

# Synthesis of Alumina Nanoparticles Using Agarose as Template

Mohd Azizi Nawawi, Mohd Sufri Mastuli, Nurul Huda Abdul Halim, Nurul Auni Zainal Abidin  
 Faculty of Applied Sciences, University Teknologi MARA, 40450 Shah Alam, Malaysia

**Abstract**— Alumina nanoparticles were synthesized from aluminum isopropoxide using agarose gel as template. The use of agarose template gives nano sized metal oxide with homogeneous and porous structure. The morphologies and structural properties of alumina nanoparticles were characterized through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) techniques. The organic template was successfully removed through calcinations process. The different concentration of agarose template used affects the morphologies of alumina nanoparticles. The higher concentration gives smaller nanoparticles with a less degree of agglomeration. The  $\gamma$ -alumina nanoparticles possess cubic crystal structure with crystallite size ranging from 8 to 16 nm.

**Index Terms**—Alumina nanoparticles, template, agarose, metal oxide

## I. INTRODUCTION

Research on synthesis of nano sized alumina has attracted great attention due to their wide spectrum of applications in catalysis, molecular separation, membranes, structural materials and adsorbents catalyst. There were several plausible routes to obtain nano sized alumina such as sol-gel, hydrothermal, template, combustion and so on [1]–[4]. Various allotropic form of alumina has been synthesized and reported in literature such as  $\alpha$ ,  $\gamma$ ,  $\delta$ ,  $\eta$ ,  $\theta$ ,  $\kappa$  and  $\gamma$ -alumina[5]. Template method offers possibility to tailor the inner structural arrangements of materials particularly pore size, pore volume as well as the outer shape and size of the samples [6]. It is well known that structural and morphological properties of materials are developed during processing stage. This point is worthy to be mentioned as the performance of the materials predetermined by preparation techniques and steps. Nowadays, there are an increased in number of studies on preparation of nanoparticles metal oxide using biomaterial as template. The template method gained popularity in synthesis of metal oxide due to the fact that templates are able to control particle size, act as stabilizers, prevent the spontaneous agglomeration of nanoparticles, provide stable frameworks against chemical degradation and play a role as pore-forming agents in producing fine ceramics [7]–[11]. In this study, an attempt to prepare alumina nanoparticles using agarose as template was carried out. Agarose is a polysaccharide derived from seaweed and has been widely used as a gel in electrophoresis. Biopolymer is preferred due to fact that it is porous, relatively cheap and environmental friendly. Agarose is readily dissolved in an aqueous solution

under appropriate heat treatment. Upon cooling process, the aqueous solution turns to gel form which possess pores in sub-micrometer range[12]. Therefore, agarose gel could be used as suitable template for preparation of alumina nanoparticles with porous structure.

## II. MATERIALS AND METHODS

### A. Materials

All chemicals were used as received. Agarose powder for routine use (Sigma) was used for template production. Aluminum isopropoxide ( $\geq 98\%$ ) from Aldrich was used as aluminum precursor. Ethanol absolute (99.8%), 2-propanol (analytical grade) and distilled water were used as solvent throughout the experiment.

### B. Template Preparation

The method for preparation of agarose template was adopted from [12]. Firstly, different weight percent of agarose powder were dissolved in distilled water under vigorous stirring at room temperature. The solution was heated until for 30 minutes until the cloudy solution turns to a clear solution. Afterwards, the solution was left overnight to allow an elastic gel to form before the gel was cut into pallets with dimension 1cm  $\times$  1cm  $\times$  1cm. Then the pallets were immersed into isopropanol in order to undergo solvent exchanged via ethanol to isopropanol. The gel pieces were transferred from water solution to water: ethanol (2:1 by volume) solution for 6 hours, followed by transferring into the water: ethanol (1:2 by volume) mixture for 6 hours and finally placed into ethanol solution. The gel pieces were then transferred from ethanol to isopropanol solution by using similar solvents ratio and soaking times. The agarose gel pieces were stored in the isopropanol solution ready for characterization and used as template for the synthesis of porous alumina.

### C. Synthesis of Alumina Nanoparticles

The template technique was applied in this synthesis procedure by soaking the alumina pallets in metal oxide precursor solution for 24 hours. The pallets then were removed from the solution and soaked in isopropanol: water of ratio 1:1 for hydrolysis and condensation reaction for another 24 hours. After that, the pallets were dried at 60°C for 24 hours and calcined at 700°C to form inorganic metal oxide.

## III. CHARACTERIZATIONS

Infrared Spectra were obtained by using the KBr wafer technique. The sample was mixed with KBr in the 1:100 ratio.

The mixture was ground to a finely divided powder and pressed under pressure for 1 minute to obtain transparent self-supporting pellet. This technique avoids excessive grinding which might cause structural degradation. The KBr disk was placed to a spectrometer disk holder and mounted the disk holder in the spectrometer to take the spectrum. The surface morphology and size of synthesized alumina nanoparticles via templating technique using various amount of agarose were evaluated by FESEM measurements. Prior to sample scanning, all the samples were coated with gold on gold sputter. The micrographs were captured using Carl Zeiss SMT Supra 40 VP FESEM operating at 5.0 kV. X-Ray diffractogram of the samples were acquired using PANalytical X'Pert Pro MPD powder diffract meter with Cu K $\alpha$  as the radiation source with  $\lambda = 1.5418 \text{ \AA}$  operating at 45 kV and 40 mA. The sample was ground to a fine powder using a mortar and then lightly pressed to form a pallet with flat and smooth surface on sample holder. Then, the sample was scanned for step size from 20° to 90°, 2 $\theta$ .

#### IV. RESULTS AND DISCUSSION

The surface functional groups of all samples were studied using infrared spectroscopy. The spectra of the framework of alumina were obtained in the region of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Fig. 1 shows characteristic IR bands representing agarose template, alumina precursor with 1% (w/w) agarose and alumina nanoparticles after calcinations at 700°C. The removal of agarose template can be studied through observing the presence and absence of a few functional groups in the samples before and after the calcinations process. The broad band at 3469 cm<sup>-1</sup> assigned to the stretching vibration of the -OH group connected to the Al cation. The peak at 1649 cm<sup>-1</sup> corresponds to the bending mode of adsorbed water. The two bands appear at 1077 cm<sup>-1</sup> and 1152 cm<sup>-1</sup> are due to C-O-C stretching vibrations which related to the functional group that present in the agarose structure. These two bands disappeared after calcinations process. The appearance of two peaks at 792 cm<sup>-1</sup> and 600 cm<sup>-1</sup> are assigned to Al-O vibrations of Al<sub>2</sub>O<sub>3</sub>. Based on FTIR analysis, the organic template was successfully removed after the sample being calcined at 700°C. In addition, all spectra in Fig. 2 are equally the same and show no obvious differences between each other which indicates that alumina samples have similar structure as proven by the XRD results.

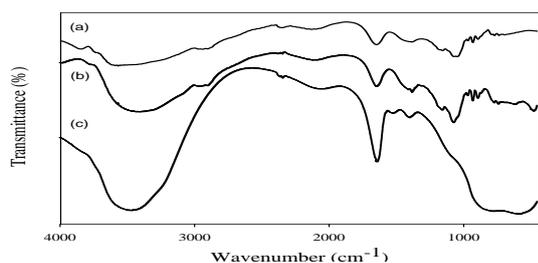


Fig. 1 FTIR spectra of (a) agarose template, (b) alumina precursor with 1%(w/w) agarose and (c) alumina nanoparticles after calcination at 700°C.

The morphologies of alumina nanoparticles formed by template method are highly dependent on the experimental condition especially the concentration of the template used. Variation of the agarose content takes control over morphologies where with the higher weight percent of agarose, the smaller the particle sizes with a less degree agglomeration. The morphologies of alumina nanoparticles prepared with different weight percent of agarose are shown in Fig. 3. The FESEM micrographs of  $\gamma$ -alumina observed with 50,000 times magnification is found to be in nano sizes range. The agglomerations among the particles can clearly be seen in the micrograph. The variation sizes of discrete agglomerated spherical particles were observed in each sample of alumina. As can be seen from the Fig. 3(a-d), the morphologies were porous with abundant wrinkles on it. The particles formed by aggregation of small nuclei rather than crystal growth.

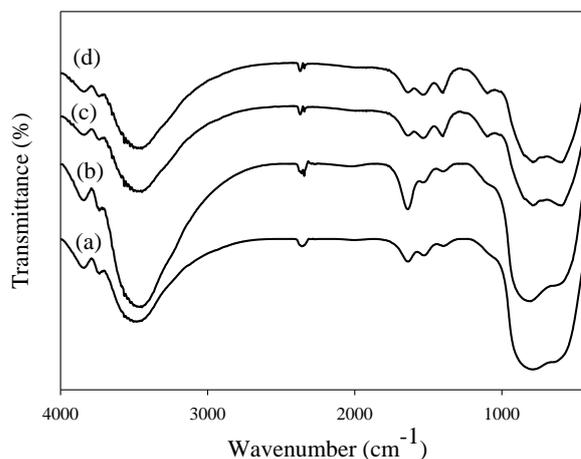
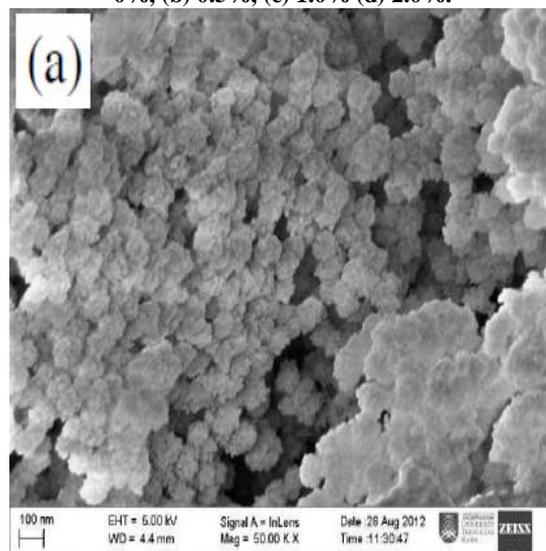
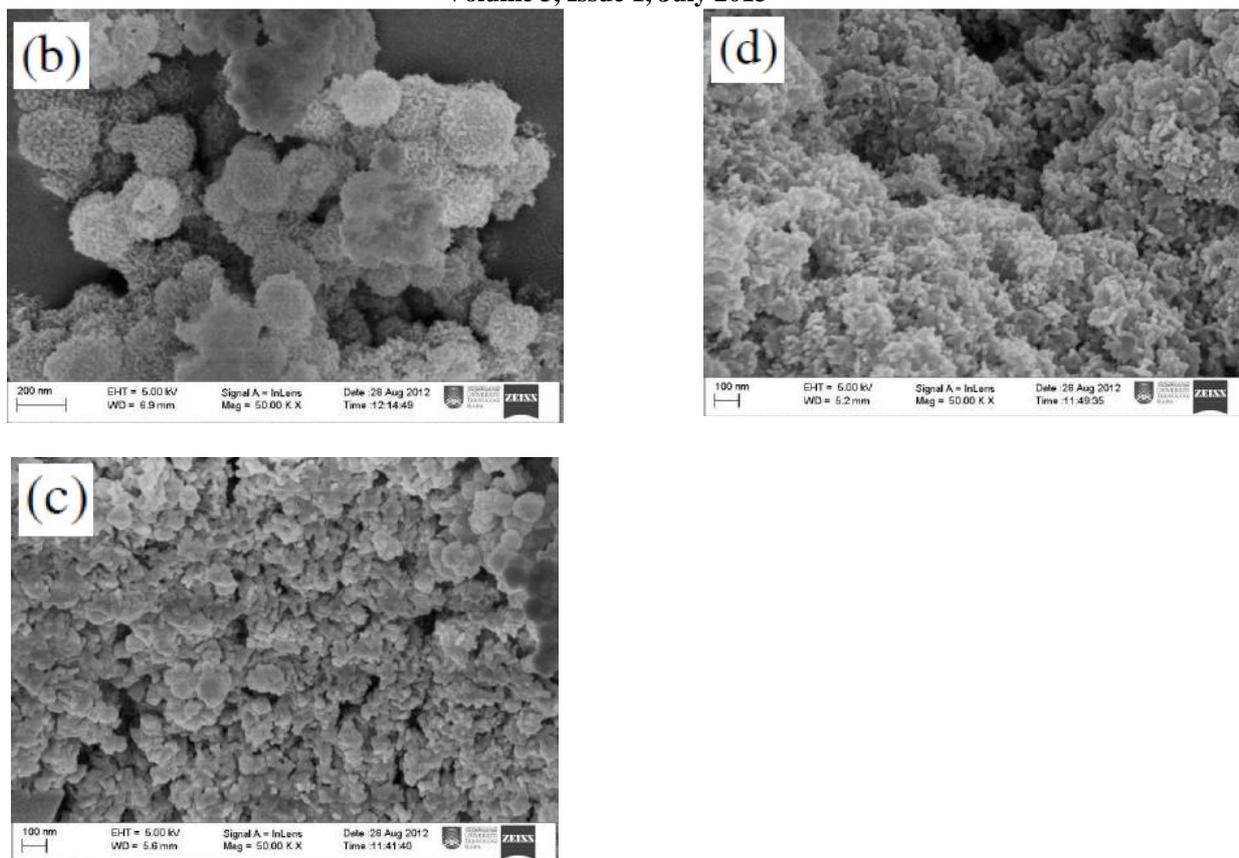


Fig. 2 FTIR spectra of calcined alumina nanoparticles prepared using different weight percent (w/w) of agarose template; (a) 0%, (b) 0.5%, (c) 1.0% (d) 2.0%.



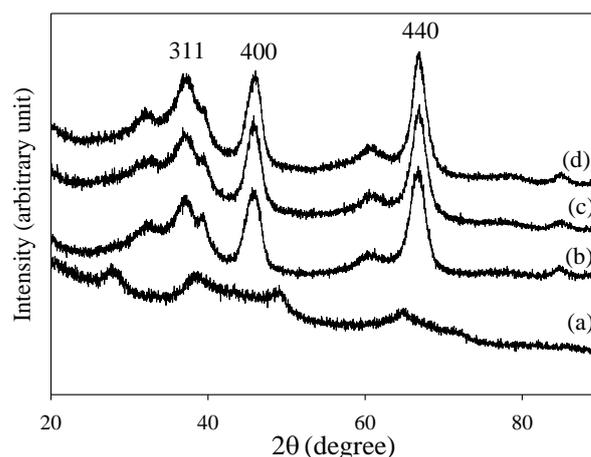


**Fig. 3 FESEM Micrographs Of Alumina Nanoparticles Prepared With Different Weight Percent (W/W) Agarose Template; (A) 0%, (B) 0.5%, (C) 1.0% (D) 2.0%.**

Fig. 4 shows the XRD diffraction patterns of alumina samples prepared with different concentrations of template. The diffraction peaks of the nanoparticles prepared without agarose template (0%) are very broad and flat which reveal the amorphous nature of the sample. However, the samples prepared with aided of agarose template show a relatively higher degree of crystallinity alumina as shown by a broad and sharper peaks at  $2\theta$  angles around  $39^\circ$ ,  $45^\circ$  and  $66^\circ$ , respectively. These peaks are correspond to (3 1 1), (4 0 0) and (4 4 0) planes which can be assigned to the cubic structure of  $\gamma$ - $\text{Al}_2\text{O}_3$ [13]. The shape and intensity of XRD peaks for alumina nanoparticles samples prepared with different concentrations of agarose template are similar in patterns and show no significant differences. These observations suggest that the samples had been converted to the crystalline alumina with a similar crystal structure. The crystallite size of alumina was estimated using the Scherrer equation as shown in (1).

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

The crystallite size (D) was estimated after quantity of the X-ray wavelength ( $\lambda$ ), the peak full width at half maximum ( $\beta$ ), the Bragg angle ( $\theta$ ) and the Scherrer constant value ( $\sim 0.9$ ) obtained from analysis. From the calculation, the crystallite sizes of the alumina are found in the range of 8 to 16 nm.



**Fig. 4 XRD patterns of calcined alumina nanoparticles prepared using different weight percent (w/w) agarose template; (a) 0% , (b) 0.5%, (c) 1.0% (d) 2.0%.**

## V. CONCLUSION

In this work, agarose gel was successfully used as an effective structural directing agent for the preparation of nano sized alumina nanoparticles. The concentration of agarose template seems to be an important factor that determines morphological properties and crystallite size of alumina

nanoparticles. This facile preparation procedures could be used to prepare other types nano sized metal oxide.

## VI. ACKNOWLEDGMENT

The authors would like to thank Ministry of Higher Education Malaysia and Universiti Teknologi MARA for the research grant no. 600-RMI/ST/FRGS 5/3/Fst (17/2011) supporting this study.

## REFERENCES

- [1] F. Mirjalili, M. Hasmaliza, and L. C. Abdullah, "Size-controlled synthesis of nano  $\alpha$ -alumina particles through the sol-gel method," *Ceramics International*, vol. 36, no. 4, pp. 1253–1257, May 2010.
- [2] T. Noguchi, K. Matsui, N. M. Islam, Y. Hakuta, and H. Hayashi, "Rapid synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles in supercritical water by continuous hydrothermal flow reaction system," *The Journal of Supercritical Fluids*, vol. 46, no. 2, pp. 129–136, Sep. 2008.
- [3] L. Qu, C. He, Y. Yang, Y. He, and Z. Liu, "Hydrothermal synthesis of alumina nanotubes templated by anionic surfactant," *Materials Letters*, vol. 59, no. 29–30, pp. 4034–4037, Dec. 2005.
- [4] K. Laishram, R. Mann, and N. Malhan, "A novel microwave combustion approach for single step synthesis of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanopowders," *Ceramics International*, vol. 38, no. 2, pp. 1703–1706, Mar. 2012.
- [5] W. Q. Jiao, M. B. Yue, Y. M. Wang, and M.-Y. He, "Synthesis of morphology-controlled mesoporous transition aluminas derived from the decomposition of alumina hydrates," *Microporous and Mesoporous Materials*, vol. 147, no. 1, pp. 167–177, Jan. 2012.
- [6] D. G. Shchukin and R. A. Caruso, "Template Synthesis and Photocatalytic Properties of Porous Metal Oxide Spheres Formed by Nanoparticle Infiltration," *Chem. Mater.*, vol. 16, no. 11, pp. 2287–2292, 2004.
- [7] A. B. Fuertes, "Template synthesis of mesoporous carbons with a controlled particle size," *Journal of Materials Chemistry*, vol. 13, no. 12, pp. 3085–3088, 2003.
- [8] Y. Zhang, Y. Chen, H. Niu, and M. Gao, "Formation of CdS nanoparticle necklaces with functionalized dendronized polymers," *Small (Weinheim an der Bergstrasse, Germany)*, vol. 2, no. 11, pp. 1314–9, Nov. 2006.
- [9] K. Naka and Y. Chujo, "Nanohybridized Synthesis of Metal Nanoparticles and Their Organization," in *Nanohybridization of Organic-Inorganic Materials SE - 1*, vol. 13, A. Muramatsu and T. Miyashita, Eds. Springer Berlin Heidelberg, 2009, pp. 3–40.
- [10] K. Joachim and K. Sabine, "Nanoparticles and Polyelectrolytes," in *Polyelectrolytes and Nanoparticles*, Springer Berlin Heidelberg, 2007, pp. 47–71.
- [11] Z. Živcová, E. Gregorová, and W. Pabst, "Alumina ceramics prepared with new pore-forming agents," *Processing and Application of Ceramics*, vol. 2, no. 1, pp. 1–8, 2008.
- [12] J. Zhou, M. Zhou, and R. A. Caruso, "Agarose Template for the Fabrication of Macroporous Metal Oxide Structures," *Langmuir*, vol. 22, no. 7, pp. 3332–3336, Feb. 2006.
- [13] B. Xu, J. Long, H. Tian, Y. Zhu, and X. Sun, "Synthesis and characterization of mesoporous  $\gamma$ -alumina templated by saccharide molecules," *Catalysis Today*, vol. 147, no. Supplement, pp. S46–S50, Sep. 2009.