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.

1. 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, 2.583 respectively[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 TiO₂. 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 TiO₂

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. The prepared titanium hydroxide precipitate was annealed at 800°C to obtain TiO₂ nanoparticles.

2.2 Characterization techniques

The obtained samples were characterized by X-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 TiO₂ nanoparticles were recorded using Varian, Cary 5000 spectrophotometer and 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 spectrometer and JASCO FP 8200 Spectrofluorometer, respectively.

III. RESULTS AND DISCUSSION

3.1 Field 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 TiO₂ 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 in the 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 TiO₂. 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.
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\textsubscript{2} nanoparticles has recorded the wavelength ranges from 200 to 600 nm. The spectrum shows maximum absorption peak at 350 nm and the blue shifted indicating the quantum confinement effect.

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.
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-Red analysis

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 spectrum is confirmed due to the presence of a strong band around 550 cm$^{-1}$ which is in connection with the 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 readsorption 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


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