubes obtained via $\text{Cd}(\text{OH})_2$ nanowires at 5°C .

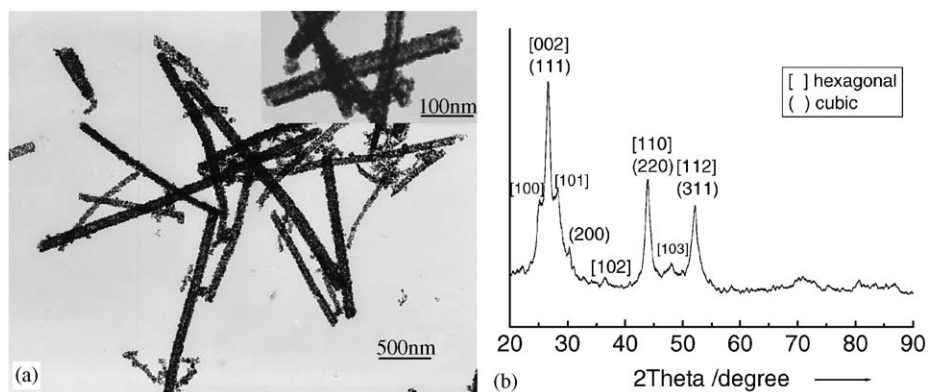


Fig. 5. The TEM image (a) and the XRD pattern (b) of the CdS nanotubes obtained through solvothermal method with thioacetamide as sulfide source.

3.4. Preparation of CdS nanotubes with insufficient sulfide source

We have shown that preformed $\text{Cd}(\text{OH})_2$ nanowires can act as good sacrificial templates for the synthesis of CdS nanotubes. However, the CdS nanotubes obtained from the two aforementioned methods have very small inner diameters. It is desirable to be able to synthesize CdS nanotubes with larger inner diameter which possesses larger specific surface area. To achieve this goal, we proposed a third synthesis route based on the following assumption: when the sulfide source was insufficient and supplied in one phase, the $\text{Cd}(\text{OH})_2$ nanowire dispersed in another phase could only be partially transformed into CdS. If we then eliminate the unreacted $\text{Cd}(\text{OH})_2$ with acetic acid, CdS nanotubes with larger inner diameter and thinner tube walls would form. To implement this two-phase synthesis route, we used water and cyclohexane as the two solvents, $\text{Cd}(\text{OH})_2$ as the Cd^{2+} source and CS_2 in cyclohexane as the S^{2-} source. The TEM image of the resulting CdS nanotubes shows that the boundaries of the walls of the CdS nanotubes are well defined (Fig. 6a). The electron diffraction (ED) result (Fig. 6b) shows that the structure of the CdS nanotubes is close to a single crystal. The high resolution TEM image (Fig. 6c) indicates that the nanotube is composed of nanoparticles and the locally magnified image (Fig. 6d) reveals that the fringe

spacing is 0.36 nm, which is very close to that of the (100) layers of hexagonal CdS. These results show that by adjusting the ratio of sulfide and cadmium sources, the inner diameter and wall thickness can be varied, and the reaction condition of insufficient sulfide source may be beneficial to the crystallization of CdS.

3.5. Photoluminescence spectra of CdS nanotubes from different methods

The photoluminescence spectra of the CdS nanotube samples all show two bands which are very typical to CdS nanomaterials (Fig. 7) [47,48]. The band around 470 nm is from the band-gap emission of CdS nanoparticles, and the broad PL peak centered between 560 and 570 nm is commonly attributed to the recombination of the charge carriers within the surface states. The latter is strongly related to the defects especially the defects in the grain surface, so sometimes it is called “defect emission”. It can be clearly seen that the intensity of the defect emission decreases from a to c. This indicates that from a to c, the concentration of the defects decreases and the degree of the crystallization increases. When the preparation is performed under room temperature, lots of defects are present in the products, therefore the defect emission of Sample a is very high. And it is known that the products will get further crystallized with the increasing of reaction temperature and

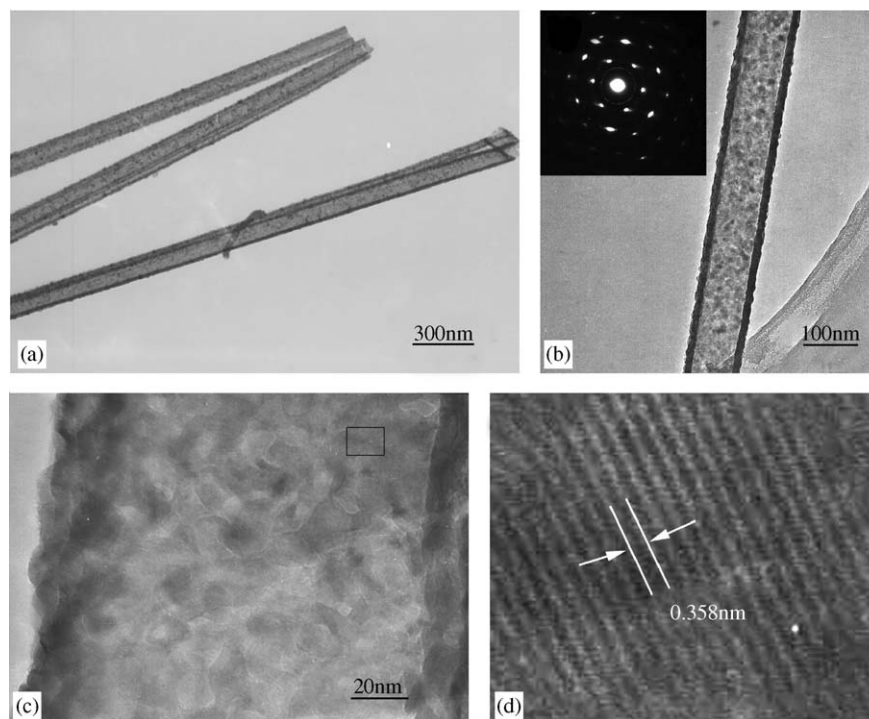


Fig. 6. The TEM (a and b) and HRTEM images (c and d) of the CdS nanotubes prepared by two-phase method. The inset in (b) is the corresponding electron diffraction pattern, (d) is the magnified image of the marked area in (c).

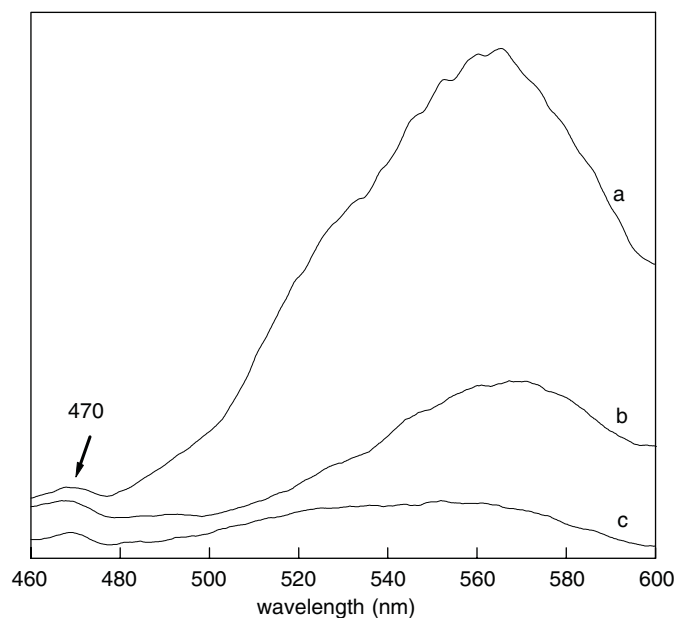


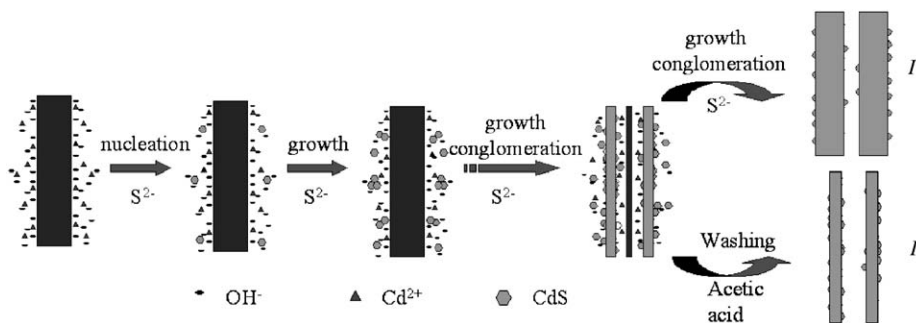
Fig. 7. Photoluminescence spectra of CdS nanotubes obtained by Cd(OH)₂ nanowires at different conditions. (a) At room temperature also with thioacetamide as the excess sulfide source; (b) by solvothermal method with thioacetamide as the excess sulfide source; (c) by two-phase solvothermal method with CS₂ as the deficient sulfide source.

the prolonging of the reaction time, hence the defect emissions of Samples b and c, which were obtained at higher temperature, are decreased. And the weakest defect emission of Sample c indicates its highest crystallization degree, which is in good accordance with what we have observed in the aforementioned structure characterization.

From the experimental results, we draw the outline of the process of converting Cd(OH)₂ nanowires to CdS nanotubes (Scheme 2). First, S²⁻ ions react with Cd²⁺ ions in the solution and aggregate nearby the surface of Cd(OH)₂ nanowires to form CdS nuclei. As the Cd²⁺ ions are consumed to form CdS, the concentration of Cd²⁺ near the CdS nuclei is decreased. Therefore, more Cd²⁺ ions are released from the Cd(OH)₂ nanowires and diffuse out, subsequently, more CdS will be formed and the CdS nuclei will grow into CdS nanoparticles. Then the CdS nanoparticles further aggregate to form CdS nanotubes. During this process, the concentration gradient of the Cd²⁺ ions between the core and the surrounding provides a great driving force for the outward diffusion of the Cd²⁺ ions [10]. Finally, CdS nanotubes composed of CdS nanoparticles are formed until the Cd(OH)₂ nanowires are completely consumed. The fact that the diameters of CdS nanotubes are larger than the diameters of Cd(OH)₂ nanowires supports the presumption that the formation of CdS nanotubes is through a diffusion-controlled mechanism. If we stop the reaction before the Cd(OH)₂ nanowires are consumed up and remove the residue Cd(OH)₂ with acetic acid, CdS nanotubes with thinner wall can be obtained.

4. Conclusion

CdS nanoparticle nanotubes have been synthesized using as-prepared Cd(OH)₂ nanowires as the precursor materials. By adjusting the ratio of the sulfide source and Cd(OH)₂, the CdS nanotubes with different wall thickness can be



Scheme 2. The mechanism of the preparation of CdS nanotube via preformed Cd(OH)₂ nanowire.

obtained. The crystal structure of the CdS nanotubes can be controlled by changing the reaction conditions (e.g. temperature). The formation mechanism of CdS nanotubes is based on a template-directed and diffusion-controlled pathway. This method has the potential to synthesize other functional nanomaterials with hollow interiors.

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