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Solvothermal synthesis of CdS nanorods using poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) as a capping agent in ethylenediamine solvent

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ABSTRACT

One-dimension (1D) cadmium sulfide (CdS) nanorods were successfully synthesized using cadmium nitrate ($Cd(NO_3)_2$) and thiourea (NH_2CSNH_2) as starting materials and poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) as a capping agent in ethylenediamine as a solvent by solvothermal reaction at 200 °C for 24 and 72 h. The phase, morphology, atomic vibration and optical property of the products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and UV–visible spectroscopy. In the present research, the products were wurtzite hexagonal CdS nanorods growing along the [001] direction, with the 1LO and 2LO vibration modes at 298 and 597 cm^{-1} and the absorption peak centered at 486 nm.

1. Introduction

One-dimensional (1D) nanostructured materials, such as nanowires, nanorods and nanotubes, which have anisotropic geometries and unique physical properties are highly potential application for a number of technologies [1–3]. CdS, one of the most advantaged direct band-gap II–VI semiconductors, has stimulated intensive interest due to its wide applications in photoelectronic conversion for solar cells, optoelectronics, light-emitting diodes and photocatalyst. It is one of the most important materials with a wide band gap of 2.5 eV for the bulk hexagonal wurtzite structure, and 3.53 eV for bulk cubic zinc blende structure [4–7]. It has been synthesized by both physical and chemical methods, including solvothermal [6], cyclic microwave radiation [7], electrochemical synthesis [8] and chemical vapor deposition [9].

Previously, 1D CdS was synthesized by solvothermal method using polymer-added solutions such as polyvinyl alcohol (PVA) [10], polyethylene glycol (PEG) [11] and polyvinyl pyrrolidone (PVP) [12] to improve the length and diameter. For the present research, 1D CdS nanostructure was synthesized by solvothermal method using ethylenediamine as a solvent and poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) as a capping agent, and compared with the non-capping solvothermal condition.

2. Experimental procedure

To synthesize CdS nanostructure, 0.005 mol of $Cd(NO_3)_2$ and NH_2CSNH_2 as cadmium and sulfur sources each was mixed in 50 ml ethylenediamine (en), and followed by 0.5 g poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) as a capping polymer adding. The mixture solution was transferred in a Teflon container and put in a home-made stainless steel autoclave, which was tightly closed, heated in an electric oven at 200 °C for 24 h, and cooled to room temperature. The 200 °C solvothermal processes were also done for two more solutions with and without polymer adding for 72 and 24 h, respectively. Finally, yellow precipitates were produced, collected, washed with distilled water and absolute ethanol for several times and dried at 80 °C for 24 h.

The products were analyzed by X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV 15 mA, and using Cu-K_α line of a copper target with the scanning angle 2θ ranging from 15 to 60°. Raman spectrometer (T64000 HORIBA Jobin Yvon) was operated by a 50 mW and 514.5 nm wavelength Ar green laser. SEM images were taken through a scanning electron microscope (SEM, JEOL JSM-6335F) operating at 15 kV, equipped with an energy dispersive X-ray analyzer (EDX, Oxford Instruments). TEM and HRTEM images of the products were taken on a transmission electron microscope (TEM, JEOL JEM-2010) using LaB_6 electron gun with an accelerating voltage of 200 kV. The samples used for TEM analysis were prepared by sonicating of dried products in absolute ethanol for 15 min and followed by putting 3–5 drops of the suspensions on carbon-coated copper grids. A room temperature absorption spectrum was carried out

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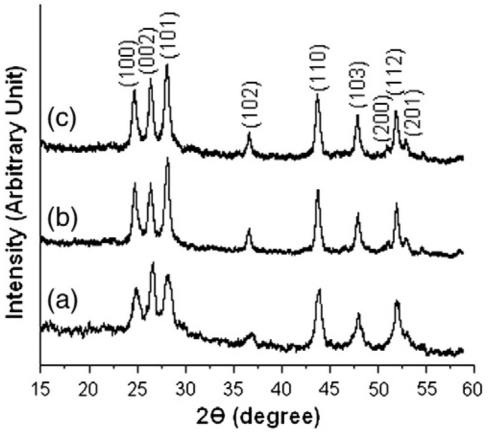

Fig. 1. XRD patterns of CdS synthesized by the 200 °C solvothermal reaction of different solutions and lengths of time: (a) polymer-free for 24 h, (b) polymer-added for 24 h and (c) polymer-added for 72 h.

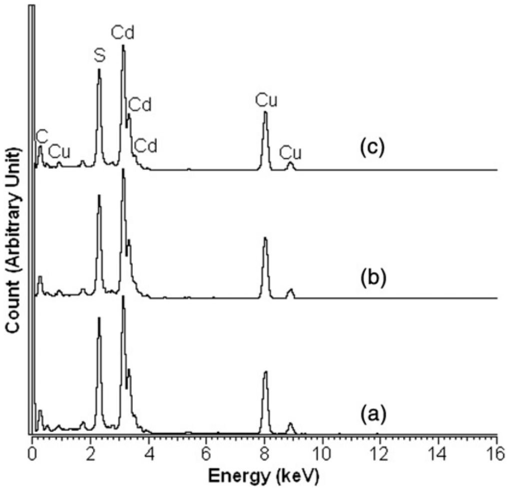

Fig. 3. EDX spectra of CdS synthesized by the 200 °C solvothermal reaction of different solutions and lengths of time: (a) polymer-free for 24 h, (b) polymer-added for 24 h and (c) polymer-added for 72 h.

on a Perkin Elmer Lambda 25 UV–visible spectrometer with the resolution of 1 nm in the wavelength range of 250–800 nm.

3. Results and discussion

XRD patterns of the as-synthesized samples prepared by solvothermal method at different conditions are shown in Fig. 1. All the diffraction peaks can be indexed to be hexagonal CdS phase, in agreement with the JCPDS no. 41-1049 [13] (a = b = 4.1409 Å and c = 6.7198 Å). No impurities such as CdO, S, and $Cd(OH)_2$ were detected. In the present research, the products were very high purity. The lattice parameters of hexagonal CdS structure of polymer-added at 200 °C for 72 h were calculated using plane-spacing equation for hexagonal structure and Bragg's law for diffraction [14]. They were a = b = 4.1395 Å and c = 6.7356 Å and were very close to the standard values. It should be noted that the c/a ratio and intensity percent of the (002) plane of the experiment were higher than those of the standard, implying that the product has preferential growth along the c axis.

The degree of c-orientation of CdS nanorods was illustrated by the relative texture coefficient [15–17], given by

$$TC_{002} = \frac{(I_{002}/I^{\circ}_{002})}{[I_{002}/I^{\circ}_{002} + I_{101}/I^{\circ}_{101}]}$$

where TC_{002} was the relative texture coefficient for diffraction peaks of (002) over (101). I_{002} and I_{101} were the experimental diffraction intensities of the (002) and (101) peaks, including I°_{002} and I°_{101} were the corresponding values of the standard measured from the randomly oriented particles. The texture coefficient of CdS with random crystallographic orientations is 0.5. TC_{002} of CdS with polymer-added at 200 °C for 72 h was 0.53, showing the product growth along the c-axis with low c-orientation.

Morphologies of the products were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images of the products are showed in Fig. 2. It should be noted that the as-synthesized CdS sample for polymer-free at 200 °C for 24 h was spherical nanoparticles with the size of 20 nm approximately. For the solvothermal reaction at 200 °C for 24 h of the polymer-added solution, morphologies of the as-synthesized CdS sample became nanorods with the length of 100–200 nm and diameter of 20–50 nm approximately, and a little amount of spherical nanoparticles. The whole CdS nanorods were synthesized by prolonging the solvothermal reaction time to 72 h. Their length and diameter were 1000 nm and 20–60 nm, respectively. It can be concluded that the poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) and reaction time have the influence on the formation and elongation of 1D CdS nanorods. The qualitative and quantitative analyses of the as-prepared CdS samples were analyzed by EDX (Fig. 3), which revealed the presence of only Cd and S as the elementary components of the products. The molar ratios of Cd to S obtained from the peak areas were very close to that of the stoichiometric CdS of 1:1 by mole. The Cu and C peaks of the copper stubs and carbon tapes were also detected.

TEM images of the products are showed in Fig 4. The TEM image and SAED pattern of CdS for polymer-free (Fig. 4a) presented mixed-morphologies of nanoparticles and nanorods with the ring pattern, confirming the product of different orientation particles. These rings were indexed to be the (100), (002), (101), (102), (110), (103) and (200) planes, corresponding to those of the standard [13]. When the polymer was added to the solution at 200 °C 24 h (Fig. 4b), CdS

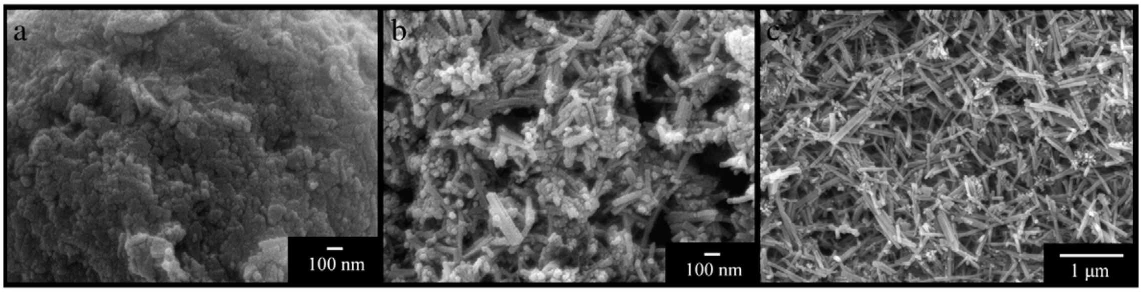

Fig. 2. SEM images of CdS synthesized by the 200 °C solvothermal reaction of different solutions and lengths of time: (a) polymer-free for 24 h, (b) polymer-added for 24 h and (c) polymer-added for 72 h.