Optical Properties of Rare-Earth Doped TiO$_2$ Nanocomposites and Coatings; A Sol-Gel Strategy towards Multi-functionality

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A novel facile sol-gel method was used to synthesize visible-light responsive and photoluminescent rare-earth modified titania nanocomposites and coatings. Titania-silica-lanthanum phosphate nanocomposite doped with terbium ions (Tb$^{3+}$) was prepared by an aqueous sol-gel process and the films fabricated on glass substrates by dip coating are investigated in the present work. Followed by heat treatment at 400 degree Celsius, Tb doped nanocomposite exhibits green luminescence under visible light excitation (484 nm) and PL spectra show intense peaks at 545 nm ($^5D_4$-$^7F_5$), characteristic of Tb$^{3+}$ ion with a lifetime of $\sim$0.34 ms. The band gap energy of the nanocomposite was red shifted with Tb doping indicating its visible light response. 0.5 mol% Tb doped nanocomposite coated glass shows $\sim$66% methylene blue dye degradation under visible light exposure for two hours while pure titania coating showed the visible light activity of $\sim$25% only. 0.5 mol% Tb doped nanocomposite is thus proposed for the development of visible light active, transparent and luminescent coatings on glass substrates. Moreover, the feasibility of a codoping approach (0.25 mol% Tb and 0.25 mol% Eu doped nanocomposite) for getting multiple emission (red and green) by a single excitation wavelength (484 nm) is also demonstrated. A higher decay time of $\sim$0.48 ms obtained for codoped system shows the possibility of an aqueous sol-gel approach useful for applications in the area of multi-color light emissive displays.

Introduction

Due to the effective emission in the visible region, doping of TiO$_2$ with rare-earth elements has recently attracted much attention, since the surface state can form suitable emission centers, such as surface trapped state, defect state and oxygen vacancy induced by the dopants.$^{[1-8]}$ Terbium is a potential phosphor material for the fabrication of visible light emitting devices, because of its intense intra-4f transitions at wavelengths in the range 400–600 nm which is less sensitive to non-radiative de-excitation processes with a long intrinsic lifetime.$^{[9]}$ Moreover, Tb$^{3+}$ luminescent activator also may result in a higher photocatalytic activity since its valence state should force the separation of the photogenerated electron-hole pairs.$^{[10]}$ The photocatalytic activity of TiO$_2$ is known to depend on the oxygen vacancy concentration and oxygen mobility.$^{[11]}$ Thus by integrating the outstanding optical properties of terbium ions$^{[5,12,13]}$ and photocatalytic activity of titania nanoparticles$^{[14-16]}$ in a nanocomposite, there is excellent possibility to develop novel self-cleaning green emissive phosphors in the form of coatings or thin films. Further, codoping of rare-earth elements is reported to enhance the photocatalytic and luminescent properties.$^{[17,18]}$ The enhancement in luminescence in such a system is reported to be due to the efficient energy transfer from one rare-earth ion to the other$^{[17]}$ while the photocatalytic enhancement is due to the better separation of the photogenerated electron-hole pairs.$^{[18]}$ The synergistic effect of Er$^{3+}$ and Ce$^{3+}$ codoping on the crystal structure of titania was reported by Xu et al. in which the co-doped titania retained anatase phase with a size of 20 nm.$^{[19]}$ Further, the codoping caused a red shift in the UV-Vis absorption spectra which enhanced the light absorption properties resulting in a better photocatalytic activity. The La–Eu-TiO$_2$ photocatalyst prepared by Shi et al. showed enhanced photocatalytic activity due to increased surface area, a red shift in UV-Visible absorbance, decreased crystallite size and prevention from electron-hole recombination.$^{[18]}$ Many papers are available on the photocatalytic activity of rare-earth doped titania without taking into account the luminescent properties whereas some others mainly deal with luminescence properties disregarding the photocatalysis property. Reports on the simultaneous photocatalysis and photoluminescence property in rare-earth doped/codoped titania are very less. Nano-titania doped with Eu/Nd and Er/Yb showing simultaneous photoluminescence and photocatalytic behavior were reported recently via an alkoxide synthesis route.$^{[20-21]}$ The effect of rare-earth metal doping/codoping on the multi-functional, luminescent and self-cleaning property of titania is not studied in detail so far.

In the present work, the multi-functional property of the rare-earth doped/codoped titania nanocomposite synthesized by an all aqueous sol-gel route is studied. Terbium doping and terbium-europium co-doping are carried out on a titania based...
nanocomposite for the development of multi-functional coatings since doping on titania matrix alone may not result in the multifunctionality. A nanocomposite of titanium dioxide containing silica and lanthanum phosphate is known to exhibit excellent photocatalytic activity and low wetting properties from our previous studies.\(^\text{[22]}\) Hence, this composition of titanium oxide is identified as a host for doping terbium ions. Titanium dioxide provides photocatalytic property while silica provides better adhesion to the substrate and enables the formation of a large amount of surface active sites facilitating easy reaction with oxygen and thus leading to enhancement in photocatalytic activity\(^\text{[23–27]}\). Lanthanum phosphate is reported to be hydrophobic\(^\text{[28]}\) and in addition, imparts increased anatase phase stability and enhanced hydrophobicity.\(^\text{[14]}\) The effect of the addition of terbium ions in imparting green emission to the titania nanocomposite, in addition to the photocatalytic and hydrophobic property of the TSL nanocomposite is investigated in the present work. Moreover, the feasibility of a co-doped system (Eu and Tb-doped TSL) for getting multiple emission (red and green) by a single excitation wavelength (484 nm) is also attempted. Such codoped systems may find application in the area of light emissive displays.

Results and Discussion

A constant pH of 1.8 and a constant temperature (30 °C) was maintained while preparing the rare-earth ion doped TSL composition. Since the synthesis of doped TSL composition involves sol- solution mixing (see Supporting Information), ensuring the stability of TSL sol during and after the process of doping with terbium and/or europium ions is important. The precursor used for doping was the salt containing the same anion as that of the acid used in peptization of the sol for ensuring chemical compatibility. The sol was kept under constant stirring while the dopant solution was added.

Particle size distribution of the TSL nanocomposite sols containing 0.1 and 5 mol% terbium ion is presented in Figure 1. A bimodal distribution pattern with an increased particle size of 45 nm was shown by the 5 mol% terbium doped sample while the particle size was 34 nm for the 0.1 mol% terbium doped samples. The photographs of the terbium doped nanocomposite sols shown as insets also exhibit an increased turbidity for higher terbium loading. This could be due to the segregation of terbium ions on the surface of TSL composite at higher doping levels.\(^\text{[29]}\)

Figure 2 shows the X-ray diffraction patterns of terbium doped TSL nanocomposites calcined at 400 °C. Diffraction peaks of anatase phase at \(2\theta = 25^\circ\) as well as traces of brookite, were observed in the XRD patterns of pure titania and terbium doped TSL nanocomposites. The sample containing higher terbium loading (5 mol%) contains traces of rutile phase also, in addition to anatase and brookite phases.

Very recently Damian et al. reported that different crystal forms of titania were formed depending on the concentration of terbium dopant. In their work, the concentration of terbium above 2 at.% resulted in rutile structure and localization of \(\text{TB}^{3+}\) ions on the surface of TiO\(_2\) nanocrystals.\(^\text{[29]}\) The crystallite sizes were calculated from the diffraction plane (101) of anatase and the doped samples showed an initial decrease in crystallite size followed by an increase at 2 mol% doping. Lattice site distortions are possible from either substitutional or interstitial dopant ion incorporation within host titania lattice,\(^\text{[30,31]}\) due to the large difference of ionic radii between \(\text{Ti}^{4+}\) (0.68 Å) and \(\text{TB}^{3+}\) (1.06 Å). The decrease in particle size can be attributed to the presence of \(\text{Tb}–\text{O}–\text{Ti}\) in the doped samples, which inhibits the growth of crystal grains. This reduction in crystal size of anatase titania by increased terbium loading can be best understood from the TEM images presented in Figure 3.

Anatase crystallite size \((D_{\text{TEM}})\) calculated for undoped TSL\(^\text{[22]}\) was ~11 nm from TEM micrographs which was reduced to
With an increased doping concentration of 5 mol%, $D_{\text{TEM}}$ changes to ~4.3 nm. TEM results were consistent with those obtained from XRD which shows a reduction in size for 5 mol% Tb doped TSL. Also, the size of amorphous spherical silica particles (marked as dotted circles) remains unchanged (~30 nm) with respect to terbium addition indicating that the doping of terbium ions selectively happens at the crystalline titania matrix which changes the anatase crystallite size.

The anatase crystal size and BET surface area of Tb-TSL nanocomposites are given in Table 1. With respect to terbium doping, the surface area did not improve appreciably with low amounts of Tb doping while it decreased considerably for higher terbium loaded samples. However, the terbium doped nanocomposite powders were mesoporous as is clear from Table 1.

The photocatalytic activity of undoped and terbium doped TSL nanocomposites was evaluated by monitoring the degradation of an aqueous solution of a standard dye, methylene blue. The degradation of dye solution upon visible light irradiation (2 hours) is presented in Figure 4. 0.5 mol% terbium doped TSL nanocomposites had the highest photoactivity among other samples with ~80% dye degradation efficiency which is only ~10% more than that of undoped TSL. The nearly identical specific surface area values for the terbium doped TSL nanocomposites (Table 1) with that of undoped TSL could be one of the reasons for this observation. Stengl et al. reported that there is an optimal dosage of rare-earth ions in TiO$_2$ particles for the most efficient separation of photoinduced electron–hole pairs.\[32\]

With the increase of dopant ions, the surface barrier becomes higher, and the space charge region becomes narrower. The electron–hole pairs are efficiently separated thereby preventing recombination which led to the higher photocatalytic activity at a low doping concentration of rare-earth ions while at excess doping levels the recombination of the photo-generated electron–hole pairs becomes easier, which led to the lower photocatalytic activity.\[32\] The photoluminescence spectra of the terbium doped TSL nanocomposites calcined at 400 °C are provided in Figure 5 and the corresponding excitation spectra are given as inset.

Excitation was done at 484 nm for collecting the emission spectra since the excitation spectra show a maximum intensity peak at 484 nm (inset of Figure 5). The PL spectra exhibit typical radiative electronic transitions from the level $^5D_4$ to the $^7F_J$ levels, where $J = 5$ and 4 which are expected for Tb$^{3+}$. For all

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**Table 1.** Textural features of terbium doped TSL nanocomposites calcined at 400 °C.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Anatase crystallite size (nm)</th>
<th>BET Surface Area (m$^2$g$^{-1}$)</th>
<th>Mesopore volume (cm$^3$g$^{-1}$)</th>
<th>Average Pore dia (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSL-0Tb</td>
<td>5.6</td>
<td>138.5</td>
<td>0.248961</td>
<td>6.3</td>
</tr>
<tr>
<td>TSL-0.1Tb</td>
<td>6.8</td>
<td>131.9</td>
<td>0.175747</td>
<td>4.6</td>
</tr>
<tr>
<td>TSL-0.5Tb</td>
<td>5.7</td>
<td>134.6</td>
<td>0.174393</td>
<td>4.5</td>
</tr>
<tr>
<td>TSL-1Tb</td>
<td>4.6</td>
<td>133.3</td>
<td>0.169232</td>
<td>4.4</td>
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<tr>
<td>TSL-2Tb</td>
<td>5.4</td>
<td>129.0</td>
<td>0.159971</td>
<td>4.1</td>
</tr>
<tr>
<td>TSL-5Tb</td>
<td>3.1</td>
<td>107.9</td>
<td>0.142000</td>
<td>3.9</td>
</tr>
</tbody>
</table>

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**Figure 3.** TEM images of (a) undoped TSL and (b) TSL-0.5 Tb nanocomposites, both calcined at 400 °C.

**Figure 4.** Methylene blue degradation of undoped and terbium doped TSL nanocomposites, all calcined at 400 °C and subjected to visible light exposure.
the samples, \(^{1}D_2\) to the \(^{7}F_2\) (543 nm) electric dipole transition is the most intensive.\(^5\) Photon absorption leads to the transition of electrons from valence to conduction band of TiO\(_2\) and then this energy is transferred non-radiatively to \(^{5}D_3\) level of Tb\(^{3+}\) ions which is followed by a multi-phonon assisted nonradiative transition of \(^{5}D_3\rightarrow^{5}D_4\). The transitions from \(^{5}D_4\rightarrow^{7}F_j\) (\(j = 5, 4\)) are radiative and correspond to the emission lines of 543 and 584 nm, respectively.\(^6\) These radiative transitions can result in the green emission of the terbium doped TSL nanocomposites. Since 0.5 mol\% Tb doping has resulted in comparatively good photoactivity, TSL-0.5Tb was further observed under a fluorescence microscope. The fluorescent microscopic image and decay curve for the emission are presented in Figure 6.

Intense green emission was observed when the powder sample was excited at 484 nm and the obtained result was in agreement with the powder PL data. Also, the TSL nanocomposite containing 0.5 mol\% terbium has a lifetime of \(~0.34\) ms.

SEM and fluorescence microscopic images of the TSL-0.5 Tb coating annealed at 400 °C are presented in Figure 7. SEM image shows the presence of a very fine coating with a few scattered agglomerates. The fluorescence microscopic image of the TSL–0.5Tb shows weak green emission when compared with a powder sample possibly due to the lesser amount of material present in the nano coating.

A cross-sectional view of Tb-doped TSL coating is provided below in Figure 8. Inset of Figure 8 shows that the coating had a thickness of \(~800\) nm. The AFM surface image of TSL-0.5Tb coating shows an average thickness of \(~200\) nm with very fine uniformly arranged particles and larger agglomerates possibly due to the segregation of terbium ions on the surface of titania crystallites as presented in Figure 9.

The UV-Visible transmittance and the tauc plot derived from the absorbance of the composite coatings are provided in Figure 10. The coating was highly transparent\(^2\) in the region 600–800 nm while it shows a significant absorption in the region 400–600 nm which can be attributed to the visible light absorbance by Tb doped titania. Although doping with 0.5 mol\% Tb did not make any essential change in transmission characteristic as compared to undoped TSL, there is a band gap narrowing from 3.6 eV to 3.1 eV. This red shift in the band gap energy revealed a shift in the absorbance towards the visible region and can be ascribed as a reason for the increased photoactivity of TSL-0.5Tb under visible light exposure.

The visible light activity of the TSL-0.5Tb coating was further evaluated by methylene blue degradation study and the results are provided in Figure 11. The TSL-0.5Tb coating has shown a dye degradation efficiency of \(~66\)\% under 2 h visible light exposure compared to \(~25\)\% for undoped titania coating under similar conditions. The advanced water contact angle measured for TSL-0.5Tb composite coating was \(~70^\circ\) against \(~83^\circ\) for the undoped TSL nanocomposite coating.\(^2\) This reduction in the water contact angle value can be attributed to the presence of large agglomerates\(^2\) on the surface of TSL-0.5Tb coating which should have altered the surface roughness as revealed from SEM image. Hence by terbium doping to the TSL nanocomposite, green emission could be integrated at very low concentration (0.5 mol\%) and such coatings possessed multi-functionalities like visible light activity, transparency, low wettability and photoluminescence.

The particle size distribution and the X-ray diffraction pattern of 0.25 mol\% Tb and Eu codoped TSL (Tb–Eu-TSL) are
shown in Figure 12. The particle size of Tb–Eu-TSL was higher than 0.1 mol% Tb and Eu-doped TSL sols. The average particle size of 0.1 mol% Tb and 0.1 mol% Eu-doped TSL sols separately was 34 and 32 nm respectively. With Tb–Eu codoping of the TSL sol, the average particle size increased to 42 nm. X-ray diffraction pattern shows the presence of anatase phase with traces of brookite. The anatase crystallite size was calculated to be 5.7 nm which is less than that of individually doped system at a lower concentration of 0.1 mol% [Crystallite size of TSL-
0.1Tb and TSL-0.1Eu (XRD is not presented here) were 6.8 and 8.5 nm respectively. The introduction of Eu and Tb ions in the TSL matrix can reduce the particle size and crystallinity of titania as reported for other codoped systems. [33]

EDS analysis and elemental mapping of Tb–Eu codoped TSL nanocomposite are provided below in Figure 13 and 14 respectively in order to affirm the presence of elements such as Ti, Si, O, La, P, Eu and Tb.

PL spectra of Tb and Eu codoped TSL nanocomposite (Figure 15), when excited at wavelength 484 nm, provide both green and red emission characteristic of the terbium and europium ions. [13, 34] These emissions correspond to the 5D4–7F5 and 5D0–7F2 transitions respectively. [35] The codoped TSL had a lifetime of ~0.48 ms. The fluorescence lifetime of europium doped titania thin film (0.25 mol%) prepared by the sol-gel method as per an earlier report was ~0.25 ms and the luminescence intensity was found to decrease with increasing temperature. However, the lifetime drops down to ~0.012 ms from ~0.2 ms at 400 °C. [36] The higher decay time of 0.48 ms obtained in the present study for the sample calcined at 400 °C shows the efficiency of Tb–Eu codoped TSL.

Figure 11. Methylen blue degradation of (a) undoped titania and (b) TSL-0.5 Tb composite coating annealed at 400 °C, under visible light exposure for two hours.

Figure 12. (a) Average particle size of Tb–Eu-TSL nanocomposite sol and (b) X-ray diffraction pattern of Tb–Eu-TSL, calcined at 400 °C.

Figure 13. EDS analysis of Eu and Tb codoped TSL nanocomposite, calcined at 400 °C.

Methylene blue degradation efficiency of 46.3% (Figure 16) was observed for the codoped TSL coating under two hours of visible light exposure. The photoactivity of thin films will be always lower than the photoactivity of powders because of the lesser amount of catalytic material present in the coating and hence an increased time of exposure is necessary to achieve successful dye degradation. Recently Samadi et al. [37] reported that Nb and Zr codoped titania-silica thin films exhibited a dye degradation efficiency (methyl orange) of ~70% in 2 hours (dye concentration - 5 μg/ml) in which the intensity of visible
The light source was 400 W (A high-intensity lamp was used in their study). In the present work, Eu and Tb codoped TSL nanocomposite coating exhibited ~46% dye degradation efficiency (methylene blue) in 2 hours for dye having an almost similar concentration (~5 μg/ml) in which the intensity of visible light source was much lesser than the reported work (112 W). This shows that the results obtained in the present work are comparable with the reported results for rare-earth codoped titania system.

The increased photoactivity of codoped TSL coating, when compared to pure titania coating (~25%), could be due to the enhanced surface area of 149.2 m²g⁻¹ and the high mesopore volume of 0.15466 cm³g⁻¹ with an average pore diameter of 3.36 nm. The BET surface areas for Tb-TSL and Eu-TSL (0.1 mol% each) were 131.9 and 122.9 m²g⁻¹ respectively while Tb–Eu-TSL was much higher (149.2 m²g⁻¹) which is the reason for the very good photoactivity. The multiple luminescence along with visible light activity makes the Tb–Eu codoped system suitable for multi-color light emissive displays.

Figure 14. Elemental mapping of Tb–Eu codoped TSL nanocomposite calcined at 400 °C showing the presence of elements such as (a) Ti (b) Si (c) O (d) La (e) P (f) Tb and (g) Eu.

Figure 15. (a) PL emission spectra and (b) lifetime curve of Eu and Tb codoped TSL nanocomposite, calcined at 400 °C when excited using a wavelength 484 nm.

Figure 16. Methylene blue dye degradation by Tb–Eu codoped TSL nanocomposite coating under visible light exposure for two hours.

Conclusions

Visible light responsive and photoluminescent titania nanocomposites by terbium doping was successfully synthesized by
an aqueous sol-gel process. Further, sol–gel-derived films were fabricated on glass substrates by dip coating method and the resultant coatings also possessed multi-functional properties. Green emission was obtained on visible light excitation at a wavelength of 484 nm in terbium doped TSL nanocomposite. PL spectra show a sharp peak at 545 nm ($\lambda_{ex}$=484 nm), characteristic of the trivalent terbium ion. Visible light activity can be induced by Tb doping on TSL as revealed from a red shift in the Tauc plot. TSL-0.5Tb composite exhibits a mesoporous structure with BET surface area of 134.6 m$^2$ g$^{-1}$. Also, TSL-0.5Tb coating has shown a dye degradation efficiency of ~66% under 2 h visible light exposure compared to ~25% for undoped titania coating under similar conditions. Such mesostructured, transparent thin coatings possessing photocatalytic activity and low wettability along with photoluminescent properties can satisfy multi-functional applications. Hence, TSL nanocomposite doped with 0.5 mol% Tb is highly promising for the development of self-cleaning and luminescent coatings. Eu and Tb codoped TSL nanocomposites and coatings were found to exhibit both red and green emission when excited using single wavelength 484 nm and were visible light active. A higher decay time of ~0.48 ms obtained for the Tb–Eu codoped TSL shows the efficiency of an aqueous sol-gel approach. Such a codoped TSL system can find application in the area of multi-color light emissive displays.

Supporting Information Available

Detailed experimental procedure and characterisations.

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