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Article

Direct electrospinning method for the construction of Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts with remarkably ameliorated photocatalytic performance

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ABSTRACT

A series of Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts are successfully constructed via a direct electrospinning technique coupled with an annealing process for the first time. They are investigated comprehensively in terms of crystal structure, morphology, composition, specific surface area, photoelectrochemical properties, photodegradation performance, etc. Compared with binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and single-component photocatalysts, ternary heterojunction photocatalysts show the best photodegradation performance for RhB under stimulated sunlight. This can be attributed to the enlarged specific surface area ($111.41 \text{ m}^2/\text{g}$), the formation of Z-scheme heterojunction, and the high separation migration efficiency of photoexcited charge carriers. A potential Z-scheme mechanism for ternary heterojunction photocatalysts is proposed to elucidate the remarkably ameliorated photocatalytic performance based on active species trapping experiments, PL detection test of hydroxyl radicals, and photoelectrochemical properties.

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1. Introduction

Organic dyes are utilized extensively in textile and other industries, which has resulted in serious water pollution and destruction of ecological equilibrium. Therefore, researchers are focusing on curbing water pollution. Many strategies have been used to solve wastewater pollution, such as flocculation, membrane filtration, adsorption, coagulation, and photocatalysis. The photocatalysis technique is regarded as an efficient method owing to the utilization of solar energy and non-polluting discharge; thus, the development of sunlight-responsive photocatalysts is a major objective for the photodegradation of organic pollution [1–5].

TiO_2 is considered as the best-known semiconductor photocatalyst for the degradation of organic contaminants [6,7]. However, it responds to only UV light owing to its wide bandgap of 3.0–3.2 eV [8]; thus, the utilization of solar irradiation is low in case of TiO_2 . $\text{g-C}_3\text{N}_4$, as a metal-free photocatalyst, has become popular owing to its abundant raw material, visible light response, tri-s-triazine ring structure, facile preparation, etc. [9–13]. In particular, its unique layered structure with a π -conjugated system can facilitate the transport of charge carriers, and the narrow band gap of approximately 2.7 eV endows $\text{g-C}_3\text{N}_4$ with perfect visible-light-harvesting ability at approximately 460 nm [14,15]. However, its practical application is hindered owing to its high photogenerated electron-hole com-

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bination and unsatisfactory photocatalytic activity.

Hitherto, binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalysts have been reported, all of which exhibit better photocatalytic performance than single-component photocatalysts. Further, various methods have been developed, such as the hydrothermal process [16–19], solvothermal strategy [20,21], integrated hydrothermal with calcination method [22–25], in situ calcination method [26–32], chemical vapor depositions [33], microwave-assisted method [34], hydrothermal coupled with in-situ microwave-heating technique [35], combined ball-milling with calcination [36], impregnation method [37], mechanical mixing [38,39], and electrospinning coupled with calcination technique [40–44].

Reduced graphene oxide (RGO) has been investigated extensively owing to its large specific surface area and excellent electron-accepting and electron-migration features. Thus, RGO is often employed for fabricating heterojunction photocatalysts to enlarge the specific surface area and reduce the recombination efficiency of electron-hole pairs to a certain extent; therefore, the photocatalytic performance is ameliorated significantly [45,46].

As demonstrated previously, ternary photocatalysts comprising TiO_2 , $\text{g-C}_3\text{N}_4$, and RGO have demonstrated the best photocatalytic activity in comparison with binary and single-component photocatalysts [47–51]. For example, Zhang et al. [47] have successfully fabricated $\text{g-C}_3\text{N}_4$ and TiO_2 co-hybridized three-dimensional graphene aerogel composites using the hydrothermal approach coupled with freeze drying; this process comprises the preparation of C_3N_4 and graphene oxide, a hydrothermal process at 180 °C for 24 h, further hydrothermal treatment in ammonia solution at 120 °C for 3 h, and subsequent freeze drying. Wu et al. [48] synthesized indirect all-solid-state Z-scheme $\text{g-C}_3\text{N}_4$ -RGO- TiO_2 nanoheterojunctions via a liquid-precipitation route that includes the preparation of C_3N_4 and GO; moreover, the mixture of $\text{g-C}_3\text{N}_4$, GO powder, and peroxy titanate acid are subjected to the reflux process at approximately 130 °C for 13 h; subsequently, the dried samples are calcined at 500 °C under N_2 atmosphere for 2 h to obtain the $\text{g-C}_3\text{N}_4/\text{RGO}/\text{TiO}_2$ nanoheterojunctions. Hafeez et al. [49] have constructed the ternary hybrid of RGO-supported $\text{g-C}_3\text{N}_4$ - TiO_2 nanocomposites using ultrasound-assisted simple wet impregnation that involves the fabrication of $\text{g-C}_3\text{N}_4$, RGO, and TiO_2 . Subsequently, the three components are mixed in an ethanol–water solution via the ultrasonic process. Finally, $\text{g-C}_3\text{N}_4/\text{RGO}/\text{TiO}_2$ are obtained by annealing at 400 °C for 1 h. Huang et al. [51] achieved a novel hybrid photocatalyst of $\text{g-C}_3\text{N}_4/\text{TiO}_2/\text{RGO}$ by a facile one-step solvothermal strategy involving the solvothermal reaction of titanium tetraisopropoxide, fluoric acid, and ethyl alcohol in the presence of prefabricated graphene and $\text{g-C}_3\text{N}_4$ at 180 °C for 12 h. However, the abovementioned preparation process is complicated and time consuming; furthermore, a facile strategy for the construction of Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts with remarkably ameliorated photocatalytic performance is still a challenge.

As is well known, electrospinning technology is a facile and versatile method to construct nanofibers, nanotubes, multipo-

rous nanotubes, nanobelts, etc. [52–59]. A one-dimensional structure can facilitate the mobility of charge carriers and the absorption of solar light, thereby reducing the recombination of charge carriers and enhance the photocatalytic activity [60,61]. However, hitherto, ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ heterojunction photocatalysts constructed by direct electrospinning and calcination have not been reported.

In this study, Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts are fabricated using direct electrospinning coupled with annealing for the first time. A series of ternary heterojunction photocatalysts are fabricated by regulating the precursor dosage of urea, and the photocatalytic degradation performances for the Rhodamine (RhB) solution are compared under simulated sunlight. Most notably, ternary heterojunction photocatalysts exhibit the best photocatalytic degradation performances among the photocatalysts constructed. Furthermore, based on the scavenger experiments of active species, the PL detection test of hydroxyl radicals, photoelectrochemical properties, and the potential Z-scheme mechanism for $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts are elucidated to clarify the remarkably ameliorated photocatalytic performance.

2. Experimental

2.1. Construction of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts

Graphene oxide (GO) was synthesized from natural graphite using an adjusted Hummers method; the detailed process is available in our previous report [45]. Ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ heterojunction photocatalysts are constructed via a facile electrospinning process coupled with calcination, as illustrated in the Fig. 1. First, 3 mg of GO and 8 mL of DMF were sonicated for 1 h to obtain a uniform GO suspension; subsequently, 6.4 mL of $\text{C}_2\text{H}_5\text{OH}$, 1.5 g of PVP, 1.15 mL of HAc, and 3.0 mL of TBT, and different dosages of urea were introduced successively into the GO suspension above, with vigorous stirring for 4 h to achieve a homogeneous sol. Subsequently, the sol was loaded into a syringe-equipped steel needle linked with a direct current high voltage of 15 kV. The distance from the collector was fixed at 15 cm, and as-spun TBT/Urea/PVP/GO precursor nanofibers were obtained, collected, and calcined at 500 °C for 3 h at a heating rate of 2 °C/min to obtain the electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary

Fig. 1. Schematic illustration of the construction of electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts via a direct electrospinning coupled with calcination method.

Table 1

Recipes of electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts and the statistical results of electrospun fibers by the Image J software.

Sample	Urea (g)	GO (mg)	Diameter range (nm)	Mean diameter (nm)
TiO_2	0	0	45–163	91
$\text{TiO}_2/\text{g-C}_3\text{N}_4$	0.6	0	74–201	145
$\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-1}$	0.3	3	60–230	112
$\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$	0.6	3	62–255	160
$\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-3}$	0.9	3	55–299	171
$\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-4}$	1.2	3	160–354	238

heterojunction photocatalysts. The resultant samples are denoted as $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-}x$ ($x = 1, 2, 3$, and 4) that correspond to the different dosages of urea (0.3, 0.6, 0.9, and 1.2 g, respectively). For comparison, TiO_2 and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ were also fabricated according to the parameters in Table 1; moreover, the calcination process parameters are the same.

2.2. Photocatalytic activity measurement

The photocatalytic performance was evaluated by the degradation of the RhB aqueous solution under the simulated solar light of a 500-W Xenon lamp. Specifically, the degradation experiment of a 50-mL RhB aqueous solution (10 mg/L) containing 50 mg of photocatalyst was performed after the absorption-desorption equilibrium for 30 min in the dark with magnetic stirring. Subsequently, the xenon lamp was opened, and 4 mL of the suspension solution was sampled at a fixed interval time and monitored using the UV-vis spectra (Beijing Purkinji Instrument Co., Ltd., China) at 554 nm after removing the photocatalysts.

2.3. Photoelectrochemical measurement

Next, 30 of mg photocatalyst, 0.15 mL $\text{C}_2\text{H}_5\text{OH}$, and 0.15 of mL Nafion aqueous solution (5 wt%) were sonicated to obtain a homogeneous mixture that was then coated on a 1 cm^2 ITO glass. A working electrode was achieved after the evaporation of $\text{C}_2\text{H}_5\text{OH}$. The standard three-electrode cell consisted of the reference electrode (Ag/AgCl), counter electrode (platinum plate), and working electrode (as-prepared photocatalyst). The photocurrent responses and electrochemical impedance spectra (EIS) tests were implemented on an electrochemical system (CHI 760D, Shanghai Chenhua Instrument Co. Ltd. China), where the electrolyte was Na_2SO_4 solution (0.1 mol/L), and a 300-W xenon lamp with a 420 nm cutoff filter was used.

2.4. Characterization

The X-ray diffraction (XRD) patterns, Fourier transform infrared (FTIR) spectra, and X-ray photoelectron spectroscopy (XPS) analysis results were obtained using the Shimadzu XRD 7000 diffractometer with $\text{Cu K}\alpha$ radiation, Nicolet Instruments Research Series 5PC FTIR spectrometer, and VG Multilab 2000 with $\text{Al-K}\alpha$ operation at 300 W, respectively. The surface morphologies and elementary composition were recorded using a

scanning electron microscope (SEM, TESCAN MAIA 3 LMH) equipped with energy-dispersive X-ray analysis (EDX). The Shimadzu UV-3600 Spectrophotometer was employed to record the UV-vis diffuse reflectance absorption spectra (DRS). The PerkinElmer LS55 fluorescence spectrophotometer was employed to detect the PL spectra with the excitation wavelength of 320 nm. Micromeritics ASAP2020 at -196°C was used to collect the N_2 adsorption-desorption isotherms. Bruker IFS 66V/FRA 106 was employed to measure the Raman spectroscopy. The JEOL JEM2100F transmission electron microscope (TEM) was utilized to collect the TEM, HRTEM, and element mapping images.

3. Results and discussion

3.1. Morphology analysis of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$

Fig. 2 shows the morphology evolution from TiO_2 to the electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction with increasing urea dosage. The bulk $\text{g-C}_3\text{N}_4$ with porous structure in Fig. 2(a) is aggregated significantly. Fig. 2(b) shows bare GO that demonstrated thin flake-like morphology with wrinkles. Fig. 2(c) displays the electrospun TiO_2 with porous structure; the fiber diameters are in the range of 45–163 nm, and the mean diameter is approximately 91 nm. As shown in Fig. 2(d), when 0.6 g of urea is introduced in the TBT/PVP precursor solution, the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ fibers possess many dinky pores and surface-wrinkled skin owing to the decomposition of urea. The fiber diameters are in the range of 74–201 nm, and the mean diameter increased to approximately 145 nm owing to the introduction of urea. When both GO and urea are charged into the TBT/PVP precursor solution, a series of electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts with different morphologies are obtained by the variation in urea dosage, as shown in Fig. 2(e–h). We observed that ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ photocatalysts are composed primarily of wrinkle-like RGO and nanofibrous $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and the wrinkle-like RGO surface are tightly wound by plenty of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanofibers. The nanofibrous $\text{TiO}_2/\text{g-C}_3\text{N}_4$ in ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ photocatalysts become shorter and thicker on increasing the urea dosage from 0.3 to 1.2 g, the mean diameter increases from 112 to 238 nm, respectively, and the fiber length shortens significantly. In particular, when the urea dosage is 0.6 g, as depicted in Fig. 2(f), the nanofibrous $\text{TiO}_2/\text{g-C}_3\text{N}_4$ in ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalysts possesses the proper length, many $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanofibers tightly wound the RGO surface, which confirms the good contact between the RGO and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanofibers, and the heterojunctions are constructed successfully. The isolation efficiency of the electron-hole pairs is improved through the intimate heterojunction interface. Furthermore, the one-dimensional (1D) fiber morphology is not only beneficial for the mobility and isolation of photoexcited charge carriers, but also for the collection and reutilization of photocatalysts [60,61]. Additionally, Fig. 2(i) displays the EDX spectrum of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$. It is noteworthy that Ti, O, C, and N elements are detected, all of which originated from

Fig. 2. SEM images. (a) g-C₃N₄; (b) GO; (c) TiO₂; (d) TiO₂/g-C₃N₄; (e) TiO₂/g-C₃N₄/RGO-1; (f) TiO₂/g-C₃N₄/RGO-2; (g) TiO₂/g-C₃N₄/RGO-3; (h) TiO₂/g-C₃N₄/RGO-4. (i) EDX spectrum of TiO₂/g-C₃N₄/RGO-2.

TiO₂/g-C₃N₄/RGO-2 photocatalysts. The results demonstrate the formation of TiO₂ and g-C₃N₄.

To verify the components and internal structure of nanofibrous TiO₂/g-C₃N₄ in TiO₂/g-C₃N₄/RGO-2 ternary heterojunction photocatalysts, TEM, HRTEM, and EDS element mapping images are obtained, as shown in Fig. 3. Based on the aforementioned SEM images, we can detect the existence of RGO. Therefore, we examine nanofibrous TiO₂/g-C₃N₄ in TiO₂/g-C₃N₄/RGO-2 ternary photocatalysts in this section. Fig. 3(a) shows the nanofibrous TiO₂/g-C₃N₄ in TiO₂/g-C₃N₄/RGO-2 ternary heterojunction photocatalysts, which displays 1D morphology with many nanopores. The results are consistent with the SEM analysis results. The lattice spacing of approximately 0.352 nm in Fig. 3(b) is recognized as the (101) lattice plane of anatase TiO₂ [41,49]. The EDS element mapping images of nanofibrous TiO₂/g-C₃N₄ in TiO₂/g-C₃N₄/RGO-2 ternary

heterojunction photocatalysts are shown in Fig. 3(c–f). The element distribution of Ti, O, and N present the 1D nanofiber profile that suggests even dispersion of TiO₂ and g-C₃N₄ components in the nanofibers. Based on the SEM, HRTEM, and EDS element mapping results, it was confirmed that ternary TiO₂/g-C₃N₄/RGO photocatalysts have the following three components: TiO₂, g-C₃N₄, and RGO. Meanwhile, the heterojunction between TiO₂ and g-C₃N₄ is demonstrated by HRTEM and EDS element mapping; the SEM images illustrate the heterojunction formation between TiO₂/g-C₃N₄ and RGO that can reduce the electron-hole recombination efficiency and ameliorate the photocatalytic property.

3.2. FTIR and Raman spectra

Fig. 4(A) represents the FTIR spectra of the as-prepared

Fig. 3. TEM (a) and HRTEM (b) images of the electrospun ternary TiO₂/g-C₃N₄/RGO heterojunction photocatalysts; EDS element mapping: (c) electron image, (d) Ti element, (e) O element, (f) N element.

Fig. 4. (A) FTIR spectra: (a) TiO₂; (b) TiO₂/g-C₃N₄; (c) TiO₂/g-C₃N₄/RGO-2; (d) g-C₃N₄. (B) Raman spectra: (a) TiO₂/g-C₃N₄/RGO-2; (b) TiO₂/g-C₃N₄.

photocatalysts. Pristine g-C₃N₄ (d) exhibits adsorption peaks at 1632 cm⁻¹ that index to the C–N stretching vibration mode; peaks located at 1243, 1319, and 1411 cm⁻¹ correspond to the typical C–N heterocyclic stretching vibration of g-C₃N₄ [47,49]. The unique absorption peak at approximately 809 cm⁻¹ is assigned to the out-of-plane flexural mode of triazine units, and a wide band in the range of 3100–3400 cm⁻¹ belongs to the stretching vibration mode of terminal NH groups [62,63]. Regarding pure TiO₂ in Fig. 4A (a), the wide band that ranged from 400 to 800 cm⁻¹ is assigned to the stretching vibration of Ti–O–Ti. Compared with the curves of TiO₂ and g-C₃N₄, the primary featured peaks of both TiO₂ and g-C₃N₄ components coexisted for the TiO₂/g-C₃N₄ and TiO₂/g-C₃N₄/RGO-2 photocatalysts, proving that TiO₂ and g-C₃N₄ are formed via a facile electrospinning method coupled with calcination. Additionally, the C=O and C–O stretching vibration bands of GO centered at 1725 and 1045 cm⁻¹ disappeared owing to the thorough reduction after the calcination process [47], which is consistent with the XRD and Raman spectra results.

Fig. 4(B) shows the Raman spectra of TiO₂/g-C₃N₄/RGO-2 and TiO₂/g-C₃N₄. The characteristic Raman fundamental modes at 148 (*E_g*), 404 (*B_{1g}*), 523 (*A_{1g}*), and 644 cm⁻¹ (*E_g*) of anatase TiO₂ are detected, indicating the existence of anatase TiO₂ [49]. Moreover, as shown from the inset, tiny peaks at approximately 1336 and 1558 cm⁻¹ in Fig. 4B(a) are observed owing to the extremely low content and complete reduction in GO; the peaks belong to the disordered (D) and graphitic (G) bands of RGO, respectively. However, g-C₃N₄ does not exhibit obvious Raman absorbance [47,49].

3.3. XRD patterns

The XRD patterns of the resultant photocatalysts are represented in Fig. 5. For pure g-C₃N₄ (a), a distinct peak centered at 2θ = 27.6° is indexed to the (002) diffraction planes of g-C₃N₄ (PDF#87-1526) [62–64]. The characteristic peaks of TiO₂ (PDF#73-1764) at 2θ = 25.4°, 37.9°, 48.1°, 54.3°, 55.2°, 62.7°, and 69.4° in Fig. 5(b) are confirmed, and are assigned to the (101), (004), (200), (105), (211), (204), and (116) lattice planes of anatase TiO₂ [41,47,49], respectively. As shown in Fig.

5(e), GO exhibits an obvious diffraction peak at the 2θ of 10.1° [51]. For TiO₂/g-C₃N₄ (c) and TiO₂/g-C₃N₄/RGO-2 (d) in Fig. 5, both the characteristic peak of g-C₃N₄ and TiO₂ can be detected, indicating the existence of TiO₂ and g-C₃N₄; however, no characteristic peaks of GO and RGO are observed owing to the low dosage of GO [3 mg] [51].

3.4. XPS analysis

XPS spectra were utilized to detect the chemical valence state and elementary composition for the TiO₂, g-C₃N₄ and electrospun TiO₂/g-C₃N₄/RGO-2 ternary heterojunction photocatalysts. Based on Fig. 6(a), the C, N, O, and Ti elements of electrospun TiO₂/g-C₃N₄/RGO ternary heterojunction photocatalysts are detected in the XPS survey, which is consistent with the results of EDX. As shown in Fig. 6(b), three peaks located at 284.8, 286.5, and 288.6 eV are observed in the magnified C1s spectrum; the peaks at 286.5 and 288.6 eV can be ascribed to the C–N–C and N–C=N backbones of g-C₃N₄, respectively. For pure g-C₃N₄, the peak appearing at 284.8 eV can be ascribed to graphitic carbon residues and *sp*² carbon in g-C₃N₄. However, the strong peak appearing at 284.8 eV can be indexed to the *sp*²-hybridized C–C bonds of RGO in the

Fig. 5. XRD patterns. (a) g-C₃N₄; (b) TiO₂; (c) TiO₂/g-C₃N₄; (d) TiO₂/g-C₃N₄/RGO-2; (e) GO.

Fig. 6. XPS spectra of TiO_2 , $\text{g-C}_3\text{N}_4$ and electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ ternary heterojunction photocatalysts. (a) XPS survey; (b) C 1s; (c) N 1s; (d) O 1s; (e) Ti 2p.

$\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ photocatalyst [49,65,66]. Three fitted peaks at 398.7, 399.5, and 401.5 eV in Fig. 6(c) of the N 1s spectrum are ascribed to the sp^2 -hybridized nitrogen ($\text{C}=\text{N}-\text{C}$), tertiary nitrogen $\text{N}-(\text{C})_3$, and amino groups with a hydrogen atom ($\text{C}-\text{N}-\text{H}$), respectively. The existence of the tertiary nitrogen $\text{N}-(\text{C})_3$ group indicates the formation of $\text{g-C}_3\text{N}_4$ [48,51]. Two peaks located at 530.0 and 531.8 eV in Fig. 6(d) of the O 1s spectrum are detected, and can be assigned to the Ti–O bonds in the TiO_2 and surface $-\text{OH}$ groups. The Ti 2p spectrum in Fig. 6(e) consist of two peaks at 458.6 and 464.2 eV that correspond to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of TiO_2 , respectively [47]. Hence, we conclude that ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ heterojunction photocatalysts have been constructed successfully.

3.5. N_2 sorption isotherm

Generally, the enlarged specific surface area of the photocatalysts is beneficial for the contact with organic pollution molecules that can enhance the photodegradation performance. Thus, both the N_2 adsorption-desorption isotherms and pore size distribution are obtained to elucidate the ameliorated photocatalytic activity, as shown in Fig. 7. The sorption isotherms in Fig. 7(A) possess the obvious hysteresis loop that can be indexed to type IV. The BET specific surface area and pore volume of binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ are $74.05 \text{ m}^2/\text{g}$, $0.177 \text{ cm}^3/\text{g}$ and $111.41 \text{ m}^2/\text{g}$, $0.199 \text{ cm}^3/\text{g}$,

Fig. 7. N_2 sorption isotherm (A) and pore size distribution (B). (a) $\text{TiO}_2/\text{g-C}_3\text{N}_4$; (b) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$.

respectively. In addition, Fig. 7(B) displays the pore size distribution of binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalysts that range from 2.5 to 20 nm. The pore size of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ binary photocatalysts are located primarily at 3 and 8 nm. However, the pore size of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ ternary photocatalysts are centered at 2.5 and 5.5 nm, and the mean pore size of binary and ternary photocatalysts are 9.87 and 7.27 nm, respectively. Therefore, the increased BET specific surface area and pore volume together with the decreased mean pore size are attributed primarily to the incorporation of GO, which is fundamental in ameliorating the photodegradation performance of electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ ternary photocatalysts.

3.6. UV-vis diffuse reflection spectra and PL spectra

Fig. 8(A) displays the UV-vis diffuse reflection spectra of the as-prepared samples. According to Fig. 8A(b), the absorption edge of $\text{g-C}_3\text{N}_4$ is located at 459.7 nm and presents splendid visible light absorption capability. However, pure TiO_2 in Fig. 8A(d) exhibits strong UV absorption ability, where the absorption edge is approximately 393.8 nm, whereas the absorption edges of binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalysts are around 440.6 and 468.3 nm, respectively, indicating the hybrid absorption feature in both the UV and visible light regions. It is noteworthy that ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ heterojunction photocatalysts exhibit a distinct red shift compared with TiO_2 and $\text{TiO}_2/\text{g-C}_3\text{N}_4$. This phenomenon may result from the outstanding synergistic interaction among TiO_2 , $\text{g-C}_3\text{N}_4$, and RGO components, which is consistent with the XRD and XPS results. Moreover, the existence of the rearranged energy level of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ is suggested. Based on the equation of $E_g = 1240/\lambda_g$, the band gap energy of the achieved photocatalysts can be estimated. Herein, λ_g and E_g denote the absorption edge and band gap energy of the semiconductor, respectively. Therefore, the corresponding band gap energy of the TiO_2 , $\text{g-C}_3\text{N}_4$, binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalysts are estimated to be 3.18, 2.70, 2.81, and 2.65 eV, respectively. It has been indicated that $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ ternary heterojunction photocatalysts

can fully utilize the UV and visible light of solar light, by which the photodegradation activity can be remarkably ameliorated.

The PL emission spectra were employed to assess which photocatalyst possessed the lowest electron-hole recombination efficiency. Based on Fig. 8(B) and the inset, it can be concluded that the ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ heterojunction photocatalyst displays the weakest peak intensity in comparison with $\text{g-C}_3\text{N}_4$ and binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$, which suggests that ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalysts possessed the lowest electron-hole recombination efficiency, and that the recombination of charge carriers are inhibited effectively owing to the heterojunction construction of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$. Moreover, RGO is crucial in the charge carriers separation and migration for $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$, thus facilitating in enhancing the photocatalytic activity.

3.7. Photodegradation activity and stability

RhB is employed as the simulated organic pollutant to evaluate the photodegradation performance of the as-prepared photocatalysts. The photocatalytic degradation and kinetics curves for the RhB aqueous solution over different photocatalysts under simulated solar light are displayed in Fig. 9. The bulk $\text{g-C}_3\text{N}_4$ in Fig. 9A (b) shows poor photocatalytic activity owing to the high recombination of photoexcited electrons and holes. The TiO_2 nanofibers shown in Fig. 9A (a) exhibit the worst photodegradation activity owing to the weak sunlight harvesting capability and charge carrier separation efficiency. Furthermore, the control experiment without photocatalyst for the degradation of RhB is negligible. The binary $\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalysts display better photocatalytic efficiency than TiO_2 and $\text{g-C}_3\text{N}_4$. In particular, the electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ ternary photocatalysts shows the best photodegradation efficiency of 99.1% within 60 min among the as-synthesized photocatalysts; this can be attributed to the following two aspects. The enhanced sunlight harvesting capability and electron-hole separation efficiency are important in ameliorating the photocatalytic performance; moreover, the enlarged specific surface area is advantageous for the enhancement in photocatalytic performance.

Fig. 8. (A) UV-vis diffuse reflection absorption spectra: (a) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$; (b) $\text{g-C}_3\text{N}_4$; (c) $\text{TiO}_2/\text{g-C}_3\text{N}_4$; (d) TiO_2 . (B) PL emission spectra: (a) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$; (b) $\text{TiO}_2/\text{g-C}_3\text{N}_4$; (c) $\text{g-C}_3\text{N}_4$.

Fig. 9. Photocatalytic degradation (A) and Kinetics curves (B) for RhB aqueous solution over different photocatalysts under simulated solar light irradiation: (a) TiO_2 ; (b) $\text{g-C}_3\text{N}_4$; (c) $\text{TiO}_2/\text{g-C}_3\text{N}_4$; (d) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-1}$; (e) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$; (f) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-3}$; (g) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-4}$; (h) no catalyst. (C) Recycled photodegradation efficiency of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$. (D) XRD patterns of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ before and after the recycling photocatalytic tests.

Based on the equation of $-\ln(C/C_0) = kt$, the kinetic curves for the photodegradation of RhB over different photocatalysts are obtained, as shown in Fig. 9B. Herein, C_0 , C , and k represent the RhB concentration at the absorption equilibrium, the RhB concentration at a given time, and the degradation rate constant, respectively. The ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ heterojunction photocatalysts show the highest kinetic constant that is approximately 6.72, 5.97, and 2.34 times larger as those of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2/\text{g-C}_3\text{N}_4$, respectively.

Fig. 9C depicts the recycled photocatalytic performance of the ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalyst, where the photodegradation efficiency of approximately 98.1% is maintained even after four runs. Moreover, the XRD patterns of the reused $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ in Fig. 9D (b) are almost the same as those of the fresh photocatalyst, thereby suggesting the good photostability of the ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ photocatalysts.

3.8. Photocurrent response and EIS analysis

In addition to the PL emission spectra, the photocurrent responses and EIS measurements of the as-synthesized photocatalysts are implemented systematically to further manifest the separation efficiency of the photoexcited charge carrier. $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ exhibits the strongest photocurrent densi-

ty in comparison with $\text{TiO}_2/\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4$, and TiO_2 , closely followed by $\text{TiO}_2/\text{g-C}_3\text{N}_4$, as shown in Fig. 10(A). Compared with $\text{TiO}_2/\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4$, and TiO_2 , the EIS Nyquist plots of $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ exhibit the smallest arc radius (Fig. 10(B)), closely followed by $\text{TiO}_2/\text{g-C}_3\text{N}_4$. Based on the analysis above and the PL emission spectra analysis, we conclude that the electrospun $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts exhibits splendid separation efficiency; thus, the recombination of electrons and holes are greatly inhibited, and the lifetime of the photogenerated electrons is prolonged, thereby ameliorating the photodegradation performance.

3.9. Trapping experiments of active species and photocatalytic mechanism

To confirm the active species that contribute to the photocatalytic degradation RhB experiments over ternary $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ heterojunction photocatalyst, the hydroxyl radical ($\cdot\text{OH}$), hole (h^+), and superoxide radical anion ($\cdot\text{O}_2^-$) were captured accordingly by the diverse trapping agents of isopropanol (IPA), triethanolamine (TEOA), and p-benzoquinone (BQ). As depicted in Fig. 11(a), when one of the three quenchers is charged into the reactive system, the photodegradation efficiency decreased; as demonstrated, $\cdot\text{O}_2^-$,

Fig. 10. Transient photocurrent response (A) and EIS Nyquist plots (B). (a) TiO_2 ; (b) $\text{g-C}_3\text{N}_4$; (c) $\text{TiO}_2/\text{g-C}_3\text{N}_4$; (d) $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$.

Fig. 11. (a) Trapping experiment of active species; (b) PL spectral variation during irradiation on the $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ using the terephthalic acid as probe molecules; (c) Proposed mechanism of the ameliorated photocatalytic performance.

$\cdot\text{OH}$, and h^+ are the active species.

Terephthalic acid (TA) was employed as the probe molecules to prove $\cdot\text{OH}$ generation detected by the PL method at approximately 425 nm. The PL spectral variation during irradiation on $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO-2}$ is shown in Fig. 11(b). The PL intensity strengthens with increasing irradiation time, indicat-

ing $\cdot\text{OH}$ generation during irradiation [11,13].

Based on the abovementioned analysis of the photocurrent response, EIS analysis, PL emission spectra, trapping experiment of active species, and PL experiments of TA molecules, the Z-scheme mechanism is proposed and schematically illustrated in the Fig. 11(c). The CB and VB positions of TiO_2 are -0.29 and

2.91 eV (vs. NHE), respectively. The CB and VB potentials of g-C₃N₄ are −1.12 and 1.58 eV (vs. NHE), respectively [51]. If the photocatalytic mechanism of TiO₂/g-C₃N₄/RGO-2 belongs to the traditional type-II heterojunction, a photoexcited e[−] will migrate from the CB of g-C₃N₄ to the CB of TiO₂. Simultaneously, h⁺ will move from the VB of TiO₂ to the VB of g-C₃N₄. However, the CB e[−] of TiO₂ cannot reduce O₂ to yield •O₂[−], because the CB position of TiO₂ is less negative than the potential of O₂/•O₂[−] (−0.33 eV vs. NHE). In addition, the VB h⁺ of g-C₃N₄ cannot oxidize H₂O to produce •OH, because the VB position of g-C₃N₄ is less positive than the potential of •OH/H₂O (2.40 eV vs. NHE) [11,13]. Thus, the hypothesis does not agree with the capturing experiments of the active species. Consequently, the Z-scheme mechanism is reasonable to elucidate the remarkably ameliorated photocatalytic performance for the ternary TiO₂/g-C₃N₄/RGO-2 heterojunction photocatalyst. When TiO₂/g-C₃N₄/RGO-2 is exposed to the stimulated sunlight, photogenerated h⁺ and e[−] are obtained. Simultaneously, the migration of e[−] from the CB of TiO₂ to the hole-rich VB of g-C₃N₄ is favored thermodynamically by the electrostatic attraction between the electrons and holes; thus, the CB e[−] of TiO₂ will transfer across the heterojunction interface to recombine with the VB h⁺ of g-C₃N₄, and the recombination between the VB h⁺ of TiO₂ and CB e[−] of g-C₃N₄ is suppressed effectively [27,67–69]. Consequently, the CB e[−] of g-C₃N₄ can reduce the O₂ to produce the •O₂[−] active species; meanwhile, the VB h⁺ of TiO₂ can directly participate in the oxidative reaction or oxidize H₂O to yield the •OH active species. Both the trapping experiment of active species and the PL experiments of TA molecules provide sufficient proof for the Z-scheme mechanism. Furthermore, the CB e[−] of TiO₂ and g-C₃N₄ can transfer to the RGO surface, and subsequently transfer freely along with the RGO network. Thus, the separation efficiencies of h⁺ and e[−] are enhanced markedly, and the lifetime and mobility of e[−] are improved significantly, both of which are manifested by the photocurrent response, EIS analysis, and PL emission spectra. Consequently, the remarkably ameliorated photocatalytic performance of TiO₂/g-C₃N₄/RGO ternary heterojunction is primarily attributed the formation of the Z-scheme [70–72].

4. Conclusions

Z-scheme TiO₂/g-C₃N₄/RGO ternary heterojunction photocatalysts with different morphologies were constructed successfully via direct electrospinning and annealing for the first time. The SEM, HRTEM, and EDS element mapping results indicated the heterojunction formation of TiO₂/g-C₃N₄/RGO. Meanwhile, the existence of TiO₂, g-C₃N₄, and RGO components were indicated. In particular, among the as-prepared photocatalysts, TiO₂/g-C₃N₄/RGO-2 with a urea dosage of 0.6 g exhibited the best photodegradation efficiency of 99.1% within 60 min for RhB under stimulated sunlight. The BET specific surface area of the ternary TiO₂/g-C₃N₄/RGO-2 heterojunction photocatalyst was 1.5 times larger than that of the binary TiO₂/g-C₃N₄ photocatalyst. Moreover, the Z-scheme mechanism for the ternary TiO₂/g-C₃N₄/RGO photocatalyst was confirmed based on the photocurrent response, EIS analysis, PL emission

spectra, active species trapping experiments, and PL detection experiments of hydroxyl radicals by TA probe molecules, thus clarifying the remarkably ameliorated photocatalytic performance.

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Graphical Abstract

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Direct electrospinning method for the construction of Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts with remarkably ameliorated photocatalytic performance

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Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ ternary heterojunction photocatalysts are constructed successfully via a direct electrospinning method coupled with annealing, and it exhibits the best photodegradation efficiency of 99.1% within 60 min among the photocatalysts achieved. Moreover, the Z-scheme mechanism is proposed to elucidate the remarkably enhanced photocatalytic performance.

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电纺法构筑高光催化活性的Z型TiO₂/g-C₃N₄/RGO三元异质结

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摘要: 太阳能光催化技术广泛应用于处理污水中。Z型光催化体系具有较强的氧化还原能力, 降低半导体的带隙, 且使导带更负, 价带更正, 有效拓宽光生电子-空穴空间距离, 抑制其复合, 大大提高了光催化剂的催化性能, 因此, 构筑直接的Z型光催化体系已成为光催化领域的研究热点之一。TiO₂具有较好的光催化性能和良好的化学稳定性, 但其禁带较宽, 只能被太阳光中约占4%的紫外光激发, 对太阳光中约占50%的可见光不响应, 且光生电子-空穴易复合。g-C₃N₄是非金属光催化剂, 具有较好的光催化活性, 可见光吸收非常强, 但比表面积较小, 光生电子-空穴易复合。还原氧化石墨烯(RGO)具有大的比表面积和优异的传输载流子能力, 可显著提高光催化剂的比表面积, 同时降低电子空穴复合效率, 从而在一定程度上改善光催化性能。大量研究证实, TiO₂/g-C₃N₄/RGO三元异质结的光催化性能明显优于单组份TiO₂, g-C₃N₄和二元TiO₂/g-C₃N₄光催化剂, 但现有制备工艺复杂且耗时, 因此, 简易地构筑具有高光催化性能的Z型TiO₂/g-C₃N₄/RGO三元异质结仍具有挑战性。

本文采用简易的直接电纺法构筑了高光催化活性的Z型TiO₂/g-C₃N₄/RGO三元异质结光催化剂, 通过调节尿素的用量成功制备了一系列不同形貌的TiO₂/g-C₃N₄/RGO三元异质结。并采用X-射线衍射、红外光谱、拉曼光谱、X射线光电子能谱、扫描电子显微镜、透射电子显微镜、紫外-可见漫反射吸收光谱、氮气吸附-脱附测试、光电化学测试和荧光光谱等技术对所制备样品的晶型、组成、形貌、光捕获能力、载流子分离能力、比表面积、光电流、阻抗、光降解性能以及羟基自由基的生成进行系统性测试。以罗丹明B为目标探针分子, 考察了模拟太阳光下所制备的光催化剂的光催化活性, 结果表明, 尿素添加量为0.6 g时, 电纺构筑的TiO₂/g-C₃N₄/RGO三元异质结在60 min具有99.1%的光催化降解效率, 显著优于纯TiO₂, g-C₃N₄, 二元TiO₂/g-C₃N₄以及制备的其它TiO₂/g-C₃N₄/RGO三元异质结光催化剂。基于光电化学测试、活性物种淬灭实验和荧光光谱分析测试羟基自由基等分析结果, 提出了一个合理的Z型增强光催化活性机理。

关键词: 电纺; Z型; 二氧化钛/氮化碳/还原氧化石墨烯; 三元异质结; 光催化

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