ADP012177

TITLE: Novel Synthesis of Aluminium Oxide Nanofibers

TITLE: Nanophase and Nanocomposite Materials IV held in Boston, Massachusetts on November 26-29, 2001

Mat. Res. Soc. Symp. Proc. Vol. 703 © 2002 Materials Research Society V1.8

# Novel Synthesis of Aluminium Oxide Nanofibers

Huai. Y. Zhu and Gao. Q. Lu*
Nanomaterials Centre and Department of Chemical Engineering, The University of Queensland, Brisbane, 4072 Australia

## ABSTRACT

This report presents a novel synthesis method of alumina nanofibers at moderate conditions in aqueous systems through a surfactant-directed crystal growth process. In the presence of polyethylene oxide (PEO) surfactants, boehmite nanofibers of about 3 nm thick and 30-60 nm long formed from aluminium hydrate colloids. During the subsequent heating, the surfactant was evaporated and boehmite nanofibers were converted into $\gamma$-alumina nanofibers. The function of the PEO surfactant and the formation mechanism of the nanofibers are discussed. Alumina nanofibers are an ideal structural reinforcement for various nanocomposite materials. They are potential adsorbents with high adsorption capacity. Furthermore, their unique structure exhibits strong resistance to heating at high temperatures. The BET surface area of a typical sample after heating at 1200°C is as high as 68 $m^2/g$. This makes the material very promising as excellent substrates for catalysts of high thermal stability.

## INTRODUCTION

In recent years, nanomaterials have attracted great attention from academe and industry because of their superior properties and their potential for a wide range of applications. Surfactants have been widely used as templates in developing uniform mesoporous structure at a scale of several nano-meters [1-3]. The concept of surfactant templating was also applied to the synthesis of mesoporous alumina molecular sieves, because activated alumina is extensively used as industrial adsorbents, catalysts and catalyst supports [4]. Successes were achieved by using neutral surfactants [5,6)] or carboxylic acids [7], as templates and aluminium alkoxide as the alumina precursor. It would be of great interest to construct alumina nano-structures of other geometry (morphology). The alumina with other geometry in nano-meter level, for instance, nano-fibers, could be important advanced engineering materials. The unique aspect ratio of nano-fibers can lead to a wide range of applications in advanced ceramics, electronic, adsorption, and catalysis etc. Here we report the first synthesis of alumina nanofibers with very large porosity from inorganic salts with non-ionic polyethylene oxide (PEO) surfactants. In such a synthesis, the surfactant micelles induce important changes in morphology and growth of the nano-sized crystallite, rather than acting as templates for gel particles to condense around them. The formation mechanism of alumina nanofibers is distinctly different from the templating mechanism as observed in M41S synthesis. This new mechanism could constitute a new strategy of nano-structuring inorganic solids.

## EXPERIMENTAL

The PEO surfactant, with a general chemical formula $C_{12\text{-}14}H_{25\text{-}29}O(CH_2CH_2O)_nH$ ($n = 5\text{-}30$) was mixed with aluminium hydrate cake prepared from common inorganic salts like $NaAlO_2$, in a designed molar ratio of surfactant to aluminium (PEO/Al ratio). Details of synthesis can be found in [8]. Boehmite (AlOOH) crystallite grows during a hydrothermal treatment at 100°C. The PEO surfactant introduced prior to the treatment can affect the crystalline growth. The hydrothermally treated samples were dried in air and calcined subsequently at 500°C. The calcination converted nano-crystallite boehmite to γ-alumina. A significant difference in crystal morphology can be observed by transmission electron microscopy (TEM). In Fig. 1, the TEM image of γ-alumina prepared with the PEO surfactant (Fig 1a) is compared with that of the γ-alumina prepared without the surfactant (Fig 1b).

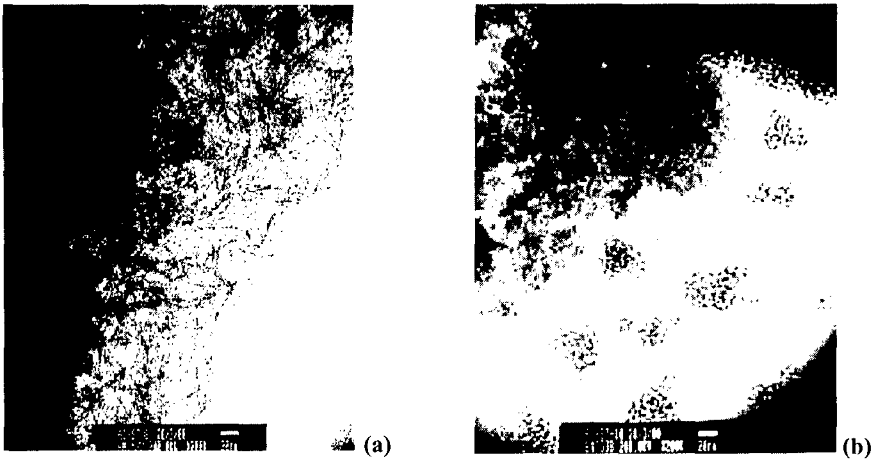


**Figure 1.** TEM images of (**a**) γ-alumina prepared with a PEO/Al ratio of 0.47, (**b**) γ-alumina prepared at the same conditions but without PEO surfactant. Nanofibers can be seen in (**a**) the sample prepared with PEO surfactant. The scale-bar is 20 nm.

## RESULTS AND DISCUSSION

The nanocrystallites in Fig 1a are nanofibers with a length over 60 nm, and a constant thickness of about 3 nm. In contrast, γ-alumina particles prepared without PEO addition as in Fig. 1b show irregular shapes. Evidently, introducing PEO surfactant results in the formation of alumina nano-crystallite with a fibrous morphology. It is postulated that boehmite nanofibers first formed from aluminium hydrate at a moderate hydrothermal condition. In the subsequent heating at 500°C, the surfactant was removed and boehmite is converted into γ-alumina, whilst the fibrous morphology was retained as shown in Fig 1a. However, the XRD patterns for the samples in Fig 1a and 1b are almost identical (Fig 2).

The random stacking of the alumina nanofibers (Fig 1a) results in a highly porous texture, as reflected by the nitrogen adsorption isotherms in Fig 3. It is known that nitrogen adsorption by a solid strongly depends on its porosity [9]. The alumina prepared without PEO adsorbed nitrogen at 77 K slightly over 300 $cm^3/g$ STP, whereas the sample prepared in the presence of PEO adsorbed as much as 1050 $cm^3/g$ STP. The extraordinarily large adsorption capacity indicates very large pore volumes in the samples prepared with PEO. The pore volume should be attributed to the inter-crystallite voids of the randomly stacked alumina nanofibers. An important feature of the nanofiber structure is that it exhibits significant resistance to heating at high temperatures. The data of BET specific surface area and porosity of the samples calcined at three temperatures are given in Table 1.

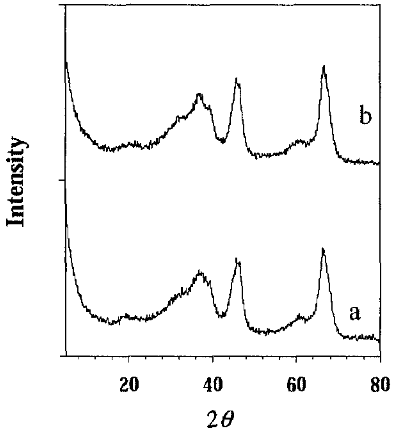


**Figure 2.** XRD patterns of γ-alumina. Patterns **a** and **b** are for samples **a** and b in Fig 1, respectively. The two patterns are almost identical

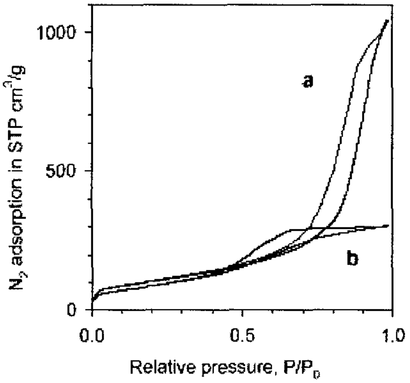


**Figure 3.** Nitrogen ads/desorption isotherms of the samples in Figure 1. For the sample prepared with PEO surfactant a steep increase in adsorption commences from a $P/P_0$ of about 0.7 (curve **a**), indicating a huge mesopore volume, whereas for sample b (w/o PEO) the adsorption capacity is low.

**Table I.** Surface area, mean pore radius and pore volume of alumina samples.

| **PEO/Al ratio** | **BET S.A. ($m^2/g$)** | **Mean R (nm)** | **Pore volume ($cm^3/g$)** |
|---|---|---|---|
| **After calcination at 500°C** | | | |
| 0 | 321.6 | 5.9 | 0.471 |
| 0.24 | 360.0 | 15.7 | 1.409 |
| 0.47 | 376.2 | 17.1 | 1.616 |
| 0.95 | 347.4 | 22.4 | 1.946 |
| 1.95 | 373.1 | 12.7 | 1.185 |
| **After calcination at 900°C** | | | |
| 0 | 154.2 | 7.2 | 0.433 |
| 0.24 | 179.4 | 15.5 | 1.131 |
| 0.47 | 198.7 | 15.5 | 1.406 |
| 0.95 | 189.3 | 21.8 | 1.545 |
| 1.95 | 183.9 | 15.5 | 1.129 |
| **After calcination at 1200°C** | | | |
| 0 | 4.6 | 10.5 | 0.032 |
| 0.24 | 13.4 | 11.4 | 0.077 |
| 0.47 | 48.6 | 16.0 | 0.391 |
| 0.95 | 50.2 | 16.1 | 0.404 |
| 1.95 | 43.4 | 15.3 | 0.333 |

To understand the function of the PEO surfactant, the weight loss of the dried sample as temperature increases from room temperature to 800°C was measured by thermogravimetric analysis (TGA). The main weight loss for the sample prepared without PEO is below 150°C, mainly due to dehydration, whereas for the samples prepared with PEO the greatest weight loss is observed between 200-300°C, due to volatilization. If heating was carried out in a nitrogen flow that passes a cooling trap, the surfactant could be readily recovered for reuse. This is an important merit in regard to environmentally friendliness and costs of the synthesis process. We also found that the pore volume (obtained from $N_2$ adsorption) is proportional to the weight loss. This suggests that the surfactant molecules were located in the inter-crystallite voids before the calcination step. The surfactant evaporates during heating, leaving a large number of mesopores in the sample. Because the pore size is far beyond the molecular size of the surfactant, the surfactant should have existed in the forms of micelles rather than in single molecule. A number of studies have also shown that PEO surfactants exist in rod-like or worm-like micelles in aqueous solutions [10-13]. It was reported that introducing polymer molecules of large molecular weight ($10^4$ to $10^6$) increased the porosity of activated alumina [14]. However, the additives, such as polyalcohols and cellulose, were simply regarded as space fillers in that work. The affinity of the additives to aluminium hydroxide surfaces was ignored. It is known that the conversion of boehmite to γ-alumina mostly takes place at above 300°C and the PEO surfactants evaporate at lower temperatures than this temperature. Because the nano-fiber morphology resulted from the presence of PEO surfactant, the surfactant-boehmite interaction should be the main force inducing the oriented growth to form nano-fiber crystallites. This morphology was retained even after the surfactant removal.

For the dried samples prepared with surfactant, a XRD peak of the greatest intensity at $2\theta = 20.8°$, corresponding to d = 4.3Å, is observed (curve c in Fig 4), whilst the rest peaks are well matched with the pattern. This peak is believed to be due to the oxide groups of the surfactants because we found the intensity of this peak is proportional to the number of oxide groups in the surfactant. For the same surfactant used, the intensity of this peak is proportional to the surfactant amount in the dried samples, and if various PEO surfactants were introduced by the same amount, this increases with n, the number of oxide groups in a surfactant molecule. Indeed, a strong peak is also found in the XRD pattern of the pristine surfactant liquid at room temperature at a lower angle, $2\theta = 18.6$ (Fig 4d), corresponding to d = 4.8Å. The comparison of XRD patterns for the same surfactant in different states, solid, partial melted, in mixture of boehmite and surfactant (in Fig 4), suggests that the surfactant in boehmite is in an intermediate state, with more close packing than that in pristine liquid. This can only be due to the interaction of the surfactant micelles with the boehmite crystallite surfaces. In liquid phase the alkyl chains of PEO surfactants prefer to stack close to each other, and so do their oxide groups, forming micelles. When the surfactant is dispersed in a polar media, such as in aqueous systems or polar surfaces, the oxide groups would form the outer surface of the micelles, being in contact with the polar media [10-12], in this case, the surface of boehmite crystallites. The shift in the diffraction peak to a lower angle is indicative of the interaction between oxide groups of the surfactants and the surface of boehmite crystallites. This hydrogen bonding seems not sufficiently strong to alter the intrinsic structure of boehmite crystallites, but could lead to changes in the stacking of oxide groups in the surfactants because the stacking of the surfactant molecules is more flexible. More importantly, this close bonding combined with the regular stacking of the PEO surfactant, regulates the growth of the boehmite crystallites to a certain direction during aging. This is the fundamental mechanism underlying the oriented growth of alumina nano-fibers, which we term as surfactant-directed oriented growth (SDOG).

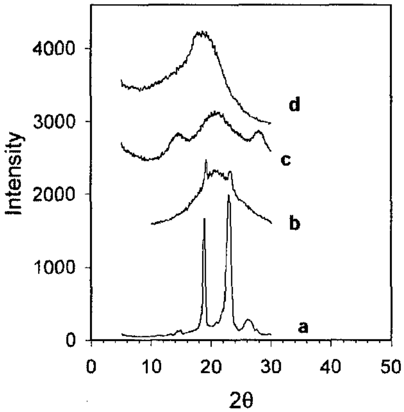
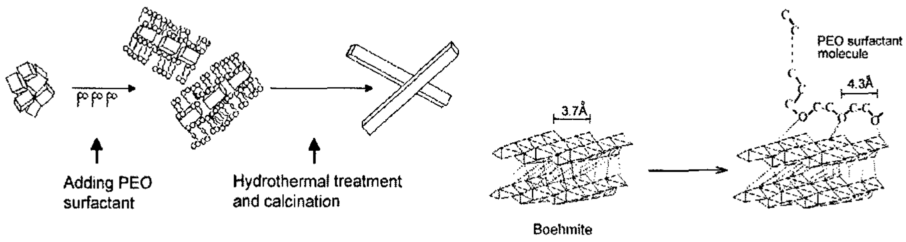


**Figure 4.** XRD patterns of a PEO surfactant in various states. **a** pure solid, b, partial melt, **c** in boehmite and **d** pure liquid.

The proposed SDOG process is schematically illustrated in Fig 5a. The structure of boehmite crystallite is given in Fig 5b. The corrugated layers of boehmite nano-crystallite are linked by hydrogen bonds. The surfactant micelles should take the configuration that the oxide chains linking to the surface of boehmite crystallite, while the alkyl chains point away from the surface (Fig 5b). The layered aggregates of boehmite crystallites are thus intercalated with surfactant micelles. The hydrogen bonding between the oxide groups and the boehmite crystallite surface reduces the chemical potential of the system. The stacking of the oxides groups of the surfactant micelles on the boehmite crystallite surface is more closely packed than in the pristine surfactant liquid. Therefore, the surfactant micelles attain a maximum number of hydrogen bonds with the -OH groups on boehmite surfaces.



**(a)** **(b)**

**Figure 5.** SDOG mechanism (**a**). boehmite in PEO surfactant, where PEO molecules form micelles of one dimension structure. The growth of boehmite crystals is regulated by the micelles through hydrogen bonding. During heating the boehmite nanofibers consolidate, and are converted to γ-alumina nano-s upon PEO removal. **b.** Boehmite corrugate structure and interaction with PEO molecules. The micelles are close packed on the surface of boehmite behaving as directing agents for the oriented growth of boehmite crystallite, thus inducing nano- morphology

High-temperature calcination may create acid sites with stronger acidity, which is more favorable for some catalytic reactions. We have found that Ni catalysts supported by our nano-alumina calcined at 900°C exhibit a superior performance for $NO_x$ reduction to catalysts supported on a commercial γ-alumina. Barium hexaaluminate (BHA) is reported to have high thermal stability above 1200°C, and it retained surface area of around 10 $m^2/g$ after heat treatments at 1200°C [16,17]. BHA has been used for catalytic combustion or steam reforming reaction. As a comparison, we simply impregnated the alumina nano- with $Ba(NO_3)_2$ solution and calcined the solid at 1200°C. The calcined catalyst still has a surface area of 35 $m^2/g$, which are a mixture of barium hexaaluminate and barium aluminate. This demonstrates that alumina nanofibers in this work are promising substrate for the synthesis of BHA catalysts.

## CONCLUSION

SDOG is a typical "synthesis with construction" mechanism [15], which is distinctly different from the conventional crystallization and the templated synthesis. The new strategy proposed in this work would be useful for low temperature, aqueous syntheses of oxides and other useful nano-structured ceramics and composites. It is expected that a comprehensive understanding of the SDOG mechanism will greatly assist us in developing new nanomaterials with desired morphology, tailorable size, porosity and surface chemistry.

## ACKNOWLEDGEMENTS

Financial Support from the Australian Research Council (ARC) and the University of Queensland's Strategic Funds are gratefully acknowledged. HYZ is also indebted to Australian Research Council (ARC) for the QE II fellowship. Thanks also to Dr. John Barry for TEM imaging and to Mr C. Lu and Ms X. Q. Yan for most of experimental data collection..

## REFERENCES

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S.Beck, *Nature* **359,** 710 (1992).
2. S. Inagaki, Y. Fukushima, K. Kuroda, *J. Chem. Soc. Chem. Commun.* **680**, (1993).
3. Q. Huo, et al., *Nature* **368**, 317 (1994).
4. K. P. Goodboy, K. C. Dowing, in *Alumina Chemicals: Science and Technology Handbook*, Hart, L. D., Lense, E., Eds. (American Ceramic Society, Westervill, Ohio, 1990), p. 93.
5. P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Nature* **396**, 152 (1998).
6. S. A. Bagshaw, T. J. Pinnavaia, *Angew. Chem. Int. Ed. Engl.* **35**(10), 1102 (1996).
7. F. Vaudry, S. Khodabandeh, M. E. Davis, *Chem. Mater.* **8**, 1451 (1996).
8. H.Y. Zhu and G.Q. Lu, Patent WO 01/74713 A1, 11 Oct, 2001
9. S. J. Gregg, K. S. W. Sing, *Adsorption, Surface Area and Porosity* (Academic Press: New York, 1982).
10. P. G. Cummins, J. B. Hayter, J. Pemfold, E. Staples, Chem. *Phys. Lett.* **138**, 436 (1987).
11. P. G. Cummins, E. Staples, J. Pemfold, *Langmuir* **5**, 1195 (1989).
12. J. Pemfold, E. Staples, P. G. Cummins, *Adv. Colloid Interface Sci.* **34**, 451 (1991).
13. Z. Lin, L. E. Scriven, H. T. Davis, *Langmuir* **8**, 2200 (1992).
14. D. Basmadjian, N. Fulford, B. I. Parsons, D. S. Montgomery, *J Catal.* **1**, 547 (1962).
15. S. Mann, *Nature* **365**, 499 (1993).
16. G. Groppi, M. Bellotto, C. Cristiani, P. Forzatti, P. L. Villa, *Appl. Catal.* **104**, 101 (1993).
17. A. J. Zarur, J. Y. Ying, *Nature* **403**, 65 (2000).