

Growth of Boehmite Nanofibers by Assembling Nanoparticles with Surfactant Micelles

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It is known that boehmite (AlOOH) nanofibers formed in the presence of nonionic poly(ethylene oxide) (PEO) surfactant at 373 K. A novel approach is proposed in this study for the growth of the boehmite nanofibers: when fresh aluminum hydrate precipitate was added at regular interval to initial mixture of boehmite and PEO surfactant at 373 K, the nanofibers grow from 40 to 50 nm long to over 100 nm. It is believed that the surfactant micelles play an important role in the nanofiber growth: directing the assembly of aluminum hydrate particles through hydrogen bonding with the hydroxyls on the surface of aluminum hydrate particles. Meanwhile a gradual improvement in the crystallinity of the fibers during growth is observed and attributed to the Ostwald ripening process. This approach allows us to precisely control the size and morphology of boehmite nanofibers using soft chemical methods and could be useful for low temperature, aqueous syntheses of other oxide nanomaterials with tailorable structural specificity such as size, dimension and morphology.

The synthesis of inorganic structures with nanoscale dimensions and morphological specificity is of great importance and interest in materials science and nanotechnology.^{1,2} An emerging synthesis strategy is to construct delicate inorganic nanostructured materials by employing surfactants in so-called “soft chemistry” approaches.^{3,4} Ultrathin γ -alumina fibers possessing nanoscale thicknesses have potential for applications including advanced catalysts, adsorbents, composite materials, and ceramics.^{5–7} Therefore, numerous studies on boehmite nanofibers have been undertaken in recent years.^{8–13} We reported recently that boehmite nanofibers can be formed from a precipitate of aluminum hydrous oxide in the presence of poly(ethylene oxide) (PEO) surfactant at 373 K.⁹ The boehmite nanofibers undergo an isomorphous transformation to nanocrystalline γ -alumina by calcination at 723 K and do retain the fibril morphology. In this communication, we report an interesting finding that the boehmite nanofibers grow rapidly when fresh precipitate of aluminum hydrate was supplied at regular intervals. The growth progress of the boehmite fiber is as follows: White precipitate is prepared by dropping 50 mL of NaAlO_2 solution containing 18.8 g of $\text{NaAlO}_2 \cdot (0.2 \text{ mol of Al})$ into 50 mL of 5 N acetic acid solution with vigorous stirring. The white precipitate is recovered by centrifugation and washed with water four times to remove the sodium ions. PEO surfactant (40 g, Tergitol 15S-7 from Aldrich), with a general chemical formula $\text{C}_{12-14}\text{H}_{25-29}\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ and average molecular weight of about 508, is mixed with the washed aluminum hydrate cake. The sticky mixture is stirred for at least 1 h and then transferred into a closed autoclave and kept in an oven at

373 K. The molar ratio of $\text{Al}(\text{OH})_3\text{:PEO:H}_2\text{O}$ in the mixture is 0.2:0.08:3.2. The autogenous pressure in the closed autoclave is about 1 atm. Fresh aluminum hydrate precipitate (prepared as described above and contain about 0.2 mol of $\text{Al}(\text{OH})_3$) is added into the autoclaved mixture every 2 days. Accordingly, the molar ratio of $\text{Al}(\text{OH})_3\text{:PEO:H}_2\text{O}$ changed to 0.4:0.08:6.4, 0.6:0.08:9.6, and 0.8:0.08:12.8, respectively, after 2, 4, and 6 days (post adding precipitate). The specimens were taken from reaction mixture after 2, 4, 6, and 8 days (prior to adding precipitate) for characterization by transmission electron microscopy (TEM) and X-ray diffraction (XRD).

A TEM based comparison of the reaction products from 2 and 8 days is provided in Figure 1a,b, respectively. A typical selected area electron diffraction (SAED) pattern is inset in Figure 1b. Indexing of the ring patterns indicated that the nanofibers possessed a crystal structure consistent with the orthorhombic form of boehmite $\text{Al}(\text{OOH})$ (unit cell parameters are $a = 0.369 \text{ nm}$, $b = 1.223 \text{ nm}$, and $c = 2.868 \text{ nm}$).

The fibers formed after 8 days are obviously longer and thicker than those formed after 2 days. We also measured the lengths and widths of isolated fibers that did not overlap other fibers in the images. The mean length of the fibers formed after 2, 4, 6, and 8 days are 40, 52, 76, and 92 nm, respectively, and the mean widths are 2.6, 3.5, 4.4, and 5.2 nm, respectively. The aspect ratios of the samples are 15.4, 14.9, 17.3, and 17.7. The narrow range of observed aspect ratios (15–18) supports our proposal that the boehmite nanofibers formed initially after 2 days grew simply by consuming the fresh precipitate supplied at regular intervals. In principle, one can make much longer fibers by continuing the growth process. The diffraction peaks in the X-ray diffraction (XRD) patterns of Figure 2 became sharper in the samples reacted for longer times, indicating a gradual improvement in the crystallinity of the fibers during growth.

The most intensive band on the Raman spectra for bulk boehmite is at 362 cm^{-1} (Figure 3). Its position and the full

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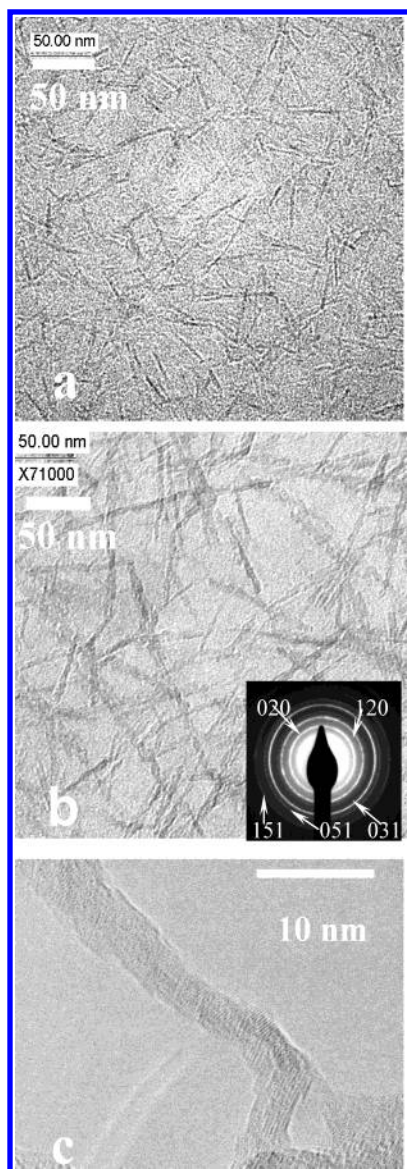


Figure 1. TEM images of the boehmite nanofibers. (a) is for the sample after 2 days, and (b) for the sample after 8 days. Comparison the two images clearly illustrates the growth of the boehmite fibers. (c) is HRTEM image of a fiber in the samples after 8 days. The fiber consists of a number of crystal grains stacking along the fiber axis, whereas the fiber thickness is same as the size of a single-crystal grain.

width at half-maximum (fwhm) are linear functions of the size of boehmite nanocrystals when the size is below 10 nm¹⁴ because the decrease in crystal size will bring about more Raman active modes because the selection rule for the infinite crystal is not valid. We found that the bands in Raman spectra of the samples become stronger and sharper, and the most intensive peak shifts to high wavenumber as the fibers grow (Figure 3). This is consistent with the literature¹⁴ and confirms that the crystals in the fibers are smaller than 10 nm.

As shown in the high-resolution TEM (HRTEM) images of the fibers formed after 8 days (Figure 1c), the thickness of the nanofiber is just 2–3 orthorhombic unit cells. The narrow range in fiber thickness, together with the facets along their length, suggests that each fiber is composed of orthorhombic unit cells stacking along the fiber axis. There has been a growth unit model, suggesting that crystals of metal oxide grow by growth units, the complexes of cations, and the coordinating hydroxyl ligands, rather than by ions.¹⁵ Each addition of fresh aluminum hydrate precipitate to the reaction system produced an increase

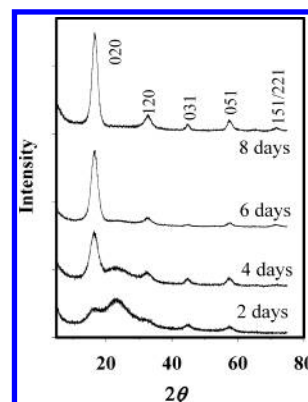


Figure 2. X-ray diffraction (XRD) patterns of the samples after reaction spanning for 2, 4, 6, and 8 day (from the bottom to top). The peaks are well matched with the patterns of boehmite in terms of peak position but the width of the peaks suggests that the crystals of these samples are small, being in nanometer range.

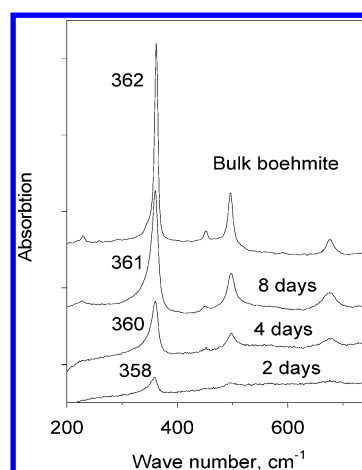


Figure 3. Raman spectra for the samples after reaction spanning for 2, 4, 6, and 8 day (from the bottom to top). The spectrum of bulk boehmite is also given for comparison.

in the length of the boehmite fibrils by at least 10 nm, meanwhile the increase in boehmite crystal size calculated from the fwhm of the 020 diffraction peak in the XRD pattern (Figure 2) using the Debye–Scherrer equation is less than 1 nm. Thus the fiber growth should not be due to the growth of boehmite crystals, but to another mechanism. The critical size of a stable crystal particle of boehmite nucleated from aluminum hydrate precipitate is estimated to be ~2–4 nm,¹⁶ we propose that the increase in fiber length involves an assembling process in which the nascent stable boehmite crystals, acting as the basic building units, aggregate and attach themselves to the ends of the fibrils, assisted by the micelles of PEO surfactant. Such an assembly process should yield polycrystalline fibers. Indeed, the steps along the boehmite nanofiber length suggest such assemblies of unit cells (Figure 1c). These results provide important insight into the growth mechanism of the fibers. We found no elongation of the fibers occurred when samples were kept under hydrothermal conditions for 8 days without the supply fresh precipitate to act as the building blocks for fiber growth.

We propose that the increase in the average crystal size of the fibers, shown by the XRD, is due to an Ostwald ripening process, in which larger crystallites grow at the expense of dissolving smaller crystallites driven by a reduction in surface energy. It is also possible that the fresh aluminum hydrate precipitate contains various species,¹⁶ and some of the small particles were dissolved and redeposited onto existing fibers.

This reprecipitation mechanism for growth should also lead to an increase in the average crystal size.

Evidently, the surfactant plays a crucial role in the formation and growth of the fibers. It is proposed that the surfactant directs the fibrils growth by forming rodlike micelles.^{17,18} In a polarized media, the ethylene oxide groups of the surfactant head toward the outside of the micelles whereas the hydrocarbon chain (of 12–14 carbon atoms) will tend to diffuse inside. The surfactant micelles interact with the hydroxyl group on the surface of boehmite particles through hydrogen bonding.^{9,19} Through this bonding, the rod-shaped micelles can direct the boehmite nanofiber growth.

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