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

Minh-Thuan Pham$^{1,2,4}$, Hong Quang Luu$^2$, Truc-Mai T. Nguyen$^5$, Hong-Huy Tran$^{2,3,*}$, Sheng-Jie You$^{2,4}$, Ya-Fen Wang$^{2,4,*}$

$^1$ Department of Civil Engineering, Chung Yuan Christian University, Taoyuan 32023, Taiwan
$^2$ Department of Environmental Engineering, Chung Yuan Christian University, Taoyuan 32023, Taiwan
$^3$ Université Grenoble Alpes, CNRS, Grenoble INP (Institute of Engineering, Université Grenoble Alpes), LMGP, 38000 Grenoble, France
$^4$ Center for Environmental Risk Management, Chung Yuan Christian University, Taoyuan 32023, Taiwan
$^5$ Center for Environmental Toxin and Emerging-Contaminant Research, Cheng Shiu University, Kaohsiung 833301, Taiwan

ABSTRACT

TiO$_2@g$-C$_3$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 TiO$_2@g$-C$_3$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 TiO$_2@g$-C$_3$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, g-C$_3$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).
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\textsubscript{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 (TiO\textsubscript{2}) 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 TiO\textsubscript{2} 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 TiO\textsubscript{2}, 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-C\textsubscript{3}N\textsubscript{4}) presents great promise in generating highly efficient photocatalysts. This effective combination originates from the unique advantages of g-C\textsubscript{3}N\textsubscript{4}, 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, TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4} heterojunction materials (TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4}) 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 TiO\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4}. However, the use of these TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4} 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 TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4} heterojunction materials for the purpose of addressing NO pollution. By forming a functional interface between TiO\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4}, TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4} heterojunctions exhibit excellent photocatalytic NO removal under visible light. The role of the main radical species, involved in the photocatalytic activity is also thoroughly investigated in the present study. Such a TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4} 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% (NH\textsubscript{2}CONH\textsubscript{2}) was purchased from Alfa Aesar. TiO\textsubscript{2} (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-C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4} is shown in Fig. 1. For the synthesis of g-C\textsubscript{3}N\textsubscript{4}, 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 TiO\textsubscript{2}@g-C\textsubscript{3}N\textsubscript{4}, 30 g of urea and a desirable amount of the TiO\textsubscript{2} (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 TiO\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4} was calculated based on the desirable ratio.
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
hydroxyl radical (•OH). These dried materials were used in the photocatalytic experiments for NOx removal as typical photocatalytic experiments.

The NO degradation, and NO2 conversion, were calculated by Eqs. (1) and (2), respectively (Ohtani, 2011; Guerrand et al., 2015):

\[
\eta = \frac{C_{NO,i} - C_{NO,f}}{C_{NO,i}} \times 100\%
\]

\[
\gamma = \frac{C_{NO_{2},i} - C_{NO_{2},f}}{C_{NO,i} - C_{NO,f}} \times 100\%
\]

where \(C_{NO}\) (ppb) is the concentration of NO. \(C_{NO_{2}}\) is the concentration of NO2, 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 (•O2) and (•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 g-C3N4, significant diffraction peaks appeared at positions of 27.3° and were indexed to the (002) plane of g-C3N4, indicating a typical graphitic structure (JCPDS 87-1526). However, no other impurity peaks were detected in the XRD pattern, indicating that the synthesized g-C3N4 exhibited high purity crystalline characteristics. The flat cell, repeating cell structure, and sandwich stack reflection of g-C3N4 have been suggested to be responsible for the sheet structure of g-C3N4 (Yang et al., 2013; Zhang et al., 2013).

After combining g-C3N4 with TiO2, the important peaks of g-C3N4 show exhibited a lower peak intensity. In TiO\(_2\)@g-C3N4 nanostructures (blue line), with most of these peaks showing the (1 0 1), (0 0 4), (1 0 5), and (2 1 1) planes of anatase TiO2. The weak diffraction peak at 63.4° (0 0 2) indicated the presence of small amounts of the rutile phase in TiO2 (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 g-C3N4 and TiO2, the diffraction peak corresponding to the g-C3N4 (0 0 2) crystal plane in the composite is relatively broader, and the intensity was weaker. The peaks of g-C3N4 and anatase TiO2 could be observed in the TiO2@g-C3N4 sample, thus indicating that the TiO2@g-C3N4 composite was successfully synthesized.

Fig. 3(b) shows the FT-IR spectra of the TiO2@g-C3N4, pure g-C3N4, and pure TiO2 composite. The absorption band of the pure g-C3N4 in the range of 1220–1650 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$_3$N$_4$ (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$_3$N$_4$ and TiO$_2$ in the TiO$_2$@g-C$_3$N$_4$ samples, suggesting that a mixture of g-C$_3$N$_4$ and TiO$_2$ was formed.

3.2 Morphology Characterizations

The morphology of the TiO$_2$@g-C$_3$N$_4$, TiO$_2$, g-C$_3$N$_4$ observed at the HR-TEM scale was 50 nm, as shown in Fig. 4. The structure of the TiO$_2$@g-C$_3$N$_4$ 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$_3$N$_4$ composites were successfully synthesized via one-step pyrolysis. In addition, the particle length of the TiO$_2$@g-C$_3$N$_4$ is shown in Fig. 5. The average particle length of TiO$_2$ in the TiO$_2$@g-C$_3$N$_4$ 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$_3$N$_4$ and bare TiO$_2$. The
Fig. 4. TEM and HR-TEM of (a, b) TiO$_2$@g-C$_3$N$_4$, (c, d) TiO$_2$, (e, f) g-C$_3$N$_4$. The SEAD of TiO$_2$@g-C$_3$N$_4$ (insert b).

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

Particle length average: 14.4 nm
Table 1. The specific surface area of g-C₃N₄, TiO₂, and TiO₂@g-C₃N₄ heterojunction.

| No. | Pollutant                  | g-C₃N₄ BET surface area (m² g⁻¹) | TiO₂ BET surface area (m² g⁻¹) | TiO₂@g-C₃N₄ BET surface area (m² g⁻¹) | References                                |
|-----|----------------------------|----------------------------------|--------------------------------|-------------------------------------|------------------------------------------|
| 1   | Methylene Blue             | 6.1                              | 9.33                           | 223.71                              | (Alfaifi and Bagabas, 2019)              |
| 2   | Methylene Blue             | 35.2                             | 40.0                           | 47.6                                | (Bairamis et al., 2019)                  |
| 3   | H₂ production              | 10                               | 46                             | 52                                  | (Jiménez-Calvo et al., 2020)             |
| 4   | Methylene Orange           | 4.72                             | 210.39                         | 222.06                              | (Chen et al., 2014)                     |
| 5   | N₂O production             | 11                               | 45                             | 53                                  | (Reli et al., 2016)                     |
| 6   | Polybrominated diphenyl ethers | 27.84                          | 47.5                           | 120.85                              | (Ye et al., 2017)                       |
| 7   | Nitrogen                   | 12.1                             | 43.6                           | 45.3                                | (Zhang et al., 2019)                    |
| 8   | Rhodamine B                | 14                               | 19                             | 49                                  | (Wang et al., 2016)                     |
| 9   | Rhodamine B                | 68.9                             | 30.7                           | 137.1                               | (Monga and Basu, 2019)                  |
| 10  | Methylene Blue             | 35.9                             | 56                             | 84.37                               | (Gündoğmuş et al., 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=N$_2$ groups. Interestingly, the strong peak at 284.7 eV in the TiO$_2$@g-C$_3$N$_4$ 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 TiO$_2$@g-C$_3$N$_4$ sample as characterized using DRS. These spectra are noticeably different between TiO$_2$@g-C$_3$N$_4$ and the two bare materials. As shown in the results, the TiO$_2$ and g-C$_3$N$_4$ both exhibited an absorption band at $\sim$380 nm and $\sim$475 nm, respectively, which is consistent with previous reports (Boonprakob et al., 2014; Huang et al., 2015; Xiao et al., 2015). Therefore, the TiO$_2$@g-C$_3$N$_4$ had coherent TiO$_2$ and g-C$_3$N$_4$ optical properties, and the absorption edge of the composite showed a remarkable redshift to a larger wavelength at $\sim$600 nm. These results suggested that the as-prepared composite can improve utilization in the visible-light region compared with the single material. As shown in Fig. 7(b), absorption occurred at wavelengths shorter than 410 nm and 460 nm, which agreed well with the bandgap of the TiO$_2$ (3.31 eV) and g-C$_3$N$_4$ (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 TiO$_2$@g-C$_3$N$_4$ 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 TiO$_2$, g-C$_3$N$_4$, and TiO$_2$@g-C$_3$N$_4$ 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 NO$_2$ that converted from NO after the degradation process was significantly decreased from 27.5%, 6.8%, and 5.3% for g-C$_3$N$_4$, TiO$_2$, and TiO$_2$@g-C$_3$N$_4$, 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 (NO$_3$), nitrogen trioxide, 

![Fig. 7. (a) DRS spectra, and (b) Kubelka-Munk function of the materials.](image-url)
Fig. 8. (a) The photocatalytic activity, (b) NO conversion of the materials.

Fig. 9. (a) The photocatalytic stability of TiO$_2$@g-C$_3$N$_4$, (b) XRD pattern before and after 4th recycling test of TiO$_2$@g-C$_3$N$_4$.

nitrous oxide, dinitrogen tetroxide, dinitrogen pentoxide, etc.) generated by the reaction of NO and O$_2$ or O$_3$ 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 TiO$_2$@g-C$_3$N$_4$ 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 TiO$_2$@g-C$_3$N$_4$ was not affected during the photocatalytic reaction. These results indicated that TiO$_2$@g-C$_3$N$_4$ is a high reusable material. Table 2 shows a comparison of this study and previous studies related to TiO$_2$@g-C$_3$N$_4$.

3.5 Photocatalytic NO Degradation Mechanism

The ESR signals of the •OH and •O$_2$ radicals were studied to validate the generation of the radical from the materials. The ESR signals of the •OH and •O$_2$ 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 •O$_2$. In contrast, there were no •OH and •O$_2$ signals under dark conditions.

A trapping experiment was conducted to consider the critical factors leading to photodegradation of NO by adding the K$_2$Cr$_2$O$_7$, KI, and IPA scavengers. Herein, the K$_2$Cr$_2$O$_7$, 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.
The photocatalytic mechanism of TiO$_2@g$-$C_3$$N_4$ for NO degradation under visible light is presented in Fig. 11. Under visible light irradiation, the generated $e^-$ moved from the valance band to the conduction band of TiO$_2$ created excess $h^+$ in the TiO$_2$ valence band. Then, the $e^-$ transferred from the TiO$_2$ conduction band to the valence band of g-$C_3$$N_4$. Finally, the $e^-$ moved to the g-$C_3$$N_4$ conduction band. The $e^-$ in the g-$C_3$$N_4$ conduction band reacted with O$_2$ to form the
Fig. 11. The proposed photocatalytic mechanism of the TiO2@g-C3N4 heterojunction base on the Z-scheme interface for NO degradation under visible light.

•O2−. The generated O2− oxidized NO to form NO3− and prevented the formation of NO2 (Huy et al., 2019a). On the other hand, the h+ in the valence band of TiO2 reacted with H2O to form •OH. The •OH degraded NO to NO2 and NO3− (Pham et al., 2021). From the ESR and trapping results, the materials generated •OH more than •O2 radicals.

4 CONCLUSIONS

A one-step pyrolysis method was employed in the present work to synthesize the TiO2@g-C3N4 heterojunction. Outstanding photocatalytic activity and stability was demonstrated for photocatalytic NO removal and low NO2 generation (5.3%) under visible light. The photocatalytic efficiency of TiO2@g-C3N4 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 TiO2 (76.34%) and pure g-C3N4 (71.6%) was lower than that of TiO2@g-C3N4. 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 TiO2@g-C3N4. Furthermore, after four reusability tests, the TiO2@g-C3N4 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 •OH were the main factors contributing to the photocatalytic activity of TiO2@g-C3N4 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 TiO2@g-C3N4 material can be considered to be a material with high applicability, a simple manufacturing method, and low cost.

ACKNOWLEDGMENTS

This research was financially supported by the Chung Yuan Christian University, Taiwan (Project No: 109609432). This work was supported by the Department of Environmental
Engineering, Chung Yuan Christian University, Taoyuan City, 32023, Taiwan; Department of Civil Engineering Chung Yuan Christian University, Taoyuan City, 32023, Taiwan; Department of Environmental Engineering, Chung Yuan Christian University, Taoyuan City, 32023, Taiwan; Center for Environmental Risk Management, Chung Yuan Christian University, No. 200, Taoyuan City, 32023, Taiwan; Center for Environmental Toxin and Emerging-Contaminant Research, Cheng Shiu University, Kaohsiung, Taiwan, ROC.

DISCLAIMER

The authors declare no competing financial interests.

REFERENCES

Abdelsalam, E.M., Mohamed, Y.M., Abdelkhalik, S., El Nazer, H.A., Attia, Y.A. (2020). Photocatalytic oxidation of nitrogen oxides (NOx) using Ag- and Pt-doped TiO2 nanoparticles under visible light irradiation. Environ. Sci. Pollut. Res. 27, 35828–35836. https://doi.org/10.1007/s11356-020-09649-5

Alfaifi, Q.M., Bagabas, A.A. (2019). Preparation, characterization, and application in water purification of g-C3N4/i-TiO2 composite photocatalysts. Adv. Mater. Sci. 4, 1–10. https://doi.org/10.15761/AMS.1000148

Bairamis, F., Konstantinou, I., Petrakis, D., Vaimakis, T. (2019). Enhanced performance of electrospray nanofibrous TiO2/g-C3N4 photocatalyst in photocatalytic degradation of methylene blue. Catalysts 9, 880. https://doi.org/10.3390/catal9110880

Baudys, M., Paušová, Š., Praus, P., Brezová, V., Dvoranová, D., Barbieriková, Z., Krýsa, J. (2020). Graphitic carbon nitride for photocatalytic air treatment. J. Mater. Res. 13, 3038. https://doi.org/10.3390/ma13133038

Boonprakob, N., Wetchakun, N., Phanichphant, S., Waxler, D., Sherrell, P., Nattestad, A., Chen, J., Inceesungvorn, B. (2014). Enhanced visible-light photocatalytic activity of g-C3N4/TiO2 films. J. Collo. Interfa. Sci. 417, 402–409. https://doi.org/10.1016/j.jcis.2013.11.072

Chen, R., Li, J., Wang, H., Chen, P., Dong, X., Sun, Y., Zhou, Y., Dong, F. (2021). Photocatalytic reaction mechanisms at the gas-solid interface for typical air pollutants decomposition. J. Mater. Chem. A 9, 20184–20210. https://doi.org/10.1039/D1TA03705F

Chen, Y., Huang, W., He, D., S itu, Y., Huang, H. (2014). Construction of heterostructured g-C3N4/Ag/TiO2 microspheres with enhanced photocatalysis performance under visible-light irradiation. ACS Appl. Mater. Interfaces 6, 14405–14414. https://doi.org/10.1021/am503674e

Cheng, S.W., Li, Y.H., Yuan, C.S., Tsai, P.Y., Shen, H.Z., Hung, C.H.J.A., Research, A.Q. (2018). An innovative advanced oxidation technology for effective decomposition of formaldehyde by combining iron modified nano-TiO2 (Fe/TiO2) photocatalytic degradation with ozone oxidation. Aerosol Air Qual. Res. 18, 3220–3233. https://doi.org/10.4209/aaqr.2018.05.0156

Dao, V.D., Nguyen, T.D., Van Noi, N., Ngoc, N.M., Pham, T.D., Van Quan, P., Trang, H.T. (2019). Superior visible light photocatalytic activity of g-C3N4/ NiWO4 direct Z system for degradation of gaseous toluene. J. Sol. State Chem. 272, 62–68. https://doi.org/10.1016/j.jssc.2019.01.030

Espina, C., Straif, K., Friis, S., Kogevinas, M., Saracci, R., Vainio, H., Schüz, J. (2015). European code against cancer 4th edition: Environment, occupation and cancer. Cancer Epidemiol. 39, S84–S92. https://doi.org/10.1016/j.canep.2015.03.017

Fu, M., Pi, J., Dong, F., Duan, Q., Guo, H. (2013). A cost-effective solid-state approach to synthesize g-C3N4 coated TiO2 nanocomposites with enhanced visible light photocatalytic activity. Inter. J. Photoener. 2013, 158496. https://doi.org/10.1155/2013/158496

Fu, M., Liao, J., Dong, F., Li, H., Liu, H. (2014). Growth of g-C3N4 layer on commercial TiO2 for enhanced visible light photocatalytic activity. J. Nanomater. 2014, 869094. https://doi.org/10.1155/2014/869094

Gahlot, S., Dappozze, F., Mishra, S., Guillard, C. (2021). High surface area g-C3N4 and g-C3N4-TiO2
photocatalytic activity under UV and visible light: Impact of individual component. J. Environ. Chem. Eng. 9, 105587. https://doi.org/10.1016/j.jece.2021.105587

Guerrand, H., Pucheault, M., Vaultier, M. (2015). Ionic liquids. Green Proc. Eng. 267. https://doi.org/10.1201/b18533

Gündoğmuş, P., Park, J., Öztürk, A. (2020). Preparation and photocatalytic activity of g-C3N4/TiO2 heterojunctions under solar light illumination. Ceramics Inter. 46, 21431–21438. https://doi.org/10.1016/j.ceramint.2020.05.241

Huang, L., Li, Y., Xu, H., Xu, Y., Xia, J., Wang, K., Li, H., Cheng, X. (2013). Synthesis and characterization of CeO2/g-C3N4 composites with enhanced visible-light photocatalytic activity. RSC Adv. 3, 22269–22279. https://doi.org/10.1039/C3RA42712A

Huang, Y., Cao, J.J., Kang, F., You, S.J., Chang, C.W., Wang, Y.F. (2017). High selectivity of visible-light-driven La-doped TiO2 photocatalysts for NO removal. Aerosol Air Qual. Res. 17, 2555–2565. https://doi.org/10.4209/aaqr.2017.08.028

Huang, Y., Zhang, J., Wang, Z., Liu, Y., Wang, P., Cao, J.J., Ho, W. (2020). g-C3N4/TiO2 composite film in the fabrication of a photocatalytic air-purifying pavements. Solar RRL 4, 2000170. https://doi.org/10.1002/solr.202000170

Huang, Z.F., Song, J., Pan, L., Wang, Z., Zhang, X., Zou, J.J., Mi, W., Zhang, X., Wang, L. (2015). Carbon nitride with simultaneous porous network and O-doping for efficient solar-energy-driven hydrogen evolution. Nano Energy 12, 646–656. https://doi.org/10.1016/j.nanoen.2015.01.043

Huy, T.H., Kang, F., Wang, Y.F., Liu, S.H., Thi, C.M., You, S.J., Chang, G.-M. (2019a). SnO2/TiO2 nanotube heterojunction: The first investigation of NO degradation by visible light-driven photocatalysis. Chemosphere 215, 323–332. https://doi.org/10.1016/j.chemosphere.2018.10.033

Jiang, L., Wang, Y., Feng, C. (2012). Application of photocatalytic technology in environmental safety. Procedia Eng. 45, 993–997. https://doi.org/10.1016/j.proeng.2012.08.271

Jiménez-Calvo, P., Caps, V., Ghazzal, M.N., Colbeau-Justin, C., Keller, V. (2020). Au/TiO2 (P25)-g-C3N4 composites with low g-C3N4 content enhance TiO2 sensitization for remarkable H2 production from water under visible-light irradiation. Nano Energy 75, 104888. https://doi.org/10.1016/j.nanoen.2020.104888

Kumar, R., Zhou, H., Cronin, S.B. (2007). Surface-enhanced raman spectroscopy and correlated scanning electron microscopy of individual carbon nanotubes. Appl. Phys. Lett. 91, 223105. https://doi.org/10.1063/1.2816905

Lin, H., Zhao, L. (2019). Novel g-C3N4/TiO2 nanorods with enhanced photocatalytic activity for water treatment and H2 production. J. Mater. Sci. 30, 18191–18199. https://doi.org/10.1007/s10854-019-02173-4

Liu, C.H., Lin, S.J., Lewis, C. (2013). Evaluation of NOx, SOx and CO2 emissions of Taiwan’S thermal power plants by data envelopment analysis. Aerosol Air Qual. Res. 13, 1815–1823. https://doi.org/10.4209/aqr.2013.03.0070

Liu, L., Zheng, C., Qu, R., Wang, J., Liu, X., Wu, W., Gao, X. (2019). Non-thermal plasma assisted preparation of MnCeOx, MnOx and CeO2 catalysts for enhancement of surface active oxygen and NO oxidation activity. Aerosol Air Qual. Res. 19, 945–958. https://doi.org/10.4209/aqr.2018.12.0456

Liu, S.H., Lin, W.X. (2019). A simple method to prepare g-C3N4-TiO2/waste zeolites as visible-light-responsive photocatalytic coatings for degradation of indoor formaldehyde. J. Hazar. Mater. 368, 468–476. https://doi.org/10.1016/j.jhazmat.2019.01.082

Monga, D., Basu, S. (2019). Enhanced photocatalytic degradation of industrial dye by g-C3N4/TiO2 nanocomposite: Role of shape of TiO2. Adv. Powder Technol. 30, 1089–1098. https://doi.org/10.1016/j.apt.2019.03.004

Nasrabadi, A.M., Todea, A.M., Wolf, C., Demirel, T., Habryka, D., Asbach, C. (2021). Investigation of the effect of aerosolized TiO2 nanoparticles on the NO2 concentrations under uva exposure. Aerosol Air Qual. Res. 21, 200612. https://doi.org/10.4209/aqr.200612

Ohtani, B. (2011). Chapter 10 - Photocatalysis by inorganic solid materials: Revisiting its definition, concepts, and experimental procedures, in: Eldik, R. van, Stochel, G. (Eds.), Advances in Inorganic Chemistry, Academic Press, pp. 395–430. https://doi.org/10.1016/8978-0-12-385904-4.00001-9

Pareek, S., Quamara, J.K. (2018). Dielectric and optical properties of graphitic carbon nitride—
titanium dioxide nanocomposite with enhanced charge separation. J. Mater. Sci. 53, 604–612. https://doi.org/10.1007/s10853-017-1506-7

Pham, M.T., Tran, H.H., Nguyen, T.M.T., Bui, D.P., Huang, Y., Cao, J., You, S.J., Van Viet, P., Nam, V.H., Wang, Y.F. (2021). Revealing deNOx and DeVOC reactions via the study of the surface and bandstructure of ZnSn(OH)₆ photocatalysts. Acta Mater. 215, 117068. https://doi.org/10.1016/j.actamat.2021.117068

Reli, M., Huo, P., Sihor, M., Ambrozova, N., Troppová, I., Matejova, L., Lang, J., Svoboda, L., Kustrowski, P., Ritz, M. (2016). Novel TiO₂/g-C₃N₄ photocatalysts for photocatalytic reduction of CO₂ and for photocatalytic decomposition of N₂O. J. Phys Chem. A 120, 8564–8573. https://doi.org/10.1021/acs.jpca.6b07236

Sahrin, N.T., Nawaz, R., Fai Kait, C., Lee, S.L., Wirzal, M.D.H. (2020). Visible light photodegradation of formaldehyde over TiO₂ nanotubes synthesized via electrochemical anodization of titanium foil. Nanomaterials 10, 128. https://doi.org/10.3390/nano10010128

Sansotera, M., Kheyli, S.G.M., Baggioli, A., Bianchi, C.L., Pedeferrì, M.P., Diamanti, M.V., Navarrini, W. (2019). Absorption and photocatalytic degradation of VOCs by perflourinated ionomeric coating with TiO₂ nanopowders for air purification. Chem. Eng. J. 361, 885–896. https://doi.org/10.1016/j.cej.2018.12.136

Song, G., Chu, Z., Jin, W., Sun, H. (2015). Enhanced performance of g-C₃N₄/TiO₂ photocatalysts for degradation of organic pollutants under visible light. Chinese J. Chem. Eng. 23, 1326–1334. https://doi.org/10.1016/j.cjche.2015.05.003

Štengl, V., Grygar, T.M. (2011). The simplest way to iodine-doped anatase for photocatalysts activated by visible light. Interna. J. Photoener. 2011, 685935. https://doi.org/10.1155/2011/685935

Sun, Q., Lv, K., Zhang, Z., Li, M., Li, B. (2015). Effect of contact interface between TiO₂ and g-C₃N₄ on the photoreactivity of g-C₃N₄/TiO₂ photocatalyst: (0 0 1) vs (1 0 1) facets of TiO₂. Appl. Catal., B 164: 420–427. https://doi.org/10.1016/j.apcatb.2014.09.043

Tang, T., You, L., Liang, P., Jia, T., Feng, W., Liu, Q., Li, F., Zhui, W., Wang, D., Wu, J. (2021). Tuning dimensionality TiO₂/g-C₃N₄ heterostructure for enhanced elemental mercury removal performance under visible-light. Chem. Phys. Lett. 782, 139027. https://doi.org/10.1016/j.cplett.2021.139027

Tasbihi, M., Čalin, I., Šuligoj, A., Fanetti, M., Štangar, U.L. (2017). Photocatalytic degradation of gaseous toluene by using TiO₂ nanoparticles immobilized on fiberglass cloth. J. Photochem. Photobiol., A 336, 89–97. https://doi.org/10.1016/j.jphotochem.2016.12.025

Toghan, A., Abd El-Lateef, H.M., Taha, K.K., Modwi, A. (2021). Mesoporous TiO₂@g-C₃N₄ composite: Construction, characterization, and boosting indigo carmine dye destruction. Diamond Relat. Mater. 118, 108491. https://doi.org/10.1016/j.diamond.2021.108491

Van Viet, P., Huy, T.H., Sang, N.X., Thi, C.M., Van Hieu, L. (2018). One-step hydrothermal synthesis and characterisation of SnO₂ nanoparticle-loaded TiO₂ nanotubes with high photocatalytic performance under sunlight. J. Mater. Sci. 53, 3364–3374. https://doi.org/10.1007/s10853-017-1762-6

Van Viet, P., Huy, T.H., Sang, T.T., Nguyen, H.M., Thi, C.M. (2019). One-pot hydrothermal synthesis of Si doped TiO₂ nanotubes from commercial material sources for visible light-driven photocatalytic activity. Mater. Res. Express 6, 055006. https://doi.org/10.1088/2053-1591/aa8d80

Van Viet, P., Nguyen, H.P., Tran, H.H., Bui, D.P., Pham, M.T., You, S.J., Thi, C.M. (2021). Constructing g-C₃N₄/SnO₂ s-scheme heterojunctions for efficient photocatalytic NO removal and low NO₂ generation. J. Sci.: Adv. Mater. Devices 6, 551–559. https://doi.org/10.1016/j.jsadvmd.2021.07.005

Wang, H., Liang, Y., Liu, L., Hu, J., Cui, W. (2018). Highly ordered TiO₂ nanotube arrays wrapped with g-C₃N₄ nanoparticles for efficient charge separation and increased photoelectrocatalytic degradation of phenol. J. Hazard. Mater. 344, 369–380. https://doi.org/10.1016/j.jhazmat.2017.10.044

Wang, M., Liu, Z., Fang, M., Tang, C., Huang, Z., Liu, Y.g., Wu, X., Mao, Y. (2016). Enhancement in
the photocatalytic activity of TiO$_2$ nanofibers hybridized with g-C$_3$N$_4$ via electrospinning. Solid State Sci. 55, 1–7. https://doi.org/10.1016/j.solidstatesciences.2016.02.002

Wang, S., Zhang, J., Li, B., Sun, H., Wang, S. (2021). Engineered graphitic carbon nitride-based photocatalysts for visible-light-driven water splitting: A review. Energy Fuels 35, 6504–6526. https://doi.org/10.1021/acs.energyfuels.1c00503

Wang, Y., Ding, X., Zhang, P., Wang, Q., Zheng, K., Chen, L., Ding, J., Tian, X., Zhang, X. (2019). Convenient and recyclable TiO$_2$/g-C$_3$N$_4$ photocatalytic coating: Layer-by-layer self-assembly construction on cotton fabrics leading to improved catalytic activity under visible light. Indus. Eng. Chem. Res. 58, 3978–3987. https://doi.org/10.1021/acs.iecr.8b05509

Wu, H.C., Ku, Y. (2021). Chemical looping combustion of isopropanol in aqueous solution with fabricated Fe$_2$O$_3$/Al$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$/ TiO$_2$ oxygen carriers. Aerosol Air Qual. Res. 21, 200455. https://doi.org/10.4209/aaqr.2020.07.0455

Xiao, H., Zhu, J., Thomas, A. (2015). Graphitic carbon nitride for photocatalytic degradation of sulfamethazine in aqueous solution under simulated sunlight irradiation. RSC Adv. 5, 105731–105734. https://doi.org/10.1039/C5RA21895K

Xiong, M., Tao, Y., Zhao, Z., Zhu, Q., Jin, X., Zhang, S., Chen, M., Li, G. (2021). Porous g-C$_3$N$_4$/TiO$_2$ foam photocatalytic filter for treating NO indoor gas. Environ. Sci.: Nano 8, 1571–1579. https://doi.org/10.1039/D1EN00318F

Yang, S., Gong, Y., Zhang, J., Zhan, L., Ma, L., Fang, Z., Vajtai, R., Wang, X., Ajayan, P.M. (2013). Exfoliated graphitic carbon nitride nanosheets as efficient catalysts for hydrogen evolution under visible light. Adv. Mater. 25, 2452–2456. https://doi.org/10.1002/adma.201204453

Yao, S., Kuo, H. (2015). Photocatalytic degradation of toluene on SiO$_2$/TiO$_2$ photocatalyst in a fluidized bed reactor. Procedia Eng. 102, 1254–1260. https://doi.org/10.1016/j.proeng.2015.01.254

Ye, W., Shao, Y., Hu, X., Liu, C., Sun, C. (2017). Highly enhanced photoelectrocatalytic degradation of polybromodiphenyl ethers with g-C$_3$N$_4$/TiO$_2$ under visible light irradiation. Nanomaterials 7, 76. https://doi.org/10.3390/nano7040076

Yu, H., Shang, L., Bian, T., Shi, R., Waterhouse, G.I., Zhao, Y., Zhou, C., Wu, L.Z., Tung, C.H., Zhang, T. (2016). Nitrogen-doped porous carbon nanosheets templated from g-C$_3$N$_4$ as metal-free electrocatalysts for efficient oxygen reduction reaction. Adv. Mater. 28, 5080–5086. https://doi.org/10.1002/adma.201600398

Yu, J., Wang, S., Low, J., Xiao, W. (2013). Enhanced photocatalytic performance of direct z-scheme g-C$_3$N$_4$/TiO$_2$ photocatalysts for the decomposition of formaldehyde in air. Phys. Chem. Chem. Phys. 15, 16883–16890. https://doi.org/10.1039/C3CP53131G

Zhang, R.Z., Chen, Q.W., Lei, Y.X., Zhou, J.P. (2019). Growth of MoS$_2$ nanosheets on TiO$_2$/g-C$_3$N$_4$ nanocomposites to enhance the visible-light photocatalytic ability. J. Mater. Sci.: Mater. Electron. 30, 5393–5403. https://doi.org/10.1007/s10854-019-00832-0

Zhang, X., Xie, X., Wang, H., Zhang, J., Pan, B., Xie, Y. (2013). Enhanced photoresponsive ultrathin graphitic-phase C$_3$N$_4$ nanosheets for bioimaging. J. Am. Chem. Soc. 135, 18–21. https://doi.org/10.1021/ja308249k

Zhang, Y., Cao, G., Yang, X. (2021). Advances in de-NO$_x$ methods and catalysts for direct catalytic decomposition of NO: A review. Energy Fuels 35, 6443–6464. https://doi.org/10.1021/acs.energyfuels.1c00330