Synthesis, Structural, Morphological and Optical Characterization of TiO₂ and Nd³⁺ Doped TiO₂ Nanoparticles by Sol Gel Method: A Comparative Study for Photovoltaic Application

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Abstract. Nano structured materials are currently receiving wide attention due their optical, electronic, magnetic, chemical, physical and mechanical properties. Semiconductor nano crystals have been widely studied for their fundamental properties. Pure and Nd³⁺ 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 scanning electron microscope (HRSEM). The HRSEM analysis shows the partial crystalline nature of undoped, and doped TiO₂ nanoparticles and it was performed to obtain the particles size. The energy dispersive X - ray (EDAX) technique was used to determine their elemental compositions. The optical properties of doped and undoped TiO₂ nano particles were investigated by UV-Vis spectroscopy and Photoluminescence (PL). The band gap of the doped TiO₂ nanoparticles was found to be less than un-doped TiO₂ nanoparticles.

1. Introduction
Titanium dioxide (TiO₂) has been extensively studied oxide as a pigment and in sunscreens, paints, ointments and toothpaste and as a photocatalytic material for self cleaning coatings. Environmental purifiers, antifogging mirrors and in many other applications. Semiconductor nano crystals have been widely studied for their fundamental properties especially titanium dioxide (TiO₂). Nano sized titanium dioxide materials have been the focus of great interest because they exhibit modified physical-chemical properties in comparison with its bulk. Inexpensiveness, excellent chemical stability, non toxicity, high photo-catalytic property, a wide band gap and high refractive index of TiO₂ make it attractive for practical applications [1]. The use and performance for a given application are strongly influenced by the crystalline structure, the morphology and the size of the particles. The use of TiO₂ nano particles is in great demand because of its properties and application in various fields such as photocatalysis, solar energy conversion and electronic...
devices. The photocatalytic performance of TiO₂ based devices is largely influenced by the particle size, apparently at the nanometer scale. Following the literature the photocatalytic activity of TiO₂ has been improved by optimizing the nanostructure size using various synthetic methods such as sol-gel, hydrothermal, solvothermal, co-precipitation etc. Furthermore, doping with alkali metals, transition metal ions or rare earth metal ions (lanthanides) or non metal ions has been considered as a promising way for improving the photocatalytic efficiency of nano sized TiO₂.

The optical and electronic properties of nano structured TiO₂ can be tailored by a variety measures including thermal treatments, supported film growth, and metal-ion doping [2]. In particular, doping with lanthanide metal ions has been shown to increase the photocatalytic efficiency for selected reaction. It is critical to assess the effects of lanthanide-ion doping on the structure of titania which will allow greater control over the desired properties. Doping of TiO₂ with neodymium ion would introduce a distortion in TiO₂ lattice [3]. The interstitial neodymium does not affect the charge balance in the anatase lattice, as a substitutional neodymium does.

Sol-gel process is one of the most successful techniques for preparing nanocrystalline metallic oxide materials due to low cost and easy for fabrication. Generally in a typical sol-gel process a colloidal suspension or a sol is formed due to the hydrolysis and polymerization reaction of the precursors, which on complete polymerization and less of solvent leads to the transition from the liquid sol into a solid gel phase, the wet gel can be converted into nano crystals with further drying and hydrothermal treatments. In this paper, we report synthesis and characterization of Nd³⁺ doped TiO₂ nanoparticles obtained by sol-gel method. The prepared samples were characterized by X-ray diffraction (XRD), High resolution scanning electron microscope (HRSEM), the energy dispersive (EDAX) studies, ultraviolet - visible spectroscopy (UV-Vis) and photoluminescence (PL) studies.

2. Experimental Details

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: C₆H₅O: CH₂COOH: Distilled H₂O = 5:30:4.4:30. Ti [OCH(CH₃)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 powder and calcined at 400°C for 4h to keep anatase phase. The neodymium (Nd³⁺) doped TiO₂ was synthesized using the same procedure as the reference sample. The doping rate with Nd³⁺is equal to 0.5% wt. The prepared sample was characterized by X-ray diffraction (XRD) measurements which were carried out at room temperature by using Siemens X-ray diffraction D500 with CuKα. Scanning electron micrograph images were taken with a JEOL (JSM-840 A), High resolution scanning electron microscope (HRSEM) equipped with an EDAX spectrometer. The absorption spectrum of the sample was measured on a UV-3101 Shimadzu visible spectrometer. Photoluminescence (PL) study was carried out on a Perkin-Elmer LS-55 luminescence spectrometer using a Xe-lamp at room temperature.

3. Results and Discussion

3.1. XRD analysis

The crystalline phase of undoped and doped TiO₂ nanoparticles was analyzed by X-ray diffraction (XRD). Figure 1a and 1b shows the powder XRD pattern of as-prepared pure and Nd³⁺ doped TiO₂ nano particles. The presence of sharp diffraction peaks in the XRD confirm that products are highly crystalline and the crystalline size was calculated by the Debye Scherrer formula D =0.89λ/β cos θ, where D is the crystalline size, λ is the wavelength of X-ray radiation (0.154 nm), ‘β’ is the full width half maximum and θ is the diffraction angle [4,5]. It was found that the
average crystalline size of pure and Nd$^{3+}$ doped TiO$_2$ surface were 18 and 20 nm respectively.

![Figure 1](image1.png)

**Figure 1.** Powder X-ray diffraction analysis of (a) Pure TiO$_2$ nanoparticles (b) Nd$^{3+}$ doped TiO$_2$ nanoparticles.

### 3.2. UV-Vis Absorption spectroscopy

Optical properties were observed by UV–Vis spectroscopy. Figure 2a and 2b demonstrates the optical absorption spectra of undoped and Nd$^{3+}$ doped TiO$_2$ nano particles. The absorption edge of TiO$_2$ nano particles at 374 nm moved to a longer wavelength after doping with Nd$^{3+}$ (0.5%) showing the absorption edge at 386 nm. After doping with Nd$^{3+}$ the response of TiO$_2$ nanoparticles to visible light was increased and showed blue shift (towards increased wavelength). The blue shift of the absorption curve results in a reduction of the band gap energy. The band gap energy of the materials were calculated using the formula, $E_g = \frac{\hbar c}{\lambda} \times 6.2415 \times 10^{18}$ eV. Where, $\hbar$ is Planck constant ($6.626 \times 10^{-34}$ J s), $C$ is Speed of light ($3.0 \times 10^8$ m/s) and $\lambda$ is Cut-off wavelength and its value is $372 \times 10^{-9}$ m. The calculated band gap energy of pure TiO$_2$ is 3.3 eV and the Nd$^{3+}$ doped TiO$_2$ is 3.02 eV. The optical band gap energy decrease with the Nd$^{3+}$ doped TiO$_2$ nanoparticles.

![Figure 2](image2.png)

**Figure 2** UV-Vis absorption spectra of (a) Pure TiO$_2$ nanoparticles (b) Nd$^{3+}$ doped TiO$_2$ nanoparticles.

### 3.3. Photoluminescence spectroscopy

Photoluminescence spectroscopy (PL) is a practical method for probing the electronic structure of nano materials [6], the PL emission spectra of the TiO$_2$ and Nd$^{3+}$ doped TiO$_2$ excited at a wavelength of 285 nm at room temperature is shown in figure 3. The TiO$_2$ nano particles showed the emission peak in a range of 350-400 nm and another one in range of 400-430 nm, there after doping with Nd$^{3+}$ one peak at 350-390 nm and another one in the range of 420-430 nm corresponds to the radioactive transition of the excited electron from fermi level. The PL intensities of Nd$^{3+}$ doped TiO$_2$ (0.5%) were
lower in comparison to those of the TiO$_2$ nanoparticles because the neodymium cause some changes in the electronic structure of the doped TiO$_2$ nanoparticles. The PL emission is directly related to the recombination of excited electrons and holes, so the lower PL intensity indicates a delay in recombination rate.

![Photoluminescence spectra](image)

**Figure 3.** Photoluminescence spectra of (a) Pure TiO$_2$ nanoparticles (b) Nd$^{3+}$ doped TiO$_2$ nanoparticles.

### 3.4. High Resolution Scanning Electron Microscopy (HRSEM)

High resolution scanning electron microscope (HRSEM) was used to examine the surface morphology of prepared samples. Figure 4a and 4b shows HRSEM images of the undoped and Nd$^{3+}$ doped TiO$_2$. The HRSEM investigation of the synthesized samples reveals that the crystallites are of nanometer size and all samples show uniform morphology in the form of TiO$_2$ nano clusters.

![HRSEM image](image)

**Figure 4.** HRSEM image of (a) Pure TiO$_2$ nanoparticles  (b) Nd$^{3+}$ doped TiO$_2$ nanoparticles.
3.5. Energy Dispersive X-Ray (EDAX) analysis
To identify the type of elements present in the sample, Energy dispersive X-ray spectroscopy (EDAX) was used. The EDAX spectra of the undoped and Nd$^{3+}$ doped TiO$_2$ nanoparticles were recorded and they are shown in figure 5a and 5b. From the results, it is confirmed that Ti, O and Nd$^{3+}$ ions are present in the sample, the presence of Nd$^{3+}$ is confirmed which indicates the doping has entered into the sample.

![EDAX spectra](image)

**Figure 5.** EDAX spectra: (a) Pure TiO$_2$ nanoparticles. (b) Nd$^{3+}$ doped TiO$_2$ nanoparticles.

4. Conclusion
The pure and Nd$^{3+}$ doped TiO$_2$ nanoparticles were synthesized by sol-gel technique. The powder X-ray diffraction analysis confirmed the crystalline phase of the synthesized TiO$_2$ nanoparticles. From the optical absorption spectra, a blue shift has been observed as compared to the bulk excitonic peak, which clearly shows the effect of quantum confinement and the presence of strong PL intensity which is due to both high crystalline and good surface states of the synthesized nanoparticles. The HRSEM and EDAX studies confirmed the morphological features of the nanoparticles and the composition of the undoped and Nd$^{3+}$ doped TiO$_2$ nanoparticles.

References

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