Rapid and Scalable Fabrication of $\text{TiO}_2@\text{g-C}_3\text{N}_4$ Heterojunction for Highly Efficient Photocatalytic NO Removal under Visible Light

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ABSTRACT

$\text{TiO}_2@\text{g-C}_3\text{N}_4$ heterojunction composites were successfully synthesized via one-step pyrolysis using commercial TiO_2 and urea. The photocatalytic performance of a composite was investigated by measuring the degradation of nitric oxide (NO) under visible light. The light absorption and bandgap of the selected materials were determined using diffuse reflectance spectroscopy (DRS), which confirmed the strong photocatalytic activity of the materials under visible light. The NO photodegradation efficiency of the composite was almost 90% under visible irradiation. The generation of by-products and nitrogen dioxide (NO_2) was calculated to determine the conversion pathway of NO during the photocatalytic reaction. Furthermore, the results for recycling indicated that the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ composite exhibited excellent stability. Also, the morphology and the chemical compositions of the materials were observed using high-resolution transmission electron microscopy (HR-TEM) images and X-ray photoelectron spectroscopy (XPS). Raman spectroscopy was used to detect the structural vibrations in the materials. Through electron spin resonance (ESR) and trapping tests, the photocatalytic mechanism of the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ composite was also elucidated, in which superoxide radical anions were found to play a significant role in NO removal.

Keywords: Photocatalysis, Nitric oxide, Visible light, $\text{g-C}_3\text{N}_4$, TiO_2

1 INTRODUCTION

Climate change has been one of the most critical problems globally and has been significantly affecting air quality. Thus, it is highly desirable to address this overwhelming problem by amending major air pollutants (nitrogen oxides (NO_x), sulfur dioxide, and volatile organic compounds). In 2012, diesel engines were identified as cancer-causing by the World Health Organization (Espina *et al.*, 2015). NO_x is primary air pollutants, causing severe impacts on human health. In particular, it causes lung problems, headaches, eye damage, loss of taste, and corroded teeth. In addition, NO_x contributes to the formation of photochemical smog when exposed to sunlight (Cheng *et al.*, 2018). People with lung diseases such as asthma may experience damage to lung tissue and reduced lung function when working outdoors when a high concentration of NO_x is present. Recent advancements in science and technology have inspired several practical approaches to addressing air pollution (Liu *et al.*, 2013; Chen *et al.*, 2021; Wu and Ku, 2021; Zhang *et al.*, 2021).

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Several strategies have been proposed to suppress air pollution, including physical, chemical, and biological treatments through recovery or degradation. In particular, methods such as adsorption, thermal oxidation, microorganisms, selective catalytic reduction, selective non-catalytic reduction, and activated carbon injections have been used. Given the high costs, poor efficiency of secondary products, and complicated operating processes (Liu *et al.*, 2019), the use of these technologies has been limited. (Jiang *et al.*, 2012). Nevertheless, plant operators should consider implementing the most advanced technology available to achieve high NO_x removal while holding operational and investment costs to a minimum.

In recent years, photocatalysis research has gained significant attention by taking advantage of the abundance of solar light for the purpose of addressing environmental pollution issues. In particular, titanium dioxide (TiO₂) has been identified as one of the most efficient photocatalysts because of its high photoactivity, low cost, non-toxicity, and highly tuneable bandgap (Huang *et al.*, 2017; Huy *et al.*, 2019a; Nasrabadi *et al.*, 2021). However, the practical use of TiO₂ in photocatalytic NO removal has been limited because of its large bandgap and rapid charge recombination (Van Viet *et al.*, 2018). Therefore, several strategies have been implemented further to improve the performance of TiO₂, such as doping, modifying its surface and bandgap, forming heterojunctions (Tran *et al.*, 2018; Van Viet *et al.*, 2019). Notably, coupling with metal-free graphitic carbon nitride (g-C₃N₄) presents great promise in generating highly efficient photocatalysts. This effective combination originates from the unique advantages of g-C₃N₄, showing an excellent response under visible light, non-toxicity, low cost, and ease of fabrication (Yu *et al.*, 2016; Wang *et al.*, 2019; Baudys *et al.*, 2020; Van Viet *et al.*, 2021; Wang *et al.*, 2021). Specifically, TiO₂@g-C₃N₄ heterojunction materials (TiO₂@g-C₃N₄) have led to great improvement in photocatalysis-induced pollutant degradation (Sun *et al.*, 2015; Pareek and Quamara, 2018; Wang *et al.*, 2018; Chen, 2021; Gahlot *et al.*, 2021; Xiong *et al.*, 2021). The underlying physics for such a successful combination comes from the proper bandgap alignment between TiO₂ and g-C₃N₄. However, the use of these TiO₂@g-C₃N₄ heterojunctions has rarely been studied in an NO pollution context. In addition, the typical approaches for generating these structures are generally complicated, laborious, have poor stability and reproducibility, and are time-consuming, which hinders their potential for scalable manufacturing.

In this study, we report on a scalable fabrication of TiO₂@g-C₃N₄ heterojunction materials for the purpose of addressing NO pollution. By forming a functional interface between TiO₂ and g-C₃N₄, TiO₂@g-C₃N₄ heterojunctions exhibit excellent photocatalytic NO removal under visible light. The role of the main radical species, involved in the photocatalytic activity is also thoroughly investigate in the present study. Such a TiO₂@g-C₃N₄ heterojunction, prepared via scalable fabrication without the generation of any harmful by-products is shown to be highly efficient in terms of removing NO pollution, and thus to have great promise for practical and industrial implementation.

2 METHOD

2.1 Materials and Chemicals

All chemicals were of analytic grade and used without being further treated. Urea 99% (NH₂CONH₂) was purchased from Alfa Aesar. TiO₂ (mass fraction 0.990) was provided by Xilong Chemical Co., Ltd., Beijing, China. Nitric oxide (NO) was purchased from Ming Yang special gas company. Deionized water (DI) was obtained from Thermal Scientific.

2.2 Synthesis of Materials

A schematic illustration for the synthesis of g-C₃N₄ and TiO₂@g-C₃N₄ is shown in Fig. 1. For the synthesis of g-C₃N₄, 30 g of Urea were ground and placed in a 100 mL crucible. This crucible was then annealed at 550°C for 120 min. The sample was then cooled down to room temperature naturally.

For the synthesis of the TiO₂@g-C₃N₄, 30 g of urea and a desirable amount of the TiO₂ (0.8 g) were ground and placed in a crucible. This crucible was then annealed at 550°C for 2 h. The sample was then cooled down to room temperature naturally. The ratio of the TiO₂ and g-C₃N₄ was calculated based on the desirable ratio.

Fig. 1. Synthesis of TiO₂@g-C₃N₄.

2.3 Photocatalytic Activity Test

The photocatalytic performance of the materials was evaluated by measuring the degradation of gaseous NO under visible light. 0.2 g of the samples were placed in a petri dish, after which it was dispersed in 10 mL DI for 5 min under an ultrasonic cleaner, and then dried at 60°C for 30 min to remove the water via evaporation. The reactor was a cylinder reactor (Fig. 2). The reaction chamber which had a volume of 4.5 L (30 cm × 10 cm × 15 cm), was made of stainless steel, and quartz was used to seal the top of the reactor to allow light to pass through. A xenon lamp (300 W) was placed vertically 40 cm above the reaction chamber. Firstly, the initial 100 ppm concentration of NO was diluted with zero-air (Zero-air generator, Model 1001, Sabio Instruments). The input flow rate and the concentration of NO and zero-air were controlled by a mass control flow rate to reach an NO concentration of 500 ppb. Finally, the lamp was turned on after the catalyst reached adsorption/desorption equilibrium. The sampling rate of the experiment was 0.5 L min⁻¹. In this study, the photocatalytic NO removal experiment followed the U.S. EPA requirements for RFNA-1289-074 and the international standard-ISO 22197-1.

The factors considered for the photocatalytic degradation of NO included the hydroxyl radicals, electrons, and hole pairs. To explain the photocatalytic mechanism, a trapping experiment was performed during the photocatalytic reaction in the presence of the materials to detect active species. The capture experiments were carried out by mixing 0.2 g of the photocatalyst with trapping agents, including potassium iodide (KI), potassium dichromate (K₂Cr₂O₇), and isopropyl alcohol (IPA), which served as a radical scavenger for the hole (h⁺), one electron (e⁻), and the

Fig. 2. The photocatalytic system.

hydroxyl radical ($\bullet\text{OH}$). These dried materials were used in the photocatalytic experiments for NO_x removal as typical photocatalytic experiments.

The NO degradation, and NO_2 conversion, were calculated by Eqs. (1) and (2), respectively (Ohtani, 2011; Guerrand *et al.*, 2015);

$$\eta = \frac{C_{\text{NO},t} - C_{\text{NO},f}}{C_{\text{NO},t}} \times 100\% \quad (1)$$

$$\gamma = \frac{C_{\text{NO}_2,t} - C_{\text{NO}_2,i}}{C_{\text{NO}_2,i} - C_{\text{NO}_2,f}} \times 100\% \quad (2)$$

where C_{NO} (ppb) is the concentration of NO. C_{NO_2} is the concentration of NO_2 , i is the initial concentration, and f is the final concentration.

2.4 Reusability of Photocatalysts

The ability to reuse the materials used for removing NO was evaluated for four cycles. After the first test, the sample was washed carefully with DI and dried in an oven at 80°C for 20 min before the rest of the photocatalytic test was performed. The degradation efficiency was almost the same as that in the previous test.

2.5 Characterizations

The X-ray diffraction (XRD) patterns were studied to determine the crystal structures of the materials in the range of 10° to 80° . Fourier-transform infrared spectroscopy (FTIR) was used to investigate the structural vibrations of the materials in the range of 4000 cm^{-1} to 400 cm^{-1} . The morphology of the materials was observed using high-resolution transmission electron microscopy (HR-TEM) images. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical compositions of the materials. Raman spectroscopy was used to detect the structural vibrations of the materials in the range of 100 cm^{-1} to 500 cm^{-1} . Diffuse reflectance spectroscopy (DRS) was used to observe the bandgap of the materials. The electron spin resonance (ESR) was implemented to capture the presence of oxygen free radicals ($\bullet\text{O}_2$) and ($\bullet\text{OH}$) in the photocatalytic processes.

3 RESULTS AND DISCUSSION

3.1 Structural and Compositional Characterizations

XRD patterns of the materials are shown in Fig. 3(a). In the XRD pattern of the pure $\text{g-C}_3\text{N}_4$, significant diffraction peaks appeared at positions of 27.3° and were indexed to the (002) plane of $\text{g-C}_3\text{N}_4$, indicating a typical graphitic structure (JCPDS 87-1526). However, no other impurity peaks were detected in the XRD pattern, indicating that the synthesized $\text{g-C}_3\text{N}_4$ exhibited high purity crystalline characteristics. The flat cell, repeating cell structure, and sandwich stack reflection of $\text{g-C}_3\text{N}_4$ have been suggested to be responsible for the sheet structure of $\text{g-C}_3\text{N}_4$ (Yang *et al.*, 2013; Zhang *et al.*, 2013).

After combining $\text{g-C}_3\text{N}_4$ with TiO_2 , the important peaks of $\text{g-C}_3\text{N}_4$ show exhibited a lower peak intensity. In $\text{TiO}_2@\text{g-C}_3\text{N}_4$ nanostructures (blue line), with most of these peaks showing the (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) planes of anatase TiO_2 . The weak diffraction peak at 63.4° (0 0 2) indicated the presence of small amounts of the rutile phase in TiO_2 (JCPDS 21-1272). It is worth mentioning that the anatase-rutile two-phase structure exhibited higher photocatalytic activity than the respective pure phases (Kumar *et al.*, 2007).

Compared with the diffraction peaks of pristine $\text{g-C}_3\text{N}_4$ and TiO_2 , the diffraction peak corresponding to the $\text{g-C}_3\text{N}_4$ (0 0 2) crystal plane in the composite is relatively broader, and the intensity was weaker. The peaks of $\text{g-C}_3\text{N}_4$ and anatase TiO_2 could be observed in the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ sample, thus indicating that the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ composite was successfully synthesized.

Fig. 3(b) shows the FT-IR spectra of the $\text{TiO}_2@\text{g-C}_3\text{N}_4$, pure $\text{g-C}_3\text{N}_4$, and pure TiO_2 composite. The absorption band of the pure $\text{g-C}_3\text{N}_4$ in the range of $1220\text{--}1650\text{ cm}^{-1}$ corresponds to the

Fig. 3. The XRD pattern (a), and FTIR spectra (b) of the materials.

typical stretching vibration of C-N heterocycles (Song *et al.*, 2015). The absorption band around 400–800 cm^{-1} was attributed to the Ti-O bonds (Fu *et al.*, 2013). The peaks at 809 cm^{-1} and 1220–1650 cm^{-1} were attributed to the characteristic stretching modes and suggest the existence of g- C_3N_4 (Fu *et al.*, 2014). In the region of 2900–3500 cm^{-1} , the O-H vibration broadband was observed. The spectrum showed the main features of the g- C_3N_4 and TiO_2 in the TiO_2 @g- C_3N_4 samples, suggesting that a mixture of g- C_3N_4 and TiO_2 was formed.

3.2 Morphology Characterizations

The morphology of the TiO_2 @g- C_3N_4 , TiO_2 , g- C_3N_4 observed at the HR-TEM scale was 50 nm, as shown in Fig. 4. The structure of the TiO_2 @g- C_3N_4 was observed as presented in Fig. 4(a). The d-spacing was 0.48 nm, which corresponded to the plane (002) of the TiO_2 (Štengl and Grygar, 2011). The TEM results further demonstrated that the TiO_2 @g- C_3N_4 composites were successfully synthesized via one-step pyrolysis. In addition, the particle length of the TiO_2 @g- C_3N_4 is shown in Fig. 5. The average particle length of TiO_2 in the TiO_2 @g- C_3N_4 was 14.4 nm. Furthermore, the effect of the synthesis method on the specific surface area of the materials and the effect of the specific surface area on the photocatalytic activity were confirmed as indicated in previous studies, as shown in Table 1. Previous studies indicated that the photocatalytic activity of these materials is better when the specific surface area is higher.

3.3 Optical and Electrical Properties Characterizations

Fig. 6(a) shows the Raman spectra from 100 cm^{-1} to 450 cm^{-1} of the materials. The characteristic peaks of TiO_2 can be observed at 139.2 cm^{-1} and 392.6 cm^{-1} in TiO_2 @g- C_3N_4 and bare TiO_2 . The

Fig. 4. TEM and HR-TEM of (a, b) $\text{TiO}_2@\text{g-C}_3\text{N}_4$, (c, d) TiO_2 , (e, f) $\text{g-C}_3\text{N}_4$. The SEAD of $\text{TiO}_2@\text{g-C}_3\text{N}_4$ (insert b).

Fig. 5. The particle length average of the $\text{TiO}_2@\text{g-C}_3\text{N}_4$.

Table 1. The specific surface area of g-C₃N₄, TiO₂, and TiO₂@g-C₃N₄ heterojunction.

No	Pollutant	BET surface area (m ² g ⁻¹)			References
		g-C ₃ N ₄	TiO ₂	TiO ₂ @g-C ₃ N ₄	
1	Methylene Blue	6.1	9.33	223.71	(Alfaifi and Bagabas, 2019)
2	Methylene Blue	35.2	40.0	47.6	(Bairamis <i>et al.</i> , 2019)
3	H ₂ production	10	46	52	(Jiménez-Calvo <i>et al.</i> , 2020)
4	Methylene Orange	4.72	210.39	222.06	(Chen <i>et al.</i> , 2014)
5	N ₂ O	11	45	53	(Reli <i>et al.</i> , 2016)
6	Polybrominated diphenyl ethers	27.84	47.5	120.85	(Ye <i>et al.</i> , 2017)
7	Nitrogen	12.1	43.6	45.3	(Zhang <i>et al.</i> , 2019)
8	Rhodamine B	14	19	49	(Wang <i>et al.</i> , 2016)
9	Rhodamine B	68.9	30.7	137.1	(Monga and Basu, 2019)
10	Methylene Blue	35.9	56	84.37	(Gündoğmuş <i>et al.</i> , 2020)

Fig. 6. (a) Raman spectra, (b) XPS survey, (c) high-resolution C 1s XPS, (d) high-resolution N 1s XPS, (e) high-resolution O 1s XPS, (f) high-resolution Ti 2p XPS of the materials.

peak at 139.2 and 392.6 corresponded to the Ti-Ti vibrational modes, and the Ti-O vibrational modes, respectively. On other hand, no peak shifts of g-C₃N₄ were observed within the Raman shift from 100 cm⁻¹ to 450 cm⁻¹ (Lin and Zhao, 2019).

The surface chemistry of the materials is shown in Figs. 6(b–f). In the XPS survey of the materials shown in Fig. 6(b), the peaks of C 1s, N 1s, O 1s, and Ti 2p can be observed at 288.2 eV, 398.8 eV, 531.7, and 460.5 eV, respectively. Furthermore, the high-resolution XPS (HR-XPS) of C 1s, N 1s, O 1s, and Ti 2p was investigated to determine the effect of the synthesis method on the surface chemistry of the materials (Tang *et al.*, 2021; Toghan *et al.*, 2021). In Fig. 6(c), the peak at 288.2 eV was attributed to the N-C=N₂ groups. Interestingly, the strong peak at 284.7 eV in the TiO₂@g-C₃N₄ was attributed to the C-C groups (Štengl and Grygar, 2011). In contrast, the N 1s, O 1s, and Ti 2p spectra were similar for the three materials.

Fig. 7(a) depicts the optical properties of the synthesized TiO₂@g-C₃N₄ sample as characterized using DRS. These spectra are noticeably different between TiO₂@g-C₃N₄ and the two bare materials. As shown in the results, the TiO₂ and g-C₃N₄ both exhibited an absorption band at ~380 nm and ~475 nm, respectively, which is consistent with previous reports (Boonprakob *et al.*, 2014; Huang *et al.*, 2015; Xiao *et al.*, 2015). Therefore, the TiO₂@g-C₃N₄ had coherent TiO₂ and g-C₃N₄ optical properties, and the absorption edge of the composite showed a remarkable redshift to a larger wavelength at ~600 nm. These results suggested that the as-prepared composite can improve utilization in the visible-light region compared with the single material. As shown in Fig. 7(b), absorption occurred at wavelengths shorter than 410 nm and 460 nm, which agreed well with the bandgap of the TiO₂ (3.31 eV) and g-C₃N₄ (2.92 eV), respectively (Huang *et al.*, 2013; Huang *et al.*, 2015). The energy bandgap of the synthesized composite was estimated using the Kubelka-Munk function, where the bandgap of the TiO₂@g-C₃N₄ composite was 3.03 eV, leading to the ability to absorb light in the visible region as well as reducing the recombination of electrons and hole pairs.

3.4 Photocatalytic Performance

The efficiency of photocatalytic NO removal of the materials is shown in Fig. 8(a). The NO photodegradation efficiency of the single TiO₂, g-C₃N₄, and TiO₂@g-C₃N₄ was 76.4 %, 71.6%, and 90.2%, respectively. The enhancement of the removal efficiency indicated that the synthesized composite can utilize visible light, parallel with the improvement in the electron and hole recombination rates.

Specifically, the products of the NO removal process were also considered, for which the results are shown in Fig. 8(b). The amount of NO₂ that converted from NO after the degradation process was significantly decreased from 27.5%, 6.8%, and 5.3% for g-C₃N₄, TiO₂, and TiO₂@g-C₃N₄, respectively. In addition, the results indicated that the other nitrogen products produced when using the synthesized composite were higher than those produced using a single catalyst. The other nitrogen products were various types of nitrogen gas (nitrate radical (NO₃), nitrogen trioxide,

Fig. 7. (a) DRS spectra, and (b) Kubelka-Munk function of the materials.

Fig. 8. (a) The photocatalytic activity, (b) NO conversion of the materials.

nitrous oxide, dinitrogen tetroxide, dinitrogen pentoxide, etc.) generated by the reaction of NO and O₂ or O₃ in the air.

The reusability of the materials was determined using a recycling test and the XRD pattern of the samples before and after the 4th recycling process. As shown in Fig. 9(a), the photocatalytic efficiency of TiO₂@g-C₃N₄ decreased slowly and reached 86.4% at the 4th recycling cycle. In addition, the XRD pattern (Fig. 9(b)) indicated that the crystal structure of the TiO₂@g-C₃N₄ was not affected during the photocatalytic reaction. These results indicated that TiO₂@g-C₃N₄ is a high reusable material. Table 2 shows a comparison of this study and previous studies related to TiO₂@g-C₃N₄.

3.5 Photocatalytic NO Degradation Mechanism

The ESR signals of the •OH and •O₂ radicals were studied to validate the generation of the radical from the materials. The ESR signals of the •OH and •O₂ radicals under dark conditions and visible conditions for 300s are shown in Fig. 10(a), (b). Under the visible condition, the generation of •OH was higher than •O₂. In contrast, there were no •OH and •O₂ signals under dark conditions. A trapping experiment was conducted to consider the critical factors leading to photodegradation of NO by adding the K₂Cr₂O₇, KI, and IPA scavengers. Herein, the K₂Cr₂O₇, KI, and IPA scavengers were mixed with the materials to trap e⁻, h⁺, and •OH, respectively. The results of the trapping experiments are shown in Fig. 10(c). The trapping results demonstrated that the contribution of e⁻ to the photocatalytic activity of the three materials was higher than that of h⁺ and •OH. These results were consistent with the ESR data signal.

Fig. 9. (a) The photocatalytic stability of TiO₂@g-C₃N₄, (b) XRD pattern before and after 4th recycling test of TiO₂@g-C₃N₄.

Fig. 10. ESR signals of (a) •OH radicals, (b) •O₂ radicals, and (c) trapping test results of the materials.

Table 2. Previous study related to TiO₂@g-C₃N₄.

No.	Catalyst	Efficiency	Air pollutant	Light Source	References
1	g-C ₃ N ₄ @TiO ₂	35%	HCHO	Visible	(Liu and Lin, 2019)
2	TiO ₂ NTs	62%			(Sahrin <i>et al.</i> , 2020)
3	g-C ₃ N ₄ @TiO ₂	95%			(Yu <i>et al.</i> , 2013)
4	TiO ₂	66.7%	Toluene		(Tasbihi <i>et al.</i> , 2017)
5	SiO ₂ @TiO ₂	53%			(Yao and Kuo, 2015)
6	g-C ₃ N ₄ /NiWO ₄	31%		Solar	(Dao <i>et al.</i> , 2019)
7	Perfluorinated coating with TiO ₂	80%	VOCs	UV	(Sansotera <i>et al.</i> , 2019)
8	g-C ₃ N ₄ /TiO ₂ composite film	70.7%	NO _x		(Huang <i>et al.</i> , 2020)
9	Pt-doped TiO ₂	35%	NO	Visible	(Huang <i>et al.</i> , 2017)
10	Ni-doped TiO ₂	45%	NO	Solar	(Huang <i>et al.</i> , 2017)
11	Ag/TiO ₂	78.3%	NO _x		(Abdelsalam <i>et al.</i> , 2020)
12	TiO ₂ @g-C ₃ N ₄	90.1%	NO	Visible	This study

The photocatalytic mechanism of TiO₂@g-C₃N₄ for NO degradation under visible light is presented in Fig. 11. Under visible light irradiation, the generated e⁻ moved from the valance band to the conduction band of TiO₂ created excess h⁺ in the TiO₂ valance band. Then, the e⁻ transferred from the TiO₂ conduction band to the valance band of g-C₃N₄. Finally, the e⁻ moved to the g-C₃N₄ conduction band. The e⁻ in the g-C₃N₄ conduction band reacted with O₂ to form the

Fig. 11. The proposed photocatalytic mechanism of the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ heterojunction base on the Z-scheme interface for NO degradation under visible light.

$\bullet\text{O}_2^-$. The generated O_2^- oxidized NO to form NO_3^- and prevented the formation of NO_2 (Huy *et al.*, 2019a). On the other hand, the h^+ in the valence band of TiO_2 reacted with H_2O to form $\bullet\text{OH}$. The $\bullet\text{OH}$ degraded NO to NO_2 and NO_3^- (Pham *et al.*, 2021). From the ESR and trapping results, the materials generated $\bullet\text{OH}$ more than $\bullet\text{O}_2^-$ radicals.

4 CONCLUSIONS

A one-step pyrolysis method was employed in the present work to synthesize the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ heterojunction. Outstanding photocatalytic activity and stability was demonstrated for photocatalytic NO removal and low NO_2 generation (5.3%) under visible light. The photocatalytic efficiency of $\text{TiO}_2@\text{g-C}_3\text{N}_4$ reached 86.1% after the first 10 min under visible light irradiation, after which it reached the highest efficiency (90.1%) 30 min later. Meanwhile, the efficiency of pure TiO_2 (76.34%) and pure $\text{g-C}_3\text{N}_4$ (71.6%) was lower than that of $\text{TiO}_2@\text{g-C}_3\text{N}_4$. This result demonstrated that the heterojunction structure greatly affects the photocatalytic performance of these materials. Herein, the heterojunction structure reduced the recombination of electron-hole pairs and extended the light absorption of the composite under visible light. The reduction in the recombination of electron-hole pairs decreased photocatalytic inactivation, which led to an increase in the photocatalytic activities of $\text{TiO}_2@\text{g-C}_3\text{N}_4$. Furthermore, after four reusability tests, the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ showed good stability with only a 3.9% decrease in reusability. The influence of the heterojunction structure on the optical properties of the materials was determined using DRS. Finally, the photocatalytic mechanism of the materials was confirmed and discussed through trapping experiments, where ESR, h^+ , and $\bullet\text{OH}$ were the main factors contributing to the photocatalytic activity of $\text{TiO}_2@\text{g-C}_3\text{N}_4$ during photodegradation of NO under visible light. The material worked well under visible light and overcame the biggest drawback of photocatalyst technology by reducing the energy consumption required for the photocatalyst reaction. From the above results, the $\text{TiO}_2@\text{g-C}_3\text{N}_4$ material can be considered to be a material with high applicability, a simple manufacturing method, and low cost.

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DISCLAIMER

The authors declare no competing financial interests.

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