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Synthesis of NiO nanorods by a novel simple precursor thermal decomposition approach

Wenzhong Wang ^{a,b}, Yingkai Liu ^a, Congkang Xu ^a, Changlin Zheng ^a, Guanghou Wang ^{a,b,*}

^a Department of Physics, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

^b Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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Abstract

Single-crystal cubic NiO nanorods with diameters of 30–80 nm and lengths of up to tens of micrometers were synthesized by using a simple precursor thermal decomposition in NaCl flux with NiCO₃ as the precursor, which was prepared by one-step, solid-state reaction of NiCl₂ \cdot 6H₂O and Na₂CO₃ at ambient temperature. The crystallinity, purity, morphology, and structure features of the as prepared NiO nanorods were investigated by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and Raman spectrum. © 2002 Elsevier Science B.V. All rights reserved.

Over the past few years, attention has been focused on the research field of one-dimensional nanostructural materials, such as nanorods or nanowires, because of their potential applications in nanodevices [1–3]. In order to obtain one-dimensional nanostructural materials of the desired materials, various preparation methods have been developed including arc discharge [4], laser ablation [5,6], template [7,8], solution [9–11], and other methods [12–14]. However, to the best of our knowledge, special conditions, tedious procedures or complex apparatus may be required for these methods. Here we report simple precursor thermal decomposition route for preparing NiO nanorods. This method requires neither complex apparatus and sophisticated techniques, nor metal catalysts and/or templates as usually needed in other methods.

NiO has received a considerable amount of attention over the last few years due to its applications in diverse fields, such as smart windows, active optical fibers [15], catalysis [16], electrochromic films [17], fuel cell electrodes [18,19], gas sensors [20,21], antiferromagnetic layers [22], ptype transparent conducting films [23], and others [24,25]. In the early studies, there are a few methods for preparing NiO. The most widespread one used is based on the calcination of almost any nickel compound in air at about 1273 K, and physical and chemical vapor deposition tech-

^{*} Corresponding author. Fax: +86-25-359-5535.

E-mail address: wangqun@nju.edu.cn (G. Wang).

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niques. However, only NiO particles or films can be prepared by these methods.

NiO nanorods were synthesized as follows: 8 g of NiCl₂ \cdot 6H₂O and 2 g of Na₂CO₃ were ground for 5 min each before mixing together. After 15 min of grinding, the product was washed several times with distilled water to remove unreacted reactants and by-product, and then dried in an oven at 333 K for 5 h.

The above prepared NiCO₃ precursor (0.2 g) was mixed with 1 g of NaCl and 3 ml of nonyl pheyl ether (9) (NP-9) with an agate mortar, and then the mixture was ground for 5 min. The mixed sample was heated in a porcelain crucible that was placed in the middle of an alumina tube with a horizontal tube electric furnace at 1173 K for 2 h, the heat treatment sample was cooled gradually to room temperature in air, washed several times with distilled water to remove NaCl flux, filtered, and dried in an oven at 373 K for 3 h.

The purity and crystallinity of the as-synthesized NiO nanorods were examined by using powder X-ray diffraction (XRD). Fig. 1 shows the diffraction pattern collected on these nanorods. All diffraction peaks can be perfectly indexed to the crystalline NiO, not only in peak position, but also in their relative intensity. The peaks can be readily indexed as (111), (200), (220), (311), (222), and (400) crystal plans of the crystalline cubic structure NiO, respectively. The NiO lattice constant calculated from the XRD data is a = 4.1730 Å, which is in good agreement with the reported data (JCPDS 4-835).

The morphology of the nanorods was observed by transmission electron microscope (TEM, JEM-200 CX, 200 kV) as shown in Fig. 2. It can be seen that NiO crystals display rod-like shape with diameters of 30-80 nm, and lengths of up to tens of micrometers, and no spherical droplets can be seen at tips of these nanorods. This observation suggests that the nanorods may not grow by vaporliquid-solid (VLS) [11] or solution-liquid-solid (SLS) [12] mechanism proposed for the nanorods growth by a catalytic-assisted technique [13,14], in which a metal liquid droplet is located at the growth front of the wire and acts as the catalytic active site. Selected area diffraction (SAED) pattern taken from a single nanorod with a diameter of 40 nm can be indexed on a cubic cell with lattice parameters of a = 4.1769 Å, consistent with the above X-ray result. The SAED pattern also confirms that the nanorod is a single crystal cubic NiO.

Fig. 3 shows a high-resolution TEM (HRTEM, JEOL-2010, 200 kV) image of a single nanorod with a diameter of 40 nm. The HRTEM image shows that the nanorod is structurally uniform, and the clear lattice fringes illustrate that the nanorod is a single crystalline. The interplanar spacing is about 0.149 nm, which corresponds to



Fig. 1. The XRD pattern of the as-prepared NiO nanorods.



Fig. 2. TEM images of NiO nanorods. Inset is a SAED image from a single nanorod.



Fig. 3. An HRTEM image of a 40 nm NiO nanorod.

the (220) plane of the cubic crystalline NiO, indicating the growth plane of the nanorods is along the (220) planes.

Fig. 4 shows the Raman spectra (LABRAM-HR Confocal Laser MicroRaman spectrometer, 514.5 nm, 250 mW) of the as-synthesized NiO nanorods. It can be seen that there are four Raman peaks at 420, 546, 712, and 1092 cm⁻¹, respectively. Compared to the predicted data of cubic NiO single crystal [26], we can assigned the peaks at 420 and 546 cm⁻¹ to the first-order transverse optical (TO) and longitudinal optical (LO) phonon modes of NiO, respectively. The remaining peaks at 712 and 1092 cm⁻¹ can be as-



Fig. 4. The Raman spectra of as-synthesized NiO nanorods.

signed as combination of 2TO and 2LO, respectively, and are all shifted down in frequency about 68 cm⁻¹. Since k = 0 phonons in the paramagnetic (cubic) phase transform as Γ_4^- , no firstorder Raman scattering is expected. Therefore the observed first-order Raman peaks near the 420 (TO) and 546 cm⁻¹ (LO) must derive from paritybreaking imperfections [26]. This conclusion is confirmed by the enhancement of the first-order Raman scattering in the black NiO, where the nickel vacancy concentration is high. The combination Raman scattering trends to vanish at the Γ point but is usually strong elsewhere in the Brillouin zone. This explains why the combination peaks are all shifted down in frequency, since both LO and TO branches are expected to be depressed in frequency away from the zone center.

In summary, a simple thermal decomposition route has been developed to synthesize single crystalline NiO nanorods with NiCO₃ as the precursor. The as-synthesized nanorods have diameters of 30–80 nm, and lengths of up to tens of micrometers. The natures of the NiO nanorods have been investigated by XRD, TEM, HRTEM, and Raman spectra. The growth mechanism of nanorods, the roles of NP-9 and NaCl in the formation of NiO nanorods will be investigated in further.

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References

- J. Hu, M. Ouyang, P. Yang, C.M. Lieber, Nature 399 (1999) 48.
- [2] D.S. Xu, G.L. Guo, L.L. Gui, Y.Q. Tang, Z.J. Shi, Z.X. Jin, Z.N. Gu, W.M. Liu, X.L. Li, G.H. Zhang, Appl. Phys. Lett. 75 (1999) 481.
- [3] J.R. Heath, P.J. Kuekes, G. Snyder, R.S. Williams, Science 280 (1998) 717.

- [4] S. Iijima, Nature 354 (1991) 56.
- [5] A.M. Morales, C.M. Lieber, Science 279 (1998) 208.
- [6] A. Thess, R. Lee, P. Nikolaev, H.J. Dai, P. Petit, J. Robert, C.H. Xu, Y.H. Lee, S.G. Kim, A.G. Kinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fisher, R.E. Smalley, Science 273 (1996) 348.
- [7] C.R. Martin, Science 266 (1994) 1961.
- [8] W. Han, S. Fan, Q. Li, Y. Hu, Science 277 (1997) 1287.
- [9] T.J. Trentler, K.M. Hickman, S.C. Goel, A.M. Viano, P.C. Gibbons, W.E. Buhro, Science 270 (1995) 1791.
- [10] Y.D. Li, Y. Ding, Z.Y. Wang, Adv. Mater. 11 (1999) 847.
- [11] J.D. Hopwood, S. Mann, Chem. Mater. 9 (1997) 1819.
- [12] W.S. Shi, Y.F. Zheng, N. Wang, C.S. Lee, S.T. Lee, Adv. Mater. 13 (2001) 591.
- [13] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 291 (2001) 1947.
- [14] S.W. Liu, J. Yue, A. Gedanken, Adv. Mater. 13 (2001) 656.
- [15] P. Lunkenheimer, A. Loidl, Phys. Rev. B 44 (1991) 5927.
- [16] B. Sheela, H. Gomathi, G. Prabhakara Rao, J. Electroanal. Chem. 394 (1995) 267.

- [17] M. Chigane, M. Ishikawa, J. Chem. Soc., Faraday Trans. 88 (1992) 2203.
- [18] P. Tomczyk, G. Mordarski, J. Oblakowski, J. Electroanal. Chem. 353 (1993) 177.
- [19] R.C. Makkus, K. Hemmes, J.H.W.D. Wir, J. Electrochem. Soc. 141 (1994) 3429.
- [20] C.B. Alcock, B.Z. Li, J.W. Fergus, L. Wang, Solid State Ion. 53–56 (1992) 39.
- [21] H. Kumagai, M. Matsumoto, K. Toyoda, M. Obara, J. Mater. Sci. Lett. 15 (1996) 1081.
- [22] E. Fujii, A. Tomozawa, H. Torii, R. Takayama, Jpn. J. Appl. Phys. 35 (1996) L328.
- [23] H. Sato, T. Minami, S. Takata, T. Yamada, Thin Solid Films 236 (1993) 27.
- [24] M. Kitao, K. Izawa, K. Urabe, T. Komatsu, S. Kuwano, S. Yamada, Jpn. J. Appl. Phys. 33 (1994) 6656.
- [25] K. Yoshimura, T. Miki, S. Tanemura, Jpn. J. Appl. Phys. 34 (1995) 2440.
- [26] R.E. Dietz, G.I. Parisot, A.E. Meixner, Phys. Rev. B 4 (1971) 2302.