Facile Synthesis of Polycrystalline NiO Nanorods Assisted by Microwave Heating

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Polycrystalline NiO nanorods have been synthesized by thermal decomposition of rod-like nickel oxide precursor achieved by microwave-assisted method. The structure, morphology, and crystalline phase of the products are characterized by transmission electron microscopy (TEM), X-ray diffractometry, Fourier-transformed infrared spectroscopy, and UV-visible absorption spectrum. TEM reveals that NiO nanorods consist of numerous NiO nanoparticles. The average size of NiO nanoparticles as a function of the calcination temperature has been investigated. The optical absorption band gap of polycrystalline NiO nanorods is 3.7 eV.

I. Introduction

OW-DIMENSIONAL inorganic nanostructures possess unique physical and chemical properties, such as the high surfaceto-volume ratio and the high fraction of chemically similar surface sites, and have been the extensive research focus in recent years.¹ As a *p*-type wide-bandgap semiconductor, NiO is a very promising material and has attracted increasing attention due to its extensive important applications such as catalyst,² electrode materials for lithium ion batteries and fuel cell,³ electrochromic films,⁴ and dye-sensitized photo-cathodes.⁵ Therefore, many methods have been observed to fabricate nanostructure NiO, such as thermal decomposition, sol-gel, surfactant-mediated synthesis, and anodic alumina membrane template synthesis.^{6–9} However, there are few researches about microwave-assisted synthesis of rod-shaped NiO. The microwave-assisted synthesis of rod-shaped metal oxides (CuO and TiO2) have been investigated.^{10,11} Pol et al. have reported a simple microwave irradiation method for the large-scale synthesis of submicrometer-sized TiO₂ rods with diameters of about 400 nm and lengths up to 5 µm. Compared with the traditional methods, microwave heating has unique effects and significant merits such as rapid volumetric heating, high reaction rate, short reaction time, and energy saving.¹²⁻¹⁵ Xia and colleagues show that the ethylene glycol-mediated synthesis of metal oxide nanowires requires heating the solution at above 170°C for 2 h by convective heating method.^{16,17} However, in our present work, we obtain the similar NiO nanorods at 110°C for 10 min under microwave irradiation, which should be contributed to the very short nonionizing electromagnetic energy waves.¹⁰ Herein, we report a facile and efficient microwave-assisted approach for fabricating rod-shaped nickel oxide precursor that can be transformed into pure polycrystalline NiO rod after calcination. The fact that the

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This work was supported by National Natural Science Foundation of China (No. 50572116) and Shanghai Nanotechnology Promotion Center (No. 0652nm022). *Member, The American Ceramic Society. synthesis protocol is fast, energy saving, and low cost for the preparation of polycrystalline NiO nanorods will promote its industrial application.

II. Experimental Procedure

(1) Preparation

All the chemicals were purchased from Shanghai Chemical Regent Co. (Shanghai, China) and used as received without any purification. In a typical experiment, 0.28 g of NiCl₂ \cdot 6H₂O was dissolved in 10 mL of ethylene glycol in a warm-water bath at 60°C, and then 0.7 g of sodium acetate (NaAc) was added into the mixture under vigorous stirring. The as-formed green transparent solution was transferred into a 50-mL round bottomed flask under magnetic stirring. The solution was heated to 110°C and kept at this temperature for 10 min by microwave heating. The microwave oven was a focused single-mode microwave synthesis system (Discover, CEM, Matthews, NC) equipped with a magnetic stirrer and a water-cooled condenser. The temperature was controlled by automatic adjusting of microwave power. The green product was separated by centrifugation and washed by ethanol several times, and then dried in a dynamic vacuum at 60°C. Finally, the green precipitate was heated at different temperature of 320°, 350°, and 400°C for 40 min.

(2) Characterization

The phase compositions of the powder were identified using X-ray diffractometry (XRD, Model D/MAX-2550V, Rigaku, Tokyo, Japan). The morphologies of the powder were examined using transmission electron microscopy (TEM, Model 2100, JEOL, Tokyo, Japan). Scanning electron microscopy (SEM) images were collected on a JSM (Tokyo, Japan) 6700F scanning electron microscope. Thermogravimetric analysis of the sample was performed in air using a thermal analyzer (Model STA449C, Netzsch Inc., Selb, Germany). Fourier-transformed infrared (FT-IR) spectrometer was used to collect the spectra of the samples (NEXUS, Nicolet, Madison, WI), and UV-visible absorption spectra analysis was performed on a PE Lambda 950 spectrophotometer (Waltham, MA).

III. Results and Discussion

The 1D morphology of the nickel oxide precursor and the asannealed nickel oxide polycrystalline rods are investigated by TEM. Figure 1(a) shows that the rod-like nickel oxide precursors with diameter from 500 to 800 nm and length up to 10 μ m are obtained. The surface of these rod-like nickel oxide precursors is smooth. The TEM image of calcined samples obtained at 350°C is presented in Fig. 1(b). It is evident that the rodlike morphology is preserved in the calcination process. However, the magnification of single polycrystalline NiO nanorod (Fig. 1(c)) demonstrates the smooth surfaces of rod-like nickel

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Fig. 1. Transmission electron microscopic images of (a) the nickel oxide precursor; (b) polycrystalline NiO nanorods obtained at 350°C for 40 min; (c) magnified picture of single polycrystalline NiO nanorod, the inset is the corresponding selected area electron diffraction pattern; (d) nitrogen adsorption/desorption isotherm of the polycrystalline NiO nanorod.

oxide precursors have transformed to rough structure with more pores, which should be a result of the degradation of organic groups and phase transformation. The selected area electron diffraction pattern shows several Debye–Scherrer rings (the inset of Fig. 1(c)), corresponding to the reflections of the NiO polycrystals. Figure 1(d) shows the nitrogen adsorption/desorption isotherms of polycrystalline NiO nanorod, indicating the isotherms are of type IV. The sharp decline in the desorption curve at $0.7 < P/P_0 < 0.8$ suggests characteristics of mesoporous materials.

Figure 2 shows the XRD patterns of the nonheated nickel oxide precursor and as-calcined nanorods at different temperature. The pattern of the rod-like precursor (Fig. 2(a)) shows that the diffraction spectra are strikingly similar to those of other metal oxide precursors reported by other groups,^{16,17} especially the strong peak locates in the low-angle region. To determine exact structure of such a precursor is usually difficult.^{18,19} Sharp reflections in the range of small angles can be assigned to the layered stacking order of brucite-like structures composed of linear coordination complexes. Chakroune *et al.*¹⁸ detected that the main lines in the XRD pattern are indexed as the (001) reflections. The strong peak around 10° is characteristic for organometallic precursors synthesized by the polyol-mediated process. Jiang *et al.*¹⁷ proposed that ethylene glycol can serve as a ligand that can form linear coordination complexes. The linear complexes can then aggregate into ordered nanobundles to generate nanowires through van der Waals interactions. Based on the similarities between our reaction and those reported in the literature, we believed that this mechanism might

be applied to explain the formation of rod-like precursors. All diffraction peaks of as-annealed samples are perfectly consistent with the cubic structure NiO (JCPDS 47-1049) and can be indexed as (111), (200), and (220) crystal planes. It is clear from XRD patterns that the peaks are broadened at relatively lower temperature, suggesting that the particle size of as-obtained NiO



Fig. 2. X-ray diffraction patterns of (a) unheated rod-like nickel oxide precursor and NiO nanorods obtained at different temperature: (b) 320°C, (c) 350°C, (d) 400°C.

nanoparticle increases with the increase of heating temperature. The average crystalline sizes of the obtained NiO nanoparticles are calculated using the Debye–Sherrer equation to be 6.7, 8.8, and 17.6 nm for 320°, 350°, and 400°C, respectively.

In the FT-IR spectra of rod-like precursor (Fig. 3(a-I)), the vibrational bands of CH_2 at 2946 and 2869 cm⁻¹ as well as the stretching band of C-OH at 1061 cm⁻¹ from ethylene glycol unit are observed; simultaneously, the strong absorption bands of C = O in acetate ion at 1569 and 1445 cm⁻¹ are also detected. The three bands appearing around 1034, 883, and 682 cm⁻ should be assigned to the stretching and bending vibrations of the C-O species in the precursor, also further confirming the presence of acetate ions.²⁰ Therefore, the chemical structure of rod-like precursor is likely CH₃COO-Ni-OC₂H₄OH. The curve (Fig. 3(a-II)) of NiO nanorod obtained after 350°C shows no such bands of rod-like precursor, indicating the complete decomposition of rod-like precursor. Furthermore, the peak at about 475 cm^{-1} assigned to Ni-O stretching vibration is clearly observed.

The thermogravimetric and differential thermogravimetry analysis results (Fig. 3(b)) further confirm that the rod-like precursor formula is CH₃COO-Ni-OC₂H₄OH. The TG curve of rod-like precursor shows two weight loss (21.2% and 45.6%), corresponding to the departure of water or excess polyol molecules and the decomposition of the precursor, respectively. The formula weight calculated from the weight loss of 45.6% is 178 g/mol, which is very close to the formula weight of CH₃COO-Ni-OC₂H₄OH (179 g/mol).

UV-vis spectrum of polycrystalline NiO nanorods is shown in Fig. 4. A strong absorption in the UV region is observed at wavelength smaller than 375 nm, which should be attributed to band gap absorption of NiO nanoparticles assembling the polycrystalline NiO nanorods. The optical transition type and the optical band gap (E_g) can be calculated by using the following equation:

$$(\alpha E_{\rm p})^n \propto K(E_{\rm p}-E_{\rm g})$$

where K is a constant, E_p is the discrete photon energy, α is the absorbance coefficient, and n is either 2 for direct transition or



Fig. 3. (a) Fourier-transformed infrared spectra of the as-obtained rod-like precursor (I) and as-annealed polycrystalline NiO nanorod (II); (b) the curves of thermogravimetric analysis and differential thermogravimetry analysis of the rod-shaped precursor.



Fig. 4. UV-vis spectrum and $(\alpha E_p)^2$ vs E_p curve (inset) for polycrystalline NiO nanorod calcined at 350°C.

1/2 for an indirect transition.²¹ Hence, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the $(\alpha E_p)^2$ vs E_p curve to zero (the inset of Fig. 4). The value of band gap of the polycrystalline NiO nanorod is about 3.7 eV, which is smaller than the value of bulk material (4.0 eV).²² It is well known that semiconductors with nanoscale size show a blue shift in their spectra due to the quantum confinement effects. However, the as-obtained samples have an E_{g} smaller than the bulk one. This effect is likely due to the chemical defects or vacancies present in the intergranular regions generating new energy level to reduce the band gap energy.²

IV. Conclusions

The microwave-assisted method has been successfully used for fast synthesis of rod-shaped CH₃COO-Ni-OC₂H₄OH that can be transformed into polycrystalline NiO nanorods at different temperature of 320° , 350° , and $400^{\circ}C$. While increasing the heating temperature, the size of NiO nanoparticles becomes larger. The optical absorption band gap of the polycrystalline NiO nanorod is determined to be 3.7 eV. This method is simple, fast, and low cost for the preparation of polycrystalline NiO nanorods.

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