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Structural and Optical Properties of Rutile Titanium Dioxide Nanoparticles Synthesized Using Titanium Tetra Isopropoxide as a Precursor

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***Abstract* - Nanoparticles of titanium dioxide was synthesized via chemical precipitation method using titanium tetraisopropoxide as a precursor and polyvinyl pyrrolidone (PVP) as a capping agent. The thermogravimetric analysis (TGA) of the samples were recorded and the phase transformation temperature of titanium hydroxide $Ti(OH)_4$ to titanium dioxide TiO_2 was noted to be at 800°C and were calcinated at this temperature to form TiO_2 nanoparticles. The synthesized nanoparticles were characterized by Field Effect Scanning Electron Microscopy (FESEM),X-Ray Diffraction (XRD), UV-Visible absorption spectroscopy (UV-Vis),Micro Raman spectroscopy, Fourier Transform Infra-Red spectroscopy (FTIR) and Photoluminescence spectroscopy (PL)techniques.The morphology of the prepared sample was studied using the Field Effect Scanning Electron Microscopy (FESEM). The X-Ray Diffraction peak well matched with the rutile phase of the nanoparticles of the titanium dioxide and average crystalline size was found to be 15nm.The optical and vibrational bands of the prepared samples were studied using UV-Visible spectrum and FTIR technique respectively. A strong emission peak was observed from the photoluminescence spectra of the recorded sample.**

Keywords: TiO_2 nanoparticles, chemical precipitation route, phase transformation.

I.INTRODUCTION

Metal oxides play an important role in the technological applications such as molecular sensors, piezoelectric devices, fabrication of electronic circuits, photovoltaic cells, solar cells, dielectric materials, semiconductor industry, chemical and petrochemical industries[1-5].The properties of bulk oxides differ from the nanoparticles of the metal oxides due to their limited size and exhibit unique physical and chemical properties[6-9].Nanoparticles of the titanium dioxide is a good photocatalytic material and it is suitable for many applications, including photonics, medicine, dye-sensitized solar cells(DSSC),antibacterial composition, controlled drug release, degrading organic contaminants and germs,cleaning ceramic and glasses, cosmetic products, long lasting soothing skin creams etc,[10-16].Hoffmann et al. and Wang et al.reported that the titanium dioxide is widely used due to its unique electrical and optical properties, high chemical stability, strong oxidizing power[17-18]. Zellen et al. reported that the titanium dioxide occurs in the anatase, brookite, rutile phases with refractive indices 2.488, 2.606, 2.583respectively[19]. The present study is an attempt to synthesis the nanoparticles of the rutile titanium dioxide through the hydroxide route using the titanium tetra isopropoxide as a precursor and polyvinyl pyrrolidone (PVP) as a capping agent and they are characterized by X-Ray Diffraction (XRD), Field Effect Scanning Electron Microscopy (FESEM), UV-Visible absorption spectroscopy (UV-Vis), Micro Raman spectroscopy, Photoluminescence spectroscopy (PL) and Fourier

Transform Infra-Red spectroscopy (FTIR) techniques.

II. EXPERIMENTAL

The chemical reagents collected were strictly analytical grade to synthesis the nanoparticles of TiO_2. Titanium isopropoxide was commercially purchased from the Sigma Aldrich Chemical Co.(97%) and other chemical reagents used in experiments were bought from the Merck India. Deionised water was used throughout the preparation of the nanoparticles of the titanium oxide.

2.1 Synthesis of TiO_2

A quantity of 15ml titanium isopropoxide was taken in a 250ml beaker and added to the 100 ml of isopropyl alcohol and well stirred for 30 minutes using the magnetic stirrer. To the mixture solution, 0.1gm of polyvinyl pyrrolidone was added and again stirred for 20 minutes and 10ml of deionised water was added drop wise to the mixed solution. A white precipitate of titanium hydroxide was formed which was refluxed for 2 hours and then it was further stirred continuously for a day. In order to remove the impurities, the precipitate was centrifuged with deionised water and ethanol. It was kept at 80°C for one day. Theprepared titanium hydroxide precipitate was annealed at 800°C to obtain TiO_2 nanoparticles.

2.2 Characterization techniques

The obtained samples were characterized byX-ray Diffraction patterns were recorded using a Philips Xpertpro Diffractometer and using CuKα radiation over the diffraction angles (2θ) from 20 to 80°. The Field Effect Scanning Electron Microscope images of the samples were recorded using Carl Zeiss Sigma HD FESEM. UV-Vis absorption and micro Raman spectra of TiO_2 nanoparticles were recorded using Varian, Cary 5000 spectrophotometerand Horiba Labram-HR, in the range of 100-1400 cm^{-1}respectively.The room temperature FT-IR in the range of 400-4000 $cm^{-1}$and photoluminescence(PL) spectra of the titanium dioxide nanoparticles were recorded using the Shimadzu FTIR-8400S spectrometerand JASCO FP 8200 Spectrofluorometer, respectively.

III. RESULTS AND DISCUSSION

3.1Field Effect Scanning Electron Microscope

The surface morphology of the nanoparticles of the titanium dioxide is examined by the FESEM is shown in the fig.1.The FESEM image of the nanoparticles of the titanium dioxide reveals that the nanoparticles show narrow size distribution and a little agglomeration.It may be due to the presence of the polyvinyl pyrrolidone, as the capping agent. The particle size is calculated by the line section method when it is in the range of 10nm which is very close to the grain size value calculated from the XRD pattern[20].

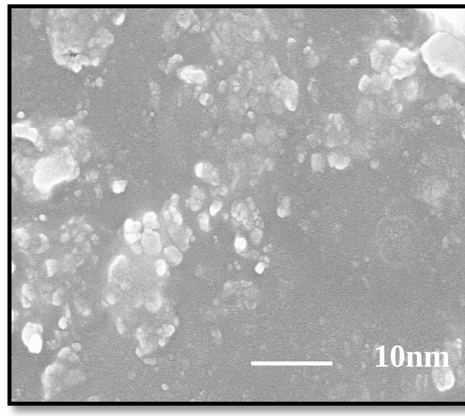

Fig.1 FESEM photograph of TiO_2 nanoparticles

3.2 X-ray Diffraction analysis

The powder X-ray diffraction(XRD) pattern of the nanoparticles of the titanium dioxide annealed at 800°C is shown inthe Fig.2. The figure shows diffraction peaks at 2θ values of 27.44°, 36.15°, 39.24°, 41.45°, 44.07°, 54.51°, 56.65°, 62.74°, 64.16°, 69.08° and 69.82°which is corresponding to the reflections from (110), (101), (200), (111), (210), (211), (220), (022), (310), (301) and (112) planes of TiO_2. The diffraction patterns show the presence of the broad peaks, is an indication of very small crystalline size[21].The obtained XRD peaks are compared with the standard JCPDS values(JCPDS card No. 89-4920)and all the diffraction peaks are assigned to the rutile phase of the titanium dioxide[22]. The average crystalline size is also calculated from the full width at the half maximum (FWHM) of the diffraction peaks using Debye–Scherer formula[23] and the grain size of the prepared titanium dioxide particle is found to be approximately 15nm.

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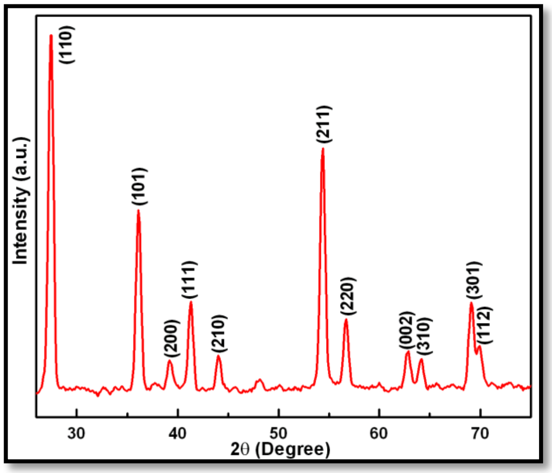

Fig.2 XRD pattern of TiO_2 nanoparticles

3.3 UV-Visible absorption analysis

The UV-Visible absorption spectrum of the nanoparticles of the titanium dioxide of the present study is shown in the fig.3. Absorption spectrum of the TiO_2 nanoparticles has recorded the wavelength ranges from 200 to 600 nm.The spectrum shows maximum absorption peakat 350 nm and the blue shifted indicating the quantum confinement effect.

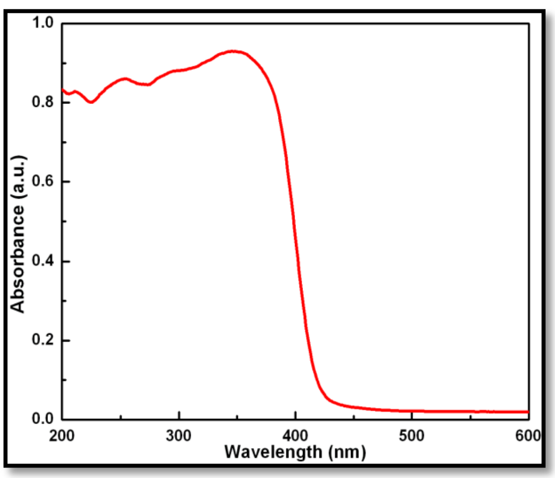

Fig.3 Absorption spectra of TiO_2 nanoparticles

A graph is plotted between$(\alpha hv)^2$ vs hv shown in the fig.6 to find the optical band gap of the nanoparticles prepared by the titanium dioxide and it is calculated as 3 eV which is low compared to the bulk band gap value of 3.84 eV. The change in the band gap of the nanoparticles of TiO_2 of the present study indicates that the bulk defects induce delocalization of the molecular orbitals in the conduction band edge and create deep traps in the electronic energy hence it red shift of absorption spectra [24 &25].

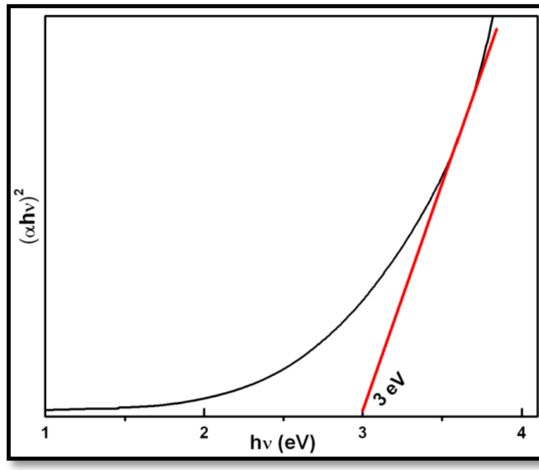

Fig.4 Band gap of TiO_2 nanoparticles

3.4 Photoluminescence analysis

The fig. 5 depicts photoluminescence spectrum of the titanium dioxide nanoparticles of samples recorded at the 450nm wavelength range. The emission peak shown at 438nm (2.84 eV) in the photoluminescence spectrum may be due to the surface defect emission. It is clear that there is a decrease in the particle size and also there is an increase in surface energy which may be ascribed to defect centres generated due to the oxygen related vacancies.

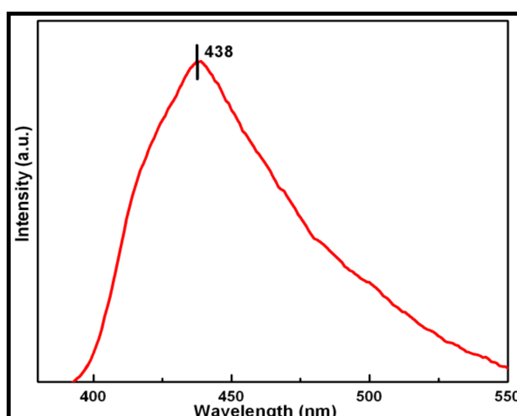

Fig.5 Photoluminescent spectrum of TiO_2 nanoparticles

3.6 Micro Raman analysis

The spectrum is typical of the rutile TiO_2 phase confirms the phase obtained from the XRD. The Eg peak at 444 cm^{-1} a characteristic of rutile TiO_2 is shifted with respect to those of the bulk TiO_2 crystal. The shift of the Raman peak observed in TiO_2 nanocrystal is attributed to phonon confinement effect that exist in the nanosized materials [26].The peak at 605 cm^{-1} corresponds to A_g rutile mode is influenced by the grain size of the TiO_2 nanocrystals, which shows red shift in frequency and increase in line width with a decrease of grain size[27].

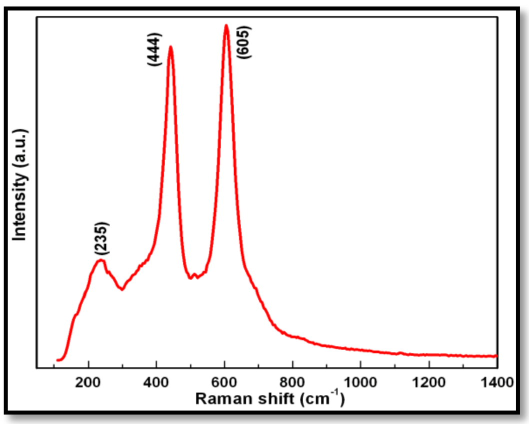

Fig.6 Micro-RAMAN spectra of TiO_2 nanoparticles

3.6 Fourier Transform Infra-Redanalysis

FT-IR spectrum of TiO_2 nanoparticles annealed at 800 °C in the range from 400 to 4000 cm^{-1} is shown in the Fig.7.FT-IR spectrumis confirmed due to the presence of a strong band around 550cm^{-1}which is in connection withthe characteristic modes of the TiO_2[28]. The absorption observed at 3410$cm^{-1}$is related to the presence of hydroxyl(stretching) which may be related to the spectrum which recorded some readsortion of water from the atmosphere[29]. The absorption at 1640 cm^{-1} may be due to hydroxyl(bending) groups of the molecular water[30].

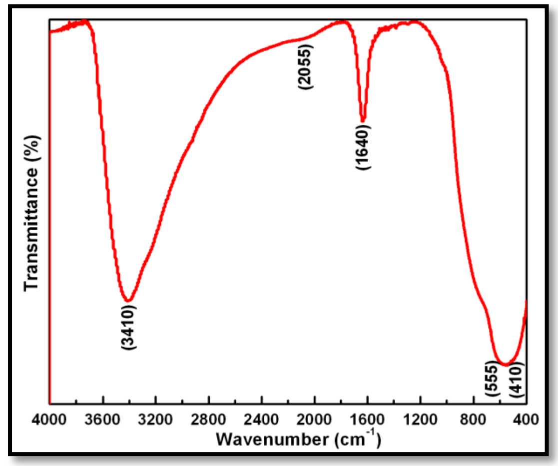

Fig.7 FTIR spectra of TiO_2 nanoparticle

IV. CONCLUSION

In the summary,nanopowders of the titanium dioxide is successfully synthesized by the chemical precipitation method using titanium tetra isopropoxide as a precursor and polyvinyl pyrrolidone as a capping agent. The prepared nanopowders are characterized by X-Ray Diffraction (XRD), Field Effect Scanning Electron Microscopy(FESEM), UV-Visible absorption spectroscopy (UV-Vis), Micro Raman spectroscopy, Photoluminescence spectroscopy (PL) and Fourier Transform Infra-Red spectroscopy (FTIR) techniques. FESEM image displays uniform morphology and narrow size distribution of the prepared sample.The XRD spectrum reveals the synthesized nanopowder is rutile phase of the titanium dioxide. UV-Vis absorption studies confirms the band gap is found to be blue shifted indicating the quantum confinement effect. The Photoluminescence spectrum indicates that the PL excitation is due to the oxygen related vacancies. FTIR spectrum shows the vibrational mode of titanium dioxide around 550 cm^{-1}.

References

[1] Kung H. H, Transition Metal Oxides:Surface Chemistry and Catalysis;Elsevier:Amsterdam,1989.
[2] Fernande GarciaM, Martinez-Arias,A; Hanson,J. C, Rodriguez J. A, Chem.Rev.vol.104,4063, 2004.
[3] Wells A.F, Structural Inorganic Chemistry, 6; Oxford University Press: New York,1987.
[4] Harrison W. A, Electronic Structure and the Properties of Solids, Dover:New York,1989.

[5] Henrich V. E and Cox P. A, The Surface Chemistry of Metal Oxides;Cambridge University Press:Cambridge,UK,1994.

[6]Valden,M.;Lai,X.;Goodman,D.W.Science1998,281,1647.
[7]Rodriguez,J.A.;Liu,G.;Jirsak,T.;Hrbek,Chang,Z;Dvorak,J.;Maiti,A.J.Am.Chem.Soc.2002,124,5247.
[8] Gleiter,H.Nanostruct.Mater.1995,6,3.
[9] Baumer,M.;Freund,H.-J.Progressin Surf.Sci.1999,61,127
[10] X. Shen, J.Zhangand B.Tian,J.Mater.Sci.,47(2012)3855.
[11] G.Tian,Y.Chen,W.Zhou,K.Pan,C.Tian,X.Huang and H.Fu,Cryst.Eng.Comm,13(2011)2994.
[12] L.Zhang,Q.Ding and Y.Zhou,Cryst.Res.Technol.,46(2011)1202.
[13] G.Wu,J.Wang,D.F.Thomas and A.Chen,Langmuir,24(2008)3503.
[14] Y.Wang,L.Zhang,K.Deng,X.Chen andZ.Zou,J.Phys.Chem.C,111(2007)2709.
[15] G.Plesch,M.Gorbar,U.F.Vogt,K.Jesenak and M.Vargova, "Reticulated macroporous ceramic foam supported TiO_2 for photocatalytic Applications," Material Letters Vol.63,No.3-4,pp.461-463,2009.
[16] S.Mahshid,M.Askeri,and M.S.Ghamsari "Synthesis of TiO_2 nanoparticles by hydrolysis and peptization of titanium isopropoxide solution",J.Mater.Prosess.Tech.,Vol.189,No.123,pp.296-300,2007.
[17] M.R.Hoffmann,S.T.Martin,W,Choi and D.W.Bahnemann, "Environmental Applications of Semiconductor Photocatalysis",Chem.Rev.,Vol.95,No.1,pp.69-96,1995.
[18] Wang W,GuB,Liang L,Hamilton W A,Wesolowski D J.Synthesis of Rutile(ὰ-TiO_2)Nanocrystals with Controlled Size and Shape by Low –temperature Hydrolysis:Effects of Solvent Composition.J.Phys.Chem.B.2004;108;14789-92.DOI;10.1021/jp0470952.
[19] Zallen R,Moret M P,The optical absorption edge of brookite TiO_2 .Solid State Commun.2006;137(3);154-157.
[20] C.Wang,Z.X.Deng,Y.Li,The synthesis of nanocrystalline anatase and rutile titania in mixed organic media,Inorg.Chem.40 (2001)5210-5214.
[21]C.L.Yeha,S.H.Yeh.,H.K.Ma,Powder Technol.145(2004)1.
[22] T. R. N. Kutty, R. Vivekanandan, and P. Murugaraj, "Precipitation of rutile and anatase (TiO_{12}) fine powders and their conversion to MTiO3 (M = Ba, Sr, Ca) by the hydrothermal method," *Materials Chemistry and Physics*, vol. 19, no. 6, pp. 533–546, 1988.
[23] L. K. Campbell, B. K. Na, and E. I. Ko, "Synthesis and characterization of titania aerogels," *Chemistry of Materials*, vol. 4, no. 6, pp. 1329–1333, 1992.
[24] L.Bras,J.Chem.Phys.80(1984) 4403-4409.
[25] L.Bras,J. Phys. Chem.90(1986)2555-2560.
[26]A. V. Prasada Rao, A. I. Robin, and S. Komarneni, "Bismuth titanate from nanocomposite and sol-gel processes," *Materials Letters*, vol. 28, no. 4–6, pp. 469–473, 1996.
[27] E. Scolan, C. Sanchez, Synthesis and characterization of surface-protected nanocrystalline titania particles, Chem. Mater. 10 (1998) 3217–3223.
[28] N. Steunou, F. Robert, K. Boubekeur, F. Ribot, C. Sanchez, Synthesis through an in situ esterification process and characterization of oxo isopropoxo titanium clusters, Inorg. Chim. Acta 279 (1998) 144–151.
[29]A.N.Jose,J.T.Juan,D.Pablo,R.P.Javier,R.Diana,I.L.Marta,Appl.Catal.,A Gen.178(1999)91.
[30]Y.Zhao, C.Li, X.Liu,F.Gu,H.Jiang,W.Shao,L.Zhang,Y.He, Synthesis and optical properties of TiO_2 nanoparticles.Mater.Letter.61(2007)79

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