Enhanced ultraviolet-visible photocatalysis of RGO/equaixial geometry TiO$_2$ composites on degradation of organic dyes in water

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Abstract
The reduced graphene oxide dopped equaixial geometry TiO$_2$ (rGO/egTiO$_2$) composite as photocatalyst was synthesized hydrothermally with various mass ratios of tetrabutyl titanate. The photocatalyst is considered to be rGO/equaixial geometry TiO$_2$ in terms of modifying the combined reduced graphene Oxide and TiO$_2$. The rGO plays a vital role in rGO/egTiO$_2$ composite as photocatalysts were analyzed in methylene blue (MB) and rhodamine B (RhB) photocatalytic degradation under UV and simulated solar light irradiation. This synthesized catalyst was characterized by various analytical techniques such as XPS, XRD, SEM, BET, and TEM. The rGO/egTiO$_2$ composite exhibits enhanced photocatalytic performance with degradation rates of 97.5 and 97% on RhB and MB for 60 min under UV radiation respectively, while the degradation rate of 94 and 92 % was observed on the same dyes for 6 h under the simulated sunlight radiation. The enhanced photocatalytic performance of the rGO/egTiO$_2$ composite under ultraviolet irradiation source was owing to a high separation efficiency of the photo-induced electron-hole pairs, while the photocatalytic performance under simulated sunlight radiation was due to the photosensitive and charge separator behavior of rGO. This offers us an excellent potential of significant photocatalytic activity for the removal of organic contaminants from wastewater.

Keywords Equaixial geometry TiO$_2$ · Reduced graphene oxide · Photocatalysis · Solar-energy utilization · Water depollution

Introduction
In the past few decades, all the industries in the world have achieved remarkable growth and their impact on the living standards of peoples has been continuously improved. However, rapid growing explosive industrial growth that mainly depends on industrial fossil fuels has severely caused global environmental pollution. The vast majority of toxic waste is emitted into the air and water, destroying nature’s ecology and causing various health and survival problems for livings organisms (Eren et al. 2020; Fu et al. 2019; Guo et al. 2020; Hasan et al. 2021; Lin et al. 2018; Luna-Sanguino et al. 2020; Velasco-Hernández et al. 2020). To overcome these environmental problems, photocatalytic technology has been widely emerged due to its high safety, cleanliness, and useful effects. It can use inexhaustible solar energy to convert it into chemical energy, which can photocatalytic electrolysis water into H$_2$ and O$_2$ or degrades some toxic compounds that are difficult to degrade (Nguyen et al. 2020; Trapalis et al. 2016). This technology has improved or auxiliary effects some conventional methods of destroying or transforming hazardous chemical waste such as high-temperature incineration activating sludge decomposition, and conventional physic-chemical treatment (Cao et al. 2019; Wu et al. 2020; Zouzelka et al. 2019), and it is also expected to replace traditional energy sources as hydrogen energy. If this technology is developed as a mature solution, it can degrade the...
hard-to-remove substances without causing secondary pollution. Currently, semiconductor materials that can be used for photo-catalysis include TiO$_2$, ZnO, ZnS, CdS, MoS$_2$, WO$_3$, and Fe$_2$O$_3$ etc. (Byrne et al. 2018; Ding et al. 2015; Hasan et al. 2020). The semiconductor catalyst for TiO$_2$ is one of the most representative materials owing to its electronic, optical, and photovoltaic applications. TiO$_2$ has a high level of photocatalytic activity and chemical stability (Rajender et al. 2018). Moreover, TiO$_2$ is inexpensive, non-toxic, and allows high oxidation and long-term stability against optical and chemical corrosion (Cerrato et al. 2019; Gunnagol and Rabinal 2019; Surikanti et al. 2019; Wang et al. 2014). Yet, the wide bandgap (3.0–3.2 V) limits the optical response in the UV region. For TiO$_2$, the highest recombination time is $10^{-9}$ s while the minimal reaction time between pollutants and the chemical reaction of electrons varies between $10^{-8}$ and $10^{-7}$ s (Lu et al. 2017; Tian et al. 2017). The electron-hole shaped through the pair is reconfigured via differences in the time period. Consequently, a wide amount of attention has been connected to enhance its catalytic efficacy and pertinent under ultraviolet light (Lu et al. 2018).

The photo catalytic activity is significantly exaggerated by means of morphology, particle size, and surface area. When the size of TiO$_2$ nanoparticles is reduced to the nanoscale, the catalytic activity must be improved owing to the quantum size effect and the increased surface area (Lim et al. 2016). There are two types of explanations for the enhancement of the photocatalytic activity of TiO$_2$, when combined with these co-materials, are first, the higher adsorption of organic pollutants because of their closeness to graphene materials and second, the enhanced separation of electron-hole pairs, due to the easy transport of charge through the π-conjugation structures (Leal et al. 2020). The synthesis of TiO$_2$ on graphene sheets is significantly beneficial for the dispersion of nanoparticles. The higher contact area between TiO$_2$ nanoparticles and contaminants has promoted the photo-degradation of pollutants. The significant contribution of graphene enhanced the photocatalysis property. Graphene is a carbon allotrope composed of a single layer of atoms arranged in the lattice of a two-dimensional honeycomb (Chang and Chen 2011; ChongYeon et al. 2013; Du and Cheng 2012; Giovannetti et al. 2016). Graphene has a broad two-dimensional sp$^2$ conjugated network that exhibits electron mobility up to 15,000 cm$^2$/Vs at room temperature (Geim and Novoselov 2010; Padmanabhan et al. 2021; Wanag et al. 2018; Wang et al. 2015a). Owing to the difference in energy level between structures of two materials when TiO$_2$ is combined with graphene, the electrons at the interface will flow from TiO$_2$ to graphene. This flow of electrons created a heterojunction at the interface (referred to as a Schottky barrier). It can separate photoexcited electron-hole pairs prevention charge recombination. In addition, graphene can display the same photosensitization as CNTs, extending the photoresponse range of the photocatalyst in the visible range. One of the effective ways of enhancing the photocatalytic efficiency of nanostructured TiO$_2$ is to combine TiO$_2$ with graphene. The aim of synthesizing TiO$_2$/graphene nanomaterial is to reduce the TiO$_2$ rate of charge recombination. Consequently, due to the decrease in the recombination of photo-generated electron-hole pairs, TiO$_2$/graphene composites could display enhanced photocatalytic activities (Gao et al. 2009). A lot of researchers have looked into using rGO/TiO$_2$ composites to extract and degrade contaminants including methyl orange, methyl blue, and rhodamine B from water. Enhanced photocatalytic degradation of atenolol using TiO$_2$/GO composites as a catalyst was recently reported (Song et al. 2018). Shehzad et al. (Shehzad et al. 2020) prepared 2.5% AgFeO$_2$/rGO/TiO$_2$ by using a simple deposition and reflux method under UV and visible light irradiation, which exhibited efficiency and completely degraded the 50 ppm of MB dye for 0.5 h. Yadav and Kim (Yadav and Kim 2016) prepared and used the anatase TiO$_2$/graphene oxide nanocomposite as photocatalysts for organic dye degradation under UV irradiation. The composite showed better photocatalytic efficiency than pure TiO$_2$ nanoparticles. Kurniawan et al. prepared TiO$_2$/GO in the degradation of MB in synthetic wastewater. Under UV–vis irradiation. Where is found that composite by a 1:2 wt ratio has the largest surface area of 104.51 m$^2$/g that observed an almost complete MB removal within 4 h (Kurniawan et al. 2020). TiO$_2$/rGO composites were prepared by the hydrothermal method under solar irradiation; the generation rate of hydroxyl HO radicals under irradiation was higher in pure TiO$_2$ than that in TiO$_2$/rGO, but they decayed with time, so TiO$_2$/rGO eventually presented a higher HO’ concentration at longer times (Monteagudo et al. 2020). Accordingly, the electron transfer efficiency and decrease of the electron-hole pair’s recombination for use of graphene oxide (GO) and reduced graphene oxide (rGO) depend on preparation conditions as well as reduction methods. Consequently, designing composites structure, hetero-structures, and coupling of 2D materials with semiconductors can be one promising approach to developing the photocatalytic performance under UV and simulated sunlight irradiation. Therefore, it has been assumed that the attachment of TiO$_2$ nanoparticles with various mass ratios of raw material on reducing graphene oxide can effectively be applied to obtain superior catalytic efficiency.

Generally, visible light and infrared radiation constitute the major fraction of solar radiation reaching the atmosphere of the Earth. About 6% of the radiation is UV radiation that has a wavelength of 200 to 400 nm, about 50% is visible radiation that has a wavelength of 400 to 700 nm, and about 40% is infrared radiation. How to make full use of solar energy to clean our environmental water is still an important scientific and technological problem to be solved. Herein, we have synthesized the reduced graphene oxide dopped equaixial geometry TiO$_2$ (rGO/egTiO$_2$) composite via the reaction of rGO.
and different mass ratios of tetrabutyl titanate by solvothermal and hydrothermal methods. The photocatalyst is considered to be rGO/egTiO$_2$ composite in terms of modifying the combined reduced graphene Oxide and TiO$_2$. The main idea is to combine TiO$_2$ with the conjugated electronic material rGO to make it the carrier of TiO$_2$ particle growth to promote particle dispersion. The outcome demonstrates that rGO/egTiO$_2$ composite has a wider range from UV to visible light and greater absorption abilities to the solar irradiation than egTiO$_2$ itself. This performance will achieve effective pollution mitigation to maintain the minimum level of environmental flows and to ensure the purity of water in the environment.

**Experimental section**

**Materials**

Potassium persulfate (K$_2$S$_2$O$_8$), isopropanol ((CH$_3$)$_2$CHOH), and hydrogen peroxide (H$_2$O$_2$) were purchased from Shanghai Guangdong Chemical Reagent Engineering Technology R&D Center, China. Tetrabutyl titanate (C$_{16}$H$_{36}$O$_4$Ti) was purchased from Chengdu Kelong Chemical Co., Ltd. Sodium nitrate (NaNO$_3$), Methylene blue (MB), and rhodamine B was purchased from Tianjin Komiou Chemical Reagent Co., Ltd. All the chemicals were of high analytical grade and used as received.

**Preparation of GO and rGO**

Graphene oxide (GO) was typically synthesized according to Hummers modified (Haag and Kung 2014) as shown in the supplementary information. Solvothermal reduction: 60 mg of GO was dispersed in 50 mL of isopropanol and a transparent brown dispersion of GO was obtained by sonication for 60 min. Follow 2 mL of distilled water was added dropwise to the dispersion, and the mixture was stirred for 30 min, then transferred into a 100-mL Teflon reactor and heated at 180 °C for 8 h. After cooling, the product was taken out and the powder was washed by centrifugation with absolute ethanol 5 times, then dried in an oven at 50 °C to obtain a gray powder product. The mass ratio of material GO: tetrabutyl titanate is 0.06:2, 0.06:4, 0.06:6, 0.06:8, and 0.06:10 in order and the mass ratio of rGO to TiO$_2$ are 12.7, 6.4, 4.3, 3.2, and 2.6%. Using the same method, pure rGO can be obtained without adding tetrabutyl titanate.

**Preparation of equaixial geometry TiO$_2$ composite**

Firstly, 60 mg of GO was dispersed in 50 mL of isopropanol and sonicated for 1 h to obtain a clear brown dispersion of GO. Two, 4, 6, 8, and 10 mL of tetrabutyl titanate was added to the dispersion, and the mixture was stirred for 0.5 h. Then, 2 mL of distilled water was added dropwise and the mixture was continuously stirred for another 30 min. Then transferred the mixture to 100 mL Teflon-lined, the reactor was heated at 180 °C for 8 h. After cooling, the product was taken out and the powder was washed by centrifugation with absolute ethanol 5 times, then dried in an oven at 50 °C to obtain a gray powder product. The mass ratio of material GO: tetrabutyl titanate is 0.06:2, 0.06:4, 0.06:6, 0.06:8, and 0.06:10 in order and the mass ratio of rGO to TiO$_2$ are 12.7, 6.4, 4.3, 3.2, and 2.6%. Using the same method, pure rGO can be obtained without adding tetrabutyl titanate.

**Photocatalyst characterization**

The crystal phases of the as-synthesized catalysts were characterized via X-ray powder diffraction (XRD, D2 PHASER X) with Cu kα with irradiation source of λ = 1.54178 Å in the (2θ) range between 5 and 90°. The morphology was analyzed using field emission scanning electron microscopy (SEM, TM4000PLUS). The surface composition and electronic states were recorded via an X-ray photoelectron spectrophotometer (XPS, Kratos, Axis Supra). The structural morphology was analyzed via transmission electron microscopy (TEM, FEI Talos F200X). The photodegradation analysis was taken by UV–Vis Spectrophotometer (UV1800, Jinghua Instruments Co. Ltd., China) under 200–800 nm scanning rate. The photochemical reactor was equipped with a 1000-W adjustable Xe lamp a 300–500 W (λ > 420 nm) as a light source, DS-GHX-V, Dusi Instruments Co. Ltd. (Shanghai, China).

**The photocatalytic activity reactor and experimental procedures**

The light source has a mercury lamp that emitted ultraviolet light, and the visible light is emitted by the xenon lamp 300–500 W (λ > 420 nm). The photocatalytic operation of the photocatalyst concerned was evaluated based on the dye decolourization and the absorption spectrum of UV-vis under ultraviolet light or visible light. In the present work, MB and RhB dyes have been preferred, and they are associated with 664 nm and 554 nm absorption wavelengths, respectively. The light source’s power is modified as per the photocatalytic reaction effect. To achieve an adsorption-desorption equilibrium, a 10-mg photocatalyst sample was scattered into 50 mL of 10 mg/L dye solution and stirred for one hour at a magnetic
stirrer (500 rpm) in a dark room. Then, the light is turned on and the photocatalytic reaction is carried out. Then, the lamp is then switched on, the photocatalytic reaction is performed, and the sampling is taken out at periodic intervals (modified according to the photocatalytic reaction effect). 3.0 mL sample aliquots were taken out from the dispersion mixture, centrifuged for 4 min at 7000 rpm to remove the catalyst particles. The concentration of dye in the residual solution was analyzed spectrophotometrically to evaluate the change in maximum absorption peak. A test tube is usually inserted in the experiment without a photocatalyst as a blank run, MB and RhB monitoring is performed. The degradation efficiency (%) was measured by the following equation (1).

\[
\text{Degradation} \% = \left( \frac{C_o - C_t}{C_o} \right) \times 100
\]

where \(C_o\) degradation concentration before illumination and \(C_t\) degradation concentration after a certain time of illumination.

**Results and discussion**

**Salient characteristics of the rGO/egTiO\(_2\) composites**

Figure 1 a shows the XRD pattern of rGO/equaixial geometry of TiO\(_2\) composite with different mass ratios. All the diffracted peaks are coincidental with the standard XRD pattern of anatase crystal TiO\(_2\) and tetragonal system (ICPDS, No.21-1272). There is no intensity increase of rGO peak at about \(2\theta =25^\circ\) was observed, while the peak at \(2\theta =9.44^\circ\) for GO was has disappeared. The disappeared peak of rGO was attributed to a lot of particles available on the surface rGO composite caused by the compounding with TiO\(_2\). A possible reason was that the most intense diffraction peak of reduced graphene (\(2\theta = 25^\circ\)) could be shielded by the main peak of anatase TiO\(_2\) at 25\(^\circ\)(Sun et al. 2012; Tan et al. 2013); thus, the peak of rGO cannot appear. The XRD of pure rGO is prepared with the same method, as shown in Fig. 1(b), there is a wide peak at about \(2\theta =25^\circ\), which proves that it has been restored. Observing several XRD patterns of rGO/equaixial geometry TiO\(_2\) composites with different ratios, it is found that with the increase of rGO content, the crystal surface strength of composites has gradually declined, which was the most obvious by observing the peak corresponding to the strongest peak (101). The compound with the lowest rGO content is 2.6%, which has the highest XRD intensity. There are double peaks at around \(2\theta=55^\circ\) is the most obvious and complete, indicating that it has high crystallinity, and also when the content of rGO is relatively high, it will slightly affect the crystallinity of TiO\(_2\) crystals. The XRD pattern preliminary confirmed that the two are successful compounding with each other. In the XRD pattern, there are no other redundant peaks except TiO\(_2\) peaks, which proves the samples are relatively pure.

The SEM image of rGO/equaixial geometry TiO\(_2\) composites with different mass ratios is shown in Fig. 2. In order to get a better comparison, the SEM image of pure rGO and TiO\(_2\) was added. Figure 2(a) is the SEM images of the pure rGO sample. Figure 2(b–f) show the SEM images of rGO/egTiO\(_2\) composite with mass ratios of 12.7, 6.4, 4.3, 3.2, and 2.6%. Figure 2(g, h) are the SEM images of pure equaixial geometry TiO\(_2\) particles with different magnification ratios. It can be clearly observed that after compounding, rGO lamellas were covered with a TiO\(_2\) particles. Some bare areas on the rGO surface are chosen; thus, the corresponding rough particle density may not be observed in the picture with proportion, which can be seen in TEM images. Although there will be aggregations of particles, it can be observed from Fig. 2 that TiO\(_2\) is equably dispersed on rGO layers, make the dispersion more equable, which indicates that the aggregations of TiO\(_2\) particles were prevented after compounding with rGO. The recombination of TiO\(_2\) particles on rGO layers also prevented the accumulation of rGO layers, the two interacted with each other. Figure 2(e) is the SEM images of rGO and TiO\(_2\) with a

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Fig. 1 The XRD pattern of rGO/egTiO\(_2\) composite with different mass ratios (a) and the XRD pattern of rGO (b)
ratio of 3.2%, which is a little different with other recombination, rGO layers wrap TiO₂ particles, but only one side is recombined, it is probably that because the oxygen-containing groups of rGO just oxidized one side, so causing one side recombination. SEM image has confirmed again that the two have been successfully combining, which is consistent with the XRD results.

TEM image of rGO/equaixial geometry TiO₂ composites with different mass ratios as display in Fig. 3, for better comparison, the TEM images of pure rGO and TiO₂ were added. Figure 3(a) is a TEM image of a pure rGO. Figure 3(b, c, d, e, and f) are TEM images of rGO/equaixial geometry TiO₂ composite samples with different magnification ratios of GO and TiO₂, whose mass ratios are respectively 12.7%, 6.4%, 4.3%, 3.2%, and 2.6%. Figure 3 (g) is a TEM representation of TiO₂ particles in pure equaixial geometry. Figure 3 (h) is an energy dispersive X-ray spectroscopy of the rGO/equaixial geometry TiO₂ composite sample with a mass ratio of 4.3%, with a lowest proportion of rGO, the average density of TiO₂ is bigger, the particles are closer, but it can be observed that the edges of rGO layers in figures from 12.7% until the proportion are 2.6%; TiO₂ particles are completely covered rGO layers. Its edges cannot be observed; the large TiO₂ particles gathering together can only be observed. The aggregation of TiO₂ particles in this period is different from the previous spontaneous aggregation of particles that is because, after the hydrothermal reaction, there was some binding force between TiO₂ and rGO that caused particles to grow together with the lamella. In Fig. 3 (b), it can be observed that growing many TiO₂ particles on rGO lamella of micron-level are very equable, whose average size of crystal particles can only reach 16.5 nm. There will be relatively more particle aggregations in fold areas, which is the normal phenomenon. However, in the surrounding areas of rGO and TiO₂ composites, there is no other scattering and single TiO₂ particles, the difference in particles density between the rGO layers and copper screen used in tests could further indicate that there is a certain strength interaction between TiO₂ particles and rGO particles, and the two cannot be separated by ultrasonic treatment. This kind of combination is unlike the mixture merely at the physical level. The results have proved again that the recombination of the two is successful, which is consistent with the results of XRD and SEM, which confirmed that the super-molecule has been successfully prepared by the hydrothermal method and solvothermal method. Besides, Fig. 3 (h) has provided supplementary data for the results; the elemental analysis of the EDX image shows that the elements composed by composites are Ti, O, and C, which also supplemented the results of XRD.
The optical properties of photocatalysts are assessed using UV-visible reflectance spectroscopy and band-gap energy. Figure 4 shows the UV-vis diffuse reflection spectrum of P25, equiaxial geometry TiO\textsubscript{2} composites with composite ratios of 12.7, 6.4, 4.3, 3.2, and 2.6%. It can be seen from the figure that P25 and equiaxial geometry TiO\textsubscript{2} have relatively strong absorption in the ultraviolet region, the absorption edge of them is approximately 370 nm, while none in the visible region. However, rGO/equiaxial geometry TiO\textsubscript{2} composites exhibited a certain intensity of absorption in the visible light region, which

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**Fig. 3** The TEM images of rGO/egTiO\textsubscript{2} composites with different composite ratios: (a) is pure rGO, and (b, c, d, e, and f) are respectively rGO/egTiO\textsubscript{2} composites with the mass ratios of 12.7, 6.4, 4.3, 3.2, and 2.6%. (g) is pure equiaxial geometries. The EDX diagram of elements composite with rGO: TiO\textsubscript{2} mass ratio of 4.3% (h)

**Fig. 4** (a) UV-Vis diffuse reflectance spectra of three different samples and (b) plots of (\(A\lambda\nu\))\textsuperscript{1/2} versus energy (\(h\nu\)) for the band gap energy of equiaxial geometry of TiO\textsubscript{2}, and P25
indicates that the absorption intensity of the samples in the visible light region has been improved after recombination. Moreover, it can be observed that qualitative red-shift towards higher wavelengths at the absorption edges of composites. The findings show that the dominance of rGO, which has excellent conductivity and π-conjugation, can significantly boost photocatalytic efficiency in this system. This mechanism is that graphene and semiconductor will produce chemical effects of a certain degree, C element may be doped in, such as carbon doping, forming a doping level, which can widen or narrowing the semiconductor to expand the response to visible light. We can calculate the band-gap energy of P25 and equiaxial geometry TiO2 according to Fig. 4, because TiO2 is the indirect band-gap semiconductor (Kurniawan et al. 2020); therefore, according to Eq. (2):

\[(\alpha h\nu)^{1/2} = C (h\nu - E_g)\]  

Since the absorption coefficient is in proportion to the absorbance A, here the \((\Delta h\nu)^{1/2}\) is replaced with the \((\alpha h\nu)^{1/2}\). Where \(\alpha\) is referred to as the absorption coefficient, \(h\) is referred to as the Planck constant (\(J s^{-1}\)), the incident light frequency (\(Hz\)), the proportional coefficient is \(C\), and prohibited band-gap energy is \(E_g\). Hence, the \(E_g\) of P25 is 2.78 eV and the \(E_g\) of TiO2 equiaxial geometry is 3.05 eV. But higher band-gap anatase has a better oxidizing ability, meaning the efficiency of photo-catalysis is better than P25.

The Raman spectrum of nanocomposite TiO2, rGO, and rGO/equiaxial geometry TiO2 is shown in Fig. 5 (a). Four characteristic bands appear at 0–800 cm\(^{-1}\) in the TiO2 spectrum at 145 cm\(^{-1}\), 385 cm\(^{-1}\), 506 cm\(^{-1}\), and 640 cm\(^{-1}\), corresponding to the main vibration modes of the anatase phase, \(E_g\), \(B_1\), \(A_1\), and \(E_g\), respectively (Guo et al. 2019; Mathpal et al. 2013). The characteristics of the disordered carbon and graphic carbon bands display a simple, subtle small change in free carbon of the pyrolysis temperature of rGO/equiaxial geometry TiO2. Two distinctive bands appear in the RGO spectrum at 1324 and 1606 cm\(^{-1}\), referring to D (disordered carbon) and G (graphic carbon) bands, respectively (Xu and Cheng 2013). Because of edge and internal structural defects (sp3 defects), the D band is due to the disruption of the symmetrical hexagonal graphitic lattice. On the other hand, the characteristics of all sp2 carbon forms (C-C bonds) constitute the G band (Garrafa-Gálvez et al. 2019). According to the Gaussian-Lorentzian fitting were calculated, the intensity ratio (I_D/I_G) of rGO/equiaxial geometry TiO2 (0.83), less than the intensity ratio of rGO (0.84), This is because of the reduced sp\(^2\) domain in the planes of carbon atoms, suggesting a large number of defects on the rGO sheets due to the TiO2 formation (Prabhu et al. 2017).

The photocurrent calculation was conducted to research the interfacial charge transfer dynamics, the higher the photocurrent value, the more effectively splitting the photogenerated electron-hole pairs (Wang et al. 2015b). Figure 5 (b, c) is a representation of rGO, geometry TiO2, and rGO/equiaxial geometry TiO2, transient photocurrent responses. For each light turned on, a sudden and uniform photocurrent increase was clearly observed, and then the photocurrent decreased to a constant value as soon as the light was turned off. Furthermore, the photocurrent for rGO/equiaxial geometry TiO2 was far higher than that of rGO and geometry TiO2, indicating that under visible light irradiation as shown in Fig. 5 b, and under solar radiation, as shown in Fig. 5c, and more efficient charge separation of electron-hole pairs in rGO/equiaxial geometry TiO2. As a result, this can be deduced that hybridization improves the separation and transfer efficiency of photoinduced electrons and holes, resulting in an increase in photocurrent density. This result is consistent with the results of the degradation curves in Fig. 7.

In addition, electrochemical impedance spectra (EIS) calculation was conducted to obtain a deeper understanding of the charge transfer properties of rGO, geometry TiO2, and rGO/equiaxial geometry TiO2. In the EIS of rGO/equiaxial geometry TiO2 spectrum, the arc size radius was smaller than that of rGO and geometry TiO2, as seen in Fig. 6 (d, e). This suggests that the rGO/equiaxial geometry TiO2 had a lower resistance, and the transition speed of electrons of the composite was higher than the others, largely due to the heterostructured construction between rGO and geometry TiO2.

An essential parameter for evaluating the photocatalytic activity of the nanostructure is the surface area. BJH and BET techniques are associated with pore size distribution and real surface area measurements. The isotherms of N\(_2\) adsorption-desorption were calculated at 200 °C for rGO, equiaxial geometry TiO2, and rGO/equiaxial geometry TiO2, and the isotherms are shown in Fig. 6. According to the IUPAC classification (Khan et al. 2019; Yu et al. 2018), isotherms are classified into three types as type IV of mesoporous nature. The specific surface area of rGO/equiaxial geometry TiO2 composite was 115.80 m\(^2\)/g, while the average pore size was 2.822 nm, as seen in Fig. 6 (a), larger than that of surface area (3.32 m\(^2\)/g), (16.38 m\(^2\)/g) and pore size (28.184 nm), (17.22 nm) of rGO and equiaxial geometry TiO2, respectively as seen in Fig. 6 (b, c). The findings suggest that the rGO/equiaxial geometry TiO2 composite BET surface area is higher than that of rGO, and equiaxial geometry TiO2. The broad heterogeneous photocatalyst surface area can provide more surface-active adsorption sites for reactant molecules, making photocatalytic process more efficient.
The photocatalytic performance of rGO/egTiO$_2$ composite on organic dye degradation

After confirming the successful recombination between equaixial geometry TiO$_2$ and rGO, we also need to simulate test its photo-catalysis performance, stimulate pollutions but still choose the organic dyestuffs RhB and MB, since they are both refractory contaminants that are commonly found in textile wastewater. Firstly, we tested the degradation curve figures of rGO/eqaixial geometry TiO$_2$ composites under ultraviolet rays with different composite ratios to RhB by using mercury lamps of 370 W, and compared with single equaixial geometry TiO$_2$ and single rGO at the same time, as showed in Fig. 7 is their whole degradation process on RhB, which includes dark absorption and photo-catalysis degradation. There will also be degradation occurring in dyestuffs in blank test tubes under ultraviolet light, they were be degraded by about 20% in...
60 min. Secondly, observe the process of dark absorption, we found that the proportion of the rGO composites increased, the dyestuffs absorbed in the process of its dark absorption were also increased until the proportion of rGO reached 12.7%. The absorption process can make the absorbance of dyestuffs decrease 50%, but the single rGO could directly absorb nearly 85%, which indicates the absorption effect of rGO on dyestuffs is very strong, it could be attributed to its shape which is the very thin lamellas with relatively large specific surface areas. It can be seen from Fig. 7 (a) that whether it is single rGO or single equaixial geometry TiO₂, its degradation rates are relatively low, but the degradation rate of other composites with various ratios has increased, which are different. Directly, when the rGO proportion reaches 12.7% and 2.6%, the degradation rate is the fastest, which degraded almost all the dyestuffs for RhB 97.5% in 60 min. The difference is that when the rGO ratio reaches 12.7%, the absorption is relatively strong, the absorption of the rGO composites with the ratio of 2.6% is relatively less strong than the former, but it can degrade dyestuffs with higher concentration to the same level, so we think the overall degradation of the rGO composites with the ratio of 2.6% is better. Figure 7 (b) showed the degraded UV-vis absorption spectrum of rGO/equaixial geometry TiO₂ composites with the mass ratio of 2.6% of rGO: TiO₂ to RhB, whose absorption on dyestuff is not very intense, but the degradation ratio is very excellent, the final results of degradation showed that its absorption peaks of all the wavelengths are almost zero. Afterwards, under the same conditions, we tested the degradation curve figures of the rGO/equaixial geometry TiO₂ composites with different composite ratios on MB and compared them with single equaixial geometry TiO₂ and single rGO at the same time, as showed in Fig. 7 (c) is the whole degradation process on MB. Its rules of the dark absorption process are consistent with that of RhB. Single rGO absorbed 88% dyestuffs in one hour. The degradation rates of composites with different ratios are relatively close, but the degradation rate of the rGO composite with the ratio of 6.4% is the fastest, which degraded almost all the dyestuff for MB around 97% in 60 min. Therefore, Fig. 7 (d) showed a UV-vis absorption spectrum of rGO/equaixial geometry TiO₂ composites with a mass ratio of 6.4% of rGO: TiO₂ on the degraded MB. It is found that comparing every single component, the photo-catalysis activity of composites increased by analyzing the degradation process of rGO and TiO₂, which can be attributed to the cooperative effect of rGO and TiO₂, making agglomerate TiO₂ dispersed on rGO lamellas, graphene lamellas are also divided. In the two shaped heterojunctions, the graphene is used as electron acceptor materials, and the character of its ready electricity conduction can effectively prevent the recombinetion of photo-electrons and holes, providing better conditions and time of the occurring oxidization process than before. The comparison of photodegradation performance is shown in Table 1. The reason for the high photo-degradation of rGO/equaixial geometry TiO₂ is its novel structure and excellent separation performance of photo-generated electrons and holes in the rGO/equaixial TiO₂ composite.

To explore the degradation process under sunlight, the sample was tested and degradation curve pictures of the rGO/equaixial geometry TiO₂ composites with three composite ratios on RhB and MB presented in Fig. 7, under the simulation sunlight via adopting a high-intensity discharge lamp of 800 W. We compared them with a single equaixial geometry TiO₂ and single rGO at the same time, as showed in Fig. 7 (c) is the whole degradation process on MB. Its rules of the dark absorption process are consistent with that of RhB. Single rGO absorbed 88% dyestuffs in one hour. The degradation rates of composites with different ratios are relatively close, but the degradation rate of the rGO composite with the ratio of 6.4% is the fastest, which degraded almost all the dyestuff for MB around 97% in 60 min. Therefore, Fig. 7 (d) showed a UV-vis absorption spectrum of rGO/equaixial geometry TiO₂ composites with a mass ratio of 6.4% of rGO: TiO₂ on the degraded MB. It is found that comparing every single component, the photo-catalysis activity of composites increased by analyzing the degradation process of rGO and TiO₂, which can be attributed to the cooperative effect of rGO and TiO₂, making agglomerate TiO₂ dispersed on rGO lamellas, graphene lamellas are also divided. In the two shaped heterojunctions, the graphene is used as electron acceptor materials, and the character of its ready electricity conduction can effectively prevent the recombinetion of photo-electrons and holes, providing better conditions and time of the occurring oxidization process than before. The comparison of photodegradation performance is shown in Table 1. The reason for the high photo-degradation of rGO/equaixial geometry TiO₂ is its novel structure and excellent separation performance of photo-generated electrons and holes in the rGO/equaixial TiO₂ composite.

| Materials                  | Light source        | Organic dyes (mg/L) | Irradiation time (min) | Rate of degradation (%) | Reference          |
|----------------------------|---------------------|---------------------|------------------------|-------------------------|--------------------|
| TiO₂ @ RGO doped nanoparticles | Visible light | 10 – 120 | 90 | (Aqeel et al. 2019) |
| TiO₂–RGO nanocomposites      | Visible light | – 30 80 | 98.8 | (Sher Shah et al. 2012) |
| TiO₂@rGO nanocomposite       | Solar-like radiation | 4.5 – 120 | 98.1 | (Kocijan et al. 2021) |
| TiO₂–RGO aerogel             | Simulated solar | – 40 240 | 84.6 | (Sun et al. 2020) |
| rGO-TiO₂ nanocomposites      | Under UV light | 3.2 – 15 75 | 90 | (Mohammadi et al. 2019) |
| RGO-TiO₂/BiVO₄               | Visible and UV light | 10 – 120 | 96.1 | (Samsudin et al. 2018) |
| TiO₂@rGO nanocomposites      | UV light | 20 – 120 | 92 | (Sohail et al. 2017) |
| Au@TiO₂/rGO                 | Visible and UV light | 7 – 180 | 98 | (Saber et al. 2021) |
| rGO/egTiO₂ composite         | UV light | 10 – 60 | 97 | Our work |
| rGO/egTiO₂ composite         | Simulated sunlight | 10 – 360 | 92 | Our work |
geometry TiO$_2$ and single rGO at the same time, took samples to test UV-vis absorption spectrum every two hours. We selected the composites with the rGO ratios of 12.7%, 4.3%, and 2.6% for RhB and 12.7%, 6.4%, and 2.6% for MB to degrade. Figure 7 (e, g) is their whole degradation process on RhB and MB. Because TiO$_2$ itself has the character of being sensitive to ultraviolet ray and of being insensitive to visible light, whose degradation process is relatively low under the simulation sunlight, and its degradation rate cannot match the absorption rate, the absorption rate still obeys previous rules. Which almost degraded all the dye stuffs for RhB and MB around 94% and 92%, respectively after 6 h of degradation. This result verified the results of UV-vis diffuse reflection tests in Fig. 4, whose visible photo-response increased, the photocatalysis got improved. Pure rGO showed the fastest “degradation” rate in the first 2 h after turning on the lights, then the rate obviously slowed down, it is probably because that its absorption effect can play the role, other than the degradation effect. Figure 7 (f, h) showed the UV-vis absorption spectrum image of the rGO/equaixial geometry TiO$_2$ compounds with the mass ratio of 4.3% of rGO: TiO$_2$ on MB, degradation respectively.

We summarized the degradation findings with samples from Photocatalysts, their $K_{app}$ numbers, and $R^2$ values as seen in Table 2. The following Eq. (3) was used to analyze the kinetic photocatalytic degradation of organic dyes:

$$\ln \left( \frac{C}{C_0} \right) = k_{app} t,$$

where the $k_{app}$ is the pseudo-first-order rate constant, $C_0$ is the initial concentration of dye, and $C$ is the dye concentration after photocatalytic degradation at time $t$.

### Table 2: Photo-catalysts samples, quantities of their $K_{app}$ and $R^2$ values

| Samples            | Photocatalytic activity % | Light sources | Times (hr) | $K_{app}$ (min$^{-1}$) | $R^2$  |
|--------------------|---------------------------|---------------|------------|------------------------|-------|
|                   | RhB  | MB  | UV   | 1   | 0.022 | 0.038 | 0.87 | 0.92 |
| rGO                | 85.0 | 88.0| UV   | 1   | 0.026 | 0.036 | 0.97 | 0.96 |
| egTiO$_2$          | 84.0 | 89.0| UV   | 1   | 0.047 | 0.056 | 0.93 | 0.95 |
| rGO/egTiO$_2$      | 97.5 | 97.0| UV   | 1   | 0.24  | 0.24  | 0.87 | 0.85 |
| rGO                | 80.0 | 80.0| Sunlight | 6   | 0.26  | 0.25  | 0.95 | 0.95 |
| egTiO$_2$          | 84.0 | 82.0| Sunlight | 6   | 0.36  | 0.35  | 0.96 | 0.97 |

### The photocatalytic mechanism of the rGO/egTiO$_2$ composite

To describe the degradation mechanism of organic dye (MB and RbB) through rGO/equaixial geometry, TiO$_2$ composites photo catalysts under UV and solar irradiation are shown in Fig. 8. In MB and RhB degradation, the enhanced performance is mainly due to the function of reducing graphene sheets present in rGO/equaixial geometry TiO$_2$. In the degradation procedure, reducing graphene sheets serve as (1) an absorbent, (2) a charge separator, and (3) a photosensitive. The compound is dual structure, and there exists close interface contact among components. In the process of absorption, rGO has a big specific surface area, which endowed it the relatively good absorption ability, which can increase the opportunities of pollutant molecules and materials to contact with each other.

Under the irradiation of light, the absorption of organic dye is increased by the function of rGO. The exceptional adsorption capability of rGO/equaixial geometry TiO$_2$ was credited to simple physical and chemical adsorption resulting from ($\pi$-$\pi$) interactions on the rGO sheets between organic dyes and the aromatic domains (Liu et al. 2016). The process of adsorption enhanced the concentration of organic dye molecules over rGO sheets, placing the organic dye closer to the TiO$_2$ photocatalytic surface, which is a requirement for photocatalytic activity improvement.

Under the UV irradiation semiconductor, TiO$_2$ will produce the match of light-generated electrons with electron holes. Light-generated electrons ($e^-$) will make simulations from VB to CB, which caused the light-generated electron holes($h^+$) in the VB as shown in Fig. 8 (a). If there is no rGO, the electrons and electron holes irritated by such light irradiation will quickly revert to the ground state due to its instability, which represents the electrons back to VB quickly, which will cause fluorescence emission and low catalytic activity on dye stuffs. However, with the presence of rGO, the interface contacts of the two makes the interface form a hetero junction. Here exists separation region of space charge in hetero junction, the electrons are prone to flow to low Fermi level
from high Fermi level to adjust Fermi level; as the calculated work function of graphene is (4.42 eV), $E_{CB}$ of anatase TiO$_2$ is about 4.21 eV (Li et al. 2021).

So firstly, graphene can accept the light-generated electrons from TiO$_2$ to prevent the recombination of the match of light-generated and electron holes, which is the first reason. Secondly, the recombination of such relatively strong and interactive forces makes TiO$_2$ crystal particles at nanolevel to disperse on the graphene slices at the micron level, which is easy to be gathered, the particles are prone to contact with dyestuffs after they dispersed, and rGO has strong absorption effect, which further improved the contact possibility.

The third reason is that graphene itself has excellent electrical conductivity when the light-generated electrons are transferred to rGO. The rGO could work as the carrier of electron flow to react with $O_2$ in dyestuff to produce $O_2^-\cdot$, which will continue to make a series of reactions to produce $\cdot OH$, the composite ratio of light-generated electron holes that left on VB below, so the free holes in TiO$_2$ react with $H_2O$ or OH$^-$ to produce $O_2^-\cdot$ and $\cdot OH$ that have strong oxidization ability, and as such reacts with organic dyes which can degrade to CO$_2$, H$_2$O, and other intermediates. In a word, there exists a synergistic effect, its photo-catalysis performance can be enhanced.

Under solar radiation, the function of rGO is to instantaneously act as a photosensitizer and a charge separator. The solar spectrum contains only about 3–5% ultraviolet light and 50% visible light (~2.8 eV), which forms electron-hole pairs in nanoparticles of TiO$_2$, which are not enough to excite TiO$_2$ nanoparticles (approximately 3.2 V) (Pitre et al. 2017).

However, as shown in Fig. 8 (b), when the rGO/equaixial geometry TiO$_2$ catalyst is irradiated via solar light, the response is provided via visible light part when the rGO photo-excitation is possible due to a higher energy level than the measured band gap of rGO/equaixial geometry TiO$_2$ composite (3.05 eV), whose function is similar to the photosensitive process of organic dyes. The rGO is photoexcited from (HOMO) level to (LUMO) level. The rGO in the excited state transference electrons into the conduction band of TiO$_2$ and the excited electrons can be trapped by molecular oxygen that is found in the reaction system, where oxygen is activated to form superoxide radicals ($O_2^-\cdot$) and other oxidative species for the degradation of organic dyes and converted into CO$_2$, H$_2$O, and other intermediates.
This mechanistic way elucidated the photo-excitation of rGO/equaixial geometry TiO$_2$ under solar irradiation (ultraviolet and visible light), where it is shown that the rGO sheets serve as a charge separator to limit electron-hole pair recombination. But at the same time, it also acts as a photosensitizer, converting the large band gap semiconductor into a visible photo-activity that lets amplified the photodegradation of organic dyes.

Conclusion

We have successfully synthesized the reduced graphene oxide doped equaixial geometry TiO$_2$ (rGO/egTiO$_2$) composite with different ratios of tetrabutyl titanate supported on rGO in isopropyl alcohol via hydrothermal followed by solvothermal method. Characterization was taken via XRD, SEM, BET, TEM, and UV-vis diffuse reflection to analyze the materials; the rGO/equaixial geometry TiO$_2$ exhibited the greatest photocatalyst activity in UV and simulated sunlight radiation for the degradation of RhB and MB dye. The degradation of the catalyst rGO/equaixial geometry TiO$_2$ was respectively 97.5 and 97.0% in 60 min under the UV radiation, 94 and 92% in 6 h under the simulated sunlight radiation, which is much greater than that realized by the rGO and geometry TiO$_2$ catalyst. The UV-vis diffuse reflectance spectrum shows that P25 and equaixial TiO$_2$ have no absorption in the visible light region, and the absorption of the composite in the visible light region is much improved which indicates that the introduction of rGO enhanced the visible light response. The rGO and TiO$_2$ play a significant role in TiO$_2$ photocatalytic activity and showing that the modification of rGO to TiO$_2$ geometry boosted the efficiency of TiO$_2$ photocatalytic activity. Thus, we believe that this type of work may open a new dimension in the degradation of pollutants to obtain a water environment free of pollutants.

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Declarations

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