

The Direct transition and not Indirect transition, is more favourable for Band Gap calculation of Anatase TiO₂ nanoparticles

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Abstract— In this study, anatase titanium dioxide nanoparticles were successfully prepared by a sol-gel method using Titanium Butoxide precursor. Hydrochloric acid was added to adjust the pH of the solution. The sols obtained were dried at 80°C and calcined at 400°C for 3hrs. The nanostructures were characterised by a Scanning Electron Microscope, FTIR, Ultraviolet Visible Spectroscopy. Highly crystalline anatase titania nanoparticles could be obtained through the controlled hydrolysis reaction rate. The sizes of synthesized particles were in the range 5 nm to 15 nm i.e. 10nm on an average and with a regular shape. The band gap is calculated for direct transition and indirect transition. Direct transition is found to be more appropriate for TiO₂ nanoparticles than indirect transition.

Index Terms—Titanium dioxide; nanoparticle; Sol-gel; band gap; SEM

I INTRODUCTION

Titanium dioxide (TiO₂) is a very useful semiconducting transition metal oxide material and exhibits unique characteristics such as low cost, easy handling, non-toxicity and resistance to photochemical and chemical erosion. The measurement of the band gap of materials is important in the semiconductor, nanomaterial and solar industries. The band gap of a material can be determined from its UV absorption spectrum. The term “band gap” refers to the energy difference between the top of the valence band to the bottom of the conduction band; electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy. An alternative strategy is to use layers of different materials coated onto the silicon base material. This is employed in the solar industry in the construction of photovoltaic (PV) solar cells. The bandgap is important as it determines the portion of the solar spectrum a photovoltaic cell absorbs. Much of the

solar radiation reaching the Earth is comprised of wavelengths with energies greater than the band gap of silicon. These higher energies will be absorbed by the solar cell, but the difference in energy is converted into heat rather than into usable electrical energy. Consequently, unless the band gap is controlled, the efficiency of the solar cell will be poor.

Using layers of different materials with different band gap properties is a proven way to maximize the efficiency of solar cells. In the semiconductor and nanomaterial industries, titanium dioxide (TiO₂, commonly known as titania) is added as an ingredient to coatings.

The band gap of the semiconductors had been found to be particle size dependent. The band gap increases with decreasing particle size and the absorption edge shifted to a higher energy (blue shift) with decreasing particle size.

A number of methods [1] such as chemical precipitation, microemulsion, hydrothermal crystallization and sol-gel have been used to enlarge specific surface area of TiO₂, mostly, by reducing the particle size down to nanoscale. Sol-gel is one of the most successful techniques for preparing nano-sized metallic oxide materials.

Shipra Mital Gupta Manoj Tripathi [1] have reviewed the most commonly used solution routes in the synthesis of TiO₂. The sol-gel method has been considered to be a promising route for the synthesis of powders for photocatalytic materials. TiO₂ nanoparticles have been prepared by a sol-gel method using different precursors such Titanium isopropoxide [2-12], Titanium tetrabutoxide [13,14,17,18], Titanium tetrachloride [20] and Titanium alkoxide [19]. Crystalline TiO₂ nanoparticles have also been synthesized by hydrolysis of titanium tetrabutoxide in the presence of acids in NP-5 (Igepal CO-520)–cyclohexane reverse micelle at room temperature [15,16]. Nanoparticles of TiO₂ anatase with mean size in the range 5–10 nm are prepared [20] by precipitation of TiCl₄ in aqueous medium in the range $2 \leq \text{pH} \leq 6$. The effect of gelling pH on the properties of the material is studied [8,11]. The synthesized nanoparticles are found to be of size 7-10nm [3] or of sizes between 10nm and 20nm [11], 0.1-0.5 μm with an

irregular particle shape [8] , and about 16 nm [13]. R. Vijayalakshmi and V. Rajendran [4] have found that the nanoparticles prepared via sol-gel route are highly crystalline and have smaller crystallite size (~ 7 nm) as compared to the one prepared by hydrothermal method (~ 17 nm) when prepared under the same ambient conditions viz temperature, pressure etc. and keeping all the parameters same viz precursors, mole ratio, solvent etc. Sanjeevkumar [9] has studied the size dependent reflective properties TiO₂ nanoparticles and found that on calcinations TiO₂ powder from 350 to 900 °C, the particle size increases from 60 to 150 nm and band gap decreases from 3.42 to 3.14 eV. Muneer [6] has investigated the effects of calcination temperatures on the crystalline structure, surface area and photocatalytic activity of TiO₂ nanoparticles. C. Su [17] has found that the crystal size of TiO₂ increased from 4 to 35 nm as the calcination temperature is increased from 400 to 700 °C. Effects of the pH value of the solution, H₂O₂ addition, TiO₂ phase composition and recycled TiO₂ on the photocatalytic degradation of methyl orange (MeO) in TiO₂ suspensions under ultraviolet (UV) illumination are primarily investigated [13]. The photocatalytic activity of titania is investigated [5] from the photodegradation of methylene blue solution under UVC irradiation. Dewi Tristantini, Slamet [12] have used Ultraviolet–Visible spectroscopy to explore the dispersion and stability of titania nanoparticles in an aqueous media with different types of dispersants. Funda SAYILKAN [10] has found that HCl, as a hydrolysis catalyst, plays an important role in the formation of the anatase crystalline form of TiO₂ at low temperatures.

II MATERIALS AND METHODS:

2.1 Materials:

All reagents used were of analytical grade purity and used as received, with no further purification. Titanium (IV)-n-butoxide (Ti(OBu)₄) (purity 98%) was used as a starting material and it was supplied by sigma-Aldrich company. Hydrochloric acid [HCl] was supplied by Highmedia and ethanol was supplied by Loba. De-ionized water was used for preparing all standard solutions.

2.2 Preparation of the sample using sol-gel route :

In this work, the precursor solution was a mixture of 5 ml titanium (IV)-n-butoxide (Ti(OBu)₄) and 50 ml ethanol .The mixture was stirred for 1 hr. The mixture of water, ethanol and HCl solution was then added drop wise into the first mixture. The reaction was performed at room temperature while stirring constantly for 3 hours. After aging for 24 hrs. the sol was transformed into gel. In order to obtain nanoparticles, the gel was dried under 80°C for 1 hr. to evaporate water and organic material to the maximum extent. Then the dry gel was sintered at 450°C for 3 hrs. to obtain desired TiO₂ nanocrystalline.

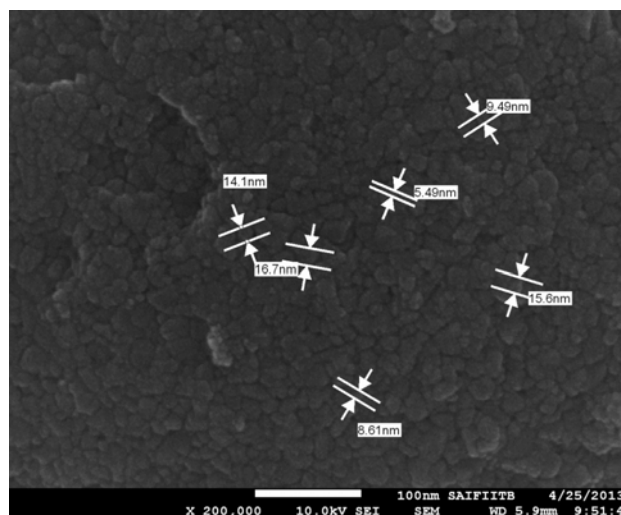
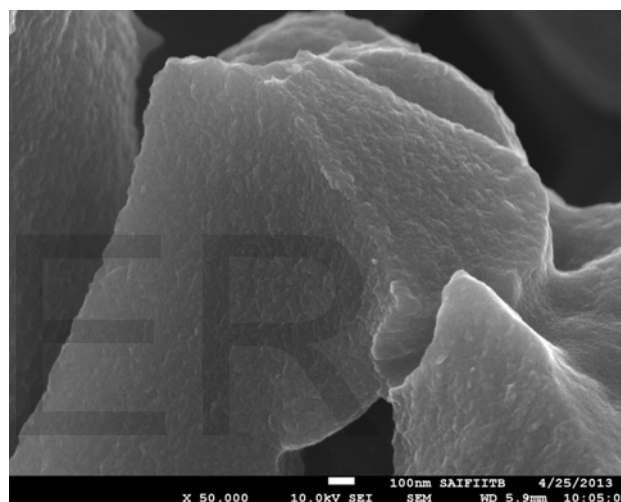
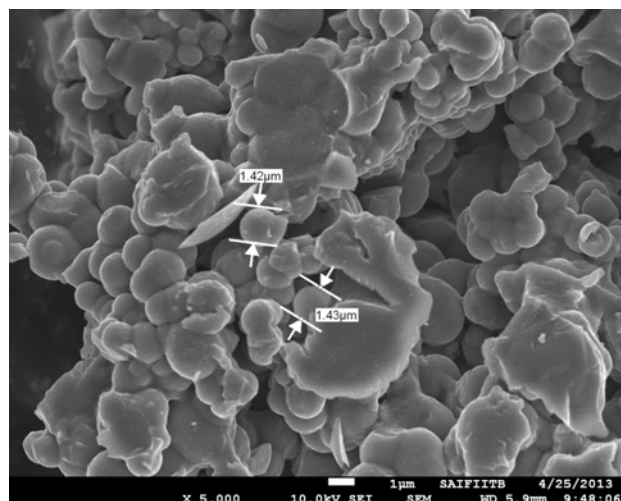


FIG. 1. SEM PICTURES OF SYNTHESIZED SAMPLE

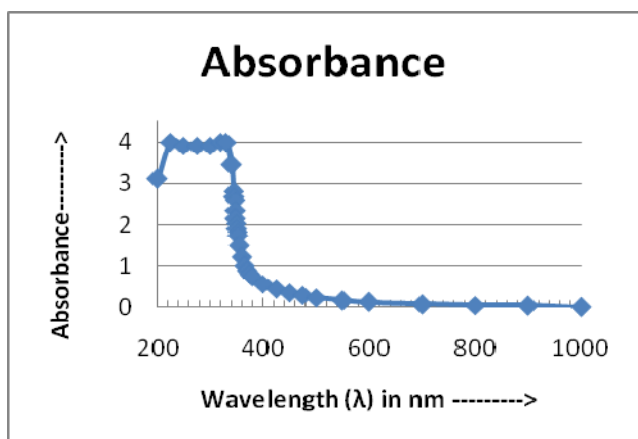


FIG. 2. VARIATION OF ABSORBANCE OF THE SAMPLE WITH INCIDENT WAVELENGTH

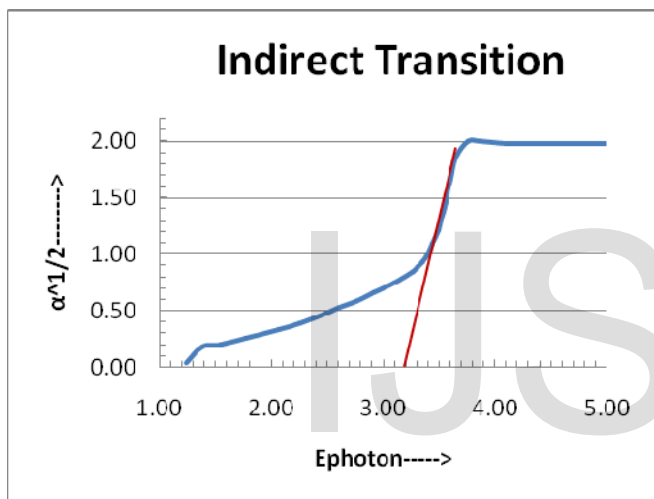


FIG. 3. PLOT OF $\alpha^{1/2}$ VERSUS E_{PHOT} FOR INDIRECT TRANSITION. BANDGAPS E_{G} ARE OBTAINED BY EXTRAPOLATION TO $\alpha = 0$.

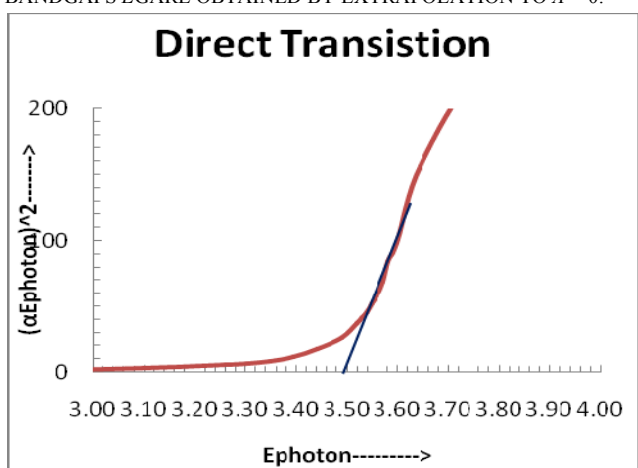


FIG. 4. PLOT OF $(\alpha E_{\text{PHOT}})^2$ VERSUS E_{PHOT} FOR DIRECT TRANSITION. BANDGAPS E_{G} ARE OBTAINED BY EXTRAPOLATION TO $\alpha = 0$.

The morphology and structure of the particles were investigated using Field Emission Scanning Electron Microscopy (JEDL JSM-7600F).

The FTIR analysis was done using MAGNA 550 Nicolet Instruments Corporation, USA.

The absorption spectra of the TiO₂ samples were measured by UV/Vis spectrophotometer equipped (Perkin Elmer (lambda 35) with an integrating sphere.

The prepared Nano particles were characterized for the crystalline structure using D8 Advance X-ray diffraction meter (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using CuK α radiation ($\lambda = 0.15406$ nm). The crystal size was calculated by Scherrer's formula.

III RESULTS AND DISCUSSION

3.1 SEM Analysis:

TiO₂ powder sample synthesized based on the different conditions are mentioned in Table 1. The SEM image studies of these samples demonstrates that the size, stability and morphology of the sol produced is not affected by the fact that whether titanium isopropoxide or titanium butoxide is used as a precursor. Also variation in the amount of water does not affect the size of particles synthesized. Also whether catalysts used is HCl or HNO₃ does not affect the particle size.

Table 1: Nanoparticle-crystallite sample preparation conditions

Precursor used	Amount of precursor	Amount of Ethanol	Amount of H ₂ O	Amount of acid	Particle size
Titanium tetra butoxide	2.5 ml	50 ml	1.25 ml	0.25 ml (HNO ₃)	8 nm to 16 nm

Fig. 1 shows SEM micrographs of the TiO₂ powders dried at 400°C for sample. The TiO₂ powder exhibits a homogeneous spherical morphology and a particle size distribution with sizes of 4 nm-16 nm. The particle morphology and particle size distribution show uniformity.

The broad view of the sample prepared using Titanium Butoxide shows spherical granules.

3.2 UV-Visible spectra

Firstly, to establish the type of band-to-band transition in the synthesized particles, the absorption data were fitted to equations for both indirect and direct bandgap transitions. Fig. 3 shows the $\alpha^{1/2}$ versus E_{phot} plot for an indirect transition and Fig. 4 shows the $(\alpha E_{\text{phot}})^2$ versus E_{phot} for a direct transition, where α is the absorption coefficient and E_{phot} is the photon energy, $E_{\text{phot}} = (1239/\lambda)$ eV, where λ is the wavelength in nanometers. The value of E_{phot} extrapolated to $\alpha = 0$ gives an absorption energy, which corresponds to a bandgap E_{g} . As

seen in Fig. 3 for indirect transition the sample shows a perfect fit and the extrapolation yields an E_g value of 3.2 eV which is in fact the bandgap of commercial titania and not nano titania. This is because for the samples with particle size 5–15 nm which is much less than the commercial particles (39 nm), there is always an increase in the bandgap energy. Hence their bandgap energy should be more than the 3.2 eV and not equal as observed in the present case.. The data, which is a much better fit than the corresponding indirect bandgap fit, result in values of E_g estimated from the $\alpha = 0$ extrapolation as 3.5 eV for sample . As can be seen from the different E_g values, the bandgap shifts estimated for the synthesized nanoparticles from the plots for indirect transition are too large and therefore it could be inferred that the direct transition plots are more appropriate.

This is the reason to suggest that the direct, and not indirect transition, is more favourable in anatase TiO₂ nanoparticles.

For direct bandgap semiconductors, electronic transition from the valence band to the conduction band is electrical dipole allowed and the electronic absorption as well as emission is usually strong. For indirect bandgap semiconductors, the valence band to the conduction band electronic transition is electrical dipole forbidden and the transition is phonon assisted, i.e., both energy and momentum of the electron–hole pair are changed in the transition. Both their absorption and emission are weaker compared to those of direct bandgap semiconductors, since they involve a change in momentum. Hence a direct bandgap transition would result in a more efficient absorption of solar energy and therefore much better photovoltaic devices. Hence, any indication in this direction would direct towards a more favourable material for the applications envisaged.

3.3 FTIR spectrum analysis :

- In the FT-IR spectrum (Fig. 4) of the collected precipitate, a broad peak appearing at 3100–3600 cm^{-1} (precisely at 3432 cm^{-1}) is assigned to fundamental stretching vibration of O–H hydroxyl groups (free or bonded) [28].
- The band at 2920 cm^{-1} is assigned to C-H vibrations . The C-H can be attributed to the organic residues, which remain in TiO₂ even after calcination [2].
- Also, the sharp peaks centred on 1621, 1451, and 1080 cm^{-1} can be attributed to C=C (in unsaturated hydrocarbon dehydrated, such as butene, propene from precursors) stretching, -C-H (methyl or methylene) bending and -C-O stretching, respectively [24]. The shoulder observed at 690 cm^{-1} may have been due to the vibration of the Ti–O–O bond [28].
- The peak between 800 and 450 cm^{-1} is assigned to the Ti-O stretching bands.[6]

IV CONCLUSIONS

- The particle morphology and particle size distribution have shown uniformity.
- The broad view of SEM micrographs of the sample prepared using Titanium Butoxide has shown spherical granules.
- The absorption spectra of my synthesized TiO₂ sample has exhibited strong absorptions below 400 nm.
- The band gap value for the synthesized sample is 3.2 eV when calculated using indirect transition. This value is same as for bulk TiO₂ whose particle size is nearly 39nm.
- The band gap value for the synthesized sample is 3.5 eV when calculated using direct transition.
- The band gap value calculated using direct transition have validated my crystallite size results according to which smaller crystallite size should have larger band gap (8 to 13 nm, 3.5 eV).
- Thus the direct, and not indirect transition, is more favourable in anatase TiO₂ nanoparticles.

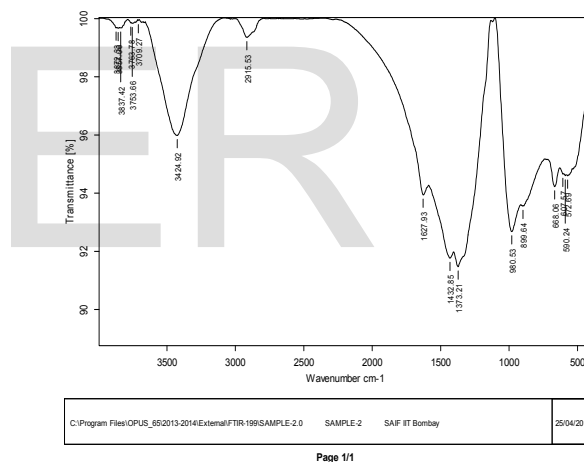


FIG. 5. FTIR SPECTRA OF NANO-TIO2

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REFERENCES

- [1] Gupta S. M.,Tripathi M.,”A review on the synthesis of TiO₂ nanoparticles by solution route”, *CEJC*,10(2),279-

- 294,(2012)
- [2] Yodyingyong S, *et al.*: Physicochemical, "Properties Of Nanoparticles Titania from Alcohol Burner Calcination", *Bull. Chem. Soc. Ethiop.*, 25(2), 263-272. ISSN 1011-3924, (2011)
- [3] Balachandran K., Venkatesh R., Shivraj R., "Synthesis of Nano TiO₂-SiO₂ Composite using Sol-Gel Method: Effect on Size, Surface Morphology and Thermal Stability", *IJEST, e-ISSN 0975-5462*, Vol.2(8), 3895-3700, (2010)
- [4] Vijayalaxmi R. and Rajendran V., "Synthesis and characterization of nano-TiO₂ via different methods". *Archives of Applied Science and research*, 4(2):1183-1190,(2012)
- [5] Vorrada Loryuenyong, Kunmutta Angamnuaysiria, Jidlada Sukcharoenponga, Athijit Suwannasria, "Sol gel template synthesis and photolytic behavior of anatase titania nanoparticles", *Science Asia* 38301-306,(2012)
- [6] Muneer M. Ba-Abbad^{1,*}, Abdul Amir H. Kadhum, Abu Bakar Mohamad, Mohd S. Takriff, Kamaruzzaman Sopian, "Synthesis and Catalytic Activity of TiO₂ nanoparticles for photochemical oxidation of concentrated Chlorophenols under direct solar radiation", *Int. J. Electrochem*, 7, 4871-4888, (2012)
- [7] Supan Yodyingyong, Chaiyuth Sae-Kung, Bhinyo Panijpan, Wannapong Triampo and Darapond Triampo, "Physicochemical Properties Of Nanoparticles Titania From Alcohol Burner Calcination", *Bull. Chem. Soc. Ethiop.* 25(2), 263-272. ISSN 1011-3924, (2011)
- [8] Pookmanee P. and Phanichphant S., "Titanium dioxide powder prepared by a sol-gel method", *J CERAM PROCESS*, Vol.10, No 2, pp.167-170, (2009)
- [9] Kumar S., Verma N.K., Singla M.L., "Size dependent Reflective properties of TiO₂ nanoparticles and Reflectors made thereof", *DIG J NANOMATER BIOS*, Vol 7, No.2, p.607-619, (2012)
- [10] Sayilkan F., Asilturk M. Sayilkan H., "Characterisation of TiO₂ Synthesized in Alcohol by a Sol-Gel Process: The Effects if Annealing Temperature and Acid Catalyst", *Turk J Chem* 29, 697-706, (2005)
- [11] Dewi Tristantini, Slamet, Rini Mustikasari, Widuri, "Modification of TiO₂ Nanoparticle with PEG and SiO₂ For Anti-fogging and Self-cleaning Application", *IJET-IJENS* Vol:11 No.2, (2011),
- [12] Safaei-Naeini Y., "Suspension Stability Of Titania Nanoparticles Studied By Uv-Vis Spectroscopy Method", *IJMSE*, Vol 9, Number 1, (2012)
- [13] Huaming Yang, Ke Zhang, Rongrong Shi, Xianwei Li Xiaodan Dong, Yongmei Yu, "Sol-gel synthesis of TiO₂ nanoparticles and photocatalytic degradation of methyl orange in aqueous TiO₂ suspensions", *Elsevier J. Alloys Compd*, ISSN: 0925-8388 413, 302-306, (2006)
- [14] Jing Tang, Franz Redl, Yimei Zhu, Theo Siegrist, Louis E. Brus, and Michael L. Steigerwald, "An Organometallic Synthesis of TiO₂ Nanoparticles", *Nano Letters* Vol.5, No. 3 543-5, (2005)
- [15] Dongbai Zhang, Limin Qi, Jiming Ma* and Humin Cheng, "Formation of crystalline nanosized titania in reverse micelles at room temperature", *J. Mater. Chem.*, 2002, 12, 3677-3680, (2002)
- [16] Dong Bai ZHANG, Li Min QI, Hu Min CHENG, Ji Ming MA, "Synthesis of Crystalline Nanosized Titanium Dioxide via a Reverse Micelle Method at Room Temperature", *CHINESE CHEM LETT*. Vol. 14, No. 1, pp 100 - 103, (2003)
- [17] Su C. Hong, B. Y., Tseng C. M., "Sol-gel preparation and photocatalysis of titanium dioxide", *Catalysis Today* 96 119-126, (2004)
- [18] Jeffrey C.S., Tseng H., Chang W.C., "Synthesis of titania-supported copper nanoparticles via refined alkoxide sol-gel process", *J NANOPART RES. Journal* ISSN: 1388-07643: 113-118, (2001)
- [19] Karami A., "Synthesis of TiO₂ Nano Powder by the Sol Gel method and its use as a Photocatalyst", *J IRAN CHEM SOC*. ISSN: 1735-207X, Vol. 7, Suppl, pp. S154-S160, (2010)
- [20] Agne's Pottier, Sophie Cassaignon, Corinne Chane' Franc, oise Villain, Elisabeth Tronca and Jean-Pierre Jolivet*, "Size tailoring of TiO₂ anatase nanoparticles in aqueous medium and synthesis of nanocomposites. Characterization by Raman spectroscopy", *J. Mater. Chem.*, 2003, 13, 877-882, (2002)
- [21] Lim C.H., *et al.*, "Reaction morphology and the effect of pH on the preparation of TiO₂ nanoparticles by a sol-gel method", *J CERAM PROCESS*. Vol. 11, No. 6, pp. 736-741, (2010)
- [22] Loryuenyonga V., *et al.*, "Sol-gel template synthesis and Photocatalytic behavior of anatase titania nanoparticles", *Science Asia* 38, 301-306, (2012)
- [23] Shinen M., Khalid I.A. Rasin F.A., "Preparation of Titanium Dioxide (TiO₂) Via the Sol-Gel Process.
- [24] Chaudhari V, Shrivastava A.K. and Kumar, "On the Sol-gel Synthesis and Characterization of Titanium Oxide Nanoparticles", *J. Mater. Res. Soc. Symp. Proc.* Vol. 1 Materials Research Society, DOI: 10.1557/opl.2011.759, (2011)
- [25] Reddy K.M., Sunkara V.M., Reddy A.R., "Bandgap studies on anatase titanium dioxide nanoparticles", *Elsevier, Materials Chemistry and Physics* 78 239-24, (2002)
- [26] Godnjavec J., *et al.*, "Stabilization of rutile TiO₂ Nanoparticles with Glymo in Polyacrylic clear coating" *Materials and technology*, 46, 19-24. ISSN 1580-2949, (2012)
- [27] Kokilal, P Senthilkumar V. Nazeer K.P., "Preparation and photo catalytic activity of Fe³⁺-doped TiO₂ nanoparticles", *Scholar research Library*, ISSN 0976-970, CODEN(USA): APRC 7
- [28] Gaoa Y., Yanfeng Gao, Yoshitake Masuda, Won-Seon Seo, Hiromichi Ohta, Kunihito Koumoto, "TiO₂ nanoparticles prepared using an aqueous peroxotitanate

- solution”,Ceramics International 30 , 1365–1368,(2004)
- [29] R. Vijayalakshmi and V. Rajendran: Synthesis and characterization of nano-TiO₂ via different methods, ISSN 0975-508X CODEN (USA) AASRC9

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