Kaolin-graphene carboxyl incorporated TiO_2 as efficient visible light active photocatalyst for the degradation of cefuroxime sodium

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Abstract

A novel solar light active photocatalyst, TiO_2 /kaolin-graphene carboxyl nanocomposite was synthesized by hydrothermal method for the degradation of cephalosporin antibiotic, cefuroxime sodium. The synthesized photocatalyst was characterized by various analytical and spectroscopic techniques, including Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) thermogravimetry (TG), UV–Vis diffuse reflectance spectroscopy (DRS) and photoluminescence (PL). The prepared TiO_2 /kaolin-graphene carboxyl nanocomposite exhibited efficient photocatalytic degradation of methylene blue (MB) upon illumination with the solar simulator as compared to unmodified TiO_2 . The incorporation of both kaolin and graphene carboxyl was found to immobilize TiO_2 , enhancing the visible light absorption range of TiO_2 . Scavenger study revealed that hydroxyl radicals act as the main active species in the photocatalytic degradation process. The hydroxyl group present on kaolin surface reacts with photo-generated holes to increase the amount of hydroxyl radical, and further the graphene carboxyl plays a role to impede the recombination of photo-generated electron–hole pairs. Furthermore, the synthesized photocatalyst was found to degrade cefuroxime sodium within 90 min of sunlight illumination, indicating that TiO_2 /kaolin-graphene carboxyl nanocomposites would be very beneficial for pharmaceutical waste management through the advanced oxidation process. Mass spectral analysis was also carried out for elucidating the photocatalytic degradation pathway of cefuroxime sodium.

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Graphical abstract

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1 Introduction

Water pollution caused by dye stuffs and antibiotics in the aquatic system has become a serious menace for human health and the environment, and is expanding in an alarming rate due to rapid industrialization [1, 2]. Cephalosporins are semi-synthetic beta-lactam antibiotics which have wide applications in human and veterinary treatment. This class of antibiotics have been spotted in variety of aqueous environments at concentrations ranging from 0.30 ng L⁻¹ to 0.03 mg L⁻¹ [3]. The exhaustion of cephalosporins into water bodies by pharmaceutical companies, hospitals and from expired and unused medications endangers human health by promoting generation of resistant strains of bacteria which have negative impact on curing diseases [4]. Cefuroxime sodium is an injectable, cephalosporin second generation antibiotic that holds promising pharmacokinetic properties [5]. Like most antibiotics, the degradation of this water-soluble contaminant through traditional treatment methods is inefficient and time consuming. The conventional wastewater treatment techniques were ineffective towards their degradation as they possess several drawbacks such as high-energy requirement, partial contaminant removal and formation of toxic byproducts [6, 7]. Hence to tackle and control their adverse effects on human beings as well as on ecosystems, removal of these types of organic

contaminants from waterbodies using efficient and environment-friendly approaches is urgently required [8].

Semiconductor-mediated photocatalysis has been considered as a promising approach to convert organic pollutants to innocuous products by harvesting solar energy [9]. Among various semiconductor photocatalysts (TiO₂, ZnO, ZnS, Fe₂O₃, CdS), TiO₂ has been the most frequently explored catalyst owing to its low cost, biological and chemical inertness, eco-friendliness, availability, and durability against photo- and chemical corrosion [10, 11]. The major drawbacks of TiO₂ photocatalysts are the requirement of UV light for activity and fast recombination rates of photoinduced electron–hole pairs [12, 13]. Also, large-scale execution of this technology is still hampered because of the technical challenges associated with post separation and recovery of the photocatalyst as it forms a milky dispersion with the waste water [14, 15]. To make TiO₂ as visible light active and practically applicable photocatalyst, researchers are focusing on the incorporation of nano-clays such as kaolin. The presence of abundant hydroxyl groups on the kaolinite surface makes it susceptible to various modifications to act as anchoring supports for TiO₂ nanoparticles to make the recycling process easier [16]. Kaolinite [Al₂Si₂O₅(OH)₄] is a 1:1-type clay mineral consisting of stacked layers of Si₂O₅²⁻ tetrahedral sheets and [Al₂(OH)₄]²⁺ octahedral sheets which are linked by common oxygen atoms [16–19].

Kaolin supports could control the crystal type of TiO_2 nanoparticles, allowing the easy recovery of catalysts from water slurries after treatment [16, 20]. Chong et al. developed titania-impregnated kaolinite to crack the problems associated with catalyst separation, and they ensured its reuse in several reaction cycles for reducing catalyst amount and treatment cost [14]. In this perspective, the incorporation of catalysts into clay structure like kaolin is an effectual method for photocatalytic applications.

Recently, attention has been also focused on the modification of TiO_2 using graphene oxide (GO) derivatives because of its exceptional properties, such as high surface area, flexible sheets, good thermal and electrical conductivity and excellent charge carrier mobility [21, 22]. GO comprises hydroxyl, carboxyl and epoxyl groups attached to sp^2/sp^3 hybridized carbon network that are responsible for its hydrophilic character and chemical reactivity [23–26]. Recently, there were several reports on the role of GO as adsorbent, electron acceptor and photosensitizer for the enhancement of photodecomposition [27, 28]. TiO_2/GO composites are widely used for the photocatalytic degradation of organic pollutants such as dyes and antibiotics [29, 30]. Incorporation of GO enhances the adsorptive property of TiO_2 and hinder the recombination of electron–hole pairs through the movement of photo-excited electron to the GO surface [31].

Literature reports several studies related to the photocatalytic activity of $\text{TiO}_2/\text{kaolin}$ and TiO_2/GO nanocomposites. However, kaolin-graphene carboxyl incorporated TiO_2 nanoparticles and their photocatalytic activity under solar light are hardly reported. Here, we have made an attempt to synthesize $\text{TiO}_2/\text{kaolin}$ -graphene carboxyl nanocomposite to attain a synergistic effect of $\text{TiO}_2/\text{kaolin}$ and $\text{TiO}_2/\text{graphene}$ carboxyl to improve the photocatalytic efficiency under solar light. This novel system is an efficient solar light active photocatalyst which employs more visible light instead of artificial UV light for the photocatalytic degradation of methylene blue and cefuroxime sodium in surface water. To the best of our knowledge, the photocatalytic degradation pathway of cefuroxime sodium under solar radiation has not been reported yet. Hence in this study, we present a plausible photocatalytic degradation pathway for cefuroxime sodium through mass spectral analysis.

2 Experimental section

2.1 Materials

Analytical grade titanium(IV) isopropoxide ($\text{Ti}[\text{OC}_3\text{H}_7]_4$), kaolin clay, graphene carboxyl and methylene blue dye were purchased from Sigma Aldrich. The antibiotic cefuroxime sodium was provided by Sance Laboratories Pvt. Ltd. All

chemicals were used without further purification. Distilled water was used throughout the experiments.

2.2 Synthesis of photocatalysts

Kaolin-graphene carboxyl (KG) was synthesized as reported in the literature [32]. $\text{TiO}_2/\text{kaolin}$ -graphene carboxyl nanocomposite was synthesized by hydrothermal reaction using titanium isopropoxide as starting material. To 3.0 mL of titanium isopropoxide, appropriate amount of water was added with vigorous stirring until the formation of white precipitate was ceased. A calculated amount of KG (1, 2, 3, 4, 5 wt%) dispersed in distilled water was added to the above solution and was stirred for 1 h. After adjusting the pH to 7.0, the mixture was transferred to a stainless-steel autoclave with Teflon liner and was placed in an oven for hydrothermal treatment. The reaction was proceeded at 180 °C for 4 h and after the completion of autoclaving treatment, the autoclave was allowed to cool naturally. The obtained powders were filtered, washed, and dried at 80 °C. The samples were designated as TKG1, TKG2, TKG3, TKG4 and TKG5 based on the wt% of KG in TiO_2 . The same procedure was followed for the synthesis of nano TiO_2 except the step involving the addition of KG.

2.3 Characterizations

IR spectra of the synthesized samples were analyzed in a Perkin Elmer spectrum Two FT-IR Spectrophotometer in the range 4000–400 cm^{-1} . X-ray diffraction patterns (XRD) were obtained on a Rigaku Miniflex 600 diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.15418 \text{ nm}$) radiation in the range of 10°–80°. Transmission electron microscopic image (TEM) of the sample was obtained on a Jeol/JEM-2100 field emission electron microscope.

Scanning electron microscopy combined with Energy dispersive X-ray spectroscopy analysis (SEM–EDX) of the sample were collected using a Jeol 6390LA/OXFORD XMX N instrument. Thermogravimetry measurements (TG) were carried out using Perkin Elmer Diamond TG/DTA equipment. The diffuse reflectance spectra (DRS) of the samples were performed using a UV-2600 Shimadzu UV–Visible spectrophotometer. The photoluminescence (PL) spectral measurements were made using Fluorolog Horiba spectrofluorometer. Systronics 2203 Double beam UV–Vis spectrophotometer was used to assess the photocatalytic activity of the nanocomposites.

2.4 Photocatalytic activity measurement

The photocatalytic properties of the synthesized nanocomposites were evaluated by monitoring the degradation of methylene blue (MB) dye using Heber solar simulator

(Heber Scientific, model no: HMV-88123) which consists of visible light source (tungsten halogen lamp) and UV light source (mercury vapor lamp) with A.M 1.5 G filter. In each experiment, 0.1 g of photocatalyst was dispersed in 20 mL of 50 ppm MB aqueous solution. The suspension was initially stirred in dark for 30 min and then exposed to solar irradiation for 40 min to study its photocatalytic degradation under sunlight. The samples were collected at regular time intervals and the separation of photocatalyst was achieved by high-speed centrifugation. The absorbance of MB solution was then analyzed using a Systronics 2203 Double beam spectrophotometer at λ_{max} 660 nm. There was no measurable degradation for MB in the absence of TiO_2 or solar irradiation alone.

The amount of dye degradation was calculated using the equation $\frac{C_0 - C_t}{C_0} \times 100$, where C_0 and C_t represent the concentration of the dye-composite solution mixture initially and after a time t , respectively.

The most active catalyst (TKG4) was used for the degradation of the antibiotic cefuroxime sodium (CS). Photocatalytic degradation was studied by dispersing 0.1 g of the photocatalyst in 30 mL of 50 ppm cefuroxime sodium aqueous solution. To reach adsorption–desorption equilibrium, the resulting suspension was stirred in the dark for 30 min before solar light illumination. The samples were collected at regular time intervals and the photocatalyst was separated by high-speed centrifugation. The absorbance of cefuroxime sodium was measured at 274 nm using a Systronics 2203 Double beam spectrophotometer. To confirm the complete degradation of cefuroxime sodium using TKG4 photocatalyst and to recognize the reaction intermediates formed during the degradation process, the antibiotic containing water (treated with photocatalyst) after 45 min and 90 min of solar irradiation were examined by liquid chromatography-mass spectroscopy (LC–MS). Electrospray ionization in positive ion mode (ES+) was performed to obtain the mass spectra. The mobile phase used for the LC–MS analysis were 0.1% formic acid in water and acetonitrile in gradient mode. The flow rate was 0.3 mL/min and injection volume was 10 μL . The mass spectra analysis provided information regarding various intermediates produced during CS degradation which aids in proposing a degradation pathway.

The active radical species involved and their role on photocatalysis were inspected by trapping the active radicals using their respective scavengers. Isopropyl alcohol (IPA), ascorbic acid (AA) and triethanolamine (TEOA) were used as scavengers for hydroxyl free radicals ($\bullet\text{OH}$), superoxide anion radicals ($\bullet\text{O}_2^-$) and holes (h^+), respectively. The experimental process involves the addition of 1 mM of scavengers to 0.1 g of photocatalyst in MB solution (20 mL of 50 ppm MB). The mixture was then placed

under solar light irradiation and the degradation of MB was monitored at 660 nm in a UV–Vis spectrophotometer.

In order to confirm the formation of hydroxyl radicals ($\bullet\text{OH}$) during the photocatalytic process, a simple standard technique involving PL instrumentation was carried out using coumarin as a fluorescent probe. For this, 0.1 g of TKG4 is dispersed in 20 mL of 10^{-4} M coumarin aqueous solution and allowed to attain adsorption–desorption equilibrium. It was then kept under sunlight and the reaction solution was centrifuged to measure the photoluminescent intensity at an excitation wavelength of 332 nm after every 15 min of solar light irradiation.

3 Results and discussion

Different TiO_2 /kaolin-graphene carboxyl nanocomposites were synthesized by varying KG loading amounts to attain the best composition that shows good photocatalytic behavior. The samples were designated as TKG1, TKG2, TKG3, TKG4 and TKG5 for 1, 2, 3, 4 and 5 wt% of KG loading, respectively. The changes occurred in the structural/optical properties of TiO_2 with KG incorporation and the consequent alterations in the photocatalytic activities were investigated.

3.1 FT-IR analysis

The bonding between TiO_2 and kaolin-graphene carboxyl was examined by measuring the FT-IR spectra of KG, TiO_2 and TKG4 samples and the results are shown in Fig. 1. In the FT-IR spectra of KG, the bands in the range 3690–3618 cm^{-1} and 936, 911 cm^{-1} correspond to vibrations of inner and outer Al–OH bonds, respectively. Bands at 1114, 1029, 1006, 793 and 468 cm^{-1} fit to vibrations of Si–O bonds, and band positions at 750, 683, 535 cm^{-1} were attributed to vibrations of Si–O–Al^(IV) [33]. The peak at 1384 cm^{-1} belongs to the carboxyl (C–OH) bending vibration [34]. The peak at 1559 cm^{-1} corresponds to aromatic C=C group of graphene carboxyl. The absorption band observed in the range of 1600–1750 cm^{-1} corresponds to C=O stretching vibration of carboxylic acid groups attached to an aromatic ring structure [35]. The peak intensity at this range was not so prominent and this may due to the electrostatic interactions between the carboxylic groups of graphene carboxyl and the positively charged edge of kaolin and/or hydrogen bonding between the carboxylic groups and hydroxyl groups on the surface of kaolin [36].

In the IR spectra of TiO_2 , a broad peak observed at 3216 cm^{-1} and band with maximum at 1632 cm^{-1} can be assigned to stretching and bending vibration of hydroxyl (OH) groups present on the surface TiO_2 nanoparticles, respectively [37, 38]. The bands at 714, 530, 440 and

Fig. 1 FT-IR spectra of **a** KG, **b** TiO₂ and **c** TKG4

411 cm⁻¹ belong to the Ti–O stretching mode of the anatase TiO₂ [39].

In the TKG4 spectrum, it is possible to spot the majority of the TiO₂ and KG peaks previously assigned with small shift and different intensity. The new band appeared at 1090 cm⁻¹ could be originated from Ti–O–C vibration [40, 41]. The resemblance in the peak positions of the individual components and the TKG4 composite with little peak intensity variation and band shifts suggest that some sort of interaction must have taken place during hybrid formation. The bands of TKG4 exhibited at 1034 and 1010 cm⁻¹ are red shifted by 5 cm⁻¹ and 4 cm⁻¹, whereas bands at 784, 739, 526 and 463 cm⁻¹ are blue shifted by 9 cm⁻¹, 11 cm⁻¹, 9 cm⁻¹ and 5 cm⁻¹, respectively, as compared to those of KG, indicating that KG interacts directly with TiO₂.

3.2 XRD analysis

The XRD pattern of TiO₂ nanoparticles and TiO₂/kaolin-graphene carboxyl nanocomposites are shown in Fig. 2. The diffraction peaks of bare TiO₂ as well as TiO₂/kaolin-graphene carboxyl composites well matched with the anatase titania (JCPDS-21-1272). Characteristic peaks observed at 25.3° and 47.9° are associated with anatase phase of TiO₂ which possesses more open structure and large surface area required for superior photocatalytic activity [31]. The diffraction peaks at 25.31°, 37.92°, 47.99°, 54.31°, 62.72°, 69.36° and 75.09° can be indexed

to (101), (004), (200), (105), (204), (116) and (215) planes of anatase titania, respectively [31, 42]. The XRD pattern of KG was well matched to the standard pattern (JCPDS No. 14-0164) and displayed several peaks at 12.28°, 24.82°, 38.36°, 45.38° and 62.18° corresponded to the (0 0 1), (0 0 2), (− 2 0 2), (− 2 0 3) and (0 6 0) lattice planes of triclinic kaolinite [43]. The peak at 26.47° was due to crystalline silica [44]. The diffraction peak for graphene carboxyl is absent in the XRD spectrum of KG and this may be due to the exfoliation of the regular stacks of graphene carboxyl during KG preparation [45]. The XRD pattern of TiO₂/kaolin-graphene carboxyl nanocomposites demonstrated that TiO₂ was still present as an anatase phase in composite photocatalyst. There is no characteristic diffraction peak of KG in the TiO₂/kaolin-graphene carboxyl composites having upto 3 wt% KG incorporation, since the diffraction peaks of KG were submerged due to the strong diffraction peak of TiO₂. Further increase in KG content on TiO₂ exhibited small diffraction peaks at 12.28° and 26.47°.

The crystallite size of synthesized TiO₂ samples were studied using Scherrer's equation, $D_{\text{XRD}} \text{ (nm)} = 0.9\lambda/\beta \cos\theta$ where D_{XRD} is the crystallite size, λ is the wavelength of X-ray used, β and θ are full width at half maximum intensity (FWHM) (in radian) of XRD diffraction lines and half diffraction angle 2θ , respectively. There is no substantial change in the crystallite size of samples due to KG incorporation and is evident from Table 1.

Fig. 2 XRD patterns of the synthesized samples **a** KG, **b** TiO₂, **c** TKG1, **d** TKG2, **e** TKG3, **f** TKG4 and **g** TKG5

Table 1 Crystallite size of various samples

Samples	Crystallite size (D_{XRD}) nm
TiO ₂	6.70
TKG1	5.79
TKG2	5.72
TKG3	5.63
TKG4	5.81
TKG5	5.61

3.3 TEM analysis

The surface morphology of the synthesized samples was examined by TEM images. The TEM images of bare TiO₂ nanoparticles, KG and TKG4 are shown in Fig. 3 with their respective SAED patterns. The sizes of TiO₂ and TKG4 particles were in the 5–7 nm range. The Fig. 3a portrays the formation TiO₂ nanoparticles holding spherical shape and the SAED pattern (Fig. 3b) demonstrates well-defined concentric circles, which shows that the synthesized TiO₂ nanoparticles are polycrystalline [46]. Figure 3c and d represent the TEM image and SAED pattern of kaolin-graphene carboxyl sample (KG) which displayed flake like structure to provide a good platform for the loading of TiO₂ nanoparticles. From Fig. 3e, it is noticed that the KG surface was almost completely coated by TiO₂ with uniform dispersion and this a desired effect which provides a large specific surface area

for photocatalytic applications [20]. The SAED pattern of TKG4 sample (Fig. 3f) also exhibited several diffraction ring patterns, which confirms the polycrystalline nature of TKG4 nanocomposite. The sizes of TiO₂ and TKG4 particles obtained by the TEM image were analogous to the crystallite size determined by applying Scherrer equation to the XRD patterns.

3.4 SEM and EDX mapping images

The microstructure as well as the elemental composition of TiO₂/kaolin-graphene carboxyl (TKG4) nanocomposite photocatalyst were explored by SEM–EDX analysis (Fig. 4). The SEM image of TKG4 nanocomposite is shown in Fig. 4a and it demonstrates that KG surface is uniformly covered with TiO₂ nanoparticles. Additionally, the EDX results (Fig. 4b) of TKG4 displayed the existence of Ti and O elements of TiO₂ and Al, Si, O and C of kaolin-graphene carboxyl, that sturdily point to the successful development of TiO₂/kaolin-graphene carboxyl nanocomposite. The EDX mapping images (Fig. 4c) portrayed the formation of a well-dispersed composite material of Ti, O, Al, Si and C elements in the prepared TKG4 catalyst system, which is in good agreement with FT-IR, XRD, TEM and SEM results. The obtained results validate the intimate connection between TiO₂, kaolin and graphene carboxyl.

Fig. 3 TEM images of **a** TiO_2 , **c** KG, **e** TKG4 and **b**, **d**, **f** represents the respective SAED pattern

3.5 Thermal analysis

Figure 5 shows the thermogravimetric analysis (TGA) results for TiO_2 , KG and TKG4 samples recorded in the temperature range 30–1300 °C. The difference in the TGA curve of TKG4 with respect to TiO_2 , proposed the successful incorporation of KG in TiO_2 .

Thermogravimetric analysis of KG (Fig. 5a) shows a continuous weight loss up to 800 °C and the total weight loss is approximately 31%. The loss of weight

below 100 °C can be attributed to the elimination of free water between the particles and the weight loss occurs at 100–300 °C presumably because of the pyrolysis of labile oxygen-containing functional groups [47, 48]. Between 300 and 500 °C, there was a greater loss of mass due to the removal of constitution water (or structural water) and also because of the loss of stable oxygen functionalities on the surface of KG [47, 49]. Above 500 °C, the KG framework is almost completely degraded.

Fig. 4 EDX images of the samples: **a** SEM image, **b** EDX spectrum and **c** elemental mapping image of TKG4

With increasing temperature, TiO_2 nanoparticles displayed a gradual mass loss until $\sim 400^\circ\text{C}$ and there is a negligible weight loss at temperatures above 400°C (Fig. 5b), indicating the thermal stability of TiO_2 as reported in previous studies [50, 51]. Figure 5c clearly shows the increased thermal stability of kaolin-graphene carboxyl incorporated TiO_2 nanocomposite (TKG4). The weight loss from 30 to 150°C for pristine TiO_2 and TKG4 nanocomposite, is due to the removal of adsorbed and bound water on the nanocomposite [52]. The study validates the increased thermal stability of TKG4 compared to TiO_2 in the temperature range of $30\text{--}500^\circ\text{C}$. The weight loss of TKG4 at $30\text{--}500^\circ\text{C}$ was only about 15.95%, (less than 16.25% of the TiO_2) and this may be due to the enhancement of surface hydrophobicity, and reduction of water adsorption and fixation capacity after the incorporation of KG [53]. The sample shows only 18.32% weight loss up to 1300°C and the total weight loss is almost similar to TiO_2 (only 1.87% higher than that of TiO_2), which indicates that TKG4 is thermally stable due to the chemical bonding between TiO_2 and KG as evident from FT-IR

spectrum. The high thermal stability of TKG4 nanocomposite shows the strong affinity of KG for TiO_2 nanoparticles, which give rise to the formation of very efficient and stable TKG4 ternary nanocomposite.

3.6 Diffuse reflectance spectra

To investigate the role of KG on the optical absorption properties of TiO_2 , the UV–Visible diffuse reflectance spectra (UV–Vis DRS) of TiO_2 and TiO_2 /kaolin-graphene carboxyl samples were performed in the wavelength range of $350\text{--}600\text{ nm}$ and the results are depicted in Fig. 6. TiO_2 displayed an absorption edge at 393 nm which is in good agreement with the previous reports [54, 55]. From the figure, it is evident that the absorption edges were extended to visible light range with the incorporation of KG into TiO_2 matrix. Table 2 shows that the red shift is maximum (425 nm) in TKG4 (TiO_2 with 4 wt% KG) and further increase in KG content shows a decrease in red shift and visible light absorption.

Fig. 5 TGA curves of **a** KG, **b** TiO₂ and **c** TKG4

Fig. 6 The UV–Vis diffuse reflectance spectra of **a** TiO₂, **b** TKG1, **c** TKG2, **d** TKG3, **e** TKG4 and **f** TKG5

Table 2 Absorption edge and Band gap values of the synthesized samples

Samples	Absorption edge	Band gap value obtained from $E_g = 1239.8/\lambda$	Band gap value obtained from $(ah\nu)^2$ to $h\nu$ plot
TiO ₂	393	3.15	3.15
TKG1	405	3.06	3.05
TKG2	410	3.02	3.03
TKG3	417	2.97	2.97
TKG4	425	2.92	2.92
TKG5	413	3	3

To validate the band gap variation upon the addition of KG to TiO₂,

The band gap energies were calculated by the equation [56],

$$E_g = 1239.8/\lambda,$$

where ' E_g ' is the band gap (eV) and ' λ ' (nm) is the wavelength of the absorption edges in the spectrum.

It is possible to determine the nature of band gap using the power expression, $(ah\nu)^n = C(h\nu - E_g)$, where α is the absorbance, $h\nu$ is the absorption energy, C is the constant that depends on transition probability, E_g is the band gap energy and n denotes the nature of the transition, viz., $n = 2$ and $1/2$ for direct and indirect bandgaps, respectively [57]. Figure 7 depicts the plots of $(ah\nu)^2$ against photon energy ($h\nu$) and the band gap energies are in agreement to the onset energy noticed in the absorption spectra, validating that the band gap is ascribed to the direct transition (Table 2). The calculated band gap for nano TiO₂ is 3.15 eV which is in good agreement with the reported value for anatase [58]. The results demonstrate a significant influence of kaolin-graphene carboxyl in the optical characteristics, where an increase in KG amount narrows the band gap of TiO₂ up to 4 wt%. Further increase in KG content causes an increase in band gap value of TiO₂ as observed in TKG5 nanocomposite. The absorption spectrum of TiO₂/kaolin-graphene carboxyl nanocomposites show more absorption in the visible region than TiO₂ which points out the existence of surface states. The enhancement in light absorption might be due to the oxygen vacancies produced by KG incorporation, which form localization levels within the band gap [59]. The lower band gap energy along with significant red shift of absorption edge in TiO₂/kaolin-graphene carboxyl nanocomposites compared with TiO₂ may be beneficial for improving the visible light absorption and thereby photocatalytic efficiency under sunlight.

3.7 Photoluminescence studies

Photoluminescence studies are executed to explore the interfacial charge separation and the nature of defects involved during TiO₂/kaolin-graphene carboxyl nanocomposite formation [60]. The PL spectra of undoped TiO₂ and TiO₂/kaolin-graphene carboxyl nanocomposite at an excitation wavelength of 300 nm are depicted in Fig. 8. PL intensity of pristine TiO₂, particularly the band-edge emission (shallow surface state) is quite low because of ultrafast exciton recombination. Thus, very weak PL emission is detected around the 415–440 nm. The higher emission around 550 nm may be due to the exciton recombination at deep defect states (inset of Fig. 8). The radiative recombination of electrons via intrinsic surface states of TiO₂ nanoparticles is responsible for the generation of this visible luminescence band [61]. However, upon binding with KG, the shallow surface state emission at 415–440 nm becomes stronger, indicating the exciton-recombination is much slower. All KG loaded samples (except TKG1, where KG content is low) could display strong PL signal in the range 400–500 nm and show a noticeable PL peak at about 417 nm and 440 nm which mainly results from band edge free excitons and binding excitons, respectively [62, 63].

The PL intensity gradually increased when KG content was changed from 1 to 5 wt%. Since the size of nanoparticles was fine, there may be numerous oxygen vacancies on the surface of TiO₂ nanoparticles with KG loading which very easily bind electrons to form excitons so that the average distance in which the electrons could move freely was very short. Hence, an exciton energy level would be developed near the bottom of the conduction band and the PL band of the excitons occur. The stronger excitonic PL spectrum denotes the presence of defects and surface oxygen vacancies [62]. The oxygen vacancies and defects trap photogenerated electrons, impeding the recombination of photoinduced charge carriers (electrons and holes) and thereby favors photocatalytic reactions [64]. Instantaneously, oxygen vacancies are beneficial in stimulating the oxygen adsorption and the photoinduced electrons bound by oxygen vacancies possess strong tendency to interact with this adsorbed oxygen. Thus, oxygen vacancies and defects promote photocatalytic degradation processes in which oxygen energetically supports the oxidation of organic substances [64].

According to this study, the KG incorporated TiO₂ samples can efficiently hinder the recombination rate of photoinduced charge carriers relative to TiO₂ resulting in the enhancement of photocatalytic activity. The surface defects and oxygen vacancies provide large number of active sites for pollutant adsorption and trap electrons triggering efficient separation of photoinduced charge carriers for better photocatalytic activity of TiO₂/kaolin-graphene carboxyl nanocomposite [65].

Fig. 7 Plot of $(\alpha h\nu)^2$ against photon energy ($h\nu$) of **a** TiO₂, **b** TKG1, **c** TKG2, **d** TKG3, **e** TKG4 and **f** TKG5

3.8 Photocatalytic activity

The photocatalytic activity of TiO₂ and KG modified TiO₂ samples were evaluated on the basis of degradation of methylene blue under solar light and the results are depicted in Fig. 9. The pristine TiO₂ exhibited low photocatalytic activity, which was observed to be enhanced by kaolin-graphene carboxyl incorporation. It is also noted that KG amount in the sample has an imperative role in increasing photocatalytic efficiency. The activity of different samples under

sunlight is in the order TKG4 > TKG3 > TKG5 > TKG2 > TKG1 > TiO₂. Modification of TiO₂ with KG caused the efficient suppression of the electron–hole recombination and enhanced the surface adsorption of chemical molecules and hence improved the photocatalytic performance. The synergic effect of adsorptive capacity of KG and catalytic ability of TiO₂ enhanced the photocatalytic activity. The optimum KG content in TiO₂ for getting maximum photocatalytic activity is 4 wt% which gives more than 90% MB degradation after 40 min irradiation. The UV–Vis absorption spectra

Fig. 8 Photoluminescence spectrum of **a** TiO₂, **b** TKG1, **c** TKG2, **d** TKG3, **e** TKG4 and **f** TKG5 (inset shows the enlarged photoluminescence spectrum of TiO₂, TKG1 and TKG2 nanocomposite)

of MB solution catalyzed by TKG4 nanocomposite is shown in Fig. 9 (inset). Photocatalytic activity is decreased with further increase in the KG content (> 4 wt%) as observed in the photocatalytic efficiency of TKG5 (Fig. 9h). When the amount of KG is increased above 4 wt%, the degradation of methylene blue is found to be decreased due to the presence of bulk oxygen vacancies. According to Kang et al. surface oxygen vacancies act as charge carrier traps in addition to its role as adsorption sites and masks the surface charge recombination, while bulk oxygen vacancies have a tendency to serve as charge carrier traps where the $e^- - h^+$ recombination happens [66].

The order of photocatalytic efficiency of different samples are supported by DRS spectra. TiO₂ shows a lower photocatalytic efficiency under sunlight due to its wide band gap, where UV radiation is required for exciting electrons from valence band to conduction band. But majority of sunlight constitutes visible light and only 3–5% is UV radiation which rules out the use of TiO₂ as solar light active photocatalyst. In bare TiO₂, the absence of intermediate level to trap the conduction band electrons of TiO₂ and the rapid recombination of photogenerated electrons and holes reduce the availability of free electrons and holes for photocatalysis and consequently leads to its lower photocatalytic

efficiency. When KG was introduced into TiO₂ nanoparticles, the absorption edge of TiO₂ shifted to wider wavelength region, which was in favor of KG incorporated TiO₂ nanocomposites to absorb visible light. The high activity of KG incorporated TiO₂ samples is mainly attributed to the decrease in band gap (3.15–2.92 eV) so that visible light is enough to excite electron from valence band to conduction band. KG could also perform as an effective electron scavenger to trap the conduction band electrons of TiO₂.

The photocatalytic degradation of the non-biodegradable pharmaceutical pollutant cefuroxime sodium was investigated using the most active photocatalyst TKG4 and the results are depicted in Fig. 10. In 90 min of photoirradiation, complete degradation of cefuroxime sodium would be expected as the absorption maxima falls near to zero as in Fig. 10. To examine the various intermediates produced and possible reaction pathways, sample was withdrawn at 0, 45 and 90 min and are designated as S₀, S₄₅ and S₉₀, respectively. The mass spectra of these samples were recorded with LC–MS system at electrospray ionization, which is ideal for cephalosporin antibiotics.

Spectrum of the sample S₄₅ recorded the presence of cefuroxime sodium (CS) base peak (m/z 447), but at very low relative intensity compared to the intensity of the base

Fig. 9 Photocatalytic degradation of MB in presence of **a** light only, **b** KG, **c** TiO₂, **d** TKG1, **e** TKG2, **f** TKG3, **g** TKG4 and **h** TKG5 (inset shows the UV–Vis absorption spectra of the time dependent photodegradation of MB in the presence of TKG4)

Fig. 10 UV–Vis absorption spectra of the time dependent photodegradation of cefuroxime sodium in the presence of TKG4 (inset shows the photocatalytic degradation of cefuroxime sodium in the presence of TKG4)

peak in the initial sample (S0). This indicates that the photodegradation of cefuroxime sodium was not completed in 45 min. However, the base peak of cefuroxime sodium was

disappeared in S90 sample, which confirm that the original structure of cefuroxime sodium was destroyed during the irradiation process. Scheme 1 shows the degradation

Scheme 1 Degradation pathway of cefuroxime sodium

pathway and possible intermediates formed during photocatalytic degradation of cefuroxime sodium using TKG4 system.

In the mass spectral analysis of the sample (S0), cefuroxime sodium with a molecular mass of 446 was detected at m/z 447 (A). Fascinatingly, in this sample the major species present is of intermediate 'B' with m/z 364 which changes to C (m/z 336) by losing CO group. Another peak at m/z 442, due to the hydrolysis of beta-lactam moiety shows the presence of intermediate F.

The mass spectrum recorded a weak parent ion peak in sample taken after 45 min of photocatalysis and only small amount of CS was expected in this sample. The mass spectrum of S45 sample shown the presence of a number of ring opened intermediates D, E, G, K, L, M, N (with m/z 209, 181, 398, 170, 276, 140, 115, respectively). The possibility of the structure for the ion at m/z 209 is due to the beta ring cleavage of intermediate C and the ion at m/z 209 losses carbonyl group ensuing ion at m/z 181(E). The removal of CO_2 group from intermediate F results G which is susceptible to further scissions. The structure proposed for the ion at m/z 170 and m/z 276 corresponding to the cleavage of

the beta ring of CS demonstrates the possibility for another degradation pathway.

The irradiation was continued for further 45 min and sample S90 was drawn to record LC–MS spectrum. In this sample (S90), the peaks corresponding to CS was not observed but shows peaks corresponding to fragments. The C–C single bond between the six membered ring and the chains in the fragment ion at m/z 398 was broken forming intermediate ions E (m/z 181), H (m/z 144), I (m/z 75). With the increasing of degradation time, the species H (m/z 144) was degraded to J (m/z 99), CO_2 and H_2O [67]. The evaluation of the outcomes of the spectra obtained for the samples, S45 and S90, gives an understanding about the degradation pathway of cefuroxime sodium by solar photocatalysis in presence of kaolin-graphene carboxyl incorporated TiO_2 nanocomposite.

The HPLC method (with UV detection at 254 nm) was used to further evaluate the changes of the cefuroxime sodium and the results were shown in Fig. 11. It is evident from figure that the peak observed for cefuroxime sodium at the beginning of degradation disappeared after 90 min of solar irradiation suggesting that cefuroxime sodium would be degraded to CO_2 , H_2O and other molecules. These results displayed the ability of 4 wt% kaolin-graphene carboxyl

Fig. 11 HPLC (254 nm) chromatograms of cefuroxime sodium solution in the presence of TKG4 during different degradation times under visible light

Fig. 12 Mechanism of pollutant degradation using TKG4 under sunlight

incorporated TiO₂ in leading the photoreaction forward with the assistance of direct sunlight. The TKG4 catalytic system helped the quicker deterioration of cefuroxime sodium, in which kaolin-graphene carboxyl acts as an efficient support for TiO₂ photocatalyst.

3.9 Proposed mechanism of pollutant degradation in presence of TKG4 nanocomposite

The adsorption of pollutants on the surface of photocatalysts, light absorption in UV as well as visible region and the generation and separation of photoinduced excitons are of utmost significance for the photocatalytic degradation of pollutants. When the charge separation is preserved, the electrons and holes can move to the photocatalytic surface and join in redox reactions with the adsorbed pollutant molecule. From the outcomes of this work, a plausible mechanism is predicted and the schematic representation is shown in Fig. 12. Pollutant molecules initially gets adsorbed to TiO₂/kaolin-graphene carboxyl surface and later undergo degradation in situ from its surface. Graphene carboxyl possess outstanding electronic transmission ability, which can effectually hinder the electron–hole pairing of TiO₂ and progress the photocatalytic efficiency [54]. Kaolin having good adsorption property makes available a large number of hydroxyl groups on its surface, which leads to the increased production of •OH via its reaction with holes. The •OH thus produced is capable to attack the pollutants adsorbed on the TiO₂/kaolin-graphene carboxyl nanocomposite surface and further decompose these pollutants to CO₂ and H₂O due to its strong oxidation ability. Molecular oxygen in ambient atmosphere combines with electrons from the conduction band of TiO₂ to generate •O²⁻ radicals. The photogenerated holes (h⁺), •O²⁻ and •OH radicals thus produced are mostly accountable for the degradation of organic pollutants by their consecutive attacks through formation of numerous intermediate products. The overall reaction may be summarized as,

Fig. 13 **a** The percentage degradation of MB in the presence of TKG4 and different radical scavengers and **b** PL spectral changes observed during solar light irradiation of TKG4 dispersed in 10⁻⁴ M coumarin aqueous solution

Scavenging studies were employed as a method to differentiate the contribution of each active species to photocatalytic activity of TiO₂/kaolin-graphene carboxyl nanocomposite. The active species accountable for the photocatalytic degradation of MB were probed by introducing specific scavengers, such as isopropyl alcohol (IPA), ascorbic acid (AA) and triethanolamine (TEOA) into the dye solution. Figure 13a illustrates the influence of various active species scavengers on the photocatalytic dye degradation in presence

of the synthesized photocatalyst under sunlight. IPA, AA and TEOA were reported as scavengers for hydroxyl free radicals ($\bullet\text{OH}$), superoxide anion radicals ($\bullet\text{O}^{2-}$) and holes (h^+), respectively. From the figure, it is clear that, the active species such as hydroxyl radical, superoxide anion radical, holes etc. play significant role in the photocatalytic degradation of pollutants. Using IPA as trapping agent, the photocatalytic reaction decreases drastically which shows that hydroxyl radical plays an important role in the photodegradation of the dye. The photocatalytic dye degradation was significantly reduced by the addition of IPA and AA whereas the addition of TEOA results only a slight reduction in photocatalytic activity. The trapping experiment confirmed that $\bullet\text{O}^{2-}$, $\bullet\text{OH}$ and h^+ all make impact on the photocatalytic reaction, and $\bullet\text{OH}$ is the main active species.

The presence of hydroxyl radicals ($\bullet\text{OH}$) as the active species during the photocatalytic process was further confirmed using coumarin as a fluorescent probe [68, 69]. For this, TKG4 and coumarin suspension was irradiated under sunlight and coumarin changes to 7-hydroxycoumarin as hydroxyl radicals are formed in the system, upon irradiation. This reaction has been exploited for identifying $\bullet\text{OH}$ formed in a photocatalytic system by measuring the photoluminescent intensity of the clear solution after centrifugation, at an excitation wavelength of 332 nm. Figure 13b gives the PL intensity after every 15 min of solar light irradiation of TKG4 and coumarin suspension. The obtained spectra displayed maximum PL intensity at 450 nm which is analogous with that of standard 7-hydroxycoumarin. From the figure, it is evident that there is a direct upsurge in photoluminescent intensity with increasing irradiation time and there was no enhancement in PL intensity in the absence of photocatalyst or irradiation. This study validates the active participation of hydroxyl radicals during photodegradation of pollutants using the as synthesized TiO_2 /kaolin-graphene carboxyl nanocomposite.

3.10 Recycling capacity of the catalyst

The reproducibility of photocatalysts is an important aspect for its practical application. For investigating the reproducibility of the synthesized photocatalyst TKG4, degradation studies on MB were conducted in five repeated experimental cycles while maintaining the same reaction settings (0.1 g catalyst + 20 mL of 50 ppm MB, 40 min of solar irradiation). After each experiment, the catalyst was segregated by centrifugation and then dried prior to subsequent experimental cycles. Figure 14a depicts that the catalyst is strong enough to degrade MB even after five cyclic runs. The FT-IR spectra of the photocatalyst recycled after five experimental runs is also identical to that of the fresh photocatalyst (Fig. 14b),

Fig. 14 **a** Cyclic runs of TKG4 for the degradation of MB under solar irradiation and **b** FT-IR spectra of TKG4 photocatalyst before and after five cyclic runs

signifying the stability, recoverability and reusability of the composite photocatalyst.

4 Conclusion

In summary, novel TiO_2 -kaolin-graphene carboxyl nanocomposite materials were developed via a facile one step hydrothermal method and were used for the degradation of the dye methylene blue and the cephalosporin antibiotic, cefuroxime sodium. We found that kaolin-graphene carboxyl incorporation prevented the recombination of photoexcited charge carriers, shifted the absorption edge to visible region, improved the visible light absorption and reduced the band gap of TiO_2 . Among various KG modified samples, TKG4 (TiO_2 with 4 wt% KG) showed highest photocatalytic efficiency and the sample gave near complete degradation for methylene blue and cefuroxime sodium within 40 min and 90 min, respectively. Radical scavenger experiment identified hydroxyl radicals, superoxide radicals and holes as reactive species and the most active species is found to be

hydroxyl radical. Thus, the study suggests the application of TiO₂-kaolin-graphene carboxyl nanocomposite for the mineralization of non-biodegradable dyes and antibiotics like cefuroxime sodium with the aid of solar light.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Ethics approval Not applicable.

Consent to participate Not applicable.

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References

1. Rathee, G., Singh, N., & Chandra, R. (2020). Simultaneous elimination of dyes and antibiotic with a hydrothermally generated NiAlTi layered double hydroxide adsorbent. *ACS Omega*, 5(5), 2368–2377. <https://doi.org/10.1021/acsomega.9b03785>
2. Jamee, R., & Siddique, R. (2019). Biodegradation of synthetic dyes of textile effluent by microorganisms: An environmentally and economically sustainable approach. *European Journal of Microbiology and Immunology*, 9(4), 114–118. <https://doi.org/10.1556/1886.2019.00018>
3. Ribeiro, A. R., Sures, B., & Schmidt, T. C. (2018). Cephalosporin antibiotics in the aquatic environment: A critical review of occurrence, fate, ecotoxicity and removal technologies. *Environmental Pollution*, 241, 1153–1166. <https://doi.org/10.1016/j.envpol.2018.06.040>
4. Kraemer, S. A., Ramachandran, A., & Perron, G. G. (2019). Antibiotic pollution in the environment: From microbial ecology to public policy. *Microorganisms*, 7(6), 180. <https://doi.org/10.3390/microorganisms7060180>
5. Wozniak, T. J., & Hicks, J. R. (1991). Analytical profile of cefuroxime sodium. *Analytical Profiles of Drug Substances*, 20, 209–236. [https://doi.org/10.1016/S0099-5428\(08\)60532-8](https://doi.org/10.1016/S0099-5428(08)60532-8)
6. Anjum, M., Miandad, R., Waqas, M., Gehany, F., & Barakat, M. A. (2019). Remediation of wastewater using various nano-materials. *Arabian Journal of Chemistry*, 12(8), 4897–4919. <https://doi.org/10.1016/j.arabjc.2016.10.004>
7. Ferroudj, N., Nzimoto, J., Davidson, A., Talbot, D., Briot, E., Dupuis, V., Bée, A., Medjram, M. S., & Abramson, S. (2013). Maghemite nanoparticles and maghemite/silica nanocomposite microspheres as magnetic Fenton catalysts for the removal of water pollutants. *Applied Catalysis B: Environmental*, 136, 9–18. <https://doi.org/10.1016/j.apcatb.2013.01.046>
8. Rasheed, T., Bilal, M., Nabeel, F., Adeel, M., & Iqbal, H. M. N. (2019). Environmentally-related contaminants of high concern: Potential sources and analytical modalities for detection, quantification, and treatment. *Environment International*, 122, 52–66. <https://doi.org/10.1016/j.envint.2018.11.038>
9. Yang, C., Li, Q., Tang, L., Bai, A., Song, H., & Yu, Y. (2016). Monodispersed colloidal zinc oxide nanospheres with various size scales: Synthesis, formation mechanism, and enhanced photocatalytic activity. *Journal of Materials Science*, 51(11), 5445–5459. <https://doi.org/10.1007/s10853-016-9848-0>
10. Irandost, M., Akbarzadeh, R., Pirsaeheb, M., Asadi, A., Mohammadi, P., & Sillanpää, M. (2019). Fabrication of highly visible active N, S co-doped TiO₂@ MoS₂ heterojunction with synergistic effect for photocatalytic degradation of diclofenac: Mechanisms, modeling and degradation pathway. *Journal of Molecular Liquids*, 291, 111342. <https://doi.org/10.1016/j.molliq.2019.111342>
11. Pawar, M., Topcu Sandoğdular, S., & Gouma, P. (2018). A brief overview of TiO₂ photocatalyst for organic dye remediation: Case study of reaction mechanisms involved in Ce-TiO₂ photocatalysts system. *Journal of Nanomaterials*, 2018, 5953609. <https://doi.org/10.1155/2018/5953609>
12. Khan, M., Yi, Z., Gul, S. R., Wang, Y., & Fawad, U. (2017). Visible-light-active silver-, vanadium-codoped TiO₂ with improved photocatalytic activity. *Journal of Materials Science*, 52(10), 5634–5640. <https://doi.org/10.1007/s10853-017-0798-y>
13. Liao, C., Li, Y., & Tjong, S. C. (2020). Visible-light active titanium dioxide nanomaterials with bactericidal properties. *Nanomaterials*, 10(1), 124. <https://doi.org/10.3390/nano10010124>
14. Chong, M. N., Vimonse, V., Lei, S., Jin, B., Chow, C., & Saint, C. (2009). Synthesis and characterisation of novel titania impregnated kaolinite nano-photocatalyst. *Microporous and Mesoporous Materials*, 117(1–2), 233–242. <https://doi.org/10.1016/j.micromeso.2008.06.039>
15. Wang, C., Shi, H., Zhang, P., & Li, Y. (2011). Synthesis and characterization of kaolinite/TiO₂ nano-photocatalysts. *Applied Clay Science*, 53(4), 646–649. <https://doi.org/10.1016/j.clay.2011.05.017>
16. Li, X., Peng, K., Chen, H., & Wang, Z. (2018). TiO₂ nanoparticles assembled on kaolinites with different morphologies for efficient photocatalytic performance. *Scientific Reports*, 8(1), 11663. <https://doi.org/10.1038/s41598-018-29563-8>
17. da Silva Lopes, J., Rodrigues, W. V., Oliveira, V. V., Braga, A. D. N. S., da Silva, R. T., França, A. A. C., da Paz, E. C., Osajima, J. A., & da Silva Filho, E. C. (2019). Modification of kaolinite from Pará/Brazil region applied in the anionic dye photocatalytic discoloration. *Applied Clay Science*, 168, 295–303. <https://doi.org/10.1016/j.clay.2018.11.028>
18. Štengl, V., Popelková, D., & Grygar, T. M. (2014). Composite pigments based on surface coated kaolin and metakaolin. *Applied Clay Science*, 101, 149–158. <https://doi.org/10.1016/j.clay.2014.07.030>
19. Li, X., & Tang, A. (2016). Pd modified kaolinite nanocomposite as a hydrogenation catalyst. *RSC Advances*, 6(19), 15585–15591. <https://doi.org/10.1039/C5RA25387J>
20. Henych, J., & Štengl, V. (2013). Feasible synthesis of TiO₂ deposited on kaolin for photocatalytic applications. *Clays and Clay Minerals*, 61(3), 165–176. <https://doi.org/10.1346/CCMN.2013.0610301>
21. Adly, M. S., El-Dafrawy, S. M., & El-Hakam, S. A. (2019). Application of nanostructured graphene oxide/titanium dioxide composites for photocatalytic degradation of rhodamine B and acid green 25 dyes. *Journal of Materials Research and Technology*, 8(6), 5610–5622. <https://doi.org/10.1016/j.jmrt.2019.09.029>

22. Li, X., Yang, S., Sun, J., He, P., Xu, X., & Ding, G. (2014). Tungsten oxide nanowire-reduced graphene oxide aerogel for high-efficiency visible light photocatalysis. *Carbon*, 78, 38–48. <https://doi.org/10.1016/j.carbon.2014.06.034>
23. Rosu, M. C., Coros, M., Pogacean, F., Magerusan, L., Socaci, C., Turza, A., & Pruneanu, S. (2017). Azo dyes degradation using TiO₂-Pt/graphene oxide and TiO₂-Pt/reduced graphene oxide photocatalysts under UV and natural sunlight irradiation. *Solid State Sciences*, 70, 13–20. <https://doi.org/10.1016/j.solidstatesciences.2017.05.013>
24. Dreyer, D. R., Park, S., Bielawski, C. W., & Ruoff, R. S. (2010). The chemistry of graphene oxide. *Chemical Society Reviews*, 39(1), 228–240. <https://doi.org/10.1039/b917103g>
25. Krishnamoorthy, K., Veerapandian, M., Yun, K., & Kim, S. J. (2013). The chemical and structural analysis of graphene oxide with different degrees of oxidation. *Carbon*, 53, 38–49. <https://doi.org/10.1016/j.carbon.2012.10.013>
26. Adán-Más, A., & Wei, D. (2013). Photoelectrochemical properties of graphene and its derivatives. *Nanomaterials*, 3(3), 325–356. <https://doi.org/10.3390/nano3030325>
27. Azira, N. M. N., Murizam, D., Halin, D. S. C., Idris, M. A., & Yunus, N. F. M. (2020). Preliminary study of hydrothermal synthesis of TiO₂-GO composites as a high performance photocatalyst. *IOP Conference Series: Materials Science and Engineering*, 957(1), 012041. <https://doi.org/10.1088/1757-899X/957/1/012041>
28. Nguyen-Phan, T. D., Pham, V. H., Shin, E. W., Pham, H. D., Kim, S., Chung, J. S., Kim, E. J., & Hur, S. H. (2011). The role of graphene oxide content on the adsorption-enhanced photocatalysis of titanium dioxide/graphene oxide composites. *Chemical Engineering Journal*, 170(1), 226–232. <https://doi.org/10.1016/j.cej.2011.03.060>
29. Najafi, M., Kermanpur, A., Rahimpour, M. R., & Najafizadeh, A. (2017). Effect of TiO₂ morphology on structure of TiO₂-graphene oxide nanocomposite synthesized via a one-step hydrothermal method. *Journal of Alloys and Compounds*, 722, 272–277. <https://doi.org/10.1016/j.jallcom.2017.06.001>
30. Zhen, Q., Gao, L., Sun, C., Gong, H., Hu, P., Song, S., & Li, R. (2018). Honeycomb-like TiO₂@ GO nanocomposites for the photodegradation of oxytetracycline. *Materials Letters*, 228, 318–321. <https://doi.org/10.1016/j.matlet.2018.06.041>
31. Khan, S. A., Arshad, Z., Shahid, S., Arshad, I., Rizwan, K., Sher, M., & Fatima, U. (2019). Synthesis of TiO₂/Graphene oxide nanocomposites for their enhanced photocatalytic activity against methylene blue dye and ciprofloxacin. *Composites Part B: Engineering*, 175, 107120. <https://doi.org/10.1016/j.compositesb.2019.107120>
32. He, K., Chen, G., Zeng, G., Chen, A., Huang, Z., Shi, J., Peng, M., Huang, T., & Hu, L. (2018). Enhanced removal performance for methylene blue by kaolin with graphene oxide modification. *Journal of the Taiwan Institute of Chemical Engineers*, 89, 77–85. <https://doi.org/10.1016/j.jtice.2018.04.013>
33. Kutláková, K. M., Tokarský, J., Kovář, P., Vojtěšková, S., Kovářová, A., Smetana, B., Kukutschová, J., Čapková, P., & Matějka, V. (2011). Preparation and characterization of photoactive composite kaolinite/TiO₂. *Journal of Hazardous Materials*, 188(1–3), 212–220. <https://doi.org/10.1016/j.jhazmat.2011.01.106>
34. Zhang, H., Wang, X., Li, N., Xia, J., Meng, Q., Ding, J., & Lu, J. (2018). Synthesis and characterization of TiO₂/graphene oxide nanocomposites for photoreduction of heavy metal ions in reverse osmosis concentrate. *RSC Advances*, 8(60), 34241–34251. <https://doi.org/10.1039/C8RA06681G>
35. Pan, N., Guan, D., Yang, Y., Huang, Z., Wang, R., Jin, Y., & Xia, C. (2014). A rapid low-temperature synthetic method leading to large-scale carboxyl graphene. *Chemical Engineering Journal*, 236, 471–479. <https://doi.org/10.1016/j.cej.2013.10.060>
36. Sun, W., Wang, C., Pan, W., Li, S., & Chen, B. (2017). Effects of natural minerals on the adsorption of 17β-estradiol and bisphenol A on graphene oxide and reduced graphene oxide. *Environmental Science: Nano*, 4(6), 1377–1388. <https://doi.org/10.1039/C7EN00295E>
37. Dodoo-Arhin, D., Buabeng, F. P., Mwabora, J. M., Amaniampong, P. N., Agbe, H., Nyankson, E., Obada, D. O., & Asiedu, N. Y. (2018). The effect of titanium dioxide synthesis technique and its photocatalytic degradation of organic dye pollutants. *Heliyon*, 4(7), e00681. <https://doi.org/10.1016/j.heliyon.2018.e00681>
38. Devi, R. S., Venkatesh, R., & Sivaraj, R. (2014). Synthesis of titanium dioxide nanoparticles by sol-gel technique. *International Journal of Innovative Research in Science, Engineering and Technology*, 3(8), 15206–15211. <https://doi.org/10.15680/IJIRSET.2014.0308020>
39. Mahalingam, T., Selvakumar, C., Kumar, E. R., & Venkatachalam, T. (2017). Structural, optical, morphological and thermal properties of TiO₂-Al and TiO₂-Al₂O₃ composite powders by ball milling. *Physics Letters A*, 381(21), 1815–1819. <https://doi.org/10.1016/j.physleta.2017.02.053>
40. Ramos, D. K. C., González, M. V., Muñoz, R. A. E., Cruz, J. S., De Moure-Flores, F. J., & Mayén-Hernández, S. A. (2020). Obtaining and characterization of TiO₂-GO composites for photocatalytic applications. *International Journal of Photoenergy*, 2020, 3489218. <https://doi.org/10.1155/2020/3489218>
41. Ashkarran, A. A., Fakhari, M., Hamidinezhad, H., Haddadi, H., & Nourani, M. R. (2015). TiO₂ nanoparticles immobilized on carbon nanotubes for enhanced visible-light photo-induced activity. *Journal of Materials Research and Technology*, 4(2), 126–132. <https://doi.org/10.1016/j.jmrt.2014.10.005>
42. Veer, D. H., Singh, R. M., & Kumar, H. (2017). Structural and optical characterization of ZnO-TiO₂-SiO₂ nanocomposites synthesized by sol-gel technique. *Asian Journal of Chemistry*, 29, 2391–2395. <https://doi.org/10.14233/AJCHEM.2017.20690>
43. Sun, Z., Li, C., Du, X., Zheng, S., & Wang, G. (2018). Facile synthesis of two clay minerals supported graphitic carbon nitride composites as highly efficient visible-light-driven photocatalysts. *Journal of Colloid and Interface Science*, 511, 268–276. <https://doi.org/10.1016/j.jcis.2017.10.005>
44. Salahudeen, N. (2018). Metakaolinization effect on the thermal and physicochemical properties of kankara kaolin. *Applied Science and Engineering Progress*, 11(2), 127–135. <https://doi.org/10.14416/j.ijast.2018.04.003>
45. Li, J., Liu, D., Li, B., Wang, J., Han, S., Liu, L., & Wei, H. (2015). A bio-inspired nacre-like layered hybrid structure of calcium carbonate under the control of carboxyl graphene. *CrystEngComm*, 17(3), 520–525. <https://doi.org/10.1039/C4CE01632G>
46. Dubey, R. S., Krishnamurthy, K. V., & Singh, S. (2019). Experimental studies of TiO₂ nanoparticles synthesized by sol-gel and solvothermal routes for DSSCs application. *Results in Physics*, 14, 102390. <https://doi.org/10.1016/j.rinp.2019.102390>
47. Souza, A. E., Teixeira, S. R., Santos, G. T. A., & Longo, E. (2013). Addition of sedimentary rock to kaolinitic clays: Influence on sintering process. *Cerâmica*, 59, 147–155. <https://doi.org/10.1590/S0366-69132013000100017>
48. Zhang, L., Shi, T., Wu, S., & Zhou, H. (2014). Graphene/polystyrene nanocomposites synthesized via pickering emulsion polymerization. *High Performance Polymers*, 26(2), 156–165. <https://doi.org/10.1177/0954008313504440>
49. Kumar, S., Reddy, N. L., Kushwaha, H. S., Kumar, A., Shankar, M. V., Bhattacharyya, K., Halder, A., & Krishnan, V. (2017). Efficient electron transfer across ZnO-MoS₂-RGO heterojunction for remarkably enhanced sunlight driven photocatalytic hydrogen

- evolution. *Chemsuschem*, 10, 3588–3603. <https://doi.org/10.1002/cssc.201701024>
50. Alamgir, K., Ahmad, S., Ahammed, N., & Naqvi, A. H. (2015). Thermal analysis and temperature dependent dielectric responses of Co doped anatase TiO₂ nanoparticles. *American Institute of Physics Conference Series*, 1661(1), 080001. <https://doi.org/10.1063/1.4915392>
 51. Dalod, A. R. M., Henriksen, L., Grande, T., & Einarsrud, M. A. (2017). Functionalized TiO₂ nanoparticles by single-step hydrothermal synthesis: The role of the silane coupling agents. *Beilstein Journal of Nanotechnology*, 8(1), 304–312. <https://doi.org/10.3762/bjnano.8.33>
 52. Sambaza, S. S., Maity, A., & Pillay, K. (2020). Polyaniline-coated TiO₂ nanorods for photocatalytic degradation of bisphenol A in water. *ACS Omega*, 5(46), 29642–29656. <https://doi.org/10.1021/acsomega.0c00628>
 53. Liu, H., Xie, S., Liao, J., Yan, T., Liu, Y., & Tang, X. (2018). Novel graphene oxide/bentonite composite for uranium (VI) adsorption from aqueous solution. *Journal of Radioanalytical and Nuclear Chemistry*, 317(3), 1349–1360. <https://doi.org/10.1007/s10967-018-5992-0>
 54. Liu, Y., Wang, L., Xue, N., Wang, P., Pei, M., & Guo, W. (2020). Ultra-highly efficient removal of methylene blue based on graphene oxide/TiO₂/bentonite sponge. *Materials*, 13(4), 824. <https://doi.org/10.3390/ma13040824>
 55. Mohammadi, R., & Sabourmoghaddam, N. (2020). TiO₂-graphene/chitosan nanocomposite: preparation and its application for removal of anionic dyes. *Asian Journal of Green Chemistry*, 4(1), 11–32. <https://doi.org/10.33945/SAMI/AJGC/2020.1.2>
 56. O'Regan, B., & Gratzel, M. (1991). A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 353, 737–740. <https://doi.org/10.1038/353737a0>
 57. Qaid, S. M. H., Al-Asbahi, B. A., Ghaithan, H. M., & Aldwayyan, A. S. (2021). Tuning the optical properties of MEH-PPV/PFO hybrid thin films via the incorporation of CsPbBr₃ quantum dots. *Coatings*, 11, 154. <https://doi.org/10.3390/coatings11020154>
 58. Karpovich, N. F., Pyachin, S. A., Pugachevskii, M. A., Burkov, A. A., Zaytsev, A. V., Makarevich, K. S., & Ri, E. K. (2015). Optical properties of anatase nanoparticles doped with tungsten. *Journal of Applied Spectroscopy*, 82(5), 767–772. <https://doi.org/10.1007/s10812-015-0178-9>
 59. Nakamura, I., Negishi, N., Kutsuna, S., Ihara, T., Sugihara, S., & Takeuchi, K. (2000). Role of oxygen vacancy in the plasma-treated TiO₂ photocatalyst with visible light activity for NO removal. *Journal of Molecular Catalysis A: Chemical*, 161(1–2), 205–212. [https://doi.org/10.1016/S1381-1169\(00\)00362-9](https://doi.org/10.1016/S1381-1169(00)00362-9)
 60. Rajender, G., Kumar, J., & Giri, P. K. (2018). Interfacial charge transfer in oxygen deficient TiO₂-graphene quantum dot hybrid and its influence on the enhanced visible light photocatalysis. *Applied Catalysis B: Environmental*, 224, 960–972. <https://doi.org/10.1016/j.apcatb.2017.11.042>
 61. Pal, M., Pal, U., Jiménez, J. M. G. Y., & Pérez-Rodríguez, F. (2012). Effects of crystallization and dopant concentration on the emission behavior of TiO₂: Eu nanophosphors. *Nanoscale Research Letters*, 7(1), 1–12. <https://doi.org/10.1186/1556-276X-7-1>
 62. Xiao, Q., Si, Z., Yu, Z., & Qiu, G. (2007). Sol-gel auto-combustion synthesis of samarium-doped TiO₂ nanoparticles and their photocatalytic activity under visible light irradiation. *Materials Science and Engineering: B*, 137(1–3), 189–194. <https://doi.org/10.1016/j.mseb.2006.11.011>
 63. Jing, L., Yuan, F., Hou, H., Xin, B., Cai, W., & Fu, H. (2005). Relationships of surface oxygen vacancies with photoluminescence and photocatalytic performance of ZnO nanoparticles. *Science in China Series B: Chemistry*, 48(1), 25–30. <https://doi.org/10.1007/BF02990909>
 64. Mandal, S., Jain, N., Pandey, M. K., Sreejakumari, S. S., Shukla, P., Chanda, A., Som, S., Das, S., & Singh, J. (2019). Ultra-bright emission from Sr doped TiO₂ nanoparticles through r-GO conjugation. *Royal Society Open Science*, 6(3), 190100. <https://doi.org/10.1098/rsos.190100>
 65. Patil, A. B., Patil, K. R., & Pardeshi, S. K. (2010). Ecofriendly synthesis and solar photocatalytic activity of S-doped ZnO. *Journal of Hazardous Materials*, 183, 315–323. <https://doi.org/10.1016/j.jhazmat.2010.07.026>
 66. Kang, Q., Cao, J., Zhang, Y., Liu, L., Xu, H., & Ye, J. (2013). Reduced TiO₂ nanotube arrays for photoelectrochemical water splitting. *Journal of Materials Chemistry A*, 1(18), 5766–5774. <https://doi.org/10.1039/C3TA10689F>
 67. Cheng, Z., & Hu, X. (2017). Performance and degradation mechanism of a sequencing batch biofilm reactor combined with an electrochemical process for the removal of low concentrations of cefuroxime. *Chemical Engineering Journal*, 320, 93–103. <https://doi.org/10.1016/j.cej.2017.03.037>
 68. Xiang, Q., Yu, J., & Wong, P. K. (2011). Quantitative characterization of hydroxyl radicals produced by various photocatalysts. *Journal of Colloid and Interface Science*, 357(1), 163–167. <https://doi.org/10.1016/j.jcis.2011.01.093>
 69. Nosaka, Y., & Nosaka, A. Y. (2019). Comment on “Coumarin as a quantitative probe for hydroxyl radical formation in heterogeneous photocatalysis.” *The Journal of Physical Chemistry C*, 123(33), 20682–20684. <https://doi.org/10.1021/acs.jpcc.9b04190>