Materials Science in Semiconductor Processing 16 (2013) 792–796

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

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

Photocatalytic degradation of methyl orange and gas-sensing performance of nanosized ZnO

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ARTICLE INFO

Available online 17 March 2013

Keywords:
ZnO nanoparticles
Gas-sensing properties
Photocatalyst

ABSTRACT

ZnO nanoparticles were synthesized by calcining composites of zinc nitrate and poly(vinyl pyrrolidone) (PVP, molecular weight 30 000) at a mass ratio of 1:2 at 500 °C for 2 h. X-Ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were used to characterize the as-synthesized ZnO nanoparticles. The particles ranged in size from 30 to 50 nm. Infrared spectra of PVP and the PVP+$Zn(NO_3)_2 \cdot 6H_2O$ composite revealed coordination between the carbonyl (C=O) of PVP and Zn^{2+} of zinc nitrate, which led to a uniform nanoparticle morphology. The gas-sensing properties and photocatalytic performance of the final product were systematically investigated. The results show that the ZnO nanoparticles exhibit both a high response for ethanol detection and excellent photocatalytic activity for degradation of methyl orange under UV irradiation for 30 min.

1. Introduction

As living standards improve, there is a greater focus on the need for good environmental quality. Effective detection of toxic and hazardous gases and the degradation of organic pollutants have become increasingly important. ZnO, as a functional n-type semiconductor with a wide bandgap of 3.37 eV [1,2], has been extensively investigated for application in dye-sensitized solar cells [3,4], optoelectronic devices [5,6], and secondary lithium batteries [7]. Many studies have investigated the fabrication of ZnO sensors for detection of various gases [8–10]. ZnO is recognized as an excellent material for photocatalysis because of its high photosensitivity and nontoxic nature among various oxide semiconductor photocatalysts other than TiO_2 [11–13]. ZnO nanoparticles (NPs) can be synthesized by various approaches including sol–gel processing, homogeneous precipitation, mechanical milling, and spray pyrolysis [14–18]. However, ZnO NPs fabricated by these methods are prone to aggregation because of their large surface area and high surface energy, which limits their application. Therefore, a simple and effective synthetic strategy is required to obtain uniformly dispersed nanosized ZnO materials.

We synthesized ZnO NPs by calcining a composite of poly(vinyl pyrrolidone) (PVP; molecular weight 30 000) and $Zn(NO_3)_2 \cdot 6H_2O$. The gas-sensing properties and photocatalytic performance of the ZnO NPs were investigated in detail. The results show that our ZnO NPs exhibits a high response for ethanol detection and excellent photocatalytic activity for degradation of methyl orange (MO) under UV irradiation.

2. Experimental

2.1. Synthesis of ZnO NPs

All raw chemicals were analytical-grade reagents used without further purification. Deionized water was used throughout the experiments. In a typical procedure, 1 g of

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http://dx.doi.org/10.1016/j.mssp.2012.12.027

$Zn(NO_3)_2 \cdot 6H_2O$ and 2 g of PVP were dissolved in 80 ml of deionized water. The resulting clear solution was incubated in a water bath at 60 °C until it became sticky. The concentrated solution was transferred to a crucible and dried in an oven at 110 °C for 12 h. Finally, the dried sticky mixture was calcined at 500 °C in a muffle furnace for 2 h to obtain the final product.

2.2. Characterization

The sample morphology was characterized using a field emission scanning electron microscope (FE-SEM; Hitachi S-4800). Transmission electron microscopy (TEM) investigations were carried out using a Tecnai F20 microscope. X-Ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2000 diffractometer with Cu K_α radiation (λ= 0.15418 nm, 40 kV, 100 mA). The optical absorption characteristics of the samples were determined by UV/Vis diffuse reflectance spectroscopy (DRS) on a spectrophotometer (Hitachi U4100) equipped with an integrating sphere. A Nicolet FT-IR spectrometer (resolution 4 cm^{-1}) was used to determine the interaction between $Zn(NO_3)_2 \cdot 6H_2O$ and PVP.

2.3. Gas-sensing measurement

Side-heated gas sensors were fabricated by dropping a suitable amount of a paste consisting of ZnO NPs and absolute ethanol on alumina ceramic tubes equipped with two Au electrodes. After evaporation of the ethanol, the alumina ceramic tubes were coated with a layer of homogeneous ZnO film. A small Ni–Cr alloy coil was placed through the tube as a heater. The working temperature of the gas sensor was controlled by adjusting the current applied to the heater. Gas-sensing tests were conducted using a PC-controlled static system (WS-30A, Weisheng Electronics, China). The gas response was measured in the static state. A given amount of the gas to be tested was injected into the test chamber and mixed with air. After each measurement, the sensor was exposed to air by opening the chamber to the atmosphere. The sensor response was defined as the ratio of resistance in air (R_a) to that in the test gas (R_g).

2.4. Photocatalytic tests

The photocatalytic activity of the samples was evaluated for degradation of a model pollutant, methyl orange (MO), under UV light generated by a 500-W high-pressure mercury lamp. Reaction suspensions were prepared by adding the photocatalyst (100 mg) into MO solution (200 ml of 10 mg/l). The mixture was stirred in the dark for 30 min to obtain good dispersion and ensure adsorption–desorption equilibrium was reached. The suspension was then exposed to light irradiation under stirring. The temperature of the suspension was maintained at 30 ± 2 °C by circulating water through an external cooling coil, and the system was open to the air. At given time intervals, samples of the reaction solution were removed and centrifuged. The decrease in

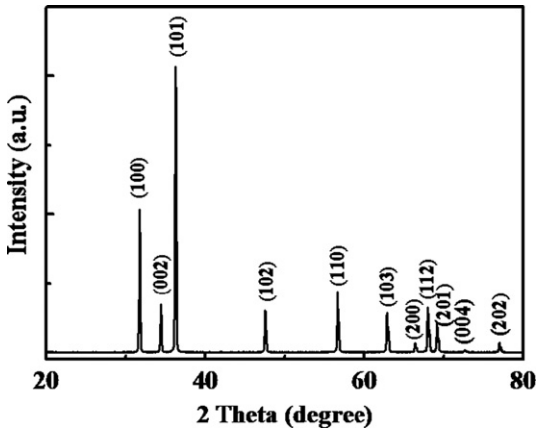

Fig. 2. XRD patterns of the as-obtained ZnO NPs.

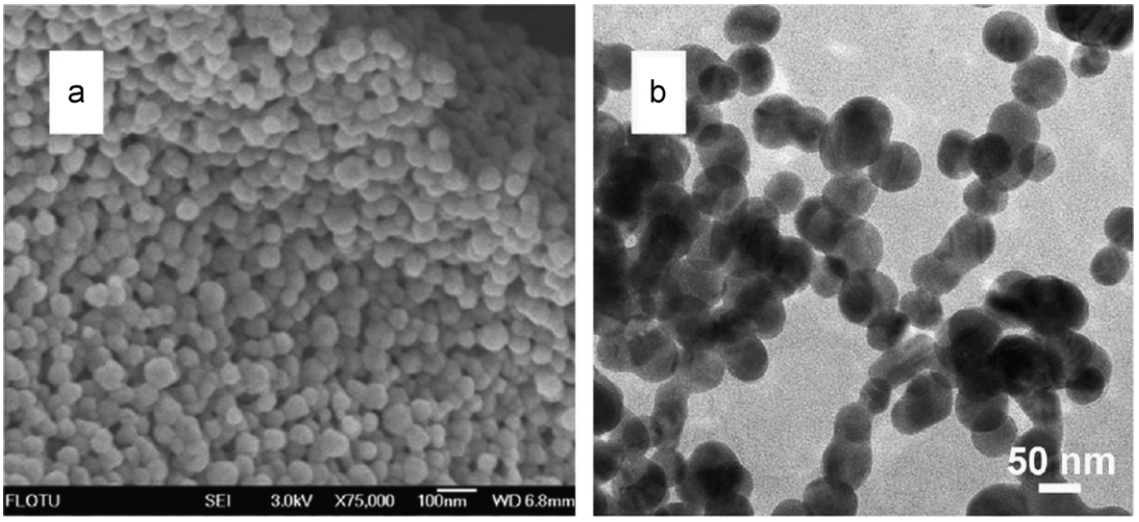

Fig. 1. (a) SEM and (b) TEM images of ZnO NPs fabricated by calcining a composite of PVP and $Zn(NO_3)_2 \cdot 6H_2O$ (mass ratio 2:1) at 500 °C for 2 h.