

A simple method of fabricating large-area α -MnO₂ nanowires and nanorods

Yi Liu^{a,b}, Meng Zhang^a, Junhao Zhang^a, Yitai Qian^{a,*}

^aHefei National Laboratory for Physical Sciences at Microscale, Department of Chemistry, University of Science & Technology of China, Hefei 230026, PR China

^bDepartment of Chemistry, Zaozhuang University, Zaozhuang 277100, PR China

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Abstract

α -MnO₂ nanowires or nanorods have been selectively synthesized via the hydrothermal method in nitric acid condition. The α -MnO₂ nanowires hold with average diameter of 50 nm and lengths ranging between 10 and 40 μ m, using MnSO₄·H₂O as manganese source; meanwhile, α -MnO₂ bifurcate nanorods with average diameter of 100 nm were obtained by adopting MnCO₃ as starting material. The morphology of α -MnO₂ bifurcate nanorods is the first one to be reported in this paper. X-ray powder diffraction (XRD), field scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were used to characterize the products. Experimental results indicate that the concentrated nitric acid plays a crucial role in the phase purity and morphologies of the products. The possible formation mechanism of α -MnO₂ nanowires and nanorods has been discussed.

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Keywords: α -MnO₂; Nanowires and nanorods; Hydrothermal reaction; X-ray powder diffraction (XRD); Field scanning electron microscopy (FESEM); Transmission electron microscope (TEM); Selected area electron diffraction (SAED); High-resolution transmission electron microscope (HRTEM)

1. Introduction

In the past few years, controlling the shape of nanostructures at the mesoscopic level is one of challenging issues presently faced by material scientists [1]. Nanowires and nanorods, which are one-dimensional (1-D) objects, have stimulated great interest among synthetic material operators due to their peculiar properties and potential application [2–9]. Several techniques for the preparation of nanowires or nanorods have been reported, such as the solid–vapor process [2], laser ablation [3], arc discharge [4], electrochemical techniques [5], virus-templating [6], exfoliating method [7,8], and hydrothermal method [9]. As a popular inorganic-function material, manganese dioxide and derivative compound have attracted special attention and been widely used not only as catalysts, molecular sieves

[10,11], but also as promising candidate materials for cathodes in lithium ion batteries [12–15]. Generally speaking, α - and γ -MnO₂ can be converted by electrochemical Li⁺ intercalation into cubic spinel, Li_{1-x}Mn₂O₄, which has channels through which Li⁺ can move [13,14]. Recently, many efforts have been focused on preparing manganese oxide 1-D nanostructures, and their synthesis methods are generally based on the redox reactions of MnO₄⁻ and/or Mn²⁺ [16–23]. For example: Y.D. Li et al. [20,21] reported a selected-control low-temperature hydrothermal method of synthesizing 1-D MnO₂ nanostructure through the oxidation of Mn²⁺ by S₂O₈²⁻, MnO₄⁻ or ClO⁻ without any existence of catalysts or templates; Z.Q. Li et al. [22] provided a simple room-temperature solution-based catalytic route to fabricate a novel hierarchical structure of α -MnO₂ core-shell spheres with spherically aligned nanorods on a large scale. The previous experimental results indicated that α -MnO₂ tended to form in acidic conditions, the pH of solution had crucial effect on the formation of 1-D nanostructural α -MnO₂ [23]. The influence of the

*Corresponding author. Fax: +86 551 3607402.

E-mail addresses: liuyi67@mail.ustc.edu.cn (Y. Liu), yqian@ustc.edu.cn (Y. Qian).

anion on growth of the products had been investigated by Kijima et al. [19], and their results showed that α -MnO₂ could be prepared in concentrated H₂SO₄ rather than HCl or HNO₃. Thus far, the synthesis of α -MnO₂ nanowires or nanorods has seldom been reported under concentrated nitric acidic conditions.

Here we report a novel, large-area synthesis method for obtaining nanowires and nanorods with uniform sizes. The α -MnO₂ nanowires have average diameter of 50 nm and lengths of 10–40 μ m, using MnSO₄·H₂O as manganese source; meanwhile, α -MnO₂ bifurcate nanorods with average diameter of 100 nm were obtained by adopting MnCO₃ as starting material. In our presentation, we choose concentrated nitric acid as acid source to tune the pH of the system. Our experiments show that pure-phase α -MnO₂ can be readily obtained in a wide range of nitric acid concentrations. This result may be a useful complementarity to previous experimental results that α -MnO₂ could be only produced in H₂SO₄ surroundings.

2. Experimental procedure

All the reagents of analytical grade were purchased from Shanghai Chemical Reagent Company and used without further purification. In a typical procedure, 1 mmol MnSO₄·H₂O or MnCO₃ and 2 mmol KClO₃ powders were successively put into a beaker with 15 mL concentrated nitric acid, the solution was magnetically stirred for 20 min at 80 °C to form brown colloid. The slurry solution was transferred into a 50 mL stainless-steel autoclave with a Teflon-liner, the beaker was washed with 25–30 mL distilled water, and washing solution was put into above-mentioned Teflon-liner. The autoclave was sealed and maintained at 120 °C for 12 h, then air cooled to room temperature. The brown products were filtered off, washed several times with distilled water and absolute ethanol, and then dried in vacuum at 80 °C for 1 h.

The X-ray powder diffraction (XRD) pattern of the as-prepared samples was determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized CuK α radiation ($\lambda = 1.541874$ Å) in the 2θ ranging from 10° to 70°. The morphology and size of the final products were determined by field scanning electron microscopy (FESEM) images, taken with JEOL-6700F scanning electronic microanalyzer. Transmission electron microscope (TEM) image and selected area electron

diffraction (SAED) pattern, which were characterized by Hitachi H-800 TEM with a tungsten filament and an accelerating voltage of 200 kV. High-resolution transmission electron microscope (HRTEM) image was recorded on a JEOL 2010 microscope. The samples used for TEM and HRTEM characterization were dispersed in absolute ethanol and were ultrasonicated before observation.

3. Results and discussion

The synthesis of α -MnO₂ nanowires and nanorods is based on the hydrothermal method in a strong acidic (nitric acid) circumstance. The experimental results by using nitric acid as acidification agent, different manganese sources, and KClO₃ as the oxidizer are summarized in Table 1. Under our experimental conditions, the different size and morphological products can be obtained by varying the concentration of nitric acid.

From this table we can see that only under concentrated nitric acid condition pure α -MnO₂ can be obtained. The volume of concentrated nitric acid can be in the range of 3–20 mL. The yields and morphology change greatly when different amounts of nitric acid were introduced. We found that the most optimal conditions of obtaining uniform α -MnO₂ nanowires were fixed on 15 mL concentrated nitric acid and reaction temperature of 120 °C. Moreover, when different Mn compounds were selected as starting materials, the size and morphologies can be changed greatly, as shown in the lines 1 and 4 of Table 1. The result of experiments clearly indicates concentrated nitric acid plays a crucial role in the formation of α -MnO₂ with 1-D structure.

The phase and purity of the products were firstly examined by XRD. Fig. 1 shows a typical XRD pattern of the as-synthesized samples at 120 °C for 12 h, all the reflection peaks can be readily indexed to body-centered tetragonal α -MnO₂ phase (space group $I4/m$), with lattice constants of $a = 9.816$ Å, and $c = 2.853$ Å, which are in agreement with the standard values (JCPDS 72-1982, $a = 9.815$ Å; $c = 2.847$ Å). No other phase was detected in Fig. 1 indicating the high purity of the final products. The morphologies and structure information were further obtained from FESEM, TEM and SAED. Fig. 2 provides FESEM images of the as-prepared α -MnO₂ single-crystal nanowires. Figs. 2(a) and (b) are the low- and high-magnification FESEM images of the as-prepared α -MnO₂

Table 1

Summary of the results on the products obtained under different manganese sources, the content of concentrated nitric acid and reaction temperature for 12 h, using KClO₃ as the oxidizer

Sample no.	Manganese source	Concentrated nitric acid (mL)	Reaction temperature (°C)	Product morphology
1	MnSO ₄ ·H ₂ O	15	120	α -MnO ₂ nanowires
2	MnSO ₄ ·H ₂ O	0	120	Nonexistence of MnO ₂
3	MnSO ₄ ·H ₂ O	0	180	Minor β -MnO ₂
4	MnCO ₃	15	120	Flowery α -MnO ₂ nanorods
5	MnCO ₃	0	120	Nonexistence of MnO ₂

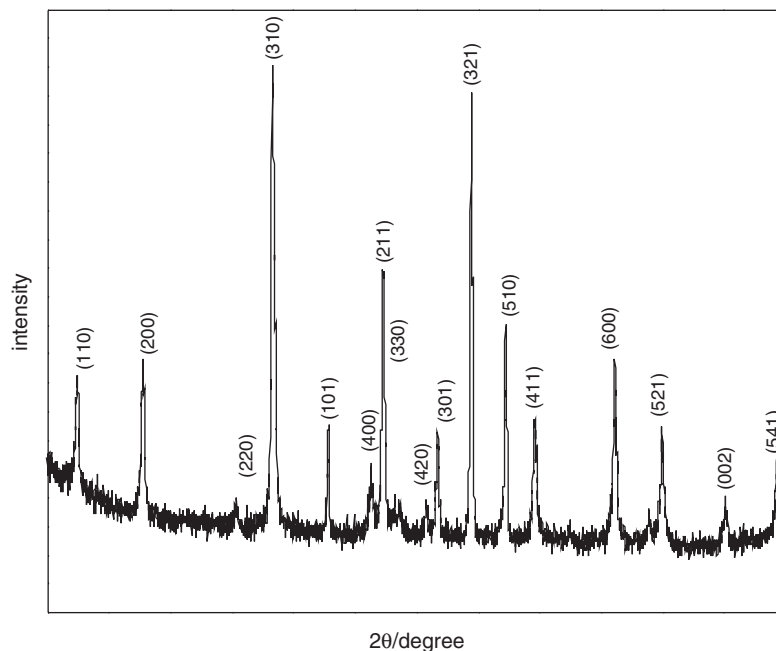


Fig. 1. Typical XRD pattern of as-prepared α -MnO₂.

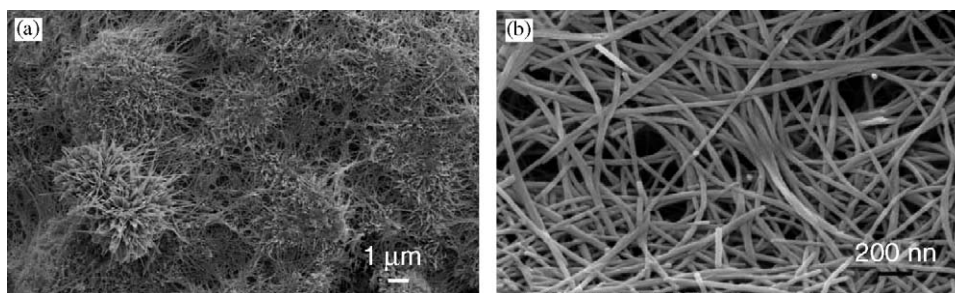


Fig. 2. Low-magnification FESEM image (a) and high-magnification FESEM image (b) of α -MnO₂ nanowires (MnSO₄ · H₂O as manganese source).

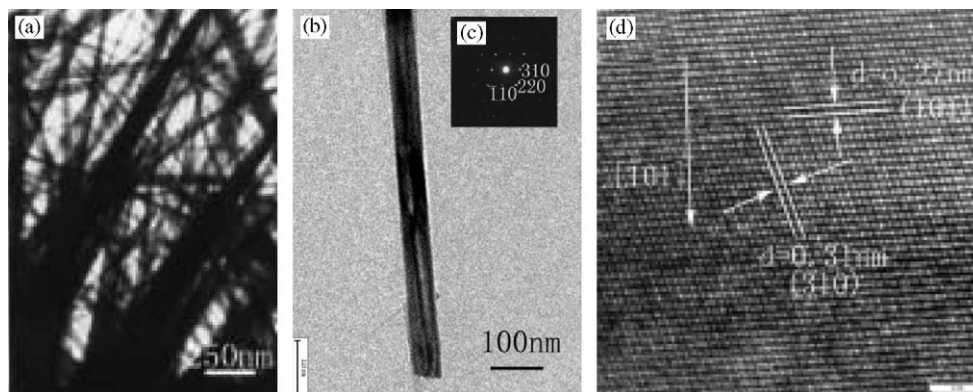


Fig. 3. TEM images of as-prepared single-crystal α -MnO₂ nanowires (a), TEM image (b), SAED pattern (c) and HRTEM image (d) of the single α -MnO₂ nanowire.

single-crystal nanowires when MnSO₄ · H₂O served as manganese source. These images show that the products of α -MnO₂ consisted of a large quantity of uniform nanowires, with diameters of 50 nm and lengths up to several hundreds of micrometers. Fig. 3(a) shows the TEM

image of as-prepared α -MnO₂ nanowires, and the TEM images further demonstrate that the obtained product has a uniform wire-like morphology. The results reveal the product of α -MnO₂ was composed of nanowires. The diameters and lengths of nanowires were consistent with

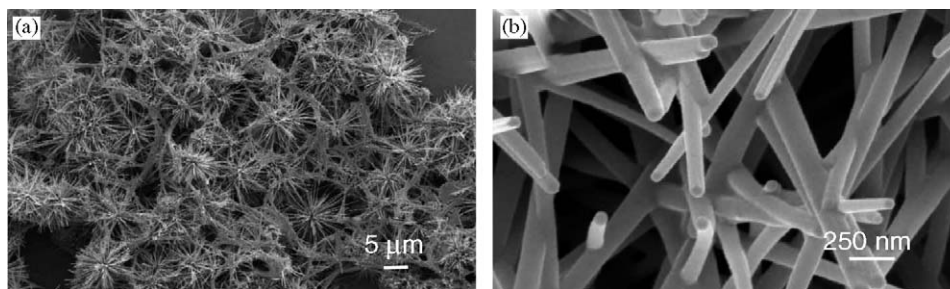


Fig. 4. Low-magnification FESEM image (a) and high-magnification FESEM image (b) of α - MnO_2 nanorods (MnCO_3 as manganese source).

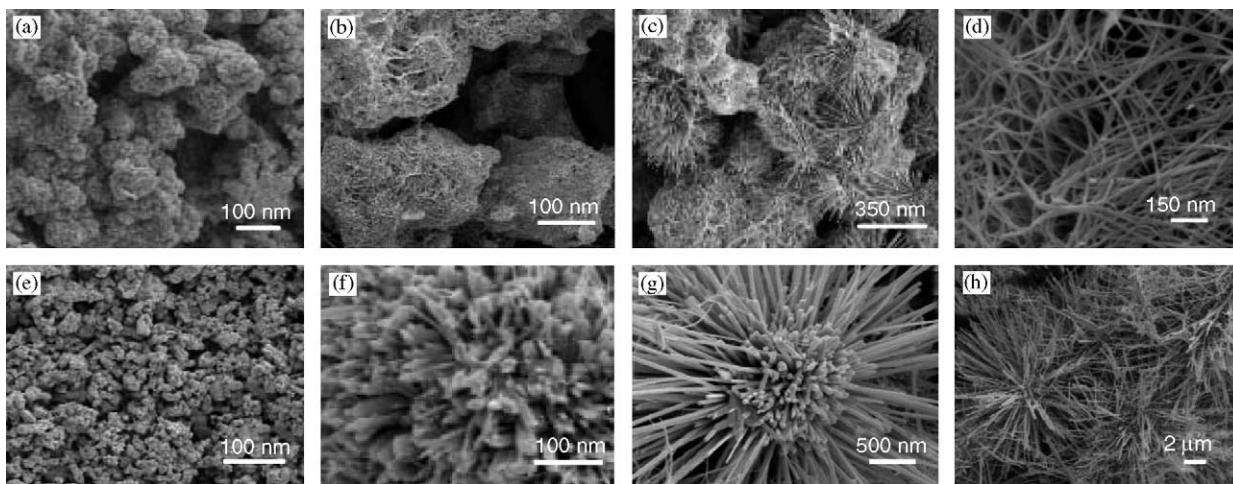


Fig. 5. The FESEM images of products obtained by heating in the acidic solution for various reaction times, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (a–d) as manganese source: (a) 0.5 h, (b) 3 h, (c) 6 h, (d) 12 h and MnCO_3 (e–h) as manganese source: (e) 0.5 h, (f) 3 h, (g) 6 h, (h) 12 h.

those of FESEM results. The TEM image (Fig. 3(b)) of representative single nanowires and HRTEM observation for individual nanowire provide additional insight into the structure of α - MnO_2 with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ as manganese source. The typical SAED pattern of the single α - MnO_2 nanowire is shown in the inset of Fig. 3(c). Fig. 3(d) is the HRTEM image taken from the single α - MnO_2 nanowire, which shows the clearly resolved lattice fringes. The separated spacings of 2.73 and 3.12 Å correspond to $(\bar{1}01)$ and (310) planar of α - MnO_2 , respectively. This image clearly reveals that the as-synthesized nanowire has no defect of dislocation and further substantiates that the nanowires are single crystalline, which is consistent with the SAED pattern. According to HRTEM image and SAED pattern recorded on the single α - MnO_2 nanowire, the deduced growth direction of nanowire is $[\bar{1}01]$.

If MnCO_3 was introduced into the reaction system, the products are mainly composed of nanorods, as revealed by the corresponding FESEM images. Figs. 4(a) and (b) are the low- and high-magnification FESEM images of the as-prepared α - MnO_2 nanorods with MnCO_3 as manganese source. The low-magnification FESEM image (Fig. 4(a)) reveals that the product of α - MnO_2 is consisted of a large quantity of flowery nanorods with average diameter of 100 nm. Fig. 4(b) is the high-magnification FESEM image of the as-prepared α - MnO_2 , in which we seem to observe

obvious features of bifurcate rod-like structure. It is worth to note that the morphology of α - MnO_2 bifurcate nanorods has never been reported previously. Comparing Figs. 4(a) and (b) to Figs. 2(a) and (b), it can be found that the nanowires with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ as manganese source are much slenderer than the bifurcate nanorods with MnCO_3 as manganese source.

Generally, pH is believed to have great impact on the crystal forms of final products [17,19,24,25]. In our experiment, a series of hydrothermal synthesis were carried out in a wide range of acidity with pH value less than 7, we found that the final products to be α - MnO_2 nanowires or nanorods with 1-D morphology whether $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ or MnCO_3 as manganese source. Therefore, this method is very effective for the large-scale synthesis of α - MnO_2 with 1-D nanostructures.

The influence of the reaction time on the growth of the nanowires and nanorods was investigated. The corresponding samples were tested by FESEM. Fig. 5 shows FESEM images of the as-obtained samples measured (a) after 0.5 h, (b) after 3 h, (c) after 6 h, (d) after 12 h, and other conditions kept constant at the same time. Thereinto, Figs. 5(a)–(d) are FESEM images of the products with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ as manganese source. As can be seen, the reaction lasted for 0.5 h; the products were composed of aggregated particles (see Fig. 5(a)). When the reaction time

prolonged to 3 h, on the surfaces of these particles, lamellar structures appeared, and some of these lamellar split to tiny nanowires, indicating the beginning of the formation of α -MnO₂ nanowires (see Fig. 5(b)). This process continued and more nanowires formed after 6 h (see Fig. 5(c)). Until the reaction time was extended to 12 h, most of the products are nanowires with average diameter of 50 nm and lengths ranging between 10 and 40 μ m, as shown in Fig. 5(d). Further elongating the reaction time shows little effects on the size and phase-purity of the products. This growth process is similar to the results of C.Z. Wu et al. [26], we call this a “rolling-broken-growth” process. According to above results and previous research [20,21,27], the possible formation mechanism of α -MnO₂ nanowires by adopting MnSO₄·H₂O as manganese source could be explained as follows: (1) when temperature was maintained at 80 °C, the interaction of KClO₃ and manganese source with Mn²⁺ ion happened only when concentrated nitric acid exists. In the synthetic process, a large number of the MnO₂ colloidal particles had been formed in concentrated nitric acid before hydrothermal operation. (2) Under hydrothermal conditions, owing to the absence of surfactants, the MnO₂ colloidal particles are prone to aggregate and form bigger particles. (3) The surface of aggregated big particles grows gradually into sheets of α -MnO₂ with lamellar structure through an elevated temperature and pressure, and then these sheets of α -MnO₂ will curl by extending reaction time to form α -MnO₂ 1-D nanostructures. (4) Much evidence has demonstrated that the lamellar structure had a strong tendency to form 1-D nanostructures [20,27]. The structure of α -MnO₂ comprises a macromolecular lamellar net with octahedral [MnO₆] units coordinated Mn and O atoms [20], which can give rise to formation of 1-D nanostructures. As the layer structure of α -MnO₂ is in a metastable state, these sheets of α -MnO₂ with lamellar structure split into nanowires. (5) Anisotropic nature of crystal growth makes the final products turn into a large number of uniform α -MnO₂ nanowires. Moreover, we found when MnCO₃ serves as manganese source, a similar growth procedure was observed, as shown in Figs. 5(e)–(h). We believe this α -MnO₂ 1-D nanostructural formation process is universal despite different manganese sources were involved in the hydrothermal process. This observation may spread to other nanomaterials synthesis. The above mechanism is in good agreement with our experiment results.

4. Conclusion

In summary, α -MnO₂ nanowires and nanorods with a uniform diameter have been successfully synthesized on a large scale via a simple nitric-acid-assisted hydrothermal process at low temperature. It belongs to firstly report that the morphology of α -MnO₂ bifurcate nanorods can be acquired when MnCO₃ serves as manganese source. The concentrated nitric acid plays a crucial role in the

formation of α -MnO₂ nanowires and nanorods. This experimental result is different from the previous conclusion that the concentrated nitric acid seems to be an unfavorable condition to form α -MnO₂. This observation may be expanded to synthesize other nanomaterials.

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References

- [1] A.P. Alivisatos, *Science* 271 (1996) 933.
- [2] Y. Wu, P. Yang, *Chem. Mater.* 12 (2000) 605.
- [3] (a) A.M. Morales, C.M. Lieber, *Science* 279 (1998) 208; (b) M.S. Gudiken, C.M. Lieber, *J. Am. Chem. Soc.* 122 (2000) 8801.
- [4] (a) S. Iijima, *Nature* 354 (1991) 56; (b) T. Seeger, P. Kohler-Redlich, M. Ruhle, *Adv. Mater.* 12 (2000) 279.
- [5] Y. Zhou, S.H. Yu, X.P. Cui, C.Y. Wang, Z.Y. Chen, *Chem. Mater.* 11 (1999) 545.
- [6] C. Mao, D.J. Solis, B.D. Reiss, S.T. Kottmann, R.Y. Sweeney, A. Hayhurst, G. Georgiou, B. Iverson, A.M. Belcher, *Science* 303 (2004) 213.
- [7] G.H. Du, L.-M. Peng, Q. Chen, S. Zhang, W.Z. Zhou, *Appl. Phys. Lett.* 83 (2003) 1638.
- [8] G.H. Du, Q. Chen, Y. Yu, S. Zhang, W.Z. Zhou, L.M. Peng, *J. Mater. Chem.* 14 (2004) 1437.
- [9] G.H. Du, Q. Chen, R.C. Che, L.M. Peng, *Appl. Phys. Lett.* 79 (2001) 3702.
- [10] M.M. Thackeray, *Prog. Solid State Chem.* 25 (1997) 1.
- [11] A.R. Armstrong, P.G. Bruce, *Nature* 381 (1996) 499.
- [12] B. Ammundsen, J. Paulsen, *Adv. Mater.* 13 (2001) 943.
- [13] Q. Feng, H. Kanoh, K. Ooi, *J. Mater. Chem.* 9 (1999) 319.
- [14] L.I. Hill, A. Verbaere, D. Guyomard, *J. Power Sources* 226 (2003) 119.
- [15] M.M. Thackeray, *J. Am. Ceram. Soc.* 82 (1999) 3347.
- [16] Y.F. Shen, R.P. Zenger, S.L. Suib, L. McCurdy, D.I. Potter, C.L. O’Young, *Science* 260 (1993) 511.
- [17] R.N. DeGuzman, Y.F. Shen, E.J. Neth, S.L. Suib, C.L. O’Young, S. Levine, J.M. Newsam, *Chem. Mater.* 6 (1994) 815.
- [18] M. Benaissa, M. Jose-Yacamán, T.D. Xiao, P.R. Strutt, *Appl. Phys. Lett.* 70 (1997) 2120.
- [19] N. Kijima, H. Yasuda, T. Sato, Y. Yoshimura, *J. Solid State Chem.* 159 (2001) 94.
- [20] Y.D. Li, X.L. Li, R.R. He, J. Zhu, Z.X. Deng, *J. Am. Chem. Soc.* 124 (2002) 1411.
- [21] X. Wang, Y.D. Li, *Chem. Eur. J.* 9 (2003) 300.
- [22] (a) Z.Q. Li, Y. Ding, Y.J. Xiong, Q. Yang, Y. Xie, *Chem. Commun.* (2005) 918; (b) Z.Q. Li, Y. Ding, Y.J. Xiong, Y. Xie, *Cryst. Growth Des.* 5 (2005) 1953.
- [23] (a) Y.Q. Gao, Z.H. Wang, J.X. Wan, G.F. Zou, Y.T. Qian, *J. Cryst. Growth* 279 (2005) 415; (b) Y. Chen, C. Liu, F. Liu, H.M. Cheng, *J. Alloy Compd.* 19 (2005) 282.
- [24] J. Luo, S.L. Suib, *J. Phys. Chem. B* 101 (1997) 10403.
- [25] T.D. Xiao, P.R. Strutt, M. Benaissa, H. Chen, B.H. Kear, *Nanostruct. Mater.* 10 (1998) 1051.
- [26] C.Z. Wu, Y. Xie, D. Wang, J. Yang, T.W. Li, *J. Phys. Chem. B* 107 (2003) 13583.
- [27] Y.D. Li, X.L. Li, Z.X. Deng, B.C. Zhou, S.S. Fan, J.W. Wang, X.M. Sun, *Angew Chem. Int. Ed. Engl.* 41 (2002) 333.