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Synthesis of Aluminum and Titanium Oxides Nanoparticles via Sol-Gel Method: Optimization for the Minimum Size

F. Kamil[1], K.A. Hubiter [1], T.K. Abed [2], A.A. Al-Amiery[2,*]

[1]*Laser & Optoelectronics Eng. Department, University of Technology (UOT), Baghdad 10001, Iraq.*
[2]*Environmental Research Center, University of Technology (UOT), Baghdad 10001, Iraq.*

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ABSTRACT

Al_2O_3 and TiO_2 nanoparticles were synthesized using sol-gel method. The structures of Al_2O_3 and TiO_2 nanoparticles were investigated using X-ray diffraction (XRD) study. The morphology of nanoparticles was investigated by scanning electron microscopy (SEM) analysis. The FE-SEM images showed that most of the nanoparticles obtained for Al_2O_3 and TiO_2 nanoparticles have spherical shape with a particle size of 14 nm and 43 nm for Al_2O_3 and TiO_2 nanoparticles respectively. The absorption spectra of Al_2O_3 and TiO_2 nanoparticles suspended in deionized water were recorded at room temperature using UV-visible spectroscopy. The absorption spectra show a strong peak at 344 nm and 483 nm for Al_2O_3 and TiO_2 respectively. The results on absorption spectra are in good agreement with those investigated by XRD which confirmed the formation of Al_2O_3 and TiO_2.

1. Introduction

Al_2O_3 nanoparticles can be synthesized by many techniques including ball milling, sol-gel, pyrolysis, sputtering, hydrothermal, and laser ablation [1–6]. In the recent years, Al_2O_3 nanoparticles were synthesized in liquid using a short pulse laser with the pulse width in the range of nanosecond [7–9]. In literature, there is information on obtaining Al_2O_3 by sol-gel method using the different precursors: aluminum triisopropylate in a hydrolysis system consisting of octanol and acetonitrile [10], aluminum nitrate – in aqueous medium [11, 12], aluminum secondary butoxide - in an alcoholic medium [13]. Titanium dioxide (TiO_2) is a versatile material with novel properties suitable for a number of technologically important applications, such as catalysis, white pigment for paints or cosmetics, electrodes in lithium batteries [14], dye-sensitized solar cells [15], and photocatalyst [16]. Although TiO_2 has wide potential application in environmental management and environmental protection, the low photocatalytic efficiency and the difficulty to separate greatly hinder its process of industrialization [17, 18]. There are various methods to synthesize titanium dioxide nanostructures such as chemical vapor deposition, microemulsion, chemical precipitation, hydrothermal crystallization, and sol-gel [19, 20]. Sol-gel is one of the most successful techniques to fabricate high photocatalytic titanium dioxide nanostructures [21], with controlled shape and porosity. Moreover, other advantages such as versatile process [22] with high purity, good homogeneity, and low processing temperature [23] can be taken into account for this synthetic technique. Recently, synthetic methods of TiO_2 nanostructures were accompanied with template-assisted approaches. The templating method is one of the frequently used methods to modify the surface properties of nanomaterials [24]. In continuation of our studies on the nanoparticles and the new organic compounds [25-31], herein, we describe the simple and efficient method for synthesis of Al_2O_3 and TiO_2 nanoparticles. The particle size and morphology of synthesized nanoparticles obtained by sol gel method were investigated by scanning electron microscopy (SEM). The optical properties of synthesized nanoparticles were carried out using UV-visible spectroscopy. The structure of the synthesized nanoparticles was investigated using X-ray diffraction (XRD) technique.

*Corresponding Author
Email Address: dr.ahmed1975@gmail.com (A.A. Al-Amiery)

2. Experimental Methods

2.1 Materials

The starting materials and solvents were purchased from Sigma Aldrich and ChemAR, without further purification. The X-Ray Diffraction spectrum for the nanomaterials were recorded on a X-Ray-STADI P(STOE/Germany). Scanning Electron Microscope was performed using SEM 54032-GE02-0002/8038 (MIRA3/Austria) which is a SEM system with the sputter coater device with gold.

2.2 Synthesis of TiO_2 Nanoparticles

Titanium oxide nanoparticles were prepared via sol-gel method using the titanium isopropoxide, de-ionized water and isopropyl alcohol as the starting materials. 100 mL of isopropyl alcohol was added to 15 mL of titanium isopropoxide. The mixture solution is stirred 10 minutes. 10 mL of de-ionized water was added drop wise to the mixed solution. Then the mixture solution was stirred continuously for 2 hours. The gel left for 24 h in dark then dried. The dried TiO_2 are calcinated at 550 °C.

2.3 Synthesis of Al_2O_3 Nanoparticles

Al_2O_3 nanoparticles were prepared via sol-gel method using the precursor aluminum trichloride as the starting materials. 28% of ammonia was added drop wise to stirred ethanolic solution of aluminum chloride (0.1 M). The gel was let to maturate for 30 hours at room temperature. After filtering in vacuum system, drying at 100 °C for 24 h in an oven, and annealing at 1000 °C.

3. Results and Discussion

3.1 SEM morphologies of the synthesized Al_2O_3 and TiO_2 nanoparticles

The morphology of Aluminum oxide and titanium oxide were examined via SEM. Figs. 1 and 2 show the SEM images for Al_2O_3 and TiO_2 respectively with the nanostructures clearly visible. The SEM images confirmed that the Al_2O_3 and TiO_2 were nearly spherical in shape with an average grain size of 14 nm for Al_2O_3 and 41 nm for TiO_2. Figs. 1 and 2 show various types of Al_2O_3 and TiO_2 nanostructures obtained by reaction of aluminum chloride ($AlCl_3$) and titanium isopropoxide respectively. The nanoparticles are entirely spherical in shape and have diameters around 14.11 nm, as can be seen from the Fig. 1 at the resolution of 100.00 kx. These nanoparticles are less than those reported previously [32, 33] and are also similar with few of literatures [34, 35]. The effect of reaction time plays a marvelous role in the morphology of nanoparticles. The influence of

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reaction conditions on physical properties of synthesized nanoparticles as well as mechanism is yet to be investigated. Fig. 2 shows the morphology of TiO_2 nanoparticles. The nanoparticles are entirely spherical in shape and have diameters around 43 nm, as can be seen from the figure at the resolution of 50.00 kx. The effect of reaction time plays a marvelous role in the morphology of nanoparticles. The influence of reaction conditions on physical properties of synthesized nanoparticles as well as mechanism is yet to be investigated [36].

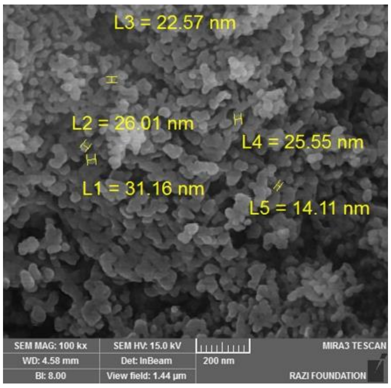

Fig. 1 The SEM test for Al_2O_3 nanoparticles

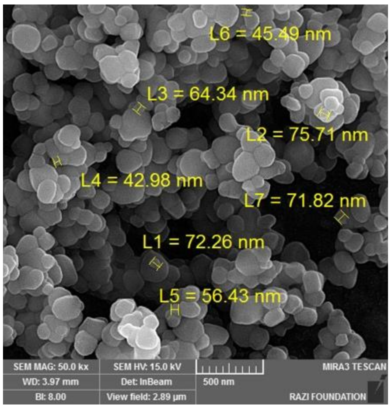

Fig. 2 The SEM test for TiO_2 nanoparticles

3.2 XRD

Structural investigation of Al_2O_3 and TiO_2 nanoparticles by XRD. The particle size was calculated for Al_2O_3 and TiO_2 NPs using the Scherrer equation based on the XRD data as

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

For Al_2O_3, $D = \frac{0.9\times1.54\times10^{-10}}{0.0625\times0.8386} = 26\ nm$

where D = particle size, K = a dimensionless shape factor, with a value close to unity, λ = the X-ray wave length, β = the line broadening at half the maximum intensity (FWHM), θ = the Bragg angle.

The XRD pattern for the Al_2O_3 and TiO_2 nanoparticles is shown in Figs. 3 and 4 respectively and indicates a single-phase with a monoclinic structure. The peak intensities and positions agree well with the library data.

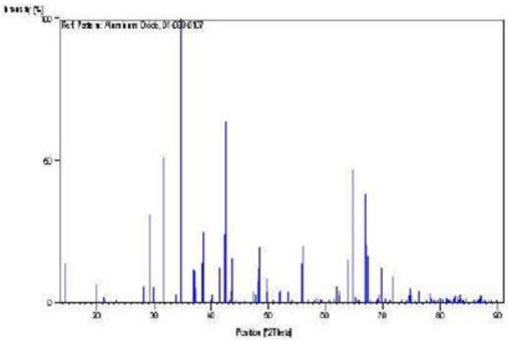

Fig. 3 the XRD for Al_2O_3 Nanoparticles

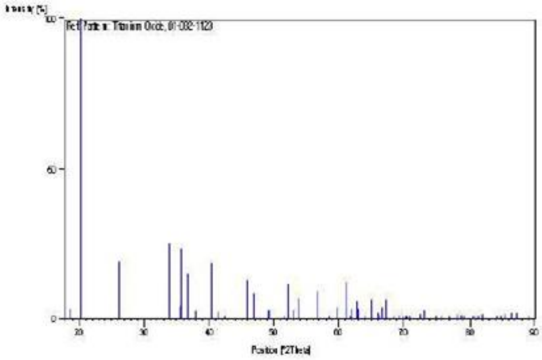

Fig. 4 The XRD for TiO_2 Nanoparticles

3.3 UV-Vis Spectroscopy

UV-Vis Absorbance Spectroscopy is a characterization techniques for Al_2O_3 and TiO_2 NPs. From Figs. 5 and 6 we can observe that Al_2O_3 and TiO_2 nanoparticles are transparent in visible region and shows almost sharp absorbance peaks at 344 nm and 483 nm respectively.

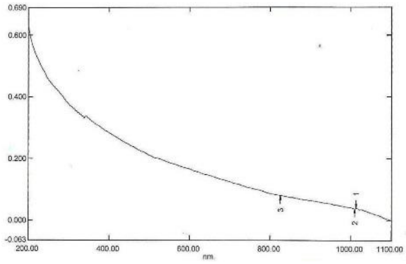

Fig. 5 The UV-Vis Spectroscopy of Al_2O_3 NPs

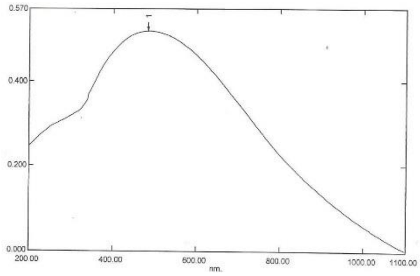

Fig. 6 The UV-Vis Spectroscopy of TiO_2 NPs

3.4 Reaction Mechanism for the Synthesized of TiO_2 and Al_2O_3 Nanoparticles

Sol-gel is a one the best techniques that can be applied to prepare and analyze the formation of TiO_2 and Al_2O_3 nanoparticles. Some effective parameters on the nature of the sol–gel process are metal precursor, temperature, pH of solution and the presence/absence of catalyst. Proposed benefits of the sol gel process are considered as easy control of formation process (nucleation and growth), high stability, better homogeneity, and high purity. The sol-gel process has been widely employed for preparing of TiO_2 and Al_2O_3 nanoparticles because the control of hydrolysis and polycondensation reactions can be easily stablished and gotten the appropriate properties [37]. TiO_2 nanomaterial can be synthesized by sol gel process with different titanium precursors. Typically, synthesizing of TiO_2 nanoparticles via sol-gel process include an acid-catalyzed hydrolysis step of titanium(IV) alkoxide followed by condensation. The development Ti-O-Ti is favorite with low water. Present of large excess of water lead to develop polymetric Ti-O-Ti chains [38, 39] The study on nucleation and growth kinetic of titania nanoparticles prepared by sol gel method shows that the rate constant for coagulation of particles increases with temperature because the velocity of monomer through the particles has high dependency of temperature. Secondary particles were formed and the growth of particles increased when they passed critical radius and became stable [40]. Researcher were found that the nucleation period was limited to a short period of time and the growth process was induced by another step [41]. On the basis of this idea it can be possible to make nucleation through super-saturation phenomena and it is possible to produce almost perfect mono-dispersed particles. During the synthesis of TiO_2 nanoparticles, the following reactions might occur according to the postulated mechanism:

$$Ti(OR)_3 + H_2O \rightarrow Ti(OH)_3 + R_2O \quad (2)$$
$$Ti(OH)_3 \rightarrow TiO_2 + H_2O \quad (3)$$

For the synthesis of Al_2O_3 nanoparticles, the following reactions might occur [46]:

$$NH_3.H_2O \rightarrow NH_4^+OH^- \quad (4)$$
$$OH^- + AlCl_3 \rightarrow Al(OH)_3 \quad (5)$$
$$Al(OH)_3 \rightarrow Al_2O_3 + H_2O \quad (6)$$

4. Conclusion

Al_2O_3 nanoparticles were prepared by sol gel method. Mole ratio of ammonia:aluminum chloride ($AlCl_3$) plays an important role in controlling the size of the Al_2O_3 nanoparticles. The size of Al_2O_3 in this method was 14 nm. With increasing the concentration of the base, the particles size becomes smaller. TiO_2 nanoparticles were prepared by sol gel method using isopropyl alcohol and titanium isopropoxide. Mole ratio of isopropyl alcohol and titanium isopropoxide have an important role in controlling the size of the TiO_2 nanoparticles.

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