Materials Letters 171 (2016) 263–267

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Facile synthesis of triangular silver nanoplate-coated flower-like ZnO nanostructures

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ARTICLE INFO

Article history:
Received 26 January 2016
Received in revised form
19 February 2016
Accepted 20 February 2016
Available online 23 February 2016

Keywords:
Triangular silver nanoplate
Flower-like ZnO
Hydrothermal
Surface plasmon resonance
Mechanism

ABSTRACT

Triangular silver nanoplate-coated flower-like ZnO nanostructures were successfully fabricated via a facile hydrothermal method combined with a dual reduction method. The morphology, composition, and structural and optical properties of the as-synthesized materials were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), UV–vis absorption spectra, X-ray diffraction (XRD), and photoluminescence (PL) spectrum. Results show that the morphology of ZnO and Ag were flower-like and triangular nanoplate, respectively. Triangular silver nanoplates exhibit unique surface plasmon resonance (SPR) absorption spectra, and the PL intensity of flower-like ZnO decreased by coating triangular silver nanoplates. In addition, the growth process and possible mechanism of flower-like ZnO and triangular silver nanoplates are discussed in certain detail.

1. Introduction

ZnO is one of the most important photocatalysts because of its wide band gap of 3.37 eV, high exciton binding energy of 60 meV, strong thermal stability and breakdown strength, high electron mobility, low cost, high oxidative capacity, and high surface area [1–5]. The physical and chemical properties of inorganic nanomaterials are known to depend not only on composition but also on structure. Therefore, the control of material morphology becomes a considerable hotspot in the research of the material [6]. ZnO possesses numerous kinds of morphology, including nanosheet, nanorod, nanosphere, nanowire, nanobridge, nanospike, dandelion-like, and nanoflower, which are achieved through different methods [7–14]. In this study, a novel and facile synthesis route is proposed for achieving a flower-like ZnO microstructure. To the best of our knowledge, flower-like ZnO on Zn foils through simple hydrothermal method has never been reported.

However, the most serious drawback of ZnO is the rapid recombination of photo-generated electrons and hole pairs, further reducing photocatalytic efficiency. Therefore, the retardation of electron–hole pair recombination is crucial for practical applications. We observed that the recombination of ZnO electron–hole pairs can be tailored for desired applications through doping, coating, and surface modification of noble metallic particles, such as Sb, Ag, and Pt [15–17]. Noble metallic triangular silver nanoplates (T-Ag) show unique surface plasmon resonance (SPR) absorption spectra in comparison with spherical silver particles, which can be applied in photocatalysis [18]. A facile route to deposit triangular silver nanoplates for coating on the surface of flower-like ZnO for the fabrication of flower-like T-Ag/ZnO nanostructures should be developed.

In this study, flower-like T-Ag/ZnO nanostructures were synthesized through a two-step method. The first step is through a simple and facile hydrothermal method for fabricating flower-like ZnO microstructure. In addition, the second step occurs through a dual reduction method for fabricating triangular silver nanoplates, followed by coating on the surface of flower-like ZnO to prepare flower-like T-Ag/ZnO nanostructures. In this study, we aim to establish the possible growth process mechanisms of flower-like ZnO and triangular silver nanoplates.

2. Experimental

The flower-like ZnO microstructure was successfully prepared by hydrothermal method. Prior to synthesis, Zn foils were polished and then cleaned by sonication in acetone, ethanol, and ultrapure

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http://dx.doi.org/10.1016/j.matlet.2016.02.091
0167-577X/

water. Afterwards, Zn foils were placed into 100 mL Teflon-lined stainless steel autoclave and then 20 mL of ethylenediamine and 5 mL ultrapure water added into it. Autoclave was subsequently kept at 150 °C for 11 h and cooled down to room temperature naturally. After hydrothermal treatment, the Zn foil was washed with ethanol and ultrapure water respectively, and then dried in an oven at 60 °C.

Flower-like T-Ag/ZnO nanostructures were successfully prepared by dual-reduction method with some modification. At room temperature, the 50 mL of 0.1 mmol L^{-1} $AgNO_3$ solution added into the 100 mL conical flask, which is completely covered with opaque tape to avoid light. As-prepared flower-like ZnO was added into the solution. Then, the following drugs, 3 mL of 30 mmol L^{-1} sodium citrate solution, 3 mL of 2.5 mmol L^{-1} polyvinyl pyrrolidone (PVP) solution, and 0.12 mL of 30 wt% H_2O_2 solution, were added into the above solution sequentially under vigorous stirring. Finally, 0.2 mL of 0.1 mol L^{-1} $NaBH_4$ solution was injected into the above solution, and the solution was continually stirred for 20 min. Triangular silver nanoplates were loaded on the surface of flower-like ZnO for 5 h under static conditions. Flower-like T-Ag/ZnO nanostructures were washed with ethanol and ultrapure water, respectively, dried in a vacuum oven at 60 °C, and stored under dark conditions.

The products were characterized by scanning electron microscopy (SEM, HITACHI S-4800 combined with EDX) and transmission electron microscopy (TEM, JEM2100F), UV–vis spectrophotometer (U-3900), X-ray diffraction (XRD, Bruker D8 Advance), and fluorescence spectrophotometer (F-7000). Samples were excited with a 325 nm wavelength light at room temperature.

3. Results and discussion

The morphologies and composition of flower-like T-Ag/ZnO nanostructures were investigated by using SEM and EDX, as shown in Fig. 1. Fig. 1a shows a low-magnification view, which confirms that the as-synthesized samples are flower shaped with a large scale. The diameters of the flowers are around 20 μm, assembled by a large number of nanowires with lengths of around 10 μm, as shown with high-magnification view in Fig. 1b and c. In addition, the diameter of the single ZnO nanowire decreases with increasing distance from the growth point. The EDX spectrum exhibits C, O, Zn, and Ag peaks. In addition, the extremely intense Zn and O peaks originate from ZnO, Ag stems from the triangular silver nanoplates, and C is from the substrate. These findings confirm that synthesized samples are flower-like T-Ag/ZnO nanostructures.

The TEM images of flower-like T-Ag/ZnO nanostructures were tested, as shown in Figs. 2a, b and c. Results show that triangular silver nanoplates coated on ZnO nanowire, the morphology of Ag shows triangular nanoplates with average diameter of 30–40 nm. The light absorbance properties of triangular silver nanoplates were also characterized using UV–vis spectroscopy measured in the range of 250–800 nm, as shown in Fig. 2d. Spherical silver nanoparticles show a characteristic peak at about 400 nm [19]. In this paper, triangular silver nanoplates exhibit a strong absorption peak at 334, 466, and 716 nm. The peak at 334 nm is due to out-of-plane quadrupole resonances. At about 466 nm, the band arises from in-plane quadrupole resonances. In addition, the peak at about 716 nm attributes to in-plane dipole resonances [20]. The TEM photograph and UV–vis absorption spectrum confirm that flower-like T-Ag/ZnO nanostructures were synthesized successfully.

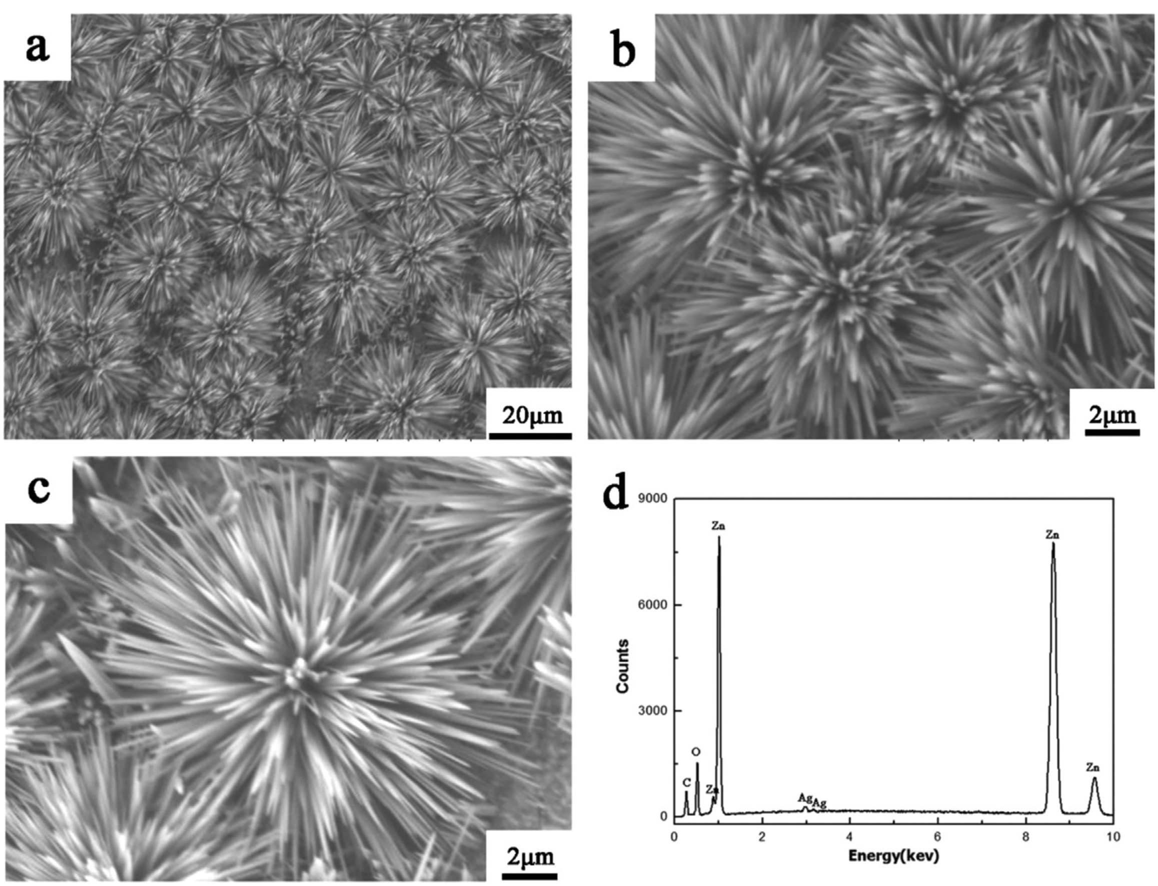

Fig. 1. (a) Low magnification SEM of the T-Ag/ZnO composites (b) high magnification SEM of the T-Ag/ZnO composites (c) SEM of a single the T-Ag/ZnO composites (d) the corresponding EDX pattern of the T-Ag/ZnO.