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Morphological characterization of sphere-like structured ZnO-NiO nanocomposites with annealing temperatures

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ABSTRACT

Three-dimensional (3D) sphere-like structured zinc oxide (ZnO) – nickel oxide (NiO) nanocomposites were prepared via a simple one-pot solution process. Their morphological properties were investigated as a function of the annealing temperature in the range 300–700 °C. Metal hydroxides ($Zn(OH)_2$ and $Ni(OH)_2$) were completely decomposed to metal oxides (ZnO and NiO), respectively, after annealing at 500 °C. Field emission scanning electron microscopy (FESEM) images revealed that the sphere-like structures maintained their shapes during the annealing treatment. The interwoven nanowalls that constituted sphere-like structures were themselves a sheet-like assembly of nanoparticles, which increased in size with increase in annealing temperature. After annealing at 700 °C, a network of interconnected nanoparticles could be observed.

1. Introduction

Metal oxide composites at the nanoscale have attracted significant attention these days due to their interesting structural, electrical, optical, and photocatalytic properties [1–12]. It was reported that zinc oxide (ZnO) – copper oxide (CuO) composites containing nanoflakes had better transparency and photoluminescence (PL) properties as compared to pure ZnO nanoparticles [7]. This is important for application in optoelectronic devices. The synthesis of nanocrystalline ZnO – nickel oxide (NiO) mixed metal oxide powers in the form of agglomerated nanoparticles was reported by Sharma et al. [8]. Preparation of novel porous structured ZnO-NiO nanocomposites for lithium-ion batteries has been effectively studied [9,10]. It is imperative to further develop and investigate the properties of unique hierarchically architectured nanocomposites for designing materials with new functionalities, which could broaden their fields of application [8–12].

In our previous study [13], we successfully fabricated discrete, porous ZnO-NiO nanocomposites via a facile one-pot solution process, which is a promising technique for large-scale fabrication due to its low cost and simplicity. The morphology and structural characteristics of the ZnO-NiO nanocomposites (rod-type structures, sphere-like structures, nanolayered structures) were strongly dependent on the amount of nickel acetate in the solution used for the synthesis. In this present paper, we have investigated the effects of annealing temperatures on the morphological properties of sphere-like structured ZnO-NiO nanocomposites.

2. Experimental

To prepare ZnO-NiO nanocomposites, an aqueous solution was prepared by dissolving zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$; Zn(NO), 10 mM), nickel acetate tetrahydrate ($Ni(CH_3COO)_2{\cdot}4H_2O$; Ni(Ac), 7 mM), and hexamethylenetetramine (HMT, $C_6H_{12}N_4$, 10 mM). This greenish solution was kept at a constant temperature of 90 °C for 6 h in a dry oven, and allowed to react. After reaction, the as-obtained powder was washed with deionized water and dispersed in ethanol. A solution containing this power was dropped on a silicon substrate. The samples were dried at 120 °C for 10 min, subsequently annealed at temperatures of 300 °C, 500 °C, and 700 °C for 1 h in air. These samples-dried but not annealed, and the samples dried and annealed at temperatures of 300 °C, 500 °C, and 700 °C were named as ZN0, ZN3, ZN5, and ZN7, respectively. The schematic flow chart for preparation of the ZnO-NiO nanocomposites was shown in the Fig. S1, in the Supporting information.

The morphology of ZnO-NiO nanocomposites was characterized by field emission scanning electron microscopy (FESEM, JSM-6701). The crystal structure and phase were identified using X-ray diffraction (XRD, D8ADVANE). The chemical bonds were analyzed by Fourier transform infrared (FTIR, JASCO, FT/IR-6100) spectroscopy in the spectral range 350–4000 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

Fig. 1 shows the FESEM images of the ZN0 (a,b), ZN3 (c), ZN5 (d),

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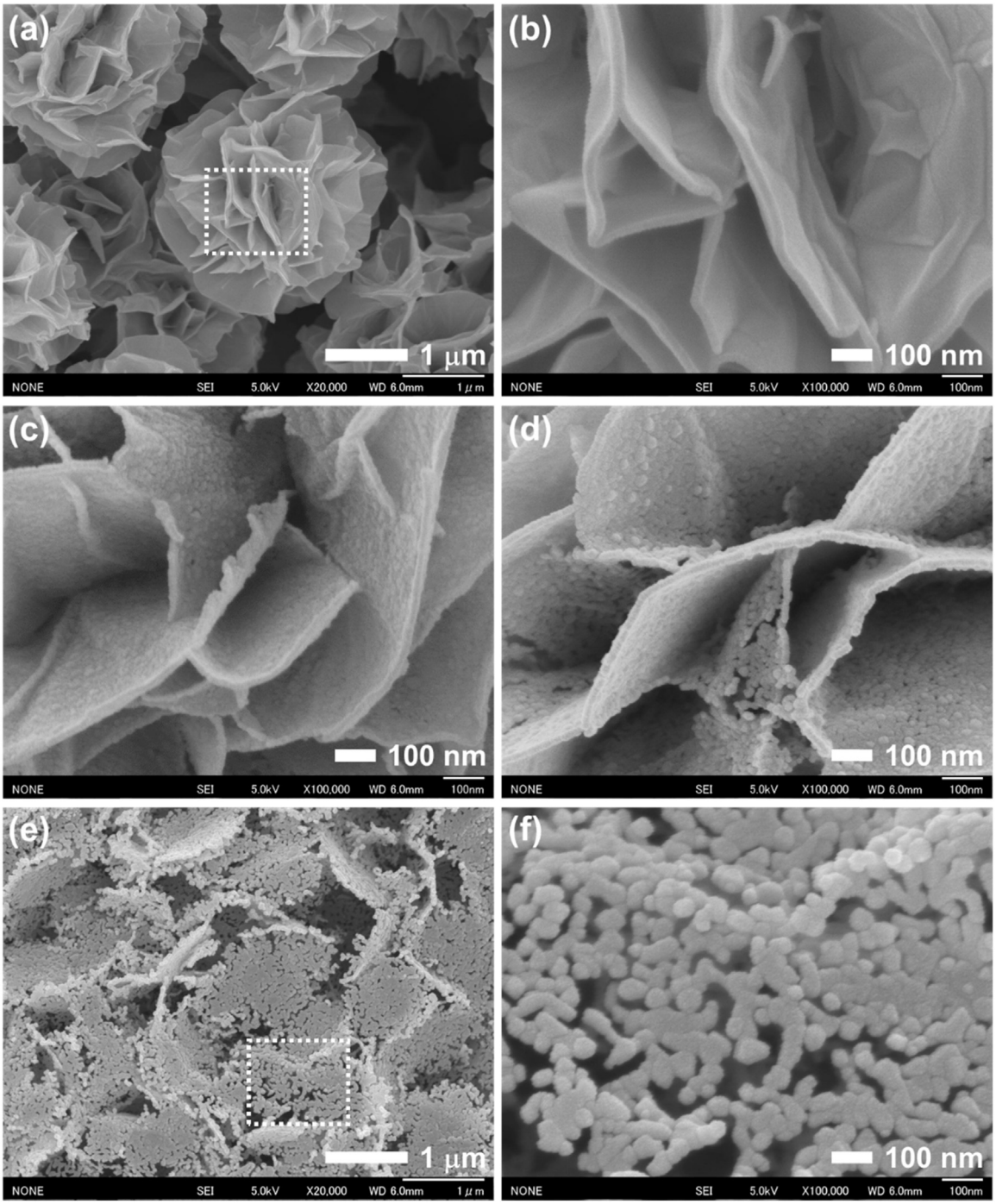

Fig. 1. FESEM images of (a) ZN0-low magnification, (b) ZN0-high magnification, (c) ZN3-high-magnification of the area marked by square in Fig. S2(a), (d) ZN5-high-magnification of the area marked by square in Fig. S2(b), (e) ZN7-low magnification, and (f) ZN7-high magnification.

and ZN7 (e,f) samples. The ZN0 sample had three-dimensional (3D) porous, sphere-like structures assembled with interwoven nanowalls (Fig. 1(a)). The overall morphology of the ZN0 sample was shown in Fig. S2. It shows that the sphere-like structures with diameter of about 3 μm are uniformly distributed. From the high-magnification image (Fig. 1(b)), it can be seen that the thickness of the nanowalls is around 25 nm. When the annealing temperature was increased to 500 °C, the sphere-like structures maintained their shapes, as shown in Fig. S3. It is worth to note that the individual nanowalls are embedded with sub-level nanoparticles, as shown in Fig. 1(c,d). On annealing at a temperature to 700 °C (ZN7), network-structured nanoparticles were observed because the sphere-like structures were aggregated and mingled each other, as shown in Fig. 1(e). The nanoparticles grew in size as the annealing temperature was increased from 300 °C to 700 °C. In the ZN7 sample (Fig. 1(f)), the nanoparticles are about 30–50 nm in size, which makes the surface noticeably rougher as compared to that of other samples.

Fig. 2 shows the XRD patterns of the ZN0 (a), ZN3 (b), ZN5 (c), and ZN7 (d) samples. The XRD pattern of ZN0 sample had a diffraction peak at 33.5°, which could be resolved into diffraction peaks at 33.5° for the (110) plane of nickel hydroxide ($Ni(OH)_2$) (JCDPS card no.22-0444), and 34.3° and 36.0° for the (224) and (317) planes of zinc hydroxide ($Zn(OH)_2$) (JCPDS card no.20-1435), respectively. The XRD pattern of the ZN0 sample in the range 2θ=30–50° was shown in Fig.