



Preparation of NiO nanoparticles in microemulsion and its gas sensing performance

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ABSTRACT

Nano-sized nickel oxides have been synthesized in a water-in-oil microemulsion. The as-synthesized samples were characterized by powder X-ray diffraction (XRD), transmission electronic microscopy (TEM) and nitrogen adsorption/desorption. The particle size of nickel oxide can be controlled from 11.5 to 31.5 nm by varying the proportion of water, surfactant and oil in the microemulsion, mixing method, and calcining temperature. Gas sensors based on as-synthesized nickel oxide are fabricated and investigated. They exhibit much higher sensitivities to hydrogen sulfide, ethanol and nitrogen dioxide, compared to those based on the conventional bulk NiO. Furthermore, the response of as-synthesized materials to various kinds of target gases increases with the decreasing of the particle size of gas sensors. It is noted that the NiO sensor with particle size of 11.5 nm displays high degree of selectivity, coupled with high response value, making it particularly interesting for H₂S-monitoring applications.

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1. Introduction

Nickel oxide (NiO) regarded as a model for p-type semiconductors has wide applications such as catalyst [1], electrochromic films [2], and fuel cell electrodes [3]. Recent works have demonstrated that NiO is also a promising functional material for chemoresistive-type gas sensors [4]. Therefore, much effort has been directed toward preparation of NiO by various methods, such as chemical precipitation [5], sputtering [6], and sol–gel [7]. However, gas sensors based on NiO could not exhibit satisfactory sensing performance including low sensitivity and high operating temperature, because of its rather higher resistance in air than that of n-type semiconductors.

In the last decade, nanostructured materials display more attractive physical and chemical properties than conventional bulk materials, due to their small particle size, large surface to volume ratio and high surface energy. These properties cause metal oxides with high porosity and nanostructure considered promising candidates in the development of gas sensor with high performance [8]. The microemulsion approach is a desirable method to prepare nanometer-sized particles. An inverse microemulsion system [9] is a thermodynamically stable isotropic dispersion of the aqueous phase in the continuous oil phase. Chemical reactions will occur when droplets containing the desirable reactant collide with each other and therefore nanometer-sized particles form. Lately, a variety of nanometer-sized materials with homogeneous dispersion and uniform particle size distribution have been successfully obtained by microemulsion processing techniques [10], such as Ag, ZrO₂, and BaTiO₃ etc.

In the present work, nano-sized nickel oxides were synthesized in reverse microemulsion. By adjusting experimental condition, we achieved four nickel oxides with different particles size. The gas sensors based on nickel oxide nanoparticles are fabricated and investigated. Notably, the enhanced sensing performance of the sensors to hydrogen sulfide, ethanol and nitrogen dioxide, compared to those based on conventional bulk NiO have been demonstrated.

2. Experimental

In a typical process, 0.666 g of nickel chloride hexahydrate was dissolved in 13.3 mL of deionized water (solution I); 2.2 mL aqueous ammonia were dissolved in 12.1 mL of deionized water (solution II); 40.4 mL of n-hexanol, 67.0 mL of Triton X-100 and 112.5 mL of cyclohexane were mixed together (solution III). The mobile phase was 44% oil (cyclohexane)/33% surfactant (Triton X-100)/16% cosurfactant (cyclohexane)/7% water (inorganic precursor) (w/w). Solution I and solution II were respectively added in two solutions III to form microemulsion. Sequentially, these two reverse microemulsions were mixed under vigorous stirring. The green precipitates were filtered, washed, and calcined at 500 °C for 2 h to produce nickel oxide. The other three sensing materials were synthesized according to conditions shown in Table 1. For comparison, conventional nickel oxide was also prepared by chemical precipitation method using 2 M aqueous ammonia solution and 0.2 M nickel chloride solution.

X-ray diffraction patterns were recorded with Rigaku X-ray diffraction D/max rA using Cu-K α radiation. Nitrogen adsorption/desorption isotherms were measured at 77 K with a Gemini VII instrument. The specific surface areas were estimated by the Brunauer–Emmett–Teller method [11]. Transmission electron microscopes were performed on a FEI Tecnai 30 electron

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Table 1
Different experimental conditions of as-prepared nickel oxide.

Experimental conduction	I	II	III	IV
Oil:surfactant:cosurfactant: water	12:36:24:28	44:33:16:7	44:33:16:7	44:33:16:7
Microemulsion mixing method	Direct	Direct	Dropwise	Dropwise
Calcining temperature	500 °C	500 °C	500 °C	450 °C

microscope of Phillips Analytical with an acceleration voltage of 200 kV. In order to fabricate the sensing device, the paste prepared from the mixture of product and deionized water was coated onto an Al₂O₃ tube on which two gold electrodes had been formed at each end. After drying at room temperature for 1 h, the devices were heated at 450 °C for 2 h in muffle furnace. A heater of Ni–Cr coil was inserted into the Al₂O₃ tube to supply the operating temperature. The different concentration target gases were obtained by diluting a definite amount of bomb gases with air. When the sensor was exposed to air or the sample gas, the electrical resistances of the sensor in air and sample gas were measured by a Fluke 8846A precision multimeter, respectively.

3. Results and discussion

3.1. Characterization of nickel oxide

Fig. 1(a) shows the X-ray diffraction patterns of NiO prepared with different experimental conditions. Compared with the JCPDS card no. 65-2901, all of the products are indexed as cubic NiO with lattice parameters of $a = 4.195 \text{ \AA}$ (the space group: Fm-3m). No characteristic peaks of impurities are detected. We can observe the diverse full-widths at half-maximum from the XRD patterns of products prepared with different experimental conditions. The calculated crystallite size (D) according to Scherrer Equation is 31.5 nm, 17.2 nm, 14.1 nm, 11.5 nm and 29.1 nm responding to experimental conditions I, II, III, IV and chemical precipitation method, respectively.

To investigate the particle size and dispersion status of sensing materials prepared with various experimental conditions, TEM images of them are provided. As seen in Fig. 1(b), a homogeneous distribution of particles can be discerned for all the samples synthesized by microemulsion method. The particle sizes are approximately consistent with values calculated from XRD patterns through Scherrer Equation. We also find that the NiO prepared with chemical precipitation agglomerated flakily that is distinct from the materials prepared by microemulsion method.

The specific surface area of the semiconducting oxide plays an important role in determining its catalytic activity of sensing material [12]. Fig. 1(c) displays the specific surface area of five materials measured by nitrogen adsorption/desorption. As expected, the smaller particle prepared by microemulsion method shows the larger specific surface area besides NiO prepared by chemical precipitation approach. Although its particle size (29.1 nm) is smaller than that of NiO prepared with experimental condition I (31.5 nm), its specific surface area is smallest which probably due to the serious agglomeration of particles in chemical precipitation process.

3.2. Gas sensing properties

Fig. 2(a) shows the sensitivities of gas sensors based on NiO with different particle size to 100 ppm H₂S, 100 ppm C₂H₅OH and 100 ppm NO₂ at their optimum operating temperature of 150, 200 and 150 °C, respectively. The sensitivity is defined as R_0/R_g for NO₂, R_g/R_0 for H₂S, C₂H₅OH, NH₃ and H₂, respectively. (R_0 is the resistance of the sensor in air, and R_g is the resistance of the sensor in target gas.) The response of the sensors using the NiO prepared by microemulsion method to various kinds of target gases increases with the decreasing of the particle size of the as-synthesized materials. As we know, the small particles can give rise to a large specific surface area and porous nanostructures, which provide high effective interaction between target gas and the semiconducting oxide. In addition, when the particle size is reduced to nanometers or in the order of the thickness of charge accumulation layer, however, the performance of the entire particles, not just the surfaces or interfaces,

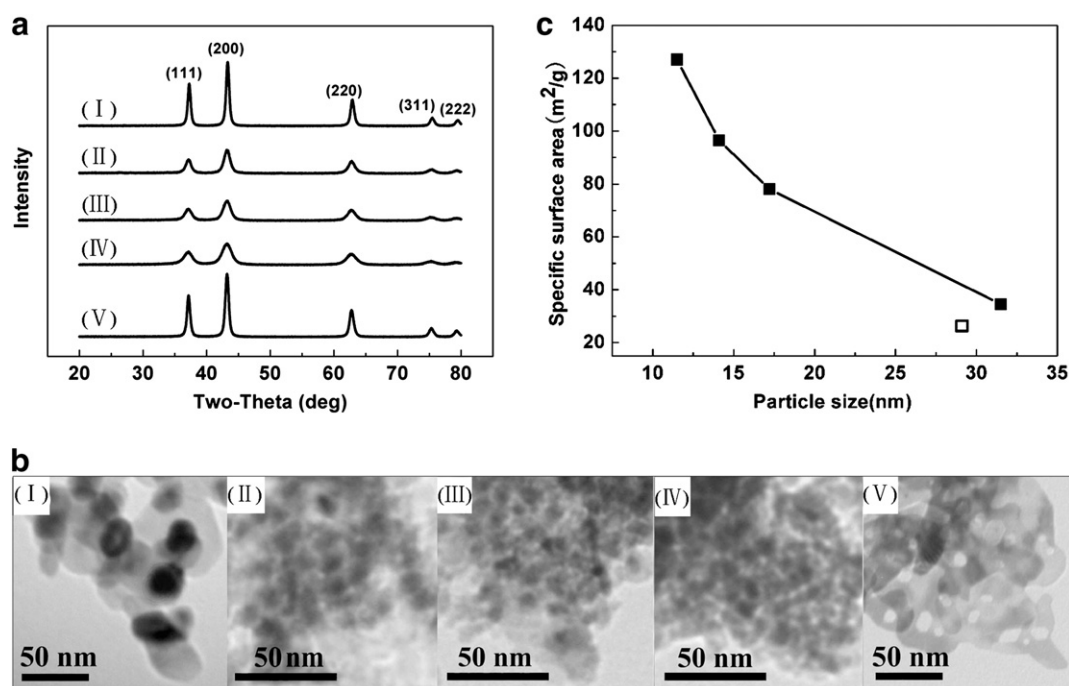


Fig. 1. (a) XRD patterns and (b) TEM images of NiO prepared with (I) experimental condition I, (II) experimental condition II, (III) experimental condition III, (IV) experimental condition IV, (V) chemical precipitation method, (c) Variation of specific surface area with the particle size of NiO prepared by microemulsion method (solid dots), and chemical precipitation method (hollow dot).

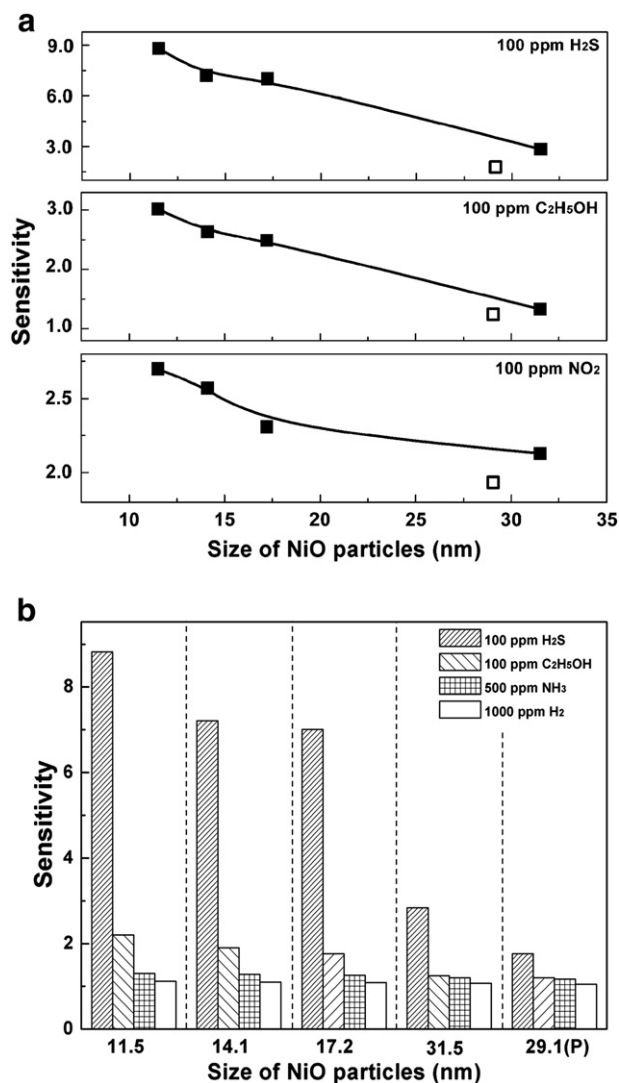


Fig. 2. (a) Response of the sensors based on NiO with different particle size to three kinds of gases, NiO prepared by microemulsion method (solid dots), and by chemical precipitation method (hollow dot). (b) Response of the sensors based on NiO with different particle size to four kinds of gases at 150 °C. P: NiO prepared by chemical precipitation method.

changes dramatically due to solid–gas interactions, leading to a substantial improvement in sensor response [13]. Therefore, the small size of as-prepared NiO is the essential factor for enhanced sensing properties of gas sensors. In our experiment, the responses of the sensor based on NiO synthesized by chemical precipitation method to all target gases are the lowest, which may be derived from the smallest specific surface area because of serious agglomeration for NiO nanoparticles (Fig. 1(c)).

The sensitivities of sensors based on NiO with different particle size to 100 ppm H₂S, 100 ppm C₂H₅OH, 500 ppm NH₃ and 1000 ppm H₂ at 150 °C are shown in Fig. 2(b). The responses of sensor based on NiO synthesized by chemical precipitation method to all target gases are the lowest. Comparably, the sensitivities of the sensors using NiO prepared by microemulsion method to various kinds of target gases totally increase with the decreasing of the particle size of nickel oxide. It is noted that an obviously increase in the responses of NiO sensors via microemulsion method to H₂S can be observed in contrast to other three target gases with the decreasing of the particle size of gas sensors. Therefore, the high degree of selectivity coupled with high response value makes the NiO sensor (11.5 nm) particularly interesting for H₂S-monitoring applications.

4. Conclusion

Nano-sized nickel oxides have been successfully synthesized in Triton X-100/n-hexanol/cyclohexane/water reverse microemulsion. By varying the proportion of surfactant, oil and water in the microemulsion, mixing method as well as calcining temperature, the particles size of nickel oxide can be adjusted from 11.5 to 31.5 nm. The gas sensors based on as-synthesized nickel oxide are fabricated and investigated. Notably, the enhanced sensitivities of the sensors to hydrogen sulfide, ethanol and nitrogen dioxide have been demonstrated in contrast to those using conventional NiO. It is suggested that the small NiO particles can give rise to a large specific surface area and porous nanostructures, as well as a high ratio of charge accumulation layer to the radius of particle, which provide high effective interaction between target gas and the semiconducting oxide and dramatic change in the performance of the material.

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