Synthesis of Nanosized Titanium Dioxide (Tio$_2$) by Sol-Gel Method

S. Ramalingam

Abstract: ***Nanosized Titanium dioxide (TiO_2) was synthesized by sol-gel method and it was characterized by XRD, EDX, SEM, FTIR and DRS-UV-Visible spectroscopy to study the structural, morphological and optical properties of the prepared nano TiO_2. The presence of elements Ti (54.5%) and O (40.5%) are confirmed by Energy dispersive X-ray spectroscopy (EDX) analysis. The X-ray diffraction analysis (XRD) confirms the presence of Nano crystalline anatase phase TiO_2. The average crystallite size calculated from the XRD data using Debye-Sherrer equation was ~15 nm and the preferred orientation plane was (101). The DRS-UV-Visible spectra analysis shows that the band gap energy (Eg) value calculated for the nano TiO_2 was 3.18 eV. The surface morphology of the nanoTiO$_2$ was studied by scanning electron microscopy (SEM) analysis, it shows that the uniform anatase phase TiO_2 with nano plate like structure.***

Keywords: ***Nanosized Titanium dioxide (TiO_2), Sol-Gel Method, Anatase, XRD analysis.***

I. INTRODUCTION

Nanostructured materials are of great interest due to its unique properties and diversity of applications. Titania (TiO_2) is a renowned nanostructured material which is used in various fields of applications from semiconductor to photo catalyst, paints and varnishes and cosmetics. The TiO_2 nanoparticles are used in waste water treatments for the removal of pollutants and in air pollution treatments. The photo catalytic property of TiO_2 nanoparticles is mainly depended on the crystallite size and structure of the nanoparticles. TiO_2 has crystalline and amorphous forms with three different polymorphos, anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Generally, the anatase phase TiO_2 is the preferred form for the photocatalytic studies [1-10]. The nanosized TiO_2 was prepared by several methods such as solvothermal [11], hydrothermal [12-13], continuous reaction [14], super critical carbon dioxide [15], chemical vapour deposition [16], sonochemical [17-18], ultrasonic irradiation [19-20], RF sputtering [21], micro-plasma oxidation method [22], microwave- hydrothermal [23] and sol-gel method [1-2] [4-5] [24-29]. Compared to other methods, the sol-gel is preferable because it is simple, economical and low temperature method and extensively used for the synthesis of TiO_2 nanoparticles [1-5] [9] [24]. The aim and scope of the present work is; (i) To synthesize nanosized Titanium dioxide (TiO_2) by sol-gel process using titanium tetraisopropoxide (TTIP) and ethanol as starting materials in acidic medium. (ii) To characterize the nano TiO_2 by XRD, EDX, SEM, FTIR and DRS-UV-Visible spectroscopy studies to determine the crystallite size, crystallite structure, elemental composition, microstructure and optical properties of the nanoparticles.

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II. EXPERIMENTAL METHODS

All the chemicals and reagents are used in this study for the synthesis of nano TiO_2 are of pure analytical grade and purchased from sigma Aldrich and Merck fine chemicals.

A. *Synthesis of TiO_2 Nanoparticles*

Nano TiO_2 was prepared by sol-gel method. The principle of this method is the formation of metal hydroxide by sol gel process and conversion of metal hydroxide in to nanocrystalline metal oxides. This process involves the following six steps; (i) hydrolysis, (ii) polymerization, (iii) gelation, (iv) drying, (v) dehydration and (vi) densification.
The precursor titanium tetraisopropoxide (TTIP) of 5 ml mixed with 25 ml of ethanol and the mixture was stirred for an hour using magnetic stirrer. To this mixture, 4.1 ml of acetic acid was added and stirring continued for an hour. After that 0.5 ml of conc. HNO_3 added in drops to this mixture and transparent clear solution was obtained. The transparent solution was then kept in an oven at 50-60^oC for 48 hours, which leads to the formation of pale yellow crystals. The crystal was then finely grained in the mortar and the grain powder was transferred into a crucible and kept in muffle furnace at 500^oC for 4 hrs. A white nano powder of TiO_2 was obtained.

B. *Characterization of Nanosized TiO_2*

The synthesized nano TiO_2 characterized by Bruker D8 Advance Eco powder X-ray difractometer with CuKα radiation source of wavelength $\lambda = 1.5406$ A° operating at 40 kV to 25 mA. The XRD Patterns for the prepared nano TiO_2 was obtained in the 2Θ angle range of 10-80° at room temperature (25°C). The surface morphology and elemental composition of the nano TiO_2 were analyzed by scanning electron microscopy (SEM) (Model: Evo18 Carl Zeiss) coupled with Energy dispersive X-ray spectroscopy (EDX) (Model: Quantax 200 with X-Flash 6130). The FTIR Spectra for the TiO_2 nanoparticles were recorded by IR Tracer-100 Shimadzu FTIR spectrometer. The optical properties of the TiO_2 nanoparticles were studied by Shimadzu UV-Visible spectrophotometer.

III. RESULTS AND DISCUSSIONS

A. *XRD Analysis*

The X-ray diffraction pattern for the synthesized nano TiO_2 is shown in Fig. 1. The diffraction peak appears at 2θ values with 25.23°, 37.69°, 47.97°, 53.84°, 55.0°, 62.67°, 62.63°, 68.89° and 74.96° correlates the crystal planes of (101), (004), (200), (105), (211), (204), (213), (116) and (215), which is matched and confirmed with the standard reference XRD pattern of TiO_2 (JCPDS Card No.21-1272). The peaks of the XRD patterns matches with the previous literature reports and confirms the prepared anatase phase TiO_2 nanoparticles by sol-gel method [8] [10] [30]. The 2Θ value of 25.23°, which is the high intense peak for the anatase TiO_2 and the preferred orientation plane was (101). The prepared nano TiO_2 were crystalline (percentage crystallinity is 67.1%) and the grain size were measured by using the Debye-sherrer equation;

$$D = \frac{0.9\lambda}{\beta \, Cos\theta}$$

Where D is the crystallite size and λ-is the wavelength of the radiation, β-is the full width at half maximum height (FWHM) of the peak. The average grain size calculated using the Sherrer formula for the synthesized TiO_2 nanoparticle was ~15 nm (JCPDS card No. 21-1272) [8] [10] [30].

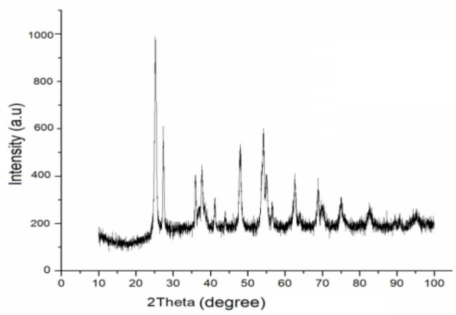


Fig. 1. XRD Pattern of synthesized TiO_2 nanoparticle.

B. *Elemental Composition by EDX Analysis*

The weight percentage of elements present in the synthesized TiO_2 nanoparticles was examined by Energy dispersive X-ray spectroscopy (EDX) analysis. The EDX spectrum of the synthesized nano TiO_2 was shown in Fig. 2. The presence of elements Ti and O are confirmed by EDX spectrum (Fig. 2) and the weight percentage composition of Ti and O are 54.5% and 40.5% respectively.

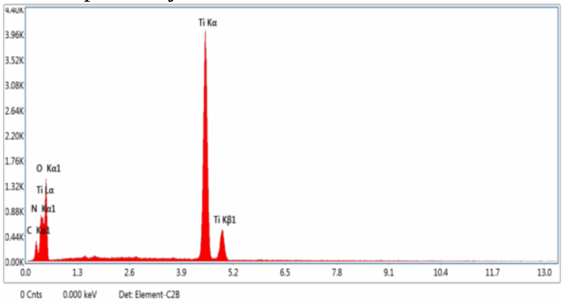
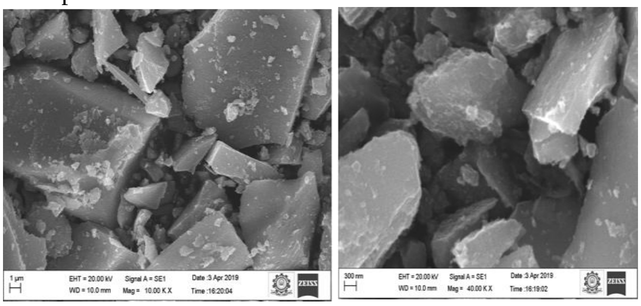


Fig. 2. EDX spectrum of synthesized TiO_2 nanoparticles.

C. *Surface Morphology by SEM Analysis*

The surface morphology of the synthesized nano TiO_2 was analyzed by scanning electron microscopy (SEM) and the corresponding SEM micrographs is shown in Fig. 3 (a&b). It shows that the uniform anatase phase TiO_2 crystallites with nano plate like structure.



(a) **(b)**

Fig. 3(a&b). SEM micrographs of synthesized TiO_2 nanoparticle.

D. *UV-Visible Spectral Analysis*

The optical properties of TiO_2 nanoparticles were studied by DRS-UV-Visible spectroscopy. The DRS–UV-Visible spectrum of TiO_2 nanoparticle is shown in Fig. 4. The UV-Visible absorption occurred at 376 nm for the synthesized TiO_2 nanoparticle. The absorption spectra of synthesized nano TiO_2 is matched with the previous reports.

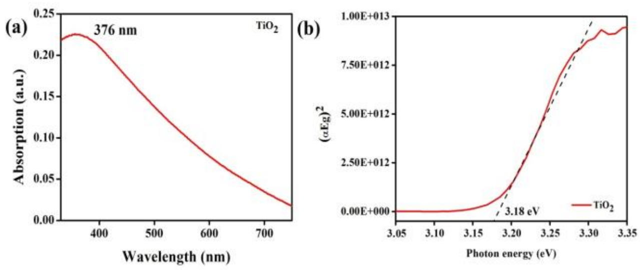


Fig. 4. (a) DRS-UV-Visible spectrum of TiO_2 nanoparticles and (b) Tacu's plot of TiO_2 nanoparticles.

The band gap energy (Eg) was calculated from the Tacu's plot for the synthesized nano TiO_2 was 3.18 eV. The band gap energy 3.18 eV signifies the energy gap between the valence band and conduction band [30]. Also, the energy required to promote a valence electron to the conduction band to free to move within the crystal lattice and to serve as a charge carrier to conduct electric current.

E. *FTIR Studies*

The FTIR spectrum for the synthesized nanoTiO_2 is shown in Fig. 5. The spectra showed the following characteristic peaks for nanoTiO_2, they are 3651.25 & 3674.39 cm^{-1}, 1541.12 & 1558.48 cm^{-1}, 1651.07 & 1701.22 cm^{-1} and 461& 501.5 cm^{-1} respectively. The peaks observed around 3650 cm^{-1} is due to the stretching vibration of the O-H group and the peaks observed between 1540 and 1700 cm^{-1} are due to the bending vibrations of the hydroxyl (O-H) groups.

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The peaks identified at 461and 501.5 cm^{-1} is due to the stretching and bending vibrations of Ti-O-Ti group [8].

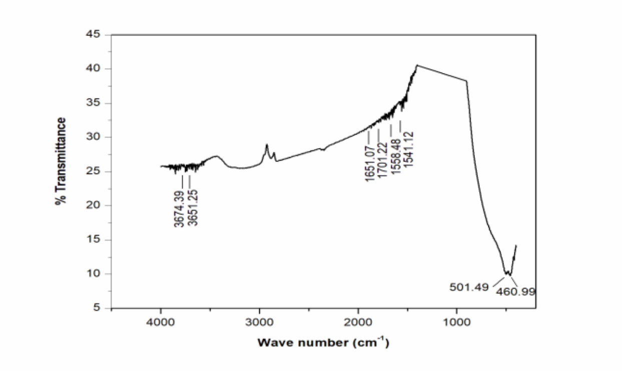

Fig. 5. FTIR Spectrum of TiO_2 nanoparticles.

IV. CONCLUSIONS

Nanosized TiO_2 was successfully prepared by sol-gel method and it is characterized by XRD, EDX, SEM, FTIR and DRS-UV-Visible spectral studies. The EDX analysis report confirms the presence of the elements Ti and O. The X-ray diffraction (XRD) analysis confirms the presence of anatase phase TiO_2 nanocrystallites. The measured grain size of nano TiO_2 was ~15 nm and the preferred orientation plane was (101). The band gap energy (Eg) value calculated from the DRS-UV–Visible spectral studies was 3.18 eV. The surface morphology of the nano TiO_2 was studied by SEM analysis, it shows that the uniform anatase TiO_2 with nano plate like structure. The results shows that the synthesized anatase phase nano TiO_2 was suitable for photo catalysis applications.

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