

# Preparation of porous zinc oxide-nickel oxide nanocomposites by facile one-pot solution process



Kyung Ho Kim\*, Yuya Yoshihara, Yoshio Abe, Midori Kawamura, Takayuki Kiba

Department of Materials Science and Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan

## ARTICLE INFO

### Keywords:

ZnO  
NiO  
Sphere-like structures  
Nanolayered structures  
Nanocomposites

## ABSTRACT

Porous zinc oxide (ZnO)-nickel oxide (NiO) nanocomposites were fabricated via a one-pot process using aqueous solutions of zinc nitrate hexahydrate (Zn(NO)<sub>3</sub>, 10 mM), hexamethylenetetramine (HMT, 10 mM), and nickel acetate tetrahydrate (Ni(Ac), 7 mM (7NZO), 10 mM (10NZO)). The structural and morphological properties of these nanocomposites were investigated and compared to those of pure ZnO nanostructures. Rod-type nanostructures were observed in the pure ZnO sample, while porous sphere-like structures and continuous nanolayered structures were observed in the 7NZO and 10NZO samples, respectively. This difference in morphology might be due to the growth of the non-polar plane instead of the polar plane of ZnO in the clusters. The nanocomposites were composed of Ni, Zn, and O, which were homogeneously distributed. Distinct morphologies of the ZnO-NiO nanocomposites were obtained via a facile one-pot solution process.

## 1. Introduction

Significant efforts have been devoted to the development of nanostructured metal oxides with unique structural morphologies that find potential applications in a wide range of electronic and optoelectronic devices [1–3]. One such metal oxide, zinc oxide (ZnO), with a wide band gap energy (3.37 eV) and large exciton binding energy (60 meV), has been of strong research interest as a typical n-type oxide semiconductor [1,2]. The electrical and optical properties of ZnO can be modified by the incorporation of dopants (Al, Ga, Sn, etc.) into its lattice in order to meet the requirements for nanotechnology applications [4–6]. Meanwhile, nickel oxide (NiO) as a p-type oxide semiconductor has been used in drug delivery systems, photocatalysts, battery cathodes, magnetic materials, electrochemical capacitors, and electrochromic films [7,8].

ZnO-based mixed nanocomposites, i.e., ZnO-SnO<sub>2</sub>, ZnO-NiO, ZnO-CuO, exhibit superior functional performance compared to single-phase metal oxides [8–12]. This study has mainly focused on the control of the dimensions and morphology of such mixed oxides, as well as use of simple, cost-effective processing methods that do not require sophisticated equipment [8,10,11]. In this study, we prepared unique porous ZnO-NiO nanocomposites via a facile one-pot solution process and compared their structural and morphological properties with those of pure ZnO nanostructures.

## 2. Experimental

For the ZnO sample, an aqueous solution of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O; Zn(NO), 10 mM) and hexamethylenetetramine (HMT, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, 10 mM) was stirred for 1 h at room temperature. The transparent aqueous solution was kept in a dry oven at 90 °C for 6 h. After reaction, the whitish powder was centrifuged and then dispersed in ethanol (C<sub>2</sub>H<sub>6</sub>O). The resulting solution was dropped on a substrate and dried at 120 °C for 10 min, in air. It was finally annealed at 500 °C for 1 h at a heating rate of 10 °C/min, in air.

For the ZnO-NiO sample, nickel acetate tetrahydrate (Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O; Ni(Ac), 7–10 mM) was added to the ZnO solution; this is a simple condition for the synthesis of ZnO-NiO nanocomposites [8,10,11]. The other parameters were kept the same as those for the ZnO synthesis. Samples without Ni(Ac), and those with 7 mM and 10 mM Ni(Ac) were indexed as 0NZO, 7NZO, and 10 NZO, respectively.

The crystalline structure and phase of the samples were identified using X-ray diffraction (XRD, D8ADVANCE) at acceleration voltage and current of 40 keV and 40 mA, respectively, with a scanning step of 0.01°. Sample morphologies were observed by a field emission scanning electron microscopy (FESEM, JSM-6701) attached with an energy dispersive X-ray (EDX).

\* Corresponding author.

E-mail address: [khkim@mail.kitami-it.ac.jp](mailto:khkim@mail.kitami-it.ac.jp) (K.H. Kim).

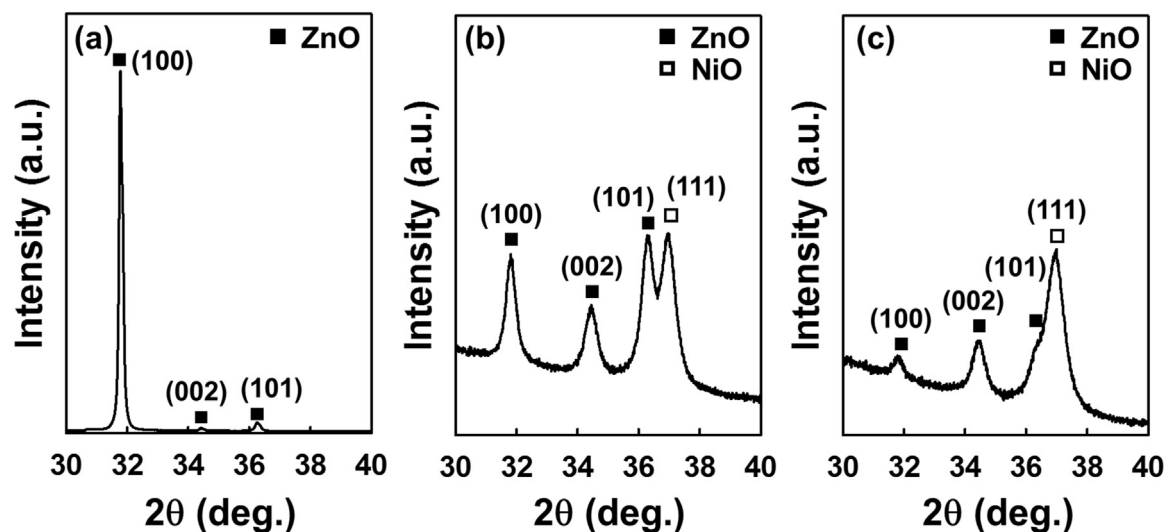


Fig. 1. XRD patterns of (a) 0NZO, (b) 7NZO, and (c) 10NZO samples.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the 0NZO (a), 7NZO (b), and 10NZO (c) samples. Detailed peak positions and lattice parameters are summarized in Table S1 in Supporting Information. In the case of the 0NZO sample (Fig. 1(a)), all the diffraction peaks could be indexed to wurtzite hexagonal structured ZnO (JCPDS card no. 36–1451). The calculated lattice parameters of the 0NZO sample were  $a=3.24$  Å and  $c=5.20$  Å. When Ni(Ac) was added, a (111) diffraction peak due to NiO (JCPDS card no. 47–1049) as a secondary phase, as well as peaks due to ZnO, were observed in the spectra of the 7NZO and 10NZO samples (Fig. 1(b) and (c)). As expected, an excess of Ni led to the formation of the oxide phase. In the 7NZO and 10NZO samples, diffraction peaks indexed to ZnO were shifted to higher  $2\theta$  values as compared to those for the pure ZnO sample (0NZO). This was due to the differences in the ionic radii of  $Zn^{2+}$  (0.74 Å) and  $Ni^{2+}$  (0.69 Å) [13], indicating that smaller Ni ions were incorporated into the ZnO lattice and caused a reduction in the lattice parameters. Meanwhile, the NiO (111) diffraction peak of the 7NZO sample was shifted to the lower  $2\theta$  values as compared to that of the 10NZO sample. Thus, it could be concluded that Ni-doped ZnO and Zn-doped NiO composites were prepared via a facile one-pot solution process, in the 7NZO and 10NZO samples.

Fig. 2 shows the FESEM images of ZnO samples with various Ni(Ac) contents. As shown in Fig. 2(a) and (b), the 0NZO sample had a flower-like structure assembled from rods and individually distributed rods. The length and width of the rods were irregular. The surface of the rods was very smooth (Fig. 2(b)). The morphology of the nanostructures was influenced by the nucleation and growth process in aqueous solution [14]. FESEM images of the 0NZO sample reacted at 90 °C for 1 h are shown in Fig. S1. It could be seen that rod-type nanostructures (Fig. S1(b)) spouted from ball-like clusters of the assembled nanostrings with a thickness of ~10 nm. After reaction for 2 h, the rods from the clusters increased in length, as shown in Fig. S2. This result is in good agreement with the study reported by Liu et al.

[15]. It was known that one-dimensional (1D) rod-type nanostructures are easily grown because of the surface energy difference between the polar and non-polar planes of ZnO [14,16,17].

Nanostructures with an interesting morphology were observed when Ni(Ac) was added to the ZnO solution. Three-dimensional (3D) sphere-like structures assembled with interwoven nanowalls were observed in the 7NZO sample, as shown in Fig. 2(c). The average diameter of the sphere-like structures was around 3 μm, and they are uniformly distributed, as shown in Fig. S3(a). From the high-magnification image (Fig. 2(d)), the thickness of the nanowalls was found to be around 25 nm. The Ni ions might have lowered the surface energy difference between the polar and nonpolar planes, leading to a distinct morphology [18]. As a result, individual clusters with interconnected nanostrings formed nanowalls rather than rods. Further studies are underway to understand the growth mechanism of the nanostructures. It is noteworthy that individual nanowalls are embedded with nanoparticles that are ~10 nm in diameter (Fig. 2(d)). Similar sphere-like structures have been reported in the other papers on ZnO, NiO, or nickel hydroxide (NiOH) [19–22]. However, this morphology is unique among ZnO-based mixed nanocomposites [10,11]. Porous nanostructures with a large surface area are important for a wide range of applications [23,24].

With an increase in the amount of Ni(Ac) in the ZnO solution to 10 mM (Fig. 2(e,f)), individual sphere-like structures that were interconnected without clear boundaries formed continuous nanolayered structures (Fig. S3(b)). The high-magnification image (Fig. 2(f)) revealed that the continuous nanolayered structures consisted of embedded nanoparticles.

Fig. 3 shows the electron image (a), EDX elemental maps (b–d), and spectrum (e) of the 10NZO sample. These images confirmed that the nanocomposites were composed of Ni, Zn, and O, which were uniformly distributed. From XRD and EDX analyses, it could be confirmed that porous ZnO-NiO nanocomposites were formed via the facile one-pot solution process.

Download English Version:

<https://daneshyari.com/en/article/5439204>

Download Persian Version:

<https://daneshyari.com/article/5439204>

[Daneshyari.com](https://daneshyari.com)