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PHASE CONTROLLING IN THE SYNTHESIS OF TIO_2 NANOSTRUCTURES BY LITTLE VARIATION OF REACTION CONDITIONS

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ABSTRACT

We have reported here, the formation of spherical shaped anatase (5-20 nm) and flower like rutile (100nm-400nm) TiO_2 nanostructure by hydrolysis of $TiCl_3$ in semi-aqueous reaction medium and drying and calcination of obtained sol.Two different structures have been obtained by little variation of reaction conditions namely usine and not using H_2O_2. Structure and size of synthesized particles have been characterized by XRD, TEM. Optical properties have been studied by absorption spectra.

KEYWORDS: Anatase andrutile TiO_2 Nanoparticles, Calcination, TiO_6 Octahedron

INTRODUCTION

Nanomaterials are at the foremost periphery of the developing field of commercial exploration of nanotechnology [1]. The advent of nanotechnology has accelerated the evolution of different nanomaterials with many exceptional size-dependent properties for use in several areas of human activity [1-4]. Titanium dioxide (TiO_2) is very well known multifunctional wide band gap semiconducting material having excellent size dependent tunable optical and photo catalytic property and less toxicity to human skin. Therefore, TiO_2 has immense application in pigments, photo catalysts, dye sensitized solar cells, water contaminant removers, antimicrobials and UV blocker in sunscreen cosmetics [5-6].

TiO_2 has several polymorphs like rutile, anatase and brookite of which the first two are commonly available in nature and easily producible in laboratory whilethe last one is less stable and less common in nature [7]. Anatase and rutile polymorphs of TiO_2can be explained to be composed of TiO_6 octahedrons joined by their edges in zigzag (anatase) and linear (rutile) fashion[8] (Figure-1.c&d). The Oxygen atoms are at the corners of the octahedrons while the Ti atoms are at centres. In both structures the Oxygen atoms are shared by neighboring octahedrons which ultimately make Ti to O ratio to be 1:2. In both structures the TiO_6 octahedrons are distorted from regular shape. In rutile there are two pairs of equal equatorial O-Ti-O bond angles, one pair of angles are$>90^o$while other pair of angles are$<90^o$, also equatorial and axial bond lengths are unequal (Figure-1.a). In anatase further asymmetry is introduced by displacement of O atoms from equatorial plane [8] (Figure-1.b).Rutile polymorph of TiO_2 is maximum closely packed and so have maximum stability. It has slightly smaller band gap (bulk rutile band gap ~3eV) as compared to that of anatase (bulk anataseb and gap ~3.2eV) [8].

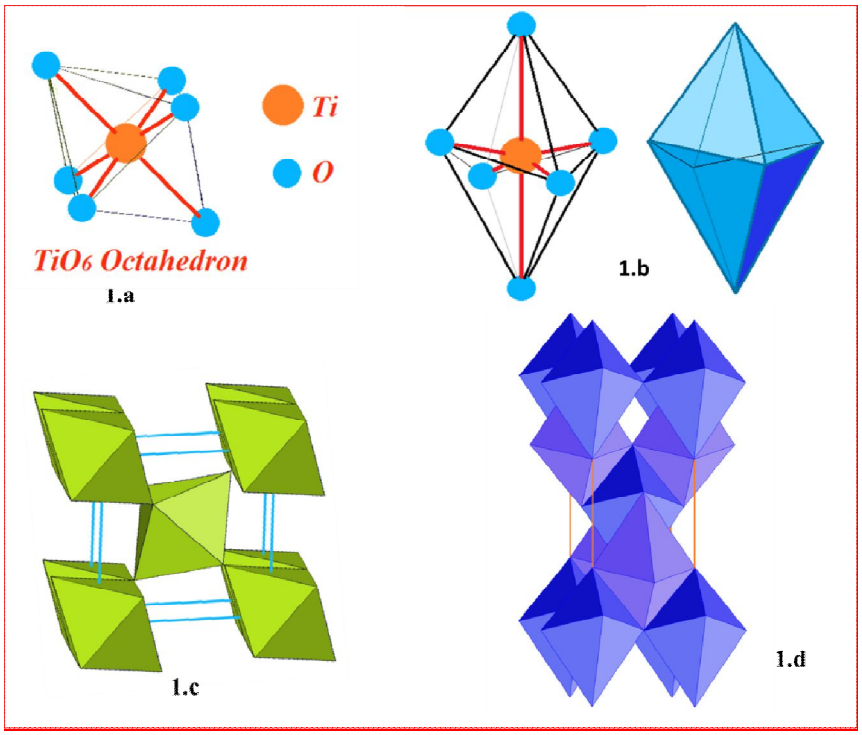

Figure 1: TiO_2 Structures: a-TiO_6 Octahedron of Rutile TiO_2; b- TiO_6 Octahedron of Anatase TiO_2, O Atoms Displaced from Equatorial Plane;c- Rutile Unit Cell; d- Anatase Unit Cell

TiO_2 nanoparticles are synthesized following different simple and complex routs of nanoparticle synthesis mechanism among which chemical methods are easier and cheaper. Aqueous medium has been employed in most cases of chemical synthesis and sol-gel method is a common technique [9-13].

Gel formation has an important role in crystallization of nano particles in sol-gel technique. In some researchers explained sol-gel synthesis of TiO_2 nano crystals by the steps like a) formation sol of Ti $(OH)_6$ by hydrolysis of chlorides or alkoxides of Ti, b) network formation of these octahedron shaped $Ti(OH)_6$molecules with water molecules as binding bridge during gel formation, c)evaporation of these water molecules, combination of $Ti(OH)_6$octahedrons leaving more water and formation of network of TiO_6 octahedrons during calcination (Figure-2). In the step c) the network formation of $Ti(OH)_6$octahedrons occurs in two different fashions – zigzag and linear –depending on the reaction condition. These zigzag and linear orientations are maintained in the next step d) and lead to anatase and rutile TiO_2 structures [17].

In our present work, we have followed a sol-gel like chemical synthesis process with $TiCl_3$ precursor using semi aqueous reaction medium where the sol has been dried and calcinated without giving any time or scope of formation of gel. The shape controlling of synthesized nanoparticles have been done by using or not using H_2O_2 in the reaction process.

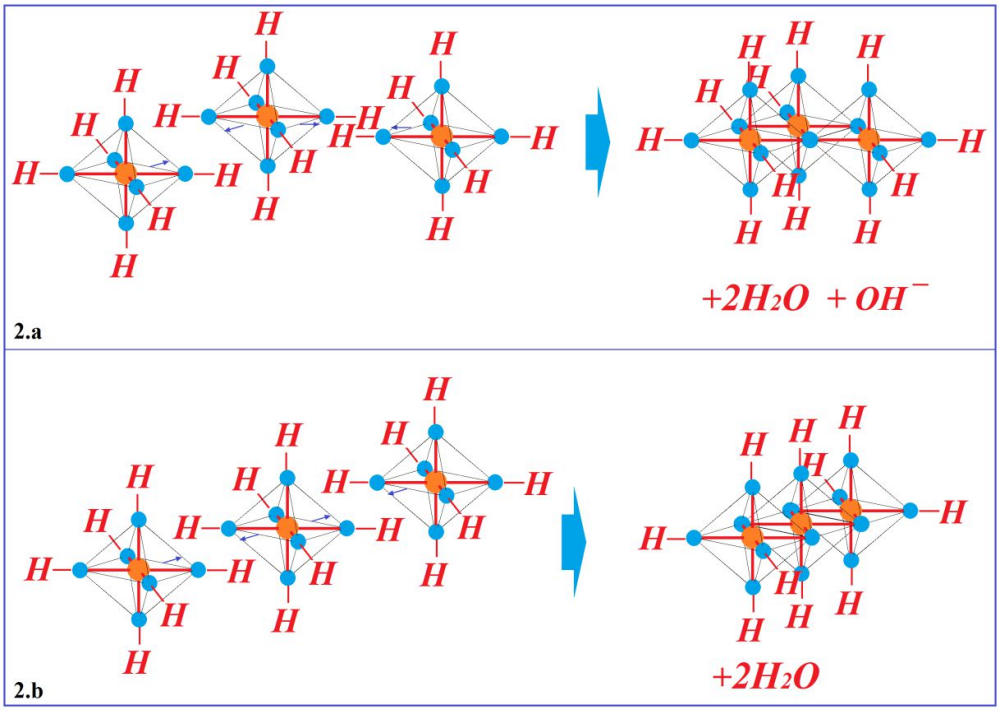

Figure 2: Formation of a) Anatase and b) Rutile TiO_2 Structures from TiO_6 Octahedrons. Asymmetry and Deviation of Octahedrons from Regular Shape are Not Shown

EXPERIMENTAL

$TiCl_3$ (12% solution in HCl) was purchased from Sigma Aldrich, USA. Ethyl Alcohol, NH_4OH and H_2O_2 were purchased from Merck, India. 5 ml $TiCl_3$ solution was mixed with 35 ml Ethyl Alcohol. The mixture was taken in a 150ml conical flask fitted with reflux condenser under moderate magnetic stirring. Temperature was increased gradually to 80°C under continuous stirring at same rate. Finally, 10 ml NH_4OH (25% solution) was added drop by drop. The stirring was continued for 3 hours at the same temperature. The reflux condenser was then removed but heating and stirring was continued for another half an hour. A thick white sol like substance [$Ti(OH)_4$/ $Ti(OH)_6$] was obtained which was dried in a petri dish on a hot plate at the same temperature i.e. 80°C in rest condition. The white solid was crushed and washed repeatedly first by ethanol and then by deionized water (for removal of chlorides). The obtained powder was calcinated at 300°C (sample-A) and 550°C (sample-B). Samples C & D were synthesized following the same route with only difference that 5 ml H_2O_2 was added drop by drop to the solution after adding NH_4OH. In this case just after adding H_2O_2 the solution becomes non transparent yellow [$HOOTi(OH)_3$], which gradually turns white [$Ti(OH)_4$ or $Ti(OH)_6$].No water was used separately in the reaction process except that remaining in the Ethyl Alcohol and NH_4OH solution.

The probable reactions are:

In the 1st route:

$$TiCl_3 + HCl + NH_4OH + H_2O + O_2 \rightarrow Ti(OH)_4 + NH_4Cl + H_2O$$

$$Ti(OH)_4 + OH^- \rightarrow Ti(OH)_6$$

$$Ti(OH)_6 \rightarrow TiO_2 + H_2O$$

In the 2nd route

$TiCl_3 + HCl + NH_4OH + H_2O + H_2O_2 \rightarrow HOOTi(OH)_3$ (yellow) $+ NH_4Cl + H_2O$

$HOOTi(OH)_3 + OH^- \rightarrow Ti(OH)_6 + H_2O$

$Ti(OH)_6 \rightarrow TiO_2 + H_2O$

The X-ray diffraction (XRD) study of the samples was done by using Rigaku Miniflex II desktop-X-ray diffract meter (40kV, 15mA) using Cu-kα radiation of wave length λ = 1.54 Å for 2Θ ranging from 10˚to 70˚.

The optical absorption spectra of the samples were recorded by using Shimadzu-Pharmaspec-1700 UV-VIS, after ultrasonication of the samples in water. The photoluminescence (PL) spectra of the as prepared samples were obtained by using Hitachi-F7000-FL spectrophotometer.

For micro structural study, small drops of ethyl alcohol dispersed samples were placed on a thin carbon film supported on the copper grids and kept for some time for drying. The high resolution transmission electron micrograph (HRTEM) of the prepared TiO_2 NPs was acquired using JEOL-JEM-200 operating at 200kV. The SAED pattern of the said NPs was also carried out.

RESULTS AND DISCUSSIONS

The XRD patterns confirmed the powder samples A and B to be anatase and C and D to be rutile TiO_2 crystals, after comparison with standard JCPDS data (JCPDS card no. 21-1272 and 21-1276 respectively) [14-15] (Figure-3). Height of XRD peaks increase with calcination temperature indicating increase in crystallization. Narrowing of peak width with increase in temperature indicates increase ingrain size. Also larger peak width and height for sample-C and Sample-D indicates larger size and higher crystallinity of nanoparticles synthesized in 2nd rout.

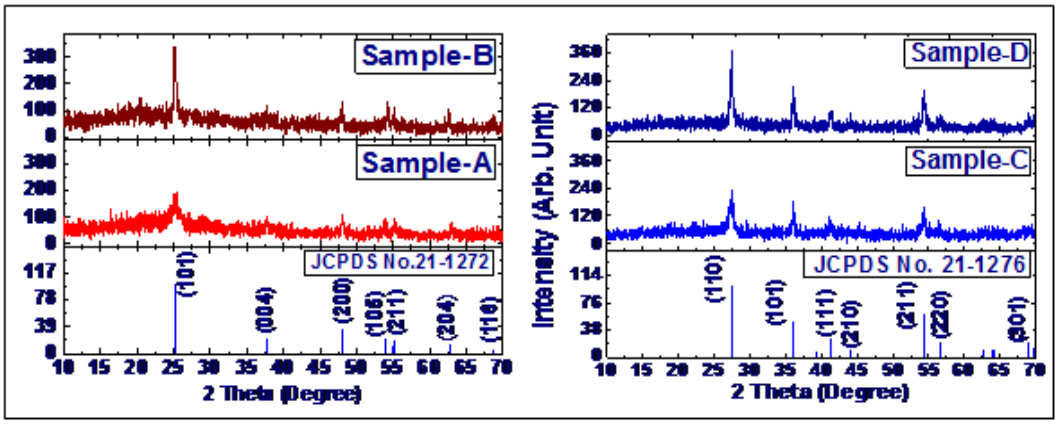

Figure 3: XRD Pattern of Synthesized Samples: Sample-A: Rout 1, Calcination Temperature 300°C, Sample-B: Rout 1, Calcination Temperature 550°C, Sample-C: Rout 2, Calcination Temperature 300°C, Sample-D: Rout 2, Calcination Temperature 550°C

TEM micrographs of sample A and B show the formation of spherical particles of diameter about 10 &20 nm (Figure-4A and B). The corresponding SAED patterns match those for anatase TiO_2 crystals. HRTEM shows formation of anatase single crystal and its characteristic (200) planes (Figure-4B.1).

TEM micrographs of sample C and D show the formation of rutile nanoflower like structures. The nanoflowers

are composed of nano-pencils of width about 40 nm and 60 nmand lengths about 100 nm and 400 nm respectively (Figure-4 C and D). The SAED patterns match those for rutile TiO_2 crystals. It is seen that increase in calcination temperature causes increase in particle size of the samples obtained by both routes. Also samples C & D synthesized in 2nd route are much larger than those synthesized in 1st route.

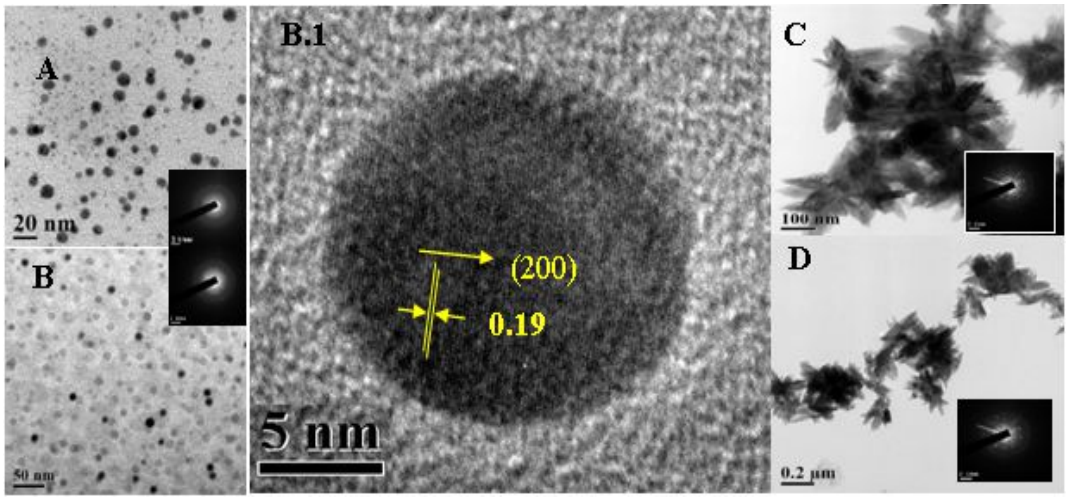

Figure 4: TEM Micrographs of A) Sample-A (Synthesis Route-1, Calcination Temperature-300°C); B) Sample-B (Synthesis Route-1, Calcination Temperature-550°C); C) Sample-C (Synthesis Route-2, Calcination Temperature-300°C); D) Sample-D (Synthesis Route-2, calcination Temperature-550°C);

The exciton absorption band maximum for samples A and B were found at 263nm and 318nm (Figure-5A and B). The exciton absorption band maximum for samples C and D were found at 362nm and 458nm (Figure-5C and D).

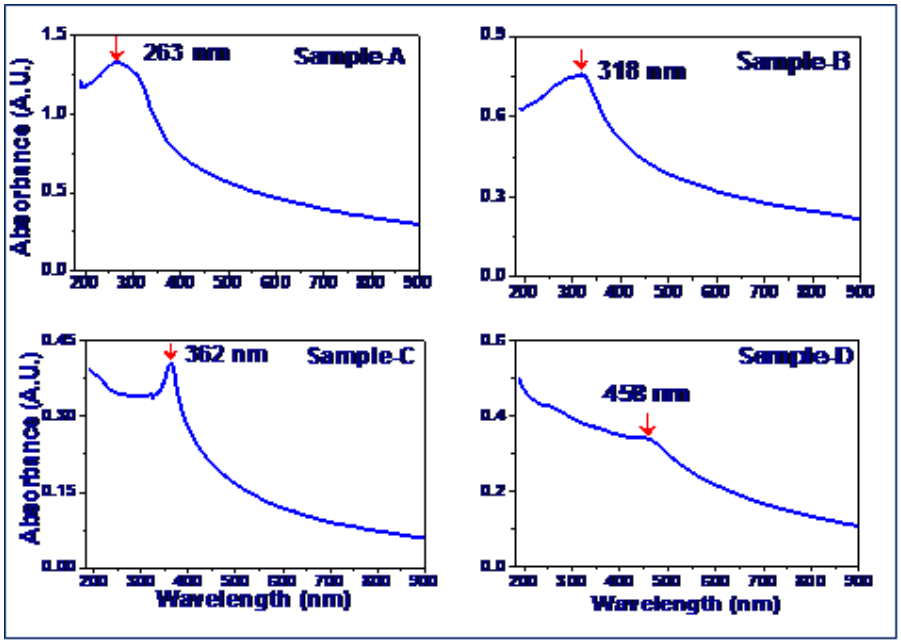

Figure 5: UV-Vis Spectra (Absorbance-Wavelength plot) for Samples A, B, and C &D

Using Tauc equation $(\alpha h\nu)^2 = C(h\nu - E_g)$ and plotting $(\alpha h\nu)^2 \; Vs. \; h\nu$ direct band gap of the samples A, B, C and D have been determined to be equal to 3.26eV, 3.02eV, 3.22eV and 2.98eV respectively[16] (Figure-6).

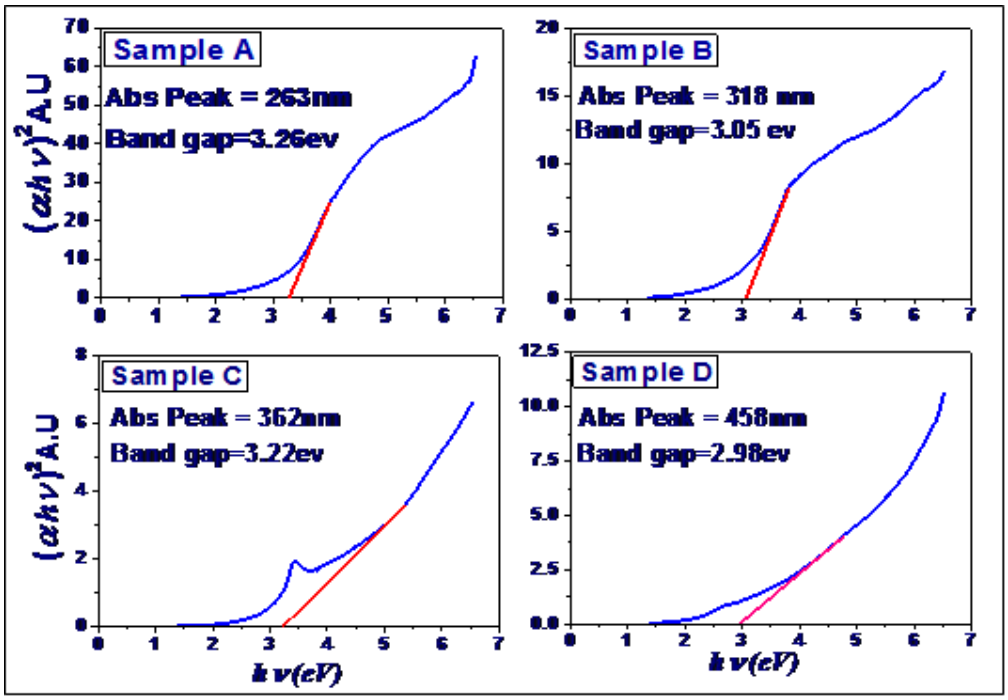

Figure 6: Direct Band Gap of Samples A, B, C & D Using Tauc Equation

Red shift in absorption maxima and decrease in direct band gap is observed with increase in calcination temperature. Also XRD and TEM analysis show that particle size increases with increase in calcination temperature. Thus smaller particles have higher band gap, which is expected as a result of quantum confinement.

Formation mechanism of anatase and rutile nanostructures: In the present synthesis no scope of gel formation from the sol, i.e. rest for hours or days, has been given. But formation of anatase and rutile nanostructures has been confirmed. This can be explained by assuming that combination of Ti (OH) $_6$ octahedrons occur in the time of drying and/or calcination to give TiO_2 nanoparticles. Use ofH_2O_2in the reaction process gives $HOOTi(OH)_3$at an intermediate step, while $Ti(OH)_4$ is obtained without usingH_2O_2. Ti (OH) $_4$ and HOOTi (OH) $_3$ have different structures and symmetry; so they should produce Ti (OH) $_6$ octahedrons of different degree of asymmetry relative to a regular octahedron. And this may lead to the difference in the combination style (zigzag or linear) of these octahedrons, giving two different TiO_2 polymorphs.

CONCLUSIONS

The formation of spherical shaped anatase (10-20 nm) and flower like (100nm - 400 nm) rutile TiO_2 nanostructures in simple chemical routes with semi-aqueous reaction medium has been confirmed. Gel formation step has been avoided and so the process is less time consuming and less costly. Different crystalline phases, namely rutile and anatase, have been obtained by little variation of reaction condition namely using and not using H_2O_2in the reaction process. Increase in percentage of crystallisation, increase in size, red shift in UV-Vis absorption spectra and decrease in band gap with increase in calcination temperature have been observed for both crystalline phases. Attempt to explain the mechanism of formation of two polymorphs has been done.

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REFERENCES

1. Mazzola L commercializing nanotechnology *Nat. Biotechnol.* 21 1137–43 (2003)
2. Vicki L Colvin the potential environmental impact of engineered nanomaterials *Nature Biotechnology* 21 1166-1170 (2003)
3. OV Salata Applications of nanoparticles in biology and medicine*J Nanobiotechnology* 2 1-6 (2004)
4. Shizhong Wang, Ruomei Gao, Feimeng Zhouand Matthias Selke Nanomaterials and singlet oxygen photosensitizers: potential applications in photodynamic therapy *J. Mater. Chem.* 1 4 487–493 (2004)
5. Daibin Kuang,Jérémie Brillet, Peter Chen, Masakazu Takata, Satoshi Uchida, Hidetoshi Miura, Kohichi Sumioka, Shaik. M. Zakeeruddin and Michael GrätzelApplication of Highly Ordered TiO2 Nanotube Arrays in Flexible Dye-Sensitized Solar Cells *acsnano* 2 6 1113–1116 (2008)
6. Yin ZF, Wu L, Yang HG and Su YH Recent progress in biomedical applications of titanium dioxide *Phys Chem Chem Phys*. 15 14 4844-58 (2013)
7. Tong Zhu and Shang-Peng GaoThe Stability, Electronic Structure, and Optical Property of TiO_2 Polymorphs*J. Phys. Chem. C* 118 21 11385–11396 (2014)
8. M Landmann, E Rauls and W G Schmidt The electronic structure and optical response of rutile, anatase and brookite TiO_2*J. Phys.: Condens. Matter* 24 19 5503 (2012)
9. Gupta S M and Tripathi M A review of TiO2 nanoparticles *Chinese Sci. Bull.* 56 16 1639-1657 (2011)
10. Gupta S M and Tripathi M A review on the synthesis of TiO2 nanoparticles by solution route *Cent. Eur. J.Chem.* 10 2 279-294 (2012)
11. Makoto Kobayashi, Hideki Kato and Masato Kakihana Synthesis of Titanium Dioxide Nanocrystals with Controlled Crystal - and Micro-structures from Titanium Complexes *Nanomaterials and Nanotechnology* 3 23 1-10 (2013)
12. R Vijayalakshmi Synthesis and characterization of nano-TiO2 via different methods *Archives of Applied Science Research*, 4 21183-1190 (2012)
13. Huaming Yang, Ke Zhang, Xianwei Li, Xiaodan Dong, Yongmei YuSol–gel synthesis of TiO2 nanoparticles and photocatalytic degradation of methylorange in aqueous TiO2 suspensions *Journal of Alloys and Compounds* 413 302–306 (2006)
14. Swarthmore, PA Joint Committee on Powder Diffraction Standards. Powder Diffraction File, Card No.21-1272
15. Swarthmore, PA Joint Committee on Powder Diffraction Standards. Powder Diffraction File, Card No.21-1276
16. R. López and R. Gómez Band-gap energy estimation from diffuse reflectance measurements on sol-

gel and commercial TiO2: a comparative study *Journal of Sol-Gel Science and Technology* 61 1 1-7(2012)

17. Y Masuda and kazumi KATO Synthesis and phase transition of TiO_2 nanocrystals in aqueous solution *Journal of Ceramic Society of Japan* 117 3 373-376 (2009)