Effect of samarium (Sm$^{3+}$) doping on structural, optical properties and photocatalytic activity of titanium dioxide nanoparticles

S. Ezhil Arasi, J. Madhavan and M. Victor Antony Raj

Department of Physics, Loyola College, Chennai, India

**ABSTRACT**

The current work reports the hydrothermal preparation of pure TiO$_2$ and Sm$^{3+}$ ion-doped TiO$_2$ nanoparticles and the influence of samarium ion doping in the TiO$_2$ host lattice. The as-synthesized both pure and Sm$^{3+}$-doped TiO$_2$ nano samples were extensively characterized by powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray spectroscopy (EDX) and UV–VIS spectroscopy. XRD pattern reveals the crystalline size and phase of the nanoparticles and the formation of spherical morphology was confirmed by HR-TEM observation. The incorporation of Sm in TiO$_2$ is confirmed by EDX. The optical properties of TiO$_2$ and Sm$^{3+}$-TiO$_2$ nanoparticles have been studied using diffuse reflectance spectroscopy analysis. The addition of the dopant ion markedly increases the bandgap from 3.39 to 3.46 eV. The photocatalytic activity of the crystalline as-synthesized nanoparticles was examined for the degradation of Rhodamine B induced by UV irradiation and the degradation efficiency is also reported.

**1. Introduction**

Nanostructured materials are studied vastly due to their enhanced properties compared to its bulk counterparts. Various preparative methods are adapted to control the structural, electrical, optical and mechanical properties of the nanomaterials. The hydrothermal method is a superior technique in which controlled diffusion is high enough in the surrounding medium to control the particle size and morphology of the synthesized material [1]. Titanium dioxide is a semiconducting material which is used in various fields because of its non-toxicity and resistance to corrosion. TiO$_2$ is used as a photocatalyst in photocatalytic degradation due to its optical activity [2]. TiO$_2$ occurs in three forms, namely anatase, rutile and brookite [3]. Anatase TiO$_2$ is more stable than rutile TiO$_2$ and also displays a better photocatalytic activity due to its wide bandgap [4]. The anatase crystalline phase TiO$_2$ with more than 3.34 eV bandgap contains relatively high reactivity and chemical stability [5]. Recently, researchers have given much attention to the rare-earth-doped luminescent materials since they have many potential applications in optical telecommunication, lasers, biochemical probes and medical diagnostics based on the electronic, optical and chemical characteristics arising from the 4f electrons of rare-earth elements. TiO$_2$ has an excellent luminescence property due to doping comparing lanthanides doped other core lattices. TiO$_2$ is the potential material in the industry due to its high optical transparency, thermal stability, chemically inactive and desirable mechanical properties [6]. The multicolour light of rare-earth ions can be directly generated from chromatic or monochromatic external displays [7]. The removal of organic dye contaminants is important in wastewater treatment, because of the non-biodegradable nature of the pollutants. Among researchers, usage of titanium oxide, zinc oxide, cobalt oxide, etc. as a potential catalyst in UV–VIS and xenon beams becomes a highly effective method to degrade organic dyes [8]. To our knowledge, nano synthesis of rare-earth ions doped TiO$_2$ particularly Sm$^{3+}$ in TiO$_2$ and their photocatalytic activities under visible light irradiation have never been reported so far. Hence, the focus of the present work is to synthesize pure and doped nanoparticles using the hydrothermal method and to explain their structural, optical and photocatalytic properties.

**2. Synthesis procedure**

Acetic acid was added to titanium (IV) isopropoxide at room temperature and then distilled water was added to a mixture of anhydrous acetic acid and titanium isopropoxide. The stirred homogenous solution was transferred to a Teflon-coated autoclave and it was kept in a furnace at 110°C for 12 h. After the heat treatment, the suspension was cooled to ambient temperature and
centrifuged to collect the nanosized TiO2 powder, which was then washed thoroughly with distilled water and ethanol to remove all possible impurities and dried at 100°C for an hour. The resulting pastes were dried at 100°C for 1 h and were sintered at 400°C for 3 h.

In the synthesis of Sm3+-doped TiO2 nanoparticles, samarium(III) oxide was added as a dopant. The same precursor method was followed here to obtain doped nanoparticles.

2.1. Characterization

The X-ray diffraction (XRD) patterns of pure and Sm3+-doped TiO2 nanoparticles are recorded on a PANalytical XPert Pro X-ray diffractometer using CuKα radiation as the X-ray source. The diffractograms were recorded in the 2θ range of 10–80° in steps of 0.02°. Transmission electron microscopic (TEM) pictures were recorded using a JEOL/JEM 2100 electron microscope operating at an accelerating voltage of 200 keV. The elemental compositions of the samples were performed by an energy dispersive X-ray spectroscopy (EDX) analyzer operated at 5 kV accelerating voltage for around 5 min and a magnification of 1000x. UV–VIS spectra were recorded using a Varian Cary 5000 spectrometer equipped with a diffuse reflectance attachment. Investigation of photocatalytic properties was characterized by a Shimadzu UV-3600 spectrophotometer.

3. Results and discussions

3.1. X-ray diffraction analysis

The phase and structure of the prepared nanoparticles are determined by XRD. The XRD patterns are illustrated in Figure 1, which is in good agreement with the pattern of anatase TiO2 reported (JCPDS Card No: 21-1272). The diffraction peaks at 25.32°, 37.90°, 48.09°, 54.10°, 55.15°, 62.85°, 68.99°, 70.49° and 75.12° corresponds to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of the pure TiO2 nanoparticles. For Sm3+-doped TiO2 nanoparticles, the prominent peak associated with the (101) plane around 2θ = 25.22° also signifies the presence of the tetragonal anatase phase.

Relatively decreased peak intensity and shifting of the peak in the XRD pattern confirmed the substitution of Sm in the host TiO2. Highly intense diffraction peaks are representing the crystalline nature.

The average crystallite size of samples was calculated using XRD data according to the Scherer equation:

\[
D = \frac{k\lambda}{\beta\cos\theta},
\]

Figure 1. XRD pattern of pure and Sm3+-doped TiO2 nanoparticles.

Figure 2. (a) HR-TEM image and SAED pattern of pure TiO2 nanoparticles. (b) TEM image and SAED pattern of Sm3+-doped TiO2 nanoparticles.
where $D$ is the crystallite size in nm, $\lambda$ is the wavelength of the incident radiation in nm, $k$ is a constant typically equals to 0.89, $\theta$ is the diffraction angle and $\beta$ is the full width at half maximum intensity.

The average particles size for pure TiO$_2$ nanoparticle is 8.1 nm and the Sm$^{3+}$-doped TiO$_2$ nanoparticle is 7.7 nm. The crystallite size seems to be decreasing from 8.1 to 7.7 nm with the substitution of samarium.

3.2. Morphological analysis

The surface morphology of the synthesized pure and Sm$^{3+}$-doped nanoparticles was examined by a high-resolution transmission electron microscope (HR-TEM). The micrographs of pure and doped TiO$_2$ nanoparticles by using high-resolution transmission electron microscopy are shown in Figure 2(a,b). The images reveal the spherical shape of the synthesized nanoparticles.

From TEM images, it is observed that the samarium doping affects the slight difference in particles size of pure TiO$_2$. The inset of Figure 2(a,b) shows the corresponding SAED pattern of pure and doped TiO$_2$ nanoparticles. The ring pattern implies that both the nanoparticles are good crystalline in nature.

3.3. EDAX analysis

The presence of particles and the distribution of elements are investigated by the EDX element analysis.
Figure 3(a,b) shows the results of the EDX analysis of pure and Sm$^{3+}$-doped TiO$_2$ nanoparticles.

Figure 3(a) displays the presence of Ti and O in the synthesized pure TiO$_2$ nanoparticles without any other impurity. The analysis of the EDAX spectrum (Figure 3(b)) concludes that the surface contains Ti, O and Sm, which confirms the formation of Sm$^{3+}$-doped TiO$_2$ nanoparticles. This accounted for a 0.75 mol.% Sm$^{3+}$ dopant in the analysed sample.

3.4. Optical properties analysis

The optical properties of semiconducting nanoparticles were observed by UV–VIS spectroscopy which is a powerful nondestructive technique [9]. Figure 4(a,b) shows the UV–VIS diffuse reflection spectra of pure and doped TiO$_2$ nanoparticles. The reflectance spectra were recorded between 200 and 2000 nm at room temperature.

The electronic structures of semiconducting nanoparticles are relevant to the process of absorption or reflectance or transmittance of light. Hence, diffuse reflectance study is the most essential role to analyse the bandgap [10]. The Kubelka–Munk function is applied to convert the diffused reflectance into equivalent absorption coefficient:

$$\alpha = \frac{(1 - R)^2}{2R},$$

where $F(R)$ is the Kubelka–Munk function, $\alpha$ is the absorption coefficient and $R$ is the reflectance. The Tauc relation was used to determine the optical bandgap [11]. Thus, the Tauc relation becomes

$$(F(R)h\nu)^n = A(h\nu - E_g),$$

where $n = 1/2$ and 2 for direct and indirect transitions, respectively. The plots of $(F(R)h\nu)^2$ versus $h\nu$ for pure and doped TiO$_2$ nanoparticles are shown in inset Figure 4(a,b). The direct bandgap values give the extrapolation of linear regions to $(F(R)h\nu)^2 = 0$. The direct bandgap value of pure and Sm$^{3+}$-doped TiO$_2$ nanoparticles are found to be 3.39 and 3.46 eV, respectively. Doped TiO$_2$ nanoparticles were considerably blue shifted due to the size quantization.

Figure 4. (a) UV–VIS diffuse reflectance spectra and optical bandgap spectrum of the pure TiO$_2$ sample. (b) UV–VIS diffuse reflectance spectra and optical bandgap spectrum of Sm$^{3+}$-doped TiO$_2$ nanoparticles.

Figure 5. (a) Photocatalytic degradation of Rhodamine B in the presence of pure and Sm$^{3+}$-doped TiO$_2$ nanoparticles. (b) Percentage degradation of Rhodamine B.
3.5. Photocatalytic activity

Photocatalytic activity for pure and Sm$^{3+}$-doped TiO$_2$ nanoparticles was investigated by measuring the degradation of Rhodamine B in the aqueous solution. The degradation reactions were carried out using 60 mg of TiO$_2$ as a photocatalyst in 60 ml of aqueous dye solutions. Before lighting, the suspension was magnetically stirred for three hours, and in the absence of light, it is assured that the mixture had attained adsorption equilibrium. Then, the aqueous solution with catalyst was irradiated with the 125 W mercury lamp and 5 ml of the suspended mixture was taken periodically and centrifuged to remove the catalyst from the solution. The photocatalytic discoloration of dye is shown in the inset figure and their concentration was determined by a UV–VIS spectrometer.

The degradation ratios ($C/C_0$) of Rhodamine B as a function of time for both the samples were investigated and it is represented in Figure 5(a). The Sm$^{3+}$-doped TiO$_2$ photo-catalysts showed enhanced activities than pure TiO$_2$. It was found that the photocatalytic performance of anatase TiO$_2$ nanoparticles is improved in the presence of the dopant ions under the irradiation in the UV and visible ranges.

From Figure 5(b), it is understood that the photocatalytic degradation efficiency has increased to 95.76% due to doping from 88% efficiency of pure TiO$_2$ nanoparticles.

4. Conclusion

In summary, pure and Sm$^{3+}$-doped TiO$_2$ nanoparticles were synthesized by the hydrothermal method. XRD analysis confirmed the presence of the anatase phase for both pure and doped TiO$_2$ nano samples. The crystal structure of the products was identified using the powder XRD analysis. The Scherrer equation gave the particle size as 8.1 for pure TiO$_2$ and 7.7 for Sm$^{3+}$-doped TiO$_2$. HR-TEM analysis revealed the spherical imaged nanoparticles. The EDX analysis reported the presence of dopant into the TiO$_2$ lattice. UV–VIS diffuse reflectance spectra and optical bandgap of pure and Sm$^{3+}$-doped TiO$_2$ nanoparticles were studied. It was found that the optical bandgap energy increases with doping. The photocatalytic activity was tested by the degradation of dye under UV light irradiation. It is concluded that the Sm$^{3+}$-doped TiO$_2$ nanoparticles act as a better catalyst than the pure TiO$_2$.

Disclosure statement

No potential conflict of interest was reported by the authors.

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