

Lanthanum doped-TiO₂ decorated on graphene oxide nanocomposite: A photocatalyst for enhanced degradation of acid blue 40 under simulated solar light

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Abstract

La-TiO₂-GO nanocomposites were successfully synthesised *via* sol-gel method. Structures, morphologies and photocatalytic activities of the as-synthesized nanocomposites were determined using X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy (RS) and scanning electron microscopy (SEM). UV-Vis diffuse reflectance spectroscopy was used to estimate band gap energies. The photocatalytic activities of the as-synthesized nanocomposites were evaluated for the degradation of Acid Blue 40 in aqueous solutions under simulated solar light. The photocatalytic results show that the as-synthesized La-doped TiO₂-GO (0.3% La) nanocomposite shows good photocatalytic activity and can be considered as a promising photocatalyst for the degradation of organic pollutants in water. The good photocatalytic efficiency is ascribed to the cooperative effect of improved visible light absorbance and separation of charge carriers due to the combined effect of La and the GO in the composite. Analysis from Total organic carbon (TOC) shows a high degree of complete mineralisation of Acid Blue 40 (TOC removal of 75%) which decreases the formation of possible degradation by-products. Due to the stability of La-TiO₂-GO (0.3% La) nanocomposite, it was reused for five times reaching 84.0% maximum degradation efficiency during the five cycles. Copyright © 2017 VBRI Press.

Keywords: Lanthanide, nanocomposite, graphene oxide, photocatalyst, acid blue 40, dye removal.

Introduction

Water is one of the essential commodities on earth and also a precious resource for human civilisation. Industries contribute about 22% of the total water usage in the world and about 70% of industrial untreated wastes find its way into streams and rivers without prior processing [1]. Researchers all over the world are looking for a novel method to treat water contaminated with organic pollutants, because about 780 million people still lack access to clean drinking water [2]. One technique, which in recent years has been gaining popularity and is promising for the treatment of organic pollutants in water, is photocatalysis. In the last decade, a lot of studies have been reported on the photocatalytic degradation of organic pollutants in water using semiconductor materials as photocatalysts [3-5]. However, the problem with semiconductors is the large band gap and the rapid recombination of photogenerated electron-hole pairs which significantly decreases their photocatalytic performance. This means that semiconductors can only absorb UV light ($\lambda < 387$ nm). UV light has carcinogenic effects and accounts for less than 5% of the solar energy

that reaches the surface of the earth. It, therefore, restricts the effective use of sunlight to propel the reaction when pure semiconductors are used as photocatalysts. The visible light ($\lambda > 400$ nm) accounts for about 50% of solar energy [6]. Therefore, enhancing visible light absorption for the efficient photocatalytic performance of the catalysts becomes important.

Semiconductors such as TiO₂, ZnO and ZnS, have proven to be efficient photocatalysts because of their unique properties such as excellent chemical and electronic structure, solar energy conversion and high photocatalytic activity [7]. Titanium dioxide (TiO₂) offers several advantages including; high chemical and thermal stability, strong oxidising power, high photocatalytic activity, relatively cost-effective and non-toxic material, and finally is one of the most predominant semiconductors which is widely used for degradation of organic pollutants in water [8-12]. However, its wide band gap (anatase 3.2 eV, rutile 3.0 eV) restricts its photocatalytic reaction in the visible region [13, 14].

Recent research has shown that the decorating TiO₂ on graphene oxide (GO) nanosheet allows the composite to exhibit a range of unique properties,

including acting as a photosensitizer [15, 16]. The GO can also act as an electron transfer channel to reduce the recombination of photogenerated charge carriers of TiO₂ and enhance its light absorption into the visible region, leading to improved photodegradation efficiency [17]. Besides, GO with its high mobility charge carrier enhances the charge transportation and separation of the electron-hole pairs leading to an increase in absorptivity of organic pollutants in water. Furthermore, studies have shown that decorating semiconductor materials on graphene oxide sheets could substantially increase the photocatalytic property of the composite over TiO₂ materials [18]. In addition, the GO have been identified to capture the electrons and enhanced the photocatalytic activity of TiO₂-GO composite during the photocatalytic process for the photodegradation of organic pollutants in water [19]. In previous studies, various attempts have been made to extend the photoresponse of TiO₂ towards the visible light and increase its photocatalytic efficiency under visible light irradiation [17]. Among the common methods which have been used to improve the photocatalytic performance of TiO₂ is dye sensitization, coupling with narrow band gap semiconductors, non-metal doping and metal doping including noble metals [20], rare earth metals [21], and transition metals [22]. Many studies have shown that lanthanide ionic doped TiO₂ such as Sm³⁺, La³⁺, Nd³⁺, Dy³⁺ and Ce³⁺ [23, 24] have also demonstrated to be more effective in promoting its photocatalytic activities than pure TiO₂ and therefore improve the performance under visible light irradiation by shifting spectra to a lower energy region, because the excellent electron scavenging characteristics of lanthanide ions enhance pollutant concentration on the photocatalyst surfaces [25-28]. For example, Oppong *et al.* [29] synthesised Nd-doped TiO₂-GO composite which was deployed in the degradation of indigo carmine dye. They observed a higher visible light and photocatalytic activity of the Nd-TiO₂-GO composite compared to the bare TiO₂ as a result of the synergic effects of both the Nd and GO. In this context, doping of TiO₂ with lanthanum and decorated on graphene oxide nanosheets could be a promising strategy to enhance the activity of the photocatalyst.

Here, we present the preparation and characterization of La-TiO₂-GO nanocomposite with its application focusing on the degradation of Acid blue 40 in water under the simulated solar light and evaluate its complete degree of mineralisation of the dye as well as the photocatalyst stability.

Experimental

Materials and reagents

All chemicals and reagents were of analytical purity and used without further purification. Titanium (IV) isopropoxide (Ti (OC₃H₇)₄ (97%)), Acid Blue 40, lanthanum (III) nitrate hexahydrate (La(NO₃)₃·6H₂O), 2-propanol (C₃H₈O) (98%) and ethylene glycol (OHCH₂CH₂OH) were purchased from Sigma-Aldrich, Germany. Deionized (DI) water was used throughout the work.

Synthesis of graphene oxide (GO)

GO was synthesised by oxidation of graphite powder using modified hummers methods [30]. A volume of 90 mL concentrated H₂SO₄ was added to a mixture of graphite flakes (2 g) and NaNO₃ (2 g) and kept in an ice bath (0-5°C) with continuous stirring for 4 h. Then KMnO₄ (12 g) was added to the suspension very slowly and the reaction temperature kept lower than 15 °C, followed by addition of 184 mL of DI water and kept under stirring for 2 h at 35 °C. After, the mixture was kept in a reflux system at 98 °C for 10-15 min and then the temperature was changed to 30 °C. The solution was finally treated with 40 mL H₂O₂ followed by slow addition of 200 mL of DI water and stirred for another 1 h. The solution was left to stand for 3-4 h and the mixture washed repeatedly by centrifugation (7500 rpm for 20 min at 4 °C) with 10 % HCl and DI water until a gel-like substance was obtained. The gel-like substance was vacuum dried at 60 °C for 12 h to obtain the GO powder.

Preparation of La-TiO₂-GO

La-TiO₂-GO nanocomposite was prepared by adding 10 mL of Ti(OC₃H₇)₄ slowly to 50 mL of 2-propanol, and the mixture stirred for 30 min. Various masses of La(NO₃)₃·6H₂O and 0.5% graphene oxide was added to the mixture and further stirred for 1 h. Then 2 mL of ethylene glycol and 10 mL of DI water were added slowly with vigorous stirring for 2 h. The resulting mixture was separated by centrifugation after washing several times with DI water and ethanol, dried (at 50 °C overnight) and collected for further characterization. TiO₂ and TiO₂-GO were synthesised in a similar manner without the addition of either La (NO₃)₃·6H₂O or both GO and La (NO₃)₃·6H₂O.

Evaluation of photocatalytic activity

The as-synthesized samples were tested for their photocatalytic activities by measuring its photo-degradation with Acid Blue 40 in aqueous solution under simulated solar light at room temperature. A mass of 100 mg of the photocatalyst was suspended in 100 mL of 20 mg/L Acid Blue 40 solution, in a quartz beaker (150 mL), which was magnetically stirred for 1 h in the dark to achieve a saturated adsorption equilibrium between the photocatalyst and dye molecules. The solar simulator light was later switched on to initiate the test. A suspension (5mL) of the Acid blue 40 was withdrawn using a disposable syringe and filtered through a 0.45 µm PVDF membrane filter at 30 min interval for 4 h. A Shimadzu UV-2450 spectrophotometer at λ = 620 nm was used to determine the concentration of the Acid Blue 40 suspension remaining after illumination in the supernatant solution. Decolourization efficiency was evaluated using the following equation:

$$\text{Decolourization efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where, C₀ is the initial concentration of the Acid blue 40 and C_t is the concentration of the Acid Blue 40 after visible light irradiation.

Characterization

X-ray diffraction (XRD) patterns were examined on the X-ray diffractometer (Philips, PANalytical X-pert PRO, X-ray diffraction system) at 40 kV and 30 mA with Cu K α radiation ($\lambda = 0.15406$) with K-beta filter. Measurements were conducted with a scintillation the counter in the range of 10-80° at a speed of 2.0 deg/min. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin Elmer FTIR spectrometer (Spectrum 100), while Raman spectra of the samples were measured on PerkinElmer Raman microscope (Raman Micro 200). Optical properties were investigated using UV-Vis diffuse reflectance spectroscopy on a Shimadzu UV-2540 (Japan). BaSO₄ was used as the reflectance standard. Scanning electron microscopy (SEM) images were taken with a TESCAN (Vega 3 XMU) and transmission electron spectroscopy (TEM) was performed with a JEOL field emission microscope (JEM -2100F). Energy dispersed X-ray spectroscopy (EDX) attached to SEM was used to determine the surface elemental composition.

Results and discussion

FT-IR analysis

The IR spectra provided information on the surface chemistry of the as-synthesized material. **Fig. 1A** shows the FTIR spectra of TiO₂, TiO₂-GO, and La-doped TiO₂ with different La concentrations. The observed characteristic features of all the spectra are the broad absorption bands below 1000 cm⁻¹ which can be assigned to Ti-O-Ti crystal [31] and Ti-O-C vibration [32]. The presence of Ti-O-C vibration confirms a strong bond between TiO₂ with GO. The disappearance of the peaks with increasing La concentration is due to the preferential formation of La₂O₃. The shift to the lower wavenumbers (from ~ 700 to ~680 cm⁻¹) may be due to La and GO co-doping. The absorption in the regions between 1620-1635 cm⁻¹ and 3000-3600 cm⁻¹ are due to bending vibrations of adsorbed water molecules and stretching vibrations [33] from the hydroxyl groups respectively. Observed peaks at 1000-1300 cm⁻¹ (C-O stretching vibrations), 1680-1450 cm⁻¹ (C=C stretching vibrations from unoxidized graphene domains) and 1706-1720 cm⁻¹ (C=O stretching vibrations) are dominant for the TiO₂-GO samples [34]. No peak originated at 1389 cm⁻¹ which would have described the bending vibrations of the C-H bond for the pure TiO₂ was observed [35]. Furthermore, no residual alkoxy peaks were observed indicating the absence of impurities in the samples.

X-ray diffraction study

XRD characterization is an effective technique to determine crystal phase and size of materials. The XRD patterns for TiO₂, TiO₂-GO and La-doped TiO₂-GO (with different concentrations of La) nanocomposites are shown in **Fig. 1B**. All the samples show anatase phase, thus the diffraction patterns were compared with the anatase TiO₂ database (JCPDS No. 21-1272) [36]. Their relative intensities and peak positions are comparable with the standard powder diffraction pattern of anatase TiO₂. XRD

patterns exhibited strong diffraction peaks at 25° and 48° [37], indicating TiO₂ in the anatase phase. The sharp, intense anatase peaks show an improvement in the degree of crystallinity with fewer lattice defects. The XRD patterns show that there was no second-phase peak and that the doping was successful. Also, in the TiO₂-GO system, the C atoms completely replaced some of the oxygen atoms in the TiO₂ crystal lattice. The absence of any residual peak(s) explains the fact that no GO residue was left on the surface of the catalysts. From the XRD results, it can be concluded that GO is in a high dissolution state in the TiO₂ lattice rather than an isolated species on the surface of TiO₂. The presence of La and GO were, however, confirmed by elemental analysis using EDX. However, no major peaks were observed for GO in the TiO₂-GO nanocomposites, and this may be due to the low amount of GO (0.5%) in the samples [38]. The average crystalline size was estimated from the Scherrer's equation [39].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where, D is the crystal size of the catalyst, λ the X-ray wavelength (1.54056 Å), β the full width at maximum (FWHM) of the diffraction peak (radian), K is a constant (0.9) and θ is the diffraction angle at the maximum. The crystallite sizes were calculated from the prominent peak (101) and found to range from 8-15 nm with an average of 12 nm.

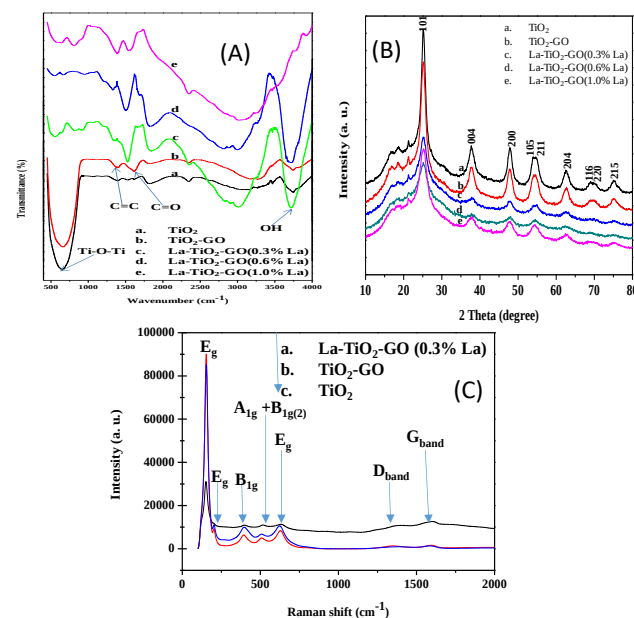


Fig. 1. (A) FT-IR spectra (B) XRD pattern and (C) Raman spectrum, of TiO₂, TiO₂-GO and La-TiO₂-GO with different concentrations of La.

Raman spectroscopy analysis

Fig. 1C shows Raman spectrum of the TiO₂, TiO₂-GO and La-TiO₂-GO (0.3% La) nanocomposite at 143, 234, 398, 518, and 614 cm⁻¹ for pure TiO₂ arising from E_g(1), E_g(2), B_{1g}(1), A_{1g} + B_{1g}(2), and E_g(3) modes indicating that the presence of anatase phase is predominant [40] in the composite and also agree with the XRD results. There is

also an additional two peaks of the nanocomposite observed at 1345 and 1581 cm^{-1} corresponding to D and G band of GO. The D-band is assigned to the breathing mode of K-point phonon of A_{1g} symmetry while the G-band corresponds to E_{2g} phonon of sp^2 bonds of carbon atoms. There is a shift in the anatase peaks suggesting a close interaction between the TiO_2 and the GO similar to a literature report of TiO_2 -RGO [41, 42].

TEM and SEM studies

TEM and SEM studies were conducted to examine the uniformity, morphology and microstructure of the pristine TiO_2 , combined TiO_2 -GO and nanocomposite La-doped TiO_2 -GO photocatalysts. **Fig. 2(a)** and **2(b)** show a typical TEM and SEM image of TiO_2 and GO respectively. The prepared TiO_2 samples show regular morphology with well define boundaries. The uniform morphology, with uniform size, is due to improvement in the sol-gel process which resulted in the mobilisation of Ti and O homogeneity in the TiO_2 crystalline structure. The SEM image of 0.3% La- TiO_2 -GO nanocomposite (**Fig. 4(c)**) shows that the TiO_2 nanoparticles are evenly decorated on the GO surface.

The elemental composition of the samples was estimated by the EDX analysis, **Fig. 2(d)** The EDX spectrum for the 0.3% La- TiO_2 -GO nanocomposite confirms the presence of Ti, La, O and C., In addition, the spectrum also indicates the principal constituents as Ti and O with low concentrations of La and GO.

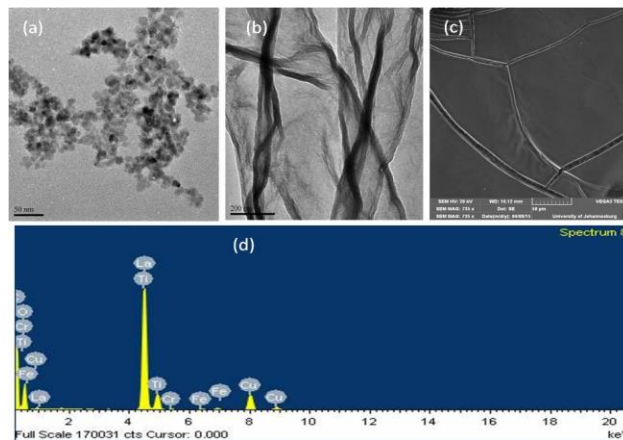


Fig. 2. (a) TEM image of TiO_2 , (b) TEM image of GO, (c) SEM image and (d) EDX spectrum of 0.3% La- TiO_2 -GO.

Optical studies

The light absorption characteristics of TiO_2 usually changes after doping with GO [43] and lanthanides [21, 44]. **Fig. 3 (A and B)** show a comparison of the UV-Vis absorption edge and UV-Vis diffuse reflectance for the as-prepared samples. The absorption spectrum of TiO_2 consists of a single broad intense absorption around 400 nm due to the charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the corresponding conduction band (mainly formed by 3d t_{2g} orbitals) of Ti^{4+} cation [45]. The onset of the absorption edge for pure TiO_2 is at ca. 385 nm which is consistent

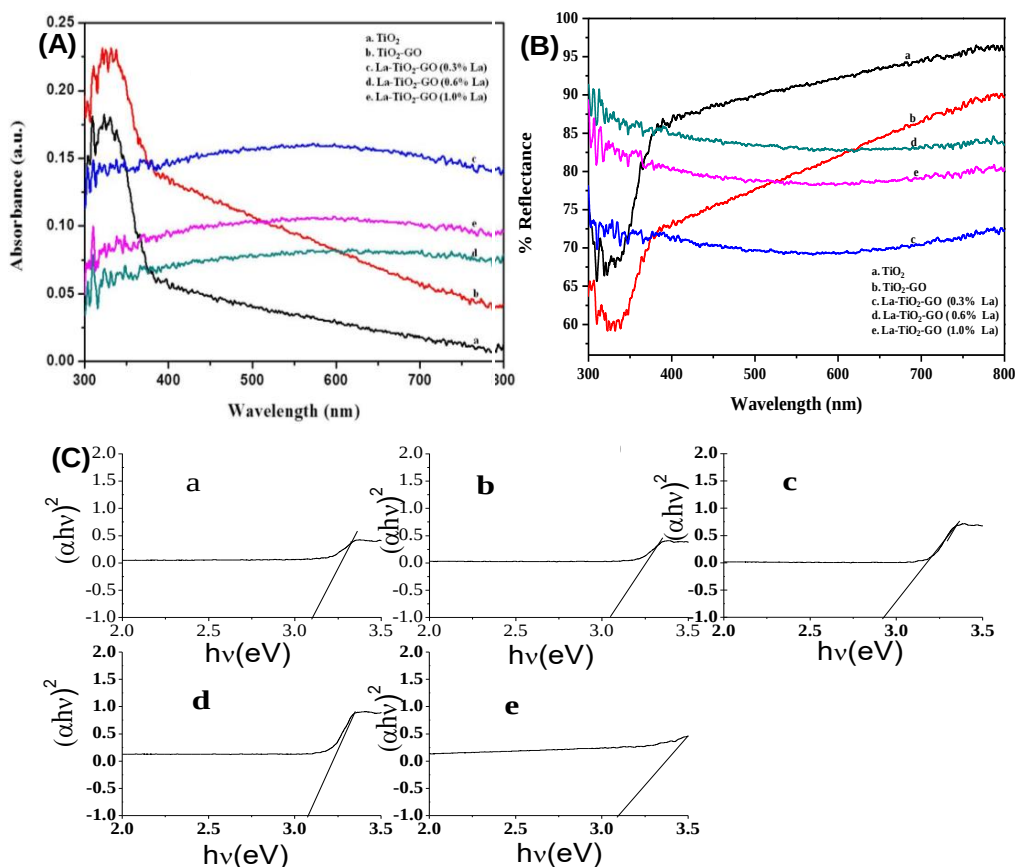


Fig. 3. (A) UV-visible spectra (B) UV-Visible diffuse reflectance spectra and (C) Tauc plots of (a) TiO_2 (b) TiO_2 -GO and (c-e) La- TiO_2 -GO with different concentrations of La.

with intrinsic band gap absorption of pure TiO_2 . However, in comparison with TiO_2 , the TiO_2 -GO composite showed an enhanced absorbance in the range of 380-800 nm. The overall visible-light absorbance increased with La doping. The visible red-shift in absorbance is partly due to the synergistic effect of La and GO co-doping. Undoubtedly, these results reveal that La and GO are indeed incorporated into the anatase TiO_2 crystal lattice, resulting in an altered crystal structure and modified electronic characteristics of the doped samples. Most importantly, to obtain a synergistic effect between TiO_2 -GO and La- TiO_2 -GO, it is vital to control [46] the addition ratios of La, so that optimum photocatalytic activity may be achieved. It was obvious that the 0.3% La- TiO_2 -GO catalyst exhibited the best visible light absorption with improved band gap.

Tauc plots [47] were used to calculate the band gaps of the as-synthesised nanocomposites (from eq. 3).

$$(\alpha h\nu)^{1/r} = h\nu \quad (3)$$

where, α is the absorption coefficient and r denote the nature of the transition [48]. For direct allowed band gap semiconductor, the plot $r = 1/2$, direct forbidden transition $r = 3/2$, indirect allowed transition $r = 2$, and indirect forbidden transition $r = 3$. Extrapolation of this line to the photon energy axis ($h\nu$) gives the indirect bandgap energy of the semiconductor which is a good signal of its visible light efficiency and shows a gradual reduction with lanthanum doping (Fig. 3C). Further increase of lanthanum doping (1.0% Nd) increases the semiconductor band gap which may arise from the domination of d-f transitions over sp-d transitions leading to a decrease in the degradation of pollutants [49].

Photocatalytic activity

The as-synthesised La-doped TiO_2 -GO (0.3% La) nanocomposite was used as a photocatalyst for the degradation of Acid Blue 40 as a model for an organic pollutant. Fig. 4(a) shows the visible absorption spectra of degraded Acid Blue 40 over La- TiO_2 -GO (0.3% La) nanocomposite after exposure to simulated solar light illumination from 0-210 min over the wavelength range of 400-800 nm. It can be observed that the intensity of the absorption peak of the Acid Blue 40 at 620 nm decreases with an increase in exposure time, thus showing the degradation of the Acid Blue 40 by the nanocomposite. The percentage degradation of the nanocomposite in Table 1 shows that under the same irradiation time La- TiO_2 -GO (0.3% La) nanocomposite degraded 92% of the dye while the bare TiO_2 degraded 15% of the dye. This clearly demonstrates that the nanocomposite exhibited higher photocatalytic performance over the latter under visible light illumination as displayed in the UV-Visible spectra. The high photocatalytic performance of the La- TiO_2 -GO (0.3% La) nanocomposite arises from the delayed recombination rate of photogenerated electron-hole pairs by enhancing its charge separation and transportation as well as its visible light absorption due to the reduction of the band gap [50]. It is observed that an increase in the photodegradation efficiency (92%) occurs with La concentration amounting to 0.3%, but when La

doping exceeds the optimum level (i.e. 1.0%), a decrease in photodegradation efficiency is observed (50%).

Table 1. Indirect band gap and percentage degradation after exposure to simulated solar light.

Sample	Indirect band gap (eV)	Degradation (%)	K_a (min^{-1})	R^2
TiO_2	3.11	15	9.2×10^{-4}	0.9974
TiO_2 -GO	3.07	41	3.0×10^{-3}	0.9827
La- TiO_2 -GO (0.3%La)	2.91	92	1.4×10^{-2}	0.9921
La- TiO_2 -GO (0.6%La)	3.09	78	9.7×10^{-3}	0.9805
La- TiO_2 -GO (1.0%La)	3.10	50	4.1×10^{-3}	0.9932

Therefore, controlling the dose of metal dopants in the nano-composites is an important factor for the enhancement of photocatalysis [48]. Below an optimum dosage level, dopants can act as charge carrier separation centre, increase separation of the charges and enhance the photocatalytic performance of the nanocomposite. The higher metal concentration or loading acts as a charge recombination centre which prevent the separation of the photogenerated charge carriers and also inhibits the production of oxygen radicals, leading to a reduction of the photocatalytic process [51].

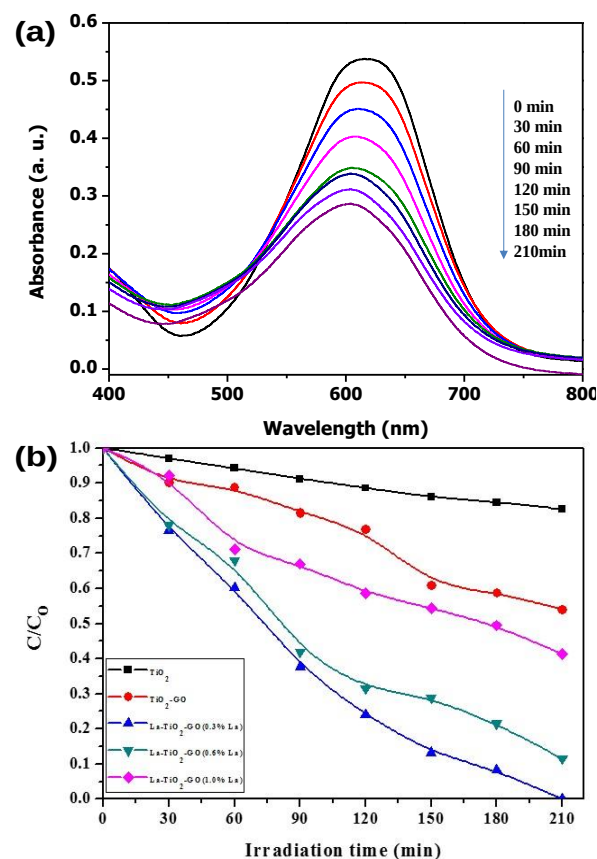


Fig. 4. (a) Acid Blue 40 photodegradation profile using 0.3% La-doped- TiO_2 -GO and (b) Acid Blue 40 degradation profile of TiO_2 , TiO_2 -GO and La- TiO_2 -GO (with a change in concentrations of La).

Fig. 4(b) shows the degradation efficiency of the Acid blue 40, for the as-synthesised materials, by plotting

C/C_0 vs t . The TiO_2 -GO and La-doped- TiO_2 -GO nanocomposites (with different La concentrations) show high degradation efficiency compared to the bare TiO_2 nanoparticle. It is observed that the La-doped- TiO_2 -GO (0.3% La) recorded a higher degradation efficiency which is eighteen (18) times higher than the bare TiO_2 nanoparticle.

Fig. 5(a) shows the plots of $\ln(C_0/C)$ vs t for the photodegradation of Acid Blue 40 by the as-synthesised materials. The results obtained shows that the reaction followed pseudo-first-order kinetics (eq. 4).

$$\ln C_0/C = kt \quad (4)$$

where, C_0/C is the normalised dye concentration, t is time taken for the reaction and k is the reaction rate constant. The k -value for the most effective photocatalyst (La- TiO_2 -GO (0.3% La)) is 1.40×10^{-2} and is sixteen (16) times faster compared to the bare TiO_2 nanoparticle. The good photocatalytic activity of (La- TiO_2 -GO (0.3%)) could be attributed to the delay of recombination rate of photogenerated electron-hole pairs by the La metal serving as a good site for scavenging electrons from conduction band thereby increasing the electron-hole life for photocatalytic activity and also extending the absorbance into the visible-light range as a results of band gap reduction. In addition, the GO has been reported to be a good acceptor of materials because of its π -conjugation structure and excellent conductivity as a result of its two-dimensional planner structure which enhances rapid transportation and separation of charge carriers, which therefore contributes to the enhancement of photocatalytic activity [31, 52, 53].

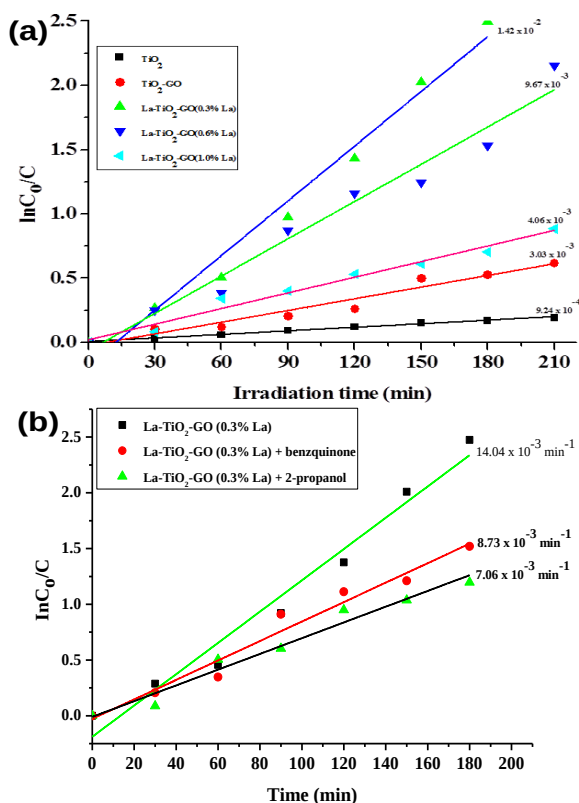


Fig. 5. (a) Kinetics of Acid Blue 40 degradation in the first 210 min under visible light irradiation and (b) Rate of reaction for Acid Blue 40 degradation in the presence of radical scavengers.

Experiment for radical scavengers

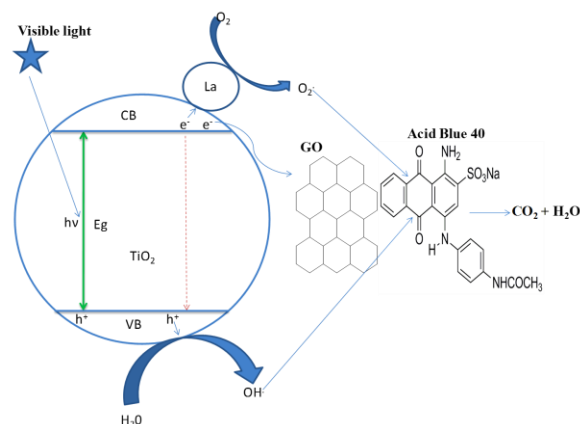
Isopropanol (scavenger for hydroxyl radical; 5 mmol/L, 10mL) and benzoquinone (scavenger for superoxide radical; 5 mmol/L, 10mL) were added to Acid blue 40 solution containing La- TiO_2 -GO (0.3% La) nanocomposite and the results after photocatalysis shows that the rate of Acid Blue 40 degradation by La- TiO_2 -GO (0.3% La) nanocomposite decreased to $8.73 \times 10^{-3} \text{ min}^{-1}$ in the presence of benzoquinone (**Fig. 5(b)**) compared to its absences ($14.04 \times 10^{-3} \text{ min}^{-1}$). Similarly, in the presences of isopropanol, the rate of Acid Blue 40 degradation decreased to $7.06 \times 10^{-3} \text{ min}^{-1}$. The dropped in the rate of degradation of Acid Blue 40 by La- TiO_2 -GO (0.3% La) nanocomposite in presences of isopropanol and benzoquinone were calculated to be 1.9 and 1.6 times slower than the absences of both radical scavengers respectively. **Table 2** shows the percentage degradation of Acid Blue 40 by La- TiO_2 -GO (0.3% La) nanocomposite in the presence and absence of the radical scavengers and the results shows that both hydroxyl and superoxide radicals are the active species responsible for the dye degradation [54]. Therefore, the addition of the radical scavengers depletes some of the hydroxyl and superoxide species leaving less amount for the degradation of the dye (Acid Blue 40) molecules, thus recording lower degradation efficiency (**Fig. 5(b)**).

Table 2. Rates of degradation and percentage degradation of Acid Blue 40 in the presence of radical scavengers.

Sample	(%) decrease in the presence of scavengers	Degr-adation (%)	Ka (min^{-1})	R ²
La- TiO_2 -GO(0.3%L a)		92	1.40×10^{-2}	0.9921
La- TiO_2 -GO(0.3%L a) + Benzoquin one	35	57	8.73×10^{-3}	0.9905
La- TiO_2 -GO(0.3%L a) + Isopropanol	43	49	7.06×10^{-3}	0.9832

Scheme 1 shows the proposed mechanism for the combined effect of La and GO co-doped photocatalyst for photocatalytic degradation of Acid Blue 40 under simulated solar light. When a semiconductor is irradiated by a photon of light equal to its band gap energy, excited electrons move from the valence band (VB) to the conduction band (CB) leaving holes in the VB. But the large band gap of this semiconductor enhanced the recombination of these photo-induced charged carriers causing a reduction in photocatalytic reaction. Therefore, the introduction of La in the composite influence the trapping of electrons to prolong the life span of photogenerated electron-hole pairs for photocatalytic activity by causing a reduction in the band gap. The GO apart from been a photosensitizer and electron sinkers increases the absorptivity of organic pollutants into the

surface of the catalyst due to its π -conjugation two-dimensional structure. The separated photogenerated electron-hole pairs, therefore, trapped the surface water or hydroxyl molecules and oxygen to form a reactive hydroxyl and superoxide radicals. These radicals are highly reactive towards the degradation of Acid Blue 40 to less complex products like carbon dioxide and water.



Scheme 1. Proposed mechanism for the photocatalytic degradation of Acid Blue 40 over La-TiO₂-GO nanocomposite under induced visible light.

Total organic carbon (TOC) analysis

The results of the photodegradation of Acid Blue 40 by La-TiO₂-GO (0.3% La) nanocomposite was carried out using Fusion UV/persulfate TOC analyser for different intervals of time up to 5 hrs. The result of this analysis is presented in **Fig. 6A**, which clearly shows a maximum TOC removal of 75 % was achieved after 5 hr indicating an appreciable degree of complete mineralisation of Acid blue 40 by the La-TiO₂-GO (0.3% La) nanocomposite has occurred. The value obtained shows that the nanocomposite is responsible for the complete mineralisation of the Acid Blue 40 to a less complex product of water and carbon dioxide. The stability of La-TiO₂-GO (0.3% La) nanocomposite was evaluated towards its recycling, for which it was reused for five (5) times, and during each experiment, it was washed with deionised water, ethanol and dried before reuse. After five cycles 84.0% maximum removal of Acid Blue 40 by La-TiO₂-GO (0.3% La) nanocomposite was attained and the decrease in the degradation efficiency is ascribed to loss of the nanocomposite through the process of washing and recovery (**Fig. 6B**).

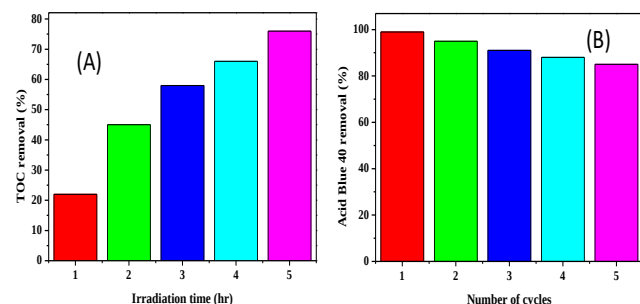


Fig. 6. (A) TOC removal by La-TiO₂-GO (0.3% La) nanocomposite and (B) Cycling studies of La-TiO₂-GO (0.3% La).

Conclusion

TiO₂, TiO₂-GO, and La-TiO₂-GO (with different concentrations of La) nanocomposites were successfully synthesised *via* the sol-gel method. The XRD and Raman analysis of the synthesised nanocomposite show they were crystalline and consist of anatase phase of TiO₂. SEM analysis also shows an even distribution of TiO₂ nanoparticles on the crumpled GO surface. The UV-Visible spectra show that dopants (La and GO) cause an increase in the absorption edge of TiO₂, leading to significant reduction in band gaps. The La-TiO₂-GO (0.3% La) nanocomposite was found to be an efficient photocatalyst for the degradation of Acid Blue 40 compared to the bare TiO₂ nanoparticle. The enhanced photocatalytic performance of La-TiO₂-GO (0.3% La) nanocomposite suggests that the presence of La and GO on the nanocomposite extends its absorbance into the visible light region because of band gap narrowing due to the formation of impurity band between VB and CB. This, therefore, decreases the recombination rate of photogenerated charged carriers considerable and enhance the photocatalytic performance of the nanocomposite for degradation of absorbed pollutant. Total organic carbon investigation shows that a high degree of complete mineralisation was achieved with the La-TiO₂-GO (0.3% La) nanocomposite which decreases the formation of any possible degradation products. Moreover, the La-TiO₂-GO (0.3% La) displayed recyclability and stability under simulated solar light illumination.

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Author's contributions

All authors contributed equally to the work. Authors have no competing financial interests.

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