INTRODUCTION

Semiconductor photocatalysis using TiO$_2$ is a promising technology for various environmental applications [1,2]. However, the photocatalytic activity of TiO$_2$ is limited to UV light, making it less practical. Its band gap is narrowed by the introduction of a metal or a non-metal ion in general to shift its optical window to visible region [3-6]. Modification of TiO$_2$ by rare earth cations is relatively less explored. Since lanthanide ions can form complexes and increase the photocatalytic activity, doping lanthanide ions like La$^{3+}$ into TiO$_2$ has become more popular as an alternative way to improve efficiency [7]. When La-doped TiO$_2$ nanosheets are exposed to light, electron-hole pairs are generated. La$^{3+}$ ions, as dopants, efficiently scavenge electrons, leading to better separation and transfer of photo-generated electrons and holes [8]. This results in the quick trapping of these electrons by La$^{3+}$ ions, results in highly reactive superoxide ions (O$_2^-$), hydroxyl radical (OH$^-$) and holes ($h^+$) in the reaction mechanism.

Effect of Lanthanum Loading on the Photocatalytic Degradation of Brilliant Yellow and Acid Blue Dyes in Visible Light and Sunlight over La$_2$O$_3$-TiO$_2$ Nanocomposites

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La-doped TiO$_2$ nanocomposites were synthesized using the sol-gel process with different proportions of lanthanum doping (1-5 wt.%). The synthesized nanocomposites were analyzed thoroughly by X-ray diffraction (XRD), nitrogen adsorption, scanning electron microscopy (SEM) with extended X-ray diffraction (EDAX), transmission electron microscopy, ultraviolet-visible DRS spectra for optical properties, photoluminescence (PL) for emission behaviours, Fourier transform infrared (FTIR) spectroscopy (FTIR) for chemical bonding analysis and X-ray photoelectron spectroscopy (XPS) for surface chemical composition. The XRD analysis confirmed the anatase phase for all synthesized La-TiO$_2$ nanocomposites. The UV-Vis spectra showed an increased absorption in the visible range and a slight red shift of binding energy as the % La doping increased from 1-5 wt.%. Similarly, the binding energy values varied from 3.02 to 2.75 eV with increased La doping. These nanocomposites exhibited the photocatalytic activity achieving 99% degradation of acid blue dye and 96% degradation of brilliant yellow dye in the presence of visible light irradiation. Scavenger studies indicated that the dye degradation was suppressed, suggesting the involvement of superoxide (O$_2^-$), hydroxyl radical (OH$^-$) and holes ($h^+$) in the reaction mechanism.

Keywords: Nanocomposites, La-doped TiO$_2$, Photocatalytic degradation, Sol-gel method.

EXPERIMENTAL

Synthesis of La-doped TiO$_2$ photocatalysts: The sol-gel synthetic procedure was employed to synthesize La$_2$O$_3$-TiO$_2$ photocatalysts with varying lanthanum content (1, 2, 3 and 5 wt.%). The synthesis involved the preparation of three independent solutions (A, B and C) containing acetic acid in ethanol,
TiO(OC_2H_5)_2 in ethanol and La(NO_3)_3·5H_2O in deionized water, respectively. These solutions were combined, leading to gel formation. Further steps included adding aqueous ammonia solution, drying at specific temperatures and calcination in air at 500 ºC for 4 h to obtain the photocatalysts. Thus, obtained catalysts were labelled as 1LT, 2LT, 3LT and 5LT, respectively as per wt.% of La present.

**Characterization:** The X-ray powder diffraction (XRD) analysis was performed using a Rigaku miniplex powder X-ray diffractometer. Surface properties were measured using N_2 adsorption and surface morphology was analyzed through field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray (EDX) analysis for element distribution. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded using a JASCO V650 UV-vis spectrophotometer.

**Photocatalytic degradation:** The experiments were carried out on a reactor with visible light irradiation and the degradation efficiency of brilliant yellow and acid blue dyes were measured using absorbance changes. The details of the experimental set up are described elsewhere [10]. The below formula was used to estimate degradation efficiency.

\[ D(\%) = \frac{C_o - C}{C_o} \times 100 = \frac{A_o - A}{A_o} \times 100 \]

where C_o and A_o are the concentration and absorbance, respectively at zero time of dye degradation; and C and A are the concentration and absorbance, respectively at every 30 min intervals during the reaction.

**RESULTS AND DISCUSSION**

**X-ray diffraction (XRD):** The XRD spectral analysis, as shown in Fig. 1, confirmed that the peaks correspond to the anatase phase for all La_2O_3-TiO_2 samples, like nano-TiO_2. This suggests that the La_2O_3 doping process did not introduce any additional phases or impurities. The absence of further peaks corresponding to La demonstrates the successful and complete doping of La into nano-TiO_2. This finding is significant since it verifies that the anatase phase remains intact even after doping.

In addition to this, the XRD investigation revealed a fascinating pattern, as the percentage of La doping increases, the most intensive diffraction peak decreases in intensity and the signal broadens. This broadening is indicative of a decrease in the crystallite size of material as presented in Table-1. It suggests that higher La percentages may lead to smaller crystallite sizes within the La_2O_3-TiO_2 structure [11].

**TABLE-1**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>XRD crystallite size (nm)</th>
<th>BET-SA (m^2 g^-1 cat)</th>
<th>UV-DRS absorption wavelength (nm) edge</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.%La_2O_3-TiO_2</td>
<td>7.3</td>
<td>83</td>
<td>402</td>
<td>3.02</td>
</tr>
<tr>
<td>2 wt.%La_2O_3-TiO_2</td>
<td>6.5</td>
<td>89</td>
<td>423</td>
<td>2.85</td>
</tr>
<tr>
<td>3 wt.%La_2O_3-TiO_2</td>
<td>6.1</td>
<td>105</td>
<td>429</td>
<td>2.82</td>
</tr>
<tr>
<td>5 wt.%La_2O_3-TiO_2</td>
<td>5.2</td>
<td>109</td>
<td>434</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Fig. 5 demonstrates the UV-Vis DRS of the La-TiO_2 nano-composites. This spectral study successfully demonstrated that La^{3+} doping in TiO_2 nanoparticles led to a red shift (which was
Fig. 2. BET-adsorption isotherms of (a) 1 wt.% La$_2$O$_3$-TiO$_2$, (b) 2 wt.% La$_2$O$_3$-TiO$_2$, (c) 3 wt.% La$_2$O$_3$-TiO$_2$ and (d) 5 wt.% La$_2$O$_3$-TiO$_2$ nanocomposites.

Fig. 3. SEM micrographs of (a) 1 wt.% La$_2$O$_3$-TiO$_2$, (b) 2 wt.% La$_2$O$_3$-TiO$_2$, (c) 3 wt.% La$_2$O$_3$-TiO$_2$ and (d) 5 wt.% La$_2$O$_3$-TiO$_2$ nanocomposites.
Fig. 4. EDAX spectra and elemental composition of (a) 1 wt.% La$_2$O$_3$-TiO$_2$, (b) 2 wt.% La$_2$O$_3$-TiO$_2$, (c) 3 wt.% La$_2$O$_3$-TiO$_2$ and (d) 5 wt.% La$_2$O$_3$-TiO$_2$ nanocomposites

<table>
<thead>
<tr>
<th>Element</th>
<th>(a) 1 wt.% La$_2$O$_3$-TiO$_2$</th>
<th>(b) 2 wt.% La$_2$O$_3$-TiO$_2$</th>
<th>(c) 3 wt.% La$_2$O$_3$-TiO$_2$</th>
<th>(d) 5 wt.% La$_2$O$_3$-TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>46.56 72.47</td>
<td>40.99 67.80</td>
<td>41.71 68.48</td>
<td>45.75 72.11</td>
</tr>
<tr>
<td>Ti K</td>
<td>52.70 27.40</td>
<td>57.93 32.00</td>
<td>57.06 31.29</td>
<td>52.28 27.53</td>
</tr>
<tr>
<td>La L</td>
<td>0.74 0.13</td>
<td>1.08 0.21</td>
<td>1.23 0.23</td>
<td>1.98 0.36</td>
</tr>
<tr>
<td>Totals</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 5. (a) UV-Vis DRS and (b) Kubelka-Munk plot of 1-5 wt.% La$_2$O$_3$-TiO$_2$ nanocomposites
increased from 1 to 5 wt.% La₂O₃-TiO₂ in the absorbance spectrum, wavelength of light absorption increases and band gap energy decreases. These changes are favourable for improving the photocatalytic performance of these nanoparticles under visible light irradiation [17].

**Photoluminescence studies:** Photoluminescence spectra of 1, 2, 3 and 5 wt.% La doped TiO₂ nanocomposites showed the emissions at 385, 451 and 469 nm (Fig. 6). These emissions are attributed to different electron-hole recombination processes, including surface state emissions. The photoluminescence characteristics are closely related to crystallinity, with lower defect density resulting in improved crystallinity [18].

**FTIR spectral analysis:** Fig. 7 shows the FTIR spectra of the La₂O₃-TiO₂ nanoparticles. In this spectrum, the peaks at 860-680 cm⁻¹ range corresponded to vibrational frequencies of Ti-O bonds. Bands at 1231, 1375 and 1740 cm⁻¹ were associated with C=O stretching frequency and the frequency of C=C bonds stretching of adsorbed atmospheric CO₂ on catalyst surface and organic precursor of titanium isopropoxide respectively, traces of which may be remaining after synthesis. Bands corresponding to O-H vibrations appeared at 3000-2900 and 3450 cm⁻¹ revealed an increased in the water adsorption on the surface of La₂O₃-TiO₂ after La³⁺ doping, leading to greater ‘OH radical production upon light irradiation. These spectra indicate that when the proportion of La increases, peaks are observed at shorter wavelengths [19].

**Raman studies:** Fig. 8 demonstrates the Raman spectrum of 5 wt.% La doped TiO₂ nanoparticles. In this, Raman modes appeared at 146 cm⁻¹ E_g (1), 197 cm⁻¹ E_g (2), 399 cm⁻¹ B_1g (1), 518 cm⁻¹ [combination of A_1g and B_1g(2)] and 642 cm⁻¹ (E_g(3)) corresponding to anatase phase [20].

**X-ray photoelectron studies:** A high-resolution spectra of 1-5 wt.% La-TiO₂ nanocomposites are shown in Fig. 9. Fig. 9a illustrates the wide scan of the aforementioned samples. The presence of peaks in spectra corresponds to the elements suggest that these elements (Ti and O) are present. The absence of peaks corresponding to La in broad scan was because of low content of La that was not detected by XPS instrument. Fig. 9b displays the XPS patterns of Ti 2p, in which the peaks of Ti 2p₃/2 and 2p₁/2 appeared at band gap energies were 458 and 464 eV, respectively for 1 wt.% and 458.7 and 464.7 eV, respectively for 5 wt.% La-TiO₂. The splitting difference in binding energy inferred that Ti exists in Ti⁴⁺ state. It is also obvious that 2p peaks of Ti slightly shifted to higher energy from 1 to 5 wt.% this implies that La percentage is increased.

**Fig. 9c shows the XPS peaks corresponding to La 3d₃/₂ and 3d₅/₂ appeared at binding energies of 839 and 852 eV, respectively attributing the presence of Ti–O–La bonds [16]. whereas Fig. 9d shows the XPS spectra of O 1s and the peaks at 530 eV for 1 wt.% La-TiO₂ and 529 eV for 5 wt.% La-TiO₂.
Photocatalytic degradation studies: The efficiency of photocatalytic processes improved from 1 wt.% La₂O₃-TiO₂ to 5 wt.% La₂O₃-TiO₂ in degrading the aqueous solutions of brilliant yellow and acid blue dyes. During the photocatalytic degradation process, dye molecules are initially adsorbed and accumulated on the surface of nanoparticles when exposed to visible and solar light. Subsequently, the continuous migration and successive photocatalytic oxidation on the nanoparticle surface enhance the efficiency of degradation.

Among the prepared La-doped TiO₂ nanocomposites, the 5% La₂O₃-TiO₂ nanocomposite exhibited high efficiency in degrading brilliant yellow and acid blue dyes, achieving degradation efficiency of 96% and 99%, respectively. The degradations for 1, 2 and 3 wt.% La₂O₃-TiO₂ in brilliant yellow dye were 43%, 57% and 86%, while in acid blue dye were 54%, 76% and 99% shown in Figs. 10 and 11, respectively. A modest 75 mg of the La-doped TiO₂ catalyst exhibited an impressive 99% degradation of 50 ppm acid blue dye (Fig. 11d).

A comparison of brilliant yellow and acid blue dye degradation using 1, 2, 3 and 5 wt.% La-doped TiO₂ particles under visible light conditions is presented in Fig. 12. Among all, 5 wt.% La-doped TiO₂ displayed the superior photocatalytic activity for both brilliant yellow dye and acid blue dyes. This enhancement is higher for acid blue when compared to brilliant yellow, which is double in case of 5 wt.% La-doped TiO₂. This enhancement was attributed to an enhancement of the anatase phase due to La doping.

The rate of photodegradation of dyes follows a pseudo-first-order reaction (Fig. 13a-b), a pattern observed in other studies as well [21,22]. The rate constants and R² values for the photodegradation of both brilliant yellow and acid blue dyes over 1-5 wt.% La-doped TiO₂ are presented in Table-3. The rate constants were varied from 1.61 × 10⁻² min⁻¹ to 2.1 × 10⁻² min⁻¹ for brilliant yellow dye and from 1.9 × 10⁻² min⁻¹ to 2.2 × 10⁻² min⁻¹ for acid blue dye, indicating the efficiency of photodegradation increased as La percentage increased and...
Fig. 10. Photodegradation of 50 ppm brilliant yellow dye using 75 mg catalyst in visible light over (a) 1LT, (b) 2LT, (c) 3LT and (d) 5LT nanocomposites.

Fig. 11. Photodegradation of 50 ppm acid blue dye using 75 mg catalyst in visible light over (a) 1LT, (b) 2LT, (c) 3LT and (d) 5LT nanocomposites.
the high intrinsic activity of catalysts. These results are correlated with the degradation efficiencies as observed earlier.

**Photocatalytic degradation of dyes in sunlight**: The comparison of brilliant yellow and acid blue dye degradation using 1, 2, 3 and 5 wt.% La-doped TiO$_2$ particles under sunlight conditions is presented in Figs. 14 and 15, respectively. Among the synthesized La$_2$O$_3$-TiO$_2$ photocatalysts with varying lanthanum content (1, 2, 3 and 5), 5 wt.% La-doped TiO$_2$ displayed superior photocatalytic activity, for both brilliant yellow and acid blue dyes (Fig. 16). This enhancement is higher for acid blue when compared to brilliant yellow, which was double in case of 5 wt.% La-doped TiO$_2$. Again, this enhancement was attributed to an enhancement of the anatase phase due to La doping. The rate constants and $R^2$ values for the
photodegradation of both brilliant yellow and acid blue dyes over 1-5 wt.% La-doped TiO₂ are depicted in Table-4.

**Reusability and stability of catalysts:** The reusability studies were monitored for five cycles of run in visible light. Fig. 17 shows the photocatalytic activity towards brilliant yellow degradation decreased slightly from 96-90% and towards acid blue degradation from 99-92%. This capability of percentage photodegradation of nanoparticles even after five successive cycles shows stability of the photocatalyst, which was also proved from used catalyst XRD analysis.

The reusability studies were monitored for five cycles of run. Fig. 18 shows the photocatalytic activity towards brilliant yellow degradation decreased slightly from 80-75% and towards acid blue degradation from 72-66%. This inferred that photocatalyst is stable. The same which was also proved from used catalyst XRD analysis (Fig. 19) that indicates no change in the structure of the catalyst after the reaction run for 5 cycles.

**Scavenger studies:** In photocatalysis, different radical scavengers are used to examine the role of various redox-active species. The hole scavenger donates the electrons to photocatalysts thereby removes the holes. Ammonium oxalate and formic acid act as holes (h⁺) scavengers in this work. In photocatalytic degradation hydroxy radicals involving mechanism includes radical addition, hydrogen abstraction, electron transfer...

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**TABLE-4**

**RATE CONSTANTS AND R² VALUES FOR THE PHOTODEGRADATION OF BRILLIANT YELLOW AND ACID BLUE DYES IN SUNLIGHT OVER 1-5 LT CATALYSTS**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Brilliant yellow dye</th>
<th>Acid blue dye</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate constant, k (min⁻¹)</td>
<td>R² values</td>
</tr>
<tr>
<td>1 wt.% La₂O₃-TiO₂</td>
<td>1.80 × 10⁻²</td>
<td>0.9002</td>
</tr>
<tr>
<td>2 wt.% La₂O₃-TiO₂</td>
<td>1.90 × 10⁻²</td>
<td>0.9880</td>
</tr>
<tr>
<td>3 wt.% La₂O₃-TiO₂</td>
<td>2.02 × 10⁻²</td>
<td>0.9449</td>
</tr>
<tr>
<td>5 wt.% La₂O₃-TiO₂</td>
<td>2.18 × 10⁻³</td>
<td>0.9875</td>
</tr>
</tbody>
</table>

---

Fig. 14. Photodegradation of 20 ppm brilliant yellow dye using 50 mg catalyst in sunlight over (a) 1LT, (b) 2LT, (c) 3LT and (d) 5LT nanocomposites
Fig. 15. Photodegradation of 20 ppm acid blue dye using 50 mg catalyst in sunlight over (a) 1LT, (b) 2LT, (c) 3LT and (d) 5LT nanocomposites and radical combination. When the hydroxy radical scavengers like isopropyl alcohol is used, this mechanism is suppressed thereby, it is understood the role of hydroxy radicals in degradation [23].

The role of the radical scavengers in the photocatalytic degradation of brilliant yellow dye rates over 5 wt.% La₂O₃-TiO₂ using sunlight (Fig. 20) showed a reduction in the degradation activity from 80% without a scavenger to 39% in the presence of benzoquinone, which is a superoxide radical scavenger and when isopropanol, used as hydroxyl radical scavenger the activity was found to be 34% and in the presence of ammonium oxalate, a-holes (h⁺) scavenger the activity was found to
Fig. 17. Reusability studies of La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanocomposites in the photodegradation of (a) brilliant yellow dye (b) acid blue dye in visible light.

Fig. 18. Reusability studies of La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanocomposites in the photodegradation of (a) brilliant yellow dye (b) acid blue dye in sun light.

Fig. 19. XRD spectrum of used 5 wt.% La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanocomposites.

Fig. 20. % Photodegradation of (a) in sunlight over 5 wt.% La<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> in the presence of scavengers, benzoquinone, isopropanol, ammonium oxalate and formic acid.
reduce to 28% whereas in the presence of formic acid, a-holes (h') scavenger the activity was found to be 29%.

The effect of the radical scavengers on acid blue dye degradation rates over 5 wt.% La$_2$O$_3$-TiO$_2$ using sunlight showed a reduction in the degradation activity from 72% without a scavenger to 36% by using benzoquinone and by using isopropanol, a hydroxyl radical scavenger the activity was found to be 29% and in the presence of ammonium oxalate, a-holes (h') scavenger the activity was found to reduce to 28% while in the presence of formic acid, a-holes (h') scavenger the activity was found to be 25%.

Conclusion

The La$_2$O$_3$-TiO$_2$ nanocomposites synthesized via the sol-gel method demonstrated high efficiency in degrading brilliant yellow and acid blue dyes. The efficiency increased with higher La doping percentages, particularly at 5 wt.%. The nanocomposites exhibited enhanced efficacy even at elevated dye concentrations, indicating their potential for practical applications in treating dye-contaminated solutions. The characterization techniques such as XRD and SEM confirmed the nanocrystalline structure and spherical morphology of the catalyst. The UV-DRS analysis revealed a clear reduction in the band gap of the La-doped catalyst. These factors contribute to the enhanced photocatalytic activity. The 5 wt.% catalyst showed high photodegradation activity for both the dyes in visible as well as sunlight. The activity of this catalyst was in the order of their rates of degradation of dyes as: $\Gamma_{\text{acid blue}}$ in sunlight > $\Gamma_{\text{acid blue}}$ in visible light > $\Gamma_{\text{brilliant yellow}}$ in sunlight > $\Gamma_{\text{brilliant yellow}}$ in visible light. The catalyst maintained stable activity over five consecutive runs, underscoring its reliability as a sunlight/visible-light degradation catalyst for brilliant yellow and acid blue dyes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

9. X. Jaramillo-Fierro and R. León, *Nanomaterials*, 13, 1068 (2023); https://doi.org/10.3390/nano13061068