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Hydrothermal fabrication of uniform hexagonal NiO nanosheets: Structure, growth and response

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ABSTRACT

Uniform hexagonal NiO nanosheets were perfectly prepared by a controlled hydrothermal method followed by calcination. The as-prepared products were characterized by X-ray powder diffraction (XRD), which illustrated the precursor $Ni(OH)_2$ and the final product NiO. The morphologies of NiO were characterized in detail by field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HRTEM). The SAED pattern is detected from a sampling area covering a collection of constituent nanoparticles. Based on the experimental results and the crystal structure theory, the chemical reaction processes and the growth mechanism for hexagonal structure were proposed. In addition, the gas-sensing performances of uniform hexagonal NiO were investigated toward 50 ppm of several reductive gases including ethanol, CO, H_2S, CH_4 and NH_3 at different working temperatures.

1. Introduction

As a significant p-type semiconductor with wide band gap energy in the range of 3.6–4.0 eV [1], nickel oxide (NiO) has long been investigated in several fields in the industry product for the extensive use such as electrochemical capacitor [2,3], magnetic property [4] and fuel cell electrodes [5]. However, it was also found that the gas sensing property of nickel oxide was outstanding and studied deeply in many literatures [6–8]. In recent years, nickel oxide was a promising material used as a particular gas sensor for detecting some inconspicuous gases such as CO, toluene, ammonia and alcohol, which had been reported by many works [9–12]. However, the gas sensing properties were relative to diversified influencing factors, such as the testing temperature, atmosphere concentration and the type of reductive gas. It was necessary to discuss systematically to confirm the quality of a gas sensor indeed.

At the meantime, in order to find out special morphologies with better gas sensing performances, nearly all kinds of morphologies of nickel oxide had been synthesized and reported, which could be classified as three obvious characteristics due to their dimensionalities. Approximate hexagonal NiO nanosheets (2-D) were mentioned by Yuan et al. [13] and Zheng et al. [14]. However, perfect uniform hexagonal NiO have not been reported and there were much less analysis about the crystal structure.

In our present work, uniform hexagonal NiO nanosheets were successfully prepared by controlling the concentration of ammonia solution and the dose of ethylene glycol (EG). The growth mechanism was elaborated according to the crystal structure and characterization. Furthermore, the gas-sensing performances of the as-prepared NiO nanostructures were investigated toward ethanol, CO, H_2S, CH_4 and NH_3 on the response and selectivity.

2. Experiment

All reagents used were of analytical purity and were directly used without further purification. In a typical procedure, 0.475 g (2.0 mmol) of $NiCl_2 \cdot 6H_2O$ is dissolved into 25.0 ml distilled water which was combined with 15.0 ml of EG to form a green clear solution in a beaker of 80 ml capacity. $NH_3 \cdot H_2O$ (25% by v/v) was added dropwise adjusting the pH to 9.50. The mixture was magnet stirred for 5 min to give a clear blue solution and transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 140 °C for 12 h. After the reaction was completed, the autoclave was cooled to the room temperature naturally. The green products were harvested by pursuing centrifugation, washing with distilled water and ethanol three times, to remove unexpected ions, then dried at 60 °C in

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vacuum. The powder was heated to 450 °C with a rate of 1.0 °C min^{-1} and then calcined at 450 °C for 2 h.

The as-prepared products were characterized by the X-Ray Diffraction (XRD), a Rigaku D/Max-1200X diffractometry with the Cu Kα radiation, employing a scanning rate 0.02 ° s^{-1} in the 2θ ranging from 10° to 80°. The morphologies and microstructures of as-prepared samples were characterized with a Nova 400 Nano field emission scanning electronic microscopy (FE-SEM) and transmission electron microscope (TEM, ZEISS, LIBRA200) with an accelerating voltage of 200 kV. Gas-sensing properties were measured with HW-30A gas sensitivity instrument (Hanwei Electronics Co., Ltd.). The sensor response (S_r) to the test gas was defined as R_g/R_a, where R_g and R_a were the resistance of the sensors in target gases and air, respectively.

3. Results and discussions

The XRD patterns and SEM images of precursor $Ni(OH)_2$ and final NiO product are shown in Fig. 1. In the Fig. 1(a), the diffraction data are all in the perfect agreement with the standard spectrum (JCPDS, no.14-0117), demonstrating that the precursors must be the $Ni(OH)_2$. In Fig. 1(c), in according with the standard spectrum (JCPDS, no. 47-1049), the diffraction peaks at the angle of 2θ=37.2°, 43.2°, 62.8°, 75.2° and 79.4° can be indexed as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) lattice planes. No peaks from other phases are found, therefore, indicating the $Ni(OH)_2$ precursors completely transform to NiO. Uniform hexagonal nanosheets can be both observed in the Fig. 1(b) and (d).

Evidently, as-synthesized NiO product presents uniform hexagonal nanosheets, which are shown in the higher resolution FE-SEM images (Fig. 2(a)). The thickness and length of these perfect hexagonal nanosheets are approximately 30 and 200 nm. It is obvious that these nanosheets are separate and do not adhere to each other in spite of their quite small size and ultrathin layer. The HRTEM image (Fig. 2(b)) gives a feature of a perfect hexagonal nanosheet and shows clear mesopores on the surface due to the decomposition of $Ni(OH)_2$. The SAED pattern in Fig. 2(c) that is detected from a sampling area covering a collection of constituent nanoparticles shows singlet spots revealing the single-crystalline structure of as-prepared NiO nanosheets. Furthermore, magnified image (Fig. 2(d)) of the original HRTEM image (Fig. 2(e)) shows the spacing between two adjacent lattice plane as 0.24 nm, which corresponds to the (1 1 1) reflection of NiO. Thus, it can be concluded that the hexagonal nanosheets orient with the top surfaces of (1 1 1) planes and the side surfaces of (2 2 0), (2 0 2) and (0 2 2) planes, which also corresponds to the main diffraction peaks in Fig. 1(c).

Based on the experimental observations and analysis, the reaction processing can be described in Eqs. (1)–(4). Initially, Ni^{2+} ions and EG molecules form one kind of complex ($EG\text{-}Ni^{2+}$), it can be described as

$$EG+Ni^{2+} \leftrightarrow EG-Ni^{2+} \text{ (complex)}. \quad (1)$$

The aqueous ammonia provides OH^- ions when the concentration reaches breakthrough point via the reaction

$$NH_3 \bullet H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

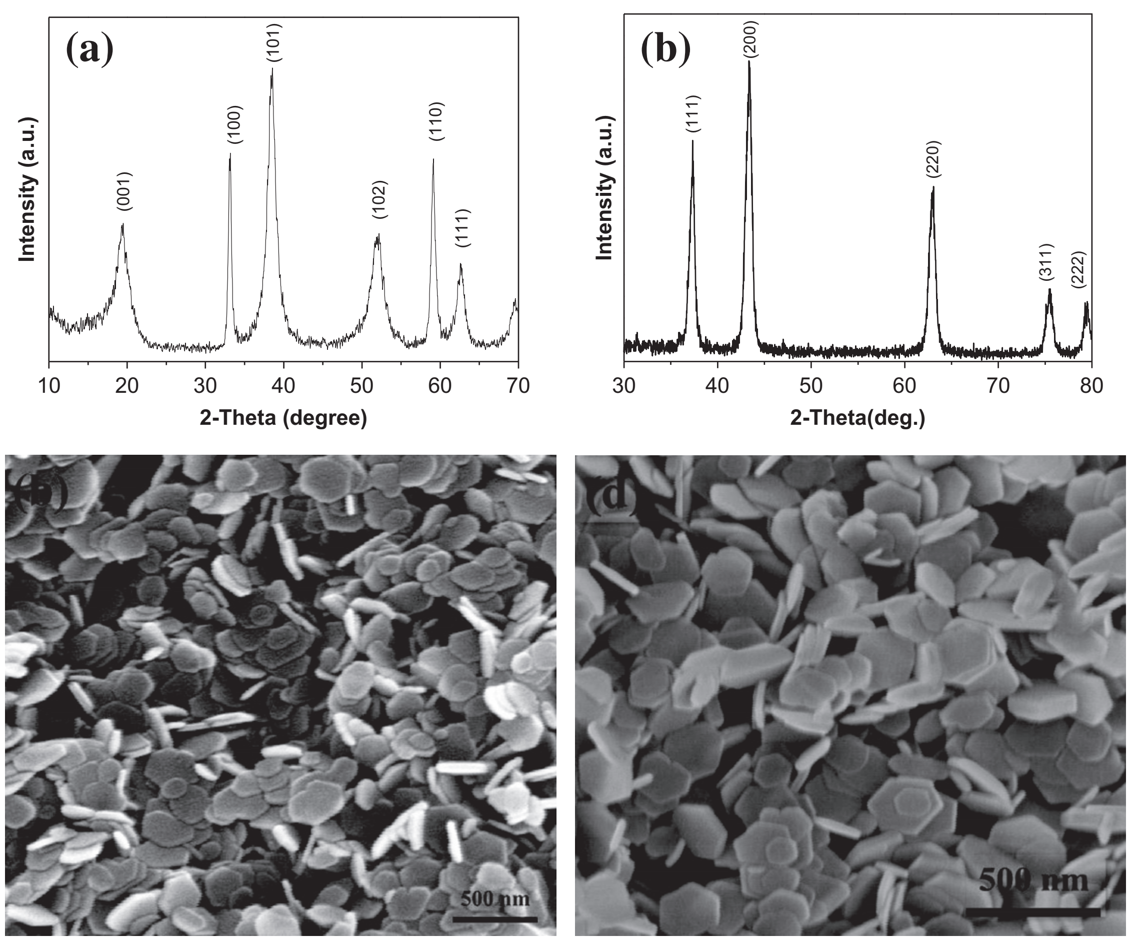

Fig. 1. XRD patterns and SEM images of the precursor (a,b) and NiO sample (c,d).