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Abstract
Enhanced photocatalytic degradation of methylene blue (MB) using graphitic carbon nitride/titanium dioxide (g-C3N4/TiO2) catalyst films has been demonstrated in this present work. The g-C3N4/TiO2 composites were prepared by directly heating the mixture of melamine and pre-synthesized TiO2 nanoparticles in Ar gas flow. The g-C3N4 contents in the g-C3N4/TiO2 composites were varied as 0, 20, 50 and 70 wt%. It was found that the visible-light-induced photocatalytic degradation of MB was remarkably increased upon coupling TiO2 with g-C3N4 and the best degradation performance of ~70% was obtained from 50 wt% g-C3N4 loading content. Results from UV–vis absorption study, Electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy suggest that the improved photoactivity is due to a decrease in band gap energy, an increased light absorption in visible light region and possibly an enhanced electron–hole separation efficiency as a result of effective interfacial electron transfer between TiO2 and g-C3N4 of the g-C3N4/TiO2 composite film. Based on the obtained results, the possible MB degradation mechanism is ascribed mainly to the generation of active species induced by the photogenerated electrons.

Keywords
tio2, c3n4, g, films, activity, enhanced, photocatalytic, light, visible

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Enhanced visible-light photocatalytic activity of g-C$_3$N$_4$/TiO$_2$ films

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ABSTRACT

Enhanced photocatalytic degradation of methylene blue (MB) using graphitic carbon nitride/titanium dioxide (g-C₃N₄/TiO₂) catalyst films has been demonstrated in this present work. The g-C₃N₄/TiO₂ composites were prepared by directly heating the mixture of melamine and pre-synthesized TiO₂ nanoparticles in Ar gas flow. The g-C₃N₄ contents in the g-C₃N₄/TiO₂ composites were varied as 0, 20, 50 and 70 wt%. It was found that the visible-light-induced photocatalytic degradation of MB was remarkably increased upon coupling TiO₂ with g-C₃N₄ and the best degradation performance of ~ 70 % was obtained from 50 wt% g-C₃N₄ loading content. Results from UV-vis absorption study, Electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy suggest that the improved photoactivity is due to a decrease of band gap energy, an increased light absorption in visible light region and possibly an enhanced electron-hole separation efficiency as a result of effective interfacial electron transfer between TiO₂ and g-C₃N₄ of the g-C₃N₄/TiO₂ composite film. Based on the obtained results, the possible MB degradation mechanism is ascribed mainly to the generation of active species induced by the photogenerated electrons.

Keywords: Titanium dioxide; Graphitic carbon nitride; Photocatalysis; Visible light

1. Introduction

Over the last few decades, the semiconductor-based photocatalysis has emerged as an alternative and environmentally benign wastewater treatment technology due to its destructive ability towards a wide range of inorganic and organic pollutants. To date, a large number of semiconductors such as ZnO, CdS, V₂O₅, WO₃, and TiO₂ have found to be active photocatalysts for photodegradation of various organic contaminants [1-5]. Among them, TiO₂ has been one of the promising
photocatalysts due to its low cost, nontoxicity and long-term stability [6-8]. However, its large band gap energy of ~3.2 eV and the high recombination rate of electron-hole pairs in excited TiO$_2$ have hindered its practical application [9, 10]. Therefore, much effort has been devoted to extend the light absorption of TiO$_2$ into visible light region as well as to reduce the photogenerated charge recombination. Various strategies have been proposed to obtain the TiO$_2$ with such properties including doping with metallic and/or non-metallic elements [11-14] and forming heterojunctions with other narrow band gap semiconductors [15, 16].

Coupling TiO$_2$ with visible light-sensitized semiconductors has shown to be beneficial to the improvement of photocatalytic performance due to the synergistic effect such as enhanced light harvesting, improved photostability and efficient photoexcited charge separation [17]. To achieve such desired coupling effect, close interfacial connection between the two semiconductors with appropriate conduction and valence band levels is necessary, so that spatially smooth charge transfer via heterojunction can proceed [18].

Recently, the metal-free graphic carbon nitride (g-C$_3$N$_4$) has attracted considerable attention as a potential visible light photocatalyst due to its high thermal and chemical stabilities together with its moderate band gap energy of ~2.7-2.8 eV depending on the degree of thermal condensation [19, 20]. The delocalized conjugated $\pi$ structure of g-C$_3$N$_4$ also offers a relatively slow charge recombination and a rapid photoinduced charge separation in the electron transfer process [21], thus making this material a sensitizer candidate for the design of efficient visible-light-driven photocatalyst. Therefore, coupling g-C$_3$N$_4$ with TiO$_2$ may be a suitable approach to achieve the improved charge separation and the enhanced light harvesting ability of the TiO$_2$ semiconductor. The application of g-C$_3$N$_4$ as a sensitizer in a composite photocatalyst has previously been
investigated. For example, Wang et al. [21] prepared g-C₃N₄/ZnO hybrid photocatalyst with a higher activity in methylene blue (MB) degradation than either a single phase of ZnO or g-C₃N₄. In addition, the excellent antiphotocorrosion ability was also observed from this composite material. Therein, the performance enhancement and the photocorrosion inhibition were attributed to the high separation efficiency of photogenerated charges. Yan et al. [22] reported that the coupling of TaON with g-C₃N₄ can increase the photocatalytic degradation of rhodamine B due to an improved electron-hole separation which results from the appropriate band structures of the composite photocatalyst. The organic-inorganic composite of g-C₃N₄ and Pt/TiO₂ with superior photocatalytic H₂ production rate was also observed by Chai et al [17]. The authors ascribed such improved H₂ evolution to the direct migration of electrons from g-C₃N₄ to Pt/TiO₂ via close interface and the effective separation of photogenerated charge carriers due to the synergistic effect.

In this study, a series of g-C₃N₄/TiO₂ photocatalyst films with different g-C₃N₄ loading contents have been investigated for their photodegradation activities towards MB under visible-light illumination (λ>400 nm). The possible mechanism for the enhancement of photocatalytic performance over the g-C₃N₄/TiO₂ heterostructured photocatalyst was also proposed.

2. Experimental

2.1. Materials

Titanium isopropoxide (Ti(OCH(CH₃)₂)₄, Pur. 97%), melamine (C₃H₆N₆, Pur. 99%) and other chemicals (analytical grade purity) were purchased from Aldrich and used without further purification. Deionized (DI) water was used throughout this study.
2.2. Catalyst preparation

Pure TiO$_2$ nanoparticles were synthesized by membrane-assisted sol-gel method [23, 24]. Briefly, a 20 ml of titanium tetraisopropoxide (TTIP) was dissolved in 250 ml of absolute ethanol. The mixture was loaded into a cellophane membrane pouch and then placed in a clear solution of 1:1 (v/v) ethanol/DI water containing 1.76 wt% of NH$_4$OH. The solution was stirred and heated at 70–80 °C for 1 h, after which the suspension was then centrifuged, washed with DI water until pH 7 was obtained and dried at 60 °C for 24 h. The dried TiO$_2$ powder was then calcined under static air at 400 °C for 3 h.

The g-C$_3$N$_4$ sample was prepared by directly heating melamine under a flow of Ar gas as described elsewhere [20]. In brief, 3 g of melamine powder was placed in a semiclosed alumina crucible with a quartz cover. The crucible was then put into a quartz tube reaction chamber and heated at 500 °C for 2 h in a flow of Ar. The sample was further heated at 520 °C for 2 h. Afterward, the obtained yellow polymeric g-C$_3$N$_4$ was ground into powder.

The g-C$_3$N$_4$/TiO$_2$ composite catalysts were prepared by mixing the pre-synthesized TiO$_2$ with different weight percentages of melamine (the nominal contents of 20, 50 and 70 wt%) in ethanol. The slurry mixture was stirred at room temperature for 3 h and sonicated for 1 h to obtain the homogeneous mixing. The sample was dried in an oven at 60°C for 24 h and subjected to the heat treatment under the same conditions as those of pure g-C$_3$N$_4$.

2.3. Characterization

To identify the crystalline phase of the obtained materials, X-ray diffraction (XRD) experiments were performed on a GBC EMMA 0133 X-ray diffractometer with Cu-K$_\alpha$ radiation of 0.15406 nm, at a scanning speed of 4 °/min. The morphology and microstructure of the photocatalyst films were examined by field emission scanning electron microscope (FESEM, JSM
-equipped with energy dispersive X-ray (EDX) spectrometer and transmission electron microscope (TEM, JEOL JEM 2010). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 510 FTIR spectrometer using conventional KBr pellets. Thermogravimetric (TG) analysis was done on TA instrument Q10 DSC. The experiment temperature ranged from 20 ºC to 800 ºC at a constant heating rate of 10 ºC min⁻¹ in air. X-ray photoelectron spectroscopy (XPS) measurement was performed using PHOIBOS 100 hemispherical energy analyser (SPECS) equipped with Al, Kα radiation in the fixed analyser transmission mode. All peaks in XPS spectra have already been calibrated with C 1s peak at 285 eV. UV–vis absorption spectra of all photocatalyst films were analyzed by Shimadzu UV–3600 spectrophotometer equipped with an integrating sphere assembly. Brunauer-Emmett-Teller (BET) surface area measurement was carried out using an Autosorb 1 MP, Quantachrome analyzer with N₂ adsorption isotherm.

2.4. Preparation of photocatalyst films

Photocatalyst films were prepared by doctor blade coating technique [25]. Typically, 1 g of the as-synthesized powders was mixed with 40 μl of acetic acid, 15 μl of Triton X100, and 0.5 ml of Milli Q water. The slurry was ground and sonicated to break up large agglomerates. The film was then prepared on a glass slide (2.00 x 5.00 cm) and the film thickness determined by a Veeco Dektak 6M stylus profilometer was 13.0 ± 2.0 μm. Finally, the prepared film was annealed at 300°C for 1 h under static air.

2.5. Photocatalytic experiments

The photocatalytic activities of catalyst films were evaluated by the decomposition of methylene blue (MB) under visible light illumination (λ>400 nm). A 50 W Halogen lamp (an intensity of ~640 W/m²) equipped with a 400 nm cut-off filter was used as a light source. In a
typical run, an aqueous MB solution (15 ml, 10 mg L\(^{-1}\)) was added into a batch reactor containing photocatalyst film. The solution pH was adjusted to ~7.0 by using 0.1 M NaOH or 0.1 M HClO\(_4\). Prior to light irradiation, the film was kept under the dark for 30 min to achieve adsorption-desorption equilibrium. At given time intervals, 2 ml samples were taken from the reaction solution and the amount of MB was determined by a Shimadzu UV–1601 spectrophotometer at 664 nm which corresponds to the characteristic absorption peak of MB. Then, the collected sample was put back into the reactor and the light was then irradiated again.

For comparison, MB photolysis was also investigated under the same experimental conditions. Investigation on the stability of g-C\(_3\)N\(_4\)/TiO\(_2\) film was carried out for five successive experiments, using a fresh MB solution for each catalytic run. After each run, the film was washed with deionized water and subsequently annealed at 300°C for 1 h.

3. Results and discussion

3.1. TG analysis

To determine the g-C\(_3\)N\(_4\) contents in the final products, thermogravimetric analysis was performed from 20 °C to 800 °C in air. As shown in Fig. 1, pure TiO\(_2\) shows almost no weight loss in the temperature range of study. However, pure g-C\(_3\)N\(_4\) presents the rapid weight loss from 550 °C to 670 °C, indicating the sublimation and/or decomposition of g-C\(_3\)N\(_4\). The weight of the g-C\(_3\)N\(_4\)/TiO\(_2\) composites decreases rapidly at the temperature above 500 °C. At the end of the analysis, total combustion of g-C\(_3\)N\(_4\) is attained. Therefore, the weight loss can be directly related to the amount of g-C\(_3\)N\(_4\) in the composite. The results from TG study indicate that the g-C\(_3\)N\(_4\) contents in the respective composites correspond to the nominal values.

[Fig. 1, single column fitting image]
3.2 Crystal phases and microstructure analyses

Fig. 1. Thermogravimetric analysis of (A) pure TiO$_2$, (B) 20 wt% g-C$_3$N$_4$/TiO$_2$, (C) 50 wt% g-C$_3$N$_4$/TiO$_2$, (D) 70 wt% g-C$_3$N$_4$/TiO$_2$ and (E) pure g-C$_3$N$_4$.

Powder XRD patterns of pure TiO$_2$, pure g-C$_3$N$_4$ and g-C$_3$N$_4$/TiO$_2$ composites are shown in Fig. 2. The diffraction peak of pure g-C$_3$N$_4$ at 2θ of ~ 27.4° is the characteristic of interlayer stacking of conjugated aromatic system, indexed as the (002) diffraction plane for graphitic materials [26]. The calculated interplanar distance of aromatic units is ~ 0.33 nm which is in good agreement with the previous reports [27-29]. The peaks of pure TiO$_2$ at 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7° and 68.7° correspond to the (101), (004), (200), (105), (211), (204) and (116) crystal planes of anatase TiO$_2$ (JCPDS 21-1272) [23]. The XRD patterns of g-C$_3$N$_4$/TiO$_2$ composites show no obvious diffraction peak attributable to g-C$_3$N$_4$ when the g-C$_3$N$_4$ content is less than 50 wt%; however, the composites with higher g-C$_3$N$_4$ loading clearly display the diffraction peak of g-C$_3$N$_4$.
at \( \sim 27.4^\circ \). It can also be seen that the relative peak intensity of g-C\(_3\)N\(_4\) gradually improves upon increasing the g-C\(_3\)N\(_4\) content.

**Fig. 2.** XRD patterns of pure TiO\(_2\), pure g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/TiO\(_2\) composites.

Morphology and microstructure of the catalyst films were examined by FESEM and TEM. Fig. 3 shows FESEM micrographs of pure g-C\(_3\)N\(_4\), pure TiO\(_2\) and g-C\(_3\)N\(_4\)/TiO\(_2\) composite films. The g-C\(_3\)N\(_4\) (Fig. 3a) appears as aggregated irregular particles whereas pure TiO\(_2\) (Fig. 3b) presents as agglomerates of small spherical-like particles. The FESEM image (Fig. 3c) of 50 wt% g-C\(_3\)N\(_4\)/TiO\(_2\) together with the corresponding EDX spectrum (Fig. 3d) reveals the agglomeration morphology and the attachment of the TiO\(_2\) particles on the g-C\(_3\)N\(_4\) surfaces. Fig. 4 shows the TEM micrographs of pure g-C\(_3\)N\(_4\), pure TiO\(_2\) and g-C\(_3\)N\(_4\)/TiO\(_2\) composites. It can be seen that g-C\(_3\)N\(_4\) (Fig. 4a) displays 2D lamellar structure whereas pure TiO\(_2\) (Fig. 4b) shows spherical particles with an average particle size of 13.7 nm. For the 50 wt% g-C\(_3\)N\(_4\)/TiO\(_2\) composite (Fig. 4c), the TiO\(_2\)
nanoparticles are found embedded in the g-C$_3$N$_4$ lamellar structure. The corresponding HRTEM image (Fig. 4d) clearly reveals the close interfacial connections between g-C$_3$N$_4$ and TiO$_2$ nanoparticles as well as the lattice spacing of 0.32 nm, corresponding to the (101) plane of anatase TiO$_2$. These observations together with the SEM result in Fig. 3c suggest the formation of heterojunction between TiO$_2$ and g-C$_3$N$_4$ which would be an ideal system to achieve the improved electron-hole separation via smooth charge transfer process [29].

[Fig. 3, single column fitting image]

![Fig. 3](attachment:image1.png)

**Fig. 3.** FESEM images of (a) pure g-C$_3$N$_4$, (b) pure TiO$_2$ and (c) 50 wt% g-C$_3$N$_4$/TiO$_2$ composite films and (d) the corresponding EDX spectrum of (c).

[Fig. 4, single column fitting image]
**Fig. 4.** TEM micrographs of (a) pure g-C₃N₄, (b) pure TiO₂ and (c,d) 50 wt% g-C₃N₄/TiO₂ composite.

### 3.3. FTIR analysis

FTIR spectra of g-C₃N₄, TiO₂ and g-C₃N₄/TiO₂ composites with different g-C₃N₄ contents are presented in Fig. 5. Pure g-C₃N₄ shows characteristic IR peaks similar to those of the previous results [17, 21, 22, 30, 31]. The peak at 1640 cm⁻¹ is assigned to C–N stretching vibration mode, while those at 1247, 1325, 1408 cm⁻¹ are associated with C–N heterocycle stretching of g-C₃N₄ [17, 21]. The peak at 810 cm⁻¹ can be attributed to the characteristic breathing mode of triazine units [21]. A broad band in the range of 3150-3300 cm⁻¹ corresponds to the stretching vibration modes of terminal NH groups [30]. Pure TiO₂ shows characteristic broad absorption band at 500-700 cm⁻¹ [17]. It can be clearly seen that the main characteristic peaks of g-C₃N₄ and TiO₂ appeared in all g-C₃N₄/TiO₂ samples suggesting the formation of a composite between g-C₃N₄ and TiO₂ [32].

*[Fig. 5, single column fitting image]*
Fig. 5. FTIR spectra of pure g-C$_3$N$_4$, pure TiO$_2$ and g-C$_3$N$_4$/TiO$_2$ composites.

3.4. XPS analysis

XPS measurement was carried out to obtain the information on oxidation state and surface chemical composition of the samples. Survey spectra in Fig. 6a indicate the peaks of Ti, O, C, and N in the 50 wt% g-C$_3$N$_4$/TiO$_2$ composite and the peaks of Ti, O and C in the pure TiO$_2$. The C 1s XPS spectrum of g-C$_3$N$_4$/TiO$_2$ sample (Fig. 6b) displays four peaks centering at 285.0, 286.4, 288.5 and 294.0 eV. The peak at 285.0 eV can be ascribed to C-C and/or adventitious carbon, and the peaks at 286.4 and 288.5 eV can be assigned to C-N-C and C-(N)$_3$ groups of g-C$_3$N$_4$ [33, 34], respectively. Another C 1s peak found at higher energy ca. 294.0 eV is attributed to carbon in aromatic rings attached to terminal uncondensed NH$_2$ species [34]. The regional spectrum of N 1s for g-C$_3$N$_4$/TiO$_2$ also presents in Fig. 6c. The spectrum can be deconvoluted into four peaks, ascribable to O-Ti-N in TiO$_{2-x}$N$_x$ at 396.2 eV [35], C-N=C at 398.6 eV [36], N-(C)$_3$ at 399.3 eV [17, 34, 36] and -NH$_2$ or =NH of uncondensed terminal amino groups at 401.0 eV [37].
Fig. 6d shows Ti 2p spectra of pure TiO₂ in comparison with that of 50 wt% g-C₃N₄/TiO₂. The binding energy values of Ti 2p₃/2 and Ti 2p₁/2 at 458.9 and 464.7 eV, respectively can be ascribed to Ti⁴⁺ species in the form of TiO₂ clusters [33]. However, the shift of 0.4 eV to the lower binding energies of 458.5 and 464.3 eV, respectively, is observed for the 50 wt% g-C₃N₄/TiO₂. This negative shift could be ascribed to an enhanced partial electron transformation to Ti and an increased electron density on Ti [38] as a consequence of the electronegativity effect due to the electronic interactions between Ti and possibly N atom as supported by the peak of O-Ti-N in N 1s region. The O 1s spectrum (Fig. 6e) of pure TiO₂ can be fitted into two peaks, and the binding energies of 530.0 and 531.4 eV can be ascribed to oxygen in TiO₂ and surface hydroxyls, respectively [17, 38]. In comparison with pure TiO₂, the negative shift of the main O 1s to 529.6 eV, with an order of ~0.4 eV, is observed for the g-C₃N₄/TiO₂ sample. This shift is the same order as that found in the case of Ti 2p peak position, suggesting the incorporation of nitrogen in TiO₂ lattice [38]. The XPS results together with those from SEM, TEM and FTIR studies clearly reveal the formation of composite material with the chemically bound interfaces between g-C₃N₄ and TiO₂ rather than a physical mixture of two separate g-C₃N₄ and TiO₂ phases.

[Fig. 6, 2- column fitting image]
Fig. 6. (a) Survey scan of TiO$_2$ and 50 wt% g-C$_3$N$_4$/TiO$_2$ composite and high-resolution spectra for: (b) C 1s and (c) N 1s of 50 wt% g-C$_3$N$_4$/TiO$_2$; (d) Ti 2p and (e) O 1s of 50 wt% g-C$_3$N$_4$/TiO$_2$ in comparison with those of TiO$_2$. 
3.5. UV–vis Absorption Spectra

The optical properties of the photocatalyst films were investigated by UV–vis absorption spectroscopy. As seen from Fig. 7a, the film color changes from opaque white to bright yellow as the amount of g-C₃N₄ loading increased from 0 to 100 wt%. The optical spectra of the films (Fig. 7b) present the absorption onsets at ~375 nm and ~490 nm for pure TiO₂ and g-C₃N₄, respectively. Superior light absorption intensity compared with pure TiO₂ is found from all g-C₃N₄/TiO₂ composite films. Additionally, upon loading TiO₂ with g-C₃N₄, the light absorption region of TiO₂ could be further extended to longer wavelength and the highest red shift appearing at ~540 nm is found from 50 wt% g-C₃N₄/TiO₂ sample. These observations suggest that the composite catalyst could provide an efficient utilization of visible light, thus producing more electron-hole pair, which would be beneficial to a photocatalytic process. The band gap energy \( E_g \) of a semiconductor can be determined by Equation (1):

\[
(ah\nu)^{1/n} = A(h\nu - E_g)
\]

where \( A \) is a proportionality constant, \( h\nu \) is photon energy, \( h \) is Planck’s constant, \( \nu \) is the frequency of vibration, and \( \alpha \) is an absorption coefficient. The value of \( n \) depends on the type of optical transition of the semiconductor (\( n = \frac{1}{2} \) for direct transition and \( n = 2 \) for indirect transition). For g-C₃N₄ and TiO₂, the \( n \) values of \( \frac{1}{2} \) and 2 are used, respectively [39-41]. Therefore, as can be seen from the inset of Fig. 7b, the corresponding band gap values of g-C₃N₄ and TiO₂ are found to be 2.83 and 3.31 eV, respectively.

[Fig. 7, single column fitting image]
Fig. 7. (a) Photocatalyst films and (b) UV–vis absorption spectra of (A) pure TiO$_2$, (B) 20 wt% g-C$_3$N$_4$/TiO$_2$, (C) 50 wt% g-C$_3$N$_4$/TiO$_2$, (D) 70 wt% g-C$_3$N$_4$/TiO$_2$ and (E) pure g-C$_3$N$_4$ films. Inset is $(\alpha h \nu)^{1/2}$ and $(\alpha h \nu)^2$ vs photon energy $(h \nu)$ plot of pure TiO$_2$ and g-C$_3$N$_4$ films, respectively.

3.6. Photocatalytic Activities of the photocatalyst films

The photocatalytic activities of the obtained films were evaluated by measuring the decolorization of MB under visible light irradiation ($\lambda > 400$ nm). As a comparison, direct photolysis and photocatalytic degradation of MB over pure TiO$_2$ were also carried out under identical conditions. Unfortunately, MB degradation activity over pure g-C$_3$N$_4$ film was not obtained due to the
problems with film-peeling off. As seen from Fig. 8a, the blank test without any catalyst shows the MB degradation of ~28% whereas the pure TiO_2 film provides ~35% degradation within 3 h of irradiation. The photocatalytic activity of g-C_3N_4/TiO_2, however, is much better than that of the pure TiO_2 sample, although at high g-C_3N_4 concentration the activity decreases slightly, suggesting an optimum g-C_3N_4 content of 50 wt%. The 50 wt% g-C_3N_4/TiO_2 film can degrade MB by 68% which is almost twice higher than that of pure TiO_2. The improved photocatalytic activity observed from the g-C_3N_4/TiO_2 films might be partially ascribed to the red-shift of the light absorption range and the strong light absorption intensity of the g-C_3N_4/TiO_2 composites as evidenced from the UV–vis study in Fig. 7b. Another possible reason responsible for the significant enhancement of the photocatalytic performance can be attributed to an improved charge separation efficiency of photogenerated electron-hole pairs due to the suitably matching conduction and valence band levels and the close interfacial connection between TiO_2 and g-C_3N_4 in the composite material [17, 21, 22]. Note that the decrease of BET specific surface area (SSA) with the increase of g-C_3N_4 loading content is observed. The SSA of pure TiO_2 is 120 m^2/g whereas that of pure g-C_3N_4 is 6 m^2/g. Upon increasing the g-C_3N_4 loading to 20, 50 and 70 wt%, the surface area decreases to 91, 49 and 31 m^2/g, respectively. Therefore, the SSA is likely not a main factor governing the observed photocatalytic activity. Since the 50 wt% g-C_3N_4/TiO_2 composite provides the best performance, this sample is selected for the following long-term stability experiments which will be an advantage for practical applications. The cyclic experiments (Fig. 8b) indicate only ~5% deactivation after five cycles, suggesting good stability and recyclability of the g-C_3N_4/TiO_2 composite film during MB photodegradation reaction.

[Fig. 8, single column fitting image]
Fig. 8. (a) MB photolysis and photocatalytic degradation over pure TiO₂, pure g-C₃N₄ and g-C₃N₄/TiO₂ composite films and (b) cycling runs using 50 wt% g-C₃N₄/TiO₂ film (the initial MB concentration of 10.0 mg/L).

A proposed mechanism for electron-hole separation and transport at the g-C₃N₄/TiO₂ interfaces under visible light irradiation is illustrated in Fig. 9. Based on the UV–vis results in Fig. 7b, the conduction band (CB) and valence band (VB) potentials of g-C₃N₄ and TiO₂ can be determined using Equation (2) [42]:
\[ E_{CB}^0 = \chi - E_C - \frac{1}{2}E_g \]  \hspace{1cm} (2)

where \( \chi \) is the Sanderson electronegativity of the semiconductor (\( \chi \) is 4.73 eV [26] and 5.81 eV [38] for g-C\(_3\)N\(_4\) and TiO\(_2\), respectively), \( E_C \) is the scaling factor relating the hydrogen electrode scale (NHE) to absolute vacuum scale (AVS) (~4.5 eV vs. AVS for 0 V vs. NHE) [42] and \( E_g \) is the band gap of g-C\(_3\)N\(_4\) (2.83 eV) and TiO\(_2\) (3.31 eV) obtained in this study. The calculated CB and VB potentials of g-C\(_3\)N\(_4\) are ~1.19 and 1.65 V, and of TiO\(_2\) are ~0.35 and 2.97 V, respectively. According to the obtained band gap energies, only g-C\(_3\)N\(_4\) can be activated under the visible light illumination, resulting in the photogenerated electrons in the CB and holes in the VB of g-C\(_3\)N\(_4\). Because the CB edge potential of g-C\(_3\)N\(_4\) (~1.19 V) is more negative than that of TiO\(_2\) (~0.35 V), the electrons in g-C\(_3\)N\(_4\) can transfer easily to the CB of TiO\(_2\) possibly via close interfacial connections [17, 22] as supported by the SEM and TEM results, while the holes remain in the VB of g-C\(_3\)N\(_4\). This direct electron transfer from g-C\(_3\)N\(_4\) to TiO\(_2\) could reduce the probability of electron-hole recombination [40], leading to efficient charge separation and the improvement of photocatalytic activity as seen in Figure 8a.

Since the CB potential of TiO\(_2\) (~0.35 V) is more negative than the standard redox potential \( E^0 \) (O\(_2^*/\text{O}_2^-\), ~0.33 V) [43], the electrons accumulated in the CB of TiO\(_2\) can be transferred to adsorbed oxygen molecules yielding \( \bullet\text{O}_2^- \) which then further react to finally produce active \( \bullet\text{OH} \) radical as follows [29]:

\[
e^- + O_2 \rightarrow \bullet\text{O}_2^- \hspace{1cm} (3)
\]

\[
\bullet\text{O}_2^- + H^+ \rightarrow \bullet\text{HO}_2 \hspace{1cm} (4)
\]

\[
e^- + \bullet\text{HO}_2 + H^+ \rightarrow \text{H}_2\text{O}_2 \hspace{1cm} (5)
\]

\[
e^- + \text{H}_2\text{O}_2 \rightarrow \bullet\text{OH} + \text{OH}^- \hspace{1cm} (6)
\]
Consequently, the generated •O$_2^-$ and •OH acting as effective oxidants will react with the MB molecules, producing CO$_2$ and H$_2$O as final products. However, since the standard redox potential $E^0$ (•OH/OH$^-$, 1.99 V) [43] is more positive than the VB position of g-C$_3$N$_4$ (1.65 V), the photoinduced holes in the VB of g-C$_3$N$_4$ cannot oxidize OH$^-$ or H$_2$O to form •OH. This suggests that the photogenerated hole is not a main effective species for the MB degradation in this study. Based on the above observations and discussion, the possible MB degradation mechanism is ascribed mainly to the generation of active species induced by the photogenerated electrons. More detailed studies to fully understand the mechanism are presently being conducted.

[Fig. 9, single column fitting image]
Fig. 9. Proposed mechanism for the photoexcited electron-hole separation and transport processes at the g-C₃N₄/TiO₂ interface under visible light irradiation.

4. Conclusions

The g-C₃N₄/TiO₂ composite films with different g-C₃N₄ weight percentages have successfully been prepared by direct heating of melamine in the presence of preformed TiO₂ nanoparticles. The improved MB degradation activity under visible light irradiation was observed from all g-C₃N₄/TiO₂ photocatalyst films with the 50 wt% g-C₃N₄/TiO₂ showing the best photocatalytic activity. Significantly, the photocatalytic performance of 50 wt% g-C₃N₄/TiO₂ increased almost twice in comparison with pure TiO₂. Such an enhanced photocatalysis is ascribed to the strong light absorption intensity and the red-shift of absorption range of the g-C₃N₄/TiO₂ composites and possibly the improved electron-hole separation efficiency originated from the suitably matching conduction and valence band potentials between g-C₃N₄ and TiO₂. Cyclic experiments also indicate the reusability and high stability of the obtained films. Based on the results obtained in this study, the possible photocatalytic mechanism of g-C₃N₄/TiO₂ heterojunction catalyst under visible light irradiation is proposed.

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References

List of Figure Captions

Fig. 1. Thermogravimetric analysis of (A) pure TiO₂, (B) 20 wt% g-C₃N₄/TiO₂, (C) 50 wt% g-C₃N₄/TiO₂, (D) 70 wt% g-C₃N₄/TiO₂ and (E) pure g-C₃N₄.

Fig. 2. XRD patterns of pure TiO₂, pure g-C₃N₄ and g-C₃N₄/TiO₂ composites.

Fig. 3. FESEM images of (a) pure g-C₃N₄, (b) pure TiO₂ and (c) 50 wt% g-C₃N₄/TiO₂ composite films and (d) the corresponding EDX spectrum of (c).

Fig. 4. TEM micrographs of (a) pure g-C₃N₄, (b) pure TiO₂ and (c,d) 50 wt% g-C₃N₄/TiO₂ composite.

Fig. 5. FTIR spectra of pure g-C₃N₄, pure TiO₂ and g-C₃N₄/TiO₂ composites.

Fig. 6. (a) Survey scan of TiO₂ and 50 wt% g-C₃N₄/TiO₂ composite and high-resolution spectra for: (b) C 1s and (c) N 1s of 50 wt% g-C₃N₄/TiO₂; (d) Ti 2p and (e) O 1s of 50 wt% g-C₃N₄/TiO₂ in comparison with those of TiO₂.

Fig. 7. (a) Photocatalyst films and (b) UV–vis absorption spectra of (A) pure TiO₂, (B) 20 wt% g-C₃N₄/TiO₂, (C) 50 wt% g-C₃N₄/TiO₂, (D) 70 wt% g-C₃N₄/TiO₂ and (E) pure g-C₃N₄ films. Inset is \((\alpha h \nu)^{1/2}\) and \((\alpha h \nu)^{2}\) vs photon energy \((h \nu)\) plot of pure TiO₂ and g-C₃N₄ films, respectively.

Fig. 8. (a) MB photolysis and photocatalytic degradation over pure TiO₂, pure g-C₃N₄ and g-C₃N₄/TiO₂ composite films and (b) cycling runs using 50 wt% g-C₃N₄/TiO₂ film (the initial MB concentration of 10.0 mg/L).

Fig. 9. Proposed mechanism for the photoexcited electron-hole separation and transport processes at the g-C₃N₄/TiO₂ interface under visible light irradiation.