Journal of Experimental Nanoscience
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t716100757

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To cite this Article Phuruangrat, Anukorn , Thongtem, Titipun and Thongtem, Somchai(2009) 'Characterisation of one-dimensional CdS nanorods synthesised by solvothermal method', Journal of Experimental Nanoscience, 4: 1, 47 — 54
To link to this Article: DOI: 10.1080/17458080802654486
URL: http://dx.doi.org/10.1080/17458080802654486

Journal of Experimental Nanoscience
Vol. 4, No. 1, March 2009, 47–54

Characterisation of one-dimensional CdS nanorods synthesised by solvothermal method

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(*Received 17 July 2008; final version received 30 November 2008*)

One-dimensional (1D) cadmium sulfide nanorods were successfully synthesised using cadmium nitrate and sulfur powder as starting materials and polyvinyl alcohol (PVA, MW = 1 25,000) as a capping agent in ethylenediamine as a solvent by solvothermal method at 200°C for 24 and 72 h. X-ray diffraction patterns (XRD) indicated a single phase of hexagonal wurtzite CdS structure, of which the results are in accordance with those of selected area electron diffraction (SAED). The morphologies of CdS were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) which showed 1D nanorods. The length and diameter of CdS nanorods were increased when PVA was added and the reaction times were prolonged. High resolution transmission electron microscopy (HRTEM) showed that growth direction of wurtzite CdS nanorods is along [001] direction or *c*-axis. Raman spectra presented the 1LO and 2LO at 299.36 and 600.72 cm^{-1}, respectively. The 2LO/1LO intensity ratios were increased when the length of CdS nanorods became longer.

Keywords: cadmium sulfide; one-dimensional structure; solvothermal method

1. Introduction

One-dimensional (1D) nanostructures, such as nanowires, nanorods, nanofibres, and nanotubes, are very interesting materials because they have anisotropic geometries and unique physical properties [1,2]. The 1D II-VI semiconductor nanocrystals are well studied and have been achieved in recent years. CdS is one of the most important materials which has a direct band gap of 2.5 eV for the bulk hexagonal wurtzite structure CdS, and 3.53 eV for bulk cubic zinc blende structure CdS [3,4]. CdS has a potential application in light-emitting diodes, solar cells, optoelectronics, and photocatalysts [5,6]. It has been synthesised by a variety of methods, including solvothermal reaction [5], thermal evaporation [7], and microwave irradiation [6]. A solution method can produce the nanostructure product without using any catalysts or templates, as well as a better crystal quality with preferable growth at lower temperature. It is a simple and economical process.

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ISSN 1745–8080 print/ISSN 1745–8099 online

DOI: 10.1080/17458080802654486
http://www.informaworld.com

Hydrothermal method is a candidate in synthesising nano-materials under high pressure and at a temperature far above its boiling point of solvent employed at 1 bar pressure in a tightly closed system. The term hydrothermal is when water is used as a solvent in the system. Solvothermal is a general term when other organic solvents are used [8,9]. The hydrothermal reaction has a lot of advantages and can be used to give high product purity and homogeneity, crystal symmetry, meta-stable compounds with unique properties, narrow particle size distributions and lower sintering temperature. It offers a wide range of chemical compositions, a single-step process, dense sintered powder, sub-micron to nano-particles with narrow size distribution using simple equipment, lower energy requirement, fast reaction time, lowest residence time, as well as for the growth of crystals with polymorphic modification and the growth of crystals with low to ultra-low solubility for other applications [8–11].

For the synthesis of 1D CdS by solvothermal method, ethylenediamine, a bidentate ligand, is the best solvent. Its lowest dielectric property is possible for providing an appropriate CdS monomer concentration for preferential growth [12]. In order to improve the length and uniformity of diameter, PVP [13] and PEG [14] were used for polymer-assisted synthesis. In the present research, 1D CdS nanostructure was synthesised by solvothermal method using ethylenediamine as a solvent and ligand, and PVA as a capping agent to obtain large aspect ratios, compared to PVA-free solution at the same condition.

2. Experiment

To synthesise 1D CdS nanostructure, each 0.005 mol $Cd(NO_3)_2$, sulfur powder and 0.75 g PVA (MW = 1 25,000) as a capping agent were mixed in a teflon-lined container, and ethylenediamine (en) was filled to 80 vol% capacity. Subsequently, the teflon-lined container was transferred into a home-made stainless steel autoclave. The autoclave was tightly closed, heated up to 200°C, held at this temperature for 24 or 72 h, and finally cooled to room temperature. Yellow precipitates were collected, washed with distilled water and absolute ethanol for several times, and dried at 80°C for 24 h. Then the products were further characterised.

X-ray diffraction (XRD, Siemens D500) analysis was carried out using Cu-Kα radiation with the scanning angle 2θ ranging from 10 to 60°, a graphitic monochrome and a Ni filter. Raman spectroscopy (HORIBA JOBIN YVON T64000) was operated using 50 mW Ar laser with 514.5 nm wavelength. Scanning electron microscopy (SEM, JEOL JSM-6335F) equipped with an energy dispersive X-ray analyzer (EDX, Oxford instruments INCA) was operated at 15 kV, and transmission electron microscopy (TEM, JOEL JEM-2010) as well as selected area electron diffraction (SAED) at 200 kV.

3. Results and discussion

Figure 1 shows XRD patterns of the products. All diffraction peaks were indexed, and found to correspond to the hexagonal wurtzite CdS (JCPDS no. 41-1049, $a = 4.1409$ Å and $c = 6.7198$ Å) [15]. No other impurities were detected, showing that the products are pure phase. Their intensities were compared with that of the standard card and the (002) diffraction peaks of the patterns were unusually stronger than the standard one. At 0.75 g

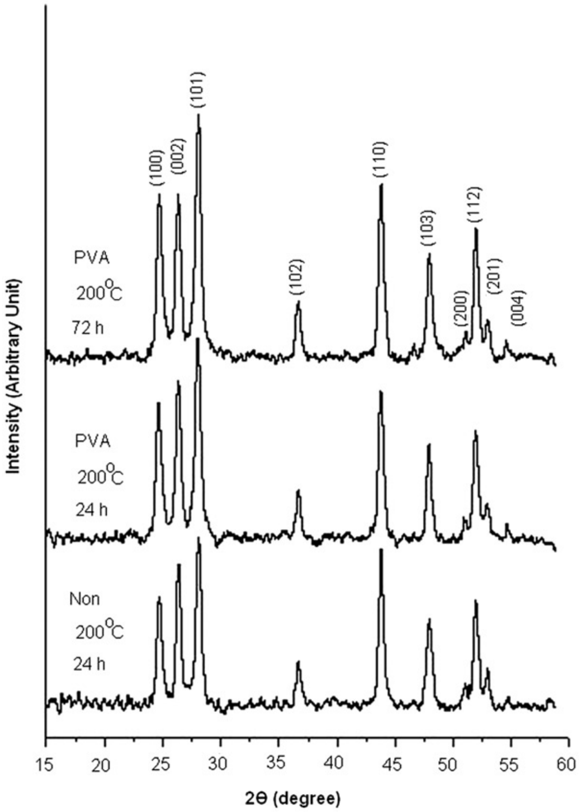

Figure 1. XRD spectra of CdS synthesised by solvothermal method at different conditions.

PVA, 200°C and 72 h, its lattice parameters were calculated using plane-spacing equation for hexagonal structure and Bragg's law for diffraction [16]. They are $a = 4.1380\,\text{Å}$ and $c = 6.7398\,\text{Å}$ which are very close to the standard values. The c/a ratio of the product is 1.6288 which is higher than that of the standard ($c/a = 1.6228$) [15]. It may ascribe as the preferential growth along the c-axis. The results are in accordance with those characterised by Raman spectroscopy and transmission electron microscopy.

Raman spectroscopy of a semiconductor is a fast characterisation to appreciate crystalline qualities, including surface condition and homogeneity. Crystalline product presents sharp Raman peaks. But for amorphous or polycrystalline materials, their Raman peaks are very broad. The hexagonal wurtzite CdS has C_{6v}^4 space group. Its Raman actives are $1A_1 + 1E_1 + 2E_2$ (E_{2H} and E_{2L}) while $2B_2$ modes are silent. For the A_1 branch, the phonon polarisation is in the z direction. But the doubly degenerate E_1 and E_2 branches, the phonon polarisations are in the x–y plane. Because the wurtzite structure is noncentrosymmetric, both A_1 and E_1 modes split into longitudinal optical (LO) and transverse optical (TO) components [1,4]. Raman spectra of the products (Figure 2) show the same position of 1LO and 2LO of A_1 mode at 299.36 and 600.72 cm^{-1}, which are polarised in the x–z face and strongly couple to the excitation along c-axis. The intensity of 1LO mode is still stronger than that of 2LO when the length of CdS nanowire

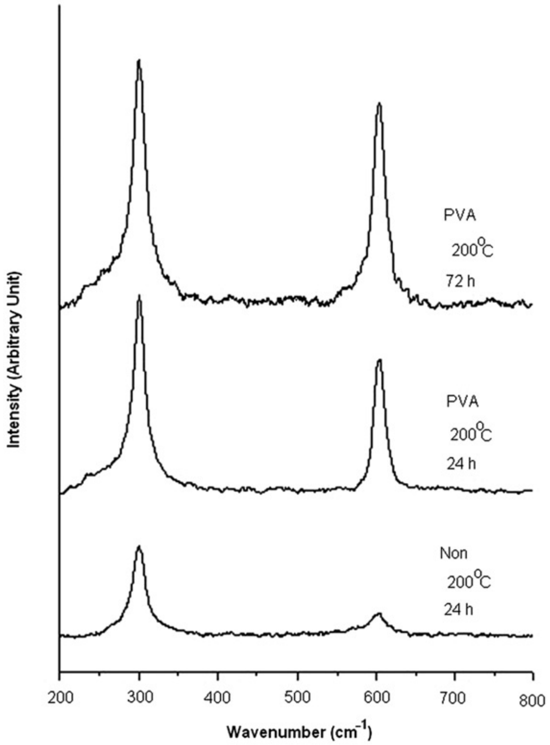

Figure 2. Raman spectra of CdS synthesised by solvothermal method at different conditions.

was increased. The exciton-LO phonon coupling in 1D semiconductor nanostructure was greatly strengthened, caused by the phonon confinement in the transverse directions and the transition of the elementary excitation (carrier, exciton, and phonon) in the longitudinal direction [4].

Morphologies of the products were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images are shown in Figure 3. CdS synthesised in PVA-free solution at 200°C for 24 h is shown in Figure 3(a), and the product is the nanorod structure. The formation of CdS nanorods can be explained below. Ethylenediamine (en) is a strongly bidentate ligand to coordinate with Cd^{2+} and reacted with sulfur powder to synthesise Cd^{2+} complex and H_2S.

$$Cd^{2+} + 2en \rightarrow Cd(en)_2^{2+}$$

$$S_n + 2NH_2CH_2CH_2NH_2 \rightarrow [NH_2CH_2CH_2NH\text{-}S_{n-1} - NHCH_2CH_2NH_2] + H_2S.$$

Finally, CdS nanorods nucleated and grew by the following reaction

$$Cd(en)_m^{2+} + S^{2-} \leftrightarrow CdS(en)_m \leftrightarrow CdS(en)_{m-n} + n(en).$$

The slow release rate of S^{2-} ion as a precursor to form complex with en and also has a relatively weak intermolecular coordinating to Cd^{2+} ion ($\log \beta_2 = 10.09$, and β_2 is a constant of the complex ion $Cd(en)_2^{2+}$). The reaction rate is relatively slow which can play

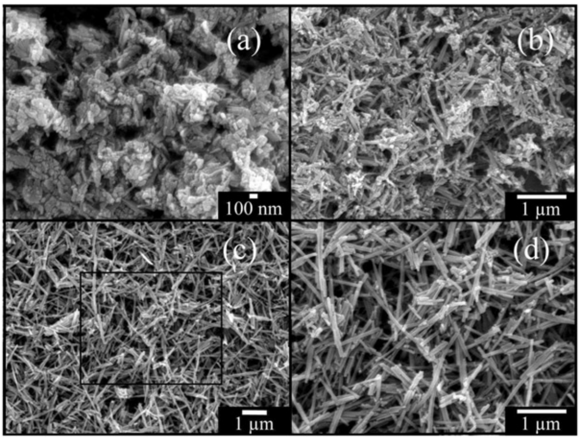

Figure 3. SEM images of CdS synthesised by solvothermal method. (a) 200 °C and 24 h in PVA-free solution, (b) 200 °C and 24 h in PVA-added solution, and (c) and (d) 200 °C and 72 h in PVA-added solution.

the role in the crystal growth towards rod-like structure [12,17]. After adding PVA as a capping agent at the same condition, the length of CdS nanorods was increased by 1–2 μm because PVA has stronger interaction with the side faces of CdS nanorods than with their ends along *c*-axis. Therefore, PVA inhibited the growth of side faces by capping them heavily, in comparison to the faces with less capping by PVA remaining as highly active to the continuous growth [18]. When the reaction time was prolonged to 72 h, the length of CdS nanorods was increased to several micrometre, but diameter showed only a little change. Therefore, PVA and reaction time have the influence on 1D growth of CdS nanorods.

TEM images of CdS nanorods synthesised in a solution of PVA at 200°C for 24 h are shown in Figure 4. CdS nanorods show the diameter around 20 nm and the length around 100–600 nm. SAED patterns in areas 1 and 2 indicated the single crystal of CdS nanorods with [−110] as zone axis. Electron diffraction was simulated using CaRIne Crystallography version 3.1 with [−110] zone axis as shown in Figure 4(f). HRTEM images of Figures 4(b) and (d) in areas 1 and 2 (Figure 4(a)) show lattice fringes which the planes are perpendicular and parallel to the nanorods with the spaces of 3.36 and 2.07 Å, respectively. They are in consistent with those of (002) and (100) planes of wurtzite CdS. SAED patterns and HRTEM images results demonstrated that the product is CdS nanorods with their growth in [001] direction [7,12].

When the reaction time was prolonged to 72 h, TEM images are shown in Figure 5. The diameter and length of CdS nanorods were increased to 30 nm and 0.2–3 μm as shown in Figure 5(a). The increase of the reaction time mainly leads to an increase in the elongation of CdS nanorods. The crystal plane space in areas 3 and 4 (Figure 5(b)), shown in Figures 5(d) and (e), were calculated to be 3.52 Å, corresponding to the space of (002) plane of wurtzite CdS. SAED patterns in areas 3 and 5 as shown in Figures 5(c) and (f), they can be indexed as [−110] zone axis. They indicated that the product is CdS nanorods with the growth along [001] direction in the same manner as those synthesised in the solution of PVA at 200°C for 24 h. The present results show that the anisotropic rod

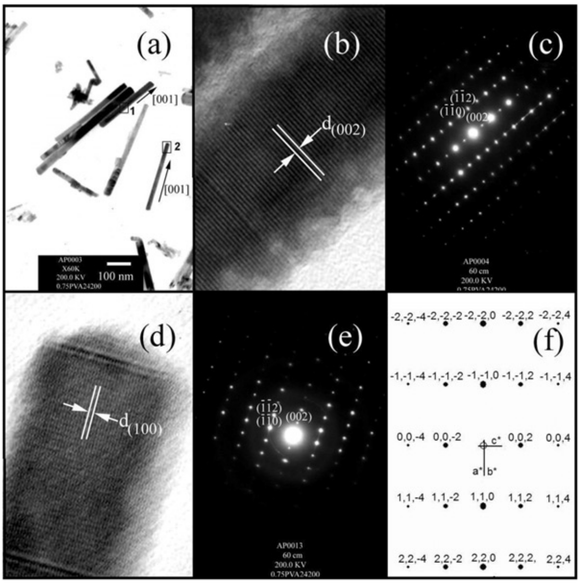

Figure 4. (a) TEM images of CdS synthesised in PVA-added solution at 200 °C for 24 h, (b) and (c) HRTEM image and SAED pattern of area 1, (d) and (e) HRTEM image and SAED pattern of area 2, and (f) electron diffraction simulation for [−110] zone axis.

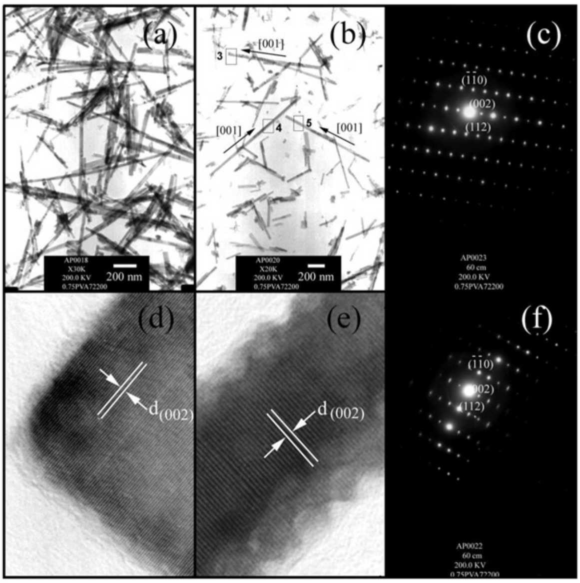

Figure 5. (a) and (b) TEM images of CdS synthesised in PVA-added solution at 200 °C for 72 h, (c) and (d) SAED pattern and HRTEM image of area 3, (e) HRTEM image of area 4, and (f) SAED pattern of area 5.

growth of hexagonal wurtzite semiconductor was driven by surface energy effect. In general, the surface energy of (001) face of wurtzite structure is much larger than those of other faces, such as (100) and (110) due to the high packing density and a large of under-coordinated atoms of the (001) face. Growth rate along the [001] direction is much faster, comparing to other directions, which finally results in progressive elongation along [001] direction of the nanocrystals and formation of 1D rod structures [19].

The elemental composition of single CdS nanorod was determined using energy disperse X-ray (EDX) analyzer. It displays cadmium $L\alpha_1$, $L\beta_1$ and $L\beta_2$ at 3.13, 3.31 and 3.53 keV peaks, respectively, and sulfur $K\alpha_1$ at 2.30 keV peak. The quantification calculation showed that the atomic ratio of Cd: S is 50.20 : 49.80, indicating that the as-prepared nanorod is exactly CdS.

4. Conclusions

One-dimensional cadmium sulfide nanorods have been synthesised by solvothermal method using cadmium nitrate and sulfur powder as starting materials and PVA as a capping agent in ethylenediamine as a solvent at 200 °C for 24 and 72 h. Comparing the morphologies of hexagonal wurtzite CdS nanorods, the length of nanorods in PVA-added solution were longer than those in PVA-free solution. The results indicated that PVA, a capping agent, played an important role in 1D growth of CdS nanorods. SAED patterns and HRTEM images showed that growth direction of wurtzite CdS nanorods is along [001] direction.

Acknowledgements

We are very grateful to the Thailand Research Fund and Commission on Higher Education for supporting the research, and the Graduate School of Chiang Mai University for general funding.

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