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Synthesis of γ-Al_2O_3 nanowires through a boehmite precursor route

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Abstract

By regulating the pH values of the reaction solution, the boehmite (γ-AlOOH) nanowires and nanoflakes were successfully synthesized with a simple hydrothermal route using anhydrous $AlCl_3$, NaOH and $NH_3{\cdot}H_2O$ as starting materials. Crystalline γ-Al_2O_3 nanowires with diameter of 10–30 nm and length of several hundreds of nanometer have been prepared by thermal decomposition of γ-AlOOH precursor. X-ray diffraction (XRD), transmission electron microscope (TEM), selected area electron diffraction (SAED), and high resolution transmission electron microscope (HRTEM) were used to characterize morphology and structure feathers of the synthesized samples. The pH values of the solution play important roles in the formation of γ-AlOOH nanowires. After calcinated at 500 °C for 2 h, the obtained γ-Al_2O_3 with a linear structure is similar to the γ-AlOOH precursor.

Keywords: γ-Al_2O_3; Boehmite; Nanowires; Hydrothermal route; pH value

1. Introduction

Since the discovery of carbon nanotubes [1], materials with one-dimensional (1D) nanostructures have received continuous attention because of their unique electronic, mechanical and chemical properties and their application on building blocks for nanodevices [2,3]. Many methods have been developed for the preparation of the 1D nanostructures, including vapor–liquid–solid (VLS) methods [3,4], chemical vapor deposition (CVD) [5], thermal evaporation [6], template assisted approaches [7], and solution-phase methods [8,9]. Among the varieties of approaches, the solution-phase methods seem to be low-cost and efficient for large-scale production [10].

As a kind of important structural ceramic materials, alumina have been used as absorbent, catalyst carrier and reinforce of ceramic composites for its high strength, corrosion resistance, chemical stableness, low thermal conductivity, and good electrical insulation [11,12]. The synthesis of nanometer-sized alumina, especially one-dimensional nanostructures, has received considerable interest due to their novel properties, such as high elastic modulus, thermal and chemical stability, and optical characteristics [13]. Up to date, the most common synthetic strategy of crystalline alumina nanowires is based on vapor-based synthetic methods. Single-crystal Al_2O_3 fibers were first produced at Lawrence Berkeley laboratory, using a basal sapphire (single crystal) substrate [14]. Zhou et al. synthesized crystalline alumina nanowires with diameter about 50 nm and length about 2 μm in a catalyst-assisted process using iron as catalyst [14]. Tang et al. grew Al_2O_3 nanowires by heating a mixture of Al, SiO_2 and Fe_2O_3 catalyst [15].

Recently, considerable efforts have been focused on the preparation of boehmite (γ-AlOOH) nanostructures by solution-phase routes because they are usually used as the precursor for the synthesis of alumina nanostructures. Chen et al. present a hydrothermal route to synthesize 1D and 2D γ-AlOOH nanomaterials under either acidic or basic conditions by using aluminum nitrate, ethylenediamine or hexamethylenetetramine as starting materials [16]. By manipulating the acidity of the reaction solution, the γ-AlOOH with two distinct 1D nanowires (or nanowire bundles) and 2D nanoplatelets was prepared under hydrothermal conditions [17]. γ-Al_2O_3 single-crystalline nanorods with diameter about 20 nm and length about 200 nm were synthesized by thermal decomposition of boehmite precursor, which was prepared by solvothermally treating $AlCl_3{\cdot}6H_2O$, NaOH, sodium dodecyl benzene sulfonate in water and dimethylbenzene mixed solvents [18]. In this paper, we report a simple hydrothermal route to the synthesis of γ-AlOOH nanostructures by using anhydrous $AlCl_3$, NaOH and

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$NH_3{\cdot}H_2O$ as starting materials. The γ-AlOOH nanowires and nanoflakes were prepared by regulating the pH values of the reaction solution. The γ-Al_2O_3 nanowires with linear structure were obtained by using γ-AlOOH nanowires as the precursor.

2. Experimental

All chemicals were of analytical grade reagents and used as received without further purification. All experiments were conducted under air atmosphere. In a typical synthesis experiment, anhydrous $AlCl_3$ (10 g) was dissolved in 50 ml distilled water under vigorous magnetic stirring at room temperature to form solution A. NaOH (4 g) was dissolved in 50 ml distilled water under magnetic stirring, and then 6.8 ml $NH_3{\cdot}H_2O$ was added dropwise to prepare solution B. Subsequently, solution B was added drop by drop to the solution A to give lacteous precipitates immediately. The obtained suspension was transferred into a 100 ml Teflon-lined

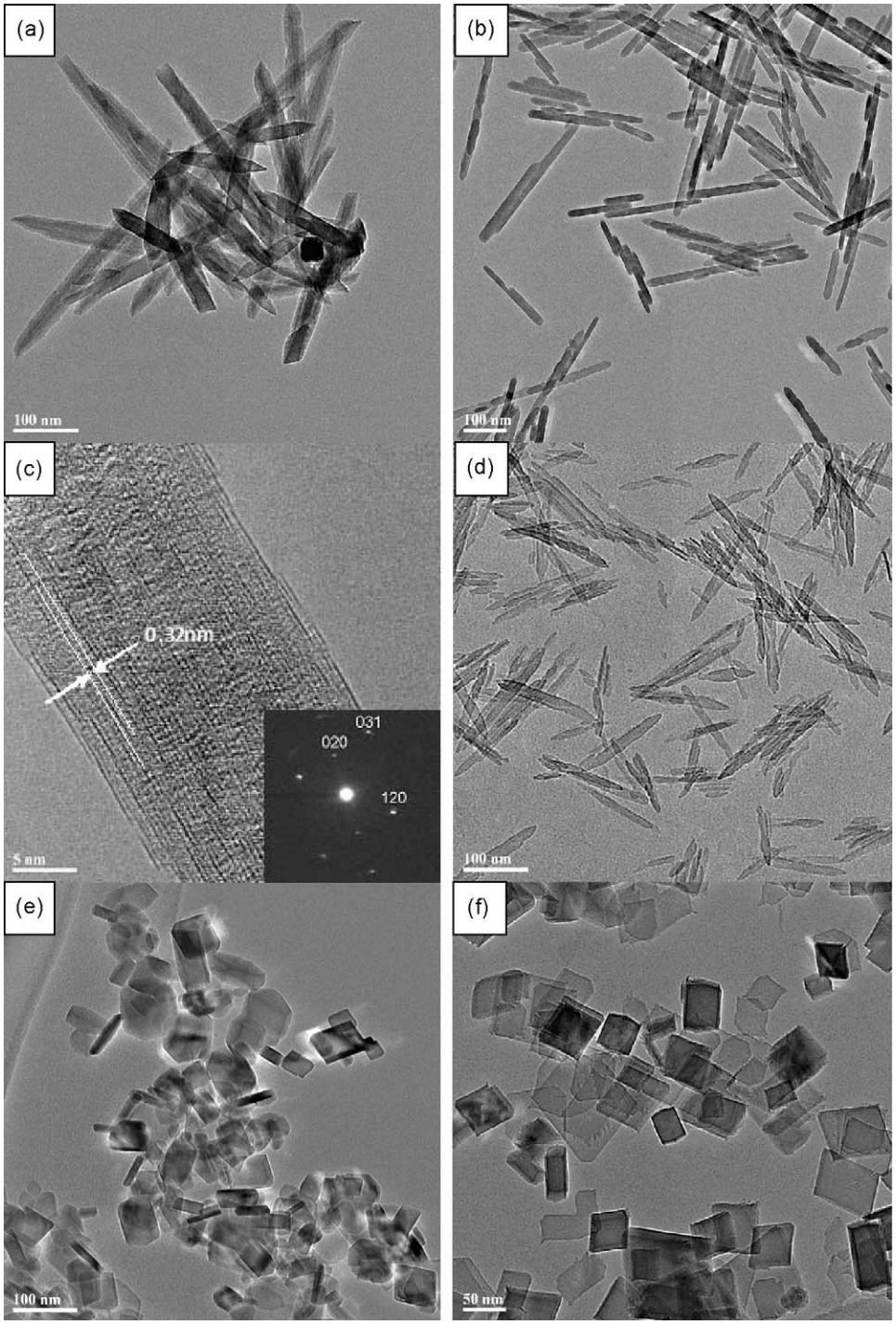

Fig. 1. TEM images of γ-AlOOH synthesized under different pH value of reaction solution: (a) pH 4, (b) pH 5, (d) pH 6, (e) pH 7, (f) pH 10, (c) HRTEM image of sample in (b) and SAED pattern (inset).

stainless steel autoclave. The autoclave was sealed and maintained at 200 °C for 12 h, then allowed to cool naturally to room temperature. The product was separated from the solution by centrifugation, washed by water and ethanol several times and dried at 60 °C in vacuum for 12 h. Finally, the white powder (boehmite) was put into an alumina crucible in a tube furnace and heated to the specified temperature for 2 h in air with a heating rate of 5 °C/min.

The X-ray diffraction (XRD) patterns of the obtained products were recorded on a BRUKER-AXS X-ray powder diffractometer with a graphite monochromator and Cu Kα radiation (λ = 0.154178 nm) at 40 kV and 60 mA in a 2θ range from 10° to 70° at room temperature. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) pattern and high resolution transmission electron microscopy (HRTEM) images were taken with a JEOL-2010 transmission electron microscope.

3. Results and discussion

It is generally accepted that many experimental factors could affect the morphologies and size of the nanomaterials. In order to investigate the influencing of processing parameters on the formation of the γ-AlOOH nanowires and the growth mechanism, different experiments were carried out by changing the reaction conditions. In our studies, the pH value of the solution played important roles in the formation of γ-AlOOH nanowires.

The morphologies of the γ-AlOOH obtained with pH value at 4, 5, 6, 7, and 10 were investigated with TEM. As shown in Fig. 1, the samples exhibit distinct morphologies when the pH values of the reaction solution vary from 4 to 10. At pH 4, the samples show linear structures (Fig. 1a). However, only a few products were obtained at this reaction condition. In the further experiment, we also found that when the pH was changed to lower values (pH < 4), no precipitates were observed in the solution after hydrothermal reaction. Fig. 1b shows the samples synthesized at pH 5, which exhibits a large quantity of nanowires with diameters of 10–30 nm and lengths of several hundreds of nanometer. A further HRTEM image of a single nanowire in Fig. 1c illustrates a lattice fringe of ∼0.32 nm, corresponding to the separation between the neighboring (120) lattices. The symmetrically scattered spots of the inset in Fig. 1c show the single crystallinity of the as-synthesized γ-AlOOH nanowires. However, when the pH value of the reaction solution varies to 6, the samples have needlelike morphology with diameters of 10–30 nm and lengths of 100–200 nm, and their surface exhibit zigzag patterns (as shown in Fig. 1d). With the increasing of pH values, the morphology of the as-synthesized samples changes dramatically. When the pH varies to 7, there are a large number of nanoflakes present in the as-synthesized products. A very few rod-like samples can also be find from Fig. 1e. Fig. 1f shows the sample prepared at pH 10 consist of nanoflakes with the width of tens of nanometers. This indicates that the γ-AlOOH nanowires are significantly sensitive to the pH value. By varying the pH from 4∼10, the 1D nanowires and 2D nanoflakes of γ-AlOOH nanostructures could be prepared by this facile hydrothermal method.

The detailed growth mechanism is still not well understood, but it is believed that the growth of γ-AlOOH nanowires could be attributed to the characteristic structure of AlOOH, which has a lamellar structure of linked octahedral AlO_6 units to form an infinite plane perpendicular to the [0 1 0] direction [19]. Hydroxyl groups sustain the lamellar structure by hydrogen bonding. The lamellar surfaces are covered with the hydroxyl groups, in which the oxygen lone pairs are directed outwards. Under acidic conditions, the reaction solution contains protons that would combine with the hydroxyl oxygen-lone pairs to give aqua ligands [19] and therefore destroy the γ-AlOOH layers. The separated layers subsequently curl to form 1D nanostructures via the scrolling-growth route [20]. By contrast, the 2D lamellar nanostructure would be retained in basic solutions, because both bases are not strong enough to deprotonate the surface OH groups to dissemble the γ-AlOOH layers [16,17].

To investigate the variety of the structure and morphology of the samples, the γ-AlOOH precursors, which were prepared via hydrothermal route with pH at 5, were calcined at different temperatures. Fig. 2 shows the XRD patterns of the samples calcined at 400 °C, 500 °C, 1200 °C, 1250 °C, and 1300 °C for 2 h, respectively. The diffraction peaks of the samples calcined at 400 °C (as shown in Fig. 2a) can be indexed to an orthorhombic phase of γ-AlOOH, indicating that the phase of precursors hardly transformed at the calcined temperature of 400 °C for 2 h. The cell parameters, $a = 5.293$ Å, $b = 5.264$ Å and $c = 5.318$ Å, are compatible with the literature values of γ-AlOOH (Ref: JCPDS No. 21-1307). When the calcined temperature increases to 500 °C, the samples transform to γ-Al_2O_3 as indexed in Fig. 2b. Fig. 2c shows the samples remain as γ-Al_2O_3 at the calcined temperature up to 1200 °C. With the increasing of the calcined temperature to 1250 °C, the γ-Al_2O_3 transform to hybrid phases with θ-Al_2O_3 and α-Al_2O_3, which was shown in Fig. 2d. At the calcined temperature of 1300 °C for 2 h, the samples completely convert to α-Al_2O_3 with a

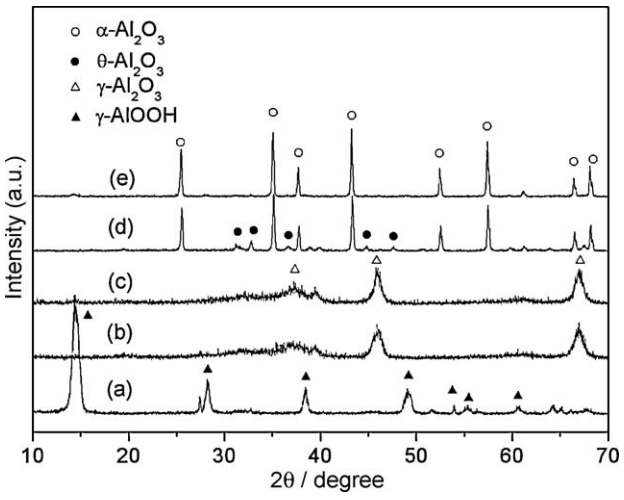

Fig. 2. XRD patterns of the samples calcined at different temperatures: (a) 400 °C; (b) 500 °C; (c) 1200 °C; (d) 1250 °C; (e) 1300 °C.

hexagonal phase (Fig. 2e). The lattice constants, $a = 9.739$ Å and $c = 2.876$ Å are also consistent with the values of α-Al_2O_3 (Ref: JCPDS No. 10-0425). Since the crystallite size of boehmite show a strong correlation with the formation temperature of γ-Al_2O_3 and the phase transition temperature of θ- to α-Al_2O_3 according to the studies by Tsukada et al. [21], it is important to investigate the detail structures of obtaining γ-, θ- and α-Al_2O_3 from boehmite.

Fig. 3 shows the morphology of the samples, which was calcined at 500 °C, 1200 °C, 1250 °C, and 1300 °C for 2 h,

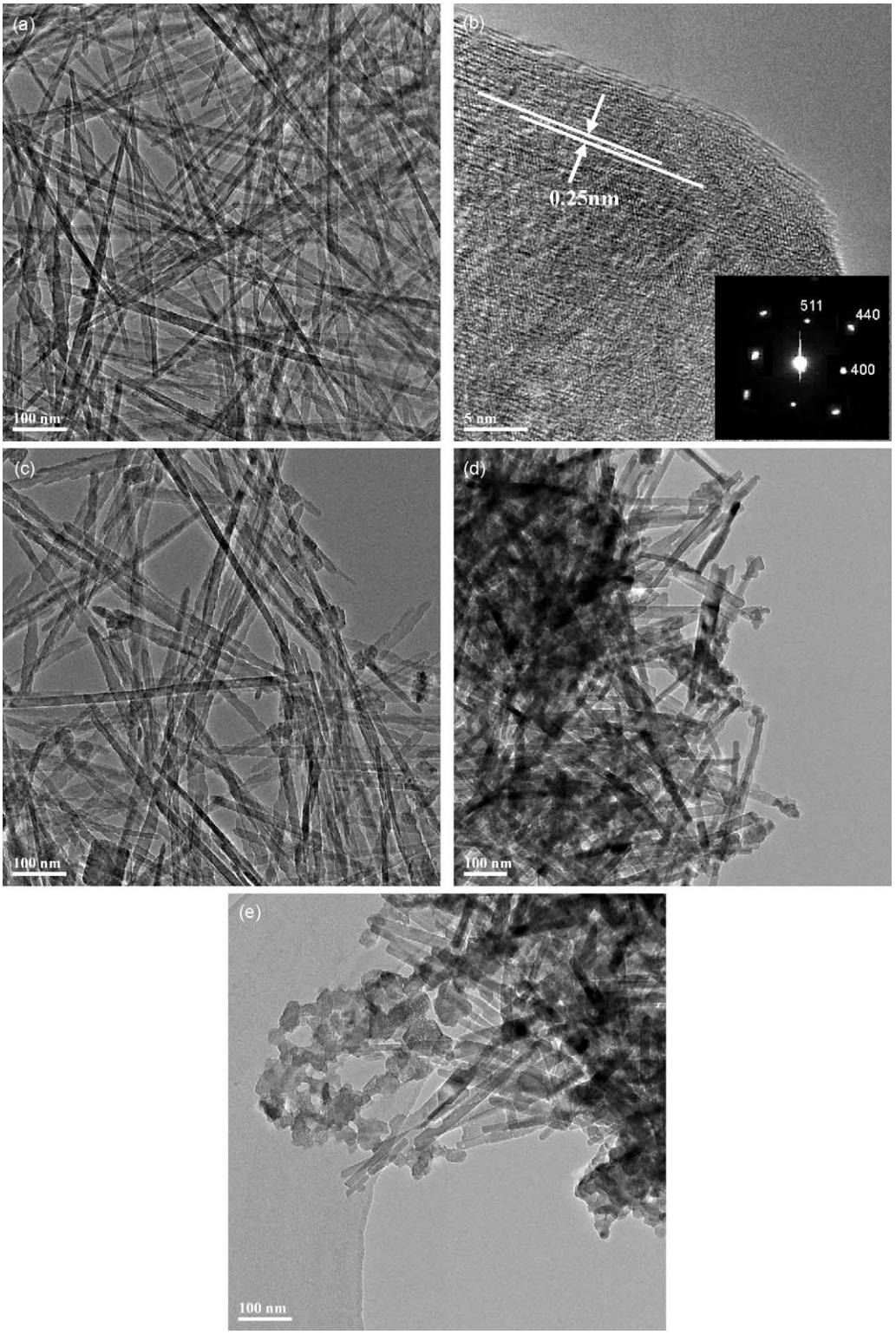

Fig. 3. TEM images of the samples calcined at different temperatures: (a) 500 °C; (c) 1100 °C; (d) 1200 °C; (e) 1300 °C, (b) HRTEM image of sample in (a) and SAED pattern (inset).

respectively. After the γ-AlOOH transformed to γ-Al_2O_3 at 500 °C for 2 h, the linear structure was retained as shown in Fig. 3a. The size and morphology of γ-Al_2O_3 are similar to those of the γ-AlOOH precursor, which exhibit the diameters at 10–30 nm and length at 1–2 μm. The HRTEM images clearly show that the lattice fringe is ∼0.2 nm, consistent well with that of the (5 1 1) plane of γ-Al_2O_3 crystals (Fig. 3b). The inset of Fig. 3b presents the selected area electron diffraction pattern taken from a single nanowire, which can be indexed as single-crystalline cubic structural γ-Al_2O_3. When the calcined temperature increases to 1200 °C, the samples remain the linear structure as shown in Fig. 3c. However, some of the samples sinter with each other after calcined at 1250 °C for 2 h (Fig. 3d). If the calcined temperature increases to 1300 °C, the samples accumulate together with severe sintered (Fig. 3e). This result indicates that the transition of γ- to α-Al_2O_3 requires a reconstructive recrystallization process because of the different cubic close-parked and hexagonal oxygen sublattice, which lead to the linear structure crimping and sintering.

4. Conclusions

In this study, the boehmite (γ-AlOOH) nanowires and nanoflakes were synthesized with hydrothermal method by regulating the pH values of the reaction solution. The growth of γ-AlOOH nanowires could be attributed to the lamellar structure of AlOOH. Crystalline γ-Al_2O_3 nanowires with diameter of 10–30 nm and length of several hundreds of nanometer have been prepared by thermal decomposition of γ-AlOOH precursor. The size and morphology of γ-Al_2O_3 can be well preserved during the transformation from γ-AlOOH to γ-Al_2O_3.

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References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56–58.
[2] R.H. Baughman, A.A. Zakhidov, W.A. Hee, Carbon nanotubes—the route toward applications, Science 297 (2002) 787–792.
[3] Z.W. Pan, Z.R. Dai, Z.L. Wang, Nanobelts of semiconducting oxides, Science 291 (2001) 1947–1949.
[4] J. Hu, T.W. Odom, C.M. Lieber, Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes, Acc. Chem. Res. 32 (1999) 435–445.
[5] C.N.R. Rao, F.L. Deepak, G. Gundiah, A. Govindaraj, Inorganic nanowires, Prog. Solid State Chem. 31 (2003) 5–147.
[6] J. Kong, H.T. Soh, A.M. Cassell, F. Calvin, Q.H. Dai, Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers, Nature 395 (1998) 878–881.
[7] W. Han, S. Fan, Q. Li, Y. Hu, Synthesis of gallium nitride nanorods through a carbon nanotube-confined reaction, Science 277 (1997) 1287–1289.
[8] Y.W. Jun, J.S. Choi, J.W. Cheon, Shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes, Angew. Chem. Int. Ed. 45 (2006) 3414–3439.
[9] X. Wang, Y.D. Li, Solution-based synthetic strategies for 1-D nanostructures, Inorg. Chem. 45 (2006) 7522–7534.
[10] Y. Xia, J.A. Rogers, K. Paul, G.M. Whitesides, Unconventional methods for fabricating and patterning nanostructures, Chem. Rev. 99 (1999) 1823–1848.
[11] H.X. Peng, Z. Fan, D.S. Mudher, J.R.G. Evans, Microstructures and mechanical properties of engineered short fibre reinforced aluminium matrix composites, Mater. Sci. Eng. A 335 (2002) 207–216.
[12] R.J. Hellmig, H. Ferkel, Using alumina nanopowder as cement in bonding of alumina ceramics, Phys. Stat. Sol. (a) 175 (1999) 549–553.
[13] C.M. Mo, L.D. Zhang, Z. Yuan, Optical absorption of nanostructured Al_2O_3, Nanostruct. Mater. 5 (1995) 95–99.
[14] J. Zhou, S.Z. Deng, J. Chen, J.C. She, N.S. Xu, Synthesis of crystalline alumina nanowires and nanotrees, Chem. Phys. Lett. 365 (2002) 505–508.
[15] C.C. Tang, S.S. Fan, P. Li, M. Lamy de la Chapelle, H.Y. Dang, In situ catalytic growth of Al_2O_3 and Si nanowires, J. Crystal Growth 224 (2001) 117–121.
[16] X.Y. Chen, S.W. Lee, pH-Dependent formation of boehmite (γ-AlOOH) nanorods and nanoflakes, Chem. Phys. Lett. 438 (2007) 279–284.
[17] X.Y. Chen, H.S. Huh, S.W. Lee, Hydrothermal synthesis of boehmite (γ-AlOOH) nanoplatelets and nanowires: pH-controlled morphologies, Nanotechnology 18 (2007) 285608.
[18] M.G. Ma, Y.J. Zhu, Z.L. Xu, A new route to synthesis of γ-alumina nanorods, Mater. Lett. 61 (2007) 1812–1815.
[19] X. Bokhimi, J.A. Toledo-Antonio, M.L. Guzma′n-Castillo, F. Herna′ndez-Beltra′n, Relationship between crystallite size and bond lengths in boehmite, J. Solid State Chem. 159 (2001) 32–40.
[20] H.W. Hou, Y. Xie, Q. Yang, Q.X. Guo, C.R. Tan, Preparation and characterization of γ-AlOOH nanotubes and nanorods, Nanotechnology 16 (2005) 741–745.
[21] T. Tsukada, H. Segawa, A. Yasumori, K. Okada, Crystallinity of boehmite and its effect on the phase transition temperature of alumina, J. Mater. Chem. 9 (1999) 549–553.