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Structural, optical and morphological analyses of pristine titanium di-oxide nanoparticles – Synthesized via sol–gel route

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HIGHLIGHTS
- Nanocrystalline TiO$_2$ was prepared by sol–gel technique.
- Phase; mean crystallite size and lattice parameters were determined by XRD analysis.
- Direct, indirect band gap energies and particle size were evaluated from DRS.
- From PL, the emission peaks were investigated.
- SEM with EDX revealed that the morphological and elemental identification.

GRAPhICAL ABSTRACT

Pure TiO$_2$ nanoparticles.

ABSTRACT

Pure titanium di-oxide nanoparticles (TiO$_2$) were synthesized by sol–gel technique at room temperature with appropriate reactants. The synthesis of anatase phase TiO$_2$ nanoparticles was achieved by tetraiso-propyl orthotitanate and 2-propanol as common starting materials and the product was annealed at 450 °C for 4 h. The synthesized product was characterized by X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), UV–VIS-DRS, Photoluminescence (PL) spectroscopy and Scanning electron microscopy (SEM) with Energy dispersive X-ray (EDX) analysis. XRD pattern confirmed the crystalline structure and tetragonal structure of synthesized composition. Average grain size was determined from X-ray line broadening, using the Debye–Scherrer relation. The functional groups present in the sample were identified by FTIR spectroscopy. Diffuse reflectance measurement indicated an absorption band edge on UV–region. The allowed direct and indirect band gap energies, as well as the crystallite size of pure TiO$_2$ nanoparticles are calculated from DRS analysis. The microstructure and elemental identification were done by SEM with EDX analysis.

INTRODUCTION

As for many oxides, properties of TiO$_2$ are directly determined by its polymorphs. TiO$_2$ occurs in nature in three different phases, namely, rutile, anatase and brookite [1]. The unit cell structures of the polymorphs together with their basic parameters are reported in earlier literature [2]. The rutile is the most stable structure of TiO$_2$, whereas the anatase and brookite are considered as metastable forms. Nevertheless, the highest photocatalytic activity is attributed to the anatase phase. From this perspective, the titania crystallinity plays a crucial role and influencing the overall photo-efficiency of the layers. On the other side, while the pure form of the anatase and rutile is relatively easy to obtain, in case of brookite it is much more difficult [3]. Among these polymorphs, rutile and anatase have been widely studied. Bookite is rarely studied...
due to its complicated structure and difficulties in sample preparation [4]. These three phases can be commonly described as constituted by arrangements of the same building block-Ti-O₆ octahedron in which Ti atom is surrounded by six oxygen atoms situated at the corners of a distorted octahedron. In spite of the similarities in building blocks of Ti-O₆ octahedra for these polymorphs, the electronic structures are significantly different [11].

Nanostructural titania is one of the most widely studied materials due to its unique and excellent properties in optics, electronics, photochemistry and biology, as well as its applications in photovoltaic cells, photocatalysis, and sensors [5–8]. A significant amount of research on TiO₂ has been performed over the last five decades and a number of reviews on various aspects of TiO₂ have been published [2,9–14] to understand and summarize the progress in this field. TiO₂ is a large band semiconductor, with band gaps of 3.2, 3.02, and 2.96 eV for the anatase, rutile and brookite phases, respectively [15]. Anatase TiO₂ is considered to be the active photocatalytic component based on charge carrier dynamics, chemical properties and the activity of photocatalytic degradation of organic compounds [16]. In the present work, we report on the synthesis and characterization of nanocrystalline TiO₂ having narrow size distribution and minimal agglomeration. Besides, the prepared nano-titania was examined using various analytical techniques. We also investigate and discuss the structure and properties of the prepared TiO₂.

### Experimental

**Sol–gel technique**

The sol–gel reaction was widely used for making transition metal oxide solids with fine-scale nanostructures. This technique consists of two step reactions: hydrolysis of metal alkoxide to produce hydroxyl groups then followed by the polycondensation of the hydroxyl groups and residual alkoxy groups to form a three dimensional network. The carboxylic acid end groups undergo a condensation reaction with titania and provide an organometallic bond. No additional coupling agents or chelating ligands were used in the preparation of the TiO₂ material [17]. The nanoparticles prepared using sol–gel method is amorphous in nature and need further heat treatment to get a crystalline product. This may lead to the grain growth and may also induce phase transformation [18].

**Preparation of TiO₂ nanoparticles**

Nano-TiO₂ was prepared by sol–gel method. All chemical reagents used in the present study were obtained from commercial sources as analytical reagent (AR) grade and used without any further purification. In a typical synthesis, 10 ml of tetra-isopropyl orthotitanate (Ti(OPr)₄), TiO₂, assay ≥98% purchased from Merck (Germany), was dissolved in 90 ml of isopropyl alcohol (Propan-2-OL, (CH₃)₂CHOH, assay ≥99%) solution obtained from Fisher scientific (Mumbai) and to this solution 5 ml of deionized water was added drop wise with vigorous stirring. The resulting colloidal suspension was stirred for 4 h at room temperature using magnetic stirrer. The white gel obtained was filtered by Whatman filter paper (110 mm) and washed several times using ethanol and deionized water. The yield gel was dried in hot air oven at 100 °C for 6 h to evaporate water and organic material to the maximum extent. Then the dried powder was ground by agate mortar using pestle to remove agglomerates. Finally, the powder was kept into muffle furnace and calcinated at 450 °C for 4 h to obtain desired pure TiO₂ nanocrystalline. The calcined powder was pulverized to fine powders using agate mortar for further characterizations.

**Characterizations**

The crystalline phase and particle size of TiO₂ nanoparticles were analyzed by X-ray diffraction (XRD) measurement, which was carried out at room temperature by using XPERT-PRO diffractometer system (scan step of 0.05°, counting time of 10.16 s per data point) equipped with a Cu tube for generating Cu Kα radiation (λ = 1.5406 Å). The incident beam in the 2-theta mode over the range of 10–80°, operated at 40 kV and 30 mA. The chemical structure was investigated by AVATAR 330 Fourier transform infrared spectrometer (FTIR) in which the IR spectrum was recorded by diluting the milled powder in KBr and in the wavelength between 4000 and 400 cm⁻¹ was used to assess the presence of functional groups in TiO₂. The diffuse reflectance spectrum (DRS) was measured at wavelength in the range of 200–800 nm by UV–Vis–NIR spectrophotometer (Varian/Cary 5000) equipped with an integrating sphere and the baseline correction was performed using a calibrated reference sample of powdered barium sulfate (BaSO₄). The photoluminescence (PL) emission spectrum of the sample was recorded with a Spectrofluorimeter (Jobin Yvon, FLUOROLOG – FL3-11). The surface morphology of pure TiO₂ was observed by a scanning electron microscope (SEM: Hitachi, S-3400N). The dispersion of titanium and oxygen in the product was characterized by energy dispersive X-ray elemental analysis (EDX: Thermo SuperDry II) equipped with the SEM instrument.

**Results and discussion**

**Phase and crystallite size analysis**

Powder X-ray diffraction pattern of pure TiO₂ nanoparticles annealed at 450 °C with miller indices (hkl) showing the crystal family of planes for each diffraction peak are depicted in Fig. 1. In the prepared product, several diffraction peaks appeared and all of them could be clearly attributed to the characteristic peaks of TiO₂ and it can be well indexed to anatase phase (JCPDS-ICDD card: 21-1272). The intense diffraction peaks appearing at about 2θ of 25.28°, 37.81°, 47.99°, 53.95°, 55°, 62.9° and 75° corresponding with those from (101), (004), (200), (105), (211), (204) and (215) orientations, respectively. The average crystallite size has been inferred from 2θ and the full width at half maximum (FWHM) of the (hkl) peaks using Debye–Scherrer relation.

Fig. 1. X-ray diffractogram of pure anatase TiO₂ nanoparticles.
$D = \frac{K \lambda}{\beta \cos \theta} \text{Å}$

where $D$ is the average crystallite size (Å), $K$ is the shape factor (0.9), $\lambda$ is the wavelength of X-ray (1.5406 Å) Cu Kα radiation, $\beta$ is the Bragg angle, and $\theta$ is the corrected line broadening of the nanoparticles [19]. The result shows that the mean crystallite size of nano-TiO$_2$ is about 15.31 nm. However, a smaller crystallite size could lead to larger surface area, which would be beneficial for increasing the photocatalytic activity of the material. Estimation of the crystallite sizes using this relation are given in Table 1. The lattice parameters ‘$a$’ and ‘$c$’ for the tetragonal structure ($a = b \neq c$, $x = \beta = \gamma = 90^\circ$) can be calculated by the following equation,

$$\sin^2 \theta = \frac{j^2(h^2 + k^2)}{4a^2} + \frac{j^2(l^2)}{4c^2} \text{Å}$$

where $h$, $k$, and $l$ are the Miller indices of the peak. From the values of ‘$a$’ and ‘$c$’, the unit cell volume ($V$) can be determined [20]. The calculated lattice parameters for anatase phase of TiO$_2$ are $a = b = 3.7881$ Å, $c = 9.5132$ Å and $V = (a^2c) = 136.51$ Å$^3$. Hence, the standard JCPDS pattern of anatase (21-1272), tetragonal, body centered, $a = b = 3.785$ Å, $c = 9.513$ Å and $V = 136.31$ Å$^3$ matches well with the recorded XRD. The calculated results are shown in Table 2. The obtained diffraction pattern shows that only anatase TiO$_2$ crystalline formation (neither rutile nor brookite structure was observed). The signal to noise ratio indicates that the synthesized nanoparticles are crystalline. It was reported that the anatase to rutile transformation in the annealing process does not occur at temperatures below 600 °C [21]. Calcination is a common treatment used to improve the crystallinity [20] of TiO$_2$ powder, however increasing the annealing temperature to 450 °C resulted in the formation of anatase TiO$_2$ with high crystallinity.

**Fourier transform infrared spectroscopy**

The FTIR transmission spectrum of TiO$_2$ nanoparticles synthesized at the temperature of 450 °C in air for 4 h is shown in Fig. 2. The reaction between precursor materials of TiO$_2$ resulted in the white powdered product. For clarifying whether TiO$_2$ particles have corresponding functional groups, the chemical structures of TiO$_2$ were characterized with FTIR spectroscopy. The FTIR study of TiO$_2$ nanoparticles shows the characteristics of the formation of high purity product and depicts the peaks correspond to TiO$_2$. From the FTIR spectrum, several peaks at 3391.72, 2920.55, 2849.32, 1747.95, 1627.28, 1342.47, 728.77 and 463.88 cm$^{-1}$ can be observed.

TiO$_2$ nanoparticles have significant hydroxyl groups on the surface. Moreover, small crystallites could result in the broadness of the peaks. The spectroscopic band is observed at around 3391.72 cm$^{-1}$, which is described to the both symmetric and asymmetric stretching vibrations of the hydroxyl group (Ti–OH) [22]. A broad band observed in between 3600 and 3000 cm$^{-1}$ is related to the O–H stretching mode of hydroxyl group, indicating the presence of moisture in the sample. The characteristic peak at 1627.28 cm$^{-1}$ is associated with the O–H bending vibrations of the absorbed water molecules. Therefore, the two observed peaks at 3391.72 and 1627.28 cm$^{-1}$ correspond to the surface adsorbed water and hydroxyl groups [23] and the presence of OH bands in the spectrum was owing to chemically and physically adsorbed H$_2$O on the surface of nanoparticles [24]. It was reported that the broad band from 1000 to 400 cm$^{-1}$ region is ascribed to the Ti–O stretching and Ti–O–Ti bridging stretching modes [25]. For the pure TiO$_2$, the peaks at 463.88 and 728.77 cm$^{-1}$ in the range of 400–800 cm$^{-1}$ are the contributions from the anatase titania. A broad absorption band between 450 and 800 cm$^{-1}$ region is ascribed to the vibration absorption of the Ti–O–Ti linkages in TiO$_2$ nanoparticles [26]. According to the standard spectra of TiO$_2$, the peak at 463.88 cm$^{-1}$ should be attributed to the vibration of Ti–O bond in TiO$_2$ (anatase titania) lattice, it indicates that the organic ligand was completely eliminated after annealing at 450 °C. At the same time, the metal oxide TiO$_2$ was formed by thermalysis of the powdered product [27]. The IR absorption band at 728.77 cm$^{-1}$ is attributed to the Ti–O–Ti stretching vibrations [22].

The prepared product has some weak absorption bands correspond to the vibrational modes of organic species such as hydroxyl, carboxilate and alkane groups. Two weak bands at 2920.55 and 2849.32 cm$^{-1}$ could be ascribed to the characteristic frequencies of residual organic species, which was not completely removed by ethanol and distilled water washing are assigned to C–H stretching vibrations of alkane groups. The peaks at 1340–1520 cm$^{-1}$ region could be attributed to carboxyl (C=O) and methylene groups. The carboxyl and methylene groups might also be resulted from residual organic species [28]. The peak at 1747.95 cm$^{-1}$ can be associated to the asymmetric stretching vibrations of C=O.

**Table 1**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>JCPDS</td>
</tr>
<tr>
<td>Anatase</td>
<td>Tetragonal</td>
<td>$a = b = 3.7881$</td>
<td>$a = b = 3.785$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 9.5132$</td>
<td>$V = 136.51$</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
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<tr>
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<td></td>
<td></td>
<td>$c = 9.5132$</td>
<td>$V = 136.51$</td>
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</table>

**Fig. 2.** FTIR spectrum of anatase TiO$_2$ nanoparticles indicating relative functional groups.
mode of titanium carboxilate. The alkane and carboxilate groups come from TiOT and 2-propanol precursors used in the synthesis process. The intensity of the bands associated with the organic groups is considerably weak because the synthesized product was annealed at 450 °C, indicating the elimination of organic species [29]. The absence of peak at 900 cm\(^{-1}\) proves the absence of peroxo groups. The FTIR spectrum firmly suggests the presence of Ti–O bonds, OH groups and the absence of peroxo groups in the final product [18]. Hence, the experimental results of FTIR spectrum indicate that the relative functional groups are presented in TiO\(_2\) nanoparticles. It is well known that the rapid condensation reactions between the large amounts of uncondensed Ti–OH existed on the surface of the amorphous mesoporous TiO\(_2\), would wall the pores of mesoporous TiO\(_2\) to collapse during calcinations [30]. The TiO\(_2\) nanoparticles prepared for the present study are of good quality and can be used for further characterizations. The infrared absorption frequencies and the corresponding vibrational assignments are represented in Table 3.

### UV–VIS–DRS analysis

**Determination of band gap energy**

The diffuse reflectance spectrum of prepared anatase TiO\(_2\) was illustrated in Fig. 3. The TiO\(_2\) material showed an intense absorption in the UV region and the absorption edge of titania can be easily discerned. Compared with bulk TiO\(_2\) [31], a shift of the reflectance spectrum of nano-TiO\(_2\) towards the lower wavelength region was observed. The band gap energy (\(E_g\)) of pure TiO\(_2\) was obtained from the wavelength value corresponding to the intersection point of the vertical and horizontal part of the spectrum, using the equation [32]:

\[
E_g = \frac{hc}{\lambda}; E_g = \frac{1240}{\lambda}\ eV
\]

The energy band gap corresponds to the absorption limit and can be roughly evaluated by the above relation. Whereas \(E_g\) is the band gap energy (eV), \(h\) is the Planck’s constant \((6.626 \times 10^{-34}\text{ J s})\), \(c\) is the light velocity \((3 \times 10^8\text{ m/s})\) and \(\lambda\) is the wavelength (nm). The absorption edge of nano-TiO\(_2\) was at 345.49 nm, corresponding to a band gap of 3.5891 eV, which is usually ascribed to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d\(_{x^2-y^2}\) orbitals of the Ti\(^{4+}\) cations) [33]. Whereas, the absorption edge of bulk TiO\(_2\) was at 385 nm, corresponding to the band gap of 3.2 eV [23]. It clearly shows that the calculated band gap energy of the nano-TiO\(_2\) is higher than that of bulk TiO\(_2\). The valence band edge of TiO\(_2\) is mainly determined by O 2p states, while the conduction band edge is of Ti 3d character predominantly; The Fermi level is at the top of the valence band. Therefore, the absorption edge corresponds to the electron transition from p states to d states. The increase in band gap of nano-TiO\(_2\) from bulk is due to the size effect [34] of the synthesized TiO\(_2\) nanoparticles (<25 nm). Notably, the band gap depends on the crystalline structure and the defects in the network of TiO\(_2\).

#### Direct and indirect band gap energy

The absorption edge of the nano-TiO\(_2\) was blue-shifted about ≤40 nm, compared with that of bulk TiO\(_2\). Manifacier model is used to determine the absorption co-efficient from the absorbance data [35]. The fundamental absorption, which corresponds to the transmission from valance band to conduction band, is employed to determine the band gap of the material. The direct band gap energy can be estimated from a plot of \((zhv)^2\) vs. photon energy (\(h\nu\)) by using the relationship,

\[
zhv = A(h\nu - E_g)^n
\]

The optical absorbance coefficient (\(\alpha\)) of a semiconductor close to the band edge can be expressed by the following equation,

\[
\alpha = A\left(\frac{h\nu - E_g}{h\nu}\right)^n
\]

where \(\alpha = 4\pi nk/\lambda\) \((k\) is the absorption index or absorbance) and \(A\) depicts constant factor. The exponent \(n\) depends on the nature of the transitions; \(n\) may have values 1/2, 2, 3/2 and 3 corresponds the allowed direct and allowed indirect, forbidden direct and forbidden indirect transitions. In this case \(n = 1/2\) for the allowed direct transition. The plot of \((zhv)^2\) vs. \(h\nu\) was presented in Fig. 4. The value of energy band gap was determined by extrapolating the straight line portion of \((zhv)^2 = 0\) axis (i.e. the zero co-efficient); as shown in Fig. 4, which is calculated from the above equation. The intercept of the tangent to the plot will give a good approximation of the direct band gap energy of the material [20]. The direct band gap energy of prepared TiO\(_2\) nanoparticles was calculated to be 3.5810 eV. Therefore, the band gap increases with decreasing particle size and the absorption edge is shifted to the higher energy region. Considering the blue shift of the absorption position from the bulk TiO\(_2\), the absorption onset of the present material can be assigned to the direct transition of electrons in the TiO\(_2\) nanocrystals [36].

The indirect band gap energy of TiO\(_2\) nanoparticles can be estimated from plot of the square root of Kubelka Munk function \(F(R)\) vs. \(h\nu\). The reflectance data was converted to the absorption coefficient \(F(R)\) values according to the Kubelka–Munk equation [37],

\[
F(R)_{\text{KM}} = \frac{(1 - R)^2}{2R}
\]

![Fig. 3. UV–Vis-Diffuse reflectance spectrum of bare TiO\(_2\) nanoparticles.](image-url)
which can be expressed as,

\[ F(R)_{\text{KM}} = C_1 (hv - E_g)^2 \]

where \( F(R)_{\text{KM}} \) is equivalent to the absorption coefficient \( \alpha_{\text{KM}} \), which can be expressed as,

\[ \alpha_{\text{KM}}(hv) = C_1 (hv - E_g)^2 \]

where \( C_1 \) is the absorption constant for indirect transition. In this case \( n = 2 \) for the allowed indirect transition. Fig. 5 shows the plot of Kubelka–Munk function (i.e., relationship of \( (\alpha_{\text{KM}}hv)^{1/2} \) vs. \( hv \)) and the linear segment of the spectra is extrapolated to intersect the \( hv \) axis to obtain the band gap value of allowed indirect transition \( E_g \) of the material. The nano-TiO\(_2\) exhibits the indirect band gap value of 3.5806 eV. This result is consistent with the fact that the conduction band edge of nano-TiO\(_2\) is about 0.38 eV more positive than that of bulk anatase. It indicates that the content of anatase in TiO\(_2\) would influence the indirect band gap value of nano-TiO\(_2\). Hence, Ti atoms rearrange to an octahedral structure when converted from amorphous titania to crystalline TiO\(_2\). It is evident that TiO\(_2\) shows large optical absorbance in the UV region. Hence, the direct and indirect band gap values are larger than the value of 3.2 eV for the bulk TiO\(_2\) and validates our crystallite size result obtained from XRD (15.31 nm) analysis according to which smaller crystallite size should have larger band gap.

**Determination of crystallite size (Brus model)**

The particle size of the prepared TiO\(_2\) nanoparticles has been determined from the relationship between band gap shift \( \Delta E_g \) and radius \( R \) of nanoparticles using the following expression [23],

\[ \Delta E_g = \frac{\pi^2 h^2}{2 \mu R^2} \frac{1.8e^2}{4R} + \text{Polarization terms} \]

where \( h \) is Planck’s constant, \( R \) is the radius of the particle, \( \varepsilon \) is the dielectric constant of the semiconductor material and \( \Delta E_g \) is the band gap shift (i.e. \( \Delta E_g = E_{g(nano) - E_{g(bulk)}} \)). The calculated band gap shift for the nano-anatase TiO\(_2\) (3.58 eV) is 0.38 eV, as compared to bulk anatase (3.2 eV). This shift typically follows the Brus model or the effective mass approximation approach, which provides a quantitative interpretation of the shift in onset of absorption energy as a function of crystallite dimension and effective mass of the electrons and holes. The onset of absorbance provides insight into the band gap of the TiO\(_2\) semiconductor material, which can be significantly different from that of the bulk material [38]. \( \mu \) is the reduced mass of the exciton, i.e., the reduced effective mass of the electron and the hole \( (1/m_e + 1/m_h) \) in the semiconductor. As the reported effective mass of the electron, \( m_e \) was in the range of 5–13\( m_0 \). The effective mass of the hole, \( m_h \) was reported to be \( \sim 2m_0 \). \( e \) is the electron charge \( (1.6 \times 10^{-19} \text{C}) \). The shifts in band gap were significantly affected by the reduced mass of exciton and the dielectric constant of the semiconductor \( \varepsilon \). The value of \( \mu = 1.63m_0 \) \( (m_0 \text{ is the electron rest mass } = 9.1 \times 10^{-31} \text{ kg}) \) and range between 1.43 and 1.73\( m_0 \). The dielectric constant of TiO\(_2\) anatase crystalline was reported to be between 23 and 184 [37]. Since the optical dielectric constant of bulk titanium di-oxide is very large \( (\varepsilon = 170) \), the columbic and polarization terms in the equation are neglected. The calculated \( \Delta E_g \) is 0.38 eV of this blue shift compared to bulk anatase TiO\(_2\), indicated a size of TiO\(_2\) nano-crystallites smaller than 25 nm. However, the particle size of TiO\(_2\) is calculated from both the reflectance spectrum as well as by analysis of the XRD data. The calculated crystallite size of the prepared TiO\(_2\) (Brus model) is 24.49 nm. Hence, the crystallite size evaluated from XRD (Debye–Scherrer) is around 15.31 nm, which is lower than the value obtained from Brus model; this may be due to aggregation of nanoparticles. The comparison of bad gap energies by direct and indirect methods and crystallite size measurement by DRS analysis with XRD are depicted in Table 4.

**Photoluminescence spectroscopy**

Information on the structural defects and the extent of charge carrier recombination was determined by PL study in order to provide rationale for the photo catalytic efficiency of the TiO\(_2\) material. The PL spectrum of pure TiO\(_2\) nanoparticles excited at 345 nm

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**Table 4** Comparisons of band gap energies and crystallite size measurements.

<table>
<thead>
<tr>
<th>Bulk TiO(_2) [31]</th>
<th>Anatase TiO(_2) nanoparticles</th>
<th>Calculated Band gap energy (eV)</th>
<th>Band gap shift ( \Delta E_g )</th>
<th>Calculated Crystallite size (nm)</th>
</tr>
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<tr>
<td>( E_g = 3.2 \text{ eV} )</td>
<td>( E_g = 1240/\lambda )</td>
<td>Direct</td>
<td>Indirect</td>
<td>XRD (Debye–Scherrer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5891</td>
<td>3.5810</td>
<td>3.5806</td>
</tr>
</tbody>
</table>
(Fig. 6) and the emission bands originating from the excited level was monitored in the spectral region between 350 and 640 nm. The wavelength corresponding to various transitions were calculated based on the Daude model [39]. The energy of the trap level identified in this spectrum at 587 nm is attributed to Ti$^{4+}$ ions adjacent to oxygen vacancies (intra gap surface states). In addition, TiO$_2$ nanoparticles could exhibit a strong PL signal at about 431 nm (400–450 nm range), possibly mainly resulting from band edge free excitons and this surface emission is attributed to indirect transition $X_{1a}$ to $\Gamma_{1b}$ and linked to exciton recombination in shallow trapped surface state [40]. From the emission spectrum, a band at 373 nm is attributed to the first vibronic fluorescence band (i.e. symmetry forbidden 0–0 band ($I_1$)) [34]. The high PL intensity of bare TiO$_2$ is indicative of emissions resulting from electron hole recombination.

There were many oxygen vacancies on the surface of TiO$_2$ nanoparticles, and the size of particles (15.31 nm, from XRD) was fine so that the average distance the electrons could move freely was very short. These factors could make the oxygen vacancies very easily bind electrons to form excitons. Thus, the exciton energy level near the bottom of the conduction band could come into being, and the PL band of the excitons showed in Fig. 6 could also occur. In general, the smaller the crystallite size, the larger the oxygen vacancy content, the higher the probability of exciton occurrence and stronger the PL signal. As the used excited energy was lower than the band gap energy of TiO$_2$, the PL signal mainly resulted from the electron transitions related to surface defects or surface state energy level other than the electron transitions between the conduction band and valence band [41]. During the process of PL, oxygen vacancies and defects could bind photoinduced electrons to form free or binding excitons so that PL signal could easily occur. However, the morphology could make impacts on the intensity of luminescence. The possible reasons are: the luminescence intensity is significantly enhanced due to the specific surface area and due to abundant local defects of the nanoparticles. Moreover, the interface effect of the nanomaterial resulted that less resonant energy could migrate to the quenching center existing at the surface of the nanoparticles, which resulted in higher luminescence intensity [42]. The PL intensity is more in case of the sintered (450 °C) nanoparticles, so that the TiO$_2$ material needs to be sintered at higher temperature to remove the binders and to get the crystalline nanoparticles.

**Morphological characterization**

**SEM with EDX analysis**

Nanostructural analysis using SEM supplemented by EDX were carried out for the anatase TiO$_2$ to establish the grain size, shape
and confirm their chemical composition. To obtain information about morphology of the product, the synthesized powder was investigated by scanning electron microscopy. SEM observed the nano-sized TiO$_2$ grains, large surface area, well-defined mesopores and the images are shown in Fig. 7. Fig. 7a–c showed the micrographs of nano-TiO$_2$ with different magnifications, confirm that the nanoparticles are grown in a very high density. From SEM micrographs, non-uniform distribution of particles was found and they consist of either single particle or cluster of particles. A closer examination of these figures reveals a well-defined particle-like morphology, having abundance of spherical shaped particles with the average agglomerated particle size in the range 16.25–22.36 nm with mean particle size of 18.98 nm and it could be suggested that the nanospheres obtained are homogenous. This average size value of nanoparticles was obtained for 20,000× magnification (Fig. 7c). The particle size distribution is illustrated in Fig. 8. It can be seen that the nanoparticles of TiO$_2$ have a well-defined shape with weak agglomeration, though the problems of agglomeration are common and expected in sol–gel synthesis. The actual size of the nanoparticles cannot be determined from the SEM images as the resolution of the SEM instrument used is limited. It was clearly seen that the surface of the pristine TiO$_2$ was smooth and porous in nature, which resulted from the growth of nanoparticles and each particle was approximately 18.98 nm (Fig. 7c) in diameter and it is near agreement with the size estimated from XRD (15.31 nm). Higher magnification of the uniform surface area of TiO$_2$ was shown in Fig. 7b and it can be estimated that TiO$_2$ has large specific surface area. However, it cannot be ruled out that some TiO$_2$ particles are too small to be observed at the resolution of the used microscope. Therefore, it is possible to assess that the pristine anatase grains have rounded shape and form sponge-like aggregates. The shape stability of TiO$_2$ nanoparticles is highly dependent on surface chemistry and the synthesis conditions play a key role [43]. However, the shape is more angular and a little more elongated in the view of higher magnifications. Energy dispersive X-ray spectroscopy (EDX) was employed here to examine the crucial information regarding the chemical composition of the titania nanoparticles as demonstrated in Fig. 7d. The EDX analysis clearly showed that the elements such as Ti and O are found in the spectrum, indicating that the TiO$_2$ matrix has composed of titanium and oxygen only. The strong X-ray peaks associated with Ti K$_\alpha$ and O K$_\alpha$ in the EDX spectrum (Fig. 7d), from that we noticed that the atomic and weight percentages of the elements Ti and O are 39.59 at.% , 66.24 wt.% and 60.41 at.% , 33.76 wt.% respectively.

Conclusions

The nanocrystals of TiO$_2$ were successfully synthesized by Sol–gel method. The XRD results reveal that the synthesized nanocrystals were of anatase phase with crystallite size of 15.31 nm. The existence of functional groups was identified by FT-IR measurement. The optical cut off wavelength was evaluated from UV–VIS-DRS analysis and the band gap energy was found to be 3.58 eV. The PL analysis shows the existence of both UV and visible emissions. This large band gap value and potential luminescence properties make TiO$_2$ as a suitable material for its usage in semiconductor and optoelectronic devices. The morphological analysis of pure TiO$_2$ nanostructures indicates that the mesoporous spherical shaped with non-uniform distribution of particles. The elemental identification was performed by EDX analysis and it represents the TiO$_2$ has relative atomic and weight percentages of titanium and oxygen.

Acknowledgements

The authors are thankful to Dr. S. Baradhan, The Professor and Head, Department of Physics, Annamalai University, who is very accommodative and has provided the necessary laboratory facilities to carry out this work in a short time. The authors also thank Sophisticated Analytical Instrumentation Facility (SAIF), Cochin and Central Instrumentation Facility (CIF), Pondicherry University, for their analytical instrument facilities.

References

Sol–gel synthesis and characterization of pure and manganese doped TiO$_2$ nanoparticles – A new NLO active material

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**Highlights**
- Crystallite sizes and lattice parameters were determined by XRD analysis.
- Direct, indirect band gap energies and particle sizes were evaluated from DRS.
- SEM with EDX revealed the morphological and elemental identification.
- PL spectra depicted the Mn–TiO$_2$ nanoparticles have enhanced intensity.
- SHG efficiency of Mn–TiO$_2$ has 0.25 times greater than that of pure TiO$_2$ with respect to KDP crystal.

**Abstract**

Pure and Manganese (4%, 8%, 12% and 16%) doped titanium di-oxide (Mn–TiO$_2$) nanoparticles were synthesized by sol–gel technique. The preparation of pure and Mn doped TiO$_2$ nanoparticles were achieved by tetra-isopropyl orthotitanate and 2-propanol as common starting materials and the products were annealed at 450 $\degree$ C and 750 $\degree$ C to get anatase and rutile phases, respectively. The prepared materials were characterized by X-ray diffraction analysis (XRD), Fourier transform infra-red spectroscopy (FT-IR), UV–VIS-Diffuse reflectance spectroscopy (DRS), Photoluminescence (PL) spectroscopy, Scanning electron microscopy (SEM) with Energy dispersive X-ray analysis (EDX) and Kurtz powder second harmonic generation (SHG) test. XRD patterns confirmed the crystalline nature and tetragonal structure of synthesized materials. The functional groups present in the samples were identified by FTIR study. The allowed direct and indirect band gap energies, as well as the crystallite sizes of obtained nanoparticles were calculated from DRS analysis. Microstructures and elemental identification were done by SEM with EDX analysis. The existence of SHG signals was observed using Nd: YAG laser with fundamental wavelength of 1064 nm. The products were found to be transparent in the entire visible region with cut-off wavelengths within the UV region confirms its suitability for device fabrications.

**Introduction**

Transition metal oxides are a fascinating class of inorganic materials, exhibiting a wide variety of structures, properties, and phenomena. Associated with their complex structures, these materials show a gamut of interesting properties: diverse electronic, magnetic, and optical properties. Metal oxides occur in nature as many minerals and are used in many applications such as pigments, catalysts, catalyst supports, ceramics, energy storage, magnetic data storage, sensors, and ferrofluids [1]. Nanocrystals generally display properties different from the bulk material or
the atomic or molecular species from which they are derived. A key to the study of their size-dependent properties is the availability of samples of high quality, internally crystalline nanoparticles. For significant physical measurements to be made, these samples must be macroscopic, and therefore a distribution in particle sizes is inevitable. This distribution ought to be as narrow as possible, and the position of its peak as controllable as possible. In large part, these latter goals have been achieved in the cases of nanocrystals of II–VI semiconductors and some of the late transition metals and coinage metals, but, by comparison, little work has been devoted to the synthesis of surface-passivated nanoparticles of transition metal oxides, despite their scientific potential and technological importance. TiO$_2$ nanoparticles are of particular interest in as much as they have been widely used in important technological applications. The dye-sensitized TiO$_2$ solar cells are inexpensive and have high photon to electron conversion efficiency [2,3]. TiO$_2$ is probably the most investigated photocatalyst system and has been found to be capable of decomposing a wide variety of organics [4]; it is becoming a promising material for lithium rechargeable batteries [5]. Syntheses of transition metal oxide nanoparticles often involve water as solvent or reactant and thus result in particles with hydroxylated surfaces that influence properties of materials significantly [6,7]. Oxide nanoparticles lacking such hydroxylated surfaces are expected to have properties that are different from their counterparts, particularly in terms of their subsequent chemical behavior [8].

Optical second harmonic (SH) spectroscopy has emerged as a new tool for the analyses of surfaces and interfaces of solid-state materials [9–12]. By using the surface and interface specificity and resonance profile of second harmonic generation (SHG), we can find the distribution of surface and interface electronic levels on the energy scale in the band-structure. By using the strong anisotropy of the SH response from asymmetric atomic bonds, we can find information on the surface and interface structures including those with adsorbates. This nonlinear optical technique offers us several significant advantages over the conventional surface spectroscopies. Unlike the method using electron or ion beams, it is free of material damage and contamination associated with charged particles. Sample surfaces in reaction in gaseous environment are accessible and so are the interfaces buried under optically transparent materials. The stoichiometric TiO$_2$ investigated in this study is a semiconductor and its surface electronic states can be studied in principle by ion or electron probes and also it can be studied with no problem by SH spectroscopy. In SH spectroscopy one can take advantage of the excellent spectral and temporal resolution given by the well-developed pulsed lasers or coherent light sources. In spite of these advantages, the analysis of the anisotropy and the spectra of SH intensity of solid-state material surfaces is not easy, and has not been performed widely. Only a limited number of attempts of systematic analyses have been made so far [13–17]. Choi et al. [18] performed a systematic study of TiO$_2$ nanoparticles doped with 21 metal ions by the sol–gel method and found that the presence of metal ion dopants significantly influenced the photoreactivity, charge carrier recombination rates, and interfacial electron-transfer rates [19]. Newly, Lu et al. [20] have investigated the Mn doped TiO$_2$ thin films with significantly improved optical and electrical properties. In our earlier works, the preparation and properties of sol–gel derived pure and transition metal elements (such as Fe, Cu, and Ag) doped TiO$_2$ nanoparticles have been analyzed [21–24]. In the present study, we report on the sol–gel synthesis and characterization of TiO$_2$ nanomaterials doped with manganese (Mn) in different atomic weight percentages (4%, 8%, 12% and 16%) capable to have enhanced optical properties. Also, the structural, functional and morphological analyses of the nanopowders were performed. The NLO activity of the TiO$_2$ nanostructures was investigated for the first time.

**Experimental**

**Sol–gel synthesis of Mn–TiO$_2$ nanoparticles**

All chemical reagents were obtained from commercial sources as analytical reagent (AR) grade and used without any further purification. In a typical synthesis, 10 ml of tetra-isopropyl orthotitanate (TITOT) and 2-propanol mixed solutions separately. The resulting colloidal suspensions were stirred for 4 h at room temperature using magnetic stirrer. The white and yellowish gray gels were obtained for pure and Mn doped TiO$_2$ respectively. Then, filtered by Whatman filter paper (110 mm Ø) and washed several times using ethanol and deionized water. The yield gels were dried in hot air oven at 100 °C for 6 h to evaporate water and organic material to the maximum extent. Then the dried powders were ground by agate mortar using pestle to avoid agglomerates. Finally, the powders were kept into muffle furnace and annealed at 450 °C and 750 °C for 4 h each subsequently carried out to obtain desired pure and Mn doped TiO$_2$ nanocrystallites. After the annealing process, the pure TiO$_2$ has white in both anatase and rutile phases. Meanwhile, Mn–TiO$_2$ has turned from yellowish gray to dark yellow when the phase transformed from anatase to rutile. The annealed powders were pulverized to fine powders using agate mortar for further characterizations.

**Characterizations**

The crystalline phase and particle size of pure and Mn doped TiO$_2$ nanoparticles were analyzed by X-ray diffraction (XRD) measurement which was carried out at room temperature by using XPERT-PRO diffractometer system (scan step of 0.05° (2θ), counting time of 10.16 s per data point) equipped with a Cu tube for generating Cu Kα radiation (λ = 1.5406 Å); as an incident beam in the 2-theta mode over the range of 10°–80°, operated at 40 kV and 30 mA. The functional groups were determined by AVATAR 330 Fourier-transform infrared spectrometer in which the IR spectra were recorded by diluting the milled powders in KBr and in the wavelength between 4000 and 400 cm$^{-1}$ was used to assess the presence of functional groups in pure and Mn doped TiO$_2$. The band-gap energy and the particle size were measured at wavelength in the range of 200–800 nm by UV–Vis–NIR spectrophotometer (Varian/Carry 5000) equipped with an integrating sphere and the baseline correction was performed using a calibrated reference sample of powdered barium sulfate (BaSO$_4$). The photoluminescence (PL) emission spectra of the samples were recorded with a Spectrofluorimeter (Jobin Yvon, FLUOROLOG – FL3–11). The surface morphology of pure and Mn doped TiO$_2$ was observed by a scanning electron microscope (SEM: Hitachi, S-3400N). The dispersion of Titanium, Oxygen and Manganese in the products was characterized by energy dispersive X-ray elemental analysis (EDX: Thermo SuperDry II) equipped with the SEM instrument. The NLO property of the materials was confirmed by the Kurtz powder second harmonic generation (SHG) test. The materials were illuminated using Spectra physics Quanta Ray DHS2. The SHG radiations of 532 nm green light were collected by a photomultiplier tube (PMT – Hamatsu R2059) after being monochromated (monochromator – Czerny – Turner) to collect only the 532 nm radiation. The optical signal incident on the PMT was converted...
into voltage output at the CRO (Tektronix-TDS 3052B). The input laser energy incident on the powdered samples was chosen to be 2.6 mL/pulse and 4.5 mL/pulse, respectively for pure and Mn doped TiO$_2$ nanoparticles.

Results and discussion

Structural analysis

The crystal structures of the synthesized powders were clarified to be single phase of anatase by XRD measurements. Fig. 1 shows the X-ray diffraction patterns for pure and Mn doped TiO$_2$ nanoparticles with different weight percentages (4%, 8%, 12% and 16%). All the peaks were indexed within the tetragonal system with body centred anatase phase, space group I4$_1$/amd, which crystal structure is composed of stacked edge sharing (TiO$_6$) octahedra. The XRD peaks are found to be broad, indicating the fine sizes of the sample grains. The pattern of pure TiO$_2$ exhibits prominent peaks at 2θ values of 25.28°, 37.81°, 47.99°, 53.95°, 55°, 62.9° and 75°, which are similar to the JCPDS-ICDD (card: 21-1272) for anatase titania. The patterns of Mn doped TiO$_2$ nanoparticles demonstrate its crystalline nature (Fig. 1a–d). In addition to anatase phase, existence of manganese peaks are also observed in Mn doped TiO$_2$ nanoparticles, which is represented by diffraction peaks corresponding to (220), (310), (400), (411), (332), (600), (541), (622) and (550) reflections (JCPDS-ICDD card: 89-4252). It is clearly evident from Fig. 1, there is an overlapping of manganese peaks on anatase titania occurs in Mn doped TiO$_2$ samples.

In the view of 4% Mn–TiO$_2$ from Fig. 1a, it looks the same as in pure TiO$_2$ but some manganese peaks are observed having orientations of (312), (332), (600), (541), (622) and (550) corresponding to 2θ values of pure TiO$_2$. All the peaks of Mn–TiO$_2$ have almost the same positions from the X-axis which were coincided well with the diffraction planes of pure TiO$_2$, except the slight deviation of 2θ values of Mn doped nanoparticles to the left side of the pattern having (101) reflection. As can be seen from Fig. 1b–d, some additional peaks are obviously obtained in the patterns with the diffractions of (220), (310), (400), (411) and (521) planes attributable to 8%, 12% and 16% Mn doped TiO$_2$ nanoparticles. When the Mn-dopant percentage increases the peaks intensities of the planes (220), (310) and (400) also increases and the characteristic Mn peak was observed with (411) orientation, indicating the presence of manganese in the TiO$_2$ lattice. However, the Mn incorporation of TiO$_2$ was not altering its anatase phase. Therefore, TiO$_2$ has retained its original structure and crystalline remained too.

Pure and Mn doped TiO$_2$ powders are well crystallized and the average crystallite sizes were obtained from 2θ and β of the (h k l) peaks using Scherrer’s relation,

$$D = \frac{K \lambda}{\beta \cos \theta} \text{Å}$$

where D is the average crystallite diameter (Å), K is the Scherrer constant (0.9), λ is the wavelength of X-ray (1.5406 Å for Cu Kα radiation), θ is the Bragg angle and β is the full width at half maximum (in radian) of the nanoparticles [25]. The mean crystallite size of pure TiO$_2$ is 15.31 nm, whereas Mn doped TiO$_2$ nanoparticles having 17.45, 18.57, 17.01 and 17.08 nm for 4%, 8%, 12% and 16% of Mn, respectively. The crystallite size of Mn–TiO$_2$ powders tends to slightly increased as compared to pure TiO$_2$. The lattice parameters ‘a’ and ‘c’ for the tetragonal structure (a = b ≠ c, α = β = γ = 90°) can be calculated by the following expression.

$$\sin^2 \theta = \frac{2(h^2 + k^2)}{4a^2} + \frac{2l^2}{4c^2} \text{Å}$$

where h, k and l are the Miller indices of the peak. From the values of ‘a’ and ‘c’, the unit cell volume (V) can be determined [26]. According to the XRD data, the calculated crystallite sizes, lattice parameters of the pure and Mn doped TiO$_2$ nanoparticles were depicted in Table 1. In 12% Mn–TiO$_2$, the lattice constants (a = 3.8019 Å, c = 9.7048 Å) and the cell volume (V = 140.27 Å$^3$) are increased predominantly as compared to pure TiO$_2$, because the radius of Mn$^{2+}$ (0.83 Å) is larger than Ti$^{4+}$ (0.68 Å) host material. Therefore, the manganese ions can easily substituted to the Ti$^{4+}$ ions.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Size (nm)</th>
<th>Lattice parameters</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
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<tr>
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<td>15.31</td>
<td>3.7881</td>
<td>9.5132</td>
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<td>4 wt% Mn–TiO$_2$</td>
<td>17.45</td>
<td>3.7912</td>
<td>9.5206</td>
</tr>
<tr>
<td>8 wt% Mn–TiO$_2$</td>
<td>18.57</td>
<td>3.7949</td>
<td>9.5642</td>
</tr>
<tr>
<td>12 wt% Mn–TiO$_2$</td>
<td>17.01</td>
<td>3.8019</td>
<td>9.7048</td>
</tr>
<tr>
<td>16 wt% Mn–TiO$_2$</td>
<td>17.08</td>
<td>3.7996</td>
<td>9.6187</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffractograms of pure and Mn (a–4%, b–8%, c–12% and d–16%) doped TiO$_2$ nanoparticles with different weight percentages.
or deposited on the surface of TiO₂. The broadening of diffraction peaks indicated the nanosized crystalline domain and the strong diffraction peaks revealed that the obtained products were crystalline in nature. Fig. 2 illustrates the variation of lattice constants on Mn doping with TiO₂.

All the patterns of pure and Mn doped TiO₂ nanoparticles exhibit an intense diffraction peak corresponding to (101) reflection. This single strong diffraction peak in the low-angle region indicated the presence of mesostructure in samples. Mesostructures with more or less regular in diameter channel packed at random often display a single peak in low-angle, implying the considerably high thermal stability of the mesoporous framework [27] in the obtained samples. The high stability of the anatase phase may be attributed to the small crystallite size and mesostructures of inorganic domains.

Hence, the XRD peaks assigned to the manganese became stronger and sharper, which indicate that the thermal annealing promotes diffusion and coalescence, leading to progressive growth of Mn clusters on the TiO₂ nanoparticles. Such findings, together with the evidence provided by SEM analysis, confirm that upon higher annealing treatment at 450 °C, there was a coexistence of Mn on/in the anatase grain boundaries [28].

Functional group analysis

The FTIR transmission spectra of pure and Mn (4%, 8%, 12% and 16%) doped TiO₂ nanoparticles annealed at 450 °C in air are shown in Fig. 3. The reaction between precursor materials of pure and Mn doped TiO₂ resulted in the white and yellowish gray powdered products, respectively. The FTIR study of these TiO₂ nanoparticles show the characteristics of the formation of high purity products and the peaks correspond to anatase titania. The spectroscopic band is observed in the range 3391–3438 cm⁻¹ for bare and manganese doped TiO₂ nanoparticles, which is attributed to the both symmetric and asymmetric stretching vibrations of the hydroxyl group (Ti–OH). Whereas, the characteristic peaks in between 1627 and 1646 cm⁻¹ are associated with the O–H bending vibration of the absorbed water molecules [29]. Hence, the presence of OH bands in the spectrum was owing to chemically and physically adsorbed H₂O on the surface of nanoparticles [30]. The existence of these bands can be attributed to the absorption of some atmospheric water during FTIR measurements. In the spectrum of pure TiO₂, the peak at 463 cm⁻¹ should be attributed to Ti–O bond in the TiO₂ lattice (anatase titania), it indicates that the organic ligand was completely eliminated after the annealing process. At the same time, the metal oxide TiO₂ was formed by thermolysis of the synthesized products [31]. The IR absorption band at 728 cm⁻¹ is attributed to the Ti–O–Ti stretching vibrations [32]. For Mn–TiO₂ nanoparticles, the vibrational bands at 663 and 668 cm⁻¹ are assigned to the Ti–O–Ti stretching modes. The peaks located in the region 593 and 568 cm⁻¹ indicating the Ti–O–O bond and the broad band at 528 cm⁻¹ illustrates the metal–oxygen bond (Ti–O) in TiO₂.

The synthesized products have some weak absorption bands correspond to the vibrational modes of organic species such as hydroxyl, carboxilate and alkane groups. Two weak bands between 2920–2926 cm⁻¹ and 2838–2853 cm⁻¹ could be ascribed to the characteristic frequencies of residual organic species, which was not completely removed by ethanol and distilled water washing and are assigned to C–H stretching vibrations of alkane groups. The peaks at 1342–1545 cm⁻¹ region could be attributed to carboxyl (C=O) and methylene groups. The carboxyl and methylene groups might also be resulted from residual organic species [33]. The peak at 1747 cm⁻¹ can be associated to the asymmetric stretching mode of titanium carboxilate. The alkane and carboxilate groups come from TiOT and 2-propanol precursors used in the synthesis process. The intensity of the bands associated with the organic groups is considerably very weak because the synthesized product was annealed at 450 °C, indicating the elimination of organic species [34]. The pure and Mn doped TiO₂ nanoparticles prepared for the present study are of good quality and can be used for the further characterizations. The infrared absorption frequencies and the corresponding vibrational assignments are represented in Table 2.

<table>
<thead>
<tr>
<th>Wavenumbers (cm⁻¹)</th>
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<td>3600–3200</td>
<td>3200–2800</td>
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<td>1200–800</td>
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<tr>
<td>800–400</td>
<td>400–300</td>
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</table>

Fig. 2. Variation of lattice constants for pure and Mn doped TiO₂ nanoparticles.

Fig. 3. FTIR spectra of pure and Mn doped TiO₂ nanoparticles (a-4% Mn–TiO₂, b-8% Mn–TiO₂, c-12% Mn–TiO₂ and d-16% Mn–TiO₂).
Table 2
Tentative vibrational assignments of pure and Mn doped TiO₂ nanostructures.

<table>
<thead>
<tr>
<th>Wavenumbers (cm⁻¹)</th>
<th>Assignments</th>
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<td>728</td>
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<td>463</td>
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<td>4% Mn–TiO₂</td>
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Linear optical study

Determination of band gap energy

The diffuse reflectance spectra of pure and Mn (4%, 8%, 12% and 16%) doped TiO₂ nanoparticles were illustrated in Fig. 4. Compared with pure TiO₂, the absorption edges of Mn–TiO₂ were shifted towards the higher energy region (i.e. blue shift). The band gap energy (E₉) of pure and Mn doped TiO₂ was obtained from the wavelength value corresponding to the intersection point of the vertical and horizontal part of the spectrum, using the equation [35]:

$$E_k = \frac{hc}{\lambda}; \quad E_k = \frac{1240}{\lambda} \text{eV}$$

The energy band gap corresponds to the absorption limit and can be evaluated by the above relation. Where E₉ is the band gap energy (eV), h is the Planck’s constant (6.626 × 10⁻³⁴ J s), c is the light velocity (3 × 10⁸ m/s) and λ is the wavelength (nm). The absorption edge of nano TiO₂ was at 345.49 nm, corresponding to a band gap of 3.58 eV, which is usually ascribed to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3dₓ²ᵧ² orbitals of the Ti⁴⁺ cations) [36]. According to the UV cut-off wavelengths 341.53, 339.79, 331.40 and 337.53 nm, the calculated band gap energies are 3.63, 3.65, 3.74 and 3.67 eV for 4%, 8%, 12% and 16% Mn doped TiO₂ nanoparticles, respectively. Hence, it can be clearly seen that the band gap energies of Mn–TiO₂ are higher than that of pure TiO₂. Furthermore, the 12% Mn–TiO₂ has relatively higher band gap energy so it has been taken for further investigation.

Direct band gap energy (plot of (zhv)² vs. hv)

The absorption edge of Mn–TiO₂ was blue-shifted about ≤14 nm, compared with that of pure TiO₂. Manifacier model is used to determine the absorption co-efficient from the absorbance data [37]. The fundamental absorption, which corresponds to the transmission from valance band to conduction band, is employed to determine the band gap of the material. The direct band gap energy can be estimated from a plot of (zhv)² vs. photon energy (hv) by using the relationship:

$$zhv = A(hv - E_k)^α$$

The optical absorbance coefficient (α) of a semiconductor close to the band edge can be expressed by the following equation,

$$\alpha = A(hv - E_k)^α/hv$$

where α = 4πk/λ (k is the absorption index or absorbance) and A depicts constant factor. The exponent n depends on the nature of the transitions; n may have values 1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. In this case n = 1/2 for allowed direct transition. The plot of (zhv)² vs. hv was presented in Fig. 5. The value of energy band gap was determined by extrapolating the straight line portions of (zhv)² = 0 axis (i.e. the zero co-efficient). The intercept of the tangent to the plot will give a good approximation of the direct band gap energy of the materials [26].

The direct band gap energy (E₉) of pure and 12% Mn doped TiO₂ nanoparticles are calculated to be 3.58 and 3.74 eV, respectively. Meanwhile, the crystallite size of pure TiO₂ was 15.31 nm and 12% Mn–TiO₂ was 17.01 nm (from XRD). This can be explained...
because the band gap energy of the materials have been found to be particle size independent when the particle size of the material is above 10 nm and hence disobey the quantum confinement effect [38]. Considering the blue shift of the absorption position from the pure TiO$_2$, the absorption onset of the present material can be assigned to the direct transition of electrons in the Mn–TiO$_2$ nanocrystals [39].

**Indirect band gap energy (Kubelka–Munk plot)**

The indirect band gap energy of pure and 12% Mn doped TiO$_2$ nanoparticles can be estimated from plots of the square root of Kubelka Munk functions $F(R)$ vs. $h\nu$. The reflectance data was converted to the absorption coefficient $\alpha(h\nu)$ values according to the Kubelka–Munk equation [40],

$$F(R)_\text{KM} = \left(1 - R^2\right)/2R$$

where $F(R)_\text{KM}$ is equivalent to the absorption coefficient ($\alpha_{\text{KM}}$), which can be expressed as,

$$\alpha_{\text{KM}}(h\nu) = C_1(h\nu - E_g)^2$$

where $C_1$ is the absorption constant for indirect transition. In this case $n = 2$ for allowed indirect transition. Fig. 6 shows the plot of Kubelka–Munk function (i.e., relationship of ($\alpha_{\text{KM}}h\nu$)$^{1/2}$ vs. $h\nu$) and the linear segment of the spectra is extrapolated to intersect the $h\nu$ axis to obtain the band gap value of allowed indirect transition ($E_g$) of the materials. The pure TiO$_2$ exhibits indirect $E_g$ of 3.58 eV, while 12% Mn–TiO$_2$ exhibits 3.75 eV when the absorption edge shifts from 345.49 to 331.40 nm (Fig. 4). This result is consistent with the fact that the conduction band edge of 12% Mn–TiO$_2$ is about 0.17 eV more positive than that of pure anatase TiO$_2$. It is evident that TiO$_2$ shows large optical absorbance in the UV region.

**Determination of crystallite size (Brus model)**

For the anatase phase TiO$_2$, the absorption wavelength ($\lambda$) and the corresponding band gap energy ($E_g$) of bulk TiO$_2$ material are well known to be $\lambda = 385$ nm and $E_g = 3.2$ eV, respectively. The particle size of the prepared TiO$_2$ nanoparticles has been determined from the relationship between band gap shift ($\Delta E_g$) and radius ($R$) of nanoparticles by using the following expression [29],

$$\Delta E_g = \frac{\pi^2 h^2}{2\mu R^2} \cdot \frac{1.8e^2}{\varepsilon R} + \text{Polarization terms}$$

where $h$ is Planck’s constant, $R$ is the radius of the particle, $\varepsilon$ is the dielectric constant of the semiconductor material and $\Delta E_g$ is the band gap shift (i.e., $\Delta E_g = E_{g(\text{nano})} - E_{g(\text{bulk})}$). The calculated band gap shift for the nano-anatase TiO$_2$ is 0.38 eV (which is determined by extrapolating the spectral curve, the $E_g$ of nano TiO$_2$ measured to be 3.58 eV corresponding to $\lambda = 345.49$ nm using $E = h\nu$ from Fig. 4), as compared to bulk anatase (3.2 eV). However, the band gap shifts are obtained to be 0.43, 0.45, 0.54 and 0.47 eV respectively for 4%, 8%, 12% and 16% Mn doped TiO$_2$ nanoparticles. These shifts typically follows the Brus model or the effective mass approximation approach, which provides a quantitative interpretation of the shift in onset of absorption energy as a function of crystallite dimension and effective mass of the electrons and holes. The onset of absorbance provides insight into the band gap of the TiO$_2$ semiconductor material, which can be significantly different from that of the bulk material [41]. $\mu$ is the reduced mass of the exciton, i.e., the reduced effective mass of the electron and the hole (1/\(m^*\) = 1/$m_e^*$ + 1/$m_h^*$) in the semiconductor. As the reported effective mass of the electron $m_e^*$ was in the range of 5–13 $m_e$. The effective mass of the hole $m_h^*$ was reported to be $\sim$2 $m_e^*$ and ‘$\varepsilon$’ is the electron charge ($1.6 \times 10^{-19}$ C). The shifts in band gap were significantly affected by the reduced mass of exciton and the dielectric constant of the semiconductor ($\varepsilon$). The value of $\varepsilon = 1.63 m_e^*$ (where, $m_e$ is the electron rest mass = 9.1 x 10$^{-31}$ kg) and range between 1.43 and 1.73 $m_e$. The dielectric constant of TiO$_2$ anatase crystalline was reported to be between 23 and 184 [40], since the optical dielectric constant of bulk titanium dioxide is very large ($\varepsilon = 170$), the coloumbic and polarization terms in the equation are neglected. However, the particle sizes of pure and Mn doped TiO$_2$ were calculated from both the reflectance spectra as well as analysis of the XRD data. The calculated crystallite size of the pure TiO$_2$ (by Brus model) is 24.49 nm. Hence, the crystallite size evaluated from XRD (by Scherrer’s relation) is around 15.31 nm, which is lower than the value obtained from UV method; this may be due to aggregation of nanoparticles. Whereas, the crystallite sizes of Mn–TiO$_2$ (by Brus model) are 23.02, 22.50, 20.54 and 22.02 nm, respectively for 4%, 8%, 12% and 16% Mn doped TiO$_2$, which are slightly larger than that of the crystallite sizes evaluated from XRD. The comparison of band gap energies by direct and indirect methods and crystallite size measurement by DRS analysis with XRD are depicted in Table 3.
Photoluminescence spectroscopy

Fig. 7 displays the PL emission spectra of pure and Mn doped TiO$_2$ nanoparticles. The excited wavelengths are 345, 341, 339, 331 and 337 nm, respectively for pure and manganese (4%, 8%, 12% and 16%) doped TiO$_2$. The emission bands originating from the excited level was monitored in the spectral region between 325 and 600 nm. In the case of pure TiO$_2$ (Fig. 7), the energy of the trap level was identified at 587 nm is attributed to Ti$^{4+}$ ions adjacent to oxygen vacancies (intra gap surface states). The obvious PL peak at about 431 nm, possibly mainly resulting from band edge free excitons and this surface emission is attributed to indirect transition X$_{12}$ to Γ$_{1b}$ and linked to exciton recombination in shallow trapped surface state [42]. A band at 373 nm is attributed to the first vibronic fluorescence band (i.e. symmetry forbidden 0–0 band (I$_{1g}$)) [43]. There were many oxygen vacancies on the surface of pure and Mn doped TiO$_2$ nanoparticles, and the sizes of particles (from XRD) were fine so that the average distance the electrons could move freely was very short. These factors could make the oxygen vacancies very easily bind electrons to form excitons [44].

For Mn–TiO$_2$ (Fig. 7a–d), the PL spectra have obvious peaks which are shifted towards the lower wavelength side. It can be found from Fig. 7 that the positions of Mn$^{2+}$ ion incorporated luminescence peaks have changed compare to pure TiO$_2$. The PL intensity for the peaks between 527 and 536 nm emission increases with Mn doping percentage, which indicates that morphology could make impacts on the intensity of luminescence. Likewise, the intensity of the peaks in higher energy region 344–365 nm decreases (when compare to pure TiO$_2$) because of more addition of Mn$^{2+}$ ions. This is due to the concentration quench effect induced by the cross-relaxation [45]. The intensity of PL peaks in between 401 and 419 nm increases with increasing Mn dopant percentage and 12% Mn–TiO$_2$ (Fig. 7c) has relatively higher intensity. On the other hand, the XRD results show that Mn$^{2+}$ ions occupied the interstitial positions of the titania host matrix partly in the formation process of Mn–TiO$_2$ nanoparticles. In fact, the Mn$^{2+}$ ions in the TiO$_2$ can be divided into two types: one is at the surface of the nanoparticles, and the other is in the interstitial position, which decreases the defects surrounding Mn$^{2+}$ ions and results in the increase of luminescent intensity. This can be attributed to the concentration luminescent quenching due to the formation of clusters among Mn$^{2+}$ ions [46]. Therefore, it could be found that the pure and Mn doped TiO$_2$ nanoparticles both could exhibit obvious PL signals with different wavelengths demonstrating that the Mn dopant has resulted into new PL phenomena. In addition, it could be found from Fig. 7 that the threshold of PL response at the shorter wavelength edge of TiO$_2$ nanoparticles has blue shifted after introducing Mn into titania host matrix.

Morphological analysis

SEM with EDX

In Fig. 8, the textural features of pure and 12% Mn doped TiO$_2$ nanoparticles were investigated using scanning electron microscopy (SEM) with corresponding energy dispersive X-ray analysis (EDX). Representative images of these nanoparticles are shown in Fig. 8a and c demonstrating specific morphology changes apart of a trend for surface particle agglomeration. SEM micrograph for pure TiO$_2$ depicted in Fig. 8a has non-uniform distribution of spherical particles and they consist of either single particle or cluster of particles. The spheres consist of many small spherical crystals of TiO$_2$ due to agglomeration. Mn doping in the sol–gel method has little influence on the particle size of TiO$_2$. The particle size distributions were illustrated in Fig. 9. As can be seen, the pure

<table>
<thead>
<tr>
<th>Materials</th>
<th>Band gap energy (eV)</th>
<th>Band gap shift ($\Delta E_g$) eV</th>
<th>Crystallite size (nm)</th>
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</thead>
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<tr>
<td>Pure TiO$_2$</td>
<td>3.58</td>
<td>0.38</td>
<td>15.31</td>
</tr>
<tr>
<td>4%Mn–TiO$_2$</td>
<td>3.63</td>
<td>0.43</td>
<td>17.45</td>
</tr>
<tr>
<td>8%Mn–TiO$_2$</td>
<td>3.65</td>
<td>0.45</td>
<td>18.57</td>
</tr>
<tr>
<td>12%Mn–TiO$_2$</td>
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<td>0.54</td>
<td>17.01</td>
</tr>
<tr>
<td>16%Mn–TiO$_2$</td>
<td>3.67</td>
<td>0.47</td>
<td>17.08</td>
</tr>
</tbody>
</table>

Table 3

Comparison of band gap energies and crystallite size measurements for pure and Mn doped TiO$_2$ nanoparticles.
TiO$_2$ has a relative particle diameter in the range of 16.25–22.36 nm with mean particle size of 18.98 nm, whereas, Mn–TiO$_2$ has diameter in 19.60–25.0 nm range and mean particle size was 22.29 nm and it could be suggests that the nanospheres obtained are homogenous. These values are in near agreement with the sizes estimated from XRD (15.31 and 17.01 nm). Therefore, it is possible to assess that the sample grains have rounded shape. The shape stability of TiO$_2$ nanoparticles is highly dependent on surface chemistry and the synthesis conditions play a key role [47]. The Mn doping on TiO$_2$ nanoparticles is clearly evident in Fig. 8c and demonstrates the particles are spherical in nature. Therefore, it is also observable that the growth of manganese was along spherical axis of nanoparticles, thus preserving the integral shape of TiO$_2$ nanoparticles after doping of Mn also. Moreover, there was a visible change was observed from white to yellowish gray after doping of manganese on TiO$_2$ nanoparticles.

The strong X-ray peaks associated with Ti K$\alpha$ and O K$\alpha$ were found in the EDX spectrum (Fig. 8b), indicating that the TiO$_2$ matrix has composed of titanium and oxygen only. Likewise, the X-ray peaks associated with Ti K$\alpha$, O K$\alpha$ and Mn K$\alpha$ were found in Fig. 8d depicted the successful doping of Mn into TiO$_2$ matrix according to the relative atomic and weight percentages of Mn. It is clear from the elemental analysis that 10.06 wt.\% Mn element is present in the doped TiO$_2$ sample and it can also be revealed that the Mn$^{2+}$ ions are incorporated in Ti$^{4+}$ lattice sites.

Meanwhile, Mn–TiO$_2$ nanoparticles also show the particle size slightly larger than that of the pure TiO$_2$. So, they both have good crystallinity and are porous in nature, which may help in the better adsorption of the dye molecules in dye-sensitized solar cell making and can be achieved better solar cell efficiencies, and may also be good for better gas sensing purpose [48]. The synthesized products were annealed at 450 °C, so the possibility of the presence of any organic impurities in the samples is very minimum. However, after Mn doping, the surface morphology of Mn–TiO$_2$ turns into uniform spherical particles from agglomeration. Hence, it is quite obvious that the Mn-doping can be deduced to have a great influence on the surface morphology and particle size.

**Nonlinear optical (NLO) study**

The oven dried powders of pure and 12% Mn doped TiO$_2$ were kept into muffle furnace and annealed at 750 °C for 4 h to obtain rutile phase of the resultant materials. In order to confirm the NLO property, the specimen was subjected to a Kurtz powder test [49] using a Q-switched, mode locked Nd: YAG laser of 1064 nm and a pulse width of 8 ns (spot radius of 1 mm). The input laser beam was directed on the synthesized powders to get maximum powder SHG. Then, the emitted light passed through an IR filter.
was measured by means of a photomultiplier tube and oscilloscope assembly. The SHG efficiency of the materials was evaluated by taking the crystalline powder of potassium dihydrogen phosphate (KDP) as the reference material. The SHG behavior was confirmed by the output of intense green light (532 nm) emission from the both sample materials (pure and Mn doped TiO$_2$) and KDP. Thus, the efficiency results show an output of 3.8 mV for pure TiO$_2$, when compared to 17.6 mV of KDP with same input laser power of 2.6 mJ/pulse. Whereas, Mn–TiO$_2$ has output of 4.8 mV with same input of 4.5 mJ/pulse compared to 10.2 mV of KDP. Hence, the conversion efficiencies of pure and Mn doped TiO$_2$ were 0.22 and 0.47 times with respect to standard KDP crystal, respectively. The SHG/NLO measurement results of pure and 12% Mn doped TiO$_2$ materials are presented in Table 4.

## Conclusions

The pure and Mn (4%, 8%, 12% and 16%) doped TiO$_2$ nanoparticles were successfully prepared by sol–gel method using relevant precursor materials and annealed at 450 °C and 750 °C for getting anatase and rutile phases, respectively. The XRD analyses reveal that the prepared products were attributed to the tetragonal system and anatase was found to be the major phase in all samples. The calculated crystallite sizes (by Scherrer’s relation), lattice constants and cell volumes were increased with increasing Mn doping percentage. The FTIR 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 Mn doping did not alter the structure of TiO$_2$ host material but it can take effect on optical and morphological properties. The allowed direct and indirect band gap energies were evaluated for pure and Mn doped TiO$_2$ nanoparticles by UV–VIS–DRS analysis, and they supported the calculated $E_g$ value. The optical cut-off wavelengths of Mn–TiO$_2$ were blue shifted towards the lower wavelength side, resulting larger band gap energies compared to pure TiO$_2$. Moreover, the 12% Mn–TiO$_2$ has relatively higher band gap energy than that of others; therefore, it has been taken as optimum dopant percentage. Hence, absorption in UV region indicates that the synthesized products are larger band gap semiconductor materials. In addition, the crystallite sizes obtained by Brus model have good agreement with that of XRD measurements. From the PL emission spectra of pure and Mn doped TiO$_2$, the bands between 344 and 373 nm were attributed to the ultraviolet emission, whereas the bands in the region 401–419 nm were attributed to the violet emission. Likewise, the bands at 431 and 587 nm were attributed to the blue and orange emissions, respectively. Finely, the bands between 527 and 536 nm were attributed to the green emission. The morphological analysis of 12% Mn–TiO$_2$ nanoparticles indicates that the uniform distribution of spherical shaped particles compared to pure TiO$_2$. The particle size distributions are consistent with the results obtained from both XRD and DRS measurements. Elemental identification was performed by EDX analysis and it represents the pure and 12% Mn doped TiO$_2$ have relative atomic and weight percentages of titanium, oxygen and manganese. NLO studies confirm that the SHG efficiency of 12% Mn–TiO$_2$ nanoparticles has 0.25 times greater than that of pure TiO$_2$ with respect to KDP crystal. All these studies indicate that the Mn doped TiO$_2$ nanoparticles can be considered as a potential candidate for the fabrication of semiconductor and optoelectronic devices.

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## References

RESEARCH ARTICLE

PREPARATION, STRUCTURAL AND OPTICAL CHARACTERIZATION OF Fe DOPED TiO$_2$ NANOPARTICLES

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ABSTRACT

Sol-gel method was employed in the preparation of pure and Iron (Fe- 4%, 8%, 12% & 16%) doped TiO$_2$ nanoparticles. The prepared Fe–TiO$_2$ nanoparticles were investigated by means of X-ray diffraction analysis (XRD) and UV-VIS-diffuse reflectance spectroscopy (DRS). The mono-anatase structure in the composite nanomaterials is indicated by XRD analysis. The Fe doped TiO$_2$ powders could apparently shift the UV-absorption band towards the higher energy region, and there was an optimal 8%Fe content in association with the larger band gap energy.

Key words:
Sol–gel; Fe–TiO$_2$; XRD; UV-VIS-DRS; Band gap

INTRODUCTION

Noble metal/TiO$_2$ composite materials have recently emerged as candidates for numerous applications ranging from nonlinear optics to photoanode materials in solar cells, optical filtering applications and potent antimicrobial coatings [1]. There have been many reports using transition metal ion or noble metal as dopants in TiO$_2$ system [2]. Shah et al. [3] successfully used the metalorganic chemical vapour deposition method to synthesize pure TiO$_2$ and Pd$^{2+}$, Pt$^{4+}$ and Fe$^{3+}$–doped TiO$_2$ nanoparticles. In recent years, the modification as well as preparation and characterization of TiO$_2$ nanomaterials has been the focus in the semiconductor photoelectric chemistry and photocatalysis fields. Doping is used to a kind of modification method [4]. Several techniques for the synthesis of nanophase titanium dioxide have been developed so far: sol–gel processing, chemical vapour deposition, supersonic cluster beam deposition, pulsed laser deposition, etc [1]. Titanium dioxide is broadly used as a photocatalyst because it is photochemically stable, non-toxic and cost little. Many studies [5] have been devoted to the improvement of photocatalytic efficiency of TiO$_2$, such as depositing noble metals and doping metal or non-metal ions. In particular, Fe$^{3+}$–TiO$_2$ has been the topic of many investigation including preparation, characterization, dynamics of charge transfer, trapping and recombination, and photocatalytic behavior, etc. [5]. In our previous work, we report on the synthesis and characterization of pure [6] and Cu doped TiO$_2$ [7] nanostructures. In the present work, TiO$_2$ nanoparticles TiO$_2$ nanoparticles with different doping Fe$^{3+}$ content were prepared by Sol-gel method. The structure and optical properties of the pure and Fe doped TiO$_2$ nanocomposites have been investigated.

Experimental

Sol-gel synthesis of Fe–TiO$_2$ nanoparticles: In a typical synthesis, 10 ml of tetra-isopropyl orthotitanate (TJOT, assay $\geq$98%) was dissolved in 90 ml of isopropyl alcohol ($\left(CH$_3$_2\right)_2CHOH$, assay $\geq$99%) and to this solution 5 ml of deionized water was added drop wise with vigorous magnetic stirring to obtain bare TiO$_2$. For Fe doped TiO$_2$ ferrocene nitrate nonahydrate (Fe(NO$_3$)$_3$9H$_2$O, assay $\geq$98%) with different atomic weight percentages (4%, 8%, 12% & 16%) were added to each 10 ml of deionized water and these solutions were added drop wise to the TiO$_2$ and 2-propanol mixed solutions separately. The resulting colloidal suspensions were stirred for 4h at room temperature using magnetic stirrer. The white and pale orange gels were obtained for pure and Fe doped TiO$_2$ respectively. Then filtered by whatman filter paper and washed several times using ethanol and deionized water. The yield gels were dried in hot air oven at 100°C for 6h to evaporate water and organic material to the maximum extent. Then the dried powders were ground by agate mortar using pestle to remove agglomerates. Finally, the powders kept into muffle furnace and annealed at 450°C for 4h to obtain desired pure and Fe doped TiO$_2$ nanocrystallites. The annealed powders were pulverized to fine powders using agate mortar for further characterizations.

Characterizations: The crystalline phase and particle sizes of pure and Fe doped TiO$_2$ nanoparticles were analyzed by X-ray diffraction (XRD) measurement, which was carried out at room temperature by using XPERT-PRO diffractometer system (scan step of 0.05°, counting time of 10.16 s per data point) equipped with a Cu tube for generating CuKα radiation ($\lambda$ = 1.5406 Å). The incident beam in the 2-theta mode over the range of 10°~80°, operated at 40 kV and 30 mA. The diffuse reflectance spectra (DRS) was measured at wavelength in the range of 200–800 nm by UV-Vis-NIR spectrophotometer (Varian/Carry 5000) equipped with an integrating sphere and the baseline correction was performed using a calibrated reference sample of powdered barium sulphate (BaSO$_4$).

RESULTS AND DISCUSSION

X-ray diffraction analysis: XRD characterization of pure and Fe (4%, 8%, 12% & 16%) doped TiO$_2$ nanoparticles are depicted in Fig.1. The
peaks marked (A) and (Fe) correspond to Anatase and Iron, respectively. Diffractions that are attributable to anatase phase of TiO₂ crystals (101) are clearly detectable at 20 ~ 25.28° (JCPDS card: 21-1272) in both the patterns of pure and Fe doped TiO₂. The orientations (101), (004), (112), (200), (105), (211), (204), (116), (220) and (215) can be assigned to the crystal planes of anatase TiO₂. Whereas, the reflections (211), (220), (110), (311), (200) and (330) can be assigned to the planes of Fe (JCPDS cards: 89-4186, 01-1267 and 01-1262). As can be seen from Fig.1, the pure and Fe doped TiO₂ samples were composed of only an anatase phase without the presence of iron oxide. It demonstrates that Fe³⁺ ions are successfully incorporated into the framework of anatase TiO₂ without the formation of iron oxide on the surface of TiO₂. All the peaks of Fe doped TiO₂ have almost the same positions from the X-axis, which were coincided well with the diffraction planes of pure TiO₂ except the characteristic peaks of iron (211), (220) and (110) (Fig. 1-a, b, c & d).

However, the peaks shifted slightly to higher 20 values when higher amounts of iron dopant were incorporated. Its incorporation gives rise to the structural expansion of the crystalline lattice. Subsequently its structural distortion. The decrease in the interplanar distance of anatase framework leads XRD peak patterns are shift to higher 20 direction according to Bragg’s law [6]. As larger amount of Fe dopant is incorporated into anatase framework, the lattice was distorted more and more. Thus, the peak shift can be regarded as indirect evidence of successful iron doping into TiO₂ crystal framework [7]. From all the diffraction patterns it is also obvious that the materials are in the form of quite small-sized nanoparticles, as the peaks are broad [8]. Hence, the new peaks appeared in Fe doped TiO₂ might be accredited to the iron content. By comparison, it can be deduced that doping Fe has a little effect on the size of anatase crystallites. The average crystallite sizes of pure and Fe doped TiO₂ nanoparticles can be estimated from the integral width of the diffraction peaks using the Scherrer formula [9]. When compared to undoped TiO₂, the peaks of 4% and 8% Fe doped TiO₂ (Fig. 1-a & b) are relatively sharper which indicate that the doped ones have increased crystallite sizes. It is the manifestation of higher particle sizes than that of the pure TiO₂. Whereas, from Fig.1-c & d the XRD peaks become broader than the pristine TiO₂ attribute the smaller particle sizes. The lattice parameters a, c and V for the tetragonal structure can also be determined [10]. The calculated average crystallite sizes, lattice parameters of pure and Fe doped TiO₂ nanoparticles are illustrated in Table 1. The lattice constants and cell volume of Fe doped TiO₂ nanoparticles are found increased due to the smaller ionic radius of Fe³⁺ (0.64 Å) than that of Ti⁴⁺ (0.68 Å), which indicates that the doping of Fe does not alter the tetragonal structure of anatase TiO₂. The variation of lattice constants on Fe doping with TiO₂ has plotted in Fig.2. The dominant peak is observed at (101) plane in both pure and Fe doped TiO₂ nanoparticles confirmed that the XRD peaks are attributed to tetragonal anatase phase. In fact, the XRD patterns of Fe doped TiO₂ does not considerably shift compared with bare TiO₂ suggesting that Fe does not come into the TiO₂ lattices to substitute Ti. This is possibly because of the valence difference between Fe³⁺ and Ti⁴⁺. Thus, it can be concluded that Fe is mainly dispersed on TiO₂ crystallite surfaces or located at interstitial sites [11].

![Figure 1: X-ray diffractograms of pure and Fe doped TiO₂ nanoparticles with different weight percentages (A: Anatase, Fe: Iron)](image)

![Figure 2: Variation of lattice constants for pure and Fe-TiO₂ nanoparticles](image)

Table 1: Comparison of crystallite size and lattice parameters for pure and Fe doped TiO₂ nanoparticles

<table>
<thead>
<tr>
<th>Material</th>
<th>Size (nm)</th>
<th>Lattice parameters</th>
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<td></td>
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<td>Pure TiO₂</td>
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<td>16%wt, Fe-TiO₂</td>
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Linear optical study

**Determination of band gap energy:** Fig. 3 shows the diffuse reflectance spectra of pure and Fe (4%, 8%, 12% & 16%) doped TiO₂ nanoparticles. Compared with pure TiO₂, the absorption edges of Fe doped TiO₂ nanoparticles shifted towards the higher energy region (i.e. blue shift) for all Fe dopant percentages. The band gap energy (E_g) of pure and Fe doped TiO₂ was obtained from the wavelength (λ) value corresponding to the intersection point of the vertical and horizontal part of the spectrum, using the equation [12]:

\[ E = \frac{hc}{\lambda} \text{ eV} \]

Where \( h \) is the Planck’s constant (6.626×10⁻³⁴ Js) and \( c \) is the light velocity (3×10⁸ m/s). The absorption edge of pure TiO₂ was at 345.49 nm, corresponding to band gap energy of 3.58 eV. According to the UV cut-off wavelengths 344.17, 339.15, 340.66 and 342.41 nm, the calculated band gap energies are 3.60, 3.66, 3.63 and 3.62 eV for 4%, 8%, 12% and 16% Fe doped TiO₂ nanoparticles, respectively. Hence, it can be clearly seen that the band gap energies of Fe doped TiO₂ are higher than that of pure TiO₂. The 8%Fe-TiO₂ has relatively higher band gap energy than other dopant percentages. Therefore, it has been taken for further investigation.

The direct band gap energy of pure and 8%Fe doped TiO₂ nanoparticles were calculated to be 3.58 and 3.67 eV, respectively. Meanwhile, the crystallite size of pure TiO₂ was 15.31 nm and 8%Fe-TiO₂ was 17.09 nm (from XRD). This can be explained because the band gap energy of the materials has been found to be particle size independent, when the particle size of the materials above 10 nm they have not obey the quantum confinement effect [13]. Considering the blue shift of the absorption position from the pure TiO₂, the absorption onset be assigned to the direct transition of electrons in the Fe doped TiO₂ nanocrystals [14]. The indirect band gap energy of pure and 8%Fe doped TiO₂ nanoparticles can be estimated from plots of the square root of Kubelka Munk functions F(R) vs. hv. The reflectance data was converted to the absorption coefficient F(R) values according to the Kubelka–Munk equation [15],

\[ F(R) = \frac{(1 - R)}{2R} \]

Where F(R)KM is equivalent to the absorption coefficient \( \alpha_{KM} \), which can be expressed as,

\[ \alpha = \frac{(hv - E)}{C} \]

Where C₁ is the absorption constant for indirect transition. In this case n=2 for allowed indirect transition. The Fig. 5 shows the plot of Kubelka-Munk function (i.e. relationship between \( \alpha_{KM} \)hv)² and hv). The pure TiO₂ exhibits an indirect band gap value of 3.58 eV, while 8%Fe-TiO₂ exhibits the value of 3.67 eV. This result is consistent with the fact that the conduction band edge of 8%Fe-TiO₂ is about 0.09 eV
more positive than that of pure anatase TiO₂. It is evident that the pure and Fe doped TiO₂ show large optical absorbance in the UV region.

Figure 5: K–M plot for (a) pure and (b) 8%Fe-TiO₂ nanoparticles

Determination of crystallite size (Brus model): The particle sizes of the prepared TiO₂ nanoparticles have been determined from the relationship between band gap shift (ΔEₜ – E₉nano ~ E₉bulk) and radius (R) of nanoparticles by using the following expression [16].

\[ \Delta E = \frac{\pi \hbar}{2\mu R} \frac{1.8e}{\varepsilon R} + \text{Polarization terms} \]

Where \( \hbar \) is Planck’s constant and \( \varepsilon \) is the dielectric constant of the semiconductor material. The calculated band gap shift for the anatase TiO₂ (E₉ = 3.58 eV) is 0.38 eV as compared to bulk anatase (E₉ = 3.2 eV). However, the band gap shifts were obtained to be 0.40, 0.46, 0.43 and 0.42 eV respectively for 4%, 8%, 12%, & 16% Fe doped TiO₂ nanoparticles. ‘\( \mu \)’ is the reduced mass of the exciton, ‘\( e \)’ is the electron charge (1.6\( \times 10^{-19} \) C). The shifts in band gap were significantly affected by the reduced mass of exciton and the dielectric constant of the semiconductor [17]. The value of \( \mu = 1.63 m_e \) where \( m_e \) is the electron rest mass (9.1\( \times 10^{-31} \) Kg) [15]. Since, the optical dielectric constant of bulk titanium dioxide is very large (\( \varepsilon = 170 \)), the coulombic and polarization terms in the equation are neglected. The calculated crystallite sizes of the pure and Fe doped TiO₂ (Brus model) are larger than the values obtained from XRD (Scherrer relation), this may be due to aggregation of nanoparticles. The comparison of band gap energies by direct and indirect methods and crystallite size measurement by DRS analysis with XRD are depicted in Table 2.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Band gap energy (eV)</th>
<th>Band gap shift (ΔEₜ eV)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₉=1240 Å</td>
<td>Band gap shift (E₉nano ~ E₉bulk)</td>
<td>XRD (Scherrer)</td>
</tr>
<tr>
<td>Pure TiO₂</td>
<td>3.58</td>
<td>0.38</td>
<td>15.31</td>
</tr>
<tr>
<td>4%Fe-TiO₂</td>
<td>3.60</td>
<td>0.40</td>
<td>23.78</td>
</tr>
<tr>
<td>8%Fe-TiO₂</td>
<td>3.66</td>
<td>0.43</td>
<td>17.89</td>
</tr>
<tr>
<td>12%Fe-TiO₂</td>
<td>3.67</td>
<td>0.43</td>
<td>11.17</td>
</tr>
<tr>
<td>16%Fe-TiO₂</td>
<td>3.62</td>
<td>0.42</td>
<td>11.31</td>
</tr>
</tbody>
</table>

Conclusions

The pure and iron doped TiO₂ nanocrystals with different doping Fe⁺ content were successfully prepared via Sol–gel method. The crystallite sizes and lattice parameters were evaluated from XRD measurements. It reveals that the resulting powders were composed of nano-sized spheres. The main discovery of this work was the blue shift of the light absorbance to the range of 344–339 nm. The allowed direct and indirect band gap energies and crystallite sizes were determined by DRS analysis. The DRS result showed that the band gap energy of 8%Fe doped anatase TiO₂ was higher than that of the others. The findings reported herein represent an innovative route to designing higher band gap energy materials that suitable for semiconductors and opto-electronic devices.

REFERENCES