Preparation of cadmium selenide nanowires and nanotubes

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1. Introduction

The synthesis, characterization and assembly of semiconductor nanowires have been extensively investigated worldwide, because they are building blocks for fabricating functional nanoscale systems with a wide range of technological applications [1–3]. CdSe nanocrystals have demonstrated robust memory effects with potential for quantum memory applications. Light has been found to restore or even increase the conduction of a CdSe nanocrystal array [4]. CdSe nanocrystals have also been used to fabricate inorganic thin-film transistors with high field mobilities [5] and hybrid polymer solar cells with a power conversion efficiency of 6.9% for green light [6]. Here, we report on, for the first time, the synthesis of a variety of CdSe 1D nanostructures, including CdSe nanowires, nanorods, nanobelts, and nanotubes, produced via a vapor–liquid–solid growth approach. The optical properties of CdSe nanowires were examined by Raman spectroscopy.

2. Sample preparation

CdSe powders (1 μm, 99.99%) were placed in an alumina boat inside a quartz tube furnace. Silicon substrates were sputtered with a layer of Au particles (about 40 Å thick). The substrate was placed at a distance of about 15 cm from the boat and the temperature of the CdSe source was set at 850 °C – 950 °C. CdSe powders were sublimated under Ar flow at a rate of 50 - 100 sccm for 30 minutes. After deposition, CdSe nanolayers were peeled off from the substrate via ultrasonication. The morphologies and structures of the CdSe nanostructures were examined by SEM and TEM. Raman spectroscopy was employed to characterize the optical properties of the CdSe 1D nanostructures.

3. Results

Fig. 1 shows SEM images of various CdSe 1D nanostructures. We found that the CdSe nanostructures were significantly influenced by the synthetic parameters such as heating temperature, the flow rate of the carrying gas, the position of the substrate, and the synthesis time. We have prepared CdSe nanostructures under different synthetic conditions. Fig 1A shows CdSe nanowires obtained at 850 ˚C and 50 sccm Ar flow. The as-prepared CdSe nanowires have diameters in the range of 40 – 50 nanometers and lengths ranging from a few micrometers to tens of micrometers. These CdSe nanowires are curly in nature. The straight CdSe nanowires and nanorods were produced under the conditions of 900 ˚C with a flow rate of 50 sccm on a substrate covering the alumina boat (Fig. 1B). At the same temperature of 900 ˚C, when the Ar flow rate was increased to 200 sccm, we collected CdSe nanobelts / nanoribbons (Fig. 1C) on a substrate placed at a distance of 50 mm from the alumina boat. As the temperature was further increased to 950 ˚C with an Ar flow rate of 30 sccm, CdSe "nanosaw" structures were obtained on a substrate covering the alumina boat (Fig. 1D).

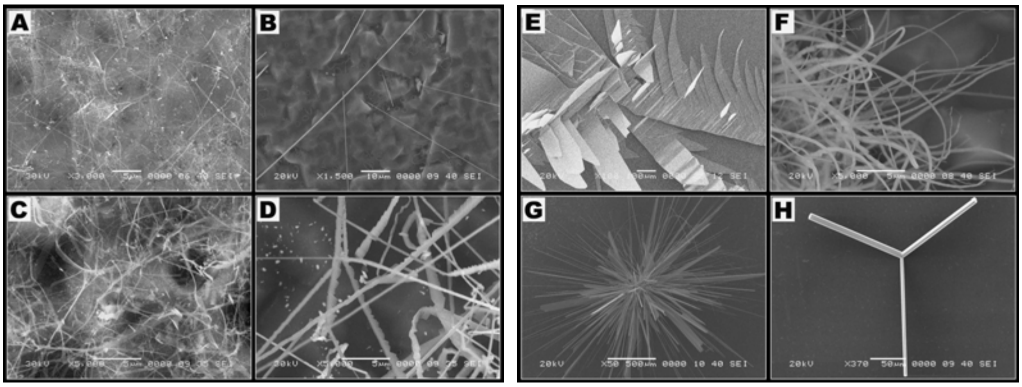

Fig. 1. SEM images of different morphologies of CdSe 1D nanostructures synthesized under various conditions: (a) 880 ˚C, 50 sccm, and substrate location: 50 mm from the Al_2O_3 boat; (b) 900 ˚C, 50 sccm, and substrate location: covering the Al_2O_3 boat; (c) 900 ˚C, 200 sccm, and substrate location: 50 mm from the Al_2O_3 boat; (d) 950 ˚C, 30 sccm, and substrate location: covering the Al_2O_3 boat; (e) 950 ˚C, 80 sccm, and substrate location: covering the Al_2O_3 boat; (f) 950 ˚C, 30 sccm, and substrate location: 60 mm from the Al_2O_3 boat; (g) 950 ˚C, 30 sccm, and substrate location: covering the Al_2O3 boat; (h) 950 ˚C, 15 sccm, and substrate location: covering the Al_2O_3 boat.

However, at the same temperature and substrate position, CdSe nanostructures resembling palm-tree leaves (Fig. 1E) were produced under the increased flow rate of 80 sccm. CdSe "nanoropes" (Fig. 1F) with diameters in the range of a few hundred nanometers were synthesized at 950 ˚C, with 30 sccm Ar flow on a substrate located at 60 mm from the alumina boat. Interestingly, CdSe flower-like structures (Fig. 1G) were obtained on a substrate covering the alumina boat under the same conditions as for Fig. 1F. When we reduced the Ar flow rate to 15 sccm, we observed a CdSe 'Y' micro-branch structure (Fig. 1H). The above SEM observations clearly demonstrate that the CdSe 1D nanostructures were dynamically influenced by the synthetic parameters.

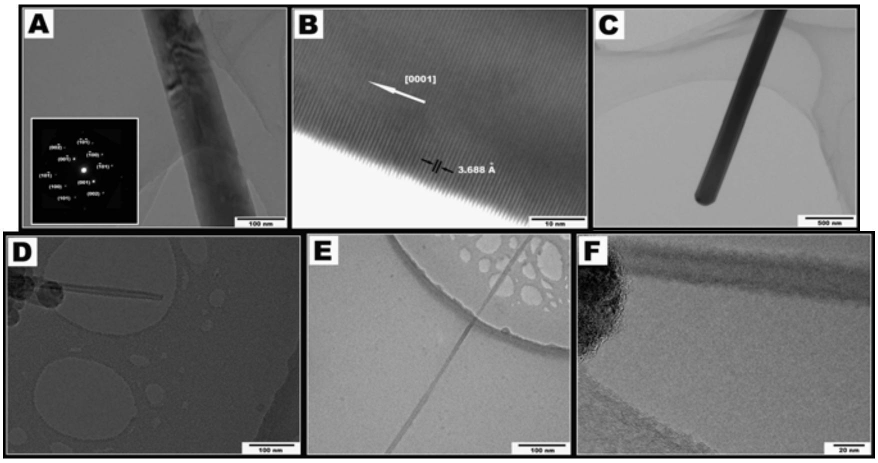

Fig. 3. Typical TEM images of CdSE 1D nanostructures: (a) a straight CdSe nanowire; (b) HRTEM lattice image of CdSe nanowire; (c) a straight CdSe nanorod; (d) a short CdSe nanotube; (e) a long and straight CdSe nanotube; (f) HRTEM image of CdSe nanotube.

Fig. 2 shows TEM images of CdSe nanowires, nanotubes and nanorods. Fig. 2A exhibits the morphology of a straight CdSe nanowire with a diameter of 50 nm. HRTEM observation can also provide insight into the structure of CdSe nanowires. Fig. 2B shows a HRTEM image of this CdSe nanowire, demonstrating the lattice details of the CdSe nanostructure. It reveals that the growth direction of the CdSe nanowire is along the <0001> direction. The fringe of the CdSe nanowire has a regular comb texture. There is no oxidation layer present at the edge of the CdSe nanowires, indicating that the CdSe nanowires are stable against oxidation. We measured the d spacing for the CdSe (100) lattice plane to be 3.688 Å. This HRTEM lattice image demonstrates that the CdSe nanowires is single crystalline in nature and free from dislocations and stacking faults. The bottom-left inset in Fig. 2A depicts a selected area electron diffraction pattern (SAED) taken on this nanowire, further confirmed the single-crystalline nature of hexagonal würtzite structure. Fig. 2C shows a straight nanorod with a diameter of 215 nm. Fig. 2D exhibits a short CdSe nanotube grown from Au nanoclusters. Fig. 2E further shows another long and straight CdSe nanotube. The detailed texture of the CdSe nanotube corresponding to Fig. 2D is shown in Fig. 2F, clearly illustrating the lattice in the edge region and the hollow core in the centre. This CdSe nanotube has an outer diameter of ~30 nm and inner diameter of ~10 nm. EDS analysis was performed on many individual CdSe nanowires, nanorods and nanotubes, showing the composition of Cd and Se with a stoichiometry ratio of 1:1.

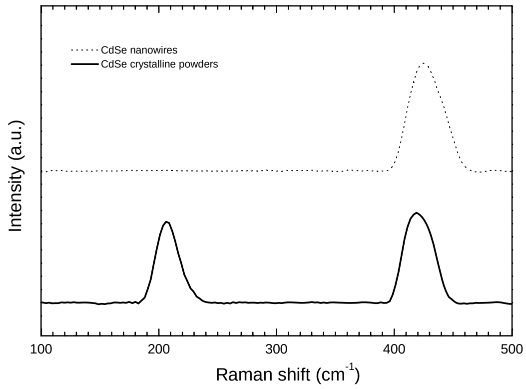

Fig. 3 Raman spectra of crystalline CdSe powders and CdSe nanowires.

Fig. 3. shows the phonon frequencies of the Longitudinal Optical (LO) and 2LO modes of CdSe at 206.2 cm^{-1} and 418.8 cm^{-1}, respectively. The corresponding Raman shift of 2LO phonons of CdSe nanowires is located at 423.9 cm^{-1}, showing an upward shift of the 2LO mode of about 5 cm^{-1}. The Raman peak of the LO mode for CdSe nanowires is very weak and almost invisible. The nanowires have much higher surface area and more surface defects than crystalline CdSe powders. This could have induced the weakening of the LO phonons and the upward shift of the 2LO modes.

Acknowledgments

This work was supported by the Australian Research Council through the ARC Discovery Project “Synthesis of nanowires and their application as nanosensors for chemical and biological detection” (DP0559891) and the ARC Centre of Excellence for Electromaterials Science.

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