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Comparative Study on Titania Nanoparticles Synthesized by Mechanical, Sonomechanical and Sol-gel methods

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Abstract- Titania nanoparticles synthesized by three different methods like mechanical method (high energy ball milling or HEBM), sonomechanical method and sol- gel method. In this work, the high energy ball milling (HEBM) was applied to synthesize nanoparticles (NPs) of TiO_2 from its microcrystalline powder for 10, 20 and 30 hours respectively. The titania NPs also synthesized by sonomechanical and sol-gel method. Eventually, they were characterized by X- ray diffraction (XRD) and UV-Vis absorption spectroscopy. XRD results stated the complete phase formation of titania nanoparticles and comparatively correlated the crystal size. UV-Vis absorption spectroscopy determines the energy band gap of titania nanoparticles by using Tauc Relationship.

Keywords- Titania naoparticles, HEBM, Sonomechanical, XRD, UV-Vis absorption spectroscopySol-gel, Band gap, Optical properties.

1 INTRODUCTION

Nanoscale materials have very attractive properties, much attention due to their unique characteristics, which are not found in bulk materials. For instance, the reactions of NPs with other materials become more efficient due to their high surface-to-volume ratios, in addition to the high percentage of atoms at the grain boundaries. Some studies have found that in last three decades, the application of semiconductor heterogeneous photocatalysts, particularly titania (TiO_2) in the photo decomposition of toxic organic pollutants has been widely examined [1-3]. Titanium dioxide (TiO_2) has potential applications to remove stain or pigment. The nano sized titania act as catalytic, photocatalytic, dye sensitized photovoltaic cells, sensors and antimicrobial agent. Their use has always expanded for novel applications such as enhancement of self-sensitizing; self-cleaning and germ free tiles for hospitals, restaurants, kitchens etc. Coating of nano sized titania on glass, decomposes the organic molecules particularly on the glass i.e. self-cleaning capability [4]. Different methods have been developed for the synthesis of TiO_2 nanoparticles like chemical precipitation [5], hydrothermal crystallization [6], vapor phase condensation, sputtering, mechanical methods, sonomechanical methods and sol-gel methods. Various studies have beenreported for the synthesis of nanocrystalline materials by mechanical milling, mechanical alloying and mechanochemical processing [7]. Not long ago, mechanical milling has proved as a simple technique which can produce nanocrystalline powders in large quantities with modified properties [8-12]. In this paper we discuss the TiO_2 nanoparticles synthesis by mechanical, sonomechanical and chemical process in order to illustrate the influence of crystallite size.

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2 EXPERIMENTAL PROCEDURE

2.1 Synthesis

Commercially available TiO_2 powder (Otto 99.9%) was milled in steel jar of 250 mL by using the hardened balls of different sizes (05 mm, 10 mm and 20 mm) from 10 to 30 hours. Bulk 150gm of TiO_2 is taken in grinding jar and 75 mL methanol is added in bulk titania powder, therefore the paste of titanium dioxide is formed then 10 mm diameter of 50 balls are added in grinding jar, finally the grinding jar is clamped in ball mill machine for 10 hrs at 350 rpm with interval 1 hr and reverse rotation 10 minute. After the completion of 10 hour, material is placed in oven at 70 ^{0}c for 3 hrs. Further the process repeated by using same material and condition for 20 hrs and 30 hrs.

Sonomechanical method is more effective because the ultra sonic waves break down the weak forces and some chemical bonding present in the material, which cannot be break down by simple milling. In this process the ultra sonic waves are provided to the sample by the instrument ultra sonic processor and bath ultra sonicator. In this new type of sonomechanical synthesis first of all 50 gm of titanium dioxide is taken in 250 mL beaker then 30 mL of methanol is added, therefore liquid suspension is formed. This liquid suspension is placed for 30 minute for ultra sonication with amplitude 40%, pulse 0.5- 1.0. After that the grinding of material takes place by ball milling.

Sol-gel method is a one of the best technique known as chemical solution deposition. In this synthesis process 7.4 mL of titanium (IV) isopropoxide (alpha acer) was added drop by drop in 1M HNO_3 aqueous solution and then

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agitate the solution for 2 hrs. The addition of NaOH (1M) solution until the gel is formed, then dilution of colloid with water. The colloidal suspension was agitated at room temperature and centrifuged and then washed with distilled water. The isolated gel was dried for overnight at 100 ^{0}c in oven. Therefore the titania nanoparticles were synthesized in powder form.

2.2 Characterization

Crystallite size and structural properties of the samples (TiO_2 unmilled, HE ball milled, sonomechanical and sol-gel) were determined by X-ray diffraction (XRD) using Rigaku-Miniflex X-ray diffractometer with Cu Kα radiations (λ = 1.5406 A0) in 2θ range from 20^0 to 70^0 with scan rate of 2^0 per minute at room temperature. Lattice parameters were calculated by applying the equation:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

UV-vis absorption spectra for the samples were taken by Perkin Elmer Lambda 35 UV-visible spectrometer. The energy band gap was calculated by using Tauc relationship:

$$\alpha h\upsilon = A(h\upsilon - Eg)^n \qquad (2)$$

For titania nanoparticles the absorption coefficient (α) is obey the above relation with n = 2 (for indirect allowed band gap semiconductor).

3 Result and Discussion

3.1 Structural Properties

Typical XRD patterns of titania nanoparticles synthesized by HEBM, sonomechanical and sol-gel recorded at room temperature is shown in Fig 1 & 2. The peak position of Fig. 1 samples (nanoparticles synthesized by HEBM) exhibit rutile phase and tetragonal structure of TiO_2, which were confirmed from the ICDD card No. 84-1284, no other impurity peak was observed which confirming the formation of single phase materials. Fig. 2 (nanoparticles synthesized by sonomechanical and sol-gel) exhibit anatase phase and tetragonal structure of TiO_2, which were confirmed by ICDD card No. 84-1286 without any characteristic peaks of impurities, revealed the single phase formation of the materials. The crystallite size of all samples was calculated by using Scherrer formula [13].

$$D = 0.9\,\lambda/\beta\cos\theta \qquad (3)$$

Where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ. The calculated crystallite size of the materials is given in Table 1 and 2. The variation in crystallite size, lattice parameters, cell volume and molecular volume of different samples of TiO_2 (rutile) nanoparticles is shown in Table 1. It is observed from Table 1 that the material taken for high energy ball milling (HEBM) was rutile in nature and the crystallite size of TiO_2 (rutile) nanoparticles reduced from 42.14 nm to 26.93 nm as a result of increasing ball milling time. As time was increased, prominent decrease in size was observed for first 10 hrs but when ball mill was further used for another 20 hrs in two steps for 10 hrs each, the change in size was megre or insignificant i.e. size decreased from 30.47 nm to 28.16 nm to 26.93 nm. When ball mill was further used there was no change in size at all. It is aurged that for long run of ball milling nanoparticles got agglomerated due to generation of high heat. Table 2 shows the variation in crystallite size, lattice parameters, cell volume and molecular volume of different nanoparticles synthesized by sonomechanical as well as sol-gel method. The particle size was observed 8.85 nm and 3.22 nm for sonomechanical and sol-gel respectively. The crystallite size of titania nanoparticles reduced by using ultra sonic waves in sonomechanical process. Since, sonomechanical and ball milling are top down approaches and not proved to be very effective as compared to sol-gel method which is a bottom up approach. Sol-gel method is far economical and easy to handle with consuming very less time than sonomechanical and ball milling methods.

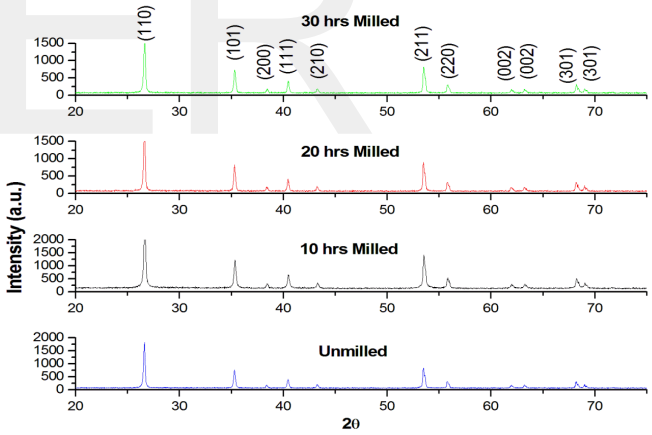

Fig.1. XRD pattern of unmilled and HE ballmilled (10 hr, 20 hr & 30 hr) TiO_2 nanoparticles.

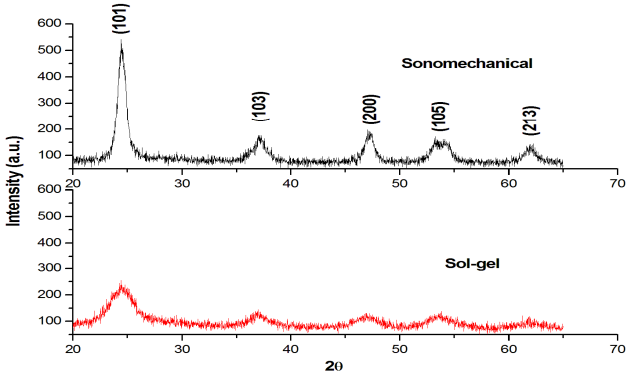

Fig.2. XRD pattern of sonomechanical and sol-gel TiO_2 nanoparticles.

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Materials	Crystallite size (nm)	Lattice parameter (a=b) (A^0)	Lattice parameter (c) (A^0)	Band gap (eV)	Volume/cell (A^0)^3	No. of molecules/cell	Volume/molecule (A^0)^3
TiO2 Unmilled	42.14	4.5931	2.9610	3.05	62.46694	2	31.23347
TiO2 10 hrs	30.47	4.5837	2.9536	3.15	62.05605	2	31.02803
TiO2 20 hrs	28.16	4.5827	2.9536	3.18	62.02897	2	31.01449
TiO2 30 hrs	26.93	4.5825	2.9534	3.20	62.01936	2	31.00968

Materials	Crystallite size (nm)	Lattice parameter (a=b) (A^0)	Lattice Parameter (c) (A^0)	Band Gap (eV)	Volume/cell (A^0)^3	No. of molecules/cell	Volume/molecule (A^0)^3
TiO_2 Sono mechanical	8.85	3.7988	9.5293	3.40	137.5161	4	34.3790
TiO_2 Sol-gel	3.22	3.7783	9.5116	3.58	135.7833	4	33.9458

Table- 1 and 2 Crystallite size, lattice parameter, band gap (Eg).

3.2 Optical properties

The properties of optical absorption are relevant to the electronic structure and features, hence are the key factors to determine the band gaps of semiconductor materials. The indirect band gap of TiO_2 nanoparticles of different samples were calculated by using Tauc relationship [14] as given below:

$$\alpha h\upsilon = A(h\upsilon - Eg)^n$$

Where A is a constant that depends on the properties of material, α is the absorption coefficient given by $\alpha = 2.303 (Ab/t)$, where, Ab is absorbance and t is the cuvette thickness (1 cm in present case), $h\upsilon$ is the photonic energy, Eg is the energy band gap. n has different values depends on electronic transition types, for a allowed direct transition n = ½, a forbidden direct transition n = 3/2, a allowed indirect transition n = 2 and for a forbidden indirect transition n = 3 [15, 16]. The plots of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for all six samples are shown in Fig.3.

The Tauc relationship was used to calculate the indirect allowed energy band gaps for all nanoparticles synthesized through different routes. The energy band gap for pure material (i.e. unprocessed) was observed to be 3.05 eV where as energy band gap increased for 10 hrs ball milled processed material and found to be 3.15 eV. There was no significant change in energy band gap for 20 hrs and 30 hrs ball milled processed material. It showed that there was no effect of ball milling after first 10 hrs and best particle size was observed after first 10 hrs only. The material was further processed using sonomechanical method and energy band gap increased sharply and found to be 3.40eV but when sol-gel method was used to synthesize nanoparticles, the band gap was found to be 3.58 eV which was excellent and showed best possible nanoparticles.

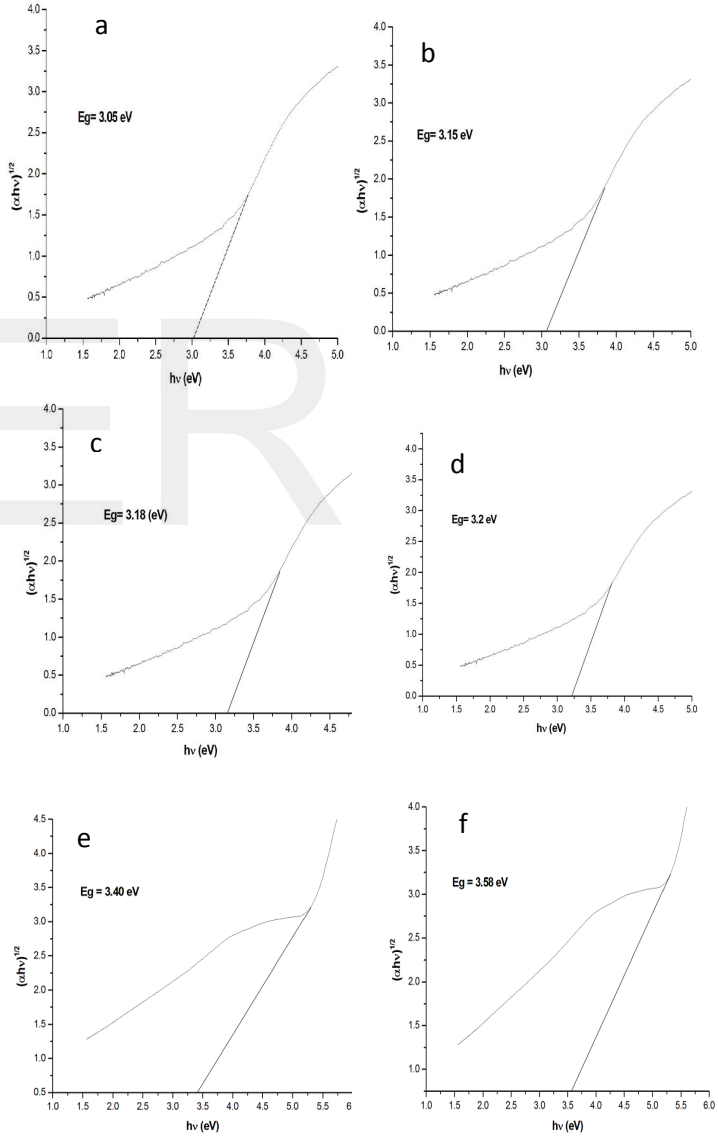

Fig- 3 Graphs (a-f) represent absorption spectra for Tauc relationship [$(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$] to calculate the indirect allowed energy band gap.

4 Conclusion

It is fairly logical that sol-gel method is far better approach to synthesize inorganic oxides nanoparticles [17-18] than sonomechanical and ball milling approaches. Also it is

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observed that top down approaches (e.g. ball milling & sonomechanical) are mechanical using high power and longer time than bottom up approaches (e.g. sol-gel method) which are easy to execute and handle with far less infrastructure.

In this study, we successfully synthesized TiO_2 nanoparticles of required sizes with well regulation in size control, where as in ball milling and sonomechanical methods size control is not so handy or practical.

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