

Fabrication of well-aligned CdS nanotubes by CVD-template method

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Abstract

Well-aligned CdS nanotubes have been synthesized within the nanochannels of the porous anodic alumina (PAA) membranes by pyrolyzing cadmium bis(diethyldithiocarbamate) [Cd(S₂CNET₂)₂] at 400 °C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that the CdS nanotubes are highly ordered with uniform diameter in range of 80–150 nm and the length up to tens of microns. X-ray diffraction (XRD), Raman spectrum, energy-dispersive spectroscopy (EDS) and selected-area electron diffraction (SAED) demonstrate that the nanotubes are composed of pure hexagonal phase polycrystalline CdS. The synthetic route can, in principle, be extended to fabricate other nanotubes of a wide range of semiconductors.

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1. Introduction

Currently, one-dimensional (1D) nanostructured materials, such as nanotubes, nanowires and nanobelts, have attracted much attention due to their intriguing properties. These new nanoscale materials are expected to have many potential applications in both mesoscopic research and development of nanodevices [1–3]. It is well known that CdS is an important II–VI semiconductor with a bandgap of 2.42 eV at room temperature. It has many commercial or potential applications in light-emitting diodes, solar cells, or other photoelectric devices [4–6]. For 1D CdS nanostructures, CdS nanowires have been

synthesized using various methods [7–10] and electrically driven laser properties have been demonstrated on a single CdS nanowire [11]. Recently, much effort has been focused on the fabrication of CdS nanotubes. A variety of methods, including surfactant-assisted synthesis [12], chemical bath deposition [13], arc-electrodeposition technique [14], microwave and ultrasonic irradiation [15,16], and electrodeposition and dissolution route [17], have been used to obtain CdS nanotubes. Furthermore, single-source metal-organic chemical vapor deposition (MOCVD) is a versatile method for preparation of thin film materials [18–21] and has recently been used to synthesize nanowires such as ZnS, CdS [22] and Ga₂O₃ [23] via a vapor–liquid–solid mechanism. More recently, we have developed a simple and efficient approach to synthesize a series of metal oxide nanotubes based on the combination of the single-source MOCVD technique with porous anodic alumina (PAA) template [24]. Herein, we extend the efficient template

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pathway to synthesis well-aligned CdS nanotubes using cadmium bis(diethyldithiocarbamate) [$\text{Cd}(\text{S}_2\text{CNET}_2)_2$] as a single-source molecular precursor.

2. Experimental

$\text{Cd}(\text{S}_2\text{CNET}_2)_2$ was synthesized according to the literature method [25]. The Commercially available PAA membranes (Whatman Ltd., Anodisc 13) with a nominal pore diameter of 20 nm and thickness of 60 μm were used as templates. The synthesis of CdS nanotubes was carried out in a quartz tube mounted inside a horizontal tube furnace. In a typical experiment, the organometallic precursor (~ 300 mg) in a ceramic boat was placed at upstream end and the PAA template was placed vertically at the central high-temperature zone of the quartz tube. After evacuating the quartz tube to ~ 2 Torr, a carrier gas of high-purity N_2 flowed via the precursor area toward the template to carry precursor into reaction zone. The gas flow rate and pressure inside the tube were kept respectively at 30 sccm and 20 Torr during the CVD. The system was then heated to 400 $^\circ\text{C}$ at the central region of the furnace at a rate of 20 $^\circ\text{C min}^{-1}$ and held at that temperature for 1 h for CVD. The precursor was situated in advance according to the temperature gradient from the center to the ends of the furnace so that its temperature could be held at about 220 $^\circ\text{C}$. After deposition, the temperature of the template was raised to 500 $^\circ\text{C}$ at a rate of 2 $^\circ\text{C min}^{-1}$ and maintained for 4 h for annealing. The resulting template was collected after the furnace was cooled to room temperature. The cover layer on the surface of the resulting templates was removed by polishing with 1500 grid sand paper for further characterization.

The as-deposited products with PAA membranes support, which were attached to the sample stub with the membrane plane being perpendicular to the X-ray beam direction, were characterized by a D/Max-RA X-ray diffractometer (XRD) with Cu K_α radiation. The morphology and the composition of the products were examined by scanning electron microscopy (SEM, JSM-840A and LEO1530VP) equipped with an energy dispersive spectrometry (EDS). The structure of the nanotubes were investigated by transmission electron microscopy (TEM, JEM-200CX). Raman spectrum was performed at room temperature using a SPEX-1403 Raman spectrometer with 514.5 nm excitation source from an Ar^+ laser. Specimens for SEM were prepared as follows: the sample was fixed at a piece of copper tape and immersed in 3 mol l^{-1} NaOH aqueous solution for ca. 2 h to remove the alumina template. After careful rinsing with deionized water and drying, the tape was attached to an SEM sample stub and was sputtered with a thin layer of gold. Samples for TEM were prepared by placing a piece of the resulting membrane in 6 mol l^{-1} NaOH aqueous solution for ca. 0.5 h to dissolve the alumina. The solution was removed carefully via syringe

and the sample was rinsed with distilled water more than twice. The sample was collected on a carbon-coated copper grid and allowed to air-dry before measurement.

3. Results and discussion

Fig. 1 shows SEM images and an EDS spectrum of the as-prepared CdS nanotubes. Fig. 1a is a top view of the CdS nanotube arrays after removing the surface cover layer. It can be seen that the nanotubes have open ends and the outer diameters of the nanotubes are in the range of 80–150 nm, which correspond to the pore diameter of PAA template. The compactness of the nanotubes is quite high of about $1.0 \times 10^{10} \text{ cm}^{-2}$, corresponding to the pore density of the PAA. Fig. 1b is a lateral view of the nanotube arrays, showing that the nanotubes are arranged in a parallel and ordered way, and their lengths are up to several tens of microns. The energy-dispersive spectroscopy (EDS) of the nanotubes shown in Fig. 1c confirmed that the nanotubes were composed of cadmium and sulphur with the atomic ratio of about 1:1 (51.7:48.3). The result indicates that the as-prepared CdS nanotubes are highly pure and there is not any detectable contaminant from carbon or oxygen.

X-ray diffraction (XRD) measurement was performed to probe the structure and phase purity of the nanotubes. Fig. 2 shows a typical XRD pattern of the CdS nanotube arrays in PAA template. All the diffraction peaks can be indexed to a hexagonal structure CdS with lattice constants of $a = 4.135$ and $c = 6.714 \text{ \AA}$, which is consistent with the standard value for bulk hexagonal CdS (JCPDS 6-0314). However, comparing the intensities of the (002) and (101) peaks of the nanotubes with those of the standard bulk hexagonal CdS, it was found that the relatively intensity of (002) peak has been dramatically improved, indicating that the nanoparticles composing nanotubes may have a different preferential growth direction from that of the bulk CdS. Because Raman scattering is very sensitive to the microstructure of nanocrystalline materials, it is also used here to clarify the structure of the CdS nanotubes. Raman spectrum of the CdS nanotubes (Fig. 3) shows characteristic Raman shifts analogous to those of pure crystalline CdS [26]. The Raman peaks located at around 301, 604, and 906 cm^{-1} correspond to the first, second, and third-order longitudinal optical (LO) phonon modes of CdS, respectively. This exhibits that the CdS nanotubes have a similar crystal structure of the bulk CdS.

The morphology and structure of individual CdS nanotubes have been characterized in further detail using transmission electron microscopy (TEM) and selected-area electron diffraction (SAED), which are shown in Fig. 4. Fig. 4a shows a typical TEM image of the CdS nanotubes. It can be seen that the nanotubes are straight and uniform along their entire length with wall thickness of about 20–30 nm. The nanotube is composed of CdS nanocrystals with sizes ca. 10–16 nm, which is consistent with the calculated

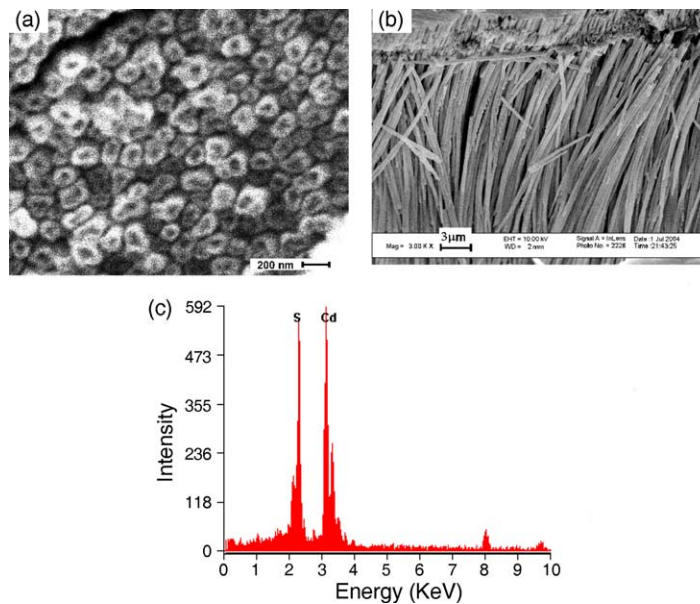


Fig. 1. SEM images and a EDS spectrum of the as-prepared CdS nanotubes. (a) Top-view of well-aligned CdS nanotubes after removing the surface cover layer. (b) Lateral view of CdS nanotube arrays. (c) EDS spectrum of the nanotubes.

value by Scherrer equation. In addition, corresponding SAED pattern (Fig. 4b) show that the CdS nanotubes are polycrystalline and the diffraction rings observed in the SAED pattern can be indexed as the (100), (002), (101), (102), (110), (103) and (112) lattice planes of hexagonal CdS.

4. Conclusions

Well-aligned CdS nanotubes have been prepared within the nanochannels of the PAA templates using cadmium bis(diethylthiocarbamate) as single-source molecular

precursors. The as-prepared CdS nanotubes with 80–150 nm in outer diameter and several tens of microns in length have been characterized by SEM, TEM, XRD, EDS, SAED and Raman spectrum. The present study demonstrates further that the efficient template-based CVD method can be used to fabricate well-aligned nanotube arrays of various semiconductors. Such nanotubes grown without catalyst can promise potential applications in optical, electric and gas sensitive nanodevices.

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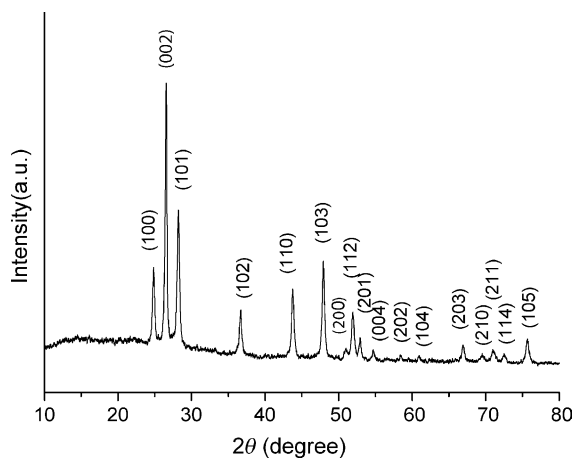


Fig. 2. XRD pattern of the CdS nanotubes embedded in PAA template.

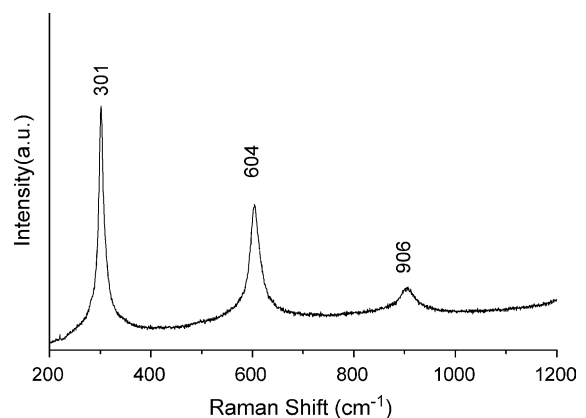


Fig. 3. Raman spectrum of the CdS/PAA assembly system.

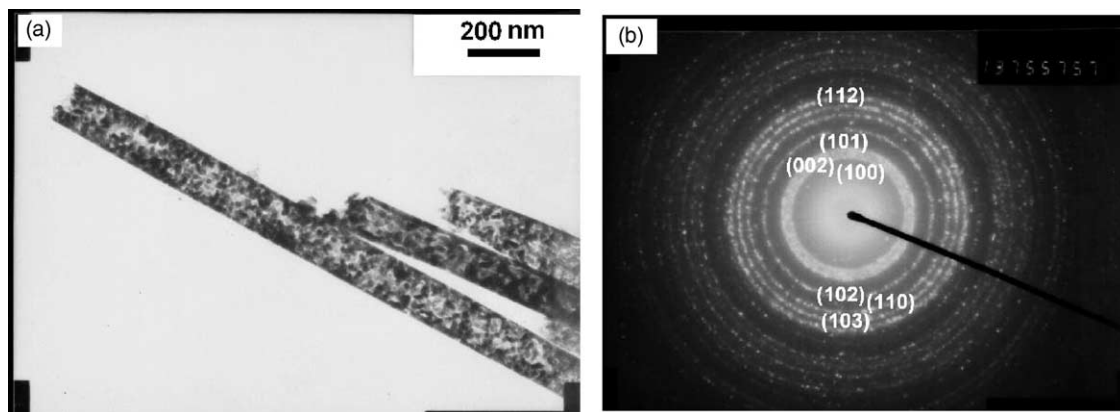


Fig. 4. (a) TEM image and (b) SAED pattern of the CdS nanotubes.

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