

A simple method to synthesize NiO fibers

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Received 29 April 2003; received in revised form 8 August 2003; accepted 19 August 2003

Abstract

Nickel oxide fibers with diameters 1–2 μm and lengths up to 100 μm were synthesized by a simple pyrolytic decomposition method in NaCl flux with NiSO_4 as precursor. X-Ray diffraction, X-ray photoelectron spectrum (XPS) and scanning electron microscopy (SEM) techniques were used to characterize these fibers. They have single-crystal structure, large aspect ratios and macroscopic quantity. Suitable precursor and molten NaCl environment are conjectured to be key factors in this method.

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Keywords: A1. Crystal morphology; B1. Oxides

1. Introduction

NiO (bunsenite) is an important transition metal oxide with a cubic rock salt-like structure ($a = 4.195 \text{ \AA}$). As an antiferromagnetic material ($T_N = 523 \text{ K}$, bulk) and p-type semiconductor, its complex band structure, magnetic character and conductivity mechanism have been the focus of many research works [1–5]. It can be used as catalyst, as fine antiferromagnetic layer in magnetic multilayers and is important components in electrochromic devices and gas sensors also [6–12]. NiO particles [13–19] can be synthesized in different ways, but many of which have similar pyrolytic processes that anneal $\text{Ni}(\text{OH})_2$ or other compounds of low-decomposition temperatures such as carbonates, oxalates at different temperatures, and as-prepared NiO particles of different sizes were granular shapes usually. A higher temperature to decompose the sulfate will increase the sizes of the obtained NiO particles, which is unsatisfactory in most occasions. So NiSO_4 was never considered before. But our work revealed that NiSO_4 also has its special use in crystal growth. Because of the potential applications of one-dimensional or quasi-one-dimensional (1D) materials, simple methods to synthesize them with high yields are valuable. In this paper, we report such a simple pyrolytic method in which NiO

fibers were synthesized in NaCl flux with NiSO_4 as precursor. It enriches our knowledge about how to choose suitable precursors in similar works.

2. Experimental

All reagents used in the experiment were analytically pure.

A typical procedure to synthesize NiO fibers is given as follows: 10 mL NiSO_4 solution (0.2 mol/L) and 20 mL saturated NaCl solution were mixed homogeneously at first, sufficient absolute alcohol was added in and the mixed solution was stirred quickly on agitator, mixture of NiSO_4 and NaCl was then deposited, the deposition was filtered, dried and green precursor was prepared. The precursor placed in ceramic boat was annealed at 820°C in electronic furnace for 1 h. Then the obtained product was cooled and washed with sufficient distilled water to clear away the residual NaCl, dark green sample was obtained after drying the product.

The as-prepared sample was characterized by X-ray powder diffraction (XRD) on a Rigaku Rotaflex d/MAX-RA rotation anode XRD using graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Its scanning electron microscopy (SEM) images were taken with a HITACHI X-650 SEM and compositions of the sample were checked by X-ray photoelectron spectrum (XPS) using a VG ESCALAB MKII spectrometer.

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3. Results and discussion

Fig. 1 shows the XRD spectrum of the sample. All the peaks could be indexed to that of the cubic phase NiO with standard value (JCPDS No 4-835) and no obvious peaks of impurity were found.

Fig. 2 shows the morphologies of the NiO sample. Fibers are the major form and some plate-like structures are also observed. These fibers have diameters about 1–2 μm and lengths up to 100 μm . The selected area electron diffraction information (not shown here) shows kikuchi lines, revealing that these fibers are single crystals, which can be verified by optic microscope with higher magnification. The proportion of fibers in sample can exceed 70%.

XPS information shown in Fig. 3 also proves that these fibers are NiO crystals. Only the Ni and O element can be detected obviously, Ni(LMM) and O(KLL) are the auger peaks of these elements. The center of the Ni_{2p} peak (calibrated with the C_{1s} peak) is 854.3 eV, which is consistent with the known value of NiO [20].

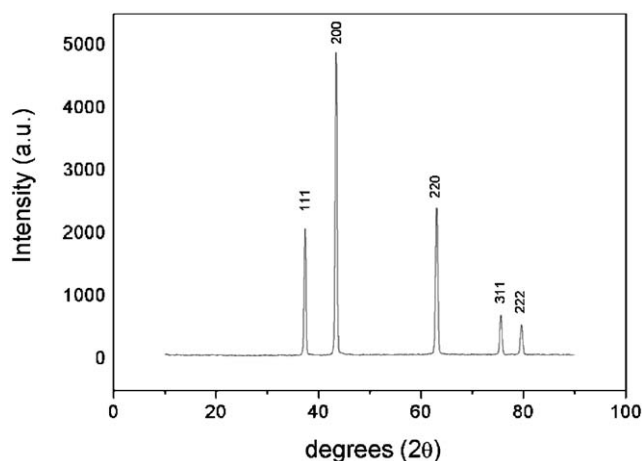


Fig. 1. XRD spectrum of an as-prepared NiO sample.

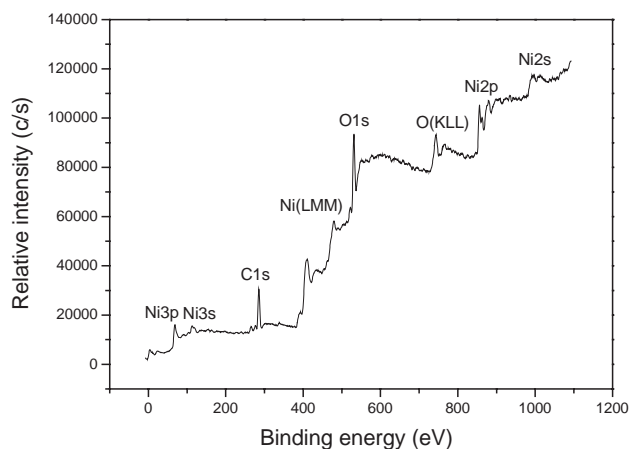


Fig. 2. XPS of NiO fibers.

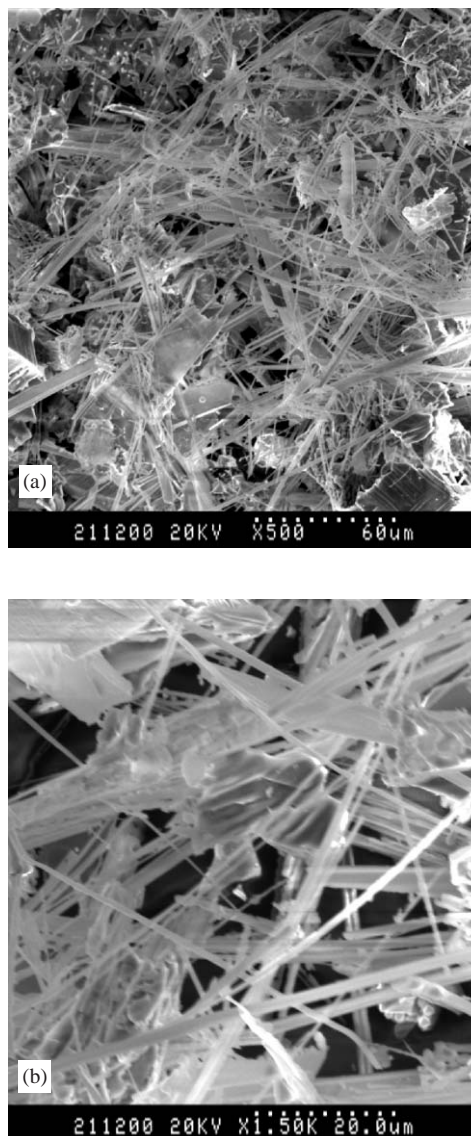


Fig. 3. SEM images of NiO fibers with different magnifications.

The chemical reaction in present work is

$$\text{NiSO}_4 \rightarrow \text{NiO} + \text{SO}_3 \uparrow (\text{at high temperature})$$

A suitable precursor is the key factor in this sort of synthesis. By similar routes other precursors such as Ni(OH)₂, NiCO₃, Ni(NO₃)₂ cannot give satisfying yields of NiO fibers at all. How to choose suitable precursors to synthesize corresponding 1D metal oxides is still unclear and further research is needed. One obvious difference between NiSO₄ and other compounds mentioned is that NiSO₄ is much steadier than those compounds at high temperature. Fig. 4 shows the DTA–TGA curves of two different precursors. Data were taken on a SETARAM TG-DTA/DSC, Labsys™, the heating-up rates are both 10°C/min. Fig. 4(a) is about NiCO₃ and Fig. 4(b) is about NiSO₄ (NiSO₄·4H₂O, the weight loss at lower temperature

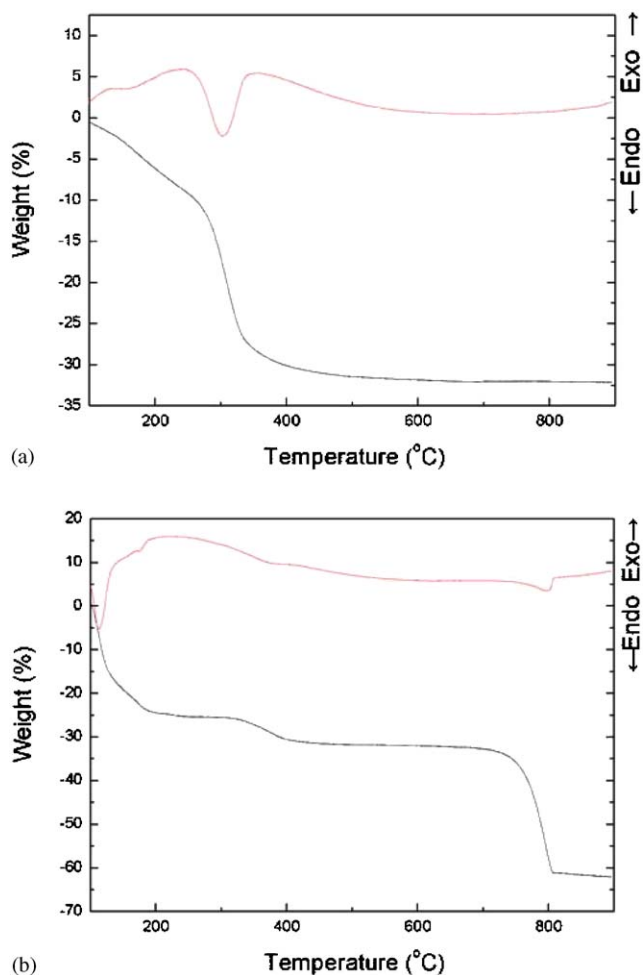


Fig. 4. DTA-TGA curves of different precursors (a) NiCO₃ (b) NiSO₄.

corresponds to the loss of its crystal water), the pyrolytic decomposition of NiCO₃ mainly happens below 400°C, whereas that of NiSO₄ mainly happens between 750°C and 800°C, which is near the experimental temperature 820°C. So it is an acceptable conjecture that the NiSO₄ precursor has a lower decomposition rate than NiCO₃ at that temperature. Such a difference leads to different nucleation rates of tiny NiO crystals. The nucleation and growth are two competitive processes in crystal growth. New-formed growth units (such as Ni–O octahedrons in our experiment) can generate new tiny particles in a nucleation process or adhere to existing particles to grow up in a growth process. The different rates of these two processes might affect the final morphologies of the NiO crystals: When compound such as NiCO₃ is selected as precursor, the reactant NiO particles may have a higher nucleation rates; because of the rapid consumption of precursor particles and the limited dissolvability of the NiO crystals in molten NaCl, the growth process of those NiO crystals are restrained; when NiSO₄ is selected as precursor, the NiO particles have lower nucleation rates and corresponding

growth times are longer. So in the same circumstance, a precursor such as NiCO₃ can form many smaller NiO particles whereas precursor NiSO₄ form relatively bigger NiO particles. A longer growth time (or a stronger growth process) will increase the possibility to change the typical granular shape of NiO crystal cores in following growth process, although it is not effective all the times.

One effect of the NaCl is to control the sizes of NiSO₄ particles. When the NaCl tiny particles were deposited together with the NiSO₄ particles, they might envelop the NiSO₄ particles to weaken their agglomeration and so control the growth of the NiSO₄ particles because of their dominance in quantity, although the aliquation effect will counteract the result. Another more important effect of NaCl is to provide a fluent circumstance full of ions, which will affect the growth rates of different NiO crystal faces and therefore change the final morphologies of the crystals. Of course only suitable precursor can create such quasi-one-dimensional structures even in this occasion. The fluent circumstance is also in favor of the transmission of the Ni–O octahedrons growth units in larger extent.

In summary, a simple template-free method to prepare NiO fibers is reported here. The directional properties of these are decided by suitable precursor and molten NaCl circumstance. These fibers have big aspect ratios, satisfying yield and good mechanic properties perhaps. This work shows an interesting and seldom-concerned aspect of pyrolytic route.

Acknowledgments

This work was financially supported by National Nature Science Foundation of China (No. 10074024, 29890210, 10023001).

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