Hierarchical nanostructures of nickel-doped zinc oxide: Morphology controlled synthesis and enhanced visible-light photocatalytic activity

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ABSTRACT

Nickel-doped zinc oxide hollow nanospheres have been synthesized using a simple solvothermal approach through a morphological transformation driven by a localized Ostwald ripening process. The saturation magnetization of the system shows that the materials have only a short-range magnetic ordering in them. Based on the visible-light photocatalytic experiment, we could confirm that, with a high doping content (10 mol%), the doping accompanied with increased recombination which reduced the energy of photoinduced electron leading to suppressed photocatalytic activity. Changing reaction parameters, i.e. the mixed reactant concentration, doping content, and different solvents, $Zn_{1-x}Ni_xO$ powders exhibited the elongated prismatic form with sharp tips, quasi-spherical structure, and hexagonal-based polyhedron, respectively. The photocatalytic results demonstrate that different crystal growth orientations, specific surface areas, particle size distributions, and doping levels have strong influences on the photocatalytic activity performances. Among the samples, hexagonal-based polyhedrons have the best photodegradation efficiency standing on higher fraction of exposed polar facets, larger specific surface area, as well as an optimal doping level. The 1 mol% nickel content showed the best photocatalytic activities among the nickel-doped zinc oxide samples.

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1. Introduction

Zinc oxide (ZnO) is a transparent semiconductor with a direct wide band gap of 3.4 eV at 300 K, large exciton binding energy (60 meV), n-type conductivity, abundant in nature and environmentally friendly. This makes it suitable for a wide range of applications in the optoelectronics industry [1–5], such as gas sensors [6,7] and anode materials [8]. Among them, photocatalysts [9–11] are one of the most important applications of nanostructured ZnO materials standing on the absorption band reaching up to 385 nm. Although the preparation of morphology controlled ZnO crystals through varying the reaction parameters and the corresponding effects on the photocatalytic activity has been extensively investigated [12–17], the comparatively narrow absorption band in UV region limits the photocatalytic efficiency to meet the requirement for practical applications, as the visible light accounts for 45% of energy in the solar radiation while UV light less than 10% [18]. Therefore the band gap of ZnO has to be narrowed or split into several sub-gaps. Modification of ZnO by doping with

metal ions is a considerable method to inhibit the recombination of photoinduced electron and holes and to promote photocatalytic activity.

Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ga^{3+} [18–23], and some other metal and non-metal ions [24,25] are often used as attractive dopants for ZnO because they are isomorphic to Zn^{2+} ions. Nair [18] and Barick [19] also found that in some cases where the additional metal ions decreased the photocatalytic activity and photodegradation rate of ZnO nanostructures because the metal ions substituted in ZnO lattice would act as the trapping or recombination centers for electrons and holes and substantially negatively affect the photodegradation efficiency. However, the metal ions are responsible for the increased recombination, but not the only reason for the change of photodegradation efficiency of ZnO. There may be another two factors contribute to this change. We could see that, in Nair and Barick's works, Co-doped ZnO nanoparticles and transition metal (Mn, Co and Ni) doped ZnO nanoclusters were synthesized, respectively, with the doping content of transition metal ⩾ 5%. But we know that the band gap energy decreased significantly when the doping level was raised over 5% [22], and that should cause the energy of photoinduced electron decrease, which accounted for the decreased photocatalytic activity of ZnO nanostructures. So

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this confirms that the doping content in ZnO nanostructures should be one of the influential factors responsible for the photocatalytic activities. The photocatalytic reaction occurs primarily at the interface between the organic pollutants and the active surface of the photocatalyst [26]. Hence, the shapes and surface morphologies of metal ions-doped ZnO materials would also play an important role in the photocatalytic performance.

In this work, we report our recent effects on the synthesis of Ni-doped ZnO (Ni/ZnO) hierarchical nanostructures through a facile selected-control solvothermal process. The experimental analysis reveals that the hollow spherical products were obtained by self-transformation from solid to hollow core–shell structure under the driving force of Ostwald ripening process. The doped oxide possessed better visible-light photocatalytic activity than pure ZnO synthesized through the same approach, but it was still unsatisfactory due to the high doping level. Therefore we also studied the effects of other synthetic parameters, such as reactant concentration, doping content and different solvents, on the morphological control and enhanced photodegradation performance of the doped oxides. In the experiments, we got several styles of Ni-doped oxides with different morphologies, such as prismatic form with sharp tips, quasi-spherical structure, and hexagonal-based polyhedron. Based on crystal growth mechanisms and photodegradation performances of the above-mentioned products, it can be concluded that the change of solvent, doping content, surface morphology, specific surface area, and particle size distribution are key factors influencing photocatalytic properties of Ni-doped ZnO, which have been discussed in the present article.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($(C_2H_3O_2)_2Zn \cdot 2H_2O$, 98+%), nickel (II) acetate tetrahydrate ($(C_2H_3O_2)_2Ni \cdot 4H_2O$, 99.8%), sodium hydroxide (NaOH, >98%), methanol (CH_3OH, >99.8%), and ethylene glycol (>99.8%) were purchased from SCRC, China and used as received without further purification.

2.2. Synthesis

Ni-doped ZnO hollow spheres were synthesized via a template-free solvothermal method reported in our previous work [27]. Briefly, to produce consistent $Zn_{1-x}Ni_xO$ hollow spheres, 1.25 mmol mixed reactants (with zinc vs. nickel molar ratio of 9.0, a dopant concentration of 10 mol%) were dissolved in 20 mL methanol with magnetic stirring for 1 h. NaOH (0.05 g) was added into the above solution with magnetic stirring and further sonicate dispersion at 0 °C. Subsequently, the suspension was put into a 50-mL Teflon-lined autoclave and heated at 200 °C for 8 h followed by naturally cooling to room temperature. The precipitates were collected and washed with ethanol, then dried under vacuum.

The influences of different precursor concentrations, solvent systems, and Ni-doping contents on particle size, specific surface area and morphology of $Zn_{1-x}Ni_xO$ were also investigated by increasing the mixed reactants from 1.25 mmol to

5.00 mmol and substituting H_2O, methanol–H_2O mixed solvent (v/v, 1:1), ethylene glycol (EG), and EG–H_2O mixed solvent (v/v, 1:1) for methanol, respectively. This was summarized in Table 1.

2.3. Characterization

The crystallinity was characterized using an X-ray diffractometer (XRD, Philips X'Pert-MPD system) with Cu Kα radiation. The microstructures of the products were analyzed by field emission scanning electron microscope (FESEM, JEOL, JSM-6700F), and transmission electron microscope (TEM, JEOL JEM-100). The magnetic property of the Ni-doped ZnO sample was investigated with Vibrating sample magnetometer (VSM, Lake Shore Model 7407). Brunauer–Emmett–Teller (BET) surface areas of the samples were determined on a NOVA 4000e surface area & pore size analyzer. Hydrodynamic diameters (i.e., particle size) were determined by Malvern NanoZS90 using three different samples of each suspension. The solid-state UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were recorded over the range of 200–800 nm in the absorption mode using a Thermo Nicolet Evolution 500 UV–vis spectrophotometer equipped with an integrating sphere. Photoluminescence (PL) spectra of oxide powders were measured at room temperature using an Edinburgh FLS 920 fluorescence spectrophotometer.

2.4. Evaluation of photocatalytic activity

The photocatalytic activities of the as-prepared Ni-doped ZnO and pure ZnO samples were evaluated by the photoassisted degradation of Rh B aqueous solution at room temperature under visible light irradiation. A Xenon lamp (CHFXQ 500 W, Global Xenon Lamp Power) with a UV cut-off filter acted as a visible light source to provide light emission at 400–800 nm. In a typical reaction, 25 mg of catalyst was dispersed in 100 mL of aqueous Rh B (10 mg L^{-1}). Prior to irradiation, the suspension was stirred in the dark for 30 min to stabilize and equilibrate the adsorption of Rh B on the surface of $Zn_{1-x}Ni_xO$. The stable aqueous dye-$Zn_{1-x}Ni_xO$ suspension was then exposed to visible light irradiation under continuous stirring. During irradiation, 10 mL of sample aliquots were extracted at 30 min intervals. After removing any suspended solid by centrifugation, a UV–Vis spectrometer (Xinmao UV-7504) was used to follow the decomposition of Rh B.

3. Results and discussion

In the present work, a controlled synthesis of nickel-doped ZnO hollow spheres with porous shells is successfully established with a solvothermal approach (see Sample 1 in Table 1 for details). The analyses on the morphology and crystallinity of the product were carried out by using FESEM, TEM, and XRD. Fig. 1a shows FESEM image of Ni-doped ZnO hollow spherical structures revealing a relatively uniform size population with main diameter of ∼200 nm. As shown by arrows in the image of broken spheres, the spherical structures have a vacancy at the center. XRD pattern (Fig. 1b) shows that all peaks match well with wurtzite ZnO (JCPDS card No. 36-1451) without any secondary phase, suggesting that the Ni^{2+} ions would occupy the Zn^{2+} site in the wurtzite structure. The magnetization curve of the hollow spherical product in Fig. 1c shows a saturation magnetization (Ms) of approximately 3.5×10^{-2} emu g^{-1} which is much lower than Ms. of $Zn_{1-x}Ni_xO$ nanorods with the similar doping level (about 7.4 emu g^{-1}) [28]. Both material composition and long-range order of the crystalline

Table 1
Detailed experimental parameters for the synthesis of typical Ni-doped ZnO samples and their morphologies, particle sizes, and BET surface areas.

Sample	Reaction system	t (h)	T (°C)	Morphology	Particle size (nm)	BET surface area (m²/g)
1	1.125 mmol ZnAc₂·2H₂O + 0.125 mmol NiAc₂·4H₂O + 1.25 mmol NaOH + 20 mL methanol	8	200	Hollow spheres with porous shells	–	–
2	4.95 mmol ZnAc₂·2H₂O + 0.05 mmol NiAc₂·4H₂O + 50 mmol NaOH + 20 mL methanol	8	200	Hexagonal prisms with sharp tips	292.5	3.601
3	20 mL EG being substituted for methanol, other terms same as Sample 2	8	200	Quasi-spherical structures	84.5	11.476
4	20 mL H₂O being used as solvent, other terms same as Sample 2	8	200	Hexagonal prisms	428.0	1.966
5	20 mL methanol–H₂O mixed solvent, other terms same as Sample 2	8	200	Quasi-spherical structures	174.3	5.257
6	20 mL EG–H₂O mixed solvent, other terms same as Sample 2	8	200	Hexagonal-based polyhedrons	101.9	10.569
7–11	Different doping levels (0.5%, 2%, 3%, 6%, 10% Ni, respectively), other terms same as Sample 6	8	200	Hexagonal-based polyhedrons to elongated prismatic structures	–	–