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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

Disciplines

Engineering | Physical Sciences and Mathematics

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Enhanced visible-light photocatalytic activity of g-C₃N₄/TiO₂ 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 graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) 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 π structure of $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ 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 ($\lambda > 400$ 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 TiO₂ 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 NH₄OH. 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 TiO₂ powder was then calcined under static air at 400 °C for 3 h.

The g-C₃N₄ 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-C₃N₄ was ground into powder.

The g-C₃N₄/TiO₂ composite catalysts were prepared by mixing the pre-synthesized TiO₂ 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-C₃N₄.

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_α 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

6335F) 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 °C to 800 °C at a constant heating rate of 10 °C min⁻¹ in air. X-ray photoelectron spectroscopy (XPS) measurement was performed using PHOIBOS 100 hemispherical energy analyser (SPECS) equipped with Al, K α 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 μ l of acetic acid, 15 μ l 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 μ m. 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 ($\lambda > 400$ 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 HClO₄. 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-C₃N₄/TiO₂ 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-C₃N₄ contents in the final products, thermogravimetric analysis was performed from 20 °C to 800 °C in air. As shown in Fig. 1, pure TiO₂ shows almost no weight loss in the temperature range of study. However, pure g-C₃N₄ presents the rapid weight loss from 550 °C to 670 °C, indicating the sublimation and/or decomposition of g-C₃N₄. The weight of the g-C₃N₄/TiO₂ composites decreases rapidly at the temperature above 500 °C. At the end of the analysis, total combustion of g-C₃N₄ is attained. Therefore, the weight loss can be directly related to the amount of g-C₃N₄ in the composite. The results from TG study indicate that the g-C₃N₄ contents in the respective composites correspond to the nominal values.

[Fig. 1, single column fitting image]

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.

3.2 Crystal phases and microstructure analyses

Powder XRD patterns of pure TiO₂, pure g-C₃N₄ and g-C₃N₄/TiO₂ composites are shown in Fig. 2. The diffraction peak of pure g-C₃N₄ at 2θ of $\sim 27.4^\circ$ 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 TiO₂ 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 TiO₂ (JCPDS 21-1272) [23]. The XRD patterns of g-C₃N₄/TiO₂ composites show no obvious diffraction peak attributable to g-C₃N₄ when the g-C₃N₄ content is less than 50 wt%; however the composites with higher g-C₃N₄ loading clearly display the diffraction peak of g-C₃N₄

at $\sim 27.4^\circ$. It can also be seen that the relative peak intensity of g-C₃N₄ gradually improves upon increasing the g-C₃N₄ content.

[Fig. 2, single column fitting image]

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

Morphology and microstructure of the catalyst films were examined by FESEM and TEM. Fig. 3 shows FESEM micrographs of pure g-C₃N₄, pure TiO₂ and g-C₃N₄/TiO₂ composite films. The g-C₃N₄ (Fig. 3a) appears as aggregated irregular particles whereas pure TiO₂ (Fig. 3b) presents as agglomerates of small spherical-like particles. The FESEM image (Fig. 3c) of 50 wt% g-C₃N₄/TiO₂ together with the corresponding EDX spectrum (Fig. 3d) reveals the agglomeration morphology and the attachment of the TiO₂ particles on the g-C₃N₄ surfaces. Fig. 4 shows the TEM micrographs of pure g-C₃N₄, pure TiO₂ and g-C₃N₄/TiO₂ composites. It can be seen that g-C₃N₄ (Fig. 4a) displays 2D lamellar structure whereas pure TiO₂ (Fig. 4b) shows spherical particles with an average particle size of 13.7 nm. For the 50 wt% g-C₃N₄/TiO₂ composite (Fig. 4c), the TiO₂

nanoparticles are found embedded in the g-C₃N₄ lamellar structure. The corresponding HRTEM image (Fig. 4d) clearly reveals the close interfacial connections between g-C₃N₄ and TiO₂ nanoparticles as well as the lattice spacing of 0.32 nm, corresponding to the (101) plane of anatase TiO₂. These observations together with the SEM result in Fig. 3c suggest the formation of heterojunction between TiO₂ and g-C₃N₄ 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. 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, 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-C₃N₄, pure TiO₂ and g-C₃N₄/TiO₂ 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-C₃N₄/TiO₂ composite and the peaks of Ti, O and C in the pure TiO₂. The C 1s XPS spectrum of g-C₃N₄/TiO₂ 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-C₃N₄ [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 NH₂ species [34]. The regional spectrum of N 1s for g-C₃N₄/TiO₂ 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 -NH₂ 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 2p_{3/2} and Ti 2p_{1/2} 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% $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composite and high-resolution spectra for: (b) C 1s and (c) N 1s of 50 wt% $\text{g-C}_3\text{N}_4/\text{TiO}_2$; (d) Ti 2p and (e) O 1s of 50 wt% $\text{g-C}_3\text{N}_4/\text{TiO}_2$ 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):

$$(\alpha h \nu)^{1/n} = A (h \nu - E_g) \quad (1)$$

where A is a proportionality constant, $h\nu$ is photon energy, h is Planck's constant, ν is the frequency of vibration, and α is an absorption coefficient. The value of n depends on the type of optical transition of the semiconductor ($n = 1/2$ for direct transition and $n = 2$ for indirect transition). For g-C₃N₄ and TiO₂, the n values of $1/2$ 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 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.

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 TiO₂ were also carried out under identical conditions. Unfortunately, MB degradation activity over pure g-C₃N₄ 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 TiO₂ film provides ~35% degradation within 3 h of irradiation. The photocatalytic activity of g-C₃N₄/TiO₂, however, is much better than that of the pure TiO₂ sample, although at high g-C₃N₄ concentration the activity decreases slightly, suggesting an optimum g-C₃N₄ content of 50 wt%. The 50 wt% g-C₃N₄/TiO₂ film can degrade MB by 68% which is almost twice higher than that of pure TiO₂. The improved photocatalytic activity observed from the g-C₃N₄/TiO₂ films might be partially ascribed to the red-shift of the light absorption range and the strong light absorption intensity of the g-C₃N₄/TiO₂ 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 TiO₂ and g-C₃N₄ in the composite material [17, 21, 22]. Note that the decrease of BET specific surface area (SSA) with the increase of g-C₃N₄ loading content is observed. The SSA of pure TiO₂ is 120 m²/g whereas that of pure g-C₃N₄ is 6 m²/g. Upon increasing the g-C₃N₄ loading to 20, 50 and 70 wt%, the surface area decreases to 91, 49 and 31 m²/g, respectively. Therefore, the SSA is likely not a main factor governing the observed photocatalytic activity. Since the 50 wt% g-C₃N₄/TiO₂ 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-C₃N₄/TiO₂ composite film during MB photodegradation reaction.

[Fig. 8, single column fitting image]

Fig. 8. (a) MB photolysis and photocatalytic degradation over pure TiO_2 , pure $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composite films and (b) cycling runs using 50 wt% $\text{g-C}_3\text{N}_4/\text{TiO}_2$ film (the initial MB concentration of 10.0 mg/L).

A proposed mechanism for electron-hole separation and transport at the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ 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 $\text{g-C}_3\text{N}_4$ and TiO_2 can be determined using Equation (2) [42]:

$$E_{CB}^0 = \chi - E^C - 1/2E_g \quad (2)$$

where χ is the Sanderson electronegativity of the semiconductor (χ is 4.73 eV [26] and 5.81 eV [38] for g-C₃N₄ and TiO₂, 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-C₃N₄ (2.83 eV) and TiO₂ (3.31 eV) obtained in this study. The calculated CB and VB potentials of g-C₃N₄ are -1.19 and 1.65 V, and of TiO₂ are -0.35 and 2.97 V, respectively. According to the obtained band gap energies, only g-C₃N₄ can be activated under the visible light illumination, resulting in the photogenerated electrons in the CB and holes in the VB of g-C₃N₄. Because the CB edge potential of g-C₃N₄ (-1.19 V) is more negative than that of TiO₂ (-0.35 V), the electrons in g-C₃N₄ can transfer easily to the CB of TiO₂ possibly *via* close interfacial connections [17, 22] as supported by the SEM and TEM results, while the holes remain in the VB of g-C₃N₄. This direct electron transfer from g-C₃N₄ to TiO₂ 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 TiO₂ (-0.35 V) is more negative than the standard redox potential E^0 (O₂/•O₂⁻, -0.33 V) [43], the electrons accumulated in the CB of TiO₂ can be transferred to adsorbed oxygen molecules yielding •O₂⁻ which then further react to finally produce active •OH radical as follows [29]:

Consequently, the generated $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ acting as effective oxidants will react with the MB molecules, producing CO_2 and H_2O as final products. However, since the standard redox potential E° ($\bullet\text{OH}/\text{OH}^-$, 1.99 V) [43] is more positive than the VB position of g- C_3N_4 (1.65 V), the photoinduced holes in the VB of g- C_3N_4 cannot oxidize OH^- or H_2O to form $\bullet\text{OH}$. 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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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.