Optical Properties of Pure and Gd3+ Doped Titanium Dioxide

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Abstract - Pure and Gd3+ doped Titanium dioxide nanocrystals were prepared using the sol – gel method. Titanium isopropoxide (TIP) was used as the precursor for Titania sol preparation. X-ray powder diffraction confirms that the particles crystallize purely in anatase phase and the broadening of Bragg’s peaks ascertain smaller particles size. The formation of uneven spherical grains composed of small primary titania particles are observed from SEM. The UV-Vis spectral analysis was carried out between 200 nm and 800 nm. More over the presence of Gadolinium had resulted in a shift of 10 nm from the undoped TiO2. The FT-IR and FT-Raman spectra confirmed the anatase phase of Titanium dioxide.

I. INTRODUCTION
Titanium dioxide (Titania, TiO2) has been fervently researched over the past few decades due to its potential applications across many different areas. Titanium dioxide (TiO2) is a large band gap semiconductor with many interesting properties. Inertness to chemical environment and long term photostability, excellent electrical and thermal conductivity, inherent high – aspect ratio, and hollow nano – geometry along with low density, corrosion resistance, and non - toxicity has made TiO2 an important component in many practical applications and commercial products, such as electronics, optics, photocatalysis, biotechnologies, solar or electrochemical cells, sensors and other material science fields [1-5].

Semiconductor nanomaterials possess interesting absorption and photoluminescence emission properties. Nanomaterials having small particle sizes exhibit enhanced optical emission due to the quantum confinement effect. Synthesis, characterization, and measurement of optical properties of nanomaterials with different anisotropic shapes have also drawn significant attention. Recently, a lot of research focuses have been given on the preparation of nanocomposite materials having potential applications in different optoelectronics and photonics devices [6]. In this paper we discuss the optical properties such as UV-Vis absorption, Photo Luminencence, FT-IR and FT-Raman studies on pure and trivalent lanthanide ions doped titania.

II. EXPERIMENTAL PROCEDURE
Pure Titanium dioxide nanocrystals were prepared using the sol – gel method. Titanium isopropoxide (TIP) was used as the precursor for Titania sol preparation. The sol corresponds to the overall volume ratio of Ti(OCH(CH3)2)4 : CH3COOH : Distilled H2O = 5:30:4:4:30. Ti(OCH(CH3)2)4 was first dissolved in iso propanol and distilled water to form titania sol and then stirred for 1h at room temperature. The pH of sol was adjusted to 2–3 by adding 1 – 2 drops of ammonia with stirring in room temperature for 12h. The prepared sol was left to stand for the formation of gel and dried at 100°C for an hour in a furnace to remove the solvents. The obtained gel was milled into powders and calcined at 400°C for 3h to keep anatase TiO2 phase. Gadolinium doped TiO2 was synthesized using the same procedure as the reference sample. The synthesized TiO2 nanoparticles were characterized by a X-ray Diffractometer (RICH SIEFERT & CO) with monochromatic CuKα (λ = 1.5406 Å) and taken over the 20 range 20° – 70° by step scanning with a step size of 0.05°. To examine the morphology of the synthesized nanoparticles SEM analysis was carried out on the JEOL JSM-6390LV SEM fitted with secondary electron detector, and equipped with an attachment for the Energy dispersive X-ray spectroscopy (EDX) to enable elemental composition analysis. UV-Vis absorption spectra and photoluminescence (PL) spectra were recorded by using Varian Cary 5E spectrophotometer and Jobinyvon Fluorolog-3-11 spectrofluorometer respectively. The FT-IR spectrum of the pure and doped TiO2 was recorded using BRUKER IFS–66V spectrometer in the range between 4000 and 400 cm⁻¹. The FRA 106 module attached to IFS 66V FT-IR Spectrometer provides the FT Raman spectral measurements.

III. RESULTS AND DISCUSSIONS
X – Ray Diffractometry (XRD) studies
The powder X-ray diffraction pattern of the synthesized Titanium dioxide nanoparticle is shown in figure 1. The diffraction peaks corresponding to 20 values are identified as (1 0 1), (1 1 0), (2 0 0), (1 0 5), (1 2 1), (2 0 4) and (1 1 6) and it matches well with the diffraction pattern of bulk anatase Titania peaks (JCPDS = 00-021-1272). The peaks corresponding to other polymorphs of Titania (namely, rutile and brookite) are not detected. The peaks are in a well-defined shape and form. This clearly indicates the crystallinity of the synthesized nano-particles. It can be noted that Gadolinium trivalent ion doped TiO2 sample have significant peaks at (1 0 1), (1 1 0), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4) and (1 1 6) as shown in figure 2. The doping Gd atoms do not cause much shift in peak position of TiO2.
The SEM micrographs of TiO$_2$ and Gd$^{3+}$ doped TiO$_2$ are shown in Figures 3 and 4 respectively. The particles are almost spherical and uniformly distributed, as observed from the SEM micrographs; the synthesized samples consisted of spherical clusters. Spherical shaped TiO$_2$ nanoparticles show an even distribution.
The energy dispersive X-ray analysis gives both qualitative and quantitative information about the elemental composition of the materials. The intensity of the spectra correlates with the amount of elements present in it. The EDX spectra of TiO$_2$, and Gd$^{3+}$ doped TiO$_2$ are shown in Figures 3a and 4a respectively. The presences of doped elements are clearly shown in the spectra. This indicates the incorporation of dopants in the Titania network.

**UV-Vis absorption spectroscopy**

The UV-Vis spectral analysis was carried out between 200 nm and 800 nm. Figures 5 and 6 show the absorption spectra of pure and Gd$^{3+}$ doped nanoparticles. The knee edge at 360 nm in the spectrum (Figure 5) shows a shift compared to its bulk counterpart which is nearly 50 nm, the shift is significant due to the weak quantum effect occurred during the growth process. There is a tail of a more intense absorption occurring at shorter wavelength due to higher energy electronic transitions as observed in low band gap semiconductor particles. The sharp optical absorption edges and well-defined excitonic features indicate that the synthesized particles have relatively narrow size distribution. More over the presence of Gadolinium (Figure 6) had resulted in a shift of 10 nm from the undoped TiO$_2$. 

![Figure 4 SEM images of Gd$^{3+}$ - TiO$_2$ nanoparticles](image)

![Figure 5. UV-Vis spectrum of TiO$_2$](image)
Photoluminescence (PL)

The photoluminescence spectrum of TiO$_2$ nanoparticles was recorded in the spectral range of 350-450 nm. The Photoluminescence spectra of TiO$_2$ and Gd$^{3+}$ doped TiO$_2$ are shown in Figures 7 and 8. The peak positioned at 388 nm of the pure TiO$_2$ is due to the radiative annihilation of the exciton after excitation at 350 nm. The charge carrier recombination in small semiconductor particles is the non-radiative path because of strong coupling of wave functions of trapped electrons and trapped holes with lattice phonons [7]. For Lanthanide doped TiO$_2$ the PL spectra have obvious peaks which are shifted towards the higher wavelength side.

FT-IR analysis

Figures 9 and 10 show the FT-IR spectra of TiO$_2$ and Gd$^{3+}$ doped TiO$_2$ samples calcinated at 400 °C respectively. The most common feature observed in both the spectra is the appearance of (i) broad bands below 1000 cm$^{-1}$ assignable to the Ti–O–Ti
crystal vibration [8]. Pure TiO$_2$ has a strong and broad band in the range of 400–1000 cm$^{-1}$, due to Ti–O stretching vibration modes, which can be observable in the anatase phase of TiO$_2$. The shift to the larger wave numbers in the doped sample ascertains the presence of dopant. The sharpening of the Ti–O–Ti bands may be due to Gd$^{3+}$ doping. The absorption band of Ti–O stretching vibration modes is observed to shift towards lower wavenumber for Gd$^{3+}$–TiO$_2$.

FT-Raman analysis

The Raman spectrum of the pure TiO$_2$ (Figure 11) shows peaks at 143.6 cm$^{-1}$, 194.2 cm$^{-1}$, 395.5 cm$^{-1}$, 515.7 cm$^{-1}$ and 638.7 cm$^{-1}$, which can be assigned to the anatase phase. The spectra of doped TiO$_2$ nanocrystals are similar to that of anatase but being slightly shifted as a result of crystal structure modification via doping. Gadolinium trivalent ion doped TiO$_2$ sample (Figure 12) shows peaks at 144.8 cm$^{-1}$, 195.7 cm$^{-1}$, 399.1 cm$^{-1}$, 513.9 cm$^{-1}$ and 636.2 cm$^{-1}$ [9]. Thus from the Raman studies we can confirm that the anatase phase was not altered by the presence of trivalent lanthanide dopant.
IV. CONCLUSION

The successfully prepared TiO$_2$ and Gd$^{3+}$ doped TiO$_2$ samples were subjected to various optical studies. From the optical absorption spectrum, a significant spectral shift in the wavelength is observed as compared to bulk TiO$_2$ crystal. The presence of Gd$^{3+}$ trivalent lanthanide ions had resulted in shifting of the absorption edge towards the visible region. The broad emission band observed in the PL spectrum is attributed to the electronic transition mediated by the defect levels such as oxygen vacancies. The FT-IR spectra signifies that the characteristic vibrational frequencies of TiO$_2$ and the chemical composition of the materials belongs to the (Ti–O, i.e. metal oxygen bond) anatase titania. Therefore, the doping did not alter the structure of TiO$_2$ host material but it can take effect on optical and morphological properties. The Raman spectrum of TiO$_2$ confirms the anatase phase. The spectra of doped TiO$_2$ nanocrystals are similar to that of anatase but being slightly shifted as a result of structure modification via doping.

V. REFERENCES