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Synthesis and investigation of novel ZnO–CuO core-shell nanospheres

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ABSTRACT

In this work, ZnO–CuO core-shell hybrid nanospheres with well-crystalline wurzite ZnO core and monoclinic CuO shell were successfully synthesized through a two-stage solution process. The as-prepared nanocomposites were carefully characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and UV/Vis diffuse reflection spectroscopy (DRS). Compared with bare ZnO cores, the ZnO–CuO core-shell 0-dimensional nanocomposites had greatly enhanced absorption strength and dramatically broadened optical response ranging from near-ultraviolet to visible light, which was probably attributed to heterojunction between n-ZnO core and p-CuO shell and defects originated from synthetic procedure. The as-synthesized p-CuO/n-ZnO core-shell hybrid structure may lead to tantalizing applications including solar energy materials, LED and optical sensor.

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1. Introduction

Zero-dimensional semiconductor material is an attractive platform for optoelectronic nanodevices [1] due to their particular optoelectronic properties and potential applications [2–5]. Core-shell type hybrid structure, as a typical structure of quantum dots system, has important theoretical research value and exhibits novel properties [6–9]. Thus it is promising to use the core-shell structure to change some properties, such as surface modification through shell building. Numerous core-shell structures have been explored in recent years, including ZnO–ZnS core-shell nanorods [7], ZnS–MgO core-shell structure [8], and Cu–ZnO core-shell nanocomposite [9].

As typical semiconductor materials, CuO [10] is a p-type semiconductor with narrow band gap of 1.2 eV and ZnO is a n-type semiconductor with direct gap of 3.3 eV. Thus the exploration of CuO–ZnO core-shell structures rendering some optical properties has attracted increasing interest in relevant research fields. Recently, reports on one-dimensional ZnO–CuO core-shell structure such as nanorods or nanowires are increasing. Ruey-Chi Wang et al [11] have reported that dip coating method was used to synthesis ZnO–CuO core-shell nanorods with ZnO obtained by chemical deposition method. Park et al [12] have reported that ZnO–CuO core-branch nanocatalysts were obtained by two-step injection method from ZnO nanospheres. However, n-p junctions of

0-dimensional core-shell nanocomposites are less reported, especially methods using the solution process, which provides a stable liquid environment for the growth of crystals and a good medium of mass transfer. In this work, ZnO–CuO core-shell nanospheres were synthesized for the first time by a two-stage solution process (seen in Fig. 1). In the salt solution of Zn^{2+} , uniform ZnO cores formed from hydrolysis of Zn^{2+} by controlling the pH and reaction temperature and their sizes were influenced by reaction time, which was perceived as the homogeneous nucleation mechanism. Thus, when dilute concentration of Cu^{2+} salt solution was added ZnO cores pseudosolution, Cu^{2+} bonded with the dangling bonds and consequently, CuO crystal nuclei formed on the surface of ZnO cores. Then the nuclei gradually grew up and finally generated a homogeneous shell, which was regarded as the heterogeneous nucleation procedure.

2. Experimental

In the present research, ZnO–CuO core-shell nanospheres were synthesized by a two-stage solution process. First of all, the homogeneous ZnO cores were obtained by sol-gel method, based on our previous researches [13,14]. Then as-prepared ZnO solution (ZnO cores) was added to the ethanol solution of cupric acetate under constant stirring at 60 °C water-bath, while the pH value was maintained at 10–11 by adding appropriate amount of sodium hydroxide. After reaction, the precipitate obtained from centrifugation was washed with deionized water several times.

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Fig. 1. Synthetic schematic diagram of ZnO–CuO core-shell nanospheres.

Finally, the powders of ZnO–CuO core-shell nanocomposites were collected, after dried at 60 °C in the air.

The microstructure and distribution of ZnO–CuO core-shell nanospheres were characterized by JEM-2100F high-resolution transmission electron microscope (HRTEM). X-ray diffraction (XRD) patterns were recorded using RIGAKU D/max-R8 diffractometer to investigate the crystal structure of the ZnO cores and ZnO–CuO core-shell nanospheres. The absorption spectra were collected by SHIMADZU UV-3600 spectrophotometer.

3. Results and discussion

Fig. 2 shows the XRD patterns of ZnO–CuO core-shell nanospheres and ZnO cores synthesized in the first step of the two-stage solution process. All diffraction peaks displayed in Fig. 2 (a) demonstrated that as-grown core-shell hybrid composites consisted of ZnO with hexagonal wurtzite structure (JCPDS Card no. 36-1451) and CuO with monoclinic structure (JCPDS Card no. 48-1548). In addition, the diffractogram in Fig. 2(a) of ZnO was highly analogous to that of CuO, suggesting a well match of crystal structure between ZnO and CuO phase, which certainly facilitated epitaxial growth of CuO phase in solution. Obviously, the peaks of ZnO particles in Fig. 2(b) were largely broadened, indicating that

those ZnO nano-materials produced a strong quantum size effect and made their diffraction peaks broadened evidently. Meanwhile, the sharpening peaks in Fig. 2(a) revealed good crystallinity of CuO phase in the process of growth.

Fig. 3 presents the transmission electron microscopy (TEM) image and high-resolution transmission electron microscopy (HRTEM) image of ZnO–CuO core-shell nanospheres, respectively. Fig. 3(a) shows that the as-prepared ZnO–CuO core-shell sample had spherical shape with diameters of 20–50 nm and a clear hierarchy configuration containing the core and shell. The HR-TEM image in Fig. 3(b) shows detailed structure of the ZnO core and CuO shell. Furthermore, the periodic lattice fringes of the ZnO core and CuO shell were distinctly observed, respectively, indicating that both the ZnO core and the CuO shell were well-crystallized in the process of synthesis in solution. Meanwhile, the lattice distance of 0.28 nm represented for (200) crystal plane of ZnO core and 0.23 nm for the (200) plane of CuO shell. The continuity of Morie fringes across certain area at the ZnO–CuO interface (Fig. 3 (b)) was sign of epitaxial growths.

Fig. 4 displays the UV/Vis absorption spectra of ZnO–CuO core-shell nanospheres and ZnO cores, respectively. In the case of ZnO cores, their optical response scope was from 360 nm to 410 nm, corresponding to an approximate band gap of 3.2 eV. The result was consistent with previous pronouncement [15]. Meanwhile, the optical absorption curve of Fig. 4(a) was unsmooth compared with that of pure species within its absorption scope, which was typical performance for composites under the irradiation of the light, implying that the ZnO–CuO core-shell complex materials were successfully synthesized in the process of solution. That was in good agreement with above characterizations. Otherwise, ZnO core possessed the –0.31 eV conduction band and 2.89 eV valence band, while the conduction band and valence band value of CuO shell were 0.46 eV and 2.16 eV, respectively. When those two species adequately formed ZnO–CuO core-shell hybrid system via heterojunction, the band structure of the composites significantly changed and differed. Herein, as-prepared ZnO–CuO core-shell hybrid composites had an approximate band gap of 1.9 eV based on the Fig. 4(a) and exhibited wide absorption from the visible light to infrared region compared with the bare ZnO. At the same time, the composites enhanced absorption strength in all regions after CuO coating.

4. Conclusions

In this research, ZnO–CuO core-shell structure was successfully synthesized by a two-stage solution process. TEM and HRTEM

Fig. 2. XRD patterns of (a) ZnO–CuO core-shell nanospheres and (b) ZnO cores.

Fig. 3. (a)TEM and (b)HRTEM images of ZnO–CuO core-shell nanospheres.

Fig. 4. Absorption spectra of (a) ZnO–CuO core-shell nanospheres and (b) ZnO cores.

images demonstrated that the as-prepared sample had spherical shape with diameters of 20–50 nm and typical core-shell structure, which directly proved the success of CuO coating. The XRD patterns suggested ZnO cores were well-crystalline wurzite phase and the outer CuO shells were monoclinic structure, respectively. Absorption measurement of the ZnO–CuO core-shell 0-dimensional nanocomposites showed a broad optical absorption from the visible light to infrared region and enhanced absorption strength compared with the bare ZnO. That was primarily attributed to heterojunction structure with multiple energy-level configuration and defects on the surface or the interface between ZnO core and CuO shell.

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