Visible-light enhancement of methylene blue photodegradation by graphitic carbon nitride-titania composites

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Abstract

Composites of graphite-like C₃N₄ (g-C₃N₄) and TiO₂ were synthesized by direct heating of melamine in the presence of different TiO₂ amounts in a semi-closed stainless steel container. The resulting samples were characterized using X-ray diffraction, X-ray photoelectron spectroscopy (XPS), UV-visible diffuse reflectance spectroscopy (DRS), photoluminescence spectrum (PLS), thermogravimetric analysis, scanning electron microscopy, and transmission electron microscopy techniques. The results reveal that the microstructure and DRS and PLS characteristics of the composites vary with the composition. XPS Ti 2p peaks for the composites exhibit a shift to lower binding energy in comparison to pure TiO₂. The photocatalytic degradation properties of the composites were evaluated using methylene blue (MB) as a model compound under visible light irradiation (400–600 nm). The results indicate that photocatalytic degradation of MB is higher for g-C₃N₄–TiO₂ composites with optimum TiO₂ content (26.4 and 80.0 wt%) than for pure g-C₃N₄ or TiO₂. Moreover, the activity of an optimum composite sample was still as high as 91% after use in four consecutive photocatalytic cycles.

1. Introduction

Over the past few decades, photocatalysis has been considered as a very promising technique for hydrogen production and removal of environmental pollutants [1–4]. Among metal oxide photocatalysts, TiO₂ has attracted much attention because of its low cost, low toxicity, photochemical stability, high photocatalytic activity, and biocompatibility [5–7]. However, the bandgap of TiO₂ is 3.0 eV for the rutile phase and 3.2 eV for the anatase phase, so UV radiation is required for activation and relatively little of the solar spectral range (4–5%) is used [8]. Therefore, the main focus of recent research into TiO₂ photocatalysis has been on how to improve the catalytic activity under visible light irradiation. There have been substantial attempts to induce absorption of visible light by TiO₂ for effective utilization of solar energy and improved separation of photogenerated electrons and holes. For instance, Moon et al. improved the visible-light photocatalytic activity of TiO₂ using acid red 44 as a modifier [9]. Asahi et al. investigated photocatalysis by nitrogen-doped titanium oxides under visible light [10]. Enhancement of photodegradation efficiency using Pt–TiO₂ catalysts [11] and B₂O₃–SiO₂–TiO₂ ternary mixed oxides [12] has also been investigated and the results revealed that these composites exhibit higher photocatalytic activity when compared with TiO₂. However, there is still a need to develop novel TiO₂-based composites to improve the activity of TiO₂ under visible light.

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Graphite-like C₃N₄ (g-C₃N₄) is a novel and metal-free photocatalyst with a conjugated π structure that absorbs visible light [13–15] and it has been used as a catalyst in several reactions [16,17]. Moreover, it is inexpensive, environmentally benign, and can be easily prepared via numerous facile methods [18,19]. However, the efficiency of pure g-C₃N₄ is limited owing to recombination of photogenerated electron–hole pairs because of its narrow bandgap energy (2.7 eV). Various strategies such as doping with metal or nonmetal species [20–22], sensitization with organic dyes [23], and coupling with other semiconductors [24] have been adopted to improve the photocatalytic performance of g-C₃N₄. Several recent reports on application of g-C₃N₄–TiO₂ in photocatalysis describe the synthesis of g-C₃N₄ and then g-C₃N₄–TiO₂. For example, a g-C₃N₄–TiO₂ composite containing 66.7% g-C₃N₄ with good photocatalytic activity was synthesized hydrothermally using g-C₃N₄ as a support [25]. Miranda et al. synthesized g-C₃N₄–TiO₂ containing 2 wt% g-C₃N₄ via an impregnation method [26]. Lu et al. prepared a g-C₃N₄–TiO₂ composite by combining sol–gel and hydrothermal methods [27]. Yang et al. synthesized an N-doped TiO₂–C₃N₄ composite by heating a mixture of the hydrolysis product of TiCl₄ and g-C₃N₄ [28]. A TiO₂–g-C₃N₄ composite was also prepared by ball-milling of TiO₂ and g-C₃N₄ powder and the product was heated at 400 °C for 1 h and used in photocatalytic production of H₂ under visible light irradiation [29]. According to the above studies, the g-C₃N₄ sheet size does not change during composite synthesis because g-C₃N₄ is synthesized first. However, g-C₃N₄ synthesis has some disadvantages, such as low yield and difficulty in controlling the quality because of sublimation of the precursor (e.g. melamine) during pyrolysis.

To the best of our knowledge, preparation methods for composites containing g-C₃N₄ mostly involve mixing of other components with prepared g-C₃N₄ and some subsequent treatment [26,27]. In most cases, the composite is g-C₃N₄–modified TiO₂ or TiO₂–modified g-C₃N₄ and the properties of a composite with one main component are investigated [30,31]. Because both TiO₂ and g-C₃N₄ are semiconductors, the two components can be used as modifiers for each other. In the present study, we synthesized g-C₃N₄– TiO₂ composites by directly heating melamine and TiO₂ in a semi-closed system. This new and facile approach can be used to prepare pure g-C₃N₄ in high yield of 95%. The preparation of g-C₃N₄– TiO₂ via thermal treatment of a mixture of TiO₂ and melamine is reported for the first time. Compared with pure g-C₃N₄ and TiO₂, the optimum g-C₃N₄– TiO₂ composite exhibits enhanced activity for photocatalytic degradation of methylene blue (MB) under visible light irradiation.

2. Experimental

2.1. Materials

TiO₂ (P25) was obtained from the Guangzhou Kosin (Evonik Degussa). Melamine was purchased from Aladdin Chemistry. Other chemicals were of analytical reagent grade and were used without further purification. MB was obtained from Zhangjiagang Chemical Plant. Deionized water was used in all experiments.

2.2. Synthesis of g-C₃N₄

g-C₃N₄ was obtained by pyrolysis of melamine powder. In brief, 1.0 g of melamine was poured into a cylindrical stainless steel container (Fig. S1) after it was fully ground in an agate mortar. The container was sealed with a screw-on lid and transferred to a muffle furnace. The temperature was increased at 3.0 °C min⁻¹ and samples were heated at temperatures ranging from 500 °C to 560 °C for 4 h. After cooling to room temperature, the resultant yellow solid (Fig. S2) was milled into powder and collected (yield ~95%).

2.3. Fabrication of g-C₃N₄–TiO₂ composites

To prepare g-C₃N₄–TiO₂ composites, a certain amount of melamine (1.0 g) was mixed with different amounts of TiO₂ powder. The mixture was ground thoroughly in an agate mortar and poured into a cylindrical stainless steel container, which was then sealed with a screw-on lid. Mixtures of different composition were heated in a muffle furnace at different temperatures (500–560 °C) for 4 h at a heating rate of 3.0 °C min⁻¹. g-C₃N₄–TiO₂ composites prepared at 540 °C containing 9.2, 16.1, 26.4, 46.9, 69.3, 80.0, and 89.1 wt% TiO₂ are denoted as g-C₃N₄–TiO₂–9, -16, -26, -47, -69, -80, and -89, respectively.

2.4. Characterization

X-Ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra DLD spectrometer (Kratos Shimadzu) using a monochromic Al Kα source at 1486.6 eV, with power of 150 W for a sample analysis area of approximately 700 μm × 300 μm. X-Ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation and a graphite monochromator. The scan speed was 5° min⁻¹ and the step size was 0.02°. The sample morphology was observed using a Jeol JSM-6701 field-emission scanning electron microscope (SEM) operating at an accelerating voltage of 10 kV and a Jeol 2010 transmission electron microscopy (TEM) operating at 200 kV. UV-Vis diffuse reflectance spectra (DRS) were recorded on a Thermo Scientific Evolution 220 UV-visible spectrophotometer. The fluorescence properties of the samples were investigated using a Hitachi F-2500 spectrophotofluorimeter at room temperature. The MB spectral absorbance during photodegradation was measured on a Varian 50 Bio UV-visible spectrophotometer. Thermogravimetric analysis (TGA) was performed on a STA449C thermogravimetric analyzer from room temperature to 800 °C at a heating rate of 10 °C min⁻¹.

2.5. Photodegradation measurements

Photocatalytic experiments were carried out using MB in solution as a model compound. In a typical run, 50.0 mL of MB solution (20.0 mg L⁻¹) containing a certain amount of photocatalyst in a 100-mL beaker was stirred for 30 min in
the dark under ambient conditions to achieve absorption–

desorption equilibrium before irradiation. The visible light

(400–600 nm) used for photocatalytic degradation was

generated by a 200-W Xe lamp equipped with a UV cutoff

filter. For irradiation, the lamp was positioned 36 cm away

from the sample beaker. The photocatalytic reaction was

initiated by turning on the Xe lamp. During photocatalysis,

MB degradation was monitored by measuring the UV

absorbance at given time intervals. During photodegrada-

tion, the temperature was kept at \( -25 \) °C and the pH at

\( \pm 7.0 \). At given time intervals, 1.0 mL of the solution

was removed and centrifuged at 12,000 rpm for 10 min

to precipitate the catalyst particles. The absorbance of

the solution was measured in an ethanol/water mixture

(3:1 v/v). Control experiments, which included irradiation

without a photocatalyst and no irradiation in the presence

of a photocatalyst, were carried out using the same proce-

dure. The solution pH was adjusted using HCl and NaOH

solutions. Catalyst stability for MB photodegradation was

also tested using the same procedure. A 30.0-mg of photo-

catalyst was initially dispersed in 50.0 mL of MB solution

(20.0 mg L\(^{-1}\)) and the same photocatalyst sample was used

in four consecutive cycles, each lasting for 3 h. After each

cycle, the catalyst was centrifuged, washed thoroughly with

water, and then added to fresh MB solution.

3. Results and discussion

3.1. Characterization

Fig. 1a shows XRD patterns for g-C\(_3\)N\(_4\) synthesized at

different temperatures. It is evident that g-C\(_3\)N\(_4\) was

successfully synthesized at \( \geq 520 \) °C, while an oligomer

is the main product at 500 °C. The g-C\(_3\)N\(_4\) samples pre-

pared at 540 °C and 560 °C show two distinct peaks at

13.1° and 27.4° corresponding to the characteristic in-plane

structural arrangement parallel to the c-axis and the long-

range interplanar stacking of aromatic systems, respec-

tively [32,33]. The g-C\(_3\)N\(_4\) size calculated using the (002)

peak is \( \sim 7.2 \) nm. However, no shift of the (002) peak to

higher angle was observed with increasing temperature, in

contrast to previous studies [26,34], which indicates that

the interplanar stacking distance does not change at

higher condensation temperatures such as 560 °C. The

XRD pattern for TiO\(_2\) reveals that it contains mainly

anatase phase and little rutile phase (Fig. 1b, curve d).

The XRD patterns for g-C\(_3\)N\(_4\)-TiO\(_2\)-26 and g-C\(_3\)N\(_4\)-TiO\(_2\)-80

(Fig. 1b, curves b and c) exhibit the characteristics of both

g-C\(_3\)N\(_4\) and TiO\(_2\), confirming that g-C\(_3\)N\(_4\)-TiO\(_2\) composites

formed during pyrolysis. It is evident that the (002)

diffraction peak for g-C\(_3\)N\(_4\) overlaps with the (110) peak

for the TiO\(_2\) rutile phase. In comparison to the patterns for

pure g-C\(_3\)N\(_4\) and TiO\(_2\), the g-C\(_3\)N\(_4\) (002) peak is relatively

weak and broad for g-C\(_3\)N\(_4\)-TiO\(_2\)-26 and is hardly detect-

able for g-C\(_3\)N\(_4\)-TiO\(_2\)-80. This can be attributed to the low

g-C\(_3\)N\(_4\) content; it is also possible that the g-C\(_3\)N\(_4\) size

along the c-axis decreases in the composites.

TGA curves for the samples are shown in Fig. 2. The

weight of TiO\(_2\) is almost unchanged in the temperature

range 25–800 °C (Fig. 2a), while g-C\(_3\)N\(_4\) exhibits a weight

loss of < 5% due to adsorbed water at 150 °C, and severe

weight loss at temperatures higher than the decomposi-

tion temperature of 600 °C, with nearly 0% weight retained

at 800 °C (Fig. 2e). However, the decomposition tempera-

ture of g-C\(_3\)N\(_4\) decreases to \( \sim 512 \) °C for the composites

(Fig. 2b–d), which indicates that TiO\(_2\) has a catalytic effect

on g-C\(_3\)N\(_4\) decomposition. The residual weight for the

Fig. 1. XRD patterns for as-synthesized g-C\(_3\)N\(_4\) samples and g-C\(_3\)N\(_4\)-TiO\(_2\). (a) g-C\(_3\)N\(_4\) prepared at 500 °C (curve a), 520 °C (curve b), 540 °C (curve c), and 560 °C (curve d). (b) g-C\(_3\)N\(_4\) (curve a), g-C\(_3\)N\(_4\)-TiO\(_2\)-26 (curve b) and g-C\(_3\)N\(_4\)-TiO\(_2\)-80 (curve c) prepared at 540 °C, and TiO\(_2\) (P25) (curve d). T, tri-s-triazine units; Ar, interlayer stacking of aromatic segments; A, anatase; R, rutile.

Fig. 2. Thermogravimetric analysis results for (a) TiO\(_2\), (b) g-C\(_3\)N\(_4\)-TiO\(_2\)-80, (c) g-C\(_3\)N\(_4\)-TiO\(_2\)-47, (d) g-C\(_3\)N\(_4\)-TiO\(_2\)-26, and (e) g-C\(_3\)N\(_4\).
composites corresponds to their TiO₂ content. Thus, the TGA data indicate that the TiO₂ content is approximately 80.0% for g-C₃N₄–TiO₂-80, 46.9% for g-C₃N₄–TiO₂-47, and 26.4% for g-C₃N₄–TiO₂-26. It is notable that the g-C₃N₄ content in the composites as determined by TGA is consistent with the nominal content when g-C₃N₄ is the major component (> 50%) but is slightly lower than the nominal content when g-C₃N₄ is the minor component, which can be attributed to sublimation of melanin.

From the SEM images of g-C₃N₄, TiO₂, and g-C₃N₄–TiO₂ composites shown in Fig. S3, it is evident that the g-C₃N₄ and g-C₃N₄–TiO₂ samples exhibit a layered and plate-like surface morphology; however, more detailed information cannot be obtained from the SEM images. To investigate the sample microstructure, TEM images were recorded and are shown in Fig. 3. g-C₃N₄ exhibits a distinct sheet-like structure (Fig. 3a) with a wide sheet size distribution. The diameter of TiO₂ particles is approximately 25 nm and the material exhibits relatively good dispersion (Fig. 3b), although there are some aggregates among the particles. The TEM image of g-C₃N₄–TiO₂-26 in Fig. 3c confirms the coexistence of sheet-like g-C₃N₄ and TiO₂ particles, with the latter dispersed on the g-C₃N₄ surface. However, g-C₃N₄ sheets are not obvious in the TEM image of g-C₃N₄–TiO₂-80 (Fig. 3d). Comparison with the image for pure TiO₂ reveals that there are some layers coated on the surface of TiO₂ particles. The TEM images indicate that g-C₃N₄ can act as a support when the TiO₂ content in the composite is low, while TiO₂ particles can act as a substrate to disperse g-C₃N₄ when TiO₂ is the main component of the composite. The results are consistent with the XRD patterns, which reveals that the presence of TiO₂ in the composites may decrease the size of g-C₃N₄ along the c-axis.

To identify the valence state of elements in the samples, XPS spectra of g-C₃N₄, TiO₂, and g-C₃N₄–TiO₂ were recorded and are shown in Fig. 4. The results indicate that the g-C₃N₄–TiO₂ composites contain C, N, O, and Ti (Fig. 4a). The C/N ratio for g-C₃N₄ is 0.76, which is close to the theoretical value of 0.75. The C/N ratios of 0.69 for g-C₃N₄–TiO₂-26 and 0.68 for g-C₃N₄–TiO₂-80 are less than the theoretical value, which can be attributed to edge defects caused by uncondensed amino groups [35]. The g-C₃N₄ C/N ratio will decrease with increasing edge defects, which are related to the g-C₃N₄ size. High-resolution C 1s, N 1s, and Ti 2p XPS spectra are shown in Fig. 4b–d. The XPS peaks can be fitted using a Gauss–Lorentz shape after Shirley background correction. For example, the C 1s spectrum can be deconvoluted into four peaks located at 284.6 (C1), 286.2 (C2), 288.2 (C3), and 289.6 eV (C4). The peak at 284.6 eV is attributed to atoms in a pure carbon environment (C–C bonds), typically ascribed to graphitic carbon [17,34,36,37]. The peak at 286.2 eV can be assigned to C bonded to N, usually ascribed to defect-containing sp²-hybridized carbon atoms present in graphitic domains [37–39]. The peak at 288.2 eV corresponds to sp²-hybridized carbon in N=C–N₂, in which C is bonded to three neighboring N atoms via one double and two single bonds [40]. The peak at 289.6 eV can be assigned to C bonded to O atoms in O=C–OR. The g-C₃N₄–TiO₂ composites exhibit similar fitted C 1s peaks, indicating the existence of graphite-like carbon nitride. The N 1s spectra for g-C₃N₄ and g-C₃N₄–TiO₂ can be deconvoluted into three peaks located at 398.6 (N1), 399.8 (N2), and 400.9 eV (N3). The peak at 398.6 eV is assigned to pyridine-type N (C–N=C) [41–43]. The N2 peak is attributed to tertiary nitrogen (N–(C)₃) and the N3 peak to an amino group carrying a hydrogen atom, which might be related to structural defects and incomplete condensation during the polymerization process [44–46]. The C 1s and N 1s XPS data provide evidence of the existence of g-C₃N₄ in the composites. The Ti 2p XPS profile for g-C₃N₄–TiO₂ is similar to that for TiO₂, but the peaks are slightly shifted to lower binding energy compared with TiO₂, indicating that electron interaction transfer from g-C₃N₄ to Ti occurs, leading to an increase in the outer electron.

![Fig. 3. TEM images of (a) g-C₃N₄, (b) TiO₂, (c) g-C₃N₄–TiO₂-26, and (d) g-C₃N₄–TiO₂-80.](image-url)
cloud density of Ti and a decrease in Ti 2p binding energy. This suggests that there is some intense interaction between TiO2 and g-C3N4 species.

UV-visible diffuse reflectance spectra (DRS) for the samples are shown in Fig. 5a. TiO2 has an absorption edge at ~400 nm, with strong absorption in the UV region and weak absorption in the range 400–800 nm (Fig. 5a curve a). g-C3N4 can absorb light at wavelengths up to 450 nm, but its absorption capacity in the UV range is weaker than that of TiO2. After combining g-C3N4 with TiO2, the absorbance edge of g-C3N4–TiO2 composites obviously shifts to longer wavelength. It is interesting that g-C3N4–TiO2-80 (Fig. 5a curve d) shows higher absorption in both the UV and visible regions than g-C3N4–TiO2-26, which may indicate that this composite has high activity due to generation of more electron–hole pairs under visible light irradiation.

PLS data were measured to determine the migration, transfer, and recombination processes for photogenerated electron–hole pairs in the samples. The photocatalytic activity of catalysts depends on the separation efficiency for photoinduced electron–hole pairs: the higher the electron–hole separation efficiency, the higher are the photocurrent and catalytic activity. For excitation at 365 nm, g-C3N4 showed a strong emission peak at ~450 nm (Fig. 5b curve a), which can be attributed to band-to-band photoluminescence, because the light energy approximately equals the bandgap energy of g-C3N4 (2.73 eV), so electrons and holes can rapidly recombine [34]. The emission peak intensity is significantly lower for g-C3N4–TiO2 composites (Fig. 5b, curves b and c), which indicates that the composites have much lower recombination rates and that TiO2 introduction can inhibit electron–hole recombination. Furthermore, the emission peaks for g-C3N4–TiO2 are shifted to shorter wavelength; for example, the peak position is 443 nm for g-C3N4–TiO2-26 and 440 nm for g-C3N4–TiO2-80. This indicates that the g-C3N4 bandgap has widened because the conjugated system has decreased in size owing to interactions between TiO2 and g-C3N4.

### 3.2. Photodegradation characteristics

A pseudo-first-order reaction model can usually describe experimental data for photodegradation according to [47]

\[
\ln \frac{C_0}{C_t} = K_{app} t, \tag{1}
\]

where \(C_0\) is the initial MB concentration, \(t\) is the reaction time, \(C_t\) is the MB concentration at reaction time \(t\), and \(K_{app}\) is the apparent first-order rate constant. During degradation, the absorbance of MB in solution decreases with increasing irradiation time (Figs. S4 and S5), indicating that the dye has decomposed. The degradation capacity of g-C3N4 prepared at different temperatures was analyzed using a pseudo-first-order reaction model and the results are shown in Fig. 6a. The largest \(K_{app}\) value...
(\(-8.83 \times 10^{-3}\) min\(^{-1}\)) is observed for g-C\(_3\)N\(_4\) prepared at 540 °C (Fig. 6a). Therefore, g-C\(_3\)N\(_4\)–TiO\(_2\) composites were prepared at the optimum temperature of 540 °C.

\(K_{\text{app}}\) for MB degradation over g-C\(_3\)N\(_4\)–TiO\(_2\) composites first increased with the TiO\(_2\) content up to 26.4%, then decreased for TiO\(_2\) content up to \(-47\%\), increased again with the TiO\(_2\) content and reached a maximum for \(-80\%\) TiO\(_2\), and decreased with further increases in the TiO\(_2\) content (Fig. 6b). These results show that the g-C\(_3\)N\(_4\)–TiO\(_2\)-26 and g-C\(_3\)N\(_4\)–TiO\(_2\)-80 composites, which contain different amounts of TiO\(_2\), exhibited good photocatalytic activity. The TEM and XRD results indicate that g-C\(_3\)N\(_4\) can be used as a support when the TiO\(_2\) content is low, while TiO\(_2\) particles can act as a substrate to disperse g-C\(_3\)N\(_4\) when TiO\(_2\) is the major component. Both g-C\(_3\)N\(_4\) and TiO\(_2\) are semiconductors, so TiO\(_2\) particles can act as modifiers that decorate g-C\(_3\)N\(_4\) when the TiO\(_2\) content is low, and g-C\(_3\)N\(_4\) sheets can act as modifiers that decorate TiO\(_2\) particles when the TiO\(_2\) content is high. Regardless of whether g-C\(_3\)N\(_4\) or TiO\(_2\) is the major component, \(K_{\text{app}}\) for MB degradation exhibits maximal values for optimal component ratios in the composites. Thus, there is a zigzag relation between \(K_{\text{app}}\) and the TiO\(_2\) content (Fig. 6b).

Control MB degradation experiments were carried out using radiation without a photocatalyst and without irradiation in the presence of a photocatalyst (Fig. 56). \(K_{\text{app}}\) for MB degradation is very low for control tests without light irradiation (6.41 \times 10^{-4} \text{min}^{-1}) and without a photocatalyst (1.49 \times 10^{-3} \text{min}^{-1}). In comparison, \(K_{\text{app}}\) for MB degradation on g-C\(_3\)N\(_4\)–TiO\(_2\)-80 under light irradiation is much greater, which clearly demonstrates that MB removal can be attributed to degradation rather than an adsorption mechanism.

MB photodegradation rates over selected samples are shown in Fig. 7a. For example, the MB degradation rate at 160 min was \(-55\%\) for TiO\(_2\) and \(-76\%\) for g-C\(_3\)N\(_4\) as catalysts. TiO\(_2\) shows low photocatalytic performance because of poor visible light absorption owing to its large bandgap (3.16 eV). The MB removal efficiency was \(-89\%\) on g-C\(_3\)N\(_4\)–TiO\(_2\)-26 and \(-92\%\) on g-C\(_3\)N\(_4\)–TiO\(_2\)-80 at 160 min, both of which are higher in comparison to g-C\(_3\)N\(_4\) and TiO\(_2\). This might be attributable to good dispersion of TiO\(_2\) on g-C\(_3\)N\(_4\) or of g-C\(_3\)N\(_4\) on TiO\(_2\), resulting in maximization of interfaces between the two semiconductors and the highest efficiency for charge carrier separation. Fig. 7b shows the corresponding pseudo-first-order kinetics plot for the samples. Under the same experimental conditions, \(K_{\text{app}}\) values for MB degradation on g-C\(_3\)N\(_4\)–TiO\(_2\)-26 (1.27 \times 10^{-2} \text{min}^{-1}) and g-C\(_3\)N\(_4\)–TiO\(_2\)-80 (1.44 \times 10^{-2} \text{min}^{-1}) are greater than for g-C\(_3\)N\(_4\) (8.08 \times 10^{-3} \text{min}^{-1}) and TiO\(_2\) (5.10 \times 10^{-3} \text{min}^{-1}). The results clearly demonstrate that photocatalytic performance can be enhanced by the formation of g-C\(_3\)N\(_4\)–TiO\(_2\) composites.
The scheme for photogenerated electron–hole separation in the g-C₃N₄–TiO₂ composite shown in Fig. S7 can be discussed as follows. The conduction band (CB) and valence band (VB) edge potentials are at approximately -1.12 and 1.57 eV for g-C₃N₄ and at approximately -0.29 and 2.91 eV for TiO₂, respectively [25]. When the system is irradiated with visible light, only g-C₃N₄ can absorb visible light and be excited. In g-C₃N₄, photogenerated electrons are excited from the VB to the CB, resulting in holes (h⁺) in the VB. Photogenerated electrons on the g-C₃N₄ surface can easily transfer to the CB of TiO₂, while photogenerated h⁺ migrate to the g-C₃N₄ surface in the composite. This effective separation of photogenerated electron–hole pairs enhances the photodegradation performance.

The effect of pH on the MB degradation efficiency was studied in the pH range 3–13 [48–50]. The g-C₃N₄–TiO₂-80 concentration was kept at 200 mg L⁻¹ for a reaction time of 30 min at room temperature and an MB concentration of 20 mg L⁻¹ (50 mL). The rate of MB photodegradation on g-C₃N₄–TiO₂-80 at different pH values is shown in Fig. 8a. It is clear that the rate of MB degradation increases with pH and reaches approximately 100% at pH 12. This may be
because a change in pH affects the adsorption behavior of MB which bears positive ion on the surface of photocatalyst where more negative charges has carried at high pH [50]. Another reason may be that OH− can act as a capture agent for h+·, which generates ·OH, so an increase in pH reduces the recombination probability for photogenerated electrons and holes, which enhances the photocatalytic activity. However, when the solution pH is greater than 12, the rate of MB photodegradation obviously decreases. This is because of competition between OH− and MB for adsorption sites on the composite surface [50].

The effect of the MB concentration on photocatalytic activity was also investigated (Fig. 8b). The rate of MB degradation decreased with increasing initial MB concentration. The reason for this behavior is that excess dye molecules decrease the number of active sites on the photocatalyst; moreover, excess dye molecules absorb light and thus reduce the number of photons that reach the photocatalyst surface [48]. \( K_{\text{app}} \) for MB photodegradation increased relatively quickly with catalyst concentration in the range 100–700 mg L\(^{-1}\), but relatively slowly when the concentration of catalyst was larger than 700 mg L\(^{-1}\). The results indicate that the catalyst does not absorb the light completely at low concentrations, so \( K_{\text{app}} \) increases with the catalyst concentration up to 700 mg L\(^{-1}\). However, \( K_{\text{app}} \) then decreases with further increases in the catalyst concentration because incident light may be reflected by excess catalyst particles [50].

3.3. Stability of g-C\(_3\)N\(_4\)–TiO\(_2\)-80

Besides activity, stability is also important for practical application of photocatalysts. Therefore, reuse of g-C\(_3\)N\(_4\)–TiO\(_2\)-80 for MB photodegradation under visible light irradiation was investigated to evaluate the optical stability of the catalyst. The results are shown in Fig. 8d. The g-C\(_3\)N\(_4\)–TiO\(_2\)-80 sample used in four consecutive photodegradation runs showed a loss of catalytic activity of only 9.0%. Therefore, g-C\(_3\)N\(_4\)–TiO\(_2\)-80 may be relatively stable during photocatalytic MB degradation.

4. Conclusion

g-C\(_3\)N\(_4\)–TiO\(_2\) composites were synthesized by directly heating melamine and TiO\(_2\) in a semi-closed system. Composites prepared at 540 °C with TiO\(_2\) content of 26.4 and 80.0 wt% showed good photocatalytic activity for MB degradation. The enhanced catalytic capability is mainly due to effective separation of photogenerated carriers and wide optical absorption up to the visible-light region owing to the formation of the heterojunction from g-C\(_3\)N\(_4\) and TiO\(_2\). The g-C\(_3\)N\(_4\)–TiO\(_2\)-80 sample was robust and could be used for at least four runs with an activity loss of only 9%. Thus, the g-C\(_3\)N\(_4\)–TiO\(_2\) composites described here may be prospective candidates for solving critical environmental and energy issues.

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**Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.mssp.2014.08.004.

**References**


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