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ORIGINAL RESEARCH PAPER

Solution Combustion Preparation of Nano-Al_2O_3: Synthesis and Characterization

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Abstract

The aluminum oxide materials are widely used in ceramics, refractories and abrasives due to their hardness, chemical inertness, high melting point, non-volatility and resistance to oxidation and corrosion. The paper describes work done on synthesis of α-alumina by using the simple, non-expensive solution combustion method using glycine as fuel. Aluminum oxide ($Al_2O_{3)}$ nanoparticles were synthesized by aluminum nitrate 9-hydrate as precursor and glycine as fuel. The samples were characterized by high resolution transmission electron microscopy (HRTEM), field effect scanning electron microscopy (FESEM), X-ray diffraction (XRD) and electron dispersive spectroscopy (EDS). As there are many forms of transition aluminas produced during this process, x-ray diffraction (XRD) technique was used to identify α-alumina. The diameter of sphere-like as-prepared nanoparticles was about 10 nm as estimated by XRD technique and direct HRTEM observation. The surface morphological studies from SEM depicted the size of alumina decreases with increasing annealing temperature. Absorbance peak of UV-Vis spectrum showed the small bandgap energy of 2.65 ev and the bandgap energy increased with increasing annealing temperature because of reducing the size.

1. Introduction

Alumina (Al_2O_3) is one of the most widely used advanced ceramic materials. Alumina is one of representative electric-insulating materials. Since it has high thermal conductivity and high chemical stability at high temperature compared to other electro-insulating materials such as glass, plastic, and paper [1-3], it is promising as the electric-insulating material used in the electronic devices.

The importance of alumina as catalyst or catalytic support has also been widely recognized for many chemical reactions [4-6]. The transparency of alumina film and wide range of properties extend its application in optics as well [7]. Aluminum oxide is the amphoteric oxide of aluminum with the chemical formula Al_2O_3 for alpha phase namely corundum as shown in Figure 1. It is also commonly referred to as alumina or aloxite in the mining, ceramic and materials science communities.

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There are various crystal structures in the alumina. Among the various crystal structures, alumina that reveals electric insulation is of α type. The α-alumina has been conventionally produced by annealing aluminum hydroxide derived from aluminum salts or minerals at temperatures higher than 1000◦C [8-11]. The α-alumina can be also produced by fabricating amorphous alumina with methods using liquid phase such as hydrothermal synthesis [12], plasma synthesis [13], the sol-gel method [14-17], freeze drying of sulfate solutions [18], controlled hydrolysis of metal alkoxide [19], decomposition of organo metallic compounds in supercritical fluids and aerosol methods [20] and precipitation method [21], precipitation and sol-gel process and then annealing it at high temperature [22–24].

These methods need the high temperatures, which brings about much consumption of energy. Accordingly, low temperature processes for producing α-alumina are desired for saving energy. Here, we have prepared Al_2O_3 nanoparticles by simple non-expensive solution combustion method using glycine as fuel.

In this paper, novel alumina ceramic nanoparticles are fabricated by using synthesis combustion method without any purification and centrifugation process to find new results and the structural, optical and surface morphological characterization of these nanoparticles are done by using XRD, HRTEM, FESEM and UV-visible analyses.

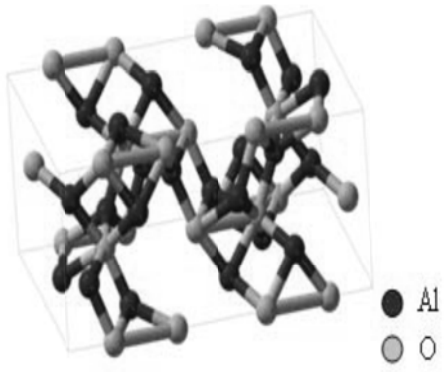

Fig. 1. Molecular structure of alpha alumina

2. Experimental detail

The γ-Al_2O_3 nanoparticles were synthesized by synthesis combustion using aluminum nitrate 9-hydrate as precursor and glycine as fuel. Firstly, 10 g $Al(NO_3)_3.9H_2O$ was completely dissolved in 10 mL pure water with stirring at room temperature and 10 g glycine was added to the solution under stirring. After that the glycine was completely solved in the solution the synthesis temperature was increased to 100^0C. The pH was maintained between 2 and 3 during the synthesis.

The brown product were evaporated for 3 hours, cooled to room temperature and finally calcined at 600^0C and 1000^oC for 4 hours to determine the gamma phase and alpha phase respectively [5-8].

All analyses were done for samples without any washing and more purification. The specification of the size, structure and optical properties of the as-synthesis and annealed Al_2O_3 nanoparticles were carried out. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2θ in the range of 4-85^o with type X-Pert Pro MPD, Cu-K_α: λ = 1.54 Å. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV. The optical properties of absorption were measured by ultraviolet–visible spectrophotometer (UV–Vis) with optima SP-300 plus. All the measurements were carried out at room temperature.

3. Result and discussion

X-Rar diffraction (XRD) at 40kV was used to identify crystalline phases and to estimate the crystalline sizes. X-ray diffraction patterns of the powder after heat treatment at1000^{o}C were done for crystal structure. Figure 1 shows the XRD pattern of aluminum oxide at1000^{o}C for 4 hours. α- Al_2O_3 was the only phase present for the powder calcined above 1000^{o}C. The exhibited picks correspond to the (012), (104), (110), (113), (024), (116), (018), (300) and (119) of a rhombohedral structure of α- Al_2O_3 is identified using the standard data. The mean size of the ordered Al_2O_3 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared Al_2O_3 nanoparticles was around between 10-25 nm from this Debye-Sherrer equation.

Figure 3a shows the SEM image of the as-prepared spherical shape Al_2O_3 nanoparticles with diameter size in the range of 35-80 nm and Figure 3b shows the SEM image of the annealed Al_2O_3 with smallest diameter of 10 nm at 600°C for 4 hours. Figure 4 shows the size measurement of 100 randomly selected particles.

TEM images show a narrow size distribution. Fitting it with a log normal curve, leads to a measured mean diameter of 60 nm, with standard deviation of about 10%.

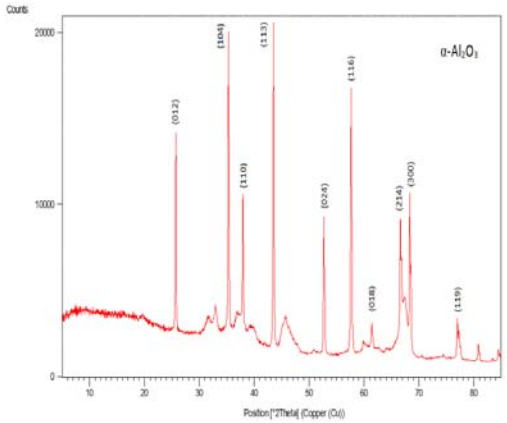

Fig. 2. XRD pattern of Alumina at 1000 °C

SEM analysis was used for the morphological study of nanoparticles of Al_2O_3 samples. With increasing temperature the smallest particle size decreases from 20 nm to 10 nm because of increasing annealing temperature [12].

The transmission electron microscopic (TEM) analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites.

Figure 5 shows the as-synthesized TEM image of alumina prepared by wet synthesis. The as-synthesized TEM image of sphere-like shaped of Al_2O_3 nanoparticles prepared by precipitation route. The average diameter of alumina nanoparticles was about 10 nm.

The principal novelty of the procedure developed is that the alumina nanoparticles were analyzed without any purification and centrifugation by ethanol or water after preparation. In fact, heat treatment processing removes all impurity from the alumina nanoparticles.

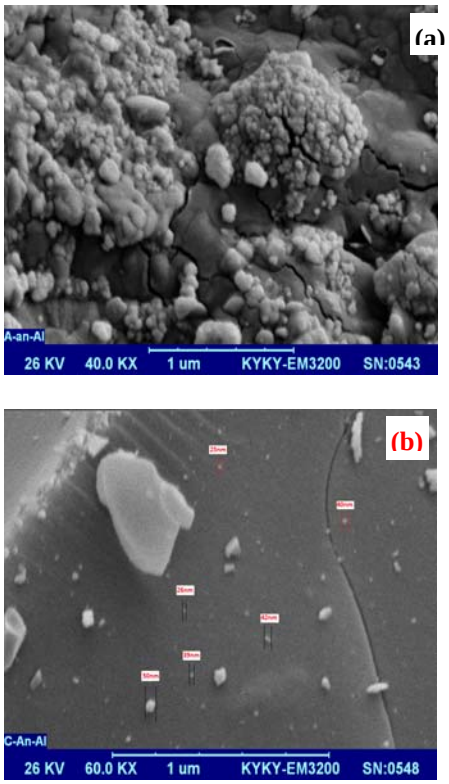

Fig. 3. SEM images of the (a) as-prepared (b) annealed Al_2O_3 nanoparticles at 600°C

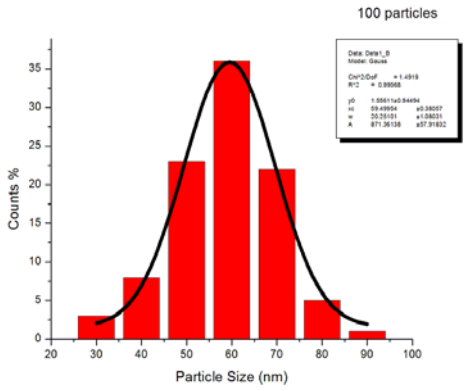

Fig. 4. Particle diameter histogram of alumina nano particles; the line plotted corresponds to fit using a log normal distribution

In most of preparation methods reported by researchers [7, 9-18], they purify nanoparticles by washing with water or ethanol. As you can see the Al_2O_3 nanoparticles prepared by using this method,

have a regular distribution, uniform size and spherical shape.

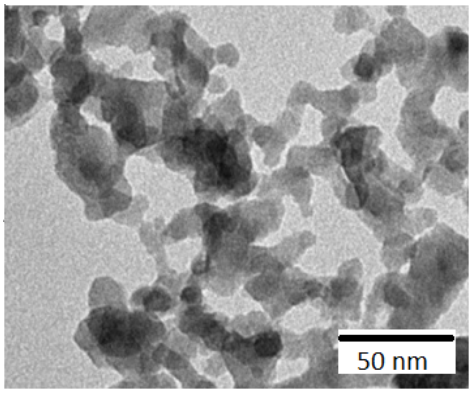

Fig. 5. TEM images of the as-prepared Al_2O_3 nanoparticles

Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. UV–Vis absorption spectra of as-prepared and annealed Al_2O_3 are shown in Figure 6. For as-synthesized Al_2O_3 nanoparticles, the strong absorption band at low wavelength near 471 nm correspond to bandgap energy of 2.65 ev (figure 5a) and for annealed Al_2O_3 at 600 ^oC and 1000^oC the strong absorption band at low wavelength near 400 nm and 402 nm correspond to 3.54 ev (figure 5b) and 3.43 ev (figure 5c) respectively. The UV absorption ability of Al_2O_3 is related with band gap energy.

The optical absorbance coefficient α of a metal close to the band edge can be expressed by the following equation:

$$\alpha = A(h\nu\text{-}Eg)^n / h\nu \qquad (2)$$

Where α is the absorption coefficient, E_g is the absorption band gap, A is constant, n depends on the nature of the transitions, n may have values ½, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. In this case n=1/2 for direct allowed transition [11].

The absorption spectra of TiO_2 nanoparticles are shown in Figure 6a. The absorption band edges were estimated around 351 and 362 nm (about 3.54 and 3.43eV).

The band gap energy can be determined by extrapolation to the zero coefficients, which is calculated from the above equation. The intercept of the tangent to the plot $(\alpha h\nu)^2$ versus hν in Figure 6b gives a good approxim-ation of the band gap energy for this direct band gap material.

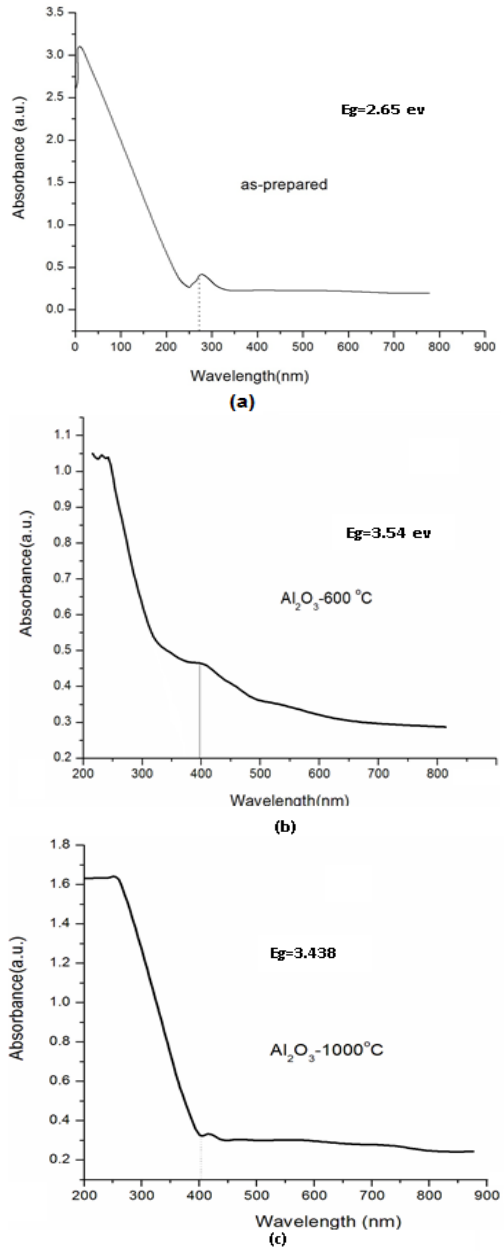

Fig. 6. UV–Vis absorption spectra of Al_2O_3 nanoparticles

4. Conclusion

Alumina ceramic nanoparticles were successfully prepared using aluminum nitrate and glycine. XRD spectrum shows rhombohedral (hexagonal) structure of α-Al_2O_3 annealed at 1000^{o}C. From SEM images, it is clear that with increasing temperature the mean size of alumina decreases from 35 nm to 80 nm. TEM image exhibits that the size of as-synthesized Al_2O_3 decreases to 10 nm. The UV–vis absorption show the small band gap is found to be 2.65 eV and the

bandgap energy increase with increasing annealing temperature because of reducing the size.

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References

[1] X. Shen, X. Nie, H. Hu, J. Tjong, Effects of coating thickness on thermal conductivities of alumina coatings and alumina/aluminum hybrid materials prepared using plasma electrolytic oxidation, Surface and Coatings Technology 207 (2012) 96–101.

[2] J. Musil, J. Blaˇzek, P. Zeman, ˇS. Prokˇsov´a, M. ˇSaˇsek, R. Cerstv´y, Thermal stability of alumina thin films containing γ-Al_2O_3 phase prepared by reactive magnetron sputtering, Applied Surface Science 257 (2010) 1058–1062.

[3] K. Vanbesien, P. De Visschere, P. F. Smet, D. Poelman, Electrical properties of Al2O3 films for TFEL-devices made with sol-gel technology, Thin Solid Films 514 (1-2) (2006) 323–328.

[4] J.-W. Lee, H.-S. Yoon, U.-S. Chae, H.-J. Park, U.-Y. Hwang, H.-S. Park, D.-R. Park, S.-J. Yoo, A comparison of structural characterization of composite alumina powder prepared by sol-gel method according to the promoters, Korean Chem. Eng. Res 43 (4) (2005) 503–510,.

[5] H.-J. Youn, J. W. Jang, I.-T. Kim, K. S. Hong, Low-temperature formation of α-alumina by doping of an alumina-sol, J. of Colloid and Interface Sci 211 (1999) 110–113,.

[6] Y. K. Park, E. H. Tadd, M. Zubris, R. Tannenbaum, Size-controlled synthesis of alumina nanoparticles from aluminum alkoxides, Materials Res. Bulletin 40 (2005) 1506–1512,.

[7] Y. Rozita, R. Brydson, A. J. Scott, An investigation of commercial gamma-Al2O3 nanoparticles, J. of Physics: Conf. Series 241(2009).

[8] V. Isupov, L. Chupakhina, G. Kryukova, S. Tsybulya, Fine α-alumina with low alkali, new approach for preparation, Solid State Ionics 141-142 (2001) 471–478.

[9] I. N. Bhattacharya, P. K. Gochhayat, P. S. Mukherjee, S. Paul, P. K. Mitra, Thermal decomposition of precipitated low bulk density basic aluminum sulfate, Materials Chemistry and Physics 8(1) (2004) 32–40.

[10] E. Ryshkewitch, Oxide Ceramics, Academic Press 1960.

[11] J. S. Reed, Principles of Ceramics Processing, Wiley-Interscience, New York, NY, USA, 2nd edition, 1995.

[12] W.L. Suchanek, Hydrothermal synthesis of alpha alumina (α-Al2O3) powders: Study of the processing variables and growth mechanisms, J. Am. Ceram. Soc 93 (2010) 399–412.

[13] P.V. Ananthapadmanabhan, K.P. Sreekumar, N. Venkatramani, P.K. Sinha, P.R. Taylor, Characterization of plasma-synthesized alumina, J. Alloy. Compd 244 (1996) 70–74.

[14] M. Nguefack, A.F. Popa, S. Rossignol, C. Kappenstein, Preparation of alumina through a sol-gel process, synthesis characterization, thermal evolution and model of intermediate Boehmite, Phys. Chem. Chem. Phys 5 (2003) 4279–4289.

[15] M. R. Karim, M. A. Rahman, M. A. J. Miah, H. Ahmad1, M. Yanagisawa, M. Ito, Synthesis of γ-Alumina Particles and Surface Characterization, The Open Colloid Science Journal 4 (2011) 32-36

[16] R. Rogojan, E. Andronescu, C. Ghitulica, B.Ş. Vasile, synthesis and characterization of alumina nanopowder obtained by sol-gel method, U.P.B. Sci. Bull 73 (2011) 67-76.

[17] F. Mirjalilia, L. Chuahb, M.Hasmaliza, Effect of stirring time on synthesis of ultra fine α-Al_2O_3 powder by a simple sol-gel Method, Journal of Ceramic Processing Research 12 (2011) 738-741.

[18] M.I. Nieto, C. Tallon, R. Moreno, Synthesis of gamma-alumina nanoparticles by freeze drying. Adv. Sci. Technol 45 (2006) 223–230.

[19] T. Ogihara, H. Nakajima, T. Yanagawa, N. Ogata, K. Yoshida, Preparation of monodisperse, spherical alumina powders from alkoxides, J. Am. Ceram. Soc 74 (1991) 2263–2269.

[20] A. Janbey, R.K. Pati, S. Tahir, P. Pramanik, A new chemical route for the synthesis of nano-crystalline α-Al2O3 powder, J. Eur. Ceram. Soc 21 (2001) 2285–2289.

[21] K. Inoue, M. Hama, Y. Kobayashi, Y. Yasuda ,T. Morita, Low Temperature Synthesis of α-

Alumina with a Seeding Technique, ISRN Ceramics (2013) 317830-317835.

[22] M. Shojaie-Bahaabad, E. Taheri-Nassaj, Economical synthesis of nano alumina powder using an aqueous sol-gel method, Materials Letters 62 (19) (2008) 3364–3366.

[23] F. Mirjalili, M. Hasmaliza, L. C. Abdullah, Size-controlled synthesis of nano α-alumina particles through the sol-gel method, Ceramics International 36 (4) (2010) 1253–1257.

[24] Q. Fu, C.-B. Cao, H.-S. Zhu, Preparation of alumina films from a new sol-gel route, Thin Solid Films 348 (1) (1999) 99–102.