RESEARCH ARTICLE OPEN ACCESS

Synthesis and Characterization Studies of Solvothermally Synthesized Undoped and Ag-Doped TiO_2 Nanoparticles Using Toluene as a Solvent

S.Perumal[1], K.MonikandaPrabu[2], C.Gnana Sambandam[3],A. Peer Mohamed [4]
[1](Principal, South Travancore Hindu College, Nagercoil-2,Tamilnadu, India)
[2](Research Scholar, Department of Physics, South Travancore Hindu College, Nagercoil-2,Tamilnadu, India)
[3](Associate Professor,Department of Physics, South Travancore Hindu College, Nagercoil-2, Tamilnadu, India)
[4](Senior Technical Officer, CSIR, NIIST, Thiruvananthapuram, Kerala, India)

ABSTRACT
Nanocrystalline TiO_2 was investigated by solvothermal synthetic method using toluene as a solvent. Titanium tetra isopropoxide (TTIP) was used as a precursor, which was decomposed at high temperature and precipitated in toluene. Subsequently, the solution was thermally treated at 250°C for five hours in stainless steel autoclave. Amorphous Nano TiO_2 was formed. When these amorphous Nano TiO_2 was calcinated to 550° C anatase Nano TiO_2 crystalline with particle size <20 nm was formed. These amorphous and anatase phase Nano TiO_2 was characterized by Powder X-ray diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and Photoluminescence (PL) studies and the results were discussed.
Keywords: Solvothermal method, Toluene solvent, TiO_2, Ag-doping, SEM.

I. INTRODUCTION

Titanium dioxide(TiO_2), a well-known oxide semiconductor material, has been extensively studied owing to its superior physical and chemical properties in photocatalysis[1]. Moreover, TiO_2 isused in solar cells for the production of hydrogen and electric energy gas sensor, whitepigment (e.g in paints and cosmetic products), corrosion-protective coating, an optical coating in ceramics and in electric devices such as varistors. TiO_2 also has many excellent properties such as non-toxicity and long term stability against photo corrosion [2,3]. TiO_2 has three polymorphs: Anatase, Rutile and Brookite. Numerous methods have been employed for the controlled formation of crystalline TiO_2 coatings and Nanoparticles. Promising technique, for example, a sol-gel method is primarily used. The hydrothermal method and solvothermal processing routes based on alkoxide (M-OR) or titanium (IV) chlorideprecursors [4-6]. Although the sol-gel method is widely used to prepare nanometre TiO_2, calcinations process will inevitably cause the grain growth and reduction in surface area of particles and even induce phase transformation. Solvothermal synthesis, in which chemical reactions can occur in aqueous or organic media under the self-produced pressure at low temperature (usually temperature lower than 250°C) can solve these problems encountered during sol-gel process [7-10].

In this study, we have prepared undoped TiO_2, Ag-doped TiO_2 Nanoparticles via solvothermalmethod using Titanium tetraisopropoxide (TTIP) as a precursor and toluene as a solvent. In Ag doping, suitable amount of silver nitrate is dissolved in DMF (N-N-Dimethyl Formamide) and well mixed with the solvent (toluene).

II. EXPERIMENTAL

2.1 Materials

Titanium tetraisopropoxide (TTIP, 97%, Sigma Aldrich), Toluene (99.8%, HPLC), N-N Dimethyl Formamide (99.5%, HPLC) and Silver Nitrate.

2.2 Preparation of undoped and Ag-doped Nano particles

TTIP ($TiOCH(CH_3)_2)_4$, 97%, Aldrich, was dissolved in toluene (99.8%,HPLC). All reagents were used without further purification process. 0.5 M of TTIP was mixed with 100 ml toluene in Teflon lined stainless steel autoclave without stirring (200 ml capacity, 80% filling). Then it was heated to 250°C with a rate of 20 C/min and maintained for five hours. After cooling gradually to room temperature, the reacted solution was kept in a beaker for a day. Now the solution slowly got transformed to gel. The gel was dried, washed and centrifuged to get TiO_2 Nanoparticles. The products were calcinated to 550°C for crystallization. The final products were characterized by Powder X-ray diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy

Dispersive Spectroscopy (EDS) and Photoluminescence (PL) studies.

III. CHARACTERIZATION

The prepared Nano TiO_2 was characterized by Powder XRD using XPERTPRO diffractometer. FTIR spectra of the as prepared NanoTiO_2 were characterized by Jasco 4100 Spectro Photometer equipped with ATR. SEM micrographs were recorded using JEOL Model JSM-6390LV Scanning Electron Microscope instrument. EDS spectra were recorded using JEOL Model JED-2300 Energy Dispersive Spectrometer. The Photoluminescence spectra of the as prepared samples were recorded using VARIAN-CARY Eclipse Fluorescence Spectrophotometer.

IV. RESULTS AND DISCUSSION

4.1. Powder XRD analysis

Fig.1 Shows the Powder X-ray diffraction (PXRD) patterns of TiO_2 Nanoparticles prepared via solvothermal synthesis and is calcinated to 550°C. As prepared TiO_2 showedno peaks, and had the characteristic appearance of an amorphous material. The samples treated to 550°C were crystallized. This showed the peaks at 2θ values about 25.58, 38.04, 48.30, 54.13, 55.24, 69.04, 70.52 and 75.31. These values corresponds to the Miller indices of (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (1 1 6), (2 2 0) and (2 1 5) planes, respectively. The observed peaks correspond to the anatase crystalline phase of TiO_2. The data obtained is in good agreement with standard JCPDS (JCPDS 21-1272) data of anatase crystalline phase of TiO_2.

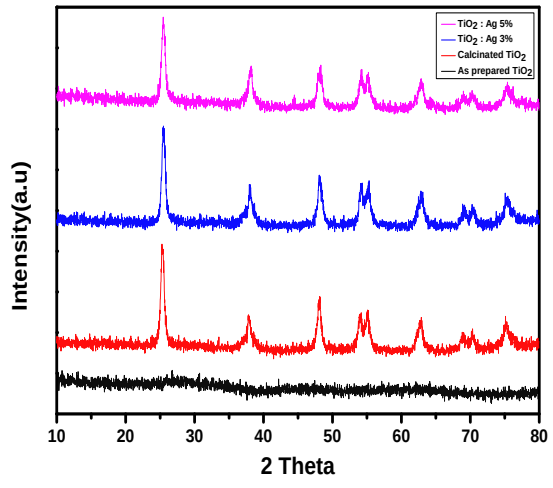

Fig 1. Powder XRD spectrum of the as prepared and Ag-doped TiO_2Nanoparticles.

The crystallite size can be determined from the classical Scherrer formula, $D=K\lambda / \beta \cos\theta$, where, D is the crystallite size, λ is the wavelength of the X-ray radiation (Cu Kα-1 radiation=1.54060 Å), K is the Scherrer constant (usually taken as 0.9) for spherical shape, and β is the full width at half-maximum height, θ is the Bragg's diffraction angle [11]. Average crystallite size of the as prepared and Ag-doped Nano TiO_2 is in the range between 17-20 nm. There is no impurity peak observed in the as prepared and Ag-doped TiO_2 Nanoparticles confirm that the samples are in pure form.

4.2 FTIR Analysis

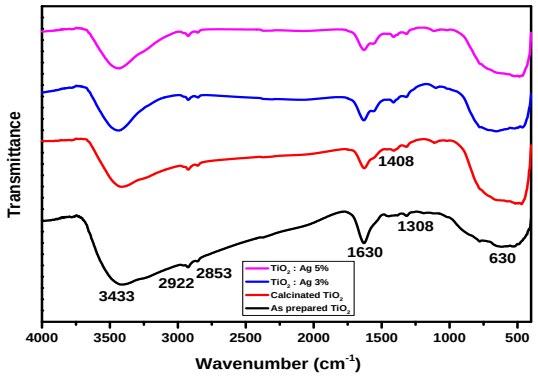

Fig 2. FTIR spectrum of the as prepared and Ag-doped TiO_2 Nanoparticles.

Fig.2 shows the FTIR spectrum of as prepared and Ag-doped TiO_2Nanoparticles. The peaks around 2922 cm^{-1} and 2850 cm^{-1} denoted as C-H vibration mode of CH_2 groups. Peak at 2922 cm^{-1} assigned to antisymmetric and 2850 cm^{-1} assigned to symmetric mode. The peaks around 630 cm^{-1} assigned to the characteristic vibrations of Ti-O-Ti network in titanium dioxide [12]. The broad peak at 3433 cm^{-1} corresponds to the stretching vibration of hydroxyl groups in water and the H-O-H bending mode at 1630 cm^{-1} is also water characteristic [13].

4.3 SEM Micrograph Analysis

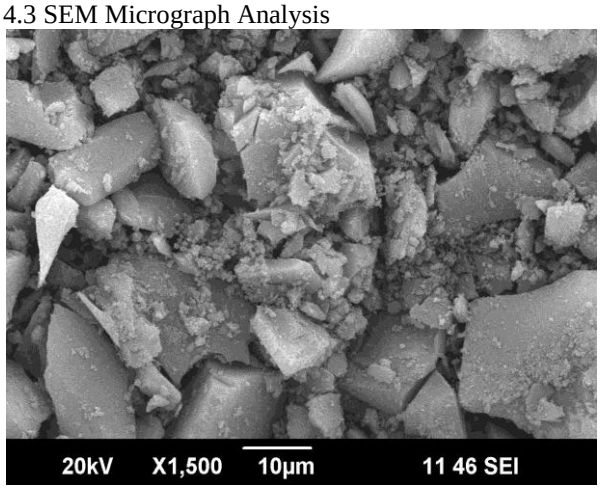

Fig 3. SEM micrograph of the as prepared TiO_2Nanoparticles.

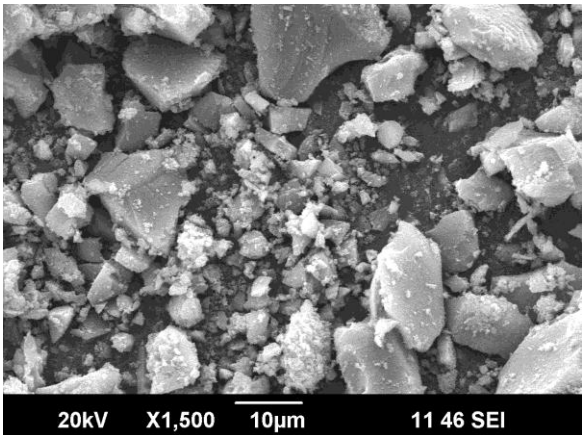

Fig 4. SEM micrograph of the as prepared calcinated TiO_2Nanoparticles.

Fig.3, 4, 5 and 6 show the SEM micrograph of the as prepared and Ag-doped TiO_2Nanoparticles. All these images have the same morphology. The morphology has different shapes of grains with irregular boundaries. With increasing the Ag loading concentration, the morphology slightly changes with mixing of Nano clusters and grain boundaries. From the SEM images, the average size of the grains is found to be in the range of 7-14 µm.

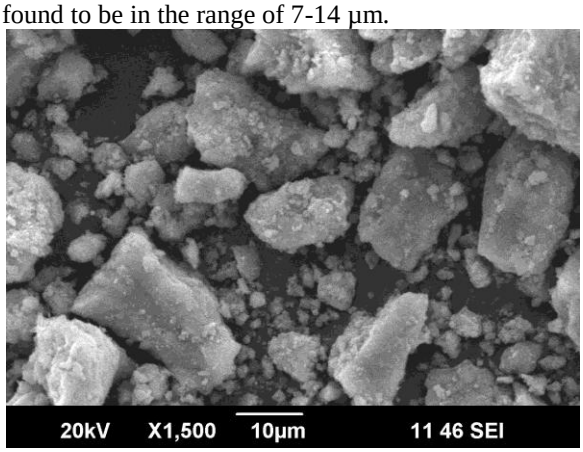

Fig 5. SEM micrograph of the 3 wt% Ag-doped TiO_2Nanoparticles.

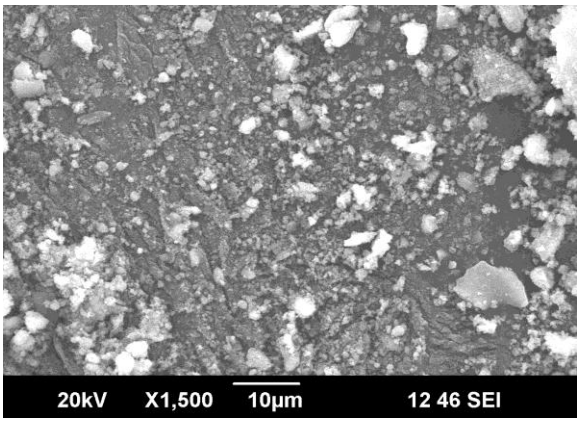

Fig 6**.** SEM micrograph of the 5 wt% Ag-doped TiO_2Nanoparticles.

The same morphology was obtained previously by N. Bahadur and et.al. using Titanium isopropyl orthotitanate as a precursor and propanol as a solvent with $AgNO_3$ as a dopant material.

4.4 EDS Analysis

Fig.7shows the EDS spectrum of the as prepared TiO_2Nanoparticles. The spectra show the only elements Ti and O. Fig. 8 shows the EDS spectrum of Ag-doped TiO_2Nanoparticles. The peaks of Ag, Ti and O can be clearly seen in the EDS spectra, which indicate that the Nanoparticles contain Ti, Ag and O elements.

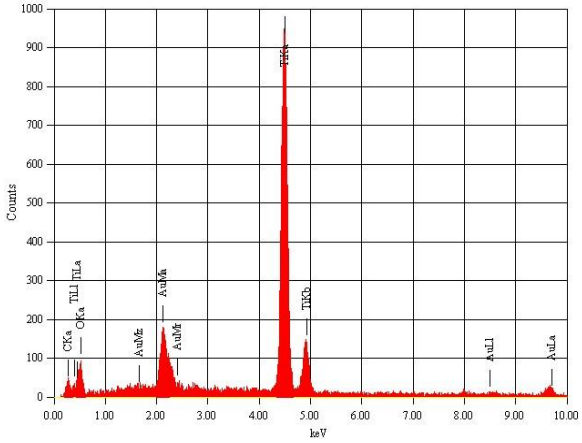

Fig 7. EDS spectra of the as prepared TiO_2Nanoparticles.

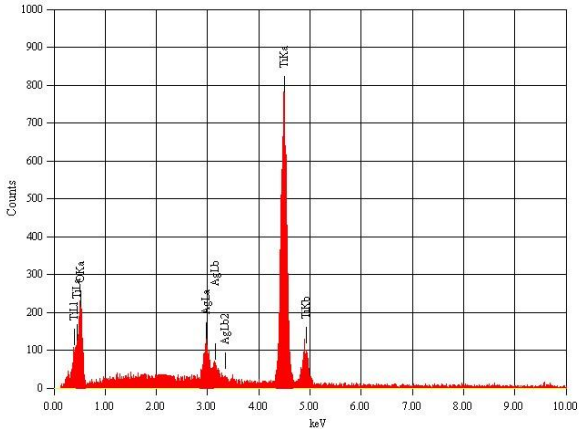

Fig 8. EDS spectra of the Ag-doped TiO_2Nanoparticles.

The presence of signal of Au can be ascribed to the Au grid. There is no impurity peaks present in the EDS spectra. This proves that the prepared samples are in pure form like XRD analysis.

4.5 PL Analysis

Fig.9 Shows the PL spectrum of the as prepared and Ag-doped TiO_2 Nanoparticles.PL spectra of as prepared and Ag-doped Nanoparticles show that the position of the peaks is almost similar except the as

prepared TiO_2 Nanoparticles. But the PL intensity of the as prepared TiO_2 is higher than the PL intensity of 3 wt% Ag -TiO_2 and 5 wt% Ag -TiO_2. It implies that the recombination of charge carriers is effectively suppressed by the doping material Ag [15].

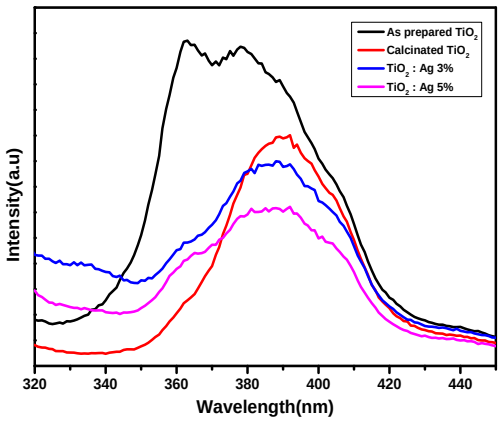

Fig 9. Photoluminescence spectrum of the as prepared and Ag-doped TiO_2Nanoparticles.

The excitation wavelength of the as prepared $TiO_2$was found to be at 378 nm. Using this wavelength the bandgap of the as prepared sample is obtained as 3.28 eV. Similarly, other excitation wavelength of calcinated, Ag-doped TiO_2 is observed at 392,388 and 392 nm. Hence, the bandgap values of Ag-doped TiO_2Nanoparticles changes from 3.16 to 3.20 eV.

V. CONCLUSIONS

TiO_2Nano particles were successfully synthesized by solvothermal method using Titanium tetra isopropoxide and Toluene. They were calcinated to 550°C to get anatasecrystalline form of TiO_2. The calcinated TiO_2Nanoparticles were characterized by Powder XRD, FTIR, SEM, EDS and PL analysis. The Powder XRD spectra reveal that anatase crystalline phase is the main phase of TiO_2 Nano particles. FTIR spectra displayed the peaks attributed to the presence of C-H groups at 2922 $cm^{-1}$and 2850 cm^{-1}. SEM image displayed the uniform morphology of all these as prepared and Ag-doped TiO_2Nanoparticles. EDS spectra confirm the samples are in pure form. Decrease of Photoluminescence intensity reveals the suppression of electron-hole recombination by the dopant material Ag. Also, using PL excitation wavelength, the bandgap of the as prepared TiO_2 and Ag-doped TiO_2 are found to be 3.28 eV and 3.16 eV.

VI. ACKNOWLEDGEMENTS

This work was supported by University Grant Commission, New Delhi, through the Major Research Project in South Travancore Hindu College Nagercoil-2, Tamilnadu, India. We thank Dr.S.Ananthakumar, Scientist, NIIST, Thiruvananthapuram, Kerala, India, for the synthesis, UV and PL characterization supports.

REFERENCES

[1] A. Fujishima and K. Honda, *Nature 238*,1972,37.[2] A. Fujishima, X. Zhang andD.A. Tryk,*Surf.Sci.Rep63*,2008,515-82.
[3] K. Pirakanniemi and M. Sillanpaa, *Chemosphere,48*,2002,1047-60.
[4] C.J. Brinker andG.W.Scherer, *Sol-gel Science*(Thephysics and chemistry of sol-gel processing,Academic Press, Inc., 1990.)
[5] G. Li and K.A. Gray, Preparation of mixed-phasetitanium dioxide nano composites viasolvothermal processing. *Chemistry of materials,19*,2007,1143-1146.
[6] G.Li, S. Ciston, Z.V. Saponjic, L. Chen, N.M.Dimitrijevic, T. Rajh and K.A. Grey,Synthesizingmixed phase TiO2 nanocompositeusingf ahydrothermal method for photo-oxidation and hoto reduction applications,*Journal ofCatalysis,253*, 2008,105-110.
[7] M. Kang and J. Mol, *Catalytic A:Chem., 3856*,2002,1.
[8] C.Wang. Z. Deng, G. Zhang, S. Fan and Y. Li,*Powder Technology,125*, 2002, 39.
[9] S.J. Chen, L.H. Li, X.T. Chen, Z. Xue, J.M.Hong andX.Z. You, *Journal of Crystal Growth252*,2003,184.
[10] J. Liu, X. Chen, M. Shao, C. An, W. Yu and Y.Qian, *Journal of Crystal Growth252*, 2003,297.
[11] D.Dastonand N.B. Chaure, Influence ofsurfactants on TiO_2 nanoparticles Grown bysol-gel technique, *Int. J. Mat.Mech. Manufact.,2*,2014,1.
[12] S. Singh, H. Kaur, V.N. Singh, K. Jain and T.D.Senguttuvan, Highly sensitive and pulse likeresponse toward ethanol of Nb doped TiO_2nanorods based gas sensors. *Sensors andActuators B, 171-172*,2012,899-906.
[13] O. Landau and A. Rothschild, Microstructureevolution of TiO_2 gas sensors produced byelectrospinning, *Sensors and Actuators B, 171-172*,2012,118-126.
[14] N. Bahadur, K. Jain, R. Pasricha, Govind and S.Chand, Selective gas sensing response fromdifferent loading of Ag in sol-gel mesoporoustitania powders, *Sensors and Actuators B, 159*,2011, 112-120.
[15] R. Velmurugan, B. Krishnakumar, B. Subashand M. Swaminathan, Preparation andcharacterization of carbon nanoparticles loadedTiO_2 and its catalytic activity driven by naturalsunlight, *Solar Energy Materials&Solar Cells108*, 2013, 205-212.