



Sacrificial template method for the synthesis of CdS nanosponges and their photocatalytic properties

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ABSTRACT

Using corresponding metal elemental nanowires as a self-sacrificed template, large-scale nanosponges consisted of curving CdS nanotubes have been successfully fabricated through a gas–solid sulfurization reaction. The products were characterized by X-ray powder diffraction, transmission electron microscopy, field-emission scanning electron microscopy and photoluminescence spectrum. The growth pathway can be described in terms of Kirkendall effect based on the experimental results. Furthermore, the CdS nanotubes exhibit high photocatalytic activity for degradation of the nonbiodegradable rhodamine B under visible irradiations probably due to the accessibility of both inner and outer surfaces through the pores in the walls.

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1. Introduction

The synthesis of tubular nanostructures has attracted much interest since the discovery of carbon nanotubes and inorganic (WS₂) nanotubes [1,2]. A variety of nanotubes with a lamellar or non-lamellar structure feature have been prepared using various synthetic techniques, because these fascinating systems are expected to have remarkable properties and a wide range of potential applications in nanoelectronic devices [3]. Especially, the preparation of nanotubes for non-lamellar compounds usually necessitates the assistance of either soft or hard templates, such as amphiphilic molecule assemblies, mesoporous silica, a porous polymer film, and an anodic aluminum oxide membrane and so forth [4–6]. Recently, a promising in situ sacrificial template method has been developed to synthesize 1D nanostructures [7–9]. Different from the pores in a membrane that can only serve as a physical template, nanowires can also be used as a chemical template to generate new types of 1D nanostructures through various reactions. During the reaction, the resultant 1D nanostructures form around the surface of the sacrificial template and the sacrificial template is gradually consumed at the same time.

Cadmium sulfide (CdS), as a member of non-lamellar compounds, is one of the most vital and classical II–VI group semiconductors with a direct band gap of 2.4 eV at room temperature, which has been used intensively in catalysts, logic gates,

field emitters and sensors [10–14]. Recently, CdS nano/microtubes have been synthesized by wet chemical route using various one dimension compounds (rods or wires) as templates. For instance, CdS or CdSe micro/nanotubes were prepared through consumption of the Cd(OH)Cl micro/nanorods sacrificial template [15,16]. Li et al. have reported the preformed Cd(OH)₂ nanowires were used as the sacrificial templates to generate CdS nanotubes [17]. In addition, hemicylindrical shell CdS nanowires (HSNWs) were synthesized by Li and Penner [18]. However, large-scale fabrication of CdS nanosponges consisted of integrated tubular, curving nanotubes by transformations of Cd nanowires via gas–solid sulfurization reaction is scarce. Herein, we have successfully fabricated CdS nanosponges, which are composed of network CdS nanotubes using corresponding metal elemental nanowires as a self-sacrificed template through a gas–solid sulfurization reaction. The formation mechanism of CdS tubular structure is discussed in detail. Furthermore, the measurement of photocatalytic activity on rhodamine B (RhB) demonstrates that the obtained CdS nanotubes show enhanced photocatalytic activity due to their high surface-to-volume ratio.

2. Experimental

Cd nanowires were prepared by evaporating corresponding bulk materials onto a Si substrate under vacuum without any catalyst, which have been reported elsewhere [19]. The obtained Cd nanowires were loaded into a glass tube and the glass tube was heated slowly in a tube furnace from room temperature to 250 °C with a heating rate of 5 °C/min and then this temperature was kept for 8 h. Afterward, the furnace was cooled to room temperature slowly, and a gray-white film was formed on the substrate. For the synthesis of CdS nanotubes, the Cd nanowires deposited on Si substrate were then transferred into a glass vessel which was purged with flowing N₂ for about 10 min to remove oxygen. Gaseous

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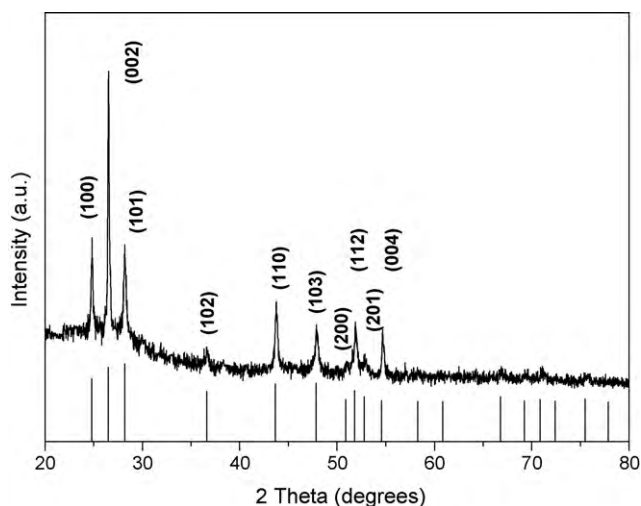


Fig. 1. Powder X-ray diffraction pattern of as-prepared CdS product on a Si substrate.

H₂S produced by mixing of H₃PO₄ (Beijing Chemical Co., 20 mL, 85 wt%) with Na₂S·9H₂O (Beijing Chemical Co., 50 g) was injected into the glass vessel immediately after stopping the N₂ purging at 250 °C for 3 h. In our work, the quantity of H₂S is excessive and the reaction time is enough long in order to guarantee the conversion of all Cd to CdS. Upon introduction of the H₂S gas into the reaction vessel, the color of the film on the substrate turned from gray-white to yellow.

The as-prepared products were characterized by powder X-ray diffraction (XRD) on a Bruker D8 Discovery-GADDS diffractometer (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$). The morphologies and microstructures of the samples were revealed with a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) and a Hitachi-8100 transmission electron microscope (TEM). For TEM imaging, the CdS nanotubes were removed from the corresponding Si substrate by careful scratching. The room-temperature photoluminescence (PL) spectra were measured using a He–Cd laser as excitation source (325 nm).

Photocatalytic experiments in aqueous solution were performed in a water-cooled quartz vessel. The visible light was generated from a 500 W xenon lamp, which is equipped with an optical filter ($\lambda > 400 \text{ nm}$) to cut off the light in the ultraviolet region. In a typical process, 25 mg CdS nanotubes was added to 50 ml RhB solution with a concentration of 10 mg l^{-1} . Prior to irradiation, the solution was sonicated for 15 min and then stirred in the dark for 30 min to establish adsorption–desorption equilibrium. At given irradiation time intervals, a series of aqueous solutions in a certain volume were collected for analysis. The concentration of RhB was determined through UV–vis spectroscopy using a Perkin-Elmer Lambda 20 UV–vis spectrometer.

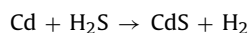
3. Results and discussion

The Cd nanowires can be sulfidized into CdS nanostructures. The phase and crystallinity of the CdS product were well-characterized using XRD techniques. As shown in Fig. 1, all of the diffraction peaks can be readily indexed to a hexagonal wurtzite-structured

CdS with the lattice parameters of $a = 4.14 \text{ \AA}$ and $c = 6.72 \text{ \AA}$, in a good agreement with the literature values (JCPDS Card, No. 41-1049). No characteristic peaks of other impurities are detected in this pattern and the sharp diffraction peaks indicate the good crystallinity.

The morphology of the as-prepared CdS product was analyzed by scanning electron microscopy and its nanotube feature was revealed by transmission electron microscopy. Fig. 2 provides the direct information of microstructures and morphologies of CdS sample. A typical SEM image of the as-synthesized CdS is shown in Fig. 2a, indicating that the CdS wire-like nanostructures have a large distribution. The high-resolution SEM image of the resulting product as shown in Fig. 2b indicates that many wire-like nanostructures with a diameter of about 200–300 nm are lying with a random distribution on the substrate. The length of nanotubes goes up to several micrometers just as the starting Cd nanowires. In addition, the typical TEM images (Fig. 3a and b) display the sharp contrast between the dark edges and the pale centers, unambiguously confirming the well-defined hollow structures. High-magnification TEM images in Fig. 3c and d further reveal the detailed structure of the shells. From the TEM images, it is clearly seen that the products are single wall nanotubes with an inner diameter of $\sim 70 \text{ nm}$ and outer diameter $\sim 120 \text{ nm}$ and the thickness of the walls of the CdS nanotubes is about 25 nm. Furthermore, the TEM image in Fig. 3d shows that many small nanocrystals are organized in an interlaced manner on the shell of CdS nanotubes.

To interrogate the formation pathway of CdS nanotubes presented above, we have observed the intermediate structures during the sulfuration of the Cd nanowires, as shown in Fig. 4. After the Cd nanowires were heated in H₂S atmosphere at 250 °C for 1 h, the surface of Cd nanowires became rough and some hollow channels inside the nanowires could be seen in the TEM image, showing the existence of Cd–CdS core–shell nanowires (Fig. 4). The thickness of the CdS layer surrounding the core Cd is about 20 nm. On the basis of these observations, the formation mechanism of CdS nanotube is proposed. In regard to our sample, the film consisted of twist Cd nanowires contains some porosity, the sulfidant species (H₂S) may easily diffuse in the interior of the film which consequently accelerates the sulfuration process. Cd nanowires were converted to CdS by exposure to flowing H₂S at 250 °C according to the reaction



When the gray-white Cd nanowires arrays are subject to reaction with H₂S, their color turns to yellow. The color change is an indication that the Cd is sulfurized to form a cadmium sulfide species.

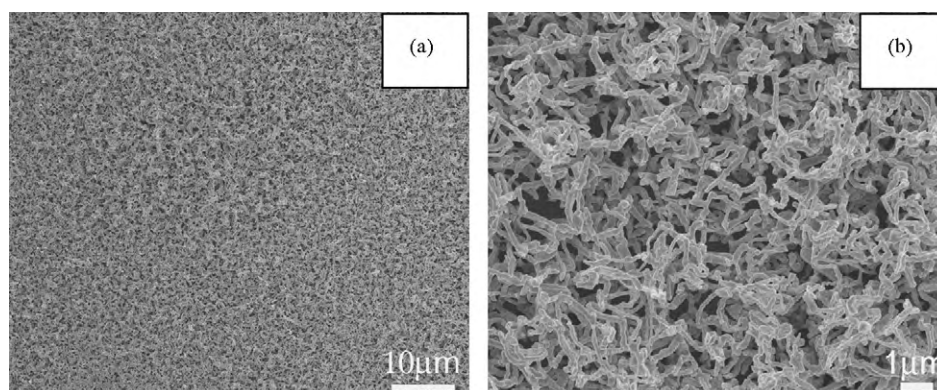


Fig. 2. Low- (a) and high- (b) magnification SEM images of CdS nanotubes on a Si substrate.

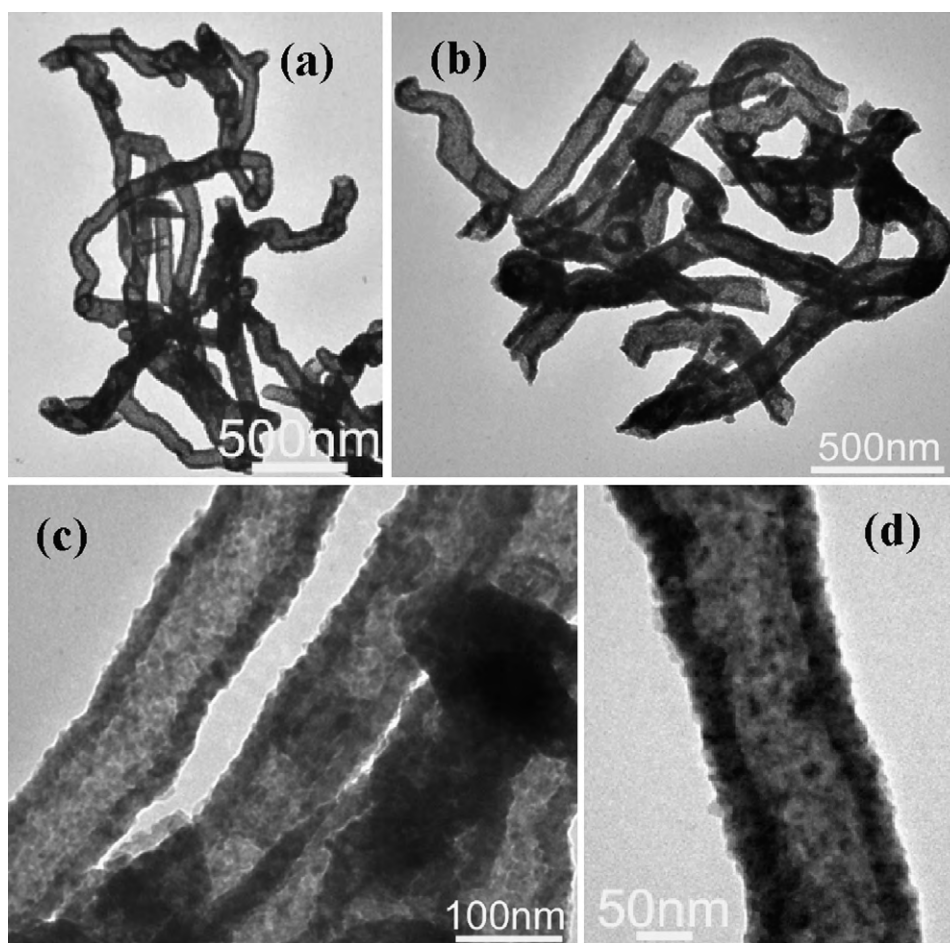


Fig. 3. TEM images of CdS nanotubes on a Si substrate. (a and b) Overall product morphology and (c and d) detailed view of CdS nanotubes.

It is well known that the melting points of Cd and CdS are 320 and 1405 °C, respectively. The temperature by slow heat treatment is lower than that of the melting point of Cd (320 °C), so the Cd in this field may be in a solid phase and the evaporation of Cd does not take place here. The formation of hollow structures is believed to be the result of non-equilibrium interdiffusion (the Kirkendall effect). Fig. 5 illustrates shape evolution process from Cd solid nanowire to CdS nanotube based on the Kirkendall effect. At the beginning of the thermal sulfurization of CdS, a thin intermediate shell was formed on the surface of these particles. This thin layer acts as an interface and separates the inner Cd from the outside atmospheric H₂S. However, the interface consists of an intermediate shell with lots of vacancies. This kind of shell structure allows the outward diffusion of inner sulfides and vacancies. A net directional flow of precursor/target materials at the template/reactant interface may lead to the formation of voids in the products. When the reaction time was prolonged, the outward diffusion of the interior Cd through the CdS crystalline wall result in the occluded voids became large and generally merged. After all Cd atoms are consumed to react with S ion absorbed on the CdS surface and finally form CdS hollow structure. This result suggests that vacancies generate at the interface are due to the imbalance of ion transport during sulfurization process. Similar phenomena had been observed in the formation of CuS nanotubes and Co₃S₄ nanotubes by our research group and Chen et al., respectively [20,21]. It is noteworthy that bulk heteroepitaxy between Cd and CdS is not favored because of the high strain energy at the interface due to relatively large lattice mismatches. So that chemical transformation of nanoparticles accompanied by

the Kirkendall effect often results in polycrystalline nanoparticle products.

Usually, two emissions are observed from CdS semiconductor nanostructures, excitonic and trapped luminescence, respectively. The green luminescence is usually attributed to near-band-edge (NBE) emission, whereas the latter (the infrared emission) could be associated with structural defects that may result from trap or surface states [22]. The room-temperature PL spectrum of CdS nanotubes excited at 389 nm is presented in Fig. 6. It is clear that the spectrum shows a strong and broad emission band located at 542 nm (2.29 eV), coupled with the lack of a strong emission near 600 nm from deep levels associated with defects, which is usually attributed to near-band-edge (NBE) emission. The lack of a broad, longer-wavelength, trap emission state, strongly suggests the high degree of purity of our samples. Similar result was also reported by Wong's research group [23].

To demonstrate the potential applicability of CdS nanotubes for the removal of contaminants from waste water, we investigated their photocatalytic activity versus CdS nanotubes by employing the photocatalytic degradation of rhodamine B (RhB) at ambient temperature. A xenon lamp is used as the irradiation source for solar light simulation (the main part of the xenon lamp radiation is in the visible region, i.e., $\lambda > 400$ nm). For comparison, the photocatalytic activities of bulk CdS under xenon lamp irradiation have also been tested. Fig. 7 shows the degradation rate of RhB over CdS nanotubes (C_0 and C are the equilibrium concentration of RhB before and after visible light irradiation, respectively). During the degradation of RhB over CdS nanotubes, the concentration of RhB quickly reduces

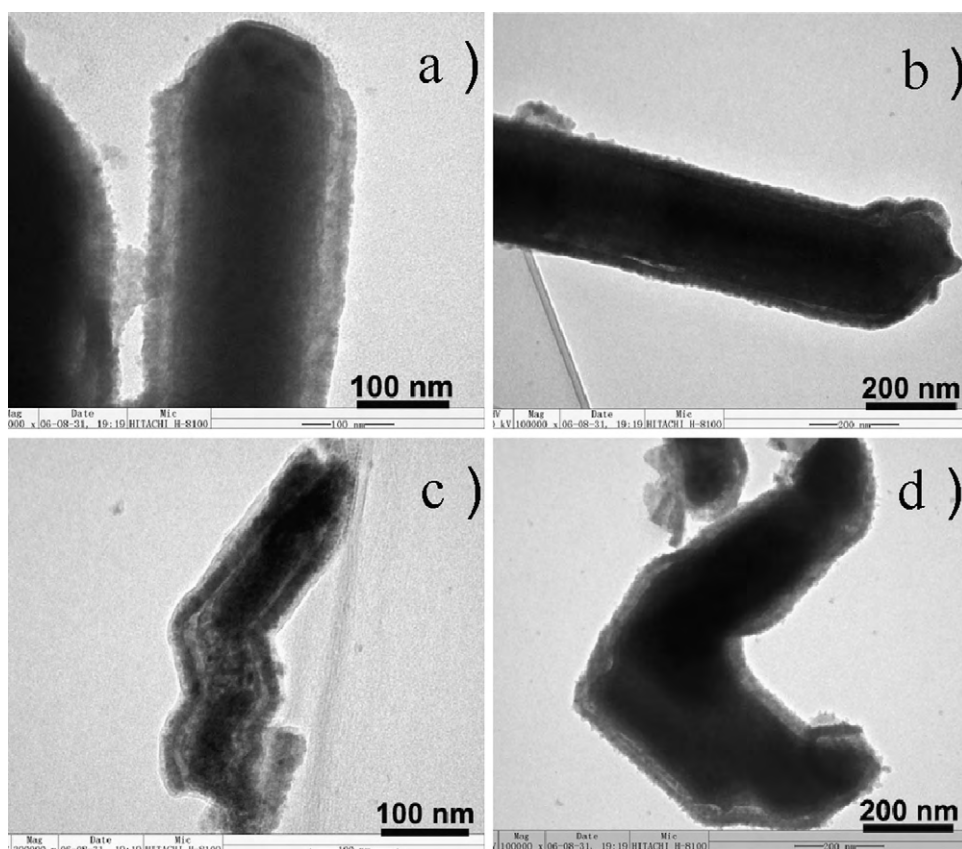


Fig. 4. TEM images of core/shell structure intermediate (Cd-CdS nanowires) when the Cd nanowires were heated in H_2S atmosphere at $250^\circ C$ for 1 h (a–d).

to 10% after visible light irradiation for about 40 min (Fig. 7a), whereas the concentration of RhB only reduces to 70% over the bulk CdS when the irradiation time is prolonged to 90 min (Fig. 7b). Xenon light illumination on RhB in the absence of a catalyst leads to no degradation of the dye at all (Fig. 7c), indicating that the RhB degradation needs an electron-transfer mediator under visible light. It is obvious that CdS nanotubes have much better photocatalytic properties than bulk CdS. The observed enhancement of photocatalytic activity of our as-prepared nanotubes herein is most likely correlated with an increase in the purity, crystallinity, and availability of surface reactive sites of our samples as compared with the bulk. It is worth noting that the CdS nanotubes are polycrystalline structures which are composed of nanocrystals. The

large amount of nanosized rough surfaces and abundant crystal boundaries of the nanocrystals make the surface-to-volume ratio of the CdS nanotubes higher and the accessibility of both inner and outer surfaces through the pores in the walls. Therefore, having a larger specific surface area would also benefit the oxidation effectiveness of CdS nanotubes as it allows more dyes to be attached to the surfaces of CdS nanotubes (catalysts) and therefore results in a larger amount of absorption and degradation of dyes (or other organic substances) [24,25].

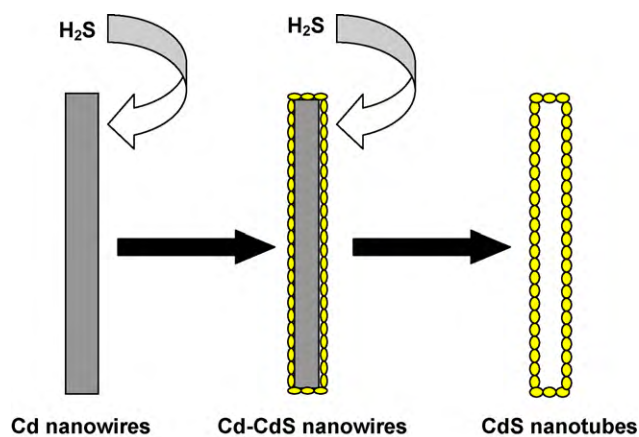


Fig. 5. Schematically illustrated shape evolution process from Cd solid nanowire to CdS nanotube based on the Kirkendall effect.

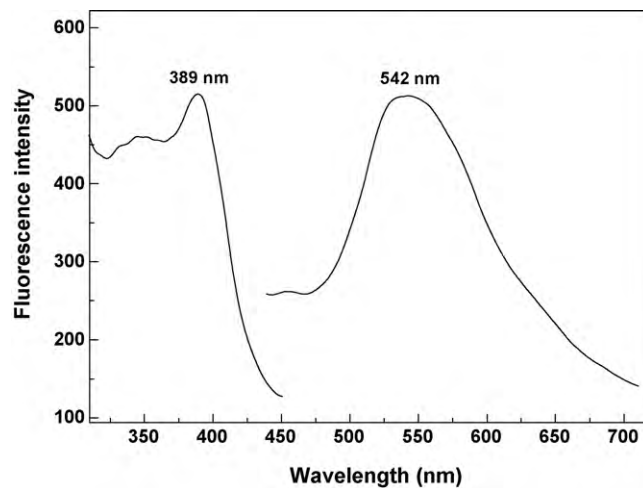


Fig. 6. Photoluminescence spectra of as-prepared CdS nanotubes at room temperature. Excitation wavelength: 389 nm.

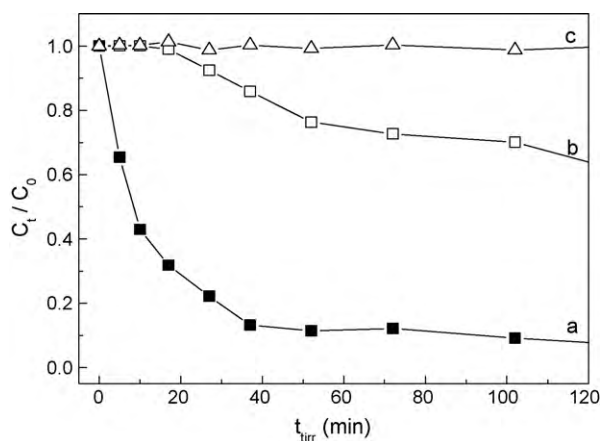


Fig. 7. Concentration change of RhB irradiated with xenon-lamp light as a function of irradiation time (t_{irr}) in the presence of (a) CdS nanotubes, (b) bulk CdS and (c) no catalyst. C_t and C_0 stand for the RhB concentrations after and before irradiation.

4. Conclusion

In summary, large-scale nanospines consisted of curving CdS nanotubes, which were assembled by many tiny nanocrystals have been fabricated using corresponding metal elemental nanowires as a self-sacrificed template through a gas–solid sulfurization reaction. The experimental results suggested that the Kirkendall effect was definitely responsible for the formation of hollow structures. In addition, enhanced photocatalytic activity is observed in the prepared samples, which is due to probably the accessibility of both inner and outer surfaces through the pores in the walls.

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