

A Two-Step Route to Self-Assembly of CdS Nanotubes via Electrodeposition and Dissolution

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Polycrystalline CdS nanotubes (CNTs) were successfully achieved by a two-step treatment, i.e. (CdS+Cd) nanowires (electrodeposition and sulfuration process in anodic alumina membrane) → CNTs (dissolution method of removing Cd in 0.5 M HCl). Having been characterized using X-ray diffraction and scanning electron microscopy, the nanowires, the intermediate products, contain Cd and CdS, and have uniform diameters of about 80 nm and lengths of up to 25 μm, which correspond to the pore size and thickness of the membrane used. The average inner and outer diameters of the as-obtained CNTs are respectively 40 and 80 nm via trans-

mission electron microscopy. Selected area electronic diffraction, X-ray diffraction and X-ray photoelectron energy spectroscopy investigations demonstrate that these CNTs with hexagonal wurtzite polycrystalline structure are pure and stoichiometric. The successful synthesis of these semiconductor CNTs may open up new possibilities for studies of fundamental properties and potential applications of semiconductor nanotubes.

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Introduction

The discovery of free-standing microscopic one-dimensional molecular structures, such as carbon nanotubes, has attracted a great deal of attention in the last decade because of the various interesting properties associated with their small dimensions, high anisotropy, and intriguing tube-like structures. These range from a variety of quantum effects to potentially useful properties such as efficient field-emission and exceptional mechanical strength.^[1] A particularly significant breakthrough in WS₂ and MoS₂ nanotubes synthesis was made by Tenne and co-workers^[2–4] through the gas-phase reaction between WO_{3–x} or MoO₃ and H₂S in a reducing atmosphere at elevated temperature. Since then many other kinds of nanotubes, such as BN,^[5] NiCl₂,^[6] InS,^[7] NbS₂,^[8] and Bi,^[9] have been reported utilizing various approaches with different growth mechanisms. More recently, Si^[10,11] and TiO₂^[12,13] nanotubes were also fabricated and a micro-templated synthesis of CdS nanotubes^[14] in aqueous solution at room temperature has also been reported. Although no generalized synthetic method for nanotubes has yet been established, self-assembly growth is a good method for producing nanotubes. For example, Remskar et al.^[15] reported the self-assembly of subnanometer-diameter single-wall MoS₂ nanotubes, and rare-earth oxide

nanotubes have been formed from dodecylsulfate assemblies.^[16] Similarly, Te,^[17] NbS₂,^[18,19] WS₂,^[20] Cu_{5.5}FeS_{6.5},^[21] and ReS₂^[22] nanotubes have also been synthesized by self- or induced-assembly. Motivated by these reports, we now report a two-step synthesis of CdS nanotubes based on a self-assembly approach.

Results and Discussion

The CdS nanotubes were synthesized as follows. First, pure metal Cd nanowires were electrodeposited inside the nanochannels of anodic alumina membrane (AAM), and then the outer walls of the Cd nanowires were sulfurized under an atmosphere of sulfur to form a CdS layer under controlled conditions; the (CdS+Cd) nanowires were formed in situ. Secondly, the CdS nanotubes were formed by removal of the Cd, together with AAM, upon dissolution in 0.5 M HCl for 1 hour. Figure 1a shows a typical cross-sectional SEM image, where the intermediate products — the (Cd+CdS) nanowires — consist of a large quantity of wire-like arrays with diameters of about 80 nm and lengths of about 25 μm, corresponding to the pore size and thickness, respectively, of the AAM used. These nanowires are highly ordered and are formed by a template, i.e. they are electrodeposited uniformly and continuously filled into the AAM pores. The composition of the nanowires was confirmed by X-ray diffraction (XRD), as shown in Figure 1b. The peak at 32.15° supports the proposal that there is metallic Cd in the nanowires, whereas no peaks from Al₂O₃ exist due to its amorphous structure at the treatment

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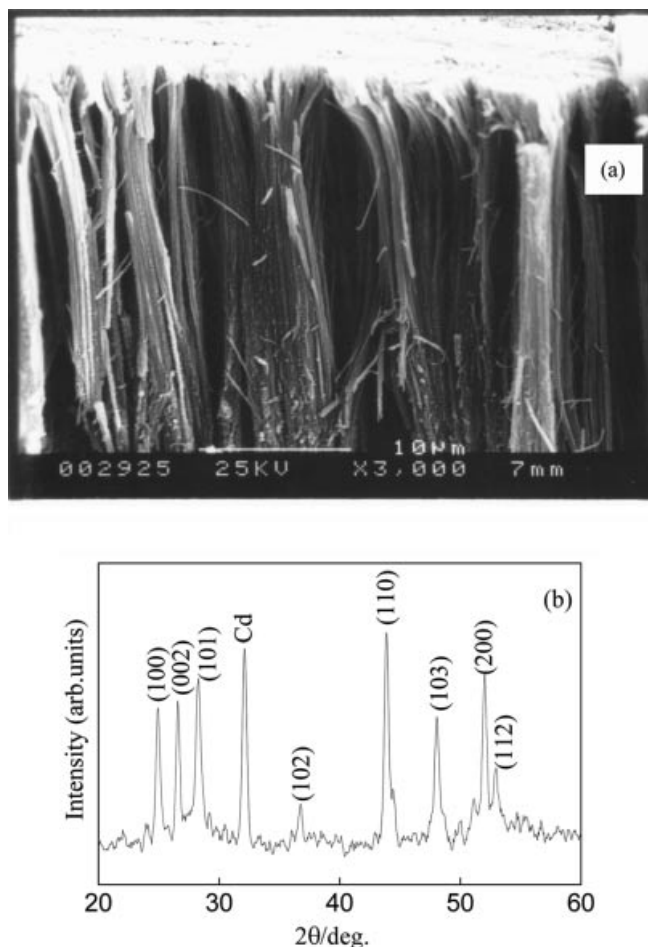


Figure 1. (a) A typical cross-sectional SEM image of (CdS+Cd) nanowires (80 nm in diameters and 25 μm in lengths) and (b) XRD pattern of (Cd+CdS) nanowires

temperature. The Miller indices of the peaks are indicated in Figure 1b where it can be seen that the whole diffractogram can be indexed from the peak positions to a crystalline CdS phase. It is also clear that the XRD pattern of the nanowires exhibits prominent peaks at scattering angles (2θ) of 24.8°, 26.4°, 28.2°, 36.6°, 43.7°, 47.8°, 51.9°, and 52.8°, of the hexagonal CdS crystal lattice (JCPDS Card File, No. 06-0314). After the AAM and the Cd had been completely removed by treatment with 0.5 M HCl for 60 min, we obtained the CdS nanotubes whose typical TEM image is shown in Figure 2a. One can clearly see that these nanotubes appear in alignment and have a hollow structure with a uniform outer diameter of about 80 nm, which is consistent with the results of SEM. A TEM image at higher magnification, taken of the open section of a single nanotube, is presented in Figure 2b; the section marked with a black loop was used for selected area electronic diffraction (SAED) analysis. From this image, it can be seen more clearly that the inner and outer diameters of the nanotube are 40 nm and 80 nm, respectively and its structure is hollow. Moreover, the open section of the nanotube has a rough surface, which might be due to the corrosion by HCl. Because of this, one can suggest that HCl dissolves AAM and Cd in the center of the wire along the nanowire axis, resulting in this kind of hollow structure. An SAED pattern (insert in Figure 2b), taken from the section mentioned above, was recorded with a W electron beam perpendicular to the nanotube axis (other SAED patterns from other sections of the nanotube are essentially identical), which reflects the characteristics of the nanotube structure. The pattern shows that the diffuse diffraction rings in the SAED pattern are due to the polycrystalline structure of the sample. The three rings in the pattern correspond to the [110], [101], and [112] direction; the [110] is the radial direction of the nanotube. Figure 3 shows the XRD pattern of

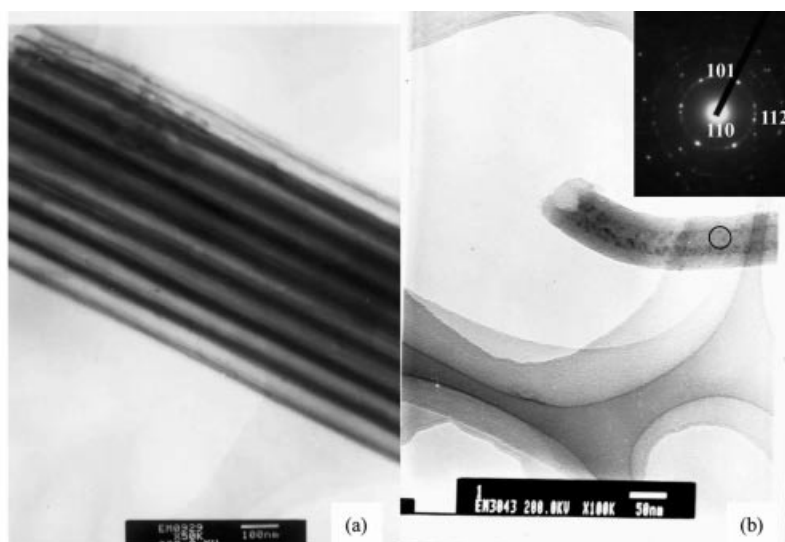


Figure 2. (a) TEM image of CdS nanotube arrays (inside diameter of 40 nm and outside diameter of 80 nm) and (b) a TEM image at higher magnification taken of an individual nanotube; inset: SAED pattern of the CdS nanotube

the final CdS nanotubes, where all the intense XRD peaks show a wurtzite (hexagonal) structured CdS with lattice constants of $a = 0.413$ nm and $c = 0.671$ nm consistent with the standard values (JCPDS Card File, No. 06-0314) and a previous report.^[23] No diffraction peaks from CdO, Cd, S or other impurities have been found in the final products.

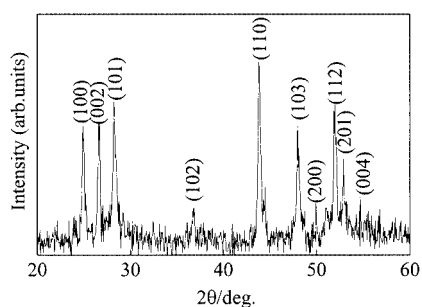


Figure 3. XRD patterns of the CdS nanotubes

A chemical composition analysis of the as-synthesized CdS nanotubes was also performed by X-ray photoelectron energy spectroscopy (XPS). The XPS spectrum (Figure 4) shows that the nanotubes are composed of S and Cd, and quantitative analysis indicates that the atomic ratio of S and Cd is 40:48 within experimental error, which is consistent with stoichiometric CdS (Cd:S = 1:1).

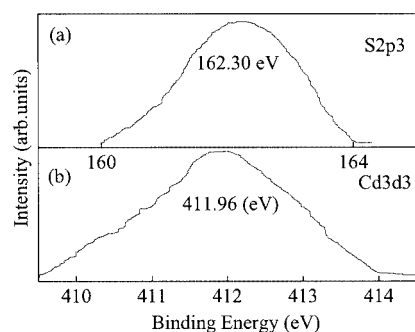
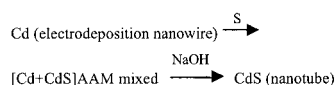


Figure 4. (a) S2p3 XPS spectrum of the CdS nanotubes: the peak binding energy is 162.30 eV and (b) Cd3d3 spectrum of the CdS nanotubes: the peak binding energy is 411.96 eV; the Cls ($E = 284.5$ eV) level serves as the internal standard

There is one other possible model for the growth of CdS nanotubes: Through the usual template approach, the parameters of Cd nanowires are strongly dependent on the size of the nanochannel in AAM. The mixture of composition CdS + Cd forms through sublimation of sulfur, the residual Cd is dissolved and then the CdS nanotubes appear. This might be a self-assembly process.



In summary, we have presented a simple, inexpensive, and reasoned method to fabricate CdS nanotubes. They were characterized by SEM, TEM, SAED, XRD, and XPS. The final products formed through self-assembly are pure CdS nanotubes with outside diameters of about 80 nm and inside diameters of about 40 nm. The CdS nanotubes have a uniform hollow structure. The growth mechanism is suggested to be a self-assembly process. The technique may serve as a model for studying the synthesis and properties of other semiconductor nanotubes such as PbS, SnS, ZnS. It is likely that these CdS nanotubes may stimulate technological interest and see many applications in optical fibers or nanodevices.

Experimental Section

The CdS nanotube was formed by a chemical method taking advantage of its low solubility in 0.5 M HCl (Cd and AAMs are readily soluble). In a typical experiment, AAM was prepared via a two-step aluminum anodic oxidation process in a 0.3 M oxalic acid solution, as described previously.^[24] The AAM had a diameter of about 80 nm in the pore size and a thickness of 25 μm . Metallic Cd was electrodeposited inside the nanochannels of the AAM with a conventional three-electrode aqueous bath, containing solutions of 0.2 M CdCl₂ and 0.1 M H₃BO₃. The deposition potentials were controlled in the range -0.68 to 0.7 V for 240 min at room temperature. Then their surfaces were polished using a 40-nm SiC polishing sandpaper to get rid of Cd particles that had grown excessively and stuck to the surface. The AAM with Cd was washed with distilled water and ethanol, put into a quartz boat and covered with a layer of S powder (99.99%). The boat was placed into the hot zone of a recrystallized alumina tube furnace. The reaction chamber was evacuated with a mechanical pump, and then it was backfilled with high purity Ar gas (0.1 MPa). The reactor was heated to 700 °C from room temperature and held at this temperature for 30 minutes to sulfurize the Cd nanowires. The AAM with CdS membranes was then cleaned with CS₂ to remove the remaining S powder, and washed with ethanol and deionized water. Then, the AAM was immersed in 0.5 M HCl for 60 min and the precipitate was separated from the solution by centrifugation and washed with toluene and absolute ethanol. The semi-finished product [i.e., (CdS+Cd) nanowires] with AAM was firstly characterized by X-ray diffraction (XRD) (PW, 1710 instrument with Cu-K α radiation, $\lambda = 0.154178$ nm at a scanning speed of 0.02°/s in the 2 θ range 20–60°). For the SEM analysis (JEOL JSM-63000 instrument) the sample was mounted directly on Cu stubs with conductive gold paint and the AAM was dissolved away. The final products were dried in vacuo at 100 °C for 3 hours and detected by using transmission electron microscopy (TEM) [JEM 200CX equipped with selected area electronic diffraction (SAED), working at 200 kV acceleration voltage], XRD, and X-ray photoelectron energy spectroscopy (XPS) [MKII XPS, employing Mg-K α , $E = 1253.6$ eV, the Cls ($E = 284.5$ eV) level served as the internal standard]. For TEM and SAED, the sample was ultrasonically dispersed in ethanol and a drop of the solution was placed on a Cu grid coated with a holey carbon film. All the chemicals used were of analytical grade and were used without further purification.

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