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Morphological Control of ZnO and ZnO@NiO Heterojunctions: Improving Sensitivity, Selectivity, and Humidity Resistance for Gas Sensing Applications

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Summary:

ZnO samples with distinct morphologies and ZnO@NiO heterostructures were synthesized via a microwave-assisted hydrothermal method. Structural characterization confirmed crystalline phases without impurities. Plate- and rod-like ZnO morphologies were obtained, each decorated with NiO in two concentrations. Gas sensing tests showed that ZnO plates had higher ethanol sensitivity, selectivity, and better humidity resistance than rods. ZnO@NiO heterostructures based on plates lowered the operating temperature and improved sensitivity and humidity resistance, despite reducing selectivity.

Keywords: zinc oxide, nickel oxide, heterostructure, chemical synthesis, gas sensor

Introduction

Metal oxide semiconductors (MOSs) are widely used in gas sensing applications due to their high sensitivity, low cost, and simple fabrication. However, challenges such as poor selectivity and humidity cross-interference limit their performance, thus reducing sensing accuracy. Some strategies to enhance selectivity and sensitivity include doping, morphological control, and the formation of heterostructures [1]. Among these, morphological control and heterojunctions are promising due to their ability to engineer surface properties, band structures, and to create preferential adsorption sites. In this work, we synthesized sub-micron zinc oxide (ZnO) structures with rod and plate morphologies, and we also combined them with nickel oxide (NiO) to form heterostructures via a single and a two-step microwave-assisted hydrothermal (MAH) method, respectively. The MAH approach allowed precise control over particle morphology. Thick films of the as-synthesized materials were fabricated using screen-printing method and evaluated as gas sensors for carbon monoxide, carbon dioxide, ethanol, benzene, hydrogen, and humidity.

Materials and Methods

The pure ZnO and ZnO@NiO heterostructures were synthesized via a single- and a two-step MAH method. The first step consisted in the synthesis of the ZnO morphologies. For such, analytical grade zinc acetate dihydrate and sodium hydroxide were used as precursors. Each precursor was separately dissolved in 40 mL of deionized water. Then, the sodium hydroxide solution was slowly added to zinc acetate dihydrate one. The mixture was poured into a PTFE autoclave and placed inside a microwave oven. The syntheses were performed at 130°C for 8 minutes. Two solutions with Zn^{2+} to OH^- molar ratios of 1:5 and 1:10 were used (1). The synthesis of the standard NiO sample followed a similar procedure. In this case, nickel nitrate hexahydrate was dissolved in 80 mL of deionized water (2), followed by an adjustment of the pH to 11 by adding a 2 M solution of sodium hydroxide. The synthesis was carried out at 140°C for 8 minutes, and the resultant product was calcined at 400°C for 1 hour. The synthesis of the heterostructures were performed by adding 600 mg of the as-synthesized ZnO samples in (1) to the Ni solution in (2), thereafter following the exact same steps of the NiO synthesis.

The as-synthesized powders were then used to fabricate the sensing films via the screen-printing method. The powders were mixed with alfa-terpineol and ethyl cellulose to prepare a paste and then printed onto alumina substrates with gold electrodes. The samples were calcined at 400°C for 1 hour to eliminate the organic compounds.

Results

X-ray diffractometry revealed crystalline samples free from phases other than wurtzite ZnO and fluorite-type NiO. For the ZnO@NiO heterostructures, both phases were detected. Rietveld analysis confirmed the increase in the NiO wt%, revealing samples with 24.30% and 41.80% for ZnO plates and 24.82% and 37.86% for ZnO rods.

The different Zn^{2+}/OH^{-} ratios resulted in two different ZnO morphologies, plates and rods, for 1:5 and 1:10 molar ratios, respectively. For the heterostructures shown in Fig. 1, it is possible to notice that the synthesis did not alter the morphology of the base ZnO sample. Also, the porous NiO nanosheets appear distributed on the surface of ZnO. The estimated band gaps were ~3.3 eV for ZnO and ~3.5 eV for NiO, consistent with literature. In the heterostructures, the absorbance edge of ZnO and NiO remained mostly unchanged.

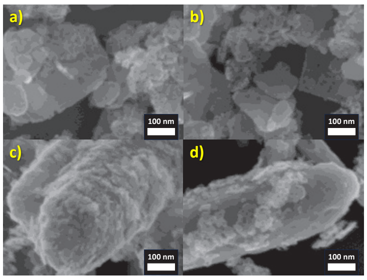

Fig. 1. Field-emission scanning electron microscopy of the heterostructures representing the base ZnO morphology, plates (a) and (b), and rods (c) and (d) decorated with NiO porous nanosheets.

Carbon monoxide was used to determine the working temperature of the sensors. As shown in Fig. 2, the ZnO plates with ~24% NiO showed the highest response to CO across all temperatures, with the best at 300°C, which is lower compared to the pure ZnO samples.

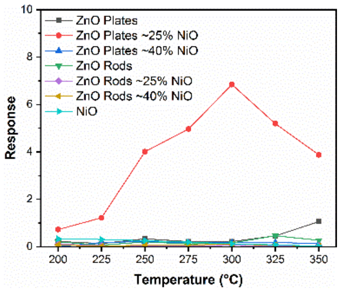

Fig. 2. Working temperature for the pure ZnO and ZnO@NiO heterostructures toward CO.

As shown in Fig. 3, the ZnO plates presented an improved humidity resistivity compared with ZnO rods, and a higher selectivity to ethanol, being able to detect it in the sub-ppm range. The heterostructure composed of ZnO plates and ~24% NiO showed an increased sensitivity compared to the pure ZnO samples and a significantly reduced cross-sensitivity to humidity, despite also presenting a decreased selectivity toward the tested gases. The other heterostructures did not present significant responses.

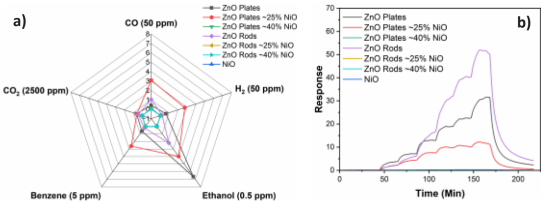

Fig. 3. Selectivity tests and dynamic response to different relative humidity levels, from ~0% to ~55% RH.

The morphological effect on the sensing results from the surface characteristics of each sample. The ZnO plates display polar surfaces with higher surface energy compared to rods, which changes their interaction with the different gaseous molecules, in this case increasing ethanol selectivity and humidity resistivity. The formation of heterostructures increases charge separation at the heterojunction, altering the depletion layer properties, which can increase the sensor sensitivity [1], as shown in Fig. 3. The improved humidity resistive of the heterostructures can be assigned to NiO on the surface since it is considered a humidity resistive material [2].

Conclusions

In this work, different ZnO morphologies were synthesized and used to prepared ZnO@NiO heterostructures. ZnO morphology improved ethanol sensitivity and decreased humidity cross-sensitivity compared with rod-shaped ZnO. The heterostructure consisting of ZnO plates and NiO improved sensitivity and humidity resistiveness but decreased selectivity. Thus, this work showed that morphological control and surface modification with other metal oxides can be a promising alternative to modify the semiconductor properties, design sensors with increased sensitivity and selectivity.

Acknowledgements

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