Nanostructures

Microwave-Assisted Synthesis of Single-Crystalline Tellurium Nanorods and Nanowires in Ionic Liquids**

Ying-Jie Zhu, Wei-Wei Wang, Rui-Juan Qi, and Xian-Luo Hu*

Many chemical processes involve volatile organic solvents that evaporate into the atmosphere with detrimental effects on the environment and human health. As the introduction of cleaner technologies has become a major concern throughout both industry and academia, the search for alternatives to the damaging volatile solvents has become a high priority. Room-temperature ionic liquids (RTILs) have aroused increasing interest worldwide due to their high fluidity, low melting temperature and extended temperature range in the liquid state, air and water stability, low toxicity, nonflammability, high ionic conductivity, ability to dissolve a variety of materials, and importantly no measurable vapor pressure.[1–4] Therefore, negative environmental and safety problems arising from the use of volatile organic solvents can be avoided by using RTILs. Because of the above reasons, RTILs are actively being explored as possible "green" solvents[5] to substitute conventional volatile organic solvents in a variety of processes, including industrially important chemical processes.[6–10] They also offer fascinating possibilities for fundamental studies of their effects on chemical reactions and synthetic processes.[1–3,11]

In contrast to their application in organic chemistry, the use of RTILs in inorganic synthesis is still in its infancy. There have been only a few reports on the formation and stabilization, by using RTILs, of hollow TiO_2 microspheres,[12] and nanoparticles of palladium,[13] iridium[14] and platinum[15] that are recyclable catalysts for biphasic hydrogenation. Electrochemical deposition of nanocrystalline metals such as Al, Fe, and Al–Mn alloys has also been reported.[16] These metal nanoparticles prepared in ionic liquids were spherical in shape, and not nanorods nor nanowires. Nanorods and nanowires represent a class of 1D nanostructures, in which the carrier motion is restricted in two directions such that they usually show interesting properties that differ from those of the bulk or spherical nanoparticles of the same chemical composition.[17–18] These nanostructures have great potential

---

[*] Prof. Y.-J. Zhu, W.-W. Wang, R.-J. Qi, X.-L. Hu
State Key Laboratory of High Performance Ceramics and Superfine Microstructure
Shanghai Institute of Ceramics, Chinese Academy of Sciences
Shanghai 200050 (P. R. China)
Fax: (+86) 215-241-3122
E-mail: y.j.zhu@mail.sic.ac.cn

[**] Financial support from Chinese Academy of Sciences under the program for recruiting outstanding overseas Chinese (Hundred Talents Program) is gratefully acknowledged. We also thank the Innovation Research Fund from the Shanghai Institute of Ceramics, Chinese Academy of Sciences. We are grateful to Dr. Long Pan for helpful discussions.

DOI: 10.1002/ange.200353101

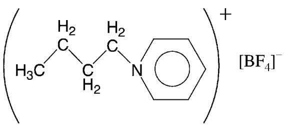
applications as important components and interconnects in nanodevices.[18–20]

The application of microwave heating in synthetic chemistry is a fast-growing area of research.[21–22] Since the first reports of microwave-assisted synthesis in 1986,[23–24] microwave heating has been accepted as a promising method for rapid volumetric heating, which results in higher reaction rates and selectivities, reduction in reaction times often by orders of magnitude, and increasing yields of products compared to conventional heating methods. As a result, this has opened up the possibility of realizing new reactions in a very short time. From the perspective of microwave chemistry, one of the key important advantages of RTILs is the presence of large organic positive ions with a high polarizability. Therefore, RTILs are very good media for absorbing microwaves, thus leading to a very high heating rate. There has been a recent report[25] on the use of ionic liquids as aids for microwave heating of nonpolar solvents, thereby allowing them to be used as media for microwave-assisted chemistry. The addition of a small quantity of an ionic liquid to a nonpolar solvent can greatly increase the rate and yield of reactions. However, the application of microwave chemistry to materials synthesis in conjunction with ionic liquids has hardly been exploited despite these advantages.

Table 1: Typical samples prepared by the MAIL method.[a]

Sample	Solution	Heating Method	T [°C]	t [min]	Morphology
1	TeO_2 (3 mg) + PVP (30 mg) + $(BPy)[BF_4]$ (0.5 mL) + $NaBH_4$ (0.12 mL, 3.67 M)	microwave	180	10	nanorods
2	PVP (24 mg) + $(BPy)[BF_4]$ (0.5 mL) + $NaBH_4$ (0.12 mL, 3.67 M) + TeO_2 (6 mg) + $(BPy)[BF_4]$ (1 mL)	microwave	180	10	nanowires
3	same as sample 1	microwave	40–130	10	spherical
4	same as sample 1	microwave	130–150	10	nanorods + spherical
5	same as sample 1	oil bath	180	10	spherical
6	same as sample 1	oil bath	180	120	spherical + nanorods (minority)
7	TeO_2 (3 mg) + PVP (30 mg) + H_2O (0.5 mL) + $NaBH_4$ (0.12 mL, 3.67 M)	microwave	80–100	10	spherical
8	PVP (24 mg) + H_2O (0.5 mL) + $NaBH_4$ (0.12 mL, 3.67 M) + TeO_2 (6 mg) + H_2O (1 mL)	microwave	80–100	10	spherical
9	same ratios as sample 7 scaled up to a total volume of 30 mL	hydrothermal	180	10–90	spherical
10	same as sample 7 except no PVP, scaled up to a total volume of 30 mL by using $(BPy)[BF_4]$ (2.3 mL)	hydrothermal	180	90	nanorods + spherical
11	same as sample 10	hydrothermal	180	600	nanowires (majority)

[a] See Experimental Section for details. PVP = polyvinylpyrrolidone, $BuPy^+[BF_4]^-$ = *N*-butylpyridinium tetrafluoroborate, the chemical structure of this ionic liquid is shown below:



By combining the advantages of both RTILs and microwave heating, we have developed a new microwave-assisted ionic liquid (MAIL) method for the fast controlled synthesis of tellurium (Te) nanorods and nanowires. Te is a p-type semiconductor with many useful and interesting properties, for example, photoconductivity, high piezoelectricity, thermoelectricity, and nonlinear optical responses. In addition, Te reacts readily with other elements to generate many functional materials. Recent progress has been made with the preparation of 1D nanostructures of Te.[26–30] Herein we demonstrate that the MAIL method is a fast, high-yield, seedless, template-free, and environmentally friendly green route for the production of Te nanorods and nanowires. This simple method does not need the subsequent complicated workup procedure required for the removal of the template or seed. This method may also be extended to the synthesis of a variety of other elemental and compound nanostructures. The conditions for preparing some typical samples by the MAIL method are listed in Table 1.

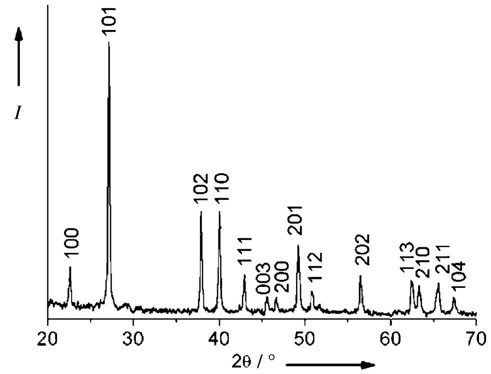


Figure 1. The XRD pattern of sample 1 prepared by the MAIL method at 180 °C for 10 min. The detailed preparation procedure is described in the Experimental Section. *I* = intensity, arbitrary units.

Figure 1 shows the XRD pattern of sample 1 prepared by the MAIL method at 180 °C for 10 min. From Figure 1 one can see that the product is a single phase of well-crystallized elemental Te with the hexagonal structure (space group: $P3_121$ (no. 152)). The measured lattice constants are $a = 4.459$ Å and $c = 5.917$ Å, which are consistent with the reported data ($a = 4.457$ Å, $c = 5.927$ Å, JCPDS file no. 36-1452). This result indicates that $NaBH_4$ has reduced TeO_2 to form Te in the ionic liquid $BuPy^+[BF_4]^-$ at 180 °C in 10 min. The yield of Te powder reached 94 % after the product was washed with absolute ethanol three times and distilled water two times, and dried at 60 °C in vacuum.

The morphologies, crystallization of samples prepared by the MAIL method were investigated with transmission electron microscopy (TEM). Figure 2 shows TEM micrographs of two typical samples consisting of Te nanorods and nanowires. The general reaction for the formation of Te may be simplified as follows:

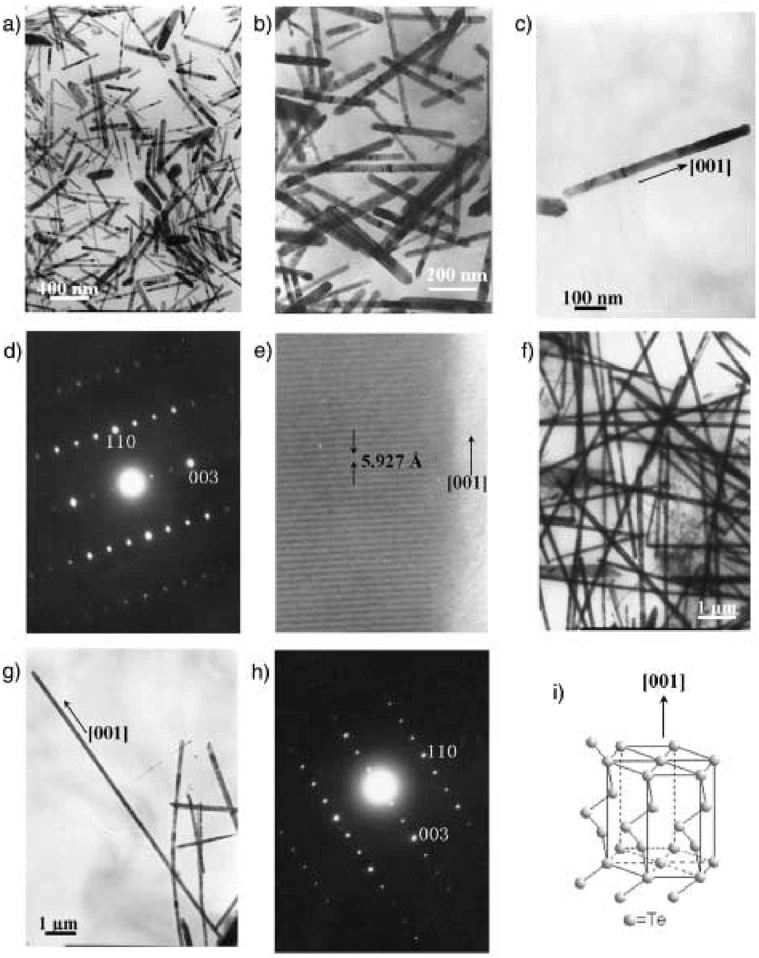


Figure 2. TEM micrographs of two typical samples prepared by the MAIL method. a) and b) sample 1; c) a single Te nanorod from sample 1 (Table 1); d) electron diffraction pattern of the same Te nanorod as shown in (c); e) high-resolution transmission electron microscopy (HRTEM) image of the same Te nanorod as shown in (c); f) and g) sample 2 (see Experimental Section); h) electron diffraction pattern of a single Te nanowire (the longest one in (g)); i) a schematic illustration showing the hexagonal crystal structure of Te and the [001] zone axis (*c* axis of the lattice).

$$\mathrm{TeO_2 + NaBH_4 \xrightarrow[\text{Microwave, }180\,^{\circ}\text{C, }10\,\text{min}]{\text{BuPy}^+[\text{BF}_4]^-,\ \text{PVP}} Te\ nanorods/nanowires} \qquad (1)$$

Figure 2a and b show TEM micrographs for the same sample as in Figure 1 (sample 1), from which one can see Te nanorods with diameters mostly ranging from ≈15 to ≈40 nm (a minority of them have diameters of 40 to 100 nm) and with lengths up to ≈700 nm. Each nanorod is straight and has a uniform diameter along its entire length. The aspect ratios of most nanorods are in the range from 10 to 20. The aspect ratio is defined as the length of the major axis divided by the width of the minor axis. Nanorods are defined as structures with widths of 1–100 nm and aspect ratios greater than 1 but less than 20; and nanowires are analogous structures with aspect ratios greater than 20.[31] Figure 2c shows a single Te nanorod with a diameter of 32 nm and a length of 610 nm (aspect ratio ≈19), its corresponding electron diffraction pattern is shown in Figure 2d which was obtained by focusing the electron beam along the $[1\bar{1}0]$ direction. Electron diffraction patterns on different nanorods or different positions of a given single nanorod were essentially the same as shown in Figure 2d, thus indicating that nanorods were single-crystalline. The electron diffraction pattern can be indexed to the hexagonal structure, which is consistent with the result obtained from XRD. Figure 2e shows the high-resolution transmission electron microscopy (HRTEM) micrograph of the same single nanorod as shown in Figure 2c, which provides more detailed structural information on these nanorods. The HRTEM shows that the nanorod is structurally single-crystalline with the periodic fringe spacing of 5.927 Å along the longitudinal axis of the nanorod, which corresponds to the interplanar spacing between the (001) planes of the hexagonal Te. This indicates that Te nanorods had the preferential growth direction along the [001] zone axis (*c* axis of the crystal lattice), which is consistent with the results obtained from Te nanorods prepared by other methods.[26,29]

By controlling the experimental parameters, exclusive nanowires or nanorods could be produced. Figure 2 f shows the TEM micrograph of sample 2 prepared under a different procedure (see Experimental Section) from sample 1 by the MAIL method. One can see that nanowires instead of nanorods were produced. Most of these nanowires have diameters ranging from 20 to 100 nm, and a minority has diameters in the range of 100–500 nm. The lengths of these nanowires are tens of micrometers. Figure 2 g shows several nanowires from sample 2. The corresponding electron diffraction pattern of the longest nanowire in Figure 2 g is shown in Figure 2 h. The electron diffraction pattern of the nanowire (Figure 2 h) is essentially the same as that of the nanorod (Figure 2d), indicating that nanorods and nanowires have the same preferential growth direction along the [001] zone axis (*c* axis of the crystal lattice).

The temperature has a significant influence on the morphology of Te. $NaBH_4$ reacts with TeO_2 to form Te even at room temperature. However, no nanorods or nanowires were observed at temperatures between room temperature and 130 °C (Table 1, sample 3). Te nanorods as well as spherical nanoparticles were observed in the temperature range of 130 to 150 °C (sample 4). When the temperature was increased to 180 °C (sample 1) or higher, only nanorods were observed. However, diameters of nanorods increased significantly when the temperature was higher than 200 °C. A similar situation exists for the preparation of Te nanowires. Therefore, the optimum temperature for the production of Te nanorods or nanowires is around 180 °C.

We investigated the influence of different heating methods on the morphology of Te. When the conventional heating method (oil bath) was used, no nanorods or nanowires were observed after heating at 180 °C for 10 min (Table 1, sample 5). Only a few nanorods could be observed if the heating time was increased to 2 h (sample 6). In contrast, exclusively nanorods or nanowires were produced by microwave-heating at 180 °C for only 10 min (samples 1 and 2). The heating time for synthesis of Te nanorods can be shortened by more than one order of magnitude by using microwave heating instead of conventional heating. The shorter microwave-heating time leads to enhanced efficiency and significant energy savings. This demonstrates the advantages of the MAIL method.

In a control experiment, we explored the possibility of using distilled water to replace ionic liquid $BuPy^+[BF_4]^-$ as the solvent. We used the same conditions and procedures as those used in samples 1 and 2 (Table 1), except with distilled water instead of $BuPy^+[BF_4]^-$ as the solvent. By microwave heating at temperatures between 80 and 100 °C (boiling point of water) for 10 min (samples 7 and 8), no nanorods or nanowires were observed. Similarly, only spherical Te nanoparticles were initially produced by reducing H_6TeO_6 by hydrazine (N_2H_4) in aqueous solution.[26] To increase the preparation temperature, each of reactant solutions was put into a 40 mL Teflon-lined stainless steel autoclave (75 % of total volume was filled). The autoclaves were sealed and hydrothermally treated at 180 °C for different times from 10 min to 1.5 h (sample 9). Nanorods or nanowires were still not observed. However, if small amount of $BuPy^+[BF_4]^-$ was added to replace PVP (sample 10), some nanorods were produced. If the hydrothermal heating time was increased to 10 h (sample 11), longer nanowires as a majority product with lengths up to tens of microns formed. These experiments show that ionic liquid $BuPy^+[BF_4]^-$ favors the formation of Te nanorods and nanowires.

The most cited classic model for shape-control is the Wulff facets theorem, which suggests that the shape of a crystal is determined by the relative specific surface energy of each facet of the crystal, giving a minimum total surface energy.[32] The shape of a single-crystalline nanostructure usually reflects the intrinsic crystal lattice symmetry. As shown in Figure 2i, Te has a highly anisotropic crystal structure consisting of helical chains of covalently bound atoms, thus having a strong tendency toward 1D growth.[26] However, the formation and growth of Te nanorods and nanowires can only be realized under appropriate conditions. Based on our experiments, we suggest that both the ionic liquid and microwave heating play an important role in the formation of Te nanorods and nanowires. The ionic liquid $BuPy^+[BF_4]^-$ consists of cation $BuPy^+$ and anion $[BF_4]^-$. The high ionic conductivity and polarizability of $BuPy^+$ make it an excellent microwave absorbing agent, thus leading to a high heating rate and a significantly shortened reaction time. The movement and polarization of ions under the rapidly changing electric field of the microwave reactor may result in transient, anisotropic micro-domains for the reaction system, facilitating the anisotropic growth of Te nanorods and nanowires. In addition to its acting as a solvent, it is likely that the ionic liquid acts as a capping reagent or a surfactant. We suggest that $BuPy^+$ ions act as a capping reagent and bind to the {001} facets less strongly than to other facets, leading to easier addition of Te atoms to the (001) facets and thus the preferential growth along *c* axis of the crystal lattice. The detailed formation mechanism of nanorods and nanowires in ionic liquids under the microwave heating needs to be further investigated.

In summary, we have developed a new MAIL method for the synthesis of Te nanorods and nanowires. This environment-friendly green method is a fast, high-yielding, seedless and template-free route, which avoids the subsequent complicated workup procedure normally needed to remove the template or seed. By controlling experimental parameters, exclusively Te nanorods or nanowires are synthesized. Our experiments show that both the ionic liquid and the microwave heating play an important role in the formation of Te nanorods and nanowires. As demonstrated by this successful example, the MAIL method may also be extended to synthesize other elemental and compound nanostructures. This will open up a new possibility for fast controlled production of a variety of 1D nanostructures in good yields by using desirable “green chemistry” methods. These related studies are in progress.

Experimental Section

All chemicals used were of analytical grade and purchased and used as received without further purification.

Sample 1 was prepared as follows: TeO_2 (3 mg) and PVP(30 mg) were mixed by a magnetic stirrer in a 10 mL tube that contained the ionic-liquid solvent $BuPy^+[BF_4]^-$ (0.5 mL) at room temperature. The suspension was microwave-heated to 180 °C (it took ≈40 s) at a power setting of 10 W, and two drops of 3.67 M $NaBH_4$ solution (≈0.12 mL) were added immediately at 180 °C. The solution was maintained at 180 °C for 10 min, then microwave heating was terminated and the solution was allowed to cool to room temperature.

Sample 2 was prepared as follows: PVP (24 mg) was dissolved in stirring $BuPy^+[BF_4]^-$ (0.5 mL) in a 10 mL tube at room temperature. Two drops of 3.67 M $NaBH_4$ aqueous solution (≈0.12 mL) were added at room temperature. The above solution was labeled solution A. TeO_2 (6 mg) was mixed into stirring $BuPy^+[BF_4]^-$ (1 mL) at room temperature, and this solution was labeled solution B. Solution A was microwave-heated to 180 °C at a power setting of 10 W (it took about 0.7 min), and solution B was immediately added dropwise at 180 °C. After the addition of solution B, the resulting solution was maintained at 180 °C for 10 min, then microwave heating was terminated and the solution was cooled to room temperature. The preparation conditions for other samples are listed in Table 1. Samples 3–6 (Table 1) were prepared under different conditions by using the same solution as that of sample 1. Samples 7 and 8 were prepared by the same means as that of sample 1 and sample 2, respectively, except using distilled water instead of $BuPy^+[BF_4]^-$. Samples 9–11 were prepared at 180 °C by the hydrothermal method. Black suspensions were obtained after microwave heating. The products were separated by centrifugation, washed with absolute ethanol three times and distilled water two times, and dried at 60 °C in vacuum.

The microwave oven (2.45 GHz, maximum power 300 W) used was a focused single-mode microwave synthesis system (Discover, CEM, USA). The unique, circular single-mode cavity ensured samples were in a homogenous highly dense microwave field. The system was equipped with an in situ magnetic stirring and a water-cooled condenser. Temperature was accurately controlled by automatic adjusting of microwave power. X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/max 2550 V X-ray diffractometer with high-intensity $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. TEM images, selected area electron diffraction and HRTEM were taken with a JEOL JEM-2010 high-resolution transmission electron microscope.

Received: October 16, 2003 [Z53101]

Keywords: ionic liquids · microwave chemistry · nanostructures · tellurium

[1] T. Welton, *Chem. Rev.* **1999**, *99*, 2071.

[2] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.

[3] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.

[4] W. Xu, E. I. Cooper, C. A. Angell, *J. Phys. Chem. B* **2003**, *107*, 6170.

[5] L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brennecke, *Nature* **1999**, *399*, 28.

[6] Y. Chauvin, H. Olivier-Bourbigou, *CHEMTECH* **1995**, *25*, 26.

[7] C. J. Adams, M. J. Earle, G. Roberts, K. R. Seddon, *Chem. Commun.* **1998**, 2097.

[8] M. J. Earle, P. B. McCormac, K. R. Seddon, *Chem. Commun.* **1998**, 2245.

[9] M. J. Earle, P. B. McCormac, K. R. Seddon, *Green Chem.* **1999**, *1*, 23.

[10] B. Ellis, W. Keim, P. J. Wasserscheid, *Chem. Commun.* **1999**, 337.

[11] K. Jin, X. Y. Huang, L. Pan, J. Li, A. Appel, S. Wherland, *Chem. Commun.* **2002**, 2872**.**

[12] T. Nakashima, N. Kimizuka, *J. Am. Chem. Soc.* **2003**, *125*, 6386.

[13] J. Huang, T. Jiang, B. X. Han, H. X. Gao, Y. H. Chang, G. Y. Zhao, W. Z. Wu, *Chem. Commun.* **2003**, 1654**.**

[14] J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, *J. Am. Chem. Soc.* **2002**, *124*, 4228.

[15] C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner, S. R. Texeira, *Inorg. Chem.* **2003**, *42*, 4738.

[16] F. Endres, M. Bukowski, R. Hempelmann, H. Natter, *Angew. Chem.* **2003**, *115*, 3550; *Angew. Chem. Int. Ed.* **2003**, *42*, 3428.

[17] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, *Science* **2002**, *295*, 2425.

[18] X. Duan, Y. Huang, Y. Cui, J. Wang, C. M. Lieber, *Nature* **2001**, *409*, 66.

[19] S. Frank, P. Poncharal, Z. L. Wang, W. A. de Heer, *Science* **1998**, *280*, 1744.

[20] H. M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **2001**, *292*, 1897.

[21] L. Perreux, A. Loupy, *Tetrahedron* **2001**, *57*, 9199.

[22] R. S. Varma, *Green Chem.* **2001**, *3*, 98.

[23] R. Gedye, F. Smith, K. Westaway, A. Humera, L. Baldisera, L. Laberge, L. Rousell, *Tetrahedron Lett.* **1986**, *27*, 279.

[24] R. Giguere, T. L. Bray, S. M. Duncan, G. Majetich, *Tetrahedron Lett.* **1986**, *27*, 4945.

[25] N. E. Leadbeater, H. M. Torenius, *J. Org. Chem.* **2002**, *67*, 3145.

[26] B. Mayers, Y. N. Xia, *J. Mater. Chem.* **2002**, *12*, 1875.

[27] B. Mayers, Y. N. Xia, *Adv. Mater.* **2002**, *14*, 279.

[28] M. S. Mo, J. H. Zeng, X. M. Liu, W. C. Yu, S. Y. Zhang, Y. T. Qian, *Adv. Mater.* **2002**, *14*, 1658.

[29] Z. P. Liu, Z. K. Hu, Q. Xie, B. J. Yang, J. Wu, Y. T. Qian, *J. Mater. Chem.* **2003**, *13*, 159.

[30] Y. J. Zhu, Y. T. Qian, H. Huang, M. W. Zhang, *J. Mater. Sci. Lett.* **1996**, *15*, 1700.

[31] J. Murphy and N. R. Jana, *Adv. Mater.* **2002**, *14*, 80.

[32] J. A. Venables, *Introduction to Surface and Thin Film Processes*, Cambridge University Press, Cambridge, **2000**, p. 4.