A Facile and Controllable Synthesis of γ-Al_2O_3 Nanostructures without a Surfactant

Bo Tang*[a] Jiechao Ge,[a] Linhai Zhuo,[a] Guangli Wang,[a] Jinye Niu,[a] Zhiqiang Shi,[a] and Yubin Dong[a]

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Boehmite [AlOOH] nanoneedles, nanorods, and nanotubes were successfully synthesized by a facile sol-hydrothermal method without using any surfactant. Calcination of the corresponding boehmite nanostructures at 700 °C gave the corresponding γ-Al_2O_3 nanoneedles, nanorods, and nanotubes. The resulting products were characterized by XRD, TEM, HRTEM, and FT-IR spectroscopy. We found that the conditions used to produce the sol and the pH value of the hydrothermal process have important effects on the nucleation and growth of nanostructured materials.

Introduction

Developing a controllable synthesis process is always one of the most important goals of materials scientists. Because of their application in adsorbents, catalysts, and catalyst supports, the synthesis of alumina nanostructured materials, especially one-dimensional (1D) nanostructures, has received considerable interest due to their novel properties, such as high elastic modulus, thermal and chemical stability, and optical characteristics.[1] However, the synthesis of these nanostructures is still a challenge owing to their extremely small size and their anisotropy. The control of nucleation and growth of nanostructured materials is therefore becoming crucial.

So far, materials scientists have succeeded in preparing various morphologies of boehmite [AlOOH] and Al_2O_3, such as nanowires,[2] nanotubes,[3] nanobelts,[2a] nanofibers,[4] nanorods,[5] and whiskers[6] by different methods. The hydrothermal synthesis of fibrillar boehmite was originally studied by Bugosh[7] and further developed by a number of researchers.[8] In particular, a surfactant-assisted hydrothermal method has been developed to synthesize 1D boehmite and γ-Al_2O_3 nanostructures in recent years.[9] However, the preparation of semiconducting oxide nanobelts,[10] MnO_2 nanowires,[11] TiO_2 nanotubes,[12] $La(OH)_3$ nanorods,[13] $Cd(OH)_2$ nanowires,[14] and CeO_2 nanowires[15] has shown that a 1D nanostructure can be prepared under properly controlled conditions, even without the presence of surfactants. This means that the formation of a 1D nanostructure is thermodynamically preferable for many substances under certain conditions. Herein, we report a facile and controllable sol-hydrothermal method for direct growth of three kinds of nanostructures of as-prepared boehmite and γ-Al_2O_3. The salient feature of this procedure is the convenient control of the morphologies, as the nucleation process of boehmite is easily tuned by the manner of adding the starting materials while the growth of the formed nucleus is adjusted by the pH value of the hydrothermal system. The subsequent calcinations do not change the shape of the synthesized boehmite, and therefore γ-Al_2O_3 with different morphologies of nanoneedles, nanorods, and nanotubes were obtained. This route is simple and controllable.

[a] College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University,
Jinan 250014, P. R. China

Results and Discussion

The crystalline phases were identified by X-ray diffraction (XRD). Representative XRD patterns of as-prepared and calcined samples are shown in Figure 1, parts A and B, respectively. All the diffraction peaks in Figure 1 (A) can be perfectly indexed to the data available in the JCPDS21-1307 powder diffraction file, thus indicating that all the samples contain only a boehmite crystalline phase. However, the samples prepared under different conditions exhibit XRD traces that differ from each other in relative peak intensities. We assumed that the relative intensities of the peaks are related to the changes in boehmite crystallization, which affects the degree of preferred orientation and, as a result, a change in the crystalline order of a sample could result in the change of the corresponding peak intensity if the crystal is perfect. The as-prepared samples were calcined at 700 °C, as previously reported.[16] The XRD patterns of the products are shown in Figure 1 (B), in which all the diffraction peaks can be indexed to the γ-Al_2O_3 phase (JCPDS29-63). The XRD patterns indicate that the nanostructures obtained by our methods consist of pure phases. Similarly, the relative intensities of the peaks corresponding to different

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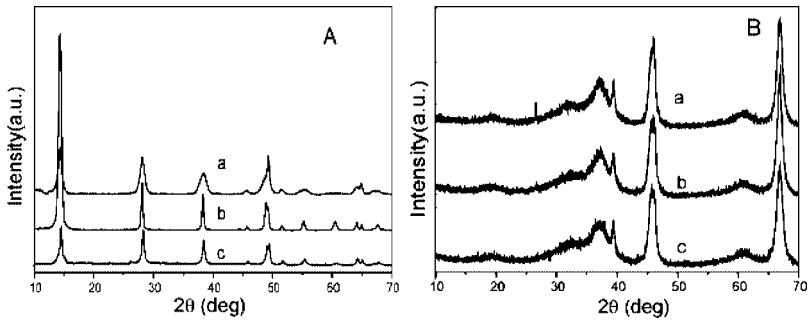


Figure 1. X-ray diffraction patterns for (A) as-prepared samples and (B) calcined samples: (a) nanoneedles, (b) nanorods, (c) nanotubes.

crystallizations of γ-Al_2O_3 are quite different, indicating that the degrees of crystallinity are different for the different nanostructures.

The morphologies and structures of the products were examined by transmission electron microscopy (TEM). As shown in Figure 2, three as-prepared products obtained by different synthetic routes display quite different morphologies, although the calcined samples exhibit almost the same morphologies as their precursors. Figure 2 (A, B) shows a needlelike shape and similar sizes, with a width of about 6 nm and a length of around 50 nm. It should be noted that when ammonia was added at room temperature during step (2), the morphology of the boehmite precursor of sample 2 changed from a needlelike shape to rodlike (Figure 2, C). These nanorods are straight, with uniform diameters of about 40 nm and lengths up to 800 nm. The cross-sectional dimensions of the calcined nanorods (sample 2) are slightly wider than the precursor (Figure 2, D). A representative HRTEM image of a nanorod (Figure 2, G) shows clear fringes, indicating that these nanorods are perfectly crystalline. Figure 2 (E) shows TEM images of the as-prepared boehmite nanotubes (precursor of sample 3). The nanotubes are typically about 40–60 nm in length with an outer diameter of around 5 nm. For the γ-Al_2O_3 nanotubes (sample 3) obtained by calcination of an as-prepared boehmite precursor (Figure 2, F), the outer diameter of the nanotubes is about 5–6 nm and the inner diameter is around 3–4 nm. The obtained nanotubes are thus characterized by their small inner diameter and thin inorganic wall, in contrast to other metal oxide nanotubes reported to date. An HRTEM image and the selected-area electron diffraction (SAED) pattern of the as-prepared nanotube are shown in Figure 2 (H), which reveals that the product is highly crystalline. According to the above XRD results, the boehmite nanostructures are converted into γ-Al_2O_3 nanostructures after calcination. It is well known that γ-Al_2O_3 is most commonly used as a high-temperature catalyst support and as a membrane due to its high surface area and mesoporous properties.[17] Therefore, the obtained γ-alumina nanostructures are expected to exhibit excellent catalytic properties.

In our synthetic system, there are three main reactions:

$$Al^{3+} + 3\,NH_3{\cdot}H_2O \rightarrow Al(OH)_3 + 3\,NH_4^+ \quad (1)$$

$$Al(OH)_3 \rightarrow AlOOH + H_2O \quad (2)$$

$$2\,AlOOH \rightarrow Al_2O_3 + H_2O \quad (3)$$

The formation of boehmite nanostructures indicates that nucleation and growth are well controlled. The manner of adding the precipitator and the pH value of the hydrothermal system play important roles in controlling the nucleation and growth of the boehmite nanostructures. In the first reaction, different conditions can lead to different morphologies of the crystal nucleus. At low temperatures, the particles form a smaller crystal nucleus faster, whereas at

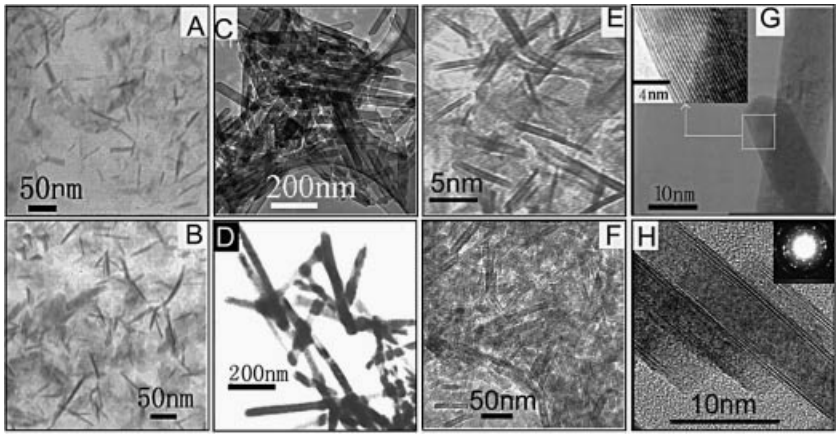


Figure 2. TEM images of the boehmite [AlOOH] samples (A, C, and E) and the corresponding γ-Al_2O_3 samples (B, D, and F): (A, B) nanoneedles, (C, D) nanorods, (E, F) nanotubes; (G) HRTEM images of γ-Al_2O_3 nanorods; (H) HRTEM images of AlOOH nanotubes.

high temperatures the reverse is the case. We suppose that more homogeneous boehmite nanostructures are formed finally in the hydrothermal process by reaction (2). In the hydrothermal system with a pH value of around 6–7, boehmite possesses a cubic crystal structure exhibiting anisotropic growth, which makes it have the tendency to grow along a certain direction quickly. Finally, the bigger crystal nucleus forms rod-like structures whereas the smaller crystal nucleus forms needle-like structures. For the formation of nanotubes, the pH values in reactions (1) and (2) are thought to be crucial. These crystal nuclei obtained in a basic environment have different morphologies for samples 1 and 2. In reaction (2), it is reasonable to suggest that *n*-butylamine acts as a structure-directing-template in the formation of nanotubes owing to its amphiphilic nature. As reported previously,[9d] these different nuclei may grow into platelet-like ones, then curve into tubes. In reaction (3), the γ-alumina is formed upon dehydration of the boehmite after calcination at 700 °C. The internal water is lost in this process (from AlOOH to Al_2O_3), while the morphologies are maintained.

Figure 3 show the characteristic IR absorption spectra for three kinds of samples in the wavenumber range from 400 to 1000 cm^{-1}, which is the characteristic region for nano-Al_2O_3 powders.[18] Although the IR spectra of all samples exhibit double peaks, they have distinct differences. Comparing the spectra of samples 1–3, for instance, it can be seen that the characteristic infrared absorption peaks of the nanoneedles, nanotubes, and nanorods are at 750.32, 608.62, and 744.87 cm^{-1}, respectively, and are blue-shifted with a decrease in sample size. In accordance with the literature,[19] however, the changes in the infrared absorption spectra of nanomaterials may actually be due to different vibrations.

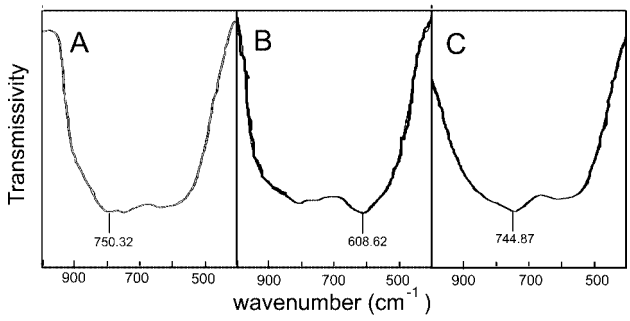


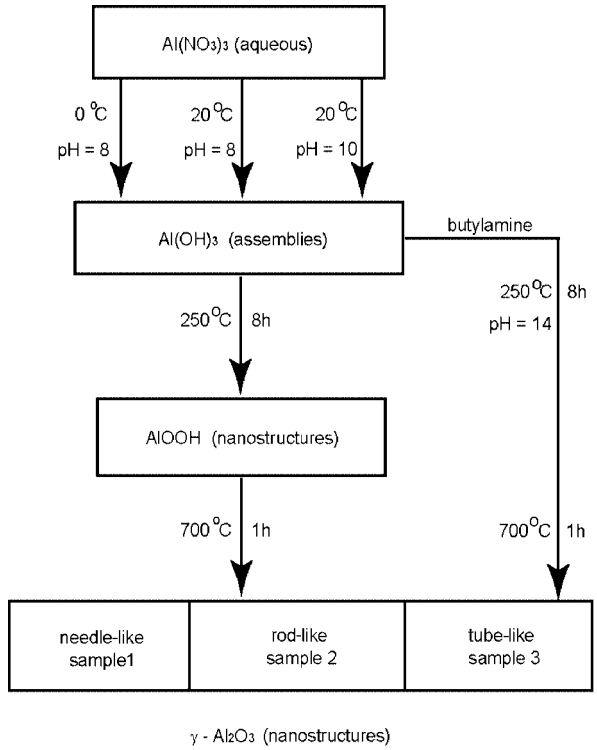
Figure 3. IR absorption spectra for three kinds of samples (A: nanoneedles; B: nanorods; C: nanotubes).

Conclusions

In summary, a facile and controllable hydrothermal synthesis method has been developed to synthesize three kinds of γ-Al_2O_3 nanomaterials without using any surfactant. These samples of nanoneedles, nanorods, and nanotubes exhibit relatively homogeneous sizes and regular morphologies, are were characterized by XRD, TEM, HRTEM, and FT IR spectroscopy.

Experimental Section

Synthesis: In a typical synthesis process there are four main steps: (1) 0.002 mol of $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 20 mL of distilled water; (2) 60 mL of 0.3 M $NH_3 \cdot H_2O$ was added to the above solution at 0 °C with vigorous stirring until the pH was around 8. This produced a transparent sol of $Al(OH)_3$. The mixture was centrifuged and washed until the pH was 6–7; (3) the obtained precipitate was redispersed in 16 mL of distilled water and then transferred into a 20-mL, Teflon-lined, stainless steel autoclave, which was sealed and maintained at 250 °C for 8 h. The resultant gels were vacuum-filtered in a Buchner funnel and washed with distilled water. The white product was dried at 60 °C for 4 h; (4) part of the product was heated at a heating rate of 3 °C min^{-1} up to 700 °C for 1 h to get sample 1 (nanoneedles). For the preparation of sample 2 (nanorods), the procedure was similar to that of sample 1 except that the ammonia was added quickly to the aqueous $Al(NO_3)_3$ solution at room temperature in step (2). To obtain sample 3 (nanotubes), the pH values of the neutral hydrothermal system and the transparent sol of $Al(OH)_3$ were adjusted to 14, with *n*-butylamine, and 10, with ammonia, respectively. The other steps were the same as for sample 1. This controllable synthetic route is shown in Scheme 1.



Scheme 1. Synthesis route of the γ-Al_2O_3 nanostructures.

Sample Characterization: The XRD patterns were recorded on a rigaku Dmax-rB X-ray diffractometer using Cu-K_α radiation (λ = 1.54178 Å) at a scanning rate of 0.02° s^{-1} in the 2θ range 10–70°. Transmission electron microscopy (TEM) analysis was conducted on a model Hitachi H-800 TEM with an accelerating voltage of 200 kV. The electron diffraction (ED) patterns and high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. FT IR spectra of the samples were recorded with a Tensor 27 (Bruker) FTIR spectrometer. Specimens for the measurements were prepared by mixing 2 mg of the sample with 100 mg of KBr and press-

ing the mixture into pellets. The spectra were acquired in a wavenumber range between 400 and 1000 at 2 cm^{-1} resolution and averaged over 30 scans.

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