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Structural, Morphological and Optical Characterization of Eu$^{3+}$ and Nd$^{3+}$ Co-Doped TiO$_2$ Nano Particles by Sol Gel Method

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ABSTRACT. Semiconductor nano crystals have been widely studied for their fundamental properties. The Eu$^{3+}$ and Nd$^{3+}$ doped titanium dioxide nano powder was successfully synthesized by sol-gel method. The morphological and structural properties of as-prepared samples were characterized by X-ray diffraction (XRD), High Resolution Transmission Electron Microscope (HRTEM). The Powder X-ray diffraction is carried out in order to examine the phase formation and substitution of Eu$^{3+}$ and Nd$^{3+}$ doped in TiO$_2$ matrix. The UV-Vis spectral analysis was carried out between 200 nm and 1200 nm. The band gap of the Eu$^{3+}$ and Nd$^{3+}$ doped TiO$_2$ nanoparticles was calculated. The functional groups of the synthesized compound have been identified by FTIR spectral analysis. The strong PL intensity confirms a blue shift.

Introduction. Titanium dioxide (TiO$_2$) nanomaterials are used in a wide range of applications such as photo catalysis, sensor devices, paints and dye-sensitized solar cells. The material properties of TiO$_2$ nanoparticles depend upon the parameters like crystal structure, nanoparticle size and morphology. However, these parameters are depending on the method of synthesize [1]. Titanium dioxide exists in three main crystallographic forms of anatase, rutile and brookite [2]. Among the various polymorphs listed above, anatase type has been selectively used for photocatalytic applications and various other applications [3]. Sol–gel method was often employed to prepare TiO$_2$ because of its simplicity and low equipment requirement. The conventional sol–gel process usually involved uncontrollable fast hydrolysis and condensation and therefore could result in formation of amorphous TiO$_2$ [4]. Sometimes, the high temperature would seriously affect the particle size and surface area and even could result in a collapse of the mesoporous structure. Therefore, it is necessary to synthesize nanocrystalline anatase under mixed conditions. Many researchers have tried to prepare nanostructure anatase TiO$_2$ in well crystalline form. Some researchers have reported that they could improve the absorption and photocatalytic activity via dye sensitizing, surface deposition with metal or doping with metal, nonmetal, or their oxides. Many nonmetal ions have been successfully doped the intensity of photoluminescence (PL) of TiO$_2$ doped with Sm$^{3+}$ ions was reported to show specific dependence on the oxygen content in the surrounding atmosphere and similar effects have been seen in case of Eu$^{3+}$ doped titania and also in the intrinsic emission of porous TiO$_2$[5-7]. This motivates further work to elaborate photoluminescent gas sensing materials based on lanthanide doped TiO$_2$. It is very necessary for researchers to explore the theory and the experimental results on such field. In the present work, we have synthesized anatase phase of Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles by sol–gel method and they were analyzed for structural and optical properties.

EXPERIMENTAL DETAILS
Synthesis 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(CH$_3$)$_2$]$_4$: C$_3$H$_6$O: CH$_3$COOH: Distilled H$_2$O = 5:30:4.4:30. Ti [OCH(CH$_3$)$_2$]$_4$ was first dissolved in isopropanol 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 4h to keep anatine TiO$_2$ phase. Europium and neodymium co-doped TiO$_2$ was synthesized using the same procedure as the reference sample.

RESULT AND DISCUSSION

XRD Analysis. The XRD pattern of the Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles are shown in Fig. 1. The Strong and sharp peaks of the pattern confirmed the crystalline structure of the samples. All the main diffraction peaks at 25.38 (101), 37.96 (002), 48.04 (042), 55.94 (361) and 63.20 (211) coincide with the JCPDS values (PDF Card No: 21-1272) which correspond to crystal structure of anatase. The variation in intensity of the diffraction peaks indicates the crystallinity behavior due to lattice distortion. When Nd$^{3+}$ and Eu$^{3+}$ ions are incorporated into the periodic crystal lattice of TiO$_2$, a strain is induced into the system, resulting in the alteration of the lattice periodicity. Furthermore, after doping, the diffraction peaks got broadened suggesting a systematic decrease in the crystallite size. The crystallite size of the co-doped nanoparticle were estimated from the most intense peak based on Scherer equation $D = k \lambda / \beta \cos \theta$ where $k$ is the shape factor taken as 0.9, $\lambda$ is the wavelength, $\beta$ is full width at half maximum and $\theta$ is the diffraction angle. Average crystallite size in co-doped TiO$_2$ matrix was calculated as 25.50 nm.

**Fig. 1.** XRD pattern of Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles.

Optical Properties. The synthesized Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles were analyzed by UV-Vis absorption spectroscopy as seen in Fig. 2 (a). The absorbance of the nanoparticles exhibits a sharp decrease in the visible region (380 nm); co-doping of Nd$^{3+}$ and Eu$^{3+}$ can have significant influence on the absorption of light. The cut-off wavelength has been enlarged to the visible regions by doping. The cut-off wavelength shifted from 380nm by increasing with Nd$^{3+}$ and Eu$^{3+}$ content. The result shows that the range of light absorption of doped TiO$_2$ is wider than undoped TiO$_2$ nanoparticles, also optical band-gap measurements of the prepared sample were carried out. The band gap for Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles was calculated using the formula:

$$a h \nu = C (h \nu - E_g)^{1/2}$$
where $\alpha$ is absorption coefficient, $C$ is a constant, $h\nu$ is energy of photons and $E_g$ is the energy band gap.

By plotting $(ah\nu)^2$ versus ‘$h\nu$’ the value of the band gap was found to be 3.02 eV for co-doped TiO$_2$ nanoparticles. Fig. 2 (b) shows the band gap plot of the Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles. As the Nd$^{3+}$ and Eu$^{3+}$ doping ratio is increasing the band gap values decreased. These band gap and absorbance spectra supported each other. These results prove that doping can reduce the wideness of forbidden band of TiO$_2$ nanoparticle.

![Fig. 2. (a) UV-vis absorption spectra of the Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles.](image)

![Fig. 2. (b) Optical band gap ($E_g$) spectra of the Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles.](image)

**HRTEM Analysis**

HRTEM allows the direct imaging of nanoparticles and provides authentic information on the distribution, size and morphology of the nanocrystalline. The morphology of the synthesized products was investigated by HRTEM analysis. Fig. 3 shows the HRTEM images of Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$. From the Fig., it is observed that most of the particles are almost spherical in shape with uniform size distribution. However, on Nd$^{3+}$ and Eu$^{3+}$ co-doping the size of the particles is increased in spherical morphology.
Photoluminescence (PL)

The PL spectra of Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticle are shown Fig.4. PL emission spectra have been widely used to investigate the efficiency of charge carrier trapping and migration and to understand the fact of electron-hole pairs in semiconductors. As shown in Fig., three emission peaks are observed for Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$. Among the three peaks one is large intense positioned at 380 nm. The peak at 380 nm is band edge luminescence of TiO$_2$ nanoparticle and other two less intense peaks are positioned at 363 and 424 nm respectively. These emission bands originated from charge recombination at the shallow-trap surface state. This surface state originated from the oxygen vacancies which act as radioactive centers. However, in Nd$^{3+}$ and Eu$^{3+}$ co-doping the above stated three peaks are largely blue shifted to 363, 380 and 424 nm as a result of doping.

Fourier Transform Infrared Spectroscopy (FT-IR).

FTIR spectroscopy is used to identify and characterize the organic species present in the Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanostructured materials. The FTIR spectra of the as prepared Nd$^{3+}$ and Eu$^{3+}$ co-doped TiO$_2$ nanoparticles is shown in Fig.5. The two weak absorption bands around 2043 cm$^{-1}$ and 2984 cm$^{-1}$ are due to C–H symmetric stretching of organic residue. The weak peak that appeared at 1124 cm$^{-1}$ and 1082 cm$^{-1}$ in Nd$^{3+}$ and Eu$^{3+}$ co-doped sample is associated to the asymmetric stretching vibration modes of Ti–O networks. The peaks observed at 3600–3000 cm$^{-1}$ is assigned to \(-\text{OH}\) of water absorbed from the molecular precursors. The band at 3000–2750 cm$^{-1}$ may be due to symmetrical stretching vibration of \(-\text{CH}_2\)
groups. The peaks 1530–1260 cm\(^{-1}\) indicates asymmetrical and symmetrical CH\(_3\) deformation vibrations from titanium-isopropoxide and C–C–O stretching vibration is positioned at 1130–820 cm\(^{-1}\) from ethylene glycol. Thus the FTIR spectra confirm the presence of functional groups and their mode of vibrations.

**Fig. 5.** FTIR spectra of the Nd\(^{3+}\) and Eu\(^{3+}\) co-doped TiO\(_2\) nanoparticles.

**Summary** We have successfully synthesized the Nd\(^{3+}\) and Eu\(^{3+}\) co-doped TiO\(_2\) nanoparticles by sol-gel method at room temperature. The XRD pattern depicted the structure and grain size of the Nd\(^{3+}\) and Eu\(^{3+}\) co-doped TiO\(_2\) nanoparticles. The UV-DRS spectra of Nd\(^{3+}\) and Eu\(^{3+}\) co-doped TiO\(_2\) nanoparticles showed an absorption peak at 380 nm in the UV region. In the co-doped TiO\(_2\), considerable blue shift was obtained for all the samples due to quantum confinement effect. The band gaps were found to be 3.02 eV on increased doping concentration doping band gap energy has been decreased. The various functional groups present in the material have been determined by FTIR analysis. The morphology of the products revealed spherical structure of Nd\(^{3+}\) and Eu\(^{3+}\) co-doped TiO\(_2\) nanoparticles which characterized using High Resolution Transmission Electron Microscopy (HRTEM). The PL emission spectra revealed the structural modification of the TiO\(_2\) matrix with doping by Nd\(^{3+}\) and Eu\(^{3+}\) ions, as well as the change in the charge transfer pairs on the surface of TiO\(_2\).

**References**


Cite the paper