International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Volume-2, Special Issue 1 (July-Aug 2014), PP. 61-64

EFFECT OF DIFFERENT ORGANIC SOLVENTS AND ANNEALING TEMPERATURES ON OPTICAL PROPERTY OF TIO_2 NANOPARTICLES

Pooja Agarwala[1,2], Vijaya Agarwala[1]
[1]Centre of Nanotechnology
Indian Institute of Technology Roorkee
Roorkee, India

Pooja Agarwala[1,2], Rajnish Garg[2]
[2]Centre for Nanotechnology -Materials Engineering University of Petroleum and Energy Studies
Dehradun, India

Abstract— **The main focus of present study is to establish the effect of boiling point of solvent on the nucleation and growth of TiO_2 nanoparticles which finally affects the particle size and consequently the surface area. Two types of titanium dioxide nanoparticles were synthesized by non-hydrolytic sol gel method. The effect of variations of annealing temperatures along with the presence of different organic solvents during the synthesis is studied in respect with particle size, absorption in visible range and band gap. The organic solvents used in this study were ethanol and benzyl alcohol. The particles were heat treated for 1 hour at 500°C when synthesized with ethanol and for 5 hours at 450°C when synthesized with benzyl alcohol. As synthesized nanoparticles were analyzed by DSC, XRD, FTIR, FESEM and UV-Vis spectroscopic techniques. Surface area and pore size was analyzed by BET. Similar XRD and IR patterns harmonized the presence of pure anatase phase in both types of TiO_2 nanoparticles. Morphological analysis by FESEM reveals that both types of nanoparticles are spherical in shape but the size is different. The average size for the particles synthesized with ethanol is 20-30 nm and for particles synthesized with benzyl alcohol is 40-60 nm. More surface area and better pore size was observed for smaller particles. It is noticed that the films fabricated by particles synthesized with benzyl alcohol demonstrate better absorption, better transparency, uniformity and fewer aggregate in comparison with that of the particles synthesized with ethanol.**

Index Terms— **TiO_2 nanoparticles, band gap, surface area, $TiCl_4$, UV-vis.**

I. INTRODUCTION

The extraordinary properties and dynamic applications of TiO_2 have made it an eye ball for many researchers across the globe. Different types of crystal densities in different phases of TiO_2 nanoparticles are the indispensable feature behind its interesting traits. It is known that TiO_2 nanoparticles exhibit three types of crystalline structures, i.e., rutile, anatase and brookite. Although anatase and rutile show tetragonal density of 3.894 g/cm^3 and 4.25 g/cm^3, respectively, brookite has orthorombic density of 4.12 g/cm^3 [1]. Its high refractive index, hydrophilicity, biocompatibility, semiconductivity, corrosion resistance, low cost and physiochemical stability are some of the properties which are highly desirable in the field of sensors, paint, cosmetics, photocatalytic and photovoltaic applications. Grain size, morphology and structure play an amicable part in deciding the role of TiO_2 nanoparticles for various applications.

For synthesis of TiO_2 nanoparticles to meet the actual demand, all these characteristics of nanoparticles are needed to be controlled at the time of synthesis [2]. Microstructure and morphology of product greatly depend upon selection of synthesis technique. It has been observed that the characteristics of nanoparticles like size, structure and morphology depend on ratio of reagents in solvent, temperature of reaction, calcination and pH of the solution. Many synthetic techniques have been used to synthesize TiO_2 nanoparticles like flame synthesis, ultrasonic irradiation, chemical vapour deposition [3], sulfate process, impregnation, hydrothermal methods [4] and sol-gel route. For enhancing mechanical properties and structurally stabilizing the product, thermal treatment is given after every synthesis.

Among all the techniques, sol-gel is the mostly used one, due to the advantages of being economical, easy and feasible. Sol-gel technique prevents co-precipitation, enables mixing at an atomic level and results in small particles which are easily sintered. The synthesis process in sol-gel technique is classified into two types, i.e., aqueous and non-aqueous sol-gel process. It has been seen that aqueous process becomes quite complex due to high reactivity of metal oxide precursors towards the water and double role of water as ligand and solvent. It leads to the strict control of large number of parameters, making the process tedious. Thus, non-aqueous sol gel processes are more in use for synthesis of nanoparticles in which organic ligand of precursors in solvent lead to in-situ formation of organic condensation products which act as oxygen suppliers for oxide formation [3].

In this study, it has been attempted to synthesize TiO_2 nanoparticles by non-aqueous sol-gel method using two different types of alcohols, i.e., ethanol and benzyl alcohol and their effect on nanoparticle size and optical properties has been investigated. The influence of higher boiling point on the mechanism of nucleation and growth of nanoparticles has been addressed. As synthesized TiO_2 nanoparticles were characterized by XRD and FTIR for particle size and phase confirmation, FESEM for ascertaining shape of the particles, BET for surface area and pore size calculations and UV-Vis to find out the band gap energy of the particles.

II. EXPERIMENTAL

TiO_2 nanoparticles were synthesized by adding $TiCl_4$ (Merck) drop wise in ethanol (Merck) and benzyl alcohol (Merck) separately at room temperature with continuous stirring in the ratio of 1:10. Reaction of $TiCl_4$ with ethanol resulted in light clear yellow solution and with benzyl alcohol a bright orange solution with white puffs was obtained. Reactions were left for aging at 70-85°C under constant stirring. The puffs which were formed during the synthesis mediated by benzyl alcohol were dissolved on aging. Colour of the solutions changed to milky brown and then off white after 24 hours of aging. A white amorphous powder was obtained in case of ethanol based synthesis which was then calcined in a furnace for 1 hour at 500 °C and coded as PA-1. In case of benzyl alcohol mediated synthesis a white dispersion was observed which was separated through a filter paper and then kept in oven for 80 °C for 12 hours. Once powder was dried, it was calcined at 450 °C for 5 hours in furnace [2]. As synthesized nanopowder was coded as PA-2 in the current study.

Thermal studies of dried TiO_2 nanopowders at different time were carried using TG/DTA (Perkin Elmer Diamond) in air at a heating rate of 10 °C /min up to 1000 °C. The phase analysis of TiO_2 powders were analyzed by X-ray diffraction (XRD) (D8 Bruker AXS diffractometer) with Cu target. BET surface area was measured by quantasorb surface analyzer. The surface morphology of calcined powders was carried out by scanning electron microscope, FESEM (Zeiss EVO-18). Particle size of the nanopowders were analyzed by XRD as well as FESEM images. The absorption spectra of the samples were studied with the help of UV–Vis–NIR spectrophotometer (Evolution 600, Thermo Scientific). Direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ vs. $h\nu$ using the absorption spectra [5].

III. Results and discussions

TiO_2 nanoparticles have been synthesized by using $TiCl_4$ as precursor with ethanol and benzyl alcohol separately at room temperature. Firstly, $TiCl_4$ reacts with alcohol and $TiCl_2(OH)_{4-X}$ was generated with the exhaustion of a large quantity of HCl gas. Produced species, i.e., $TiCl_2(OH)_{4-X}$, absorbs some amount of water from atmospheric moisture and Ti-OH is formed which generates …-Ti-O-….-Ti-OH strings. Hydrolysis process develops Ti-O-Ti strings and later $Ti(OH)_4$ molecules were formed. TiO_2 nanoparticles were generated as per the equation (1) [6, 1]:

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (1)$$

The DSC data of PA-1 and PA-2 is shown in Figure 1 and Figure 2, respectively, where green graph shows reaction thermodyanamics and blue graph represents weight loss. PA-1 exhibits the exothermic reaction and no endothermic reaction was observed. PA-2 shows exothermic reaction in the beginning only, which turns into the endothermic reaction later, on increasing the temperature. There is a constant weight loss observed in case of PA-1 with increasing temperature up to 500 °C after which it became stagnant. In case of PA-2 the weight loss is gradual from 100-1400 °C. There is a sudden weight drop of around 25.6 % at 245 °C, 29 % at 515 °C and then 49.4 % at 1289 °C in case of PA-2.

Figure 3 and Figure 4 depict the XRDs of PA-1 and PA-2, in which black graphs represent dried TiO_2 nanopowders synthesized by reactions of $TiCl_4$ with ethanol and benzyl alcohol, respectively. Since peaks are broad in these graphs, the amorphous structures of TiO_2 particles are portrayed. The particle sizes of both types of TiO_2 were calculated by Scherrer's equation. Much broader peaks of PA-1 than that is of PA-2 suggests that the particle size of PA-1 was smaller than PA-2 even before annealing (black graphs in Figure 3 and Figure 4). The larger particle size of PA-2 could be due to the much higher boiling point of benzyl alcohol (205°C) than that of ethanol (78.37°C) which facilitates more nucleation and growth of nanoparticles by allowing longer duration for the reaction to complete. Red graphs represent intensities of calcined TiO_2 nanopowders. In case of PA-1, after it was annealed at 500 °C for 1 hour, peaks became steep. The characteristic peak of anatase phase at 25.24 degree is observed which represents pure anatase structure (JCPDS-01-071-1167) of TiO_2 [7]. In case of PA-2, similar pattern of XRD graph is observed after the calcination of TiO_2 powder at 450°C for 5 hours, which confirms the presence of pure anatase phase (JCPDS-00-001-0562) [8]. The peaks in PA-2 XRD graph are more intense and the baseline is also clearer and more straight which portrays higher purity of anatase phase in PA-2 than that is in PA-1. This could be due to longer annealing of PA-2 than of PA-1.

The BET surface area of PA-1 was found to be 66.6200 m²/g with the pore size of 107.1184 Å and for PA-2 it was 40.0879 m²/g with the pore size of 74.1372 Å. The surface area and pore size of both the synthesized nanoparticles are correlated and in agreement with the particle size calculated by XRD analysis. Since the particle size of PA-1 is much smaller than that of PA-2, its surface area and pore size is observed to be much higher in comparison with PA-2.

The synthesis of TiO_2 anatase nanoparticles has also been confirmed by IR spectroscopy. IR pattern for TiO_2 nanoparticles synthesized by both types of alcohols are very similar and shown in Figure 5. The characteristic band of Ti-O bond at 548 cm^{-1} and 555 cm^{-1} for PA-1 and PA-2, respectively, assure the synthesis of TiO_2 nanoparticles as a result of both the synthesis. IR data is found to be coherent with the findings of XRD which ascertains the presence of anatase phase in both TiO_2 nanoparticles. It was observed that annealing for longer period of time led to significant sharpening of absorption bands in the region of 600-400 cm^{-1} in case of PA-2 and clearly indicates the formation of anatase phase. The absorptions at 1310 and 1410 cm^{-1}, recorded for the films prepared by PA-1, could belong to asymmetrical and symmetrical vibration of M-O-C groups [9, 10] and alkyl groups, respectively [11]. The absence of above-mentioned absorptions in case of PA-2 indicates relatively pure TiO_2 which could be resulted due to the longer calcination. The bands at 3560 cm^{-1} in case of both types of TiO_2 correspond to hydroxyl group (-OH bond) which are attributed to the atmospheric water or alcohol used during synthesis process. As the calcination time was increased to 5 hours for PA-2, the band corresponding to physically absorbed water narrowed than that in case of PA-1, shows the removal of water on longer annealing of PA-2 [12].

Figure 6 shows the pictures of the thin films prepared by spin coating the suspension of PA-1 and PA-2 on glass substrates. A good transparency of the film made by PA-2 and opaque surface of film made by PA-1 is observed. The reason behind such appearance of the films could be explained by FESEM images of the films which are shown in Figure 7 and Figure 8. The SEM images are taken of films spin coated by both types of nanoparticles (PA-1 and PA-2) at the same magnification on different glass substrates. Both nanoparticles show similarity in morphology i.e. both are spherical in shape. The average size is 20-30 nm for PA-1 and 40-60 nm for PA-2 nanoparticles. The agglomeration is very much significant in case of PA-1 and can be observed as big clusters of nanoparticles which are present all over unevenly. No such agglomeration is seen in the films made by PA-2. Films are uniform, with compact packaging of particles on the surface.

The absorption spectra of PA-1 and PA-2 are shown in Figure 9 which demonstrates that the absorption band is shifted to longer wavelength region in case of PA-2. The effective coverage of visible region extended from 350 nm in PA-1 to 400 nm in case of PA-2. Figure 10 gives an idea about the calculated band gap energies of both TiO_2 nanoparticles as 3.54 eV and 3.37 eV for PA-1 and PA-2, respectively. Increased band gap of PA-1 can be explained on the basis of effective mass model (EMM) of small semiconductor particles which was observed to increase as the particle size decreases [13, 14]. Such properties of small semiconductor particles have also been explained quantitatively by the tight binding model [15-17].

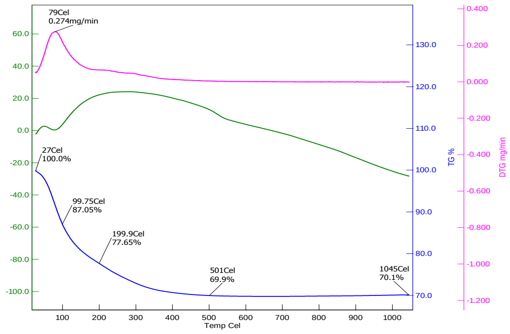

Figure 1: DSC analysis of TiO_2 nanopowder generated by reaction with ethanol.

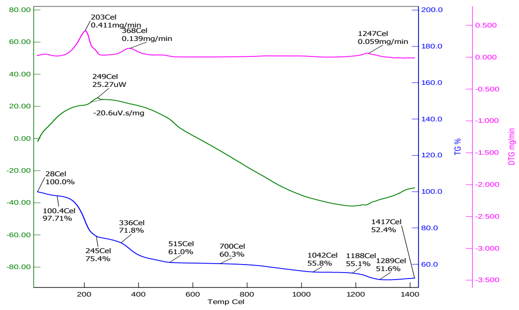

Figure 2: DSC analysis of TiO_2 nanopowder generated by reaction with Benzyl Alcohol.

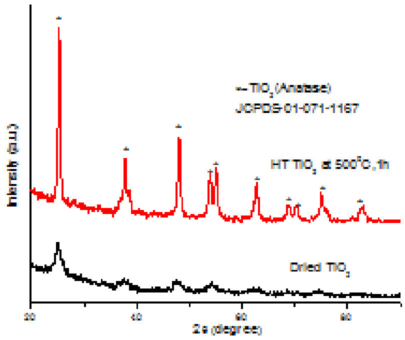

Figure 3: XRD analysis of TiO_2 nanopowder generated by reaction with ethanol.

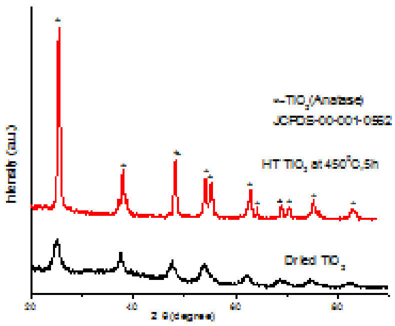

Figure 4: XRD analysis of TiO_2 nanopowder generated by reaction with Benzyl Alcohol.

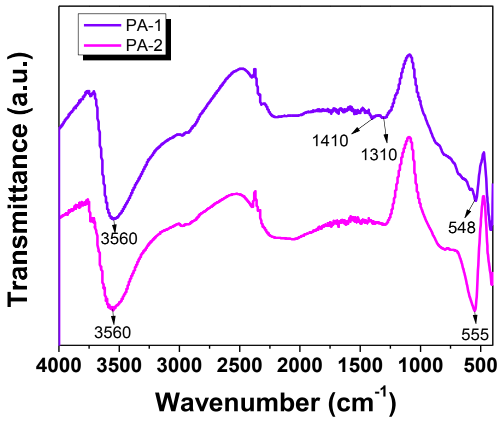

Figure 5: IR spectra of PA-1 and PA-2

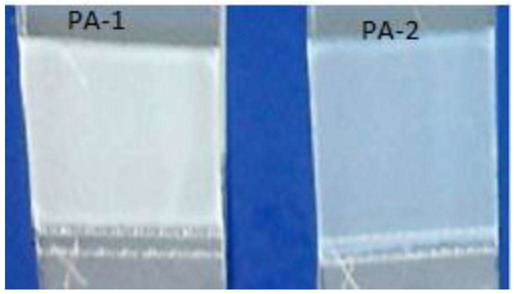

Figure 6: Pictures of spincoated films of PA-1 and PA-2.

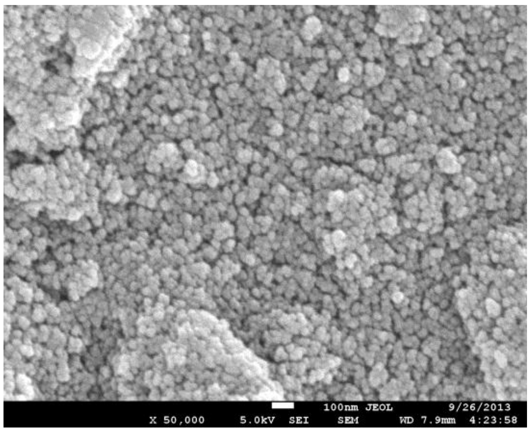

Figure 7: FESEM images of PA-1 nanoparticles

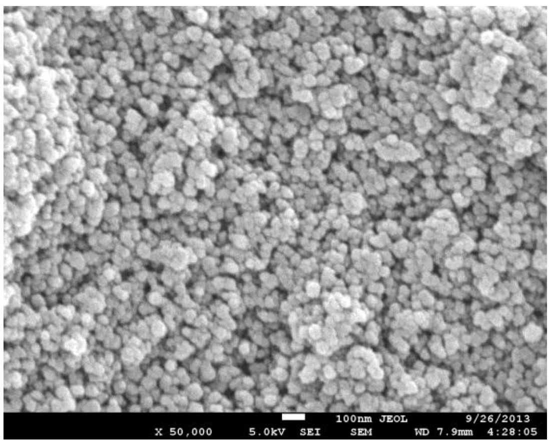

Figure 8: FESEM images of PA-2 nanoparticles

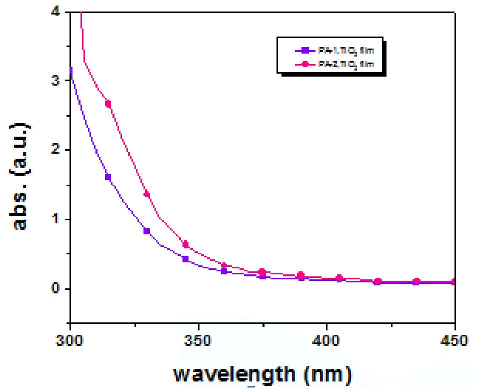

Figure 9: Absorption spectra of PA-1 and PA-2 films

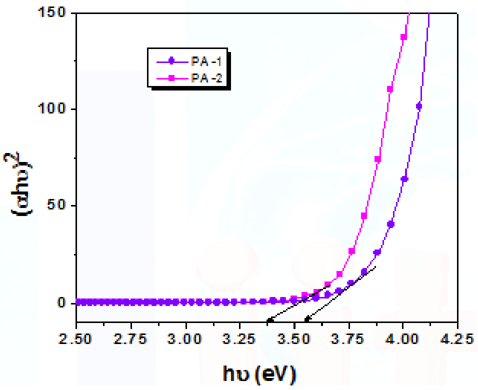

Figure 10: Band gap energy of PA-1 and PA-2.

IV. CONCLUSIONS

Present work evidences the effect of the boiling points of different organic solvents used during the synthesis of TiO_2 nanoparticles with $TiCl_4$ as precursor. Since the mechanism of reaction of $TiCl_4$ with ethanol and butyl alcohol is very straightforward and found to be opportune for the synthesis of TiO_2 nanoparticles, a lot of work has been done already. But this work deliberates the effect of high boiling of benzyl alcohol in comparison with the low boiling point of ethanol on the nanoparticle size and other properties. In short, the conclusion of the study is listed below:

- Benzyl alcohol with the boiling point 205 °C, when used with $TiCl_4$ as precursor creates the bigger sized nanoparticle than is comparison with ethanol having considerably low boiling point of 78.37 °C.
- The nanoparticles were formed in the particle size 20-30 nm and 40-60 nm with ethanol and benzyl alcohol, respectively.
- The BET surface area of the particles synthesized in this study is calculated as 66.6200 m²/g and 40.0879 m²/g with ethanol and benzyl alcohol, respectively. The pore size of 107.1184 Å and 74.1372 Å was observed.
- The threshold of spectra in UV-vis of the bigger particles is shifted towards longer wavelength in comparison with smaller particles from 350 nm to 400 nm.
- The band gap energy of bigger particles is more than smaller particles which is in harmony with previous findings.

ACKNOWLEDGEMENT

Authors acknowledge UCOST and Department of science and technology (DST) for funding.

REFERENCES

[1] Nasirian Shahruz, Milani Moghaddam Hossain, "Synthesis and size-control of TiO_2 photocatalyst nanoparticles preparation using sol-gel method", World Appl. Sci. J., 12 (11): 1981, (2011).

[2] Markus Niederberger, Michael H. Bartl and Galen D. Stucky, "Benzyl alcohol and titanium tetrachloride-a versatile reaction system for the nonaqueous and low-temperature preparation of crystalline and luminescent titania nanoparticles",Chem Mater, 14, 4364, (2002).

[3] Metal Oxide Nanoparticles In Organic Solvents, Aqueous and Non Aqueous Sol-Gel Chemistry (Chapter-2).K. Elissa, "Title of paper if known," unpublished.

[4] A. Ahmad, Gul Hameed Awan and Salman Aziz, "Synthesis and application of TiO_2 nanoparticles", Pakistan Engineering Congress, 70th Annual Sessions Proceedings.

[5] C. S. Pathak, V. Agarwala, "Synthesis and characterization of zinc sulphide nanoparticles prepared by mechanochemical route",Superlattices and Microstructures, 58, 135, (2013).

[6] Zhu,Y., L. Zhang, C. Gao, L. Cao,"The synthesis of nanosized TiO_2 powder using a sol-gel method $TiCl_4$ as a precursor",J. Math. Sci., 35: 4049, (2000).

[7] Roohollah Azizia, Sousan Rasoulib, Naghi Parvini Ahmadic, Amin Jafari jafar kolaeid and Mohammad Azizie," A systematic investigation of experimental conditions on the particle size and structure of TiO_2 nanoparticles synthesized by a sol-gel method", Journal of Ceramic Processing Research, 13, 2, 164, (2012).

[8] PDF Card #00-001-0562 PCPDFWIN Version 2 JCPDS-ICDD 2009.

[9] M. Burgos, M. Langlet," The sol-gel transformation of TIPT coatings: A FTIR study",Thin Solid Films Vol. 349, 19, (1999).

[10] O. Harizanov, A. Harizanova," Development and investigation of sol-gel solutions for the formation of TiO_2 coatings",Sol. Energy Mat. and Solar Cells Vol 63, 185, (2000),

[11] Y. Djaoued, R. Taj, R. Brüning, S. Badilescu, P.V., Ashrit, G. Bader, T. Vo-Van," Study of the phase transition and the thermal nitridation of nanocrystalline sol-gel titania films", J. Non-Cryst. Solids Vol. 297, 55, (2002).

[12] Xuchuan Jiang, Yuliang Wang, Jhruston Herricks and Younan Xia,"Ethylene glycol-mediated synthesis of metal oxide nanowires ",J. Mater Chem. 14, 695, (2004).

[13] Efros, AI. L.; Efros, A. L. Fiz.,"Interband absorption of light in semiconductor sphere", Tekh. Poluprovodn, 16, 1209, (1982).

[14] L. E.Brus," Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state", J. Chem. Phys., 80, 4403, (1984).

[15] Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. J. Chem. Phys., 87, 7375, (1987).

[16] Lippens, P. E.; Lannoo, M.," Calculation of the band gap for small CdS and ZnS crystallites",Phys. Rev. B, 39, 10935, (1989).

[17] Rama Krishna, M. V.; Friesner, R. A.," Quantum confinement effects in semiconductor clusters",J. Chem. Phys., 95, 8309, (1991).