PVA - Assisted Synthesis and Characterization of Nano α -Alumina

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Abstract- This paper is trying to explore the effect of polyvinyl alcohol (PVA) on the synthesis of nano α-alumina particles. α -Al_2O_3 is widely used and studied as high temperature structural material, electronic packaging, corrosion resistant and translucent ceramics. Sol-gel method was adopted for synthesis. PVA was used as surface stabilizing agent. The results indicated that the addition of PVA affected the particle size and reduces the degree of aggregation. The X-ray diffraction (XRD) patterns for nano powders indicated the presence of a single phase nano α-Al_2O_3 particles. The surface morphology of aluminium oxide nano particles was characterized using Scanning Electron Microscopy (SEM) which shows that the particles are having irregular spherical shape. The formation of alumina nano particles were also confirmed by Fourier Transform Infrared (FTIR) and UV-visible spectrometry measurements. A plausible mechanism is proposed for the formation of alumina nano particles and is expected that this synthetic technique can be extended to obtain other metal oxides.

Index Terms- Nanoparticles, α -alumina, sol-gel, polyvinyl alcohol, synthesis.

I. INTRODUCTION

Nanoparticles constitute a crucial and intensive area of research and development in the burgeoning field of nanotechnology. The attraction of nanoparticles lies in the myriad characteristics which can be achieved by reducing suitable materials from the bulk to the nanometer size. Alumina is one of the most widely used ceramic materials and owing to its special properties, such as high elastic modulus, thermal and chemical stability, high strength, toughness and excellent dielectric properties; alumina has been regarded as a material of outstanding performance, especially under tension or bending conditions. In contrast to metals and polymers, however, the thermal stability of ceramics above 700 ^{0}C makes them suitable materials for high temperature applications [1].

In recent years, considering their diverse properties, substantial research works have been conducted for the preparation of alumina nanoparticles [2-4]. It is well known that the physical and mechanical characteristics of alumina nano particles are largely governed by the particle size, morphology, surface and phase homogeneity and these can be controlled by selecting a proper synthetic route. Several attempts have been conducted to control the characteristics of the resulting alumina powders, including the introduction of surface controlling agents. The introduction of polymer in the system has attracted more attention and has been used to prepare both ceramic particles and metal oxide nano particles [5].

Alumina exists in several metastable crystalline structures: η-, γ-, δ-, θ-, β-, κ-, χ, and α-alumina. According to Gitzen [6], γ-Al_2O_3 transforms to δ-Al_2O_3 when calcined above 800 °C. The δ-Al_2O_3 transforms to θ-Al_2O_3, when calcined above 1000 °C. Finally, θ-Al_2O_3 transforms to α-Al_2O_3, when calcined above 1100 °C. However, the presence of impurities alters the barrier of phase transformations. Factors such as particle size, heating rate, impurities and atmosphere may influence the sequence of phase transformations of alumina [7].

Various wet chemical methods such as co-precipitation [8], hydrothermal [8]; sol-gel technology [9] and combustion method [10, 11] have been developed for the synthesis of nano alumina. Wu et al. [12] prepared the alumina gel from $Al(NO_3)_3.9H_2O$ by NH_4OH, where plate-like nano α-Al_2O_3 particles were crystallized by heating around 900 °C. Pathak et al. [13] synthesized the nano crystalline alumina powder by a chemical reaction using citric acid and ammonia at 1200 °C. Wen et al. [14] and Yen et al. [15] prepared α-Al_2O_3 nano powder using Al $(NO_3)_3.9H_2O$ and NH_4OH as precursors. Yen et al. [16] and Yu et al. [17] reported Al_2O_3 nano powder preparation by calcination of boehmite. Pang et al. [18] synthesized alumina nano powder with $AlCl_3$ using aqueous NH_4OH as precipitant. Pacheco et al. [19] reported α-Al_2O_3 nano powder prepared by sol-gel method. Wang et al. [20] synthesized α-Al_2O_3 at 1100 °C via accelerator-free polyacrylamide gel system, prepared at 80 °C and compared their route with other methods such as precipitation and calcination methods. They observed that the particle size of nano powders produced by sol-gel method was smaller than that of the nano powders made by other methods.

The present study tends to synthesize nano sized Al_2O_3 using sol-gel method by controlling the particle size distribution and shape employing polyvinyl alcohol (PVA). The PVA is a water-soluble synthetic polymer. It has the idealized formula $[CH_2CH (OH)]_n$. It is known that size of the nano particles can be controlled easily through the use of polymers in the system. Sol-gel synthesis offers relatively inexpensive scale processing of mixed oxide materials with a good control over the stoichiometry and morphology which helps to tailor the required materials on atomic scale to suit specific applications. The synthesis by this method generally produces α-Al_2O_3 by calcination at high temperature. The work also investigates the effect of PVA additions on morphology of the alumina nano particles.

II. EXPERIMENTAL

2.1 Synthesis of alumina nanoparticles

The nanoparticles were prepared by the sol-gel technology. All chemicals used were analytical reagents. Aluminium chloride, $AlCl_3$ (s.d.fine-CHEM Ltd., Mumbai), 25% NH_3 solution (s.d.fine-CHEM Ltd., Mumbai) and polyvinyl alcohol (Loba Chemie Pvt. Ltd.) were used as raw materials for the synthesis of nano alumina.

0.1 M alcoholic $AlCl_3$ solution was prepared, followed by addition of 25% ammonia solution. The resulting solution turned to a white sol. This was followed by the addition of PVA (0.5M). The sol was stirred continuously using a magnetic stirrer until it became a transparent sticky gel. The gel was allowed to mature for 24 hours at room temperature. The resultant gel was heat treated at 100 °C for 24 hours which leads the formation of light weight porous materials due to the enormous gas evolution. Dried gel was, then calcined at 1200 °C for 4 hours and finally, the calcined powders were crushed using mortar and pestle to get the fine homogeneous dense powder. The same procedure was repeated without employing PVA and the results were compared.

2.2 Characterization

The structure of particles was investigated using X-ray diffraction using PANalytical, XRD machine (DY-1656). Monochromatic CuKα radiations were used as a source of 40 kV/35 mA power and the pattern was recorded in the 2θ range of 3^o– 80^o with a scan step of 0.02 in a scan time of 65.6seconds. IR spectrophotometer (Shimadzu, FTIR-8900, Japan) was used for obtaining IR spectra (KBr) operating in the 400–4000 cm^{-1} range. The transmission spectra of the films were measured by an ultraviolet-visible spectrophotometer (Shimadzu, UV-1800) with a wavelength range 200 nm - 1100 nm and the optical band gap was measured from the transmission spectra. The morphology of particles was investigated using Scanning Electron Microscopy (Hitachi, JEOL-JSM 5800) [22].

III. RESULTS AND DISCUSSIONS

3.1 XRD Analysis

X-ray diffraction patterns were taken to examine the crystal structure of the synthesized nano alumina particles. The average crystallite sizes of synthesized samples were calculated from the full width at half maximum (FWHM) of the peaks using Debye-Scherrer formula:

$$\mathbf{D = 0.9\lambda / \beta \cos \theta}$$

Where, D - crystallite size, λ - wavelength of CuKα radiation, β - corrected full width half maximum (FWHM) of the diffraction peak, θ – Bragg's angle of the X-ray diffraction peak.

The peaks in the pattern significantly indicate the formation of crystalline nano sized α-Al_2O_3 powders. The average crystalline size of nano alumina particles without PVA was in the range of 35 - 45 nm and the PVA assisted nano alumina was in the range of 20 – 30 nm. Three main reflections were obviously observed at 2θ angles around 35 ^{0} (104), 43 ^{0} (113) and 57 ^{0} (116). The peaks in the pattern significantly supported the formation of nano sized α-Al_2O_3 (corundum) from JCPDS file (77- 2135). Figure 1(a) and 1(b) shows XRD pattern of α-Al_2O_3 nanoparticles without PVA (AI) and with PVA (API) respectively.

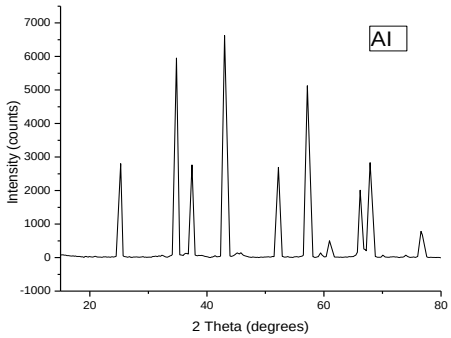

Figure 1(a) XRD pattern of nano Al_2O_3 without PVA

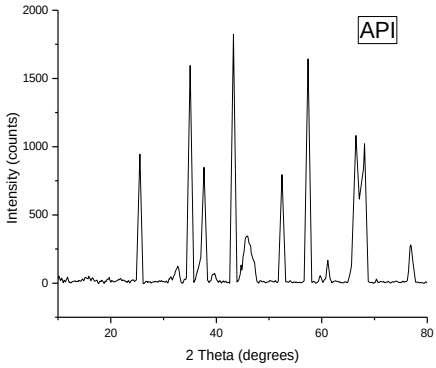

Figure 1(b) XRD pattern of nano Al_2O_3 with PVA

3.2 FTIR analysis

For nano alumina synthesized with and without PVA, an intense band centered around 3500 cm^{-1} and the other around 1600 cm^{-1} was assigned to O–H stretching and bending modes of water or alcohol respectively. The wide band appearing between 500 cm^{-1} and 900 cm^{-1} corresponds to the vibrational frequencies of co-ordinate O–Al–O bond. This wide band was divided into two peaks. The peaks in the region 500 –750 cm^{-1} were assigned to ν-AlO_6 and the other at 800 cm^{-1} was assigned to ν-AlO_4 in nano Al_2O_3 [23].

However, the prominent difference between the two kinds of powders was in the depth of the Al–O bond appearing between 500 cm^{-1} and 900 cm^{-1}. For the nano powders synthesized with PVA, the peak in the region 500–750 cm^{-1} was much sharper than in the samples without PVA, indicating more crystalline Al–O bonds [24]. Figure 2(a) and 2(b) shows FTIR spectra of α-Al_2O_3 nanoparticles without PVA and with PVA respectively.

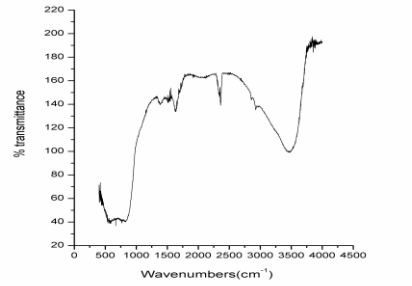

Figure 2(a) FTIR spectrum of nano Al_2O_3 without PVA

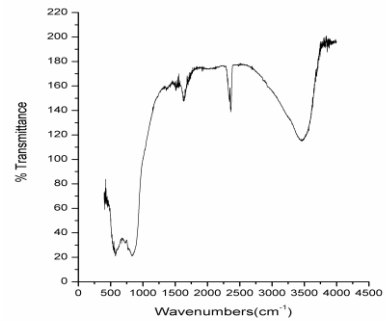

Figure 2(b) FTIR spectrum of nano Al_2O_3 with PVA

3.3 UV-visible analysis

Figure 3 shows the UV-visible absorption spectra of Al_2O_3 nano particles suspended in deionized water [25]. A strong absorption peak between 200 nm and 400 nm was clearly observed which confirmed the presence of Al_2O_3 nano particles. UV- visible absorption spectroscopy is one of the important tools to probe the energy band gap. The absorption peak of nano alumina without PVA was found at around 242 nm and 382 nm [Figure 3(a)]. PVA capped alumina nano particles had absorption peaks at 242 nm and 377 nm. A blue shift of about 5 nm was observed with addition of PVA. Band gap of the nanoparticles is calculated from

$E = hc / \lambda$

where, E is Band gap energy, h is Planck's constant, c is velocity of light; λ is wavelength of absorption edge in reflectance spectra. Band gap energy of PVA capped alumina nano particles (3.30eV) is slightly greater than for the uncapped alumina nanoparticles (3.25eV). This showed the decrease in particle size of alumina in presence of PVA [26].

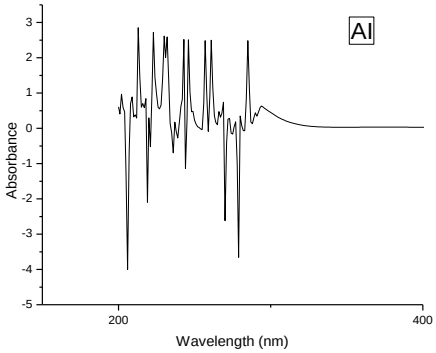

Figure 3(a) UV- visible Spectra of nano Al_2O_3 without PVA

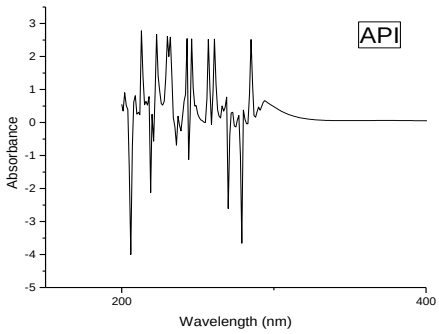

Figure 3(b) UV- visible Spectra of nano Al_2O_3 with PVA

3.4 SEM Analysis

Scanning electron microscope is a very useful tool for studying morphology of nano powders. Figure 4(a) and 4(b) shows SEM pictures of α-Al_2O_3 nanoparticles without PVA and with PVA respectively. For nano alumina particles synthesized without PVA, only a little dispersion with lot of agglomeration was observed which appears to be a major problem in producing nano powders. As shown in figures, by adding PVA, less agglomeration occurs. Particles capped with PVA possessed a better dispersion than the particles synthesized without PVA [27].

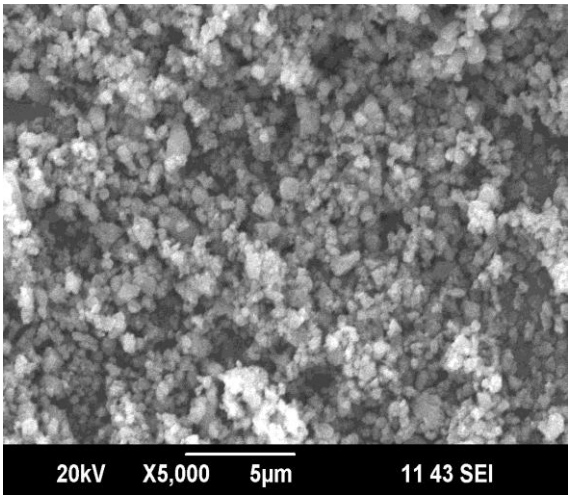

Figure 4(a) SEM of nano Al_2O_3 without PVA

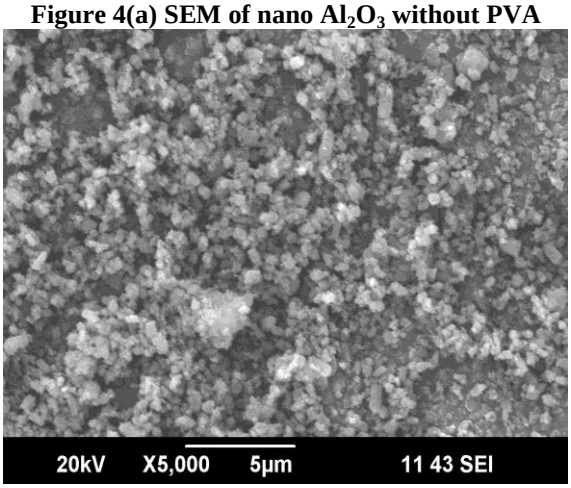

Figure 4(b) SEM of nano Al_2O_3 with PVA

IV. Conclusions

Nano crystalline Al_2O_3 powders have been synthesized by sol-gel method employing PVA. This is a direct and efficient route, extendable to other metal or alloy oxide nano particles and has the potential to be further scaled up towards production of large quantities. The synthesized alumina powders were characterized using XRD, FTIR, UV-visible spectroscopy and SEM. The XRD pattern revealed that the synthesized nano alumina particles were crystalline in nature and had more stable corundum phase. The addition of PVA produced nano sized alumina with small size distribution. FT-IR analysis confirmed that the synthesized alumina nano powder had the characteristic wide band appearing between 500 cm^{-1} and 900 cm^{-1} which corresponds to the vibrational frequencies of Al_2O_3. UV-visible absorption peaks between 200 nm and 400 nm was clearly observed which supported the formation of Al_2O_3 nano particles. The increase in bang gap energy revealed the decrease in particle size with addition of PVA. The SEM images also indicated less aggregation for the PVA addition. Alumina powders obtained at the nano metric scale, may have superior properties as compared to the powders obtained in larger particle sizes and can be used in medical applications as a biomaterial.

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