

Synthesis of Tapered CdS Nanobelts and CdSe Nanowires with Good Optical Property by Hydrogen-Assisted Thermal Evaporation

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Abstract The tapered CdS nanobelts and CdSe nanowires were prepared by hydrogen-assisted thermal evaporation method. Different supersaturation leads to two different kinds of 1D nanostructures. The PL measurements recorded from the as-prepared tapered CdS nanobelts and CdSe nanowires show only a bandgap emission with relatively narrow full-width half maximum, which means that they possess good optical property. The as-synthesized high-quality tapered CdS nanobelts and CdSe nanowires may be excellent building blocks for photonic devices.

Keywords Nanomaterials · II-VI semiconductors · Chemical vapor deposition · Vapor–liquid–solid · Photoluminescence

Introduction

One-dimensional (1D) nanostructures such as nanowires, nanorods, nanobelts, and nanotubes have become the focus

of intensive research owing to their novel physical properties and applications in the fabrication of nanoscale devices [1]. In particular, considerable efforts have been made to synthesize 1D II-VI semiconductors and investigate their electronic and optical properties because of their wide applications in optoelectronic devices, such as lasers [2, 3]. In order to achieve their full potential in optical applications, it is essential to prepare 1D II-VI semiconductors, which possess predominantly bandgap emission without defect-related emission, namely good optical property [4]. In principle, the optical property can vary with the growth process, i.e., it is condition dependent and process dependent [5]. For example, Barillet et al. [6] reported that CdS nanowires, synthesized by thermal decomposition of the single-source molecular precursors via the vapor–liquid–solid (VLS), possessed only a bandgap emission. Defect-related emission (750 nm) appeared in the PL spectra of CdS nanobelts and nanowires prepared by direct reaction of Cd and S and thermal evaporation of CdS, respectively [7, 8]. The photoluminescence (PL) spectrum of 1D CdS nanostructures synthesized with solvothermal route consisted of bandgap and defect-related emission [5, 9–11]. This may be attributed to that the relatively bad crystallinity is commonly achieved in solvothermal method [12]. That is, it is still a challenge to develop synthetic methods to prepare 1D II-VI semiconductors with high-quality optical property.

In this paper, we utilize the hydrogen-assisted thermal evaporation method, with which Jiang et al. [13] synthesized ZnS nanoribbons on a large scale, to prepare CdS and CdSe 1D nanostructures based on VLS process. The PL measurements recorded from the as-synthesized tapered CdS nanobelts and CdSe nanowires show only a bandgap emission, which means they possess high-quality optical property.

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Experimental Details

For the synthesis of tapered CdS nanobelts, CdS powders (Strem Chemicals, 99.999%) placed in a ceramic boat was put at the center of a quartz tube, which was inserted into a horizontal tube furnace. The silicon wafer coated with ~2 nm Au film was perpendicularly placed on the other ceramic boat located downstream, 10 cm away from the source material. Prior to heating, high-purity Ar was introduced into the quartz tube to purge the air inside for 60 min. After that, a carrier gas of high-purity Ar mixed with 5% H₂ was kept flowing at a rate of 60 sccm (standard cubic centimeter per minute). The furnace was heated to 800 °C with a heating rate of 100 °C min⁻¹ and maintained at this temperature for 40 min. Then, the furnace was cooled down to room temperature slowly (~5 °C min⁻¹). CdSe nanowires were synthesized through the same procedure by using CdSe powders (Strem Chemicals, 99.999%) as source material and the source zone temperature of 650 °C.

Samples collected from the silicon substrates were characterized by a field-emission scanning electron microscopy (FE-SEM, Sirion 200), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), and X-ray diffraction (XRD, Philips X'pert PRO).

Photoluminescence (PL) measurements were conducted at room temperature with a He–Cd laser using 325 nm and 514.5 nm as excitation source for CdS nanobelts and CdSe nanowires, respectively.

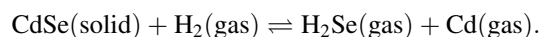
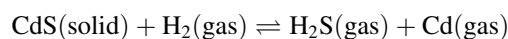
Results and Discussion

Figure 1a shows a FE-SEM image of as-synthesized tapered CdS nanobelts. These nanobelts have the thickness of 20–40 nm, the base width of 2–5 μm, and the length of 10–30 μm and possess triangle morphology. They have smooth surfaces, and their width reduces sharply with the increase of length. Figure 1b shows a FE-SEM image of the CdSe nanowires. These nanowires have diameter of ~100 nm and length of 10–20 μm. Figure 1c, d shows the X-ray diffraction (XRD) patterns of CdS nanobelts and CdSe nanowires, respectively. They are both of hexagonal wurtzite structure, which correspond to respective bulk wurtzite CdS (JCPDS 77-2306) and CdSe (JCPDS 77-2307) crystals.

Microstructure analysis of the samples was carried out with TEM. The Au particles were found atop the tapered CdS nanobelts, as shown in Fig. 2a. The HRTEM image of the CdS nanobelt was shown in Fig. 2b, and the lattice spacings are about 0.68 nm and 0.36 nm, which agree with the (0001) and (01–10) lattice planes of CdS, respectively.

The HRTEM image shows that the tapered CdS nanobelts possess good crystallinity. From the TEM image of CdSe nanowire in Fig. 3a, Au particle can be observed at the end of the nanowire. In the HRTEM in Fig. 3b of the CdSe nanowire, the lattice spacings are about 0.36 nm and 0.16 nm, which agree with the (0002) and (21–10) lattice planes, respectively. The HRTEM image suggests that the prepared CdSe nanowires have good crystallinity. The good crystallinity of tapered CdS nanobelts and CdSe nanowires may enable that they possess high-quality optical property.

Similar to the work of Jiang et al. [13], the growth process can be understood as following:



In source zone with high temperature, the oxidation–reduction reaction between CdS (CdSe) and H₂ forms H₂S (H₂Se) gas and Cd gas, which are transported to deposition zone with lower temperature where they react with each other and form CdS (CdSe) and H₂. After heating for 40 min, CdS exhausts and most CdSe remains, which means the reaction between CdS and H₂ is rapid while the one between CdSe and H₂ is slow.

The presence of Au particle on the tip of CdS nanobelt (Fig. 2a) and CdSe nanowire (Fig. 3a) illuminate that the growth process includes VLS mechanism [14–20]. For the formation of CdSe nanowires, CdSe vapor was deposited onto liquid Au particles in the initial stage. When the dissolution of CdSe in the Au particles became supersaturated, CdSe nanowires extruded from the liquid Au catalysts and precipitated at the liquid–solid interface. In this process, a liquid cluster of metal catalyst provides energetically favored sites for the absorption of gas-phase reactants, and sizes of the catalysts are considered to be responsible for the resultant diameters of nanowires. In our experiment, the low supersaturation due to the slow reaction between CdSe and H₂ favors the 1D nucleation [21, 22], and the CdSe nanowire growth proceeds by VLS mechanism. While the rapid reaction between CdS and H₂ produces very large vapor pressure of CdS gas in source zone and high supersaturation in deposition zone, which makes for 2-dimensional nucleation [21, 22]. Besides the metal catalyst, the side surface of the CdS nanobelts formed previously may become the preferred nucleation site for CdS growth. So the CdS nanobelt growth proceeds by VLS mechanism in axial direction and vapor–solid mechanism in lateral direction, which is similar to the prior reports [23–25]. As a result, the nanobelt's width increases gradually along the axial direction starting from the contact region between liquid Au nanoparticle and CdS, i.e., the tapered CdS nanobelts form.

Fig. 1 SEM images of tapered CdS nanobelts (a) and CdSe nanowires (b), respectively. XRD patterns of tapered CdS nanobelts (c) and CdSe nanowires (d), respectively

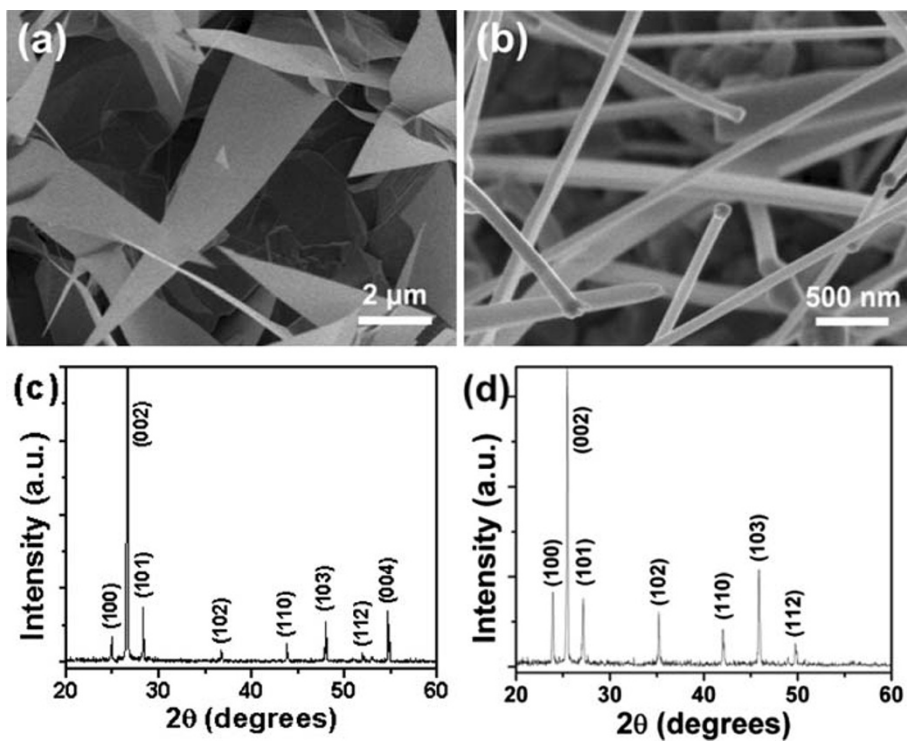


Fig. 2 TEM (a) and HRTEM (b) image of a single tapered CdS nanobelt

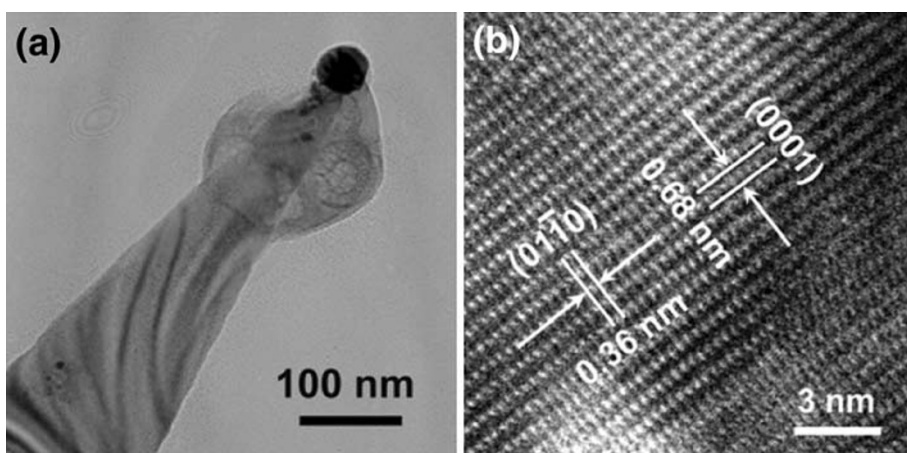
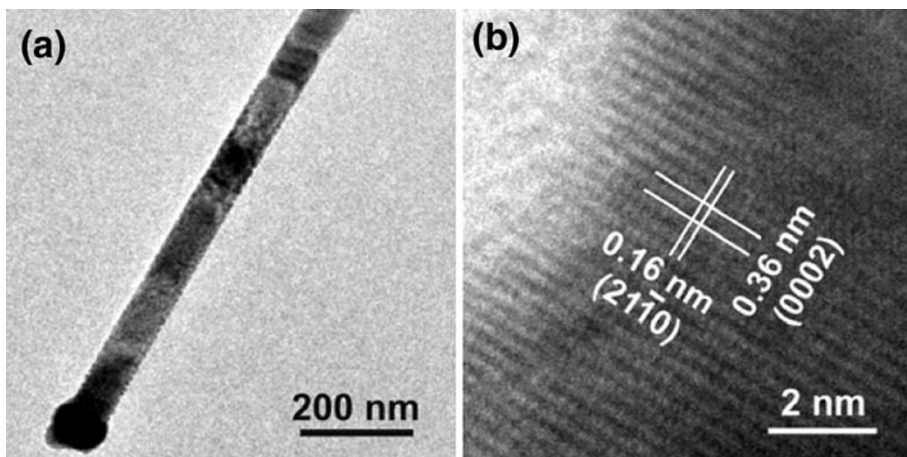


Fig. 3 TEM (a) and HRTEM (b) image of a single CdSe nanowire



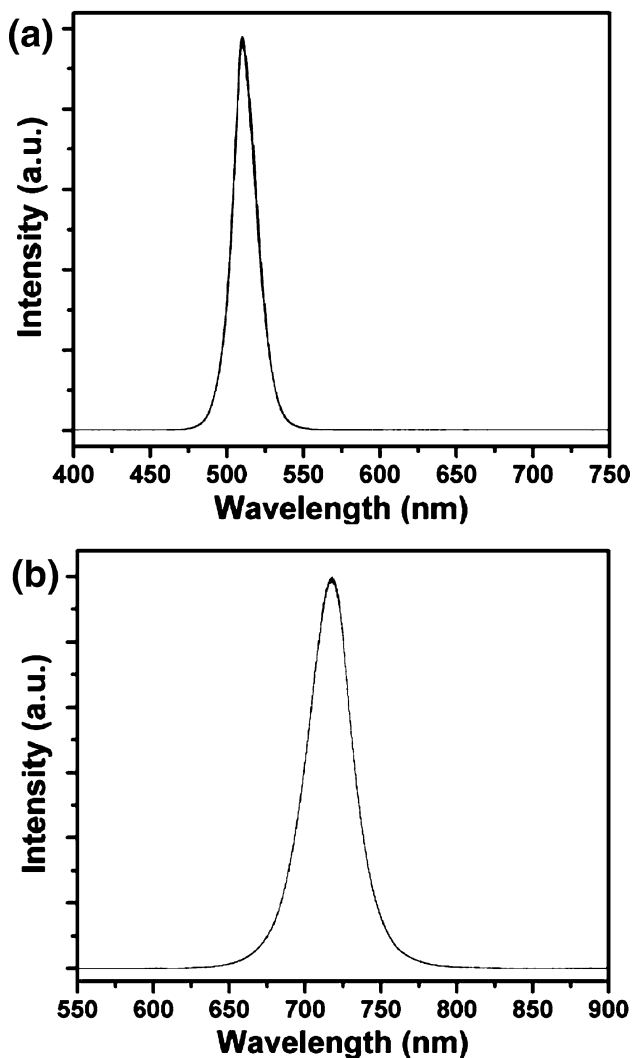


Fig. 4 PL spectra of tapered CdS nanobelts (a) and CdSe nanowires (b), respectively. PL measurements were conducted at room temperature with a He–Cd laser using 325 nm and 514.5 nm as excitation source for CdS nanobelts and CdSe nanowires, respectively

The optical properties of tapered CdS nanobelts and CdSe nanowires were studied by PL at room temperature. Figure 4a, b shows the PL spectra of CdS nanobelts and CdSe nanowires, recorded with 325 nm and 514.5 nm excitation, respectively. The spectrum of CdS nanobelts shows only a single peak centered at 510 nm with narrow full-width half maximum (fwhm) of 20 nm. The peak can be attributed to the band gap emission, because the peak position is very near the band gap of CdS (2.47 eV) at room temperature [26, 27]. The relatively narrow fwhm and absence of defect-related emission demonstrate that the tapered CdS nanobelts, synthesized by hydrogen-assisted thermal evaporation in this work, possess high-quality optical property. Wang et al. [8] reported that only a defect-related emission (750 nm) could be observed in PL spectrum of CdS nanowires, synthesized by thermal

evaporation of CdS powders based on VLS mechanism. In previous works [28, 29], the defect-related emission was considered to originate from the sulfur vacancies V_s^+ . Without hydrogen, sulfur in CdS may be oxidized by the residual oxygen in the furnace [30, 31], and consequently many V_s^+ exist in the CdS samples, which results in the defect-related emission. While in the reductive ambience with the addition of hydrogen, sulfur in CdS may be prevented to oxidize, and V_s^+ in the CdS samples may decrease and even disappear. Therefore, we think that the addition of hydrogen should be critical to obtain the excellent optical property of tapered CdS nanobelts in this work. In Fig. 4b, the spectrum of CdSe nanowires shows a single peak centered at 717 nm with fwhm of 31 nm, which is attributed to the band gap emission (1.74 eV at room temperature). The tapered CdS nanobelts and CdSe nanowires with high-quality optical property should be good building blocks for photonic devices.

Conclusions

In summary, tapered CdS nanobelts and CdSe nanowires were prepared by hydrogen-assisted thermal evaporation method. Tapered CdS nanobelt growth process includes VLS mechanism in axial direction and vapor–solid mechanism in lateral direction under high supersaturation. CdSe nanowires growth proceeds by VLS mechanism under low supersaturation. The PL measurements recorded from the as-prepared CdS and CdSe 1D nanostructures show only a bandgap emission with relatively narrow fwhm, which means they possess high-quality optical property. The as-synthesized high-quality tapered CdS nanobelts and CdSe nanowires may be good building blocks for photonic devices.

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