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Visible light responsive mesoporous graphene-Eu₂O₃/TiO₂ nanocomposites for the efficient photocatalytic degradation of 4-chlorophenol

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Abstract

Mesoporous graphene-Eu₂O₃/TiO₂ nanocomposites with different weight percentages were synthesized by hydrothermal method using Pluronic P123 as the structure directing template. The synthesized materials were characterized by XRD, HRTEM, SEM-EDAX, N₂ adsorption-desorption studies, XPS, UV-vis DRS, FT-IR and photoluminescence spectroscopy. The photocatalytic activity of the catalysts for the degradation of 4-chlorophenol, a model pollutant was evaluated under visible light irradiation. 0.7 wt% GR-Eu₂O₃/TiO₂ nanocomposites showed higher efficiency under visible light among the synthesized materials due to high surface area with narrow band gap and effectively suppressed electron-hole recombination. UV-Vis DRS showed the shift in the light absorption band-edge position to visible region for GR-Eu₂O₃/TiO₂ nanocomposites than GR-TiO₂, Eu₂O₃-TiO₂ and bare meso TiO₂. Eu³⁺ ions were trapping and transferring the exited electrons to graphene layer and adsorbed oxygen efficiently, hence the co-doping of europium and graphene synergistically suppressed the electron-hole recombination. The suppressed electron-hole recombination enhanced 'OH radicals formation and subsequently the photocatalytic degradation of 4-chlorophenol.

Keywords: Mesoporous, Eu/TiO₂, Graphene, Photocatalysis, 4-Chlorophenol, Charge carriers

Introduction

Titanium dioxide (TiO₂) is the most widely used photocatalyst in environmental applications because of its green, clean, low-cost, and sustainable innovation.¹ However, the quantum efficiency of TiO₂ is low because of the fast recombination of photo induced electron hole pairs, and its wide band gap energy (3.2 eV) limits its use as a light source in solar light (with 3% to 5% UV light).^{2,3} The limited optical absorption results in low activity of TiO₂ as photocatalysts. Therefore, a lot of approaches have been explored to extend the optical absorption of TiO₂ into the visible light region, and thus aim to enhance its photocatalytic activity. These approaches include dye-sensitizing, compositing of semiconductors with a narrow band gap, non-metal (e.g. N, C, S) doping and transition metal doping, etc.⁴⁻⁶

Surfactant assisted sol-gel and hydrothermal methods have been employed to prepare the mesoporous TiO₂ nanoparticles for enhancing the surface area and pore volume. Several surfactants and Pluronic-type copolymers such as P123 and F127 have been used as structural directing agents for synthesis of mesoporous nanomaterials.^{7,8} In particular, highly porous nanostructured materials with either large pore volumes or ordered pores have been fabricated.⁹ In addition, many articles have reported that doping metal ions could improve the mesopore structure, meanwhile increase the photocatalytic activity of TiO₂.¹⁰⁻¹² Rare-earth-metal compounds, especially their oxides, have become of increasing interest in recent years because of their special photoluminescence and catalytic properties.^{13,14} Lanthanide ions are known for their ability to form complexes with various Lewis bases (e.g., acids, amines, aldehydes, alcohols, thiols, etc.) in the interaction of these functional groups with the f-orbitals of lanthanides.¹⁵ The doping with Eu³⁺, Pr³⁺, and Yb³⁺ increased the adsorption capacity and also adsorption rate of TiO₂ catalysts simultaneously in aqueous salicylic acid, t-cinnamic acid, and p-chlorophenoxy-acetic acid solutions.¹⁶ It is expected that incorporation of lanthanide ions into a TiO₂ matrix could provide a means to concentrate the organic pollutant at the semiconductor surface and therefore enhance the photoactivity of titania. Eu³⁺, Nd³⁺ and Ce⁴⁺ increased the photocatalytic activities of TiO₂ catalysts in aqueous azo dye (X-3B) under visible light irradiation.¹⁷ Rare earth metals having incompletely occupied 4f and empty 5d orbitals often serve as catalyst and promote catalysis. The europium element, might have an ability to improve the photocatalytic activity of TiO₂ because of its electrons trap effect. However, until now, there were only a few reports on

Eu-doped mesoporous TiO_2 .^{18,19} A systematic study about the preparation, characterization and photocatalytic properties of Eu-doped mesoporous TiO_2 is needed.

The carbonaceous materials are of tremendous interest due to their unique pore structure. electronic properties and adsorption capacity. These materials include activated carbon, carbon nanotubes, and graphene.²⁰ Graphene, which is a monolayer of carbon atoms closely packed in a honeycomb lattice, has attracted a great deal of scientific interest due to its unique structure and outstanding mechanical, electrical, thermal and optical properties.²¹ Compared with CNTs, graphene has many advantages including high surface area (a theoretical value of 2630 $m^2/g)^{22}$ and the honeycomb-like graphene has a very large π -conjugated system and a two-dimensional planar structure, and these improve the mobility of charge carriers ($\approx 200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{23,24} Since the first report of the synthesis of graphene/TiO₂ nanocomposites have been developed as efficient composite systems for many applications.²⁵ Some studies have been focused on graphene-based materials in capacitors,²⁶ biosensors,²⁷ solar cells²⁸ and liquid crystalline displays.²⁹ P25-graphene composite from P25 and graphite oxide in ethanol solution using a hydrothermal method, where graphite oxide was reduced to GS during the hydrothermal process. Thus, the combination of TiO_2 and graphene is promising to simultaneously possess excellent adsorptivity, transparency and conductivity which could facilitates the charge separation in the photocatalysis process.³⁰

In this study, synthesis of mesoporous GR-Eu₂O₃/TiO₂ with different weight percentage using triblock copolymer (Pluronic P123) as the structure directing template in ethanol-water solvent mixture by hydrothermal method. Both europium and graphene dopants can shift the light absorption edge to the visible light region and can enhance the photocatalytic activity by efficiently separating charge carriers (electrons / holes). To the best of our knowledge, there has been no report on mesoporous GR-Eu₂O₃/TiO₂ as a visible light photocatalyst. Hence both europium and graphene were selected for this co-doping work. The spectroscopic characterization of the obtained photocatalysts, photocatalytic activities and the degradation pathway of 4-chlorophenol under visible light irradiation were also discussed.

Experimental section

Materials

All the reagents and chemicals were of analytical grade and used without further purification. Titanium (IV) isopropoxide (Aldrich), europium (III) nitrate pentahydrate (Aldrich) were used as the source materials for Ti and Eu respectively. Triblock copolymer, [poly (ethylene glycol)-block-poly (propylene glycol)-blockpoly(ethylene glycol)] (Pluronic P123, molecular weight = 5800, EO₂₀PO₇₀EO₂₀; Aldrich) was used as the structure directing template. Graphite powder (Aldrich), absolute ethanol (Merck) and triple distilled water were used for the preparation of catalyst. 4-chlorophenol (SRL, 98%) dye was used as the model pollutant for the degradation study.

Synthesis of mesoporous Eu₂O₃/TiO₂ nanocomposites

Mesoporous europium doped TiO₂ materials were synthesized by hydrothermal method using soft template mechanism with Pluronic P 123 as the structure directing agent. The gel composition of the synthesis with absolute ethanol as co-solute was 1 Ti(OiPr)₄: 18 H₂O. The optimum ethanol/water ratio was maintained as 50:1 for this synthesis method. Triblock copolymer Pluronic P 123 (1g) was added to absolute ethanol (30 mL). After stirring for 4 h, a clear solution was obtained. Titanium (IV) isopropoxide (3 mL) was added to the above clear solution and stirred for 2 h at room temperature. Then water (18 mL) was added to the mixture and the stirring was continued for 24 h at room temperature. The pH of the mixture was maintained at 3.0 using 0.2M H₂SO₄. Subsequently, a given amount of Eu(NO₃)₃.5H₂O were added to the above solution and stirred for 1 h. After this, the resulting suspension was put into 200 ml Teflon sealed autoclave and maintained at 180°C for 6 h. Finally, the suspension was washed with deionized water and centrifuged several times to get pH 7. Then samples were dried at 100°C in the vacuum oven for 6 h and calcined at 400°C to obtain Eu-doped TiO₂ nanopowder. It was denoted as 0.5 wt % Eu doped TiO₂ sample. The different wt% of Eu to TiO₂ (0.7 and 0.9 wt%) were also prepared by the same procedure.

Synthesis of mesoporous GR- Eu₂O₃/TiO₂ nanocomposites

Graphene oxide (GO) was synthesized from graphite powder by a modified Hummers method.³¹ In a typical synthesis, 2.0 g of graphite powder was put into cold (0 °C) concentrated H₂SO₄ (100 mL). Then, KMnO4 (8.0 g) was added gradually under stirring, and the temperature of the mixture was kept below 10 °C by cooling. The reaction mixture was continued for 2 h below 10 °C. Successively, the mixture was stirred at 35 °C for 1 h, and then diluted with 100 mL of deionized (DI) water. After adding 100 mL of DI water, the mixture was stirred for 1 h, and was then further diluted to approximately 300 mL with DI water. After that, 20 mL of 30% H₂O₂ was added to the mixture to terminate the reaction. The mixture released a large amount of bubbles, and the color of the mixture changed into brilliant yellow. Finally, the mixture was filtered and washed with 5% HCl aqueous solution (800 mL) to remove metal ions, followed by 1 L of DI water to remove the acid until pH reached to 6. For further purification, the as-obtained graphene oxide was re-dispersed in DI water, and after sonication for 1 h, the suspension was centrifuged and filtered. The resulting solid was dried at 60 °C for 24 h.

GR-Eu₂O₃/TiO₂ nanocomposite was obtained via a hydrothermal method based on Zhang's work with a slight modification.³² Briefly, 0.0115g of GO was dissolved in a solution of DI H₂O (80 mL) and ethanol (40 mL) by ultrasonic treatment for 3 h, and then 200 mg of (TiO₂ or Eu/TiO₂) was added to the obtained GO solution and stirred for another 2 h to get a homogeneous suspension. The suspension was then placed in a 300 mL Teflon-lined autoclave, and maintained at 120 °C for 5 h to simultaneously achieve the reduction of GO and the deposition of TiO₂. Finally, the resulting composite was recovered by filtration, rinsed by DI water several times, and dried at 120 °C for 6 h. It was denoted as 0.5 wt% GR-Eu₂O₃/TiO₂. In the similar procedure, 0.7 wt% GR-Eu₂O₃/TiO₂ and 0.9 wt% GR-Eu₂O₃/TiO₂ composites were synthesized when 0.0161 g and 0.0207 g starting material GO were used respectively.

Catalysts characterization

The X-ray diffraction (XRD) patterns of mesoporous TiO₂ were recorded on Bruker D2 Phaser desktop X-ray diffractometer using CuK α radiation (λ = 1.542 Å) as the X-ray source. The average crystallite size (D) was determined from the broadening of the diffraction peak using the Scherrer formula $D = K\lambda / \beta \cos\theta$ where D is the average particle size in (nm), K is the Scherrer constant (0.89) λ is the wavelength of X-ray source, β is the full width at half-maximum and θ is the Bragg's angle. Transmission electron microscopic (TEM) images were taken using a electron microscope (TECHNAI G² 305-twin D 905) operated at an accelerating voltage of 200 keV. Scanning electron microscopic (SEM) pictures were recorded using a scanning electron microscope with energy dispersive X-ray spectrometer (SEM-EDAX, Hitachi S 3400 N). The N₂ adsorption-desorption isotherms were measured using Micromeritics ASAP 2020 sorption analyzer. Prior to analysis, the samples were degassed for 3 h at 300 °C under vacuum (10⁻⁵ mbar) in the degas port of the adsorption analyzer. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated using adsorption branch of Barrett- Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was recorded with XPS K-Alpha surface analyzer using AlKa as the radiation source operated at 200 W hemispherical electron energy analyzer. Diffuse reflectance spectra of the synthesized materials were collected in the scan range 200–800 nm using UV-visible spectrophotometer (Shimadzu model 2450) equipped with an integrating sphere and BaSO₄ was used as the reference. The FT-IR spectra were recorded on PerkinElmer FT-IR spectrometer using KBr pellet technique. The pellet was scanned at 4 cm⁻¹ resolution in the range of 4000-400 cm⁻¹. Photoluminescence (PL) spectra were recorded on PerkinElmer LS-45 model fluorescence spectrometer using Xenon lamp as the excitation source with 10 nm slit width and photomultiplier tube as the detector.

Photocatalytic degradation studies and analysis

The visible-light photocatalytic efficiency of the synthesized catalysts were investigated by studying the degradation of 4- chlorophenol (4-CP) aqueous solution. Photocatalytic degradation was performed in aqueous medium in a slurry batch visible-light photoreactor. A cylindrical photochemical reactor of 30 cm \times 2 cm (height \times diameter) with a water circulation arrangement to maintain the temperature in the range 25–30 °C, was used in all the experiments. A 300 W tungsten Xenon lamp built into a housing with polished anodized aluminum reflectors was

used as the visible-light source and placed 6 cm away from the reactor tube. These lamps emit predominantly in the visible region at a wavelength above 410 nm with an intensity of 17 mW/cm². The light intensity was measured using LX-101 digital lux meter.

4-chlorophenol stock solution containing 1000 mgL^{-1} was prepared in triple distilled water and diluted to the required concentration. In a typical procedure, 100 mg of the catalyst was added to 100 mL 4-chlorophenol solution of 30 mg L^{-1} in a glass tube and oxygen was bubbled into the solution throughout the experiment. The resultant slurry was stirred for 30 min to attain equilibrium. It was then irradiated with visible-light of wavelength above 410 nm with continuous purging of air free from CO₂. An aliquot of 5 mL of samples were withdrawn at the specific time intervals of 30 minutes and analyzed after centrifugation followed by filtration with 0.2 µm membrane to remove the catalyst particles. The photocatalytic activities were evaluated by detecting 4-chlorophenol at the wavelength of 280 nm using UV- Visible spectrophotometer (Elico SL 218 double beam). The extent of mineralization of 4-chlorophenol was followed by the decrease in TOC value with irradiation time using a total organic carbon analyzer (Analytikjena multi N/C 2100). The degradation products, obtained during the photocatalytic degradation were analyzed using GC-MS (Jeol GCMS GC-Mate II). The GC-MS conditions were as follows: DP-1 (100% dimethylpolysiloxane) column, helium as carrier gas, initial temperature 80 °C, increment of 10 °C/min, injection port temperature 220 °C and detector temperature 250 °C.

Adsorption study

The extent of adsorption of 4-chlorophenol on the various synthesized catalysts were studied by mixing 100 ml of aqueous solution of 4-chlorophenol (30 mg/L) with 0.1 g of the catalyst under dark condition. The solution was kept in stirring to have uniform concentration throughout the samples. All the experiments were carried out under identical conditions. Aliquots were withdrawn at specific time intervals of 10 minutes and the change in 4-chlorophenol concentration was determined from the decrease in 4-chlorophenol concentration as C_t/C_0 . Where C_0 is the initial concentration of 4-chlorophenol and C_t is the concentration of 4-chlorophenol at time t.

Results and discussion Catalysts characterization

The crystal structures of the synthesized bare and GR-Eu₂O₃ co-doped TiO₂ samples were analyzed using XRD. As shown in Fig.1a, all the patterns showed characteristic diffraction peaks at $2\theta = 24.80, 37.78, 48.10, 53.89, 55.12, 62.86$ and 68.85° which could be perfectly indexed to the (101), (004), (200), (105), (211), (204) and (116) crystal faces of anatase phase of TiO₂ (JCPDS No. 21-1272). The average crystallite size of the synthesized materials calculated using the Scherrer's equation from the (101) crystal plane of anatase phases were 14.9, 12.3, 14.3, 10.8, 9.9 and 8.5 nm for bare meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂ respectively. Since Eu₂O₃ crystals on TiO₂ lattice surface suppressed the crystallite growth of TiO₂ nanoparticles, the average crystallite size was found to decrease with an increase of Eu loading. The ionic radius of Eu^{3+} is 0.95 Å which is much larger than that of Ti^{4+} (0.68 Å), hence Eu^{3+} could not replace Ti⁴⁺ in TiO₂ lattice.³³ It can be seen that the diffraction peak of anatase TiO₂ was not shifted to higher or lower angle after europium doping. The diffraction peaks of Eu₂O₃ were not found since the dopant concentration was very low. Fig. 1b shows the enlarged diffraction peak (002) for graphene at 25.07° and anatase (101) peak at 24.80° for both bare meso TiO₂ and 0.7 wt% GR-TiO₂ samples. Since the (002) diffraction peak of graphene was exactly overlaping with the (101) diffraction peak of TiO₂ a small shoulder peak could be observed in the composite sample which revealed the presence of graphene.^{34,35}

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Fig. 1 XRD patterns of (a) meso TiO_2 , 0.7 wt% Eu_2O_3 - TiO_2 , 0.7 wt% GR- TiO_2 , 0.5, 0.7 and 0.9 wt% GR- Eu_2O_3/TiO_2 samples. (b) enlarged (002) peak for graphene and anatase (1 0 1) peak for both bare meso TiO_2 and 0.7 wt% GR- TiO_2 samples.

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The HRTEM images clearly demonstrated the morphology and structure of the synthesized samples. The HRTEM images of mesoporous TiO_2 and 0.7 wt% GR-Eu₂O₃/TiO₂ catalysts were recorded and shown in Fig. 2. The graphene layer, the spherical nanostructure of TiO₂ nanoparticles and the particle size distributions in the range of 9-15 nm were seen in the TEM images. These values are consistent with the typical crystallite sizes calculated from XRD results. The well resolved lattice fringes were observed in the magnified images of meso TiO₂ and 0.7 wt% GR-Eu₂O₃/TiO₂ catalysts shown in Fig. 2b and d which revealed the crystalline nature of the samples. In Fig. 2d, the lattice fringes with 0.354 and 0.314 nm spacings are assigned to the tetragonal anatase phase of TiO₂ (101) and cubic form of Eu₂O₃ (222) planes respectively. This indicates that europium nanoparticles are on the TiO₂ surface, not incorporating into the lattice of TiO₂. The graphene layers could serve as a supporting material for in situ growth of anatase TiO₂ nanocrystals and also suppress the particles aggregation.³⁶ This kind of interfacial interaction would facilitate the transfer of photoinduced electrons from TiO₂ to graphene, which improve the charge transfer efficiency.



Fig. 2 HRTEM images of (a) meso TiO₂, (b) magnified image of meso TiO₂ (c) HRTEM image of 0.7 wt% GR-Eu₂O₃/TiO₂ (d) magnified image of 0.7 wt% GR-Eu₂O₃/TiO₂.

SEM images generally give information about the shape, size and EDAX tells about the composition of the synthesized catalysts. The SEM images of meso TiO_2 and 0.7 wt% GR-Eu₂O₃/TiO₂ are shown in Fig. 3a and b. The large aggregates of spherical shapes with different particle sizes are seen in the SEM images. The composition of the 0.7 wt% GR-Eu₂O₃/TiO₂ sample is determined by energy dispersive X-ray spectroscopy (EDAX) experiments. Fig. 3c showed the obvious signals for C, O, Ti and Eu. The EDAX analysis results showed the atomic percentages of C, O, Ti and Eu are 4.34, 70.75, 24.85 and 0.07% respectively.



Fig. 3 SEM images of (a) meso TiO₂, (b) 0.7 wt% GR- Eu₂O₃/TiO₂ and (c) EDAX spectrum of 0.7 wt% GR- Eu₂O₃/TiO₂ samples.

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The textural properties of meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂, 0.5, 0.7 nd 0.9 wt% GR-Eu₂O₃/TiO₂ were obtained from N₂ adsorption- desorption analyses are shown in Fig. 4A. All the obtained isotherms belong to type IV with H2 hysteresis loop at higher relative pressure, which confirmed the characteristics of mesopores. Type H2 hysteresis loop indicates that pore structure is made up of interconnected networks of different size and shape. Table 1 summarizes the crystallite size, specific surface area, pore volume and pore diameter of various samples. The average pore sizes were obtained from the maximum of pore size distribution curves for all the synthesized samples. The specific surface area of the photocatalysts are varied in the region of 91 to 122 m^2/g . Among all the prepared photocatalysts, BET surface area of 0.7 wt% GR-Eu₂O₃/TiO₂ catalyst was found to be maximum of 122 m²/g. A greater specific surface area of photocatalysts can supply more surface active sites and make charge carriers transport easier. Thus, graphene may play a role in enhancing the photocatalytic activity. The pore size distribution was investigated by adsorption branch of the Barrett-Joyner-Halenda (BJH) method is shown in Fig. 4B and inset. Particle size decreases with an increase of dopant concentration, hence the surface area increased upto 0.7 wt% GR-Eu₂O₃/TiO₂. At higher dopant concentration though particle size decreases, the well dispersed Eu₂O₃ and graphene may cover the surface sites of TiO₂ and thus obstruct the pores of the TiO_2 , resulting in a decrease of the specific surface area.

Table 1 Physico-chemical and textural properties of meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂

Catalysts	Crystallite	Bandgap	Specific surface	Pore volume	Pore diameter
si	size (nm)	(eV)	area (m ² /g)	(cm^3/g)	(nm)
meso TiO ₂	14.9	3.16	91	0.45	13.4
$0.7 \text{ wt\% Eu}_2O_3\text{-}TiO_2$	11.3	3.06	98	0.47	13.6
0.7 wt% GR-TiO ₂	14.3	3.10	105	0.46	14.8
0.5 wt% GR-Eu ₂ O ₃ /TiO ₂	2 10.8	3.01	116	0.53	10.8
0.7 wt% GR-Eu ₂ O ₃ /TiO ₂	₂ 9.9	2.90	122	0.56	15.4
0.9 wt% GR-Eu ₂ O ₃ /TiO ₂	2 8.5	2.80	118	0.54	13.6



Fig. 4 (A) N₂ adsorption-desorption isotherms of meso TiO_2 , 0.7 wt% Eu_2O_3 - TiO_2 , 0.7 wt% GR- TiO_2 , 0.5, 0.7 and 0.9 wt% GR- Eu_2O_3 / TiO_2 . (B) Pore size distribution curves of meso TiO_2 , 0.7 wt% Eu_2O_3 - TiO_2 , 0.7 wt% GR- TiO_2 and inset figure shows (a) 0.5, (b) 0.7 and (c) 0.9 wt% GR- Eu_2O_3 / TiO_2 .

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The chemical components of the synthesized GR-Eu₂O₃/TiO₂ samples were analyzed by X-ray photoelectron spectroscopy. The XPS survey spectrum of 0.7 wt% GR-Eu₂O₃/TiO₂ (Fig. 5a) catalyst indicates that the sample contains Ti, O, C, and Eu atoms. The C element could be ascribed to the adventitious carbon-based contaminant, and the binding energy for C 1s peak at 284.5 eV was used as the reference for calibration. The high-resolution XPS spectra with scanning over the area corresponding to the binding energies for the Ti 2p region around 470 eV were analyzed in Fig. 5b. For Ti 2p, the two peaks observed at 459.5 and 465.2 eV were respectively assigned to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spin-orbital splitting photoelectrons in the Ti⁴⁺ chemical states.³⁷ Fig. 5c shows the O 1s core level spectrum of 0.7 wt% GR-Eu₂O₃/TiO₂. The shoulder peak at 529.5 eV can be ascribed to the lattice oxygen in Ti-O bond on the TiO₂ surface. The peak at 532.1 eV was associated to the surface adsorbed hydroxyl groups³⁸ and residual oxygen-containing groups in reduced graphene oxides.³⁹ The XPS spectrum for the Eu 3d is shown in Fig. 5d. The characteristic peaks at 1121.1 and 1164.9 eV, which are assigned to Eu 3d_{5/2} and Eu 3d_{3/2} respectively. The spin orbital has 43 eV splitting of the Eu 3d doublets, which is a character of Eu³⁺ anion in the form of Eu₂O₃.⁴⁰

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Fig. 5 XPS spectrum of 0.7 wt% GR-Eu₂O₃/TiO₂ nanocomposite. (a) survey spectrum (b) Ti 2p spectrum (c) O 1s spectrum and (d) Eu 3d spectrum.

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The diffuse reflectance UV-Vis absorption spectra of meso TiO₂ and doped TiO₂ are shown in Fig. 6. The onset of absorption for meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂ were observed at 392, 404, 400, 411, 420 and 428 nm respectively. The band gap energy values calculated using Kubelka-Munk equation Eg = $1240 / \lambda$ (where λ is the wavelength in nm) based on the onset of absorbance were found to be 3.16, 3.06, 3.10, 3.01, 2.90 and 2.80 eV for meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂ respectively. The optical absorption onset showed a red-shift with the increasing graphene and Eu dopant concentration. Europium ion doping will produce lattice deformation and form vacancy, which will probably result the impurity states in the band gap of TiO₂. The existence of impurity states can narrow the band gap and improve the absorption.⁴¹ The hybridization of O2p and C2p atomic orbits to form a new valence band above the valence band of TiO₂ because of their similar energy levels reduced the band gap energy on the graphene loading.⁴² Graphene incorporation in the composite samples modified the optical properties of TiO₂ similar to TiO₂-CNT and C-doped TiO₂.⁴³ Thus, the band gap energy was reduced in the graphene and europium doped TiO₂. Hence, the graphene and europium co-doping improved the photocatalytic activity of TiO₂ under visible light.



Fig. 6 UV- Vis diffuse reflectance absorption spectra of meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂.

The reduction of graphene oxide was also confirmed using FT-IR measurements. The FT-IR spectra of pure meso TiO₂, graphene oxide, GR-TiO₂ and 0.7 wt% GR-Eu₂O₃/TiO₂ are shown in Fig. 7. All the spectra, the intense broad band observed in the region around 3200–3500 cm⁻¹ was due to O-H stretching vibration of surface adsorbed water. The corresponding bending vibration occurred close to 1625 cm⁻¹. The characteristic peaks of graphene oxide at 1134, 1558, 1705 and 3432 cm⁻¹ were assigned to oxygen-containing functional groups i.e., C-O (alkoxy) stretching, O-H deformation, C=O stretching and O–H stretching respectively.⁴⁴ In the spectrum of GR/TiO₂ sample, these characteristic absorption peaks especially the C-O stretching decreased dramatically which revealed the significant reduction of graphene oxide. Hence the broad absorption band between 500-800 is attributed to the Ti-O-Ti stretching vibrations in TiO₂ based composites. The absence of CH₂ and C-O stretching and bending vibrations in the spectra of bare meso TiO₂ and 0.7 wt% GR-Eu₂O₃/TiO₂ calcined samples revealed the complete removal of alcohol and polymer template in the samples.



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Fig. 7 FT-IR spectra of meso TiO₂, graphene oxide, 0.7 wt% GR-TiO₂ and 0.7 wt% GR-Eu₂O₃/TiO₂.

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Photoluminescence (PL) emission spectra are commonly used to investigate the efficiency of the trapping, transfer and separation of charge carriers, within an activated semiconductor photocatalyst. PL spectra of and pure meso TiO₂ and doped composite samples are recorded in the wavelength range 320-600 nm are shown in Fig. 8. The emission intensity of 0.7 wt% GR-Eu₂O₃/TiO₂ was much lower than meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂ and GR-TiO₂, indicating the recombination of electron and hole was effectively prohibited. It was reported that Eu doping has the ability to trap the electrons, which can effectively reduce the photogenerated electron-hole pairs.⁴⁰ The exited electrons are trapped by Eu³⁺ and transported to the graphene layer. Further, the graphene layers with a two-dimensional π -conjugated structure could serve as an effective electron-accepting material to transport on the surface thereby the direct recombination of electron-hole pairs in TiO₂ was inhibited.



Fig. 8 Photoluminescence spectra of meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂ and 0.7 wt% GR-Eu₂O₃/TiO₂.

Evaluation of photocatalytic activity of graphene and europium oxide co- doped TiO₂ nanoparticles

The photocatalytic activities of different synthesized catalysts were evaluated. The adsorption profile of the bare meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂ and 0.7 wt% GR-Eu₂O₃/TiO₂ catalysts are shown in Fig. 9. All the catalysts showed linear increase in adsorption of 4-chlorophenol for the initial 60 min with different adsorption rate and attained equilibrium after 60 min. The adsorption of 4-chlorophenol on 0.7 wt% GR-Eu₂O₃/TiO₂ was higher than on the other catalysts due to the enhanced surface area with sufficiently large pore volume and pore diameter. The 0.7 wt% GR-Eu₂O₃/TiO₂ composite sample has the superior adsorption capability for 4-chlorophenol than other samples due to giant π - conjugation system and two-dimensional planar structure of graphene with enhanced surface area. Moreover, the enhanced adsorption of 4-chlorophenol was driven by the π - π stacking between 4-chlorophenol and aromatic regions of graphene.⁴⁵



Fig. 9 Adsorption profile of 4-chlorophenol on various catalysts. Reaction conditions: 4-chlorophenol concentration - 30 ppm; catalyst concentration - 0.1 g; in dark under stirring conditions; in the absence of air flow.

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The photocatalytic degradation rates of 4-chlorophenol using Degussa P-25, meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂ catalysts were evaluated under visible light irradiation at above 410 nm are shown in Fig. 10. The degradation efficiency of Degussa P-25 was lower than bare meso TiO₂ due to the enhanced surface area and meso porosity. The rate was also found to be lower on bare mesoporous TiO₂ than europium doped samples. This is due to the fact that the band gap of TiO₂ is wide and visible light cannot be utilized effectively. On europium doping, a new impurity energy level was formed below the conduction band of TiO₂ due to the shift in the light absorption edge to the visible region. Hence europium doped samples exhibited higher photocatalytic activity under the visible region with enhanced surface area. The electron trap effect of europium due to the alterable valence states is also playing (Eu³⁺ and Eu²⁺) an important role in inhibiting the electron-hole recombination.⁴⁶ The rare earth elements have the ability of oxygen storage, hence europium facilitates more adsorbed oxygen on the surface of the catalyst. The trapped electrons were subsequently transferred to the adsorbed oxygen to form superoxide radicals by the following process.⁴⁷

$$Eu^{3+} + e^{-} \longrightarrow Eu^{2+}$$
$$Eu^{2+} + O_2 \longrightarrow O_2^{--} + Eu^{3-}$$

Neverthless, GR-Eu₂O₃/TiO₂ showed higher photocatalytic activity than Eu₂O₃-TiO₂, since graphene is a competitive candidate as an electron acceptor material due to its π -conjugation structure. The excited electrons in impurity energy state could also be transferred to graphene and further transferred to adsorbed oxygen to form superoxide radicals.⁴⁸ Thus, the simple recombination between exited electrons and holes were greatly inhibited, the redox probability increased and hence the photocatalytic activity was enhanced for the GR-Eu₂O₃/TiO₂ composite material. Among all the synthesized catalysts 0.7 wt% GR-Eu₂O₃/TiO₂ showed the highest photocatalytic activity. Further increase in the dopant concentration beyond the 0.7 wt%, the photocatalytic degradation efficiency was decreased due to the lower specific surface area. The higher concentration of surrounding europium ions influences the activity significantly, because they will act as recombination centers for photogenerated electrons and holes.¹⁸ In addition, the excessive graphene in composite increases the opportunity for the collision of

electrons and holes and hence promotes the recombination of the photogenerated electron-hole pairs, thus decreasing the photocatalytic activity.⁴⁹



Fig. 10 The rate of degradation of 4-chlorophenol using Degussa P-25, meso TiO₂, 0.7 wt% Eu₂O₃-TiO₂, 0.7 wt% GR-TiO₂, 0.5, 0.7 and 0.9 wt% GR-Eu₂O₃/TiO₂ catalysts.

The higher photocatalytic activity of 0.7 wt% GR-Eu₂O₃/TiO₂ catalyst was also confirmed by total organic carbon (TOC) analysis. The TOC analysis was performed and the plot of TOC versus irradiation time is shown in Fig. 11. Among the various synthesized catalysts, the photocatalytic mineralization of 4-chlorophenol was also found to be high with 0.7 wt% GR-Eu₂O₃/TiO₂ catalyst.



Fig. 11 TOC profile of 4-chlorophenol with irradiation time on various catalysts. Reaction conditions; 4- chlorophenol concentration – 30 ppm; catalyst concentration – 0.1 g; visible light source – tungsten halogen vapour lamp ($\lambda > 410$ nm); in the presence of oxygen flow.

Photocatalytic mechanism

GR-Eu₂O₃/TiO₂ displayed the highest photocatalytic activity towards 4-chlorophenol under visible light, which could be ascribed to the synergistic effect of graphene and europium co-doping. The proposed mechanism for the photocatalytic degradation of 4-chlorophenol on GR-Eu₂O₃/TiO₂ catalyst is shown in Fig. 12. Upon irradiation, the electrons excited from the new valence band of C2p above the valence band of TiO₂ due to the graphene loading to the impurity energy level formed below the conduction band of TiO₂ due to europium doping. Since the band gap was narrowed, more photons were absorbed in the visible region and utilized to generate exited electrons and holes. The surface electrons can be trapped by the Eu³⁺ ion to form a reduction species Eu²⁺ ions.⁵⁰ The standard reduction potential of Eu³⁺/Eu²⁺ is more negative (-0.43 eV) than the standard reduction potential of O₂/O₂⁻⁻ (-0.33 eV). Hence, the Eu²⁺ could be easily oxidized back to Eu³⁺ by the transferring the electrons to the surface adsorbed oxygen.⁵¹

Additionally, lanthanide ions have special electronic structure of $4f^{x}5d^{y}$ which would be able to form the labile oxygen vacancies with the relatively high mobility of bulk oxygen species,⁵² hence the availability of oxygen on the surface of the catalyst was enhanced by europium loading.

The excited electrons in impurity energy state could also be transferred to graphene in the nanocomposite via percolation mechanism.²⁰ Graphene could act as electronic conductive channels and transfer the electrons to the adsorbed oxygen. The excited electrons could be either directly transferred to graphene or Eu^{2+} ions could de-trap the electrons to graphene.⁵³ Therefore, rapid transport of photogenerated electrons could be achieved and an effective charge separation is subsequently accomplished. As a result, the electron hole recombination rate was suppressed and more superoxide anion radicals (O_2^{--}) were formed. The produced holes migrated to the catalyst surface and formed OH radicals with surface adsorbed OH⁻ ions. The well reduced photoluminescence intensity revealed that a better charge separation for GR-Eu₂O₃/TiO₂ nanocomposites than other catalysts. These superior properties contributed by both europium and graphene loading greatly inhibited the electron-hole recombination, which results in more charge carriers to form reactive species and promotes the degradation of organic compounds. Thus, co-doping of europium and graphene synergistically enhanced the photocatalytic activity due to the high surface area, large shift in the light absorption edge to the visible region and great suppression in the electron-hole recombination.

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Fig. 12 The proposed mechanism for the photocatalytic degradation of 4-chlorophenol on $GR-Eu_2O_3/TiO_2$.

Photodegradation products

The photodegradation products formed at 60 min and 150 min irradiations were analyzed using GC-MS technique. Table 2 summarizes the degradation products and their molecular weights after 60 min and 150 min irradiation. The intermediate products hydroquinone (1), benzoquinone (2), 4-chlorocatechol (3), hydroxyhydroquinone (4) were identified at 60 min irradiated sample. The hydroxybenzoquinone (5) and muconic acid (6) were identified at 150 min irradiated sample. Based on the intermediate products found and earlier reports on the products,⁵⁴⁻⁵⁶ the plausible degradation pathway for 4-chlorophenol was proposed as shown in Scheme 1. In 4-chlorophenol, the attack of hydroxyl radical to the para position leads to the formation of hydroquinone (1). It undergoes oxidation and reduction to form benzoquinone (2). The degradation product 4-chlorocatechol (3) is obtained by the addition of a hydroxyl radical to the ortho position of the hydroxyl group of 4-chlorophenol. The 4-chlorocatechol (3) is converted into hydroxyhydroquinone (4) by oxidation with another hydroxyl radical followed by Cl abstraction. The hydroxybenzoquinone (5) is formed either by the oxidation followed by reduction of hydroxyhydroquinone (4) and the hydroxyl radical attack of benzoquinone (2). An attack of hydroxyl radicals on hydroxybenzoquinone (5) and benzoquinone (2) lead to the ring opening to form muconic acid (6). The aliphatic compound, muconic acid (6) is further oxidized into the smaller molecular weight aliphatic compounds and finally mineralized into CO₂ and H₂O.

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Product No	Retention time (minutes)	MW (m/z)	Structure of intermediates
1	2.8	110	OH OH OH
2	1.65	108	
3	7.27	144	benzoquinone OH OH CI
4	4.93	126	4-chlorocatechol OH OH OH
5	3.05	124	hydroxyhydroquinone
6	4.45	142	HO HO muconic acid

Table 2 The intermediates identified in the photocatalytic degradation of 4- chlo	rophenol
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Scheme 1 Plausible pathway for the photocatalytic degradation of 4- chlorophenol on 0.7 wt% GR-Eu $_2O_3/TiO_2$

Conclusion

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A high photocatalytic degradation efficiency under visible light irradiation has been achieved over the GR-Eu₂O₃/TiO₂ nanocomposite synthesized by a hydrothermal method. Europium and graphene co-doped nanocomposite enhanced the specific surface area, shifted the light absorption to the visible region and improved the charge transfer efficiency. The optimal weight percentage of graphene and europium was found to be 0.7 wt %. The results demonstrated that the unique features of graphene and europium were excellent supporting materials for semiconductor nanoparticles to separate the photogenerated electron-hole pairs. The electron trap effect, high oxygen availability on surface of the catalyst due to europium and electron accepting ability of graphene efficiently suppressed the electron-hole recombination,which was revealed by PL study. It can be concluded that both europium and graphene synergistically enhanced the photocatalytic activity of TiO₂ nanoparticles for the degradation of 4-chlorophenol under visible light irradiation.

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Graphical Abstract

Visible light responsive mesoporous graphene-Eu₂O₃/TiO₂ nanocomposites for the efficient photocatalytic degradation of 4-chlorophenol

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We report that graphene and europium co-doped on TiO_2 nanoparticles synergistically enhanced the photocatalytic activity for the degradation of 4-chlorophenol under visible light irradiation due to the enhanced specific surface area, shift in the light absorption edge to the visible region and improved charge transfer efficiency.

