

Research Article

Hybrid Ag₂O/ZnO Heterostructures

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The well-aligned Ag₂O/ZnO microflowers heterostructure was synthesized by a straightforward two-step procedure. The diameters of the as-synthesized products were as much as 1.5 μm. The as-grown Ag₂O/ZnO heterostructure was investigated by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and photoluminescence (PL) spectroscopy analysis. A possible growth mechanism for flowerlike Ag₂O/ZnO heterostructure was proposed based on the experimental results. Compared with pure ZnO microflowers, PL spectrum of the composite with only one strong peak at 383 nm showed good intrinsic emission.

1. Introduction

In recent years, nanostructured materials have been a wide research focus due to their versatile morphologies and excellent physical and chemical properties superior to the corresponding bulk counterparts [1–5]. Therefore, nanostructured materials have been used widely in gas sensors [6–8], photocatalysts [9–13], solar cells [13–15], and luminescent materials [16, 17]. However, in view of applications, it is restricted because single materials seldom meet actual demands. Thus, the challenge is to find some nanocomposites consisting of two or more semiconductors, which is considered a great choice to improve outstanding performance [18–21]. Zhou et al. reported Ag₂O/TiO₂ nanobelts heterostructure with better ultraviolet and visible photocatalytic activity than single TiO₂ materials [22]. Khanchandani and his coworkers demonstrated that type II ZnO/CdS core/shell nanorod arrays show enhanced simulated solar light absorption and high transfer efficiency of photogenerated electrons [23]. Li's group synthesized Ag-doped ZnO nanowires with excellent electrical and optical properties [24].

ZnO, as a very important wide bandgap semiconductor material with large exciton binding energy of 60 meV at room temperature, has been a research focus in recent years for its three prominent characteristics: semiconductor, piezoelectricity, and biocompatibility. Therefore, it has been used

in various fields such as optics, gas sensors, piezoelectronics, and self-clean energy [25, 26]. As mentioned above, since nanocomposites represent better properties, herein, we report the synthesis Ag₂O/ZnO nanohybrid with a feasible two-step method. A possible growth mechanism of the as-prepared Ag₂O/ZnO nanohybrid is proposed. The as-synthesized flowerlike Ag₂O-ZnO nanohybrid possesses an average diameter of 1.5 μm with uniformly distributed Ag₂O nanoparticles on ZnO microflowers. Room temperature photoluminescence properties of the as-prepared ZnO microflowers and Ag₂O/ZnO nanohybrid products were investigated. The spectrum presents only an ultraviolet emission peak at 383 nm for Ag₂O/ZnO nanohybrid, revealing an excellent optical quality.

2. Experiment Details

All the reagents in this experiment are analytically pure and used without further purification. A typical experiment procedure is described as follows.

2.1. Synthesis of ZnO Microflowers. In a typical procedure, 3 mmol Zn(NO₃)₂ was dissolved into 10 mL deionized water, and 12 mmol NaOH was dissolved into 20 mL deionized water in a 50 mL glass beaker with constantly stirring until

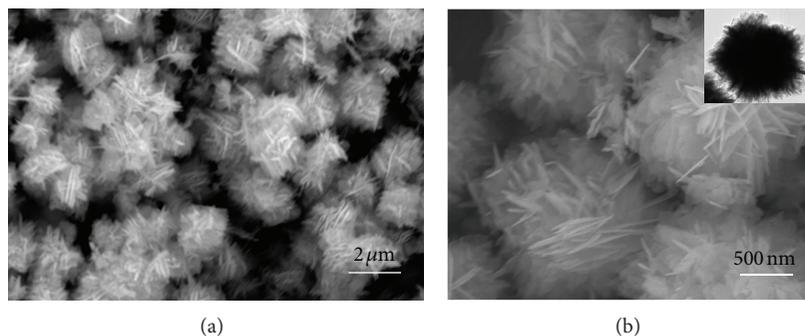


FIGURE 1: SEM images of ZnO microflowers: (a) low magnification SEM image, (b) high magnification SEM image. The inset is TEM image.

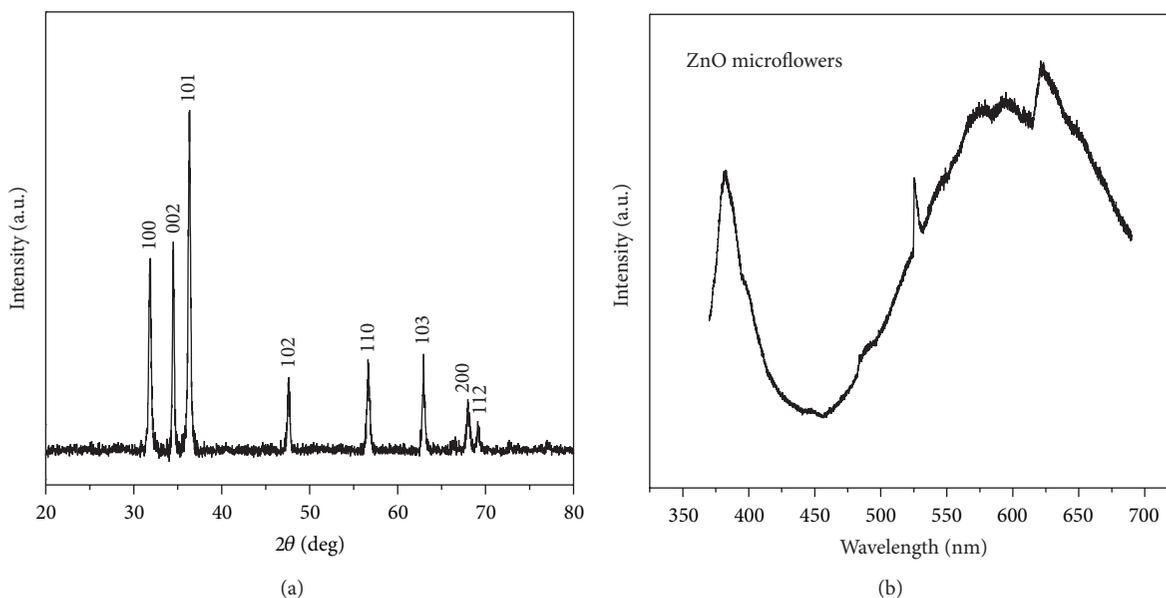


FIGURE 2: (a) XRD patterns of the as-synthesized ZnO microflowers. (b) Room-temperature photoluminescence spectrum of the as-synthesized ZnO microflowers.

the solution becomes transparent, respectively. Then, NaOH solution was added dropwise into the above solution under ceaselessly magnetic stirring for 1 h. The mixed solution was then put into a sealed Teflon-lined autoclave, followed by hydrothermal reaction at 90°C for 1.5 h. After that, the autoclave was naturally cooled to room temperature. The precursor precipitation was taken out and washed several times with deionized water and ethanol and dried at 60°C for 12 h in air.

2.2. Synthesis of Ag₂O/ZnO Heterostructures. In a typical experiment, 0.2 g Ag(NO₃)₃ and 0.48 g NaOH were dissolved into 20 mL deionized water in 100 mL glass beaker with constantly stirring until the solution becomes transparent, respectively. Then NaOH solution was added dropwise into the Ag(NO₃)₃ solution under ceaselessly magnetic stirring for 30 min. 0.20 g of ZnO was added to the suspension. The obtained mixture solution was illuminated with 250W metal-halide lamp for 1 h under magnetic agitation. After

illumination, the products were thoroughly washed with water and ethanol and then dried at 60°C for 12 h in air.

The obtained product was characterized by scanning electron microscope (SEM, Hitachi-4800), transmission electron microscope (TEM, JEOL-2010), and X-ray powder diffraction (XRD, Rigaku Dmax-2600/PC, CuK α radiation, $\lambda = 0.1542$ nm, 40 KV, 100 mA). Optical property of the as-synthesized ZnO nanoflowers was investigated by photoluminescence spectroscopy (PL SPEX FL-2T2).

3. Results and Discussion

The morphology and microstructural details of the as-prepared ZnO microflowers were investigated by SEM and TEM observation. Figure 1(a) shows a low magnification SEM image of the as-obtained product. It may clearly be found that the as-obtained product possesses many flowerlike structures. Further, high magnification SEM image reveals that individual microflower is assembled from numerous

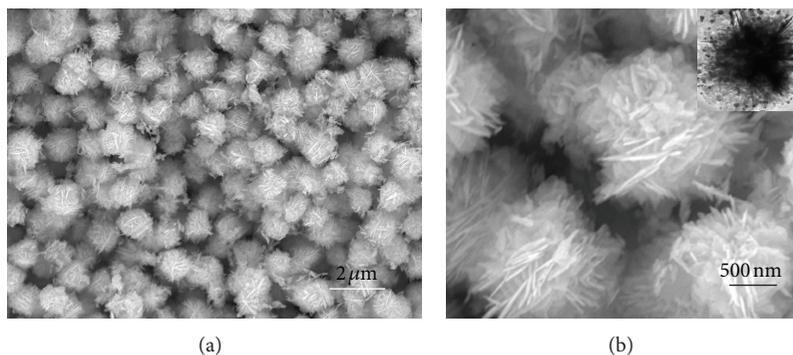


FIGURE 3: SEM images of $\text{Ag}_2\text{O}/\text{ZnO}$ heterostructure: (a) low magnification SEM image, (b) high magnification SEM image. The inset is TEM image.

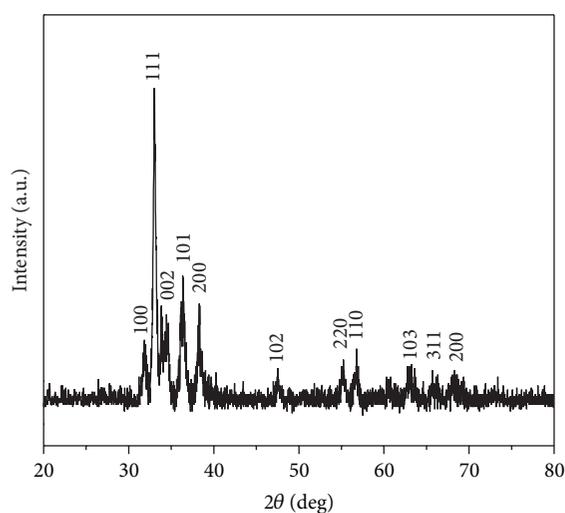


FIGURE 4: XRD patterns of the as-synthesized $\text{Ag}_2\text{O}/\text{ZnO}$ heterostructure.

nanosheets, and the diameter of the product is about $1.5 \mu\text{m}$ as shown in Figure 1(b). The inset is TEM images, which further confirm that the as-prepared products are flower-like structures by some nanosheets assembled. The typical XRD pattern of the prepared ZnO sample is presented in Figure 2(a). All the diffraction peaks can be perfectly indexed to hexagonal wurtzite-type ZnO (JCPDS no. 36-1451). No peaks of other impurities are detected in this case. The strong and sharp peaks indicate that the as-prepared product is highly crystalline.

To investigate optical properties of the nanostructures, photoluminescence (PL) spectra were measured with an excitation wavelength of 325 nm at room temperature, as presented in Figure 2(b). The PL spectra of the flowerlike ZnO nanostructures prepared were dominated by a sharp emission band with a λ_{max} at 380 nm along with a broad, strong band in the higher wavelength region of 500–660 nm. The UV peak could be generally attributed to the near-band-edge emission (NBE), and the visible band (known as deep level emission, DLE) is usually caused by impurities and structural defects [27]. The strong, broad emission band in the

higher wavelength region is termed a deep-level or trap-state emission band, which might be the superposition of green emission around 520 nm and a near-yellow emission around 640 nm as reported elsewhere [28, 29]. This trap-state emission is usually associated with various types of defects resulting from various oxygen vacancies in the valence band of ZnO nanostructures [30, 31]. Figure 3 shows SEM image of the as-obtained $\text{Ag}_2\text{O}/\text{ZnO}$ nano hybrid product. In contrast, ZnO microflowers with coated Ag_2O exhibited a rough surface where a number of Ag_2O particles were absorbed on the surface of ZnO microflowers. The inset shows the corresponding TEM image, which demonstrates clearly some Ag_2O nanoparticles coated on the surface of ZnO microflowers. XRD patterns of $\text{Ag}_2\text{O}/\text{ZnO}$ heterostructure are shown in Figure 4. The hexagonal ZnO and Ag_2O phases coexist in the $\text{Ag}_2\text{O}/\text{ZnO}$ heterostructure crystals, and the XRD patterns match their JCPDS files nos. 36-1451 and 41-1104, respectively. No peaks of other phases were detected, indicating high purity of the as-synthesized product.

On the basis of the above observations, a possible growth mechanism of the $\text{Ag}_2\text{O}/\text{ZnO}$ heterostructure is proposed in Figure 5. First, OH^- reacts with Zn^{2+} to form $\text{Zn}(\text{OH})_2$, then $\text{Zn}(\text{OH})_4^{2-}$ ions. Synthesis of ZnO micro/nanostructures from aqueous solution containing $\text{Zn}(\text{OH})_4^{2-}$ ions has been reported. As reaction time proceeds, $\text{Zn}(\text{OH})_4^{2-}$ ions dehydrate and form ZnO nuclei under hydrothermal conditions. These particles have a tendency to aggregate due to large surface energy. Surface energy is substantially reduced when the neighboring nanosheets are grown. With the crystal growth continuing, each nanoparticle in the aggregates or nanosheet has its own orientation and acts as a nucleus for further growth. These growth processes are not only related to the anisotropic ZnO crystal structure, but also the involved reaction conditions [32]. The growth habit can control the ZnO crystals to grow into nanosheets. At the same time, conventional nucleation on the nanosheet occurs for the high concentration of $\text{Zn}(\text{OH})_4^{2-}$ transforming to ZnO. Then, flowerlike ZnO hierarchical structures are formed by two-step nucleation and growth process [33, 34]. Some Ag_2O particle seeds are then partially deposited on the surface of ZnO microflowers to form nucleation sites for subsequent growth of Ag_2O particles. During early stages of the reaction,

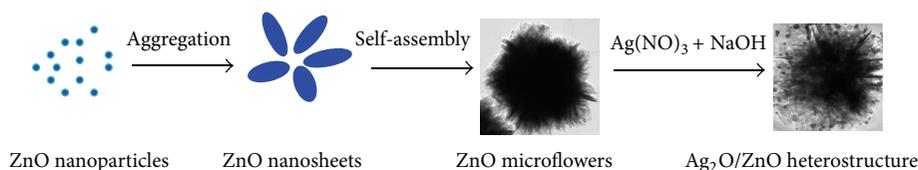


FIGURE 5: Schematic illustration of the possible formation mechanism of the as-synthesized Ag₂O/ZnO heterostructure.

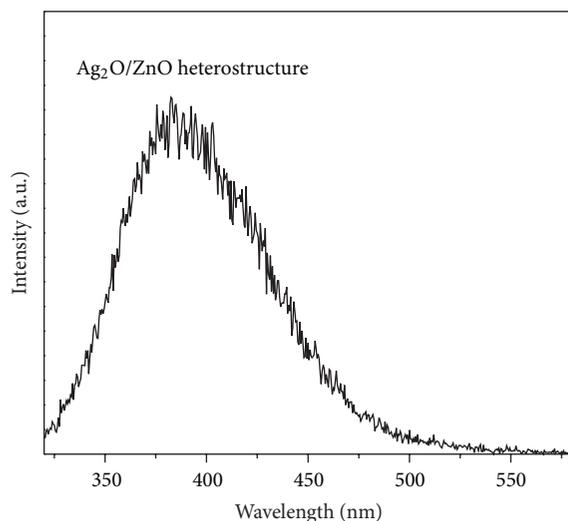


FIGURE 6: Room-temperature photoluminescence spectrum of the as-synthesized Ag₂O/ZnO heterostructure.

Ag₂O crystal nuclei are formed on the ZnO lateral surface by the reduction reaction of Ag(NO)₃. With increasing reaction time, initial particle seeds continuously aggregate and crystallize, leading to increasing diameters of the Ag₂O nanoparticles. At last, a dense and complex Ag₂O/ZnO microflowerlike heterostructure is formed.

Finally, room-temperature photoluminescence property of the as-synthesized Ag₂O/ZnO heterostructure was also investigated. Figure 6 shows a PL spectrum of the obtained Ag₂O/ZnO heterostructure. Only a single wide emission peak centered at 383 nm was observed, which may be attributed to the recombination of free excitons through an exciton-exciton collision process [27]. No other peaks were found, illustrating that the as-synthesized Ag₂O/ZnO heterostructure have a better crystal quality and stoichiometry compared with single ZnO microflowers materials.

4. Conclusions

In summary, flowerlike Ag₂O/ZnO heterostructure hybrids have been successfully synthesized by a simple two-step procedure without any surfactants. The as-prepared heterostructure composite showed Ag₂O nanoparticles coated uniformly on the surface of ZnO microflowers. The possible growth mechanism of the products is proposed based on these experimental results. PL measurements reveal a strong UV band-edge emission peak at 383 nm. Comparing with pure ZnO

microflowers, the composite exhibited greatly optical properties.

Acknowledgments

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