Enhanced Ultraviolet-Visible Photocatalysis of RGO/Equaixial Geometry TiO₂ Composites on Degradation of Organic Dyes in Water

Jaafar Hasan

Northwestern Polytechnical University

Jing Wang

Northwestern Polytechnical University

Zhentao Wang

Northwestern Polytechnical University

Muhammad Idrees

Shenzhen University

Saima Batool

Shenzhen University

Caiwei Zhang

Northwestern Polytechnical University

Chuanguang Qin (✉ qinchg@nwpu.edu.cn)

Northwestern Polytechnical University <https://orcid.org/0000-0003-4849-0187>

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Abstract

The reduced graphene oxide doped equiaxial geometry TiO_2 (rGO/eg TiO_2) composite as photocatalyst was synthesized hydrothermally with various mass ratios of tetrabutyl titanate. The photocatalyst is considered to be rGO/equiaxial geometry TiO_2 in terms of modifying the combined reduced graphene Oxide and TiO_2 . The rGO plays a vital role in rGO/eg TiO_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/eg TiO_2 composite exhibits enhanced photo-catalytic performance with degradation rate 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/eg TiO_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 photo catalytic activity for the removal of organic contaminants from wastewater.

1. 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 have been continuously improved. However, with rapid growing explosive industrial growth that mainly depends on industrial fossil fuels have severely caused global environmental pollution. The vast majority of toxic waste emitted into the air and water, destroying nature's ecology and causing various health and survival problems for living organism (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, photo catalytic 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 photo catalytic electrolysis water into H_2 and O_2 , or degrade 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 physicochemical 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 developed semiconductor materials that can be used for photo catalysis include TiO_2 , ZnO, ZnS, CdS, MoS_2 , WO_3 and Fe_2O_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 material owing to its electronic, optical and photovoltaic applications. The TiO_2 has a high level of photo catalytic activity and chemical stability (Rajender et al. 2018). Moreover, The TiO_2 is inexpensive, non-toxic, and allows high oxidation and long-term stability against optical and chemical corrosion (Cerrato et al. 2019,

Gunnagol & Rabinal 2019, Surikanti et al. 2019, Wang et al. 2014). Yet, the wide band gap (3.0-3.2V) limits the optical response in the UV region. For TiO_2 , the highest recombination time is 10^{-9} seconds while the minimal reaction time between pollutants and the chemical reaction of electrons varies between 10^{-8} - 10^{-2} seconds (Lu et al. 2017, Tian et al. 2017). The electron-hole shaped through the pair is reconfigured via difference 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 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 dispersion of nanoparticles. The higher contact area between TiO_2 nanoparticles and contaminants has promoted the photo-degradation of pollutants. 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 & Chen 2011, ChongYeon et al. 2013, Du & Cheng 2012, Giovannetti et al. 2016). Graphene has a broad two-dimensional sp^2 conjugated network that exhibits electron mobility up to $15,000 \text{ cm}^2/\text{Vs}$ at room temperature (Geim & 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 hetero-junction 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 photo response range of the photocatalyst in 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 nanomaterials 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 & 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. prepped 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 m²/g that observed an almost complete MB removal within 4 h (Kurniawan et al. 2020). TiO₂/rGO composites were prepared by the hydrothermal method under solar irradiation, the generation rate of hydroxyl HO. radicals under irradiation was higher in pure TiO₂ than that in TiO₂/rGO, but they decayed with time, so TiO₂/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 TiO₂ 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 wavelength 200 to 400 nm, about 50% is visible radiation that has wavelength 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 doped equiaxial geometry TiO₂ (rGO/egTiO₂) 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/egTiO₂ composite in terms of modifying the combined reduced graphene Oxide and TiO₂. The main idea is to combine TiO₂ with the conjugated electronic material rGO to make it the carrier of TiO₂ particle growth to promote particle dispersion. The outcome demonstrates that rGO/egTiO₂ composite has a wider range from UV to visible light and greater absorption abilities to the solar irradiation than egTiO₂ 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.

2. Experimental Section

2.1. Materials

Potassium persulfate (K₂S₂O₈), isopropanol ((CH₃)₂CHOH) and hydrogen peroxide (H₂O₂) were purchased from Shanghai Guangdong Chemical Reagent Engineering Technology R&D Center, China. Tetrabutyl titanate (C₁₆H₃₆O₄Ti) was purchased from Chengdu Kelong Chemical Co., Ltd. Sodium nitrate (NaNO₃), Methylene blue (MB), and rhodamine B was purchased from Tianjin Komio Chemical Reagent Co., Ltd. All the chemicals were of high analytical grade and used as received.

2.2. Preparation of GO and rGO

Graphene oxide (GO) was typically synthesized according to Hummers modified (Haag & 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 stainless steel autoclave and heated at 180 ° C for 8 h. After cooling, the product was taken out. The product was washed 5 times with absolute ethanol and dried in a vacuum oven at 50 ° C. A black rGO powder product is obtained.

2.3. Preparation of equiaxial geometry TiO_2

50 mL of isopropanol solution, add 10 mL of tetrabutyl titanate, and stir for 30 min. 2 mL of distilled water was added dropwise and the mixture was stirred for another 30 min. The light gray sol was transferred to a 100 mL Teflon reactor and heated at 180°C for 8 h. After completion, the product was taken out after cooling and the powder was washed with absolute ethanol 5 times and then dried in an oven at 50°C. A white powder product is obtained.

2.4. Preparation of rGO/ equiaxial 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. (2 mL, 4 mL, 6 mL, 8 mL 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 drop wise 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 for 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%, 2.6%. Using the same method, pure rGO can be obtained without adding tetrabutyl titanate.

2.5. Photocatalyst Characterization

The crystal phases of the as-synthesized catalysts were characterized via X-ray powder diffraction (XRD, D2 PHASER X) with Cu $\text{K}\alpha$ with irradiation source of $\lambda = 1.54178 \text{ \AA}$ in the (2θ) range between 5–90°. The morphology were analyzed using a 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 were taken by UV–Vis Spectrophotometer (UV1800, Jinghua Instruments Co. Ltd., China) under 200–800 nm scanning rate. The photochemical reactor was equipped with 1000 W adjustable Xe lamp a 300–500 W ($\lambda > 420 \text{ nm}$) as a light source. DS-GHX-V, Dusi Instruments Co. Ltd. (Shanghai, China).

2.6. 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 ($\lambda > 420 \text{ nm}$). The photocatalytic operation of the photocatalyst concerned was

evaluated based on the dye decolorization and the absorption spectrum of UV-vis under ultraviolet light or visible light. In present work, MB and RhB dyes have been preferred, and the associated with 664 nm and 554 nm absorption wavelengths, respectively. The light source's power is modified as per 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 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 Eq. (1).

$$\text{Degradation (\%)} = [(C_o - C_t)/C_o] \times 100 \quad (1)$$

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

3. Results And Discussion

3.1 The XRD analysis of rGO/egTiO₂ composites

Figure 1a shows the XRD pattern of rGO/equaixial geometry of TiO₂ composite with different mass ratio. All the diffracted peaks are coincidence with the standard XRD pattern of anatase crystal TiO₂ and tetragonal system (JCPDS, 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 TiO₂, it is surface cannot sustain the original shape and the original stack-up rules, 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 TiO₂ 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 crystalline, and also when the content of rGO is relatively high, it will slightly affect the crystallinity of TiO₂ 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 TiO₂ peaks, which proves the samples are relatively pure.

3.2 The morphology observation of rGO/egTiO₂ composites under SEM

The SEM image of rGO/equaixial geometry TiO₂ composites with different mass ratios as shown in Fig. 2. In order to get a better comparison, the SEM image of pure rGO and TiO₂ was added. Figure 2(a), is the SEM images of the pure rGO sample. Figure 2(b, c, d, e, and f) successively show the SEM images of rGO/equaixial geometry TiO₂ composite samples with mass ratios of 12.7%, 6.4%, 4.3%, 3.2% and 2.6%. Figure 2(g and h) are the SEM images of pure equaixial geometry TiO₂ particles with different magnification ratios. It can be seen clearly after compounding with each other rGO lamellas covered by a lot of TiO₂ particles to observe the presence of rGO. Some bare areas on the rGO surface are chosen, thus the corresponding rough particle density maybe not be observed in the picture with proportion, which will be seen in TEM images. Although there will be aggregations of particles, it can be observed from Fig. 2 that TiO₂ is equably dispersed on rGO layers, make the dispersion more equable, which indicates that the aggregations of TiO₂ particles were prevented after compounding with rGO. The recombination of TiO₂ 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 TiO₂ with a 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.

3.3 The TEM morphology and the EDX diagram of rGO/egTiO₂ composites

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 lowerest 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 is 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 very equable, whose average size of crystal particles can only reach 16.5nm. 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.

3.4 The UV-Vis diffuse reflectance spectra of rGO/egTiO₂ composites

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 TiO₂ composites with composite ratios of 2.6%. It can be seen from the figure that P25 and equiaxial geometry TiO₂ 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 TiO₂ composites exhibited a certain intensity of absorption in the visible light region, which 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 the Eq. (2):

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

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

3.5 The Raman shift spectrum and Electrochemical impedance spectra of rGO/egTiO₂ composites

The Raman spectrum of nanocomposite TiO₂, rGO, and rGO/equaixial 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_{1g}, B_{1g}, A_{1g}, 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/equaixial 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 & 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/equaixial geometry TiO₂ (0.83), less than the intensity ration of rGO (0.84), This is because of the reduced sp² 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/equaixial 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/equaixial geometry TiO₂ was far higher than that of rGO and geometry TiO₂, indicating that under visible light irradiation as shown in Fig. 5b, and under solar radiation, as shown in Fig. 5c, and more efficient charge separation of electron-hole pairs in rGO/equaixial 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/equaixial geometry TiO₂. In the EIS of rGO/equaixial 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/equaixial 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.

3.6 Nitrogen absorption – desorption isotherms and pore size of rGO/egTiO₂ composite

As 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 N₂ 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 m²/g, while the average pore size was 2.822 nm, as seen in Fig. 6(a), larger than that of surface area (3.32 m²/g), (16.38 m²/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.

3.6 The photocatalytic performance of rGO/egTiO₂ composite on organic dye degradation

After confirming the successful recombination between equiaxial geometry TiO₂ and rGO, we also need to simulate test its photo-catalysis performance, stimulate pollutions but still choose the organic dye stuffs 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/equiaxial geometry TiO₂ composites under ultraviolet rays with different composite ratios to RhB by using mercury lamps of 370W, and compared with single equiaxial geometry TiO₂ 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 minutes. 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 equiaxial geometry TiO₂, its degradation rates are relatively low, but the degradation rate of other composites with various ratios have 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 minutes. 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/equiaxial geometry TiO₂ composites with the mass ratio of 2.6% of rGO: TiO₂ to RhB, whose absorption on dye stuffs 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. Afterward, under the same conditions, we tested the degradation curve figures of the rGO/equiaxial geometry TiO_2 composites with different composite ratios on MB and compared them with single equiaxial geometry TiO_2 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 dyestuffs for MB around 97% in 60 minutes. Therefore, Fig. 7(d) showed a UV-vis absorption spectrum of rGO/equiaxial geometry TiO_2 composites with a mass ratio of 6.4% of rGO: TiO_2 on the degraded MB. It is found that comparing each single component, the photocatalysis activity of composites increased by analyzing the degradation process of rGO and TiO_2 , which can be attributed to the cooperative effect of rGO and TiO_2 , making agglomerate TiO_2 dispersed on rGO lamellas, graphene lamellas are also divided. The two shaped hetero junctions, the graphene is used as electron acceptor materials, and the character of its readily electricity conduction can effectively prevent the recombination of photo-electrons and holes, providing better conditions and time of the occurring of oxidization process than before.

To explore the degradation process under sunlight the sample was tested and degradation curve pictures of the rGO/equiaxial geometry TiO_2 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 800W. We compared them with a single equiaxial 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 hours 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 hours 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/equiaxial geometry TiO_2 compounds with the mass ratio of 4.3% of rGO: TiO_2 on RhB and 6.4% 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 1. The following Eq. (3) was used to analyze the kinetic photocatalytic degradation of organic dyes:

$$\ln\left(\frac{c}{c_0}\right) = k_{\text{app}} t, \quad (3)$$

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 1
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			RhB	MB	RhB	MB
rGO	85.0	88.0	UV	1	0.022	0.038	0.87	0.92
egTiO ₂	84.0	89.0	UV	1	0.026	0.036	0.97	0.96
rGO/egTiO ₂	97.5	97.0	UV	1	0.047	0.056	0.93	0.95
rGO	80.0	80.0	Sunlight	6	0.24	0.24	0.87	0.85
egTiO ₂	84.0	82.0	Sunlight	6	0.26	0.25	0.95	0.95
rGO/egTiO ₂	94.0	92.0	Sunlight	6	0.36	0.35	0.96	0.97

3.7 The photocatalytic mechanism of the rGO/egTiO₂ composite

To describe the degradation mechanism of organic dye (MB and RhB) through rGO/equaixial geometry TiO₂ 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 TiO₂. 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 TiO₂ was credited to simple physical and chemical adsorption resulting from (π - π) 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 nano-level 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 $\text{O}_2^{\cdot-}$, which will continue to make a series of reactions to produce $^{\cdot}\text{OH}$, 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 $\text{O}_2^{\cdot-}$ and $^{\cdot}\text{OH}$ that have strong oxidization ability, and as such reacts with organic dyes which can degrade to CO_2 , H_2O , 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 acts 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/equiaxial 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/equiaxial 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_2O , 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.

4. Conclusion

We have successfully synthesized the reduced graphene oxide dopped equaixial geometry TiO_2 (rGO/eg TiO_2) composite with different ratios of tetrabutyl titanate supported on rGO in isopropyl alcohol via hydrothermal followed by solvothermal method. Characterizations 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 from the catalyst rGO/equaixial geometry TiO_2 was respectively 97.5 and 97.0% in 60 minutes under the UV radiation, 94 and 92% in 6 hours 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.

5. Declarations

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Declaration of interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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6. References

1. Byrne C, Subramanian G, Pillai SC (2018): Recent advances in photocatalysis for environmental applications. *Journal of Environmental Chemical Engineering* 6, 3531-3555.
2. Cao L, Li Y-F, Tong Y, Yang R, Sun L, Cao Q, Chen R (2019): A novel $\text{Bi}_{12}\text{TiO}_{20}/\text{g-C}_3\text{N}_4$ hybrid catalyst with a bionic granum configuration for enhanced photocatalytic degradation of organic pollutants. *Journal of Hazardous Materials* 379, 120808.
3. Cerrato G, Galli F, Boffito DC, Operti L, Bianchi CL (2019): Correlation preparation parameters/activity for microTiO_2 decorated with SilverNPs for NO_x photodegradation under LED light. *Applied Catalysis B: Environmental* 253, 218-225.
4. Chang K, Chen W (2011): In situ synthesis of MoS_2 /graphene nanosheet composites with extraordinarily high electrochemical performance for lithium ion batteries. *Chemical Communications* 47, 4252-4254.
5. ChongYeon P, Ghosh T, ZeDa M, Kefayat U, Vikram N, WonChun O (2013): Preparation of CuS -graphene oxide/ TiO_2 composites designed for high photonic effect and photocatalytic activity under visible light. *Chinese Journal of Catalysis* 34, 711-717.
6. Ding Y, Zhou Y, Nie W, Chen P (2015): MoS_2 -GO nanocomposites synthesized via a hydrothermal hydrogel method for solar light photocatalytic degradation of methylene blue. *Applied Surface Science* 357, 1606-1612.
7. Du J, Cheng HM (2012): The fabrication, properties, and uses of graphene/polymer composites. *Macromolecular Chemistry and Physics* 213, 1060-1077.
8. Eren MŞ, Arslanoğlu H, Çiftçi H (2020): Production of microporous Cu-doped BTC (Cu-BTC) metal-organic framework composite materials, superior adsorbents for the removal of methylene blue (Basic Blue 9). *Journal of Environmental Chemical Engineering* 8, 104247.
9. Fu C, Liu X, Wang Y, Li L, Zhang Z (2019): Preparation and characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ -Co/rGO magnetic visible light photocatalyst for water treatment. *RSC Advances* 9, 20256-20265.
10. Gao B, Chen GZ, Puma GL (2009): Carbon nanotubes/titanium dioxide (CNTs/TiO_2) nanocomposites prepared by conventional and novel surfactant wrapping sol-gel methods exhibiting enhanced photocatalytic activity. *Applied Catalysis B: Environmental* 89, 503-509.

11. Garrafa-Gálvez HE, Alvarado-Beltrán CG, Almaral-Sánchez JL, Hurtado-Macías A, Garzon-Fontecha AM, Luque PA, Castro-Beltrán A (2019): Graphene role in improved solar photocatalytic performance of TiO₂-RGO nanocomposite. *Chemical Physics* 521, 35-43.
12. Geim AK, Novoselov KS (2010): The rise of graphene, *Nanoscience and technology: a collection of reviews from nature journals*. World Scientific, 11-19.
13. Giovannetti R, Rommozzi E, Zannotti M, D'Amato C, Ferraro S, Cespi M, Bonacucina G, Minicucci M, Di Cicco A (2016): Exfoliation of graphite into graphene in aqueous solution: An application as graphene/TiO₂ nanocomposite to improve visible light photocatalytic activity. *RSC Advances* 6, 93048-93055.
14. Gunnagol RM, Rabinal MHK (2019): TiO₂/rGO/CuS Nanocomposites for Efficient Photocatalytic Degradation of Rhodamine-B Dye. *ChemistrySelect* 4, 6167-6176.
15. Guo H, Jiang N, Wang H, Shang K, Lu N, Li J, Wu Y (2019): Enhanced catalytic performance of graphene-TiO₂ nanocomposites for synergetic degradation of fluoroquinolone antibiotic in pulsed discharge plasma system. *Applied Catalysis B: Environmental* 248, 552-566.
16. Guo H, Shu Z, Chen D, Tan Y, Zhou J, Meng F, Li T (2020): One-step synthesis of S-doped g-C₃N₄ nanosheets for improved visible-light photocatalytic hydrogen evolution. *Chemical Physics* 533, 110714.
17. Haag D, Kung HH (2014): Metal free graphene based catalysts: a review. *Topics in Catalysis* 57, 762-773
18. Hasan J, Li H, Tian G, Qin C (2020): Fabrication of Cr₂S₃-GO-TiO₂ composite with high visible-light-driven photocatalytic activity on degradation of organic dyes. *Chemical Physics*, 110950.
19. Hasan J, Ouyang G, Wang J, Li H, Tian G, Qin C (2021): Efficient Visible-light-driven Photocatalysis of Flower-like Composites of AgI nanoparticle/BiOI nanosheet. *Journal of Solid State Chemistry*, 122044.
20. Khan SA, 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.
21. Kurniawan TA, Mengting Z, Fu D, Yeap SK, Othman MHD, Avtar R, Ouyang T (2020): Functionalizing TiO₂ with graphene oxide for enhancing photocatalytic degradation of methylene blue (MB) in contaminated wastewater. *Journal of environmental management* 270, 110871.
22. Leal JF, Cruz SM, Almeida BT, Esteves VI, Marques PA, Santos EB (2020): TiO₂-rGO nanocomposite as an efficient catalyst to photodegrade formalin in aquaculture's waters, under solar light. *Environmental Science: Water Research & Technology* 6, 1018-1027.
23. Li X, Zhang J, Huo Y, Dai K, Li S, Chen S (2021): Two-dimensional sulfur-and chlorine-codoped g-C₃N₄/CdSe-amine heterostructures nanocomposite with effective interfacial charge transfer and mechanism insight. *Applied Catalysis B: Environmental* 280, 119452.

24. Lim J, Um JH, Lee KJ, Yu S-H, Kim Y-J, Sung Y-E, Lee J-K (2016): Simple size control of TiO₂ nanoparticles and their electrochemical performance: emphasizing the contribution of the surface area to lithium storage at high-rates. *Nanoscale* 8, 5688-5695.
25. Lin Y, Zou J, Yang W, Li C-Q (2018): A review of recent advances in research on PM_{2.5} in China. *International Journal of Environmental Research and public health* 15, 438.
26. Liu X-w, Shen L-y, Hu Y-h (2016): Preparation of TiO₂-graphene composite by a two-step solvothermal method and its adsorption-photocatalysis property. *Water, Air, & Soil Pollution* 227, 141.
27. Lu W-C, Tseng L-C, Chang K-S (2017): Fabrication of TiO₂-reduced graphene oxide nanorod composition spreads using combinatorial hydrothermal synthesis and their photocatalytic and photoelectrochemical applications. *ACS Combinatorial Science* 19, 585-593.
28. Lu Y, Zhang X, Chu Y, Yu H, Huo M, Qu J, Crittenden JC, Huo H, Yuan X (2018): Cu₂O nanocrystals/TiO₂ microspheres film on a rotating disk containing long-afterglow phosphor for enhanced round-the-clock photocatalysis. *Applied Catalysis B: Environmental* 224, 239-248.
29. Luna-Sanguino G, Ruíz-Delgado A, Tolosana-Moranchel A, Pascual L, Malato S, Bahamonde A, Faraldos M (2020): Solar photocatalytic degradation of pesticides over TiO₂-rGO nanocomposites at pilot plant scale. *Science of The Total Environment* 737, 140286.
30. Mathpal MC, Tripathi AK, Singh MK, Gairola S, Pandey S, Agarwal A (2013): Effect of annealing temperature on Raman spectra of TiO₂ nanoparticles. *Chemical Physics Letters* 555, 182-186.
31. Monteagudo J, Durán A, Martínez M, San Martín I (2020): Effect of reduced graphene oxide load into TiO₂ P25 on the generation of reactive oxygen species in a solar photocatalytic reactor. Application to antipyrine degradation. *Chemical Engineering Journal* 380, 122410.
32. Nguyen CH, Tran ML, Van Tran TT, Juang R-S (2020): Enhanced removal of various dyes from aqueous solutions by UV and simulated solar photocatalysis over TiO₂/ZnO/rGO composites. *Separation and Purification Technology* 232, 115962.
33. Padmanabhan NT, Thomas N, Louis J, Mathew DT, Ganguly P, John H, Pillai SC (2021): Graphene coupled TiO₂ photocatalysts for environmental applications: A review. *Chemosphere*, 129506.
34. Pitre SP, Yoon TP, Scaiano JC (2017): Titanium dioxide visible light photocatalysis: surface association enables photocatalysis with visible light irradiation. *Chemical Communications* 53, 4335-4338.
35. Prabhu S, Cindrella L, Kwon OJ, Mohanraju K (2017): Superhydrophilic and self-cleaning rGO-TiO₂ composite coatings for indoor and outdoor photovoltaic applications. *Solar Energy Materials and Solar Cells* 169, 304-312.
36. Rajender G, Kumar J, Giri P (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.
37. Shehzad N, Zafar M, Ashfaq M, Razzaq A, Akhter P, Ahmad N, Hafeez A, Azam K, Hussain M, Kim WY (2020): Development of AgFeO₂/rGO/TiO₂ Ternary Composite Photocatalysts for Enhanced

- Photocatalytic Dye Decolorization. Crystals 10, 923.
38. Song J, Ling Y, Xie Y, Liu L, Zhu H (2018): One-pot engineering TiO₂/graphene interface for enhanced adsorption and photocatalytic degradation of multiple organics. Nanotechnology 29, 395701
 39. Surikanti GR, Bandarapu AK, Sunkara MV (2019): A Facile One Pot Synthesis of Cu₂O@ TiO₂: A Nanocomposite Catalyst for Enhanced Visible Light Driven Photocatalysis#. ChemistrySelect 4, 2249-2257.
 40. Tian Z, Yu N, Cheng Y, Wang Z, Chen Z, Zhang L (2017): Hydrothermal synthesis of graphene/TiO₂/CdS nanocomposites as efficient visible-light-driven photocatalysts. Materials Letters 194, 172-175
 41. Trapalis A, Todorova N, Giannakopoulou T, Boukos N, Speliotis T, Dimotikali D, Yu J (2016): TiO₂/graphene composite photocatalysts for NO_x removal: a comparison of surfactant-stabilized graphene and reduced graphene oxide. Applied Catalysis B: Environmental 180, 637-647.
 42. Velasco-Hernández A, Esparza-Muñoz R, de Moure-Flores F, Santos-Cruz J, Mayén-Hernández S (2020): Synthesis and characterization of graphene oxide-TiO₂ thin films by sol-gel for photocatalytic applications. Materials Science in Semiconductor Processing 114, 105082.
 43. Wanag A, Rokicka P, Kusiak-Nejman E, Kapica-Kozar J, Wrobel RJ, Markowska-Szczupak A, Morawski AW (2018): Antibacterial properties of TiO₂ modified with reduced graphene oxide. Ecotoxicology and Environmental Safety 147, 788-793.
 44. Wang J, Li Y, Ge J, Zhang B-P, Wan W (2015a): Improving photocatalytic performance of ZnO via synergistic effects of Ag nanoparticles and graphene quantum dots. Physical Chemistry Chemical Physics 17, 18645-18652.
 45. Wang S, Guan Y, Wang L, Zhao W, He H, Xiao J, Yang S, Sun C (2015b): Fabrication of a novel bifunctional material of BiOI/Ag₃VO₄ with high adsorption–photocatalysis for efficient treatment of dye wastewater. Applied Catalysis B: Environmental 168, 448-457.
 46. Wang Y, He Y, Lai Q, Fan M (2014): Review of the progress in preparing nano TiO₂: An important environmental engineering material. Journal of Environmental Sciences 26, 2139-2177
 47. Wu K, Chen D, Lu S, Fang J, Zhu X, Yang F, Pan T, Fang Z (2020): Supramolecular self-assembly synthesis of noble-metal-free (C, Ce) co-doped g-C₃N₄ with porous structure for highly efficient photocatalytic degradation of organic pollutants. Journal of Hazardous Materials 382, 121027.
 48. Xu L, Cheng L (2013): Graphite oxide under high pressure: a Raman spectroscopic study. Journal of Nanomaterials 2013.
 49. Yadav HM, Kim J-S (2016): Solvothermal synthesis of anatase TiO₂-graphene oxide nanocomposites and their photocatalytic performance. Journal of Alloys and Compounds 688, 123-129.
 50. Yu L, Wang L, Sun X, Ye D (2018): Enhanced photocatalytic activity of rGO/TiO₂ for the decomposition of formaldehyde under visible light irradiation. Journal of Environmental Sciences 73, 138-146.

51. Zouzelka R, Remzova M, Plsek J, Brabec L, Rathousky J (2019): Immobilized rGO/TiO₂ photocatalyst for decontamination of water. Catalysts 9, 708.

Figures

Figure 1

The XRD pattern of rGO/egTiO₂ composite with different mass ratios (a) and the XRD pattern of rGO (b).

Figure 2

The SEM images of rGO/egTiO₂ composites with different composite ratios: (a) is pure rGO, (b, c, d, e, and f) are respectively rGO/egTiO₂ composites with the mass ratios of 12.7%, 6.4%, 4.3%, 3.2% and 2.6%, and (g, h) is pure equiaxial geometries.

Figure 3

The TEM images of rGO/egTiO₂ composites with different composite ratios: (a) is pure rGO, and (b, c, d, e, and f) are respectively rGO/egTiO₂ 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: TiO₂ mass ratio of 4.3% (h).

Figure 4

(a) UV-Vis diffuse reflectance spectra of three different samples and (b) Plots of $(Ah\nu)^{1/2}$ versus energy $(h\nu)$ for the band gap energy of equiaxial geometry of TiO_2 , and P25.

Figure 5

(a) Raman shift spectrum of TiO₂, rGO, 2.6, 6.4, and 12.7% of rGO/egTiO₂, the photo-current response of rGO, geometry TiO₂, and rGO/egTiO₂, (b) under visible light irradiation and (c) under solar radiation, and Electrochemical impedance spectra of TiO₂, rGO, 2.6, 6.4, and 12.7% of rGO/egTiO₂, (d) under visible light irradiation and (e) under solar radiation.

Figure 6

Nitrogen absorption–desorption isotherms and pore size of (a) rGO/equiaxial geometry TiO₂ composite, (b) TiO₂, and (c) rGO.

Figure 7

The degradation curve image of the rGO/equiaxial geometry TiO₂ composites with different composite ratios on RhB and MB (a, c) under ultraviolet irradiation, and (e, g) under simulated sunlight ray, and UV-vis absorption spectrum of RhB and MB of rGO/equiaxial geometry TiO₂ composites with the mass ratio of 2.6% and 6.4% of rGO: TiO₂ (b, d) under ultraviolet irradiation, and the mass ratio of 4.3% and 6.4% of rGO: TiO₂ (f, h) under simulated sunlight.

(a) UV irradiation

(b) solar irradiation

Figure 8

Mechanism of the photocatalytic activity of the rGO/equaiaxial geometry TiO₂ composite.

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