International Journal of Advance Research in Science and Engineering
Volume No 06, Special Issue No. 03, September 2017, AFM-2017
www.ijarse.com
IJARSE
ISSN: 2319-8354

INVESTIGATION ON PHASE TRANSFORMATION OF TIO_2 NANOPARTICLES WITH DIFFERENT ANNEALING TEMPERATURES

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Abstract

Nanocrystalline TiO_2 nanoparticles was prepared via solution combustion method. Structural and optical variations based on the influence of different annealing temperatures were investigated. Phase transformation of TiO_2 nanoparticles were confirmed by XRD. Morphological information of the samples were obtained through SEM. Vibrational frequencies between the bonds of atoms for synthesized TiO_2 nanoparticles were analyzed by Fourier Transform Infra-Red (FTIR).UV-Visible spectroscopy helped in studying the influence of temperature on optical band gap of the samples. The study reveals that phase transformation decreases the band gap of corresponding sample.PL emission spectrum indicate that mixed phase shows remarkable luminescence than pure phase.

Keywords: Photoluminescence, nanopartcle, combustion method

I. INTRODUCTION

Titanium dioxide has received a lot attention due to its chemical stability, non-toxicity, low cost, chemical, thermal, optical, and dielectric properties[1-5]. Nanosized TiO_2 particles are ideal semiconducting materials for applications in the field of photocatalysis, gas sensors, pigments, paints, toothpaste, chemical sensors, microelectronics, electrochemistry, and solar cell etc. In nanoscale, large surface-to-volume ratios and quantum-size effect play an important role in controlling the properties of particles than their bulk counterparts[6-9].Titanium dioxide has been accepted as a polymorph materials because it can exist in three main structures, anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Among these anatase and rutile phase exhibit highest photocatalytic applications due to their high reactivity[10].Different preparation methods were used for the synthesis of TiO_2 nanoparticles such as sono-chemical method, electrochemical method, microwave irradiation, solid state reaction method, Sol-gel technique, thermal decomposition technique, Hydrothermal and hydrolysis techniques[11-14]. All of these methods, simple solution combustion method is an ideal method for rapid and easiest preparation of metal oxides nanoparticles in air at ambient pressure[15].

In the present study, we have made an approach to synthesis TiO_2 nanoparticle by solution combustion

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method followed by annealing at different temperatures.

Prepared samples are characterized by XRD,SEM,FTIR,UV-Visible and photoluminescence spectroscopy.

II. EXPERIMENTAL DETAILS

Here all chemical reagents used were of analytical grade. The Titanium isopropoxide and glycene were used as starting materials in this synthesis. Glycene used as fuel in solution combustion method. Titanyl nitrate solution was prepared by controlled hydrolysis of Titanium isopropoxide and distilled water forming titanyl hydroxide. It react with nitric acid gives tianyl nitrate. Chemical reaction occurred during the processes are given below:

$$Ti(OC_4H_9)_4 + 3\,H_2O \longrightarrow TiO(OH)_2 + 4\,C_4H_9OH$$

$$TiO(OH)_2 + 2\,HNO_3 \longrightarrow TiO(NO_3)_2 + 2\,H_2O$$

Titanyl nitrate and glycene were mixed with distilled water and stirred well using a magnetic stirrer for about 30 min. After it placed in a hot plate which boils and forming a highly viscous fluid. After certain time it catches fire and ignited with flames on the surface forming a white powdered product. The powder was annealed at temperatures of 200^0C,600^0C and 700^0C. The overall chemical reaction can be written as:

$$3TiO(NO_3)_2 + 5C_2H_5NO_2 \longrightarrow 3TiO_2 + 8N_2 + 5CO_2 + 10H_2O$$

Crystalline phases and to estimate the crystallite size of nanoparticles were identified by Bruker AXS D8 Advance with Cu target radiation (λ =1.5406 A^0).Morphology of nanoparticles were studied through JEOL, JSM - 6390LV Scanning electron microscopy. Functional group determination of the prepared samples are identified through a Fourier Transform Infra- Red (IR Prestige-21) Spectrometer in the wave number in the range of 400-4000cm^{-1}.Optical absorption spectra of synthesized samples were recorded by UV-2450 spectrophotometer. LS Fluorescence Spectrometer was used to measure emission spectra of nanoparticles.

III. RESULTS AND DISCUSSIONS

3.1.X-Ray Diffraction

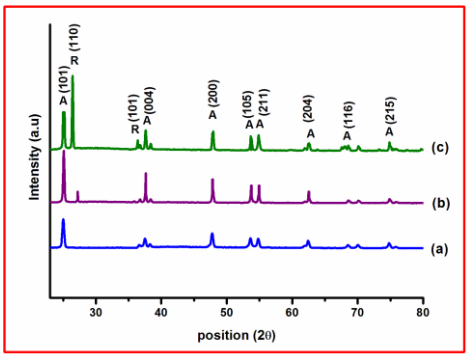

Fig1.XRD pattern of TiO2 nanoparticles annealed at (a)200^0C,(b)600^0C and (c)700^0C

Diffraction analysis provides detailed information on the crystal structure and phase purity of nanoparticles. Diffraction peaks at 25°, 37°, 48°, 54°, 55°, 62°, 69°, 75° corresponds to anatase phase of TiO_2 nanoparticles which are in consistent with the JCPDS file no. 861157 data. An additional diffraction peak at 36 ° appeared on increasing annealing temperature. It found to be in good agreement with those from JCPDS file no. 781510.It belongs to rutile phase of TiO_2 nanoparticles. Further annealing enhance the intensity of peak corresponding to rutile phase. It represents the anatase- rutile mixed phase of TiO_2 nanoparticles. The average crystallite size of nanoparticles were estimated by using Scherer equation[16]:

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

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Lattice parameter of TiO_2 nanoparticle can be determined by using the formula:

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

Weight fraction of anatase phase of TiO_2 nanoparticle was calculated by using the expression[17-18]:

$$X_A = \frac{100}{1 + 1.265\frac{I_R}{I_A}} \quad (3)$$

Where X_A is the weight fraction of anatase in the mixture, I_A and I_R is the integrated intensity of anatase (101) and rutile (110) peak respectively.

Table 1. Crystallographic parameters obtained from TiO_2 nanoparticles

Sample Detail	Calcination Temp.(^{0}C)	Lattice parameter (A^0)		Crystalline Size D (nm)	Anatase (%)	Rutile(%)	Band gap (eV)
		a = b	c				
TiO_2 nanoparticle	200	3.67	9.72	25.4336	100	_	3.3
	600	3.80	9.86	40.6969	92	8	3.29
	700	3.36	5.32	42.0497	40	60	3.28

Table 1 summarizes parameters obtained from XRD. Crystallite size increases during phase transformation from anatase to rutile phase. It indicate the enhancement in crystallinity with rise in annealing temperature[19].As listed in table 1,weight fraction of anatase phase decreases with rise in annealing temperature.Also weight fraction of rutile phase is higher in 700^0 C than that of 600^0C.This is because the phase conversion from anatase to rutile starts from 600^0C and increases with rise in annealing temperature.

3.2.Scanning Electron MICROSCOPY

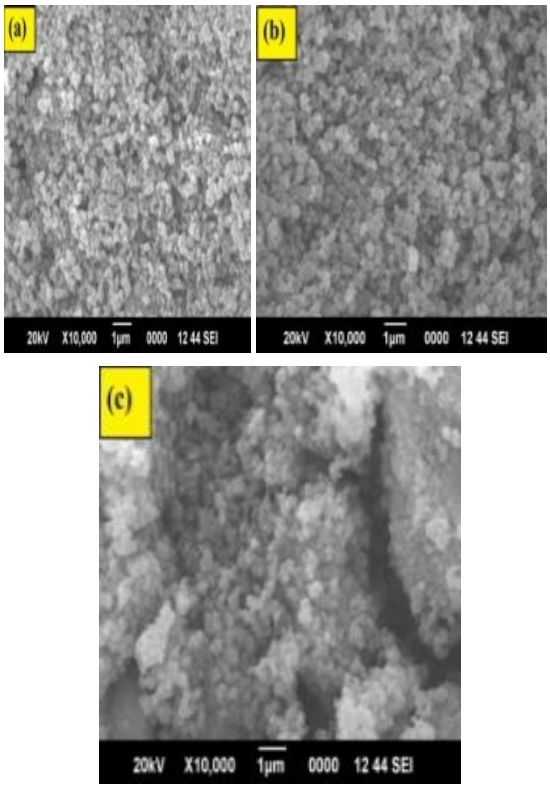

Fig2.SEM image of TiO2 nanoparticles annealed at (a)200^{0}C,(b)600^{0}C and (c)700^{0}C

SEM image taken for TiO_2 nanoparticles annealed at different temperatures are shown in fig2.Morphology revealed that nanoparticles appeared more like an assembly of spherical particles. Porous nature attributed to the liberation of liberation of large amount of gaseous products like H_2O vapours, CO_2 and N_2 during combustion process.

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3.3.FTIR Spectroscopy

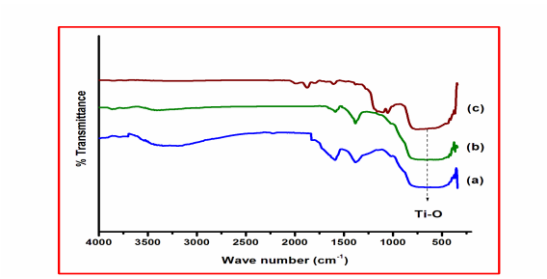

Fig3.FTIR pattern of TiO2 nanoparticles annealed at (a)200^{0}C,(b)600^{0}C and (c)700^{0}C

Various functional group present in the prepared samples are obtained through IR spectroscopy. Spectrum recorded in the wave number range of 400-4000 cm^{-1}.Fig 3 represents the FTIR pattern of TiO_2 nanoparticles.Frequency absorption band of Ti-O-Ti band lies in the range of 600-400 cm^{-1}[20]. Peak appearing at 595 cm^{-1} show stretching vibration of Ti-O bond.Peak observed at 3200 cm^{-1} and 1583 cm^{-1} corresponds to bending vibration mode of physically appeared water. Peak located at 1369 cm^{-1} due to C=O bending vibrations.As annealing temperature increases frequency absorption band corresponding to Ti-O bond get sharpened. It clearly indicate the phase transformation of TiO_2 nanoparticles from anatase to rutile.

3.4.UV-VISIBLE SPECTROSCOPY

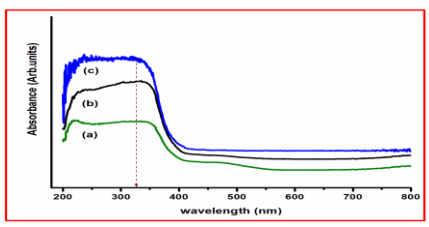

Fig4.Absorbance spectra of TiO2 nanoparticles annealed at (a)200^{0}C,(b)600^{0}C and (c)700^{0}C

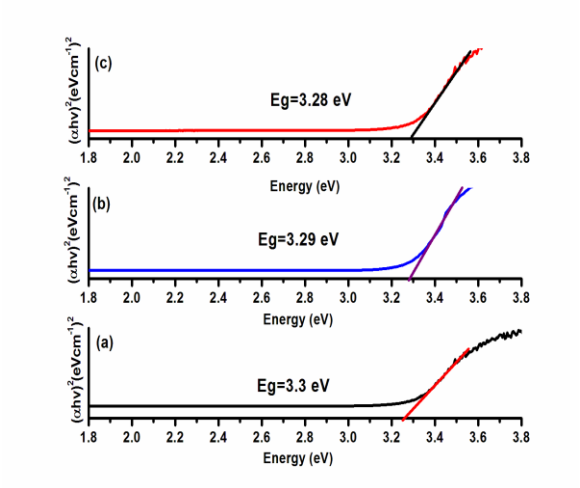

Fig5.Tauc plot of TiO2 nanoparticles annealed at (a)200^{0}C,(b)600^{0}C and (c)700^{0}C

The optical properties of the samples were characterized by UV absorbance spectroscopy. The optical absorption spectra of TiO_2 nanoparticles are shown in Fig 4.Optical absorption maximum lies in the range of 300-350 nm. As annealing temperature increases optical absorption edge shift towards higher wavelength region. This red shift may be due to change in the particle size[21-23].

The optical absorption co-efficient of prepared nanoparticles are expressed by the equation:

$$\alpha = A(h\nu - E_g)^n \quad (4)$$

Where α is the absorption coefficient, Eg is the absorption band gap, A is constant, n depends on the nature of the transitions, n may have values ½, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. In this case n=1/2 for direct allowed transition[24].Optical band gap of prepared samples are obtained by the plot of $(\alpha h\nu)^2$ vs (hν).Extrapolation of linear region to the X axis gives Eg. Nature of plot suggests a direct interband transition. Obtained band gap values corresponding samples are shown in Fig 5.It can be

seen that as increasing annealing temperature reduces the band gap of synthesized samples. Reduced band gap indicate the presence of relatively densily packed crystal structure. It is known that as crystallite size increases band gap decreases[25].

3.5.Photoluminescence Spectroscopy

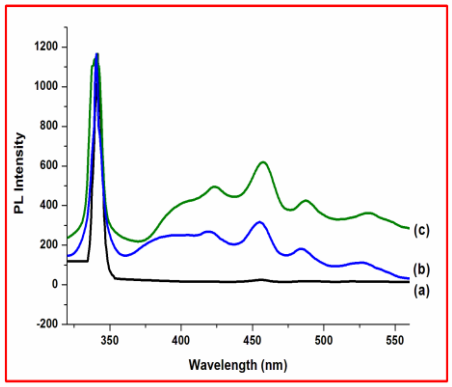

Fig6.PL spectra of TiO2 nanoparticles annealed at (a)200^{0}C(b)600^{0}C and (c)700^{0}C

The efficiency of charge carrier trapping and migration, and to understand the fate of electron-hole pairs in semiconductors can be investigated by PL spectra[26]. Fig 6 represents the PL spectra of TiO_2 nanoparticles annealed at different temperatures, at an excitation wavelength of 325 nm. Emission peaks are placed at 420 nm,455 nm,480 nm and 526 nm. Herewith most intense emission originated from 455 nm. It may be assigned to charge recombination at the shallow-trap surface state which act as radiative centers[27]. Violet emission originated from shallow traps with oxygen vacancies[28]. Self-trapped excitons localized on TiO_6 octahedral have also been identified at 480 nm[29]. Green emission may also due to the presence of oxygen vacancies. The band edge emission at 340 nm can be attributed to recombination of exitons [30].The PL intensity of anatase-rutile mixed phase is much more intense than anatase phase. It may due to increase in the rate of recombination of electron and holes in mixed phase[31].

IV. CONCLUSION

In summary,TiO_2 nanoparticles were successfully synthesized and characterized by solution combustion method. Phase transformation of TiO_2 nanoparticles from pure anatase to anatase-rutile mixed phase can be identified with increase in annealing temperature. Average crystallite size of nanoparticles increases during phase conversion. Morphological analysis can be achieved by SEM. Chemical bonding stability of Ti-O can be identified by FTIR spectroscopy. It can be seen that optical band gap of prepared samples decreases during phase change from anatase to rutile. PL intensity of mixed phase is higher when compared to pure phase. This wide band gap and efficient light emission nature of synthesized samples make suitable for solar cell and photocatalytic applications.

V. ACKNOWLEDGEMENTS

The authors are grateful to NIIST, Trivandrum and STIC, Cochin for providing facilities for the analysis of the prepared samples. The authors Bhagyalekshmi G L and Neethu Sha A P wish to acknowledge University of Kerala, Trivandrum for providing financial support for doing the research work.

REFERENCES

[1] E. Formo, E. Lee, D. Campbell, Y. Xia, Nano Lett. 8, 668–672,2008.

[2] S. Jeon, P.V. Braun, Chem. Mater. 15, 1256–1263,2003.

[3] J.B. Yin, X.P. Zhao, J. Phys. Chem. B 110,12916–12925,2006.

[4] K. Das, S.N. Sharma, M. Kumar, S.K. De, J. Phys. Chem. C 113, 14783–14792,2009.

[5] W.Q. Luo, R.F. Li, X.Y. Chen, J. Phys. Chem. C 113,8772–8777,2009.

[6] H.C. Choi, Y.M. Jung, S.M. Kim. Vibrational Spectroscopy. 37,33–38,2005.

[7] Yu-Chuan Liu, Ping-I Lin, Yit-Tsong Chen, Ming-Der Ger, Kuo-Lung Lan andChih-Lung Lin. J. Phys. Chem. B 2004, 108, 14897-14900.

[8] Yang ,Y.Hirose,S. Nakao, N.L.H. Hoang, Appl. Phys. Lett. 101, 052101 (2012).

[9] A. Lotnyk, S, Senz,D.Hesse, Thin Solid Films 515,3439–3447,2007.

[10] Z. He, Q. Cai, H. Fang, G. Situ, J. Qiu, S. Song, J. Environ. Sci. 25,2460–2468,2013.

[11] X. Quan, S.G. Yang, X.L. Ruan, H.M. Zhao, Sci. Technol. 39,3770 –3775,2005.

[12] Y.F. Zhu, L. Zhang, L. Wang, Y. Fu, L.L. Cao, J. Mater. Chem. 11 (2001) 1864–1868.

[13] H.R. Madan, S.C. Sharma, Udayabhanu, D. Suresh, Y.S. Vidya, H. Nagabhushana, H. Rajanaik, K.S. Anantharaju, S.C. Prashantha, P. Sadananda Maiya, Spectrochim. Acta Part A: Mol. Biomol. Spectro. 152,404–416,2016.

[14] H. Zhang, X. Quan, S. Chen, H. Yu, N. Ma, Chem. Mater. 21,3090 –3095,2009.

[15] M. Silambarasan, S. Saravanan, N. Ohtani and T. Soga,Jpn. J. Appl. Phys. 53, 05FB16 ,2014.

[16] H.P.Klug and L.E. Alexander,X-ray Diffraction Procedures for polycrystalline and Amorphous Materials.1974.

[17] R. Debnath and J. Chaudhuri, J. Mater. Res.7, 3348.1992.

[18] C.R. Hubbard, E.H. Evans and D.K. Smith,J. Appl.Cryst.9, 169,1976.

[19] Mohan Chandra Mathpal, Anand Kumar Tripathi, Manish Kumar Singh, Shiv Prasad, Gairola, S. N. Pandey, Arvind Agarwal, Chemical Physics Letters.2012

[20] Adawiya J. Haider, N. Zainab , Jameel, Y. Samar, Taha, Eng. &Tech.Journal.33,5, 2015..

[21] Y. Lei ,L.D. Zhang ,J.C. Fan , Chem Phys Lett. 338, 231,2001.

[22] K. Mogyorosi ,I. Dekany ,J.H. Fendler, Langmuir. 19, 2938-2946,2003.

[23] T. Wang ,H. Wang ,P. Xu ,X. Zhao ,Y. Liu ,S. Chao, Thin Solid Films.334, 103,1998.

[24] T.S. Moss, Optical properties of solids. 34,1961.

[25] R. J. Tayade, P. K. Surolia, R. G. Kulkarni, R. V. Jasra, Sci. Technol. Adv. Mater. 8, 455,2007.

[26] Y. Cong, J. Zhang, F. Chen, M. Anpo, D. He, J. Phys. Chem. C.111, 10618,2007. 2

[27] M. Yoon, M. Seo, C. Jeong, J. H. Jang, K. S. Jeon, Chem. Mater. 17, 6069,2005.

[28] N. Serpone, D. lawless, R. Khairutdinov, J. phys. Chem. 99,16646,1995.

[29] H. Tang, H Berger, P.E. Schmid, F. Levy, Solid state commun. 87,847,1993.

[30] A. Maurya, P. Chauhan, S. K. Mishra, R. K. Srivastava, J. Alloys and Comp. 509, 8433,2011.0

[31] J. Xu, L. Li, Y. Yan, H. Wang, X. Wang, X.Fu,G. Li, Journal of Colloid and Interface Science. 318,29–34, 2008.