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Original Research Paper

Synthesis, characterization, and dispersion behavior of ZnO/Ag nanocomposites

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ABSTRACT

ZnO/Ag nanocomposites that are composed of quasi-spherical nanoparticles with diameters of several nanometers have been successfully generated by a two-step liquid precipitation method. The as-prepared ZnO/Ag nanocomposites were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM). The dispersion behaviors of the ZnO/Ag nanocomposites in isopropanol with using nonionic dispersants such as stearic acid, PVP K17, and PVP K30 were investigated by conventional sedimentation method, dynamic light scattering method (DLS) and TEM observation. Both the PVP K17 and PVP K30 could disperse the ZnO/Ag nanoparticles effectively in isopropanol. It is proposed that the nonionic dispersants could form absorbed PVP molecule layers on the surfaces of the ZnO/Ag nanoparticles, prohibiting their agglomeration and enhancing their dispersion stability in isopropanol. This work is helpful for further investigating the potential applications of ZnO/Ag nanocomposites in the fields of medical plastics and sterilization.

1. Introduction

In recent years, nanometer-sized particles, namely the so-called nanoparticles, have attracted tremendous interest due to their unique chemical and physical properties [1–4]. Zinc oxide, as one of the most widely-investigated semiconducting oxide nanostructures, are attracting considerable attention because they can act as potential candidates for applications in sensors, energy generators, light-emitting diodes, lasers, and optoelectronics [5–9]. In particular, ZnO have been proven to exhibit better photocatalytic performance for the degradation of some organic compounds than that of the TiO_2, which is currently the most extensively-studied photocatalyses. ZnO is also biocompatible, biodegradable, and nontoxic for environmental applications, making it more competitive than the TiO_2. However, the photocatalytic efficiency of the ZnO photocatalysts is still not high enough for practical application because of the fast recombination of photogenerated electron–hole pairs [10]. Recent researches revealed that modification with noble metals, such as Ag, Au, or Pt, is an effective way to prohibit the recombination of charge carriers and to enhance the photocatalytic performance of ZnO photocatalysts for degrading toxic organic pollutants [11–14]. The photo-induced electrons in the conduction band of ZnO can transfer to the metal surfaces, which act as electron sinks due to the Schottky barrier at the metal–semiconductor interface. The photo-induced holes that remain in the valence band ZnO could be trapped by the hydroxyl to produce the active hydroxyl radicals, which is one of the primary oxidizing species [15]. Typical examples include the dendrite-like ZnO@Ag heterostructure nanocrystals produced by a two-step chemical method and the Au–ZnO hybrid nanopyramids prepared by regulating the heterogeneous nucleation and selective growth of ZnO on presynthesized Au seeds, both of which have been proved to possess higher photocatalytic activity than that of pure ZnO nanocrystals [16,17]. The ZnO/Ag nanocomposites were also found to exhibit high photocatalytic property for the decomposition of some bacterial, making them potential candidates as additive in the medical plastics [18–20].

In comparison to their bulk counterparts, nanometer-sized noble metal-ZnO composite photocatalysts could be more easily aggregated due to their large surface area, which could inevitably decrease their photocatalytic efficiency [21–23]. Up to now, numerous investigations have been focused on the photocatalytic properties of noble metal-ZnO nanocomposites. However, little attention has been given to the dispersion behavior of the noble metal-ZnO nanocomposites. In this paper, the ZnO/Ag nanocomposites were firstly synthesized by a two-step liquid precipitation method. The Ag nanoparticles are in situ produced during the precipitation process and strongly anchored onto the surface of ZnO

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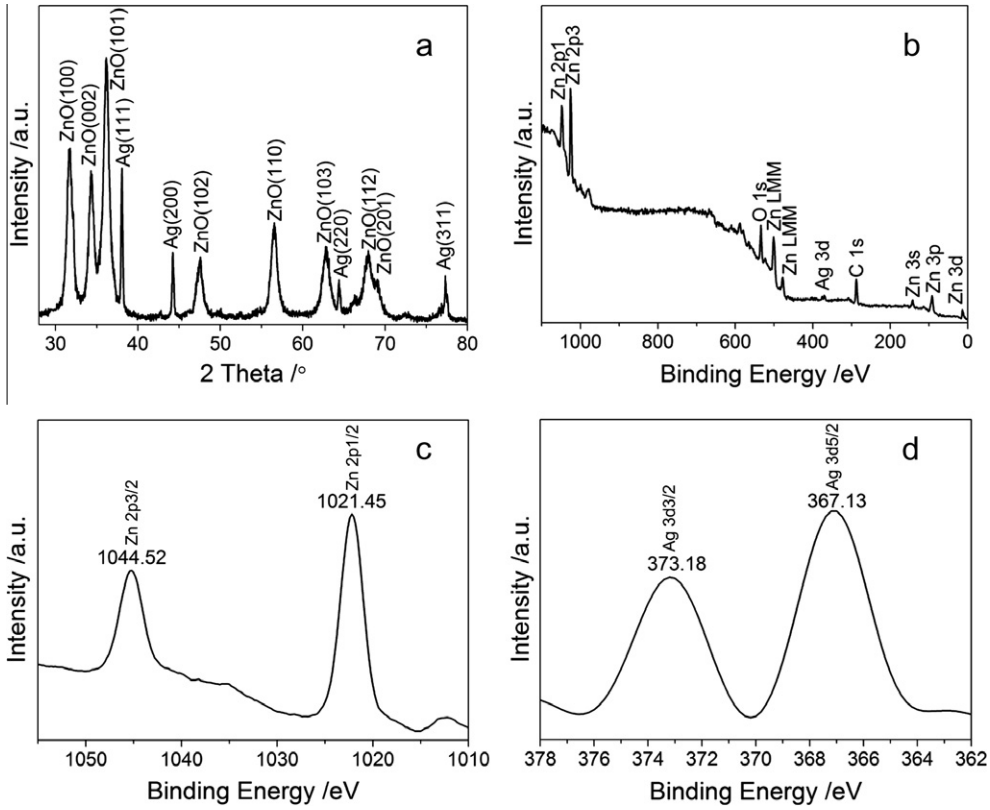

Fig. 1. (a) XRD pattern, (b) XPS spectrum of the ZnO/Ag nanocomposite, (c) and (d) core-level XPS spectra of Zn 2p and Ag 3d.

nanocrystals. In addition, the dispersion behavior of the ZnO/Ag nanocomposites in isopropanol with using nonionic dispersants was investigated. The present study is helpful for investigating the potential applications of ZnO/Ag nanocomposites in the fields of medical plastics and sterilization.

2. Experimental

ZnO/Ag nanocomposite was prepared by a two-step liquid precipitation method. Typically, 100 mM of zinc sulfate was dissolved in 100 mL of deionized water. 200 mM of Ammonium bicarbonate dissolved in 200 mL of deionized water was slowly added to the solution of zinc sulfate and stirred for 2 h at 20 °C. Then 8.4 mM of silver nitrate dissolved in deionized 50 mL of water was dropwise added to the solution. The mixture was stirred for 2 h at 20 °C. Finally, the gray powers were allowed to dry at 60 °C for 24 h. The as-prepared ZnO/Ag nanocomposites were then calcined at 400 °C in air for 4 h.

Stearic acid (SA), polyvinylpyrrolidone K17 (PVP K17), and polyvinylpyrrolidone K30 (PVP K30) were used as nonionic dispersants. 0.05 g of ZnO/Ag nanocomposites and different concentrations of the dispersant solutions were added into an agate mortar to form a solid–liquid mixture, which were ground for 20 min, stirred magnetically for 40 min, and ultrasonicated for 30 min, respectively. Finally, the dispersant-modified ZnO/Ag nanocomposites were prepared.

The as-prepared ZnO/Ag nanocomposites were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM). The particle size distribution of the ZnO/Ag suspension was measured using laser particle size analyzer. Evaluation of dispersion stability of the modified ZnO/Ag suspension in isopropanol was carried out using the conventional sedimentation method in a graduated cylinder. 10 ml of the ZnO/Ag suspension was poured into the graduated cylinder and allowed to deposit under gravity. The sedimentation rate was then calculated after 7 days.

3. Results and discussions

Fig. 1a shows the XRD pattern of the as-prepared products by the two-step liquid precipitation method. The diffraction peaks could be categorized into two sets. The main one can be indexed to ZnO with hexagonal structure (JCPD No. 36-1451), while the other one can be indexed to metallic Ag with face-centered-cubic structure (JCPDS No. 04-0783), evidencing the formation of the ZnO/Ag composites. The sharp diffraction peaks indicates that the ZnO/Ag composites are highly crystallized. Comparing with the XRD pattern of pure hexagonal ZnO (Fig. S1), no shift of diffraction peaks that corresponds to ZnO occurs, indicating that no solid solution was formed and the as-prepared composite are composed of individual ZnO and Ag. The surface compositions of the as-synthesized ZnO/Ag nanocomposites is also investigated by using XPS analysis and the corresponding survey XPS spectrum is shown in Fig. 1b. The carbon peak (C 1s) at 285 eV is due to the carbon paste used to stick the samples on the mount. It is clear that all the peaks are ascribed to Zn, O, Ag, and C elements, and no peaks characteristic of impurities are observed. The peak positions at 1021.45 eV and 1044.52 eV corresponds to the Zn 2p3/2 and Zn 2p1/2, which confirms that the Zn in the as-prepared sample mainly exists in the form of Zn^{2+} [24]. The core-level XPS spectrum of Ag consists of two peaks with energies of 373.18 and 367.13 eV, corresponding to Ag 3d3/2 and Ag 3d5/2 of metallic Ag, as shown in Fig. 1d. Both the XRD and XPS results indicate that the present two-step precipitation method is feasible to produce pure ZnO/Ag nanocomposites with high crystallinity.