Growth of Mesoscale Tubular CdS Crystals via a Hydrothermal Method

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(Received June 8, 2004; CL-040655)

Cadmium sulfide tubular crystals, with the range of 0.5–2 mm in length, 10–20 µm in the external diameter and 3–6 µm in the wall thickness, were successfully grown in sodium hydroxide solution via a hydrothermal method at 350 °C. XRD, SEM, and XPS methods characterized the products. A possible growth mechanism for the tubular structure was also proposed.

In the past years there has been growing interest in materials with specific morphologies because of the expectation of novel properties. Among them, the mesoscale tubular structure objects are useful in many areas. For example, they can provide more inert platforms for host–guest chemistry[1,2] because of their ability to act as containers or capsules.[3,4] Therefore, tubular structure materials may have potential applications in catalysts, photonic band gap materials, and chemical separations media.[5–7] In recent years, various approaches, such as hydrothermal method,[8–10] solvent-relief-self-seeding (SRSS) process,[11] self-assembly method,[12] and template methods[13–16] or CVD growth in a confined environment,[17] have been used to grow tubular structure objects. By these methods, a wide spectrum of materials with tubular structure has been processed, including both inorganic materials (Sb_2S_3, β-Ag_2Se, CuS, Sb_2E_3 (E = S, Se)) and organic materials (biomolecules, polymer).

Cadmium sulfide, a member of II–VI semiconductor compounds, has widely spread applications in the field of electronics ranging from phosphors to photovoltaic cells. In the past years, many methods have been used to synthesize CdS crystal, such as chemical vapor transport (CVT) method, physical vapor transport (PVT) method, sublimation method, Bridgeman–Stockbarger technique, and flux method. In our experiments, via a hydrothermal method, mesoscale tubular CdS crystals were prepared successfully by using nanoparicles CdS as raw material in basic media at a relative low temperature 350 °C for 24 h. A possible growth mechanism of the CdS tubular crystals is discussed.

In our route, the reactions take place as follows:

$$Cd^{2+} + OH^- \rightarrow Cd(OH)_2(sol) \tag{1}$$

$$Cd(OH)_2(sol) + S^{2-} \xrightarrow{180\,^\circ C} CdS\ (nanoparticles) + 2OH^- \tag{2}$$

$$CdS\ (nanoparticles) + H_2O + NaOH \xrightarrow{350\,^\circ C} Na_2Cd(OH)_4 + HS^- \tag{3}$$

$$Na_2Cd(OH)_4 + HS^- \xrightarrow{350\,^\circ C} CdS + H_2O + NaOH \tag{4}$$

All reagents were of 99.9% purity from Shanghai Chemical Reagents Co. and were used without further purification. The whole experiment included two stages. Firstly, cadmium hydroxide sol was synthesized by adding $Cd(AC)_2.2H_2O$ (0.01 mol) to 20 mL of sodium hydroxide aqueous solution (1 M) and then the sol was mixed with 50 mL of Na_2S aqueous solution (0.2 M) in Teflon vessel kept at 180 °C for 10 h. The obtained yellow precipitates of CdS were filtered and washed with distilled water and absolute alcohol several times. Finally, they were dried under vacuum at 50 °C for 4 h. The second stage was: the mixture of about 0.3 g as-prepared CdS nanoparticles and 40 mL of sodium hydroxide aqueous solution (2 M) was transferred to a stainless autoclave (50 mL), which was then filled to 80% of the capacity. The autoclave was heated to 350 °C in 90 min, and maintained at the temperature for 24 h. Then it was cooled to room temperature on standing. The products were carefully collected and washed with absolute ethanol and distilled water several times to remove the residues, and then dried in a vacuum at 50 °C for 4 h.

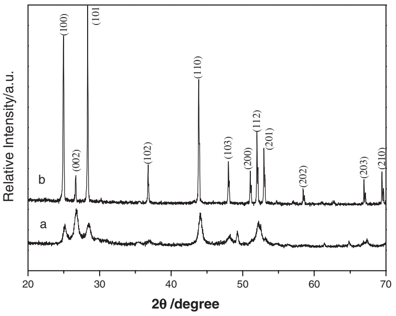

Figure 1. XRD pattern of as prepared samples, (a) nanoscale CdS powder, (b) tubular structure CdS.

X-ray powder diffraction (XRD) was obtained on a Japan Rigaku D/max-γA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 0.1541874$ nm). Figures 1a and 1b show the XRD patterns of the nanoscale CdS powder and the tubular CdS crystals, respectively. Figure 1a is the XRD patterns of the as-prepared CdS nanoparticles. The peaks are in agreement with hexagonal CdS (JCPDS file No. 41-1049). The average size of the precursors calculated from Scherrer equation is about 14.5 nm. Figure 1b shows the XRD patterns of the hexagonal tubular CdS crystals. All diffraction peaks could be indexed as hexagonal structure CdS with cell constants $a = 4.12$, $c = 6.68$, which are in agreement with the reported value (JCPDS file No.41-1049, $a = 4.1409$, $c = 6.7198$), and no obvious impurity phases, such as $Cd(OH)_2$, CdO or cubic CdS, were found in the XRD patterns. The XRD patterns (Figure 2b) of the sample showed that the majority of the products were well crystallized. Compared with the standard diffraction patterns of CdS, it is found that the diffraction peaks of (100) and (101) are stronger, and the peak of (002) decreases obviously. This result shows that (100) and (101) planes of the hexagonal CdS single crystals parallel the shaft of the tubular single crystals. This unusual relative intensity of (100) and

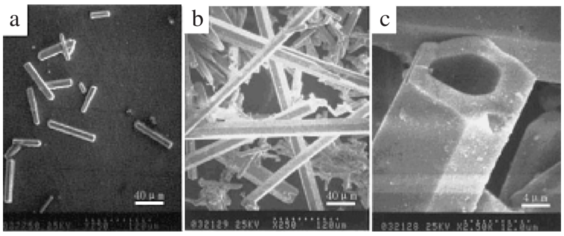

Figure 2. SEM images of CdS crystal (a) microrod and (b, c) tubes.

(101) to (002) indicates a preferential orientation along the *c* axis.

The scanning electron microscopy (SEM) images of CdS crystals are shown in Figure 2. Figure 2a shows the CdS microrod that is about 13 μm in width and up to 80 μm in length. Figures 2b and 2c show the tubular CdS crystals. Figure 2c illustrates the typical straight hollow tubular crystals. In general, this structure is 0.5–2 mm in length, and the external diameter is in the range of 10–20 μm while the wall thickness is in the 3–6 μm range.

The samples were also characterized by X-ray photoelectron spectra (XPS) (the spectra not shown). The binding energy of Cd3d^5 at 405.2 eV and S2p at161.65 eV revealed that this sample could be identified with CdS.[18] The atom ratio of Cd/S calculated from the peak areas of Cd3d^5 and S2p was 9.08:11.18. The result revealed that the obtained tubular crystals were stoichiometric within the experimental errors.

The crystallization temperature was critical factors in the formation of CdS tubes. In the hydrothermal route, the appropriate temperature for the formation of CdS tubes was at 350 °C. In our growth process, sodium hydroxide (NaOH) acted as mineralizer. Because of the formation of $Na_2Cd(OH)_4$ (Eq 3), the solubility of CdS powders in NaOH solution was higher than that in water. Experiments indicated that the suitable conditions were that the temperature was not lower than 350 °C, the reaction time was not shorter than 24 h, and the concentration of NaOH was 2 M.

The growth mechanism for the tubular CdS crystals is discussed as follows. CdS exists in two polymorphic form—wurtzite (hexagonal) and zincblende (cubic). Indeed, the thermodynamically stable crystal structure of CdS is wurtzite and occurs in nature as the mineral greenokite. This ionic and polar structure can be described as hexagonal close packing of sulfur and cadmium atoms in space group *P*63*mc* with cadmium atoms in tetrahedral sites (point group 3*m*). The occupancy of four of the eight tetrahedral sites of the hexagonal lattice controls the structure. The velocities of wurtzite structure crystal growth in different directions are reported to be $[\bar{1}00] > [\bar{1}01] > [001] \approx [00\bar{1}]$.[19] Accordingly, the theoretical and most stable crystal habit is a hexagon elongated along the *c* axis. In the early stage of our crystallization process, the nucleation and growth of the highly 3-D crystalline CdS microrod array of typically about 13 μm in width and up to 80 μm in length is produced (Figure 2a). Subsequently, in the second stage, the preferential chemical dissolution of the metastable (001) Cd faces of the fully grown oriented microrods shall lead to the required highly porous and oriented hollow structure (Figures 2b and 2c). The system undergoes variations of morphology, size, or structural properties as a result of the aging mechanism (e.g., Ostwald ripening).[20]

In summary, CdS mesoscale tubes were synthesized successfully via a hydrothermal method at 350 °C. The possible growth mechanism of CdS tubes was proposed. It is expected that the hollow tubular crystals should have novel properties, and may offer exciting opportunities for both fundamental research, and technological application. Deeper understanding of growth mechanism of CdS tubes and controlling the reaction kinetics should be further investigated.

This work supported by the Chinese National Foundation of Natural Science Research.

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Published on the web (Advance View) September 4, 2004; DOI 10.1246/cl.2004.1284