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## Synthesis and Characterization of Boehmite Nanofibers

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### **Abstract**

Boehmite nanofibers of high quality were synthesized through a wet-gel conversion process without the use of a surfactant. The long nanofibers of boehmite with clear-cut edges were obtained by steaming the wet-gel precipitate at 170 °C for 2 days under a pH 5. Hydrothermal treatment of the boehmite gels enabled self-assembly through directed crystal growth. Detailed characterization using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Infrared Emission Spectroscopy (IES) and Raman Spectroscopy is presented.

**Keywords** Boehmite; Nanofibres; Hydrothermal treatment; Nanomaterials

## Introduction

The  $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$  polymorphs have found numerous applications in technical ceramics, thin solid films, catalysis, and many others. In many cases, boehmite  $\gamma$ - $\text{AlO}(\text{OH})$  is the starting material in the applications of alumina phases. As a typical oxyhydroxy compound, boehmite is also extensively used as absorbents,[1] [2] a catalyst,[3] and optical materials.[4] Nanosized materials are well known for their quantum size effects [5] and are expected to gain novel physical and chemical properties, with many more potential applications in a wide range of areas. In recent years, boehmite with nanoscale dimensions and morphological specificity has attracted enormous interest from both fundamental and practical viewpoints.

Boehmite nanofibers were reported to be assembled with the assistance of poly(ethylene oxide) (PEO) surfactant [6] and tubular  $\gamma$ - $\text{Al}_2\text{O}_3$  was fabricated via soft solution route using *N*-cetyl-*N,N,N*-trimethylammonium bromide surfactant.[7] It has been reported a solution-based chemical synthesis of boehmite nanofibers and alumina nanorods by a modified sol-gel process in the presence of organic solvents.[8] Shen et al. reported that a steam-assisted solid-phase conversion of amorphous aluminium hydroxides wet gel to well crystallized 1D nanostructure of boehmite nanorods without using surfactants and solvents.[9] The process is unique in the simplicity of preparation and the high efficiency of crystal growth, which can be operated on a large scale.

In this work, long, large boehmite nano/microfibers with high crystallinity and purity were synthesized based on Shen's methodology[9], and the characterisation of these the nano/microfibers are reported.

## **Experimental**

### *Preparation Procedures*

15 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 25 mL ultrapure water, and 28% ammonia was diluted into 10% solution. At room temperature 10% ammonia solution was added dropwise into  $\text{Al}(\text{NO}_3)_3$  solution at a constant rate of 5 mL/min while stirring vigorously. Ammonia was ceased to be added when the pH value of the reaction mixture reached pH 5. The reaction mixture was stirred constantly in air at room temperature for 1 hour. The obtained white gel was filtrated to obtain the dry gel-cake, which was then transferred into a glass beaker (25 mL). Before adding the gel-cake to a Teflon vessel (200 mL), 2 ml of ultrapure water was added. The Teflon vessel was sealed and heated at 170 °C for 2 days. The resulting white material was washed with ultrapure water, centrifuged and dried at 35 °C for 2 days.

### **Characterization**

X-ray Diffraction analyses were performed on a PANalytical X'Pert PRO X-ray diffractometer, with a Cu X-ray tube ( $\lambda = 1.54 \text{ \AA}$ ), operating at 40 kV and 40 mA. The scanning electron microscopy (SEM) images were taken with a FEI Quanta 200 operating at 25 kV. The specimens were mounted on SEM mounts with carbon tape and sputter-coated with a thin layer of gold. The Infrared Emission Spectroscopy was carried out on a Nicolet Nexus 870 FTIR spectrometer. The emission spectra were collected at an interval of 50 °C, over the range 100 °C – 850 °C. Further details have been published [10-13]. Raman spectra were obtained using a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge

Coupled Device (CCD). 64 Raman spectra were collected using 5 mW of power at the sample using 20 sec. scans. Further details of the Raman technique have been published [14-19].

## **Results and Discussion**

### *X-ray Diffraction*

X-ray diffraction is normally used to determine the phase and phase purity of the synthesized boehmite. Figure 1 displays well-defined XRD patterns observed and all diffraction peaks were perfectly indexed to the XRD pattern of pure boehmite (JCPDS card 01-083-2384). No XRD peaks representing other crystalline phases were detected, indicating that the nanofibers of the synthetic boehmite exhibited excellent crystallinity and a high purity.

### *SEM*

Whilst TEM images are normally used to show the morphology of the boehmite nanomaterials, if the nanofibres are large enough in length then scanning electron microscopy can be used to prove the nature of the nano/micro-material. Figure 2 presents the SEM images of the synthetic boehmite nanofibers. It is clearly seen the long nanofibers in bundles. Zhu [20] et al. reported that through a soft-templated process with PEO surfactant micelles at 100 °C, the nanofibers could be assembled, the maximum length of which was 100 nm. In this study, the nanofibers were synthesized in the absence of surfactant, and in a supersaturated hydrothermal condition, which was reported by Shen et al. [9]. This steam-assisted self-assembly fabrication of boehmite

yielded high-quality 1D nanostructures with clear-cut edges and high purity. The structure was confirmed by the XRD patterns.

### *Infrared Emission Spectroscopy (IES)*

Infrared Emission Spectroscopy (IES) is known as a measurement of discrete vibrational frequencies emitted by thermally excited molecules. The major advantages of IES are that the samples are measured in situ at the elevated temperature and IES requires no sample treatment other than making the sample of submicron particle size. Figure 3 clearly shows such a suite of the dehydroxylation of the synthetic boehmite nanofibers. The dehydroxylation is followed by the decrease of intensity of the hydroxyl deformation modes and the loss of intensity of the hydroxyl stretching frequencies. The hydroxyl deformation frequencies are observed at  $840\text{ cm}^{-1}$  and  $757\text{ cm}^{-1}$ . The spectral changes in these low-frequency bands show that dehydroxylation commenced at  $250\text{ }^{\circ}\text{C}$ . The three bands displayed at  $3671\text{ cm}^{-1}$ ,  $3360\text{ cm}^{-1}$ ,  $3140\text{ cm}^{-1}$  are recognized in the hydroxyl stretching region. Above  $450\text{ }^{\circ}\text{C}$  the hydroxyl stretching bands are no longer observed. These spectral changes confirm that dehydroxylation starts at  $250\text{ }^{\circ}\text{C}$  and is completed by  $450\text{ }^{\circ}\text{C}$ . Each of the hydroxyl stretching bands shows an increase in bandwidth with temperature increase, and this indicates that the molecular structure of the boehmite nanofibers was becoming more disordered during the dehydroxylation process.

### *Raman Spectroscopy*

Many minerals both natural and synthetic lend themselves to analysis by Raman spectroscopy. The great advantage of Raman spectroscopy is that just so long as the materials are 1 micron in size or larger then individual nanofibres can be analysed as is the case for the boehmite fibres shown above.

Figure 4 depicts the Raman spectra of the synthetic boehmite nanofibers. The bands at 3216, 3077 and 2989  $\text{cm}^{-1}$  are in the region of the hydroxyl stretching vibrations. Frost et al., [21] characterized hydroxyl stretching bands in the Raman spectrum of boehmite and reported bands at 3413, 3283, 3096 and 2997  $\text{cm}^{-1}$ . The low-wavenumber region (1100-200  $\text{cm}^{-1}$ ) of boehmite consists of hydroxyl deformation modes (1050-900  $\text{cm}^{-1}$ ) and hydroxyl translation modes (800-400  $\text{cm}^{-1}$ ). The doubly degenerate mode of the  $\text{AlO}_6$  octahedron caused the observation of the bands at 495 and 675  $\text{cm}^{-1}$ . [22] The band at 362  $\text{cm}^{-1}$  was attributed to the vibration of fully symmetric  $A_g$  mode, in which all aluminium and oxygen atoms move parallel to the  $b$ -axis. [23] The weak bands at 732, 448, 340  $\text{cm}^{-1}$  were attributed to  $\text{OH}^-$  deformation modes. [24]

## **Conclusions**

In this research, long boehmite nanofibers with high crystallinity and purity were formed under steam-assisted hydrothermal treatment at 170 °C for 48 hours with pH 5. The structure and morphology of the nanofibers were detected by XRD and SEM, while the IES spectra illustrated their thermal properties. Raman spectroscopy was applied to characterize the 1D-nanostructured boehmite.

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Figure 1 XRD pattern of the synthetic boehmite nanofibers, after hydrothermal treatment at 170 °C for 2 days under pH 5.

Figure 2 SEM images of the synthetic boehmite nanofibers, after hydrothermal treatment at 170 °C for 2 days under pH 5.

Figure 3 IES spectra of the synthetic boehmite nanofibers, collected at an interval of 50 °C, over the range 100 °C – 850 °C.

Figure 4 Raman spectra of the synthetic boehmite nanofibers, after hydrothermal treatment at 170 °C for 2 days under pH 5.