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Letter

Selective growth of TiO_2 tips on CdSe nanowires

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ABSTRACT

We developed a solvothermal route to one-dimensional TiO_2–CdSe heterostructures using wurtzite CdSe nanowires and TiO_2 nanotubes as source materials. Amorphous TiO_2 nanoparticles are selectively deposited at one tip of the CdSe nanowires, resulting in the unique TiO_2 capped CdSe nanowire heterostructures. It is found that the differences of chemical reactivity among various facets are the main reason for the heterostructures. Chemical reactivity of the Se terminated $(000\bar{1})$ is most reactive, and the selective nucleation and growth of TiO_2 nanoparticles only occur on the most reactive Se-terminated $(000\bar{1})$ facets of the CdSe nanowires.

1. Introduction

As is well known, one-dimensional (1D) semiconductor-based heterostructures possess better physical and chemical properties than the homostructures because these heterostructures can modulate the intrinsic properties of the materials [1–6]. For example, depositing noble metals on the surface of semiconductors can facilitate electrons transferring out conduction band of the semiconductors after irradiation, thus further enhance photocatalytic, photosensing and photodetective properties [7,8]. Moreover, semiconductor–semiconductor heterostructures possess the enhancement of the performances of the solar cell device, catalyst and electronic conductivity because one semiconductor can pair with the other semiconductor to form heterojunction that separates the photogenerated electron–hole pairs [9–13]. Recently, selective deposition of nanoparticles at tips of semiconductor nanowires has attracted considerable attention due to their novel functionalities such as high-density data storage, enhanced activity for oxygen reduction, excellent photocatalysis and enhanced solar energy efficiency. Various heterostructures that originates from the selective deposition of metal and binary metal nanoparticles at the tips of wurtzite semiconductor nanorods have been successfully synthesized [14–19]. It was suggested that the anisotropic reactivity of the polar (0001) and $(000\bar{1})$ tips of the wurtzite nanorods resulted in special attachment of metal nanoparticles on tips of the nanorod. The difference in chemical reactivity of various facets is an important reason for the unique selective growth. In this work, we extended the mechanism to synthesize 1D TiO_2–CdSe heterostructures. The chemical composition and microstructure of the unique heterostructures were investigated, and the probable reaction mechanism was proposed.

2. Experimental

The 1D TiO_2–CdSe nanowires were synthesized by using CdSe nanowires and TiO_2 nanotubes as sources materials. First, the polar CdSe nanowires with [0001] growth direction were fabricated by a chemical vapor deposition method [20], and the TiO_2 nanotubes were synthesized by a reported hydrothermal method [21]. Then, 0.05 mmol CdSe nanowires, 0.05 mmol TiO_2 nanotubes and 40 mL ethanol solution of NaOH (0.5 M) were added in the 50 mL Telfon-lined stainless steel autoclave. The obtained mixture was conducted by ultrasonic treatment for an hour. The autoclave was then sealed and maintained at 160 °C in oven for 18 h, and then cooled to room temperature naturally. The final precipitates were filtered off and washed with ethanol and deioned water for several times, and finally stored in pure ethanol solvent for further characterization. The morphology, chemical composition and microstructure of the products were examined by scanning electron microscope (SEM, FEI XL30 S-FEG), transmission electron microscopy (TEM, Tecnai 20 at 100 kV) equipped with energy-dispersive X-ray spectroscopy (EDS) and high-resolution TEM (HRTEM, Tecnai 20 at 200 kV), respectively.

3. Results and discussion

Fig. 1a shows the TEM image of the TiO_2 products. It is found that the products exhibit 1D nanotubes morphology and the nanotubes are straight along their grown direction. The enlarged TEM image (Fig. 1b) clearly indicates the multi-wall nature of the nanotubes. The SEM image of the fresh CdSe nanowires (Fig. 1c) indicates the diameter of the nanowires range from 50 to 200 nm and the length up to tens of micrometers. Fig. 2a shows the SEM image of the CdSe nanowires treated by the solvothermal process for

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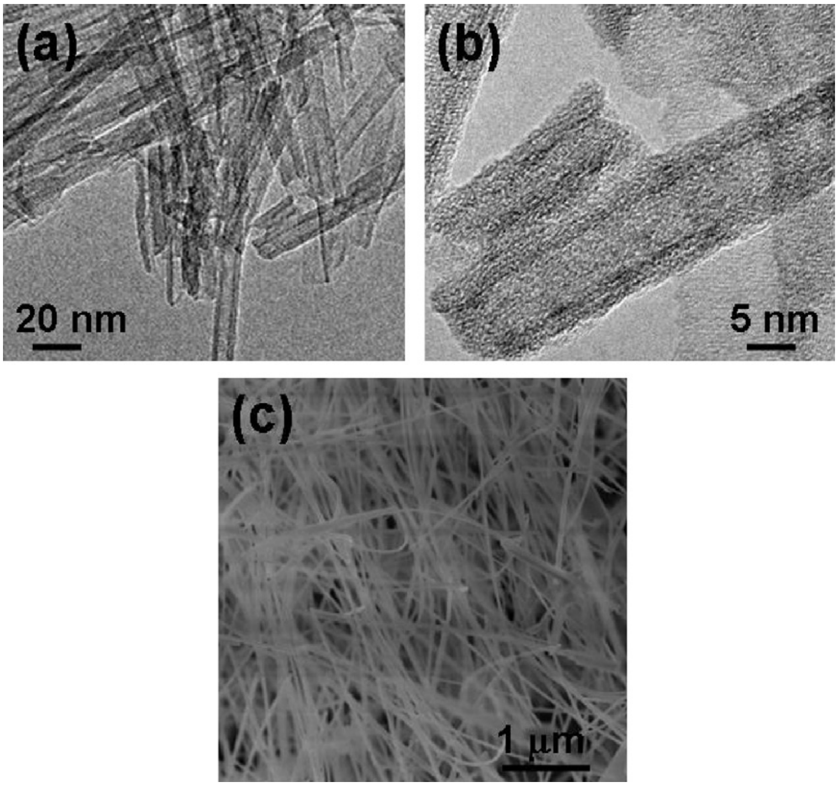

Fig. 1. (a, b) TEM and enlarged TEM images of the TiO_2 nanotubes, respectively; (c) SEM image of the fresh CdSe nanowires.

18 h. The average length of the treated CdSe nanowires *ca.* 1 μm, much shorter than that of the fresh nanowires shown in Fig. 1c. It is may be ascribed to the unstability of the CdSe nanowires in the solvothermal process. Fig. 2b shows a typical SEM image of the products obtained by using the TiO_2 nanotubes and CdSe nanowires as source materials. Regular 1D nanoparticle capped CdSe heterostructures are observed in addition to few nanoparticles. The corresponding TEM images (Fig. 3a and b) clearly indicate that the nanoparticles are selectively deposited at one tip of the nanowires. Fig. 3c shows the TEM image of interface between the nanoparticle and nanowire, revealing that the nanoparticle is grown instead of simply attached at one tip of the nanowire. The EDS spectra collected from the area "A" and "B" (Fig. 3d and e) indicate that the nanoparticle is composed of Ti and O elements, and the nanowire body consists of Cd and Se elements. The atomic ratio of Ti and O is close to stoichiometric formation of TiO_2, demonstrating that the heterostructures is TiO_2 capped CdSe nanowires. The lattice-resolved HRTEM image taken from the wire body (Fig. 3f) shows the (0 0 0 1) lattice plane of wurtzite CdSe with an inter-planar *d*-spacing of 0.69 nm, in accordance with the polar [0 0 0 1] growth direction. The TiO_2 nanoparticle is amorphous, as confirmed by the HRTEM measurement (Fig. 3g).

As is well known, nonpolar facets have much lower growth rates that the polar facets for the polar wurtzite CdSe nanowires. The CdSe nanocrystals therefore can be preferentially grown along [0 0 0 1]. For the polar wurtzite CdSe nanowires, the tips including Cd terminated (0 0 0 1) and Se terminated $(000\bar{1})$ facets are never equivalent and have higher chemical reactivity, than other nonpolar facets [22,23]. Some literatures had demonstrated that Cd terminated (0 0 0 1) facets expose Cd atoms with one dangling bond and Se terminated $(000\bar{1})$ facets expose Se atoms with three dangling bonds [23,24]. Moreover, surface reconstruction can occur in the polar CdSe nanowires, resulting in that the dangling bonds of surface cations Cd are empty whereas the surface anions Se are filled [25–27]. So the surface Cd atoms are passivated while surface Se atoms are more reactive. Therefore, the $(000\bar{1})$ facet is the most reactive one as it can expose Se atoms with more dangling bonds that serve as active sites for the selective nucleation and

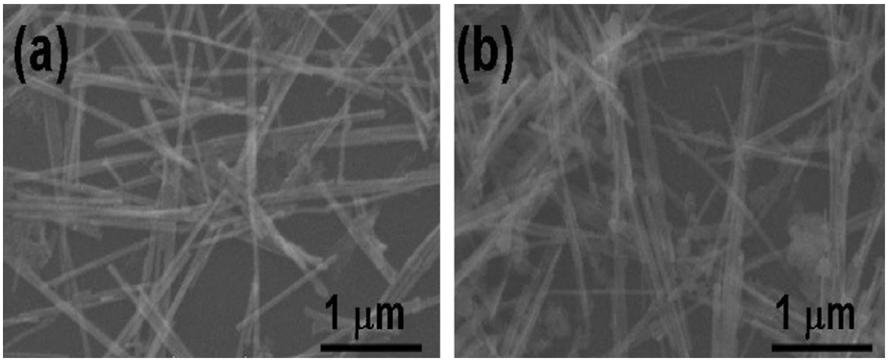

Fig. 2. (a) SEM image of the CdSe nanowires treated in the solvothermal process; (b) SEM images of the TiO_2–CdSe heterostructures.

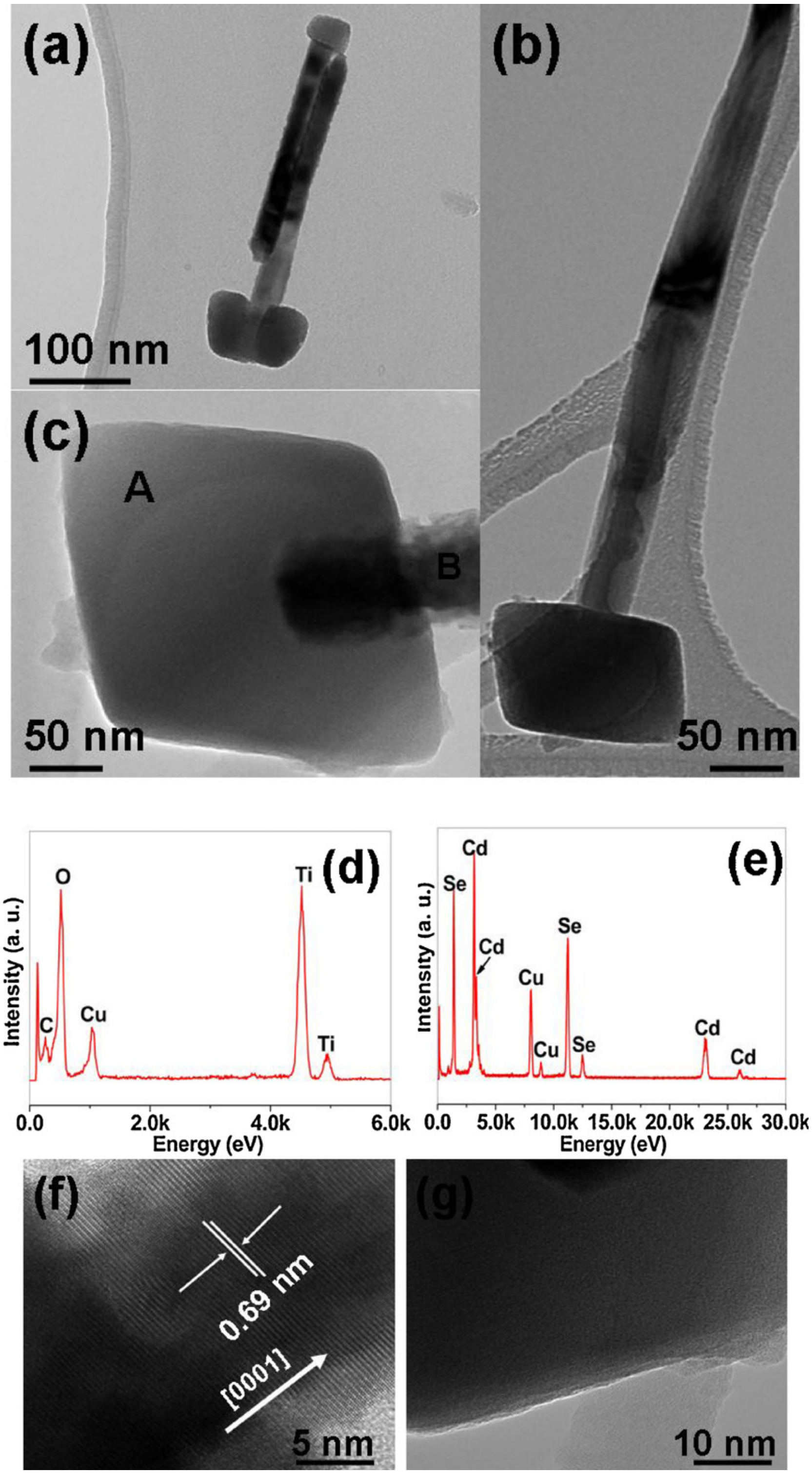

Fig. 3. (a) TEM image of the heterostructures; (b) enlarged TEM image of an individual heterostructure; (c) TEM image of interface between the nanoparticle and the nanowire; (d, e) EDS spectra of the area "A" and "B", respectively; (f) HRTEM image of the wire body and nanoparticles, respectively.

growth of TiO_2. So, the reaction process can be concluded as follows: TiO_2 nanotubes are first transmitted into a large number of species. Because Se terminated $(000\bar{1})$ facets with more dangling bonds are most reactive, the $(000\bar{1})$ facets serve as active sites for selective growth of the TiO_2 species on the Se terminated tip of the nanowire. These TiO_2 species can be continuously deposited and ripen at the Se terminated tip with time, resulting in the unique 1D heterostructures.

4. Conclusions

1D TiO_2–CdSe heterostructures were fabricated via a solvothermal route by using wurtzite CdSe nanowires and TiO_2 nanotubes as source materials. Amorphous TiO_2 nanoparticles are selectively grown at one tip of the polar CdSe nanowires. The difference in chemical reactivity of various facets is an important reason for the selective growth of TiO_2. The reactivity among various facets, even between the polar facets Cd terminated $(0\,0\,0\,1)$ and Se terminated $(0\,0\,0\,\bar{1})$ is different for the polar wurtzite nanowires. Se terminated $(0\,0\,0\,\bar{1})$ facet is demonstrated to be most reactive one as it can expose Se atoms with excessive dangling bonds. These dangling bonds provide active sites for the selective growth of TiO_2, finally resulting in the unique 1D heterostructures.

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