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Well improved photoswitching characteristic of CdSe nanorods via CdS nanoparticle-decoration

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Abstract

Synthesis of CdSe nanorods decorated with CdS nanoparticles and investigation into their optical, electrical properties are reported. CdS-decorated CdSe nanorods were assembled across gold microelectrode pairs, forming a prototype photoswitch, and showed superior photoelectrical property to the nude CdSe ones. Mechanism accounting for the improvement on the photoswitching behavior of CdS-decorated CdSe nanorods was presented as well. The excellent response of CdS-decorated CdSe nanorods to the visible light promises the appealing application in fabrication of photoelectric devices.

Keywords: Semiconductors; Core/shell structure; Photoconduction; Sensors

1. Introduction

It is pretty interesting to tailor the optical and electrical properties of II–VI group semiconductor nanomaterials by tuning their size[1–5] and shape[6–8], making them suitable for fabrication of different kinds of devices. More interestingly, tailoring the physical properties of semiconductor nanomaterials could also be achieved by alternating compositional layers of semiconductor nanomaterials to form a complex structure [9–11], such as core/shells of CdSe/ZnS, ZnS/CdS, CdSe/ZnSe, CdSe/CdS, and CdS/CdSe. Of which, CdSe and CdS, as two kinds of functional optoelectronic materials potentially applied in high density logic, memory, sensing, and energy conversion devices, such as nanoscale rectifiers, field-effect transistors, light emitting diodes and solar cells [6,7], have been drawing a great interest in scientific community.

In the present work, we reported a complex structure, CdS nanoparticle-coated CdSe nanorod, which was synthesized by a simple two-step chemical solution routes. The optical and photoconductive properties of CdS nanoparticle-coated CdSe nanorods and nude CdSe nanorods were investigated respectively. CdS nanoparticle-coated CdSe nanorods show an excellent photoswitching behavior.

2. Experimental section

2.1. Materials

Analytical pure cadmium sulfate ($3CdSO_4{\cdot}8H_2O$), selenium dioxide (SeO_2), and thiourea (H_2NCSNH_2) were purchased from Beijing Chemical Reagents Company, China.

2.2. Preparation of CdSe nanorods

CdSe nanorods were solvothermally prepared with polyacrylamide as a soft template according to a previously reported procedure [12]: 1 mmol $Cd(NO_3)_2{\cdot}4H_2O$ was dissolved in 22 g polyacrylamide gel, and the gel was kept at room temperature for one day, followed by dehydration at 60 °C. The polymers gel doped with Cd^{2+} and 1 mmol selenium dioxide were put into a Teflon-lined stainless steel autoclave of 50 ml capacity. The tank was filled with 35 ml ethylenediamine, which was maintained at

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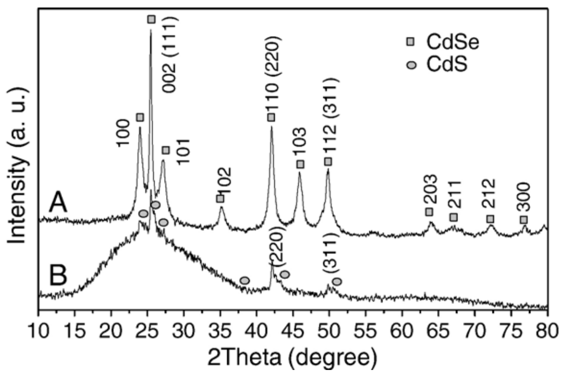

Fig. 1. XRD patterns of (A) uncoated CdSe nanorods and (B) CdSe/CdS composites.

170 °C for 48 h and then allowed to cool down to room temperature. The red product was washed with deionized water and ethanol for several times. Then the CdSe nanorods were collected.

2.3. Preparation of CdS nanoparticle-coated CdSe nanorods

In a typical case, 10 mg of as-synthesized CdSe nanorods, 0.2 mmol $Cd(NO_3)_2{\cdot}4H_2O$, and 0.2 mmol thiourea were dissolved in 20 ml deionized water to obtain a reactant mixture. Before heating, nitrogen gas was bubbled through the reactant mixture for 10 min to purge oxygen. The reactant mixture was vigorously stirred for 2 h in water bath at 80 °C. During the reaction, the red mixture turned brown, indicating the generation of CdS. Then, CdS nanoparticle-coated CdSe nanorods were collected by centrifugation, and washed thoroughly with deionized water and ethanol and dried naturally in air before characterization.

2.4. Structural and property characterization

The morphology and structure of CdS nanoparticle-coated CdSe nanorods were investigated by XRD, TEM and HR-TEM. Photoluminescence measurement was carried out using a CARY Eclipse Fluorescence spectrum. The photoconductive properties of CdS nanoparticle-coated CdSe nanorods and nude CdSe nanorods were investigated through prototype switches fabricated by assembling CdSe nanorods onto gold microelectrod arrays, which were fabricated using a conventional photolithographic method with a finger width of 10 μm and a gap size of

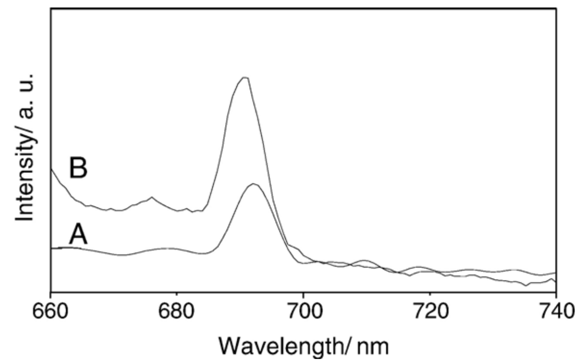

Fig. 3. Room temperature PL spectra of (A) uncoated CdSe nanorods, and (B) CdSe/CdS composites.

1.2 μm, and thickness of. 30-nm Ti and 100-nm Au on a silicon wafer.

3. Results and discussions

3.1. Structural characteristics of CdS nanoparticle-coated CdSe nanorods and nude CdSe nanorods

Fig. 1A shows the XRD patterns of the uncoated CdSe nanorods. All the diffraction peaks can be indexed to wurtzite and zinc blende structured CdSe, revealing that the core material of CdSe was a mixture of wurtzite and zinc blende phase. No diffraction peaks from another crystalline form were detected. After the CdSe nanorods were heated in an aqueous solution of cadmium ions and thiourea, some additional diffraction peaks corresponding to the hexagonally structured CdS phase (JCPDS Card No. 41-1049) appeared, revealing that hexagonally structured CdS was produced in the reaction mixture during heating and stirring. The broading of the CdS XRD peaks (Fig. 1B) shows that the CdS nanoparticles are very tiny.

Fig. 2(A–D) shows typical TEM images of CdS nanoparticle-coated CdSe nanorods. In Fig. 2(E), we can see the very smooth surface of the uncoated CdSe nanorods of approximately 20–30 nm in diameter, and several hundred nanometers in length. Clearly, in Fig. 2(A–C), we can see the CdS nanoparticles adhered to the CdSe nanorods in two ways: layer (Fig. 2C) and aggregates (Fig. 2B). The latter fashion can be attributed to the fact that PAM residual on the surface of CdSe nanorods may absorb the Cd^{2+} through electrostatic interaction during the synthesis and, subsequently, the CdS nanoparticles grow along the CdSe nanorods as cores; On the other hand, it is a fact that the chemical properties of selenium and sulfur are similar to each other, and consequently, the sulfur anions generated in the solution would have a tendency to be captured by the selenium vacancies located mainly on the surface of CdSe nanorods. Absorption of sulfur anions on the CdSe

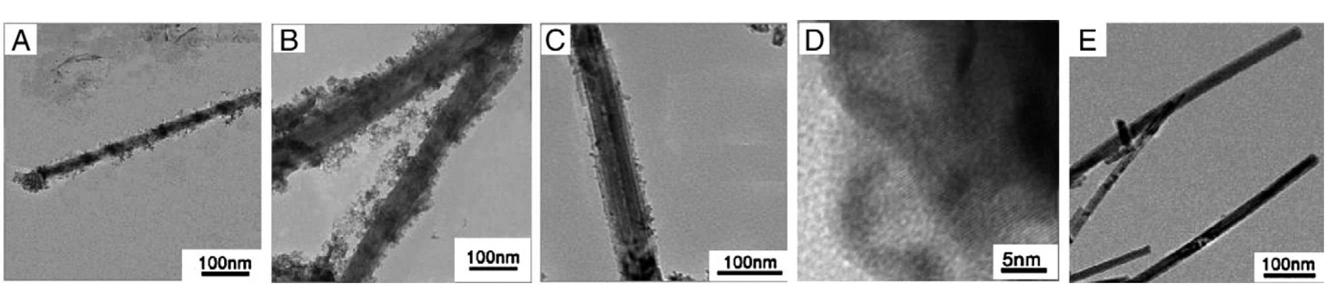

Fig. 2. (A–C) Typical TEM images of CdSe/CdS composites. (D) CdSe–CdS heterojunction interface. (E) TEM images of uncoated CdSe nanorod.