

CHARACTERIZATION OF MULTIPOD CADMIUM SULFIDE NANOSTRUCTURES SYNTHESIZED BY AMINETHERMAL METHOD

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Multipod (monopod, bipod, tripod and tetrapod) CdS nanostructures have been successfully synthesized under aminothermal method at 200 °C for 10 h without using any templates and surfactants. The product was characterized by X-ray diffraction (XRD), Raman spectroscopy, fast Fourier transformation (FFT), transmission electron microscopy (TEM), and high resolution TEM (HRTEM). XRD pattern shows wurtzite CdS structure. Its Raman spectrum respectively shows the LO₁ and LO₂ of A₁ vibration mode at 300 and 601 cm⁻¹, which are polarized in the x-z face, and strongly couple to the excitons along the c axis. The structures of multipod CdS were characterized using TEM and HRTEM.

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1. Introduction

Nanoscale inorganic materials have been widely studied, due to their wide range of different technological applications: composite materials, chemical sensing materials, biomedicine, optoelectronics and nanoelectronics. They are very interesting materials, due to their special characteristics which are different from the corresponding bulks. Recently, the polymorphic shapes of IV-IV, III-V and II-VI semiconductors show higher efficient in the properties than their one dimensional structure [1-4]. For example, CdTe tetrapod nanocrystals can potentially lead to a variety of interesting mechanical, electrical and optical properties, and display higher degree of solubility comparing to the separate rods with the same length and diameter [4]. However, the synthesis of polymorphic inorganic materials is unpredictable and difficult to understand. Cheon et al [2], who synthesized CdS nanorods, nanobipods, nanotripods and nanotetrapods using a monosurfactant system under atmospheric standard condition, found that the shapes of CdS nanocrystallines were controlled by simple varying either the growth temperature or precursor concentration.

In this paper, CdS multipod (monopod, bipod, tripod and tetrapod) nanostructures were synthesized by aminothermal method, and formation of the polymorphic CdS nanostructures was investigated using TEM analysis.

2. Experiment

To synthesize CdS multipod nanostructures, 0.005 mole CdCl₂ was dissolved in 25 ml butylamine solution and stirred for 30 min at room temperature. The 1.80 ml 20 % (NH₄)₂S in water was added to cadmium solution, which was transferred into a home-made Teflon-lined stainless steel autoclave. Close it tightly and heat it up in an electric oven to 200 °C for 10 h, and finally cool it down 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.

The product was characterized by X-ray diffraction (XRD) - carried out using Cu K α radiation with the scanning 2θ angle ranging from 15° to 60° , a graphitic monochromer and a Ni filter, Raman spectroscopy with 50 mW Ar laser and 514.5 nm wavelength, transmission electron microscopy (TEM) and fast Fourier transformation (FFT).

3. Results and discussion

Fig. 1a shows an XRD pattern of the product, which was synthesized using CdCl $_2$ and (NH $_4$) $_2$ S as cadmium and sulfur sources in butylamine solution at 200 °C for 10 h. The pattern shows hexagonal CdS structure, composing of the (100), (002), (101), (110), (103) and (112) peaks - corresponding to the JCPDS no. 41-1049 [5] ($a = b = 4.1409$ Å and $c = 6.7198$ Å). Intensity of the (002) peak of the product appears as the sharpest and strongest - implying that CdS crystals preferred to orient along the c axis, and the product grew in the [002] direction [6,7]. In addition, the growth direction was further confirmed by relative texture coefficient from XRD pattern and TEM analysis.

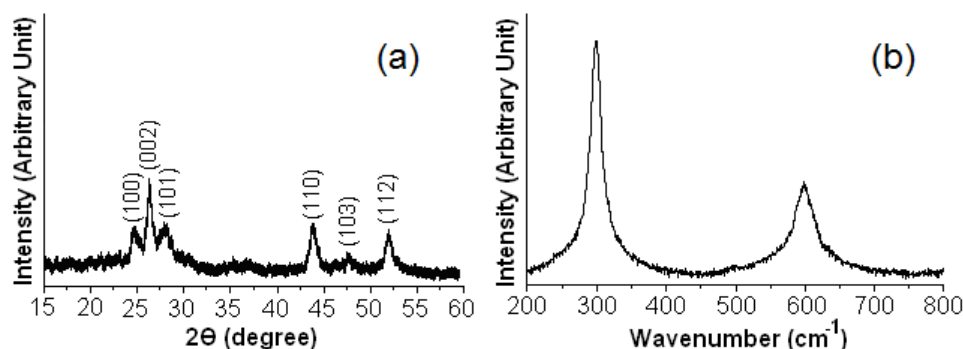


Fig. 1 (a) XRD pattern and (b) Raman spectrum of CdS synthesized by aminothermal method at 200 °C for 10 h.

The degree of the c orientation of CdS nanorods was determined using the relative texture coefficient (TC) [8,9] and preferred (P) orientation [10]. The relative texture coefficient of the (002) peak was calculated using the formula,

$$TC_{002} = \frac{(I_{002}/I^{\circ}_{002})}{[I_{002}/I^{\circ}_{002} + I_{101}/I^{\circ}_{101}]} \quad (1)$$

TC_{002} is the relative texture coefficient of the (002) over (101) diffraction peaks. I_{002} and I_{101} are the measured diffraction intensities of the (002) and (101) peaks, respectively. I°_{002} and I°_{101} are the corresponding values of the standard, measured from the randomly oriented powder. For random crystallographic orientation, the texture coefficient of CdS is 0.5. Calculated TC_{002} was 1.63, which supports growth of the nanorods along the c direction.

An estimate of the preferred orientation was determined from

$$P_{hkl} = \frac{I_{(hkl)} \sum I'_{(hkl)}}{I'_{(hkl)} \sum I_{(hkl)}} \quad (2)$$

$I_{(hkl)}$ and $I'_{(hkl)}$ refer to the integrated intensity of the experimental and random (simulated) XRD diffraction, respectively. For random orientation, P equals to 1. But for a particular CdS (hkl) plane, which has preferred orientation, P is greater than 1. The P of the (002) plane is 2.67, implying that CdS grew along the c axis.

Wurtzite CdS structure is C^4_{6v} space group material. It has four vibration modes, which are active by Raman interaction. They are $1A_1$, $1E_1$, and $2E_2$ (E_{2H} and E_{2L}). The $2B_2$ modes are silent. For the A_1 branch, the phonon polarization is in the z direction. But the doubly degenerate E_1 and

E_2 branches, the phonon polarizations are in the x-y plane. The wurtzite structure is noncentrosymmetric; therefore, both A_1 and E_1 modes split into longitudinal optical (LO) and transverse optical (TO) components. Raman spectrum of the product (Fig. 1b) respectively shows the vibrations of LO_1 and LO_2 of A_1 mode at 300 and 601 cm^{-1} , which were polarized in the x-z face, and strongly couple to the excitons along the c axis [6,7].

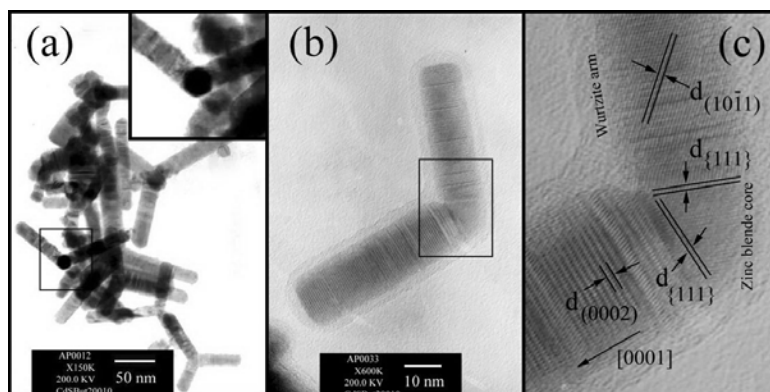


Fig. 2 TEM and HRTEM images of (a) multipod CdS, and (b, c) single bipod nanostructures synthesized by aminothermal method at $200\text{ }^\circ\text{C}$ for 10 h.

Fig. 2 shows TEM and HRTEM images of CdS nanostructures synthesized under aminothermal at $200\text{ }^\circ\text{C}$ for 10 h. The product (Fig. 2a) is mainly composed of bipods, tripods, tetrapods (more than 90%) and the less extent of monopods or monorods (less than 10%). The widths x lengths of CdS multipods are $10\text{-}15\text{ nm} \times 20\text{-}70\text{ nm}$. The high magnification at the square (inset of Fig. 2a) shows a tripod with its two arms 109.5° apart. The third appears as the hexagonal shape of the rod (pod, arm), and is at right angle to the plane through the two arms. The TEM image of a single bipod CdS and HRTEM image of core of CdS bipod are shown in Fig. 2b and c. The bipod structure shows the regular wurtzite CdS with perfect tetrahedral symmetry – composing of two crystalline pods (arms) of the (10-11) and (0002) hexagonal planes. Each of the CdS bipods is 12 nm wide and 25 nm long. HRTEM image shows the detail structure of CdS bipod. These indicate that the crystalline bipod was composed of a zinc blende core, and epitaxially grown wurtzite arms. The lattice fringe shows two families of the $\{111\}$ faces of zinc blende structure triangular core with its angle of 60° , and the wurtzite CdS arms grown on families of the $\{111\}$ faces of zinc blende CdS core along the $[0001]$ direction [2-4].

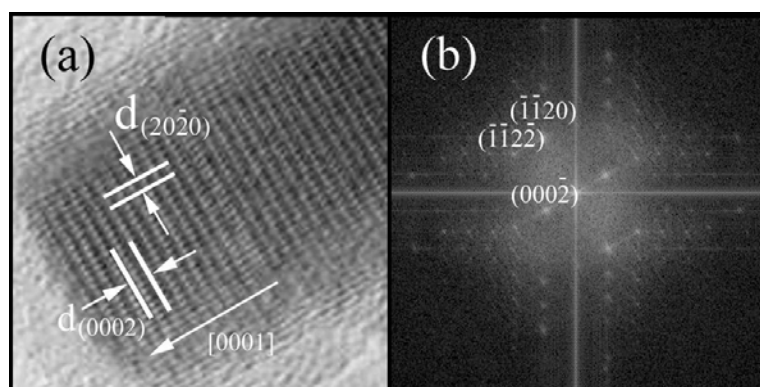


Fig. 3. (a) HRTEM image and (b) FFT pattern of the lower arm of the bipod in Fig. 2b.

Fig. 3 shows HRTEM image and fast Fourier transformation (FFT) pattern characterized on the lower arm of the bipod in Fig. 2b. The lattice planes are both at right angle and parallel to the arm of the bipod with the spaces of 3.36 \AA and 2.07 \AA , corresponding to the (0002) and (20-20) planes of wurtzite CdS hexagonal structure, respectively. Growth direction of the arm of bipod wurtzite CdS hexagonal structure indicates that the bipod structure extends along the $[0001]$

direction, in accordance with the previous report [2-4]. The fast Fourier transformation (FFT) pattern of CdS was specified as wurtzite CdS structure with zone axis in the [-1100] direction. The TEM analysis concluded that the multipod CdS structures were composed of the zinc blende CdS cores and the wurtzite CdS arms grew on the (111) faces of zinc blende CdS cores along the [0001] direction [2-4].

4. Conclusions

Multipod CdS nanostructures have been successfully synthesized under aminothermal method at 200 °C for 10 h. XRD pattern shows the hexagonal CdS structure corresponding to the JCPDS standard. Its Raman spectrum shows the vibration of LO₁ and LO₂ at 300 and 601 cm⁻¹, respectively. The TEM images present the multipods of CdS nanostructures, which were composed of zinc blende CdS cores and wurtzite CdS arms growing on the (111) faces of zinc blende CdS cores in the [0001] direction.

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