Facile Hydrothermal Synthesis of Sm and Eu doped TiO2/Graphene Oxide Nanocomposites for Photocatalytic Applications

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LANTHANIDE (Ln3+) doped TiO2 supported on Graphene oxide (GO) (Ln3+ = Eu3+ and Sm3+ ions) were prepared by using a low cost and facile hydrothermal method. Structural, morphological and optical properties of the un-doped and Ln3+-doped nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-Ray (EDX), transmission electron microscopy (TEM), (SBET) Barrett–Joiner–Halenda surface area analysis, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy (RS) and diffuse reflection spectrometry (DRS). The photocatalytic activities of the catalysts were investigated by studying photo decolorization and photodegradation of Methylene Blue (MB). The XRD results showed that all the TiO2 prepared samples exhibit anatase phase and no other peaks have been observed indicating the absence of impurities in the prepared samples. SEM images demonstrated that the TiO2 nanoparticles are well dispersed on the GO surface. A red shift in the UV-Vis absorption of the prepared samples have been observed indicating the charge transfer between the dopants and TiO2. The photocatalytic activity results showed that 0.015 mol% Eu3+-doped TiO2/GO nanocomposite possesses the highest photocatalytic activity. Chemical oxygen demand (COD) analysis indorsed the photodegradation results. This promising photocatalyst led to almost complete mineralization of MB dye after only 90 min upon expose to UV light. The results clearly demonstrated the beneficial role of both GO as a supporting material and lanthanide metal ions as dopants on the degradability of MB.

Keywords: Photocatalysis, Lanthanide doped Titania, Graphene oxide, Methylene blue (MB), UV light.

Introduction

Environmental contaminations as wastewater and air pollution have become a very serious problem, the world is facing today. For water treatment, photocatalysis is one of the most powerful and environment friendly techniques [1,2]. Titanium dioxide is one of the most promising semiconductors that have been widely studied because of its unique photoelectric properties, high chemical stability, non-toxicity and low cost [3]. It has been reported that anatase phase is more photoactive than rutile or brookite forms because of the low recombination rate of its photogenerated electrons and holes on the surface.
of TiO₂. Despite its role as a good photocatalyst semiconductor material its efficiency is limited by its wide bandgap and the fast electron–hole recombination [4]. A lot of approaches have been studied to extend the optical absorption of TiO₂ into the visible light region, aiming to modify its photocatalytic activity. One of these approaches is doping. The photocatalytic activity of TiO₂ can be increased by doping with Lanthanide elements [5-8]. Because of their unique 4f electronic configuration and spectral characteristics, lanthanides are ideal elements for modifying the crystal structure, electronic structure, optical properties, surface adsorption of TiO₂ and forming a series of novel promising photocatalysts [5]. Lanthanides provide an opportunity for an in-depth study of the electronic structure that can enhance the photocatalytic activity of TiO₂ [9,10]. In addition, it has been found that loading TiO₂ nanoparticles on a mesoporous material as zeolites, alumina, silica or carbon-based materials can also enhance the photocatalytic activity of TiO₂ [11-14]. Carbon is used as support material for catalysts because of its high surface area [15]. Carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene oxide (GO) increase the surface area of TiO₂ for trapping more organic pollutants and enhance the rate of photocatalytic process [16].

In the present work, we have investigated a simple hydrothermal procedure for the preparation of some lanthanide doped TiO₂ nanomaterials that are decorated on GO forming a new composite nanomaterial (Sm³⁺- and/or Eu³⁺-doped TiO₂/GO). The new catalysts would be characterized by standard techniques. Its potential applications as photocatalysts were also studied. As a test material we have chosen MB dye, which is considered as a model organic dye pollutant that may exist in water.

**Experimental**

**Materials and Reagents**

All chemicals and reagents were of analytical purity and used without any additional purification. Graphite flakes, hydrochloric Acid 37%, sulphuric Acid 98%, potassium permanganate (KMnO₄), hydrogen peroxide 30%, Titanium (IV) isopropoxide (Ti(OC₃H₇)₄ (99%)), Methylene blue (MB), Samarium (iii) nitrate hexahydrate (Sm(NO₃)₃·6H₂O), Europium (iii) nitrate pentahydrate (Eu(NO₃)₃·5H₂O), isopropanol (C₃H₆O (99%)) and ethanol (C₂H₅OH (99%)) were purchased from Sigma-Aldrich, Sigma-Aldrich Chemie GmbH, Taukirchen, Germany. The chemical structure of MB dye is shown in Fig. 1. Deionized (DI) water was used throughout this work.

**Preparation Methods**

Graphene oxide sheets (GO) were prepared from graphite powder by improved Hummer method as previous paper reported [17]. Ln(III)-TiO₂/GO were prepared by adding 30 mg GO in 25 mL isopropanol and sonicated at room temperature for 90 min to ensure the dispersion of graphene oxide in the alcoholic solution. Then, a certain amount of titanium isopropoxide was added into the solution and kept stirring for 10 min. Then 1 mL of water containing an appropriate amount of the dopant metal ions (Eu³⁺ or Sm³⁺) was added dropwise to the above solution with different molar ratios ranging from (0.01 to 0.03 mol% relative to TiO₂). The resulting mixture was placed in an oven at 80 °C for 1 h. The resulting powder was washed by ethanol for several times and then dried at 50 °C overnight. Pure TiO₂ and TiO₂/GO (1:100) were prepared under the same conditions without the addition of the lanthanide metal ions.

**Characterization**

X-ray diffraction (XRD) patterns were investigated by the X-ray diffractometer (X-ray 6100 Shimadzu-Japan) with Cu Kα radiation (λ= 0.15406) with Kβ filter at 30 kV and 30 mA. The Bragg angle (2θ) had the range from 10° - 80° and scan rate 5 °/min. The morphologies were characterized by a scanning electron microscope (SEM) (JEOL JSM 6360LA, Tokyo, Japan). The samples were coated with gold using sputtering coater (model: S150B, Edwards High Vacuum Ltd., England) in order to avoid the buildup of local electrical charges. SEM instrument equipped with Energy dispersive X-ray (EDX, Oxford Instruments NanoAnalysis, Concord, MA, USA, Shimadzu, Kyoto-Japan). PG Instruments Ltd., Woodway Lane, Alma Park, Leicestershire LE17 5FB, UK. Edwards High Vacuum Ltd, The Hamlyn Centre Bessemer Building, South Kensington Campus, Imperial College London, London, UK) for semiquantitative elemental analysis of the prepared samples. Transmission electron spectroscopy (TEM) was performed.

with a JEOL JEM 100CX, Tokyo, Japan. Optical properties of the prepared samples were investigated using UV-Vis diffuse reflectance spectroscopy on a Shimadzu UV-2550 (Japan). BaSO₄ was used as the reflectance standard. The Brunauer–Emmett–Teller (BET) specific surface area (S BET) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P₀) range of 0.05–0.25. Desorption isotherm was utilized to measure the distribution of pore sizes using the Barret–Joyner–Halender (BJH) method [18]. The nitrogen adsorption volume in the relative pressure was utilized to measure the average pore size and the pore volume. The IR spectra were recorded on FTIR spectrometer (8400s, Shimadzu, Japan) using KBr disc method while the sample’s Raman spectra were investigated using Raman spectroscopy (BRUKER, OPTIK, GMBH, Senterra, Germany). The UV-Vis absorption spectrum of the prepared samples and the concentration of MB dye were determined by a UV-Visible spectrophotometer (TS200, PG instruments Ltd., UK). The total organic carbon obtained from the photodegradation of the organic dyes was measured by a Multi parameter Bench Photometer with chemical oxygen demand (COD) and accompanied with COD test tube bench heater model C-99 from HANNA Company 270 George Washington Hwy, Smithfield, RI 02917, USA.

Photocatalytic Activity

The photodegradation experiments of the prepared samples were carried out in a Homemade UV-A photoreactor with a UV-light intensity of 3 mW.cm⁻². Briefly, 100 mL dye solutions were prepared in appropriate concentrations using bi-distilled water. Dye solutions were stirred in the dark for 30 min after the addition of 50 mg of the catalyst to establish an adsorption/desorption equilibrium. Samples of suspension were withdrawn at regular intervals and were immediately centrifuged at 10000 rpm for 5 min to remove the catalyst particles completely. The progress of the photocatalytic decolorization was monitored by measuring the absorbance of the solution samples at the maximum wavelength of MB dye (664 nm). The total mineralization test was examined by measuring the COD of the samples before and after UV-light irradiation.

Result and Discussion

Morphological and Crystallographic Characterization

XRD characterization is an effective and useful technique to determine the crystallite phase and the size of the nanomaterials. The XRD patterns of GO, TiO₂, TiO₂/GO (1:100) and Sm³⁺ and Eu³⁺-doped TiO₂/GO (0.015 mol %) nanocomposites are shown in Fig. 2. XRD pattern of GO (Fig. 2a) shows two distinct peaks at 2θ = 10.6º and 42.5º, which are assigned to (0 0 2) and (1 0 0) crystallographic planes of the carbon hexagonal structure. The interlayer spacing value for GO is 0.83 nm. The distance between consecutive carbon layers is increased indicates the successful oxidation of the starting graphite [19]. XRD pattern of pure TiO₂ nanoparticles (Fig. 2b) is well ascribed to the standard powder diffraction pattern of anatase TiO₂ (JCPDS No. 21–1272) [20]. In the un-doped and doped-TiO₂/GO nanocomposite system (Fig. 2e-c), no other diffraction peaks are assigned for GO or the dopant (Sm³⁺ or Eu³⁺ oxides). This firstly confirms that the C atoms are completely replace some of the oxygen atoms in the TiO₂ crystal lattice in the TiO₂/GO composite indicating that no GO is left on the catalyst’s surface. This confirms that GO is in a high dissolution state in the TiO₂ lattice rather than an isolated species on the surface of TiO₂ [21]. This may be due to the low amounts of GO (1%) and the dopant ion concentrations (0.015%) in the samples. The average crystallite size of the prepared samples are calculated by using Debye-Scherer formula [22]. The average crystallite size of the prepared samples are given in Table 1.

\[
d = \frac{k \lambda}{β \cos θ}
\]

where d is the crystallite size, k is a constant of 0.9, λ is the X-ray wavelength of Cu which is 1.5406 Å, is the Bragg angle in degree and B is the full width at half maximum (FWHM) of the peak. Due to the much lower crystalline extent of graphene than that of TiO₂, it has been observed that the crystallite size of the prepared samples decrease after being doped with lanthanides [23-24]. This may be due to the segregation of the doping ions at the grain boundary. In turn, due to bigger ionic radii of Sm³⁺ (1.086 Å) and Eu³⁺ (1.036 Å) than Ti⁴⁺ (0.68 Å), it is difficult for Sm³⁺ and Eu³⁺ to replace Ti⁴⁺ in the crystalline lattice [6].

The morphology of GO, TiO$_2$, TiO$_2$/GO (1:100) and Sm$^{3+}$ and Eu$^{3+}$-doped TiO$_2$/GO (0.015 mol%) photocatalysts are shown in Fig. 3 and Fig. 4. The SEM image of GO (Fig. 3a) shows a porous sponge-like structure with the graphene sheet not well connected together. This is an indication that the graphite has been exfoliated during the oxidation process. This also may be due to the distorted graphene sheets when oxygen and other functionality groups are attached to the sheets of graphene to form GO [25]. The SEM image of TiO$_2$ (Fig. 3b) shows small spherical distributed TiO$_2$ particles. The SEM images of undoped and doped TiO$_2$/GO composite (Fig. 3c-e) demonstrate that the TiO$_2$ nanoparticles are well dispersed on the GO surface. The TiO$_2$ nanoparticles are attached onto the surface of GO sheets and they are intercalated between the graphene oxide “Sandwich” constructed in an aggregation [26]. These images show the presence of TiO$_2$ agglomerates. Due to the high amount of TiO$_2$ compared with the GO, the latter are less visible [27].

The TEM images of pure GO and TiO$_2$/GO are shown in Fig. 4(a,b), respectively. The regular shapes of TiO$_2$ with good defined boundaries and uniform size distribution show a successful preparation method. The TEM study displays that the size of the TiO$_2$ nanoparticles are in the range of 6–12 nm with an average size of 9 nm. The TEM image of the TiO$_2$/GO (Fig. 4b) shows that there is a complete bounding between TiO$_2$ nanoparticles with wide distribution on very thin and transparent graphene oxide sheet. Figs. 4c and 4d show the TEM images of Sm$^{3+}$ and Eu$^{3+}$-doped TiO$_2$/GO, respectively. The TiO$_2$ nanoparticles are found to be completely embedded into the GO sheets. Therefore, good contact and interaction between lanthanide-doped TiO$_2$ nanoparticles and GO has been achieved during the hydrothermal process, which is believed to be favorable for transferring the photogenerated electrons into a Ln(III) doped-TiO$_2$/GO composites during the photocatalytic process.

The elemental compositions of the prepared samples have been done by EDX analysis (Supplement1). The results confirm the presence of Ti, Sm, Eu, O and C. Also, the spectra indicate that the principal constituents are Ti and O with low concentrations of lanthanide ions and GO, as well as the obtained samples are free from impurities [21].

**Optical Characterization**

The FTIR spectra of GO, TiO$_2$, TiO$_2$/GO (1:100) and Sm$^{3+}$ and Eu$^{3+}$-doped TiO$_2$/GO (0.015 mol%) nanocomposites are shown in Fig. 5. The FTIR spectrum of GO contains the characteristic peaks of GO at 3453 and 1087.9 cm$^{-1}$, due to O-H and C-O stretching vibrations, respectively. The peaks at 1626.1 cm$^{-1}$ and 1722.5 cm$^{-1}$ are due to C=O stretching vibration in the carboxylic acid group. The peak at 1400.4 cm$^{-1}$ is due to C=C stretching vibration from un-oxidized sp$^2$ C-C bonds. The peak at 2348.1 cm$^{-1}$ is due to O=O stretching vibration [18]. FTIR results of the present study are consistent with previous reports [21, 28]. The presence of polar oxygen containing functional groups strongly changes the Vander Waals interactions between GO layers and makes them hydrophilic. Due to the hydrophilic nature, GO can easily be dispersed in water and forms a stable colloidal aqueous suspension [29]. The FTIR spectra of the TiO$_2$, un-doped and Ln$^{3+}$-doped TiO$_2$/GO show a broad band about 3406 cm$^{-1}$ which is assigned to the OH stretching frequency from the surface hydroxyl groups. The band at 1633 cm$^{-1}$ corresponds to Ti-O-C vibration, which may result from the interaction between the surface hydroxyl groups of TiO$_2$ and the functional groups of graphene oxide. The bands observed in the region below 700 cm$^{-1}$ are characteristic to the Ti-O vibration modes of the Ti$^{3+}$-O-Ti$^{4+}$ in TiO$_2$. These results show the chemical coupling of TiO$_2$ and GO [30]. The peak at 1634 cm$^{-1}$ is assigned to the bending vibrations of adsorbed water molecules [31]. The observed peak at 1415 cm$^{-1}$, which is due to C=C stretching vibrations from unoxidized graphene domains, is dominant for the TiO$_2$/GO samples [32]. Furthermore, no residual alkoxy peaks have been observed indicating the absence of impurities in the samples.

The typical Raman spectrum of GO, obtained at an excitation wavelength of 517 nm, is shown in Fig. 6a. The D peak at 1348 cm$^{-1}$, with an intensity comparable to the G peak at 1592 cm$^{-1}$, along with their large band width are indicative of significant structural disorder in GO [17]. Fig. 6 (b-e) shows the Raman spectra of the TiO$_2$, un-doped and Ln$^{3+}$-doped TiO$_2$/GO prepared by using the hydrothermal method. The Raman active peaks at 143 cm$^{-1}$ (E$_g$), 395 cm$^{-1}$ (B$_{1g}$), 515 cm$^{-1}$ (A$_{1g}$), and 638 cm$^{-1}$ (E$_g$) modes are for the as-prepared composites indicate the anatase structure of TiO$_2$. The (E$_g$) modes for all prepared composites were broader and blue-shifted from...
144 cm\(^{-1}\) to 153 cm\(^{-1}\). The peak shift of TiO\(_2\), which appeared in the Raman spectrum is due to the doping with lanthanide [6]. The 1343 cm\(^{-1}\) and 1602 cm\(^{-1}\) modes are referred to the D and G bands of GO, respectively [17].

The light absorption characteristics of the obtained samples are investigated in Fig. 7. Fig. 7(a,b) shows the UV-Vis diffuse reflectance spectra for the TiO\(_2\), TiO\(_2\)/GO and Ln\(^{3+}\)-doped TiO\(_2\)/GO with different lanthanide metal ions (Eu\(^{2+}\) and Sm\(^{3+}\)) concentrations ranging from 0.01 to 0.03 molar ratios. It may be seen very well that the undoped TiO\(_2\)/GO and Ln\(^{3+}\)-doped TiO\(_2\)/GO (with different Sm\(^{3+}\) and Eu\(^{3+}\) molar ratios) nanocomposites experienced increased light absorption in the visible range showing a red shift in the absorbance compared with the bare TiO\(_2\). This can be attributed to the charge transfer between the dopant (f electrons of lanthanides and/or p electrons of carbon) and the TiO\(_2\) conduction or valence band. As a result, the un-doped and Ln\(^{3+}\)-doped TiO\(_2\) can absorb lower photo energy and this leads to higher photocatalytic activity. The band gap energies (E\(_g\)) of the prepared samples are calculated using Tauc’s equation;

\[
\alpha h\nu = B(h\nu - E_g)^{n/2} \tag{2}
\]

where \(\alpha\), \(h\nu\), and \(B\) are the absorption coefficient, the light frequency and proportionality constant, respectively [33]. The value of \(n\) depends on the characteristics of the transition in the semiconductor. The E\(_g\) values are calculated by the extrapolation of the linear parts of the curves (Fig. 7c,d) and listed in Table 2.

**BET Surface Area Analysis**

The textural properties of as-prepared TiO\(_2\), TiO\(_2\)/GO, Sm\(^{3+}\)-doped TiO\(_2\)/GO and Eu\(^{3+}\)-doped TiO\(_2\)/GO nanocomposite samples have been investigated using Brunauer–Emmett–Teller (BET) analysis. The BET surface area \(S_{\text{BET}}\), total pore volume \(V_t\) and the mean pore volume of the samples are calculated and presented in Table 1. From the data in Table 1, it has been observed that doping with Sm\(^{3+}\) and Eu\(^{3+}\) leads to an increase of the total surface area of the TiO\(_2\)/GO composite. This will be favorable for photocatalytic applications, as the higher specific surface area of the photocatalysts doped with Ln(III) lead to increase the adsorption of more dye particles on its surface. This demonstrates that Ln(III) doped TiO\(_2\) supported on GO composites are excellent candidate for adsorption and photocatalysis.

**Photocatalytic Activity**

The photocatalytic activities of the as-synthesized undoped and Ln(III)-doped TiO\(_2\)/GO (with different Ln(III) molar ratios) nanocomposite compared with that of the pure TiO\(_2\) as a photocatalyst are tested on the degradation of MB as a model for an organic pollutant. Fig. 8(a-d) shows the visible absorption spectra of degraded MB over TiO\(_2\), TiO\(_2\)/GO, 0.015 mol% Sm\(^{3+}\)- TiO\(_2\)/GO and 0.015 mol% Eu\(^{3+}\)- TiO\(_2\)/GO photocatalysts, respectively after exposure to UV-light illumination. It can be observed that the absorption peak intensity of MB at 664 nm decreases with the exposure time increasing, thus showing the decolorization of MB by the photocatalysts under investigation.

The decolorization rate kinetics of MB dye is found to obey first order rate kinetics confirmed by the linear fit eq. (3)

\[
\ln A_t = \ln A_o - kt \tag{3}
\]

where \(k\) is the rate constant (min\(^{-1}\)), \(t\) is the irradiation time, \(A_o\) and \(A_t\) are the initial and final absorption values of the dye solution, respectively. A plot of \(\ln (A_t/A_o)\) versus \(t\) yields a straight line. The photocatalytic initial decolorization rate kinetics of MB with the different photocatalysts under investigation are shown in Fig. 9(a,b) and summarized in Table 2. The results demonstrated that all Ln(III)-TiO\(_2\)/GO catalysts achieved higher rates of MB degradation than the pure TiO\(_2\) and TiO\(_2\)/GO catalysts. Moreover, it can be clearly seen that increasing the lanthanide dopant ion concentration leads to an increase of the photodegradation rate of MB till an optimum concentration (0.015 mol%). However, further increase in the lanthanide metal ion concentration, as a dopant metal ion, leads to retardation in the photo degradability of the dye solution (Fig. 9(c,d)).

This can be explained that below an optimum dopant metal ion concentration, the dopant acts as a charge carrier separator which increases the charge separation and enhances the photocatalytic performance of the nanocomposite. However, at higher metal concentration, the dopant can act as a charge recombination center which prevents the separation of the photogenerated charge carriers and furthermore represses the generation.
TABLE 1: XRD and S_{BET} analysis of pure TiO_2, TiO_2/GO, 0.015% Sm-TiO_2/GO and 0.015% Eu-TiO_2/GO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal Size (nm)</th>
<th>S_{BET} (m^2 g^{-1})</th>
<th>V_{t} x 10^{-1} cc g^{-1}</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO_2</td>
<td>6.6</td>
<td>172</td>
<td>0.3596</td>
<td>8.3631</td>
</tr>
<tr>
<td>TiO_2/GO</td>
<td>5.4</td>
<td>212</td>
<td>0.2862</td>
<td>5.3972</td>
</tr>
<tr>
<td>0.015% Sm- TiO_2/GO</td>
<td>4.9</td>
<td>213</td>
<td>0.5543</td>
<td>10.405</td>
</tr>
<tr>
<td>0.015% Eu- TiO_2/GO</td>
<td>5.4</td>
<td>249</td>
<td>1.0499</td>
<td>16.815</td>
</tr>
</tbody>
</table>

TABLE 2: Absorption edge, band gap values and initial rate constants of MB dye (k) with TiO_2, TiO_2/GO and different x mol% of Ln(III)-doped TiO_2/GO catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical characterization</th>
<th>Photocatalytic Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption edge (nm)</td>
<td>Band gap (eV)</td>
</tr>
<tr>
<td>TiO_2</td>
<td>383.9</td>
<td>3.23</td>
</tr>
<tr>
<td>TiO_2/GO</td>
<td>413.3</td>
<td>3.00</td>
</tr>
<tr>
<td>0.01% Sm- TiO_2/GO</td>
<td>387.5</td>
<td>3.21</td>
</tr>
<tr>
<td>0.015% Sm- TiO_2/GO</td>
<td>376.8</td>
<td>3.29</td>
</tr>
<tr>
<td>0.025% Sm- TiO_2/GO</td>
<td>374.6</td>
<td>3.31</td>
</tr>
<tr>
<td>0.03% Sm- TiO_2/GO</td>
<td>372.4</td>
<td>3.33</td>
</tr>
<tr>
<td>0.01% Eu- TiO_2/GO</td>
<td>380.4</td>
<td>3.26</td>
</tr>
<tr>
<td>0.015% Eu- TiO_2/GO</td>
<td>372.4</td>
<td>3.33</td>
</tr>
<tr>
<td>0.025% Eu- TiO_2/GO</td>
<td>381.5</td>
<td>3.25</td>
</tr>
<tr>
<td>0.03% Eu- TiO_2/GO</td>
<td>370.1</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Fig. 1: The Chemical structure of MB dye
Fig. 2: XRD patterns of a) GO, b) TiO$_2$, c) TiO$_2$/GO, d) 0.015% Sm-TiO$_2$/GO and e) 0.015% Eu-TiO$_2$/GO
Fig. 3: SEM images of a) GO, b) TiO$_2$, c) TiO$_2$/GO, d) 0.015% Sm-TiO$_2$/GO and e) 0.015% Eu-TiO$_2$/GO
Fig. 4: TEM images of a) GO, b) TiO$_2$/GO, c) 0.015% Sm-TiO$_2$/GO and d) 0.015% Eu-TiO$_2$/GO
Fig. 5: FTIR spectra of GO, TiO$_2$, TiO$_2$/GO, 0.015% Sm-TiO$_2$/GO and 0.015% Eu-TiO$_2$/GO

Fig. 6: Raman spectra of a) GO b) TiO$_2$, c) TiO$_2$/GO, d) 0.015% Sm-TiO$_2$/GO and e) 0.015% Eu-TiO$_2$/GO
Fig. 7(a, b) UV-Vis diffuse reflectance spectra of TiO$_2$, TiO$_2$/GO and different x mol % Ln(III) doped TiO$_2$/GO catalysts; (c, d) Tauc plot of TiO$_2$, TiO$_2$/GO and different x mol % Ln(III) doped TiO$_2$/GO catalysts.
FACILE HYDROTHERMAL SYNTHESIS OF SM AND EU ...
Fig. 8 Decay of the UV-Vis absorption spectrum of (1.5X10^-5 M) MB aqueous solution during UV irradiation in the presence of 50 mg (a) TiO₂, b) TiO₂/GO, c) 0.015 mol% Sm-TiO₂/GO and d) 0.015 mol% Eu-TiO₂/GO catalysts.
FACILE HYDROTHERMAL SYNTHESIS OF SM AND EU...

\[ \ln \left( \frac{A}{A_0} \right) \]

**Graph a:**
- TiO\(_2\)
- TiO\(_2\)/GO
- 0.01% Sm-TiO\(_2\)/GO
- 0.015% Sm-TiO\(_2\)/GO
- 0.025% Sm-TiO\(_2\)/GO
- 0.03% Sm-TiO\(_2\)/GO

**Graph b:**
- TiO\(_2\)
- TiO\(_2\)/GO
- 0.01% Eu-TiO\(_2\)/GO
- 0.015% Eu-TiO\(_2\)/GO
- 0.025% Eu-TiO\(_2\)/GO
- 0.03% Eu-TiO\(_2\)/GO

Time (min)
Fig. 9(a,b) 1st order rate kinetics of the photocatalytic degradation of \(1.5 \times 10^{-5} \) M aqueous solution of MB in the presence of 50 mg TiO\(_2\), TiO\(_2\)/GO, x mol% Sm- TiO\(_2\)/GO and x mol% Eu- TiO\(_2\)/GO catalysts; Fig. 9(c, d) Influence of the different molar ratios of the Sm\(^{3+}\) and Eu\(^{3+}\) dopant ion conc. on the decolorization rate of MB.
Fig. 10 COD% decay of MB dye solution under UV-illumination in the presence of 0.015% Eu\textsuperscript{3+}-TiO\textsubscript{2}/GO photocatalyst

Fig. 11 Proposed mechanism of photocatalytic degradation of MB over Ln(III)-TiO\textsubscript{2}/GO photocatalyst under UV irradiation
Supplement 1: EDX analysis of a) pure TiO$_2$, b) TiO$_2$/GO, 0.015% Sm-TiO$_2$/GO and d) 0.015% Eu-TiO$_2$/GO nanocomposite materials
of oxygen radicals prompting a decrease of the photocatalytic process [34]. Therefore, controlling the dose of metal dopants in the nanocomposites is an important factor for the enhancement of photocatalysis [35].

**Mineralization Study**

The photocatalytic activity of the highest active 0.015% \( \text{Eu}^{3+} \)-\( \text{TiO}_2 \)/GO photocatalyst has been quantitatively assessed by measuring the COD% decay during the photodegradation experiments (Fig. 10). Fig. 10 indicates that 99.9% of COD was removed after only 90 min of UV-illumination. This (COD% removal) analysis confirms the potentiality of this photocatalytic nanomaterial to efficiently mineralize the MB organic dye pollutant.

**Proposed Photocatalytic Mechanism:**

The explanation of the enhancement of the photocatalytic activity of the prepared catalysts due to lanthanides doping and graphene oxide incorporation can be explained according to Equations (4-10) [18, 35]. Firstly, up on UV-light illumination, the excited \( \text{TiO}_2 \) particles generate electron-hole pairs (eq. 4). Then the photogenerated electrons excited from the valence band (VB) to the conduction band (CB) of \( \text{TiO}_2 \). Ln\(^{3+}\) dopant in \( \text{TiO}_2 \) act as electron scavenger and reduce their recombination with \( h^+ \) and produce Ln\(^{2+}\) (eq. 5) [36,37]. The produced Ln\(^{2+}\) ions are very unstable, so that \( e^- \) can be easily descavenged either by passing to the adsorb \( \text{O}_2 \) molecules (eq. 6), promoting \( O_2^- \) and \( \cdot\text{OH} \) formation or by transferring to GO as well to produce superoxide anion (eq. 7). The reactive superoxide radical ion (\( O_2^- \)) can easily react with adsorbed water molecules to produce the very reactive oxidizing species (\( \cdot\text{OH} \)) (eq. 8). On the other hand, the positive holes (\( h^+ \)) in the \( \text{TiO}_2 \) valance band can also promote the MB degradation by either direct oxidation of MB or by generating (\( \cdot\text{OH} \)) radicals (eq. 9). The powerful oxidizing species (\( \cdot\text{OH} \)) can easily lead to degradation of MB dye (eq. 10).

Moreover, the possible mechanism involved in the photocatalytic degradation of Ln(III) doped \( \text{TiO}_2 \)/GO photocatalyst can be represented in Fig. 11.

**Conclusion**

Different molar ratios of Eu\(^{3+}\) and Sm\(^{3+}\)-doped \( \text{TiO}_2 \), loaded on GO nanocomposite photocatalysts were successfully prepared by a facile and low-cost hydrothermal method. The photocatalytic activity of the prepared Ln(III) nanocomposite photocatalysts was tested for the decolorization and degradation rate of methylene blue (MB) as a model of organic dye pollutants. The results clearly showed the beneficial role of both the GO and the lanthanide metal ions as a dopant on the degradability of MB. The high specific surface area of GO and its oxygen containing functional groups resulted in increase the absorptivity and hence the degradability of MB. The GO content acted as a photosensitizer and an electron scavenger to decrease the photogenerated electron–hole pair’s recombination and in this way expand its absorbance in the visible region leading to a great photocatalytic activity. Doping the as-synthesized nanocomposite with an appropriate amount of Ln(III) metal ions such as Sm\(^{3+}\) and Eu\(^{3+}\) led to further enhancement in the photocatalytic activity of the \( \text{TiO}_2 \)/GO and \( \text{TiO}_2 \) relatively and expanded the quantity of electron–hole pairs to take part in the photocatalytic reaction. The 0.015% Eu\(^{3+}\)-doped \( \text{TiO}_2 \)/GO photocatalyst showed the highest photocatalytic activity. The high photocatalytic performance combined with its higher absorbance in the visible region confirmed the synergistic impacts of the Ln(III) dopants.

**Conflict of interest**

The authors declare that they have no conflict of interest regarding the publication of this paper.

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الأكسيد التيتانيوم المطعم بأيونات السماريوم والايروبيم وحمل على أكسيد الجرافين حراري سهل تحضيره و tiêuخدامه كحفازات ضوئية فعالة.

تم تحضير الأكسيد التيتانيوم المطعم بأيونات السماريوم والايروبيم وحمل على أكسيد الجرافين بطريقة حرارية بسيطة. تم تحليل الخصائص التركيبية والمورفولوجية والضوئية للتركيبات النانوية بواسطة جهاز حيود الأشعة السينية (XRD) وتحليل مساحة (TEM) وتحليل طيفي للأشعة تحت الحمراء (FTIR) وتحليل منافذ الرياح (RS) وتحليل فورية الطيفي (SBET). وتم التحقق من الكفاءة الحفازية الضوئية للعينات المحضره بقدرها على إزالة لون صبغة الميثيلين الأزرق عن طريق الأشعة فوق البنفسجية. وتظهر نتائج التحفيز الضوئي أن متراكم (MB) ذو نشاط تحفيزي ضوئي عالى من حيث الكفاءة في إزالة اللون، وتكوين الصبغة المستقرة. مما يوضح أن هذه المادة النانوية المركبة المطعمة بأيونات اللانثينيدات تعتبر محفز ضوئي واعد واعد لتقوم مولثات الأصباغ العضوية في المحاليل المائية. وقد أظهر تحليل الطلب على الأكسجين الكيميائي (COD) درجة عالية من التمعدن الكامل لصبغة الميثيلين الأزرق بعد 90 دقيقة فقط تحت ضوء الإشعة فوق البنفسجية.