Research Article

Growth of g-C₃N₄ Layer on Commercial TiO₂ for Enhanced Visible Light Photocatalytic Activity

Min Fu, Jiazhen Liao, Fan Dong, Hongmei Li, and Hongyan Liu

Chongqing Laboratory of Catalysis and Functional Organic Molecules, College of Environmental and Biological Engineering, Chongqing Technology and Business University, Chongqing 400067, China

Correspondence should be addressed to Min Fu; fumin1022@126.com

Received 17 January 2014; Accepted 2 March 2014; Published 30 March 2014

Academic Editor: Haiqiang Wang

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Novel visible light photocatalytic graphitic carbon nitride/TiO₂ (g-C₃N₄/TiO₂) composite samples were synthesized by heating mixtures of melamine and commercial TiO₂ (TO) at different weight ratios. The samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL), Fourier transform infrared spectroscopy (FTIR), and UV-visible diffused reflectance spectroscopy (UV-vis DRS). Characterization confirms formation of nanocomposites of g-C₃N₄/TiO₂. At the optimized precursor weight ratio ($m_{\text{elamine}} : m_{\text{TiO}_2} = 2.5$), the samples exhibited highest adsorption capacity and visible light photocatalytic activity, measured by degradation of methylene blue (MB). Under visible light irradiation, the excited electrons on the surface of g-C₃N₄ transfer easily to the conduction band (CB) of TiO₂ via the well-built heterojunction. The g-C₃N₄/TiO₂ nanocomposites exhibit enhanced visible light catalytic activity due to increased visible light adsorption and effective separation of photogenerated electron-hole pairs. These g-C₃N₄/TiO₂ nanocomposites could find broad applicability in environmental protection due to their excellent visible light photocatalytic property and facile, cost-effective preparation process.

1. Introduction

Visible light photocatalysis has attracted much attention due to its extensive application in the fields of hydrogen generation [1, 2] and environmental protection [3, 4]. TiO₂ has been proved to be a competent photocatalyst for environmental applications; however, due to the wide band gap of anatase TiO₂ (3.2 eV), it cannot be excited under visible light irradiation ($\lambda > 400$ nm) [5]. Therefore, there is much interest in developing visible light-responsive TiO₂ with catalytic activity high enough for practical applications.

Recently, graphite-like carbon nitride (g-C₃N₄) has drawn wide attention for its potential application in the fields of catalytic support, gas storage, drug delivery, and optical and electronic materials [6] and as a metal-free, *n*-type semiconductor with tri-s-triazine units [7]. The band gap of g-C₃N₄ is 2.73 eV, imbuing a response wavelength of up to 450 nm, creating enormous potential in the photocatalysis field. Research has focused on synthesizing the g-C₃N₄ with several precursors [8–11]. Ma et al. reported a strategy

for enhancing the photoactivity of g-C₃N₄ via doping of nonmetal elements [9].

Recently, Yan and Yang reported a TiO₂-g-C₃N₄ composite material for photocatalytic H₂ evolution under visible light irradiation [2]. The TiO₂-g-C₃N₄ composites were prepared by thermal treatment of the mixture of TiO₂ and g-C₃N₄. Yang et al. reported that N-doped TiO₂/g-C₃N₄ composites with enhanced daylight photocatalytic properties were prepared by heating titanium tetrachloride ethanol solutions with C₃N₄ [10]. However, commercial g-C₃N₄ is not readily available and easily obtainable; inexpensive precursors for g-C₃N₄ need to be used requiring tedious preparation which may prevent large-scale application. Fu et al. reported a solid-state approach to synthesizing g-C₃N₄ coated TiO₂ nanocomposites from urea and commercial TiO₂ precursors [12]; however, the preparation conditions and proposed mechanism for enhancing photocatalytic activity of g-C₃N₄/TiO₂ require further research.

In the present work, all raw materials were purchased from commercial sources. The g-C₃N₄/TiO₂ composite

photocatalysts were prepared by a facile solid-phase method of directly heating melamine and commercial TiO_2 mixtures. In the process of melamine pyrolysis, sublimation and thermal condensation of melamine occurred simultaneously in temperature range of 297–390°C [13] and triazine-ring-based radicals and NH_x were formed as a result of the decomposition [11]. Based on XPS, FTIR, and TEM results, it was confirmed that $\text{g-C}_3\text{N}_4$ existed in prepared composites. Photocatalytic efficiency of the as-prepared $\text{g-C}_3\text{N}_4$ coated TiO_2 nanocomposites was determined by degradation of methylene blue (MB) dye under visible light irradiation.

2. Experimental

2.1. Synthesis of Photocatalysts. $\text{g-C}_3\text{N}_4$ - TiO_2 photocatalysts with various mass ratios ($m_{\text{melamine}} : m_{\text{TO}} = 1.5, 2.5, 3.5$, and 4.5 , denoted TO-M-1.5, 2.5, 3.5, and 4.5, resp.) were prepared as follows. 2 g of TiO_2 (TO) and Xg of melamine were combined in an alumina crucible and stirred with deionized water at room temperature. The mixture was dried at 60°C for 1 h and then annealed to 520°C in a covered muffle furnace for 5 h. Finally, the sample was cooled to room temperature to yield the $\text{g-C}_3\text{N}_4$ - TiO_2 photocatalyst. The $\text{g-C}_3\text{N}_4$ photocatalyst was also synthesized through pyrolysis of melamine, via direct heating of melamine at 520°C for 4 h. For comparison, TO-520-5 and M-520-5 were prepared analogously in the absence of melamine and TiO_2 , respectively. Finally, precursors with the same mass ratios ($m_{\text{melamine}} : m_{\text{TO}} = 2.5$) were prepared at temperatures of 320°C, 420°C, 520°C, and 620°C to yield TO-M-320, TO-M-420, TO-M-520, and TO-M-620 for 5 h, respectively.

2.2. Materials Characterization. Comprehensive structural characterization of as-prepared samples was undertaken. The crystal structures of samples were determined by an X-ray diffractometer with Cu-K α radiation (XRD: modelD/max RA, Rigaku Co., Japan). The surface area and porosity of the samples were estimated by measuring the nitrogen adsorption-desorption isotherms on a Quantachrome Autosorb-1 system. FTIR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. XPS spectra of the products were collected on a photoelectron spectrometer (Kratos Co., UK). The morphology of samples was characterized by TEM (JEM-2010). UV-vis diffuse reflection spectra were taken on a scan UV-vis spectrophotometer (UV-vis DRS: UV-2550, Shimadzu, Japan). Photoluminescence spectra of samples were obtained by using a fluorescence spectrometer (HITACHI, F-7000) at room temperature.

2.3. Evaluation of Photocatalytic Activity. Methylene blue (MB) oxidation reactions were performed on a photochemical reactor (BL-GHX) using a 500 W Xe lamp fitted with a thimble containing NaNO_2 solution (1 mol/L) to block UV light ($\lambda < 400$ nm). Additionally, immediate heat removal from the lamp was achieved via water flow through the inner thimble of the annular quartz tube. 0.02 g of catalyst was dispersed in MB aqueous solution (50 mL, 5 mg/L) with

FIGURE 1: XRD patterns for $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites fabricated from varying ratios of precursors, $\text{g-C}_3\text{N}_4$, and TiO_2 .

stirring for 40 min without irradiation until adsorption-desorption equilibrium was reached. During the irradiation, 5 mL aliquots were taken from the reaction cell at hourly intervals for subsequent dye concentration analysis following centrifugation. The degradation rate of MB was evaluated via the intensity of UV-vis absorption spectra at 665 nm.

3. Results and Discussion

3.1. XRD. Figure 1 depicts the XRD patterns of the as-prepared, mass ratio differentiated photocatalysts alongside $\text{g-C}_3\text{N}_4$ and TiO_2 . The $\text{g-C}_3\text{N}_4$ has two main diffraction peaks at 13.1° and 27.5° as a result of a polymeric layered structure [14]. The characteristic peaks at 27.5° and 13.1° correspond to the stacking of the conjugated aromatic system and the periodic arrangement of the condensed tri-s-triazine units of $\text{g-C}_3\text{N}_4$, respectively. The peak intensity at 27.5° corresponding to $\text{g-C}_3\text{N}_4$ increases with increasing weight ratio of melamine, which confirms that $\text{g-C}_3\text{N}_4$ has been produced in the as-prepared samples and the yield of it also gradually increased. For all $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites and TiO_2 , characteristic anatase TiO_2 peaks with similar position, intensities and widths were detected. This implies that the phase structure and the crystallite size of TiO_2 particles in as-prepared samples are conserved.

3.2. Visible Light Catalytic Activity. The degradation of MB is carried out under visible light ($\lambda > 400$ nm) illumination in aqueous sample suspensions. Figure 2(a) shows degradation of MB in the presence of samples fabricated from varying precursor ratios ($m_{\text{melamine}} : m_{\text{TO}} = 1.5, 2.5, 3.5$, and 4.5). Contrastingly, TO-520-5 and M-520-5 were prepared from single precursors by heating TiO_2 and melamine, respectively, under analogous reaction conditions. The photocatalytic activity of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ nanocomposites first increases and then decreases with the increasing melamine additive. The excess $\text{g-C}_3\text{N}_4$ prevented pollutants from being in contact with TiO_2 . As shown in Figure 2(a), during adsorption and

FIGURE 2: Evolution of MB with photodegradation time for g-C₃N₄, TiO₂ (TO), M-520-5, TO-520-5, and composite photocatalysts (TO-M-1.5, -2.5, -3.5, and -4.5) (a). Evolution of MB with photodegradation time for composite photocatalysts prepared by different temperatures (TO-M-320, -420, -520, and -620) (b).

the 5 hours of visible light photocatalytic degradation, TO-M-2.5 exhibits the highest visible light catalytic activity of all compounds including TiO₂ (TO) and g-C₃N₄. The degradation rate η (%) can be calculated as

$$\eta(\%) = \frac{(C_0 - C)}{C_0} \times 100\%, \quad (1)$$

where C_0 is the initial concentration of dye and C is the time dependent concentration. Degradation rate of MB induced by TO-M-2.5 is about 91%. It is surmisable that when combined TiO₂ and g-C₃N₄ produce a synergistic effect and effectively enhance the visible light photocatalytic efficiency.

The photocatalytic activity of the samples prepared at different temperatures is shown in Figure 2(b). The variation in degradation observed (Figure 2(b)) suggests that the calcination temperature is also a key factor with regard to photocatalytic activity.

3.3. Microstructure Analysis. The BET surface areas and porous structures of TiO₂ and TO-M-2.5 were investigated by nitrogen adsorption/desorption. In Figure 3, the two samples show a type IV adsorption isotherm with a H₂ hysteresis loop in the range (P/P_0) of 0.6–1.0. The surface area and pore volume (Table 1) of pure TiO₂ are 81.63 m²/g and 0.221 cm³/g, higher than those of the TO-M-2.5 (50.57 m²/g, 0.154 cm³/g). Compared with TiO₂, the specific surface area of TO-M-2.5 is reduced, potentially due to the presence of g-C₃N₄ layers on the TiO₂ surface. However, the surface area of g-C₃N₄/TiO₂ is not a positive factor. The enhanced visible light activity of g-C₃N₄/TiO₂ should be ascribed to the enhanced visible light adsorption and dispersion of TiO₂ resulting in increased

TABLE 1: Specific surface area, pore volume, and average pore radius.

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)
TiO ₂	81.63	0.221	5.41
TO-M-2.5	50.57	0.154	6.09
M-520-5	26.09	0.161	12.35

adsorption capacity due to the presence of g-C₃N₄ (Figures 6(c) and 7).

3.4. FTIR. The FTIR spectra (Figure 4) of TO-M-2.5, TO-M-3.5, and TO-M-4.5 were similar to that of g-C₃N₄, particularly in three regions: 805 cm⁻¹, 1200–1650 cm⁻¹, and 3100 cm⁻¹ ~ 3400 cm⁻¹. The peaks at 805 cm⁻¹ and 1200–1650 cm⁻¹, in the spectra of TO-M-2.5, TO-M-3.5, and TO-M-4.5, are assigned to the characteristic stretching modes of g-C₃N₄, indicating the existence of g-C₃N₄. The band at 805 cm⁻¹ corresponds to the characteristic breathing mode of the triazine units [8, 13]. The absorption peak at ca. 1329 cm⁻¹ and ca. 1635 cm⁻¹ can be attributed to C–N and C=N stretching modes, respectively [15, 16]. Additionally, the wide band between 3100 cm⁻¹ and 3400 cm⁻¹ corresponds to the N–H and O–H stretching vibration [14, 17]. These characteristic peaks were largely absent in the FTIR patterns of TO-M-1.5, which probably results from the low content of g-C₃N₄ in the sample.

3.5. XPS. The elemental chemical states of TO-M-2.5 were detected by XPS as shown in Figure 5 and were consistent with the FTIR results. The C 1s peaks (Figure 5(a)) at 284.8 eV and 288.1 eV were assigned to the C–C bond [15, 18] and

FIGURE 3: Adsorption-desorption isotherm of TiO_2 and TO-M-2.5 (a) and pore size distribution (b).

FIGURE 4: FTIR spectra for $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites fabricated from varying precursors ratios ($m_{\text{melamine}} : m_{\text{TiO}_2} = 1.5, 2.5, 3.5, \text{ and } 4.5$), $\text{g-C}_3\text{N}_4$, and TiO_2 ranging from 400 to 2000 (a) and from 2000 to 4000 (b).

the sp^3 C–N bond [15, 16, 18], respectively. The N 1s XPS spectrum of TO-M-2.5 can be deconvoluted into two peaks at 400.1 eV and 398.6 eV (Figure 5(b)), which were attributed to the binding energy of N–(C)₃ and C–N–C, respectively. These C 1s and N 1s binding energies were consistent with previously reported XPS data [8, 9], which further confirms that our as-prepared samples contain the graphite-like carbon nitride. The O 1s XPS spectrum (Figure 5(c)) included two peaks at 529.8 eV and 531.6 eV, which were closely related with C–O functional groups and surface hydroxyl groups [19]. The adsorbed water molecule was a major cause of surface hydroxyl groups benefitting capture of photogenerated holes and inhibition of electron-hole recombination. The peaks located at 458.7 and 464.4 eV in the Ti 2p spectra correspond to the $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ (Figure 5(d)). There were no Ti–C

or Ti–N bond peaks, which implied that C and N elements do not enter the lattice of TiO_2 . By the analysis of XPS, it can be ensured that the $\text{g-C}_3\text{N}_4$ coated TiO_2 composites were prepared by heating mixture of melamine and TiO_2 .

3.6. TEM. Figure 6(a) shows the TEM images of pure TiO_2 , consisting of nanoparticles with ca. 10 nm radius, consistent with the size of TiO_2 from microstructure analysis (Table 1). Figure 6(d) shows clear lattice fringes for the identification of crystallographic spacing of ca. 0.35 nm, matching well with an anatase TiO_2 (101) plane. The TEM and HRTEM images of TO-M-2.5 samples (Figures 6(b), 6(d), and 6(e)) also indicate that partial surface of TiO_2 was covered with a secondary phase and in Figures 6(b) and 6(d), it is clearly

FIGURE 5: N 1s (a), C 1s (b), O 1s (c), and Ti 2p (d) XPS spectra of TO-M-2.5.

shown that TiO_2 is well distributed on a layered structure. The XPS and FTIR have confirmed the existence of $\text{g-C}_3\text{N}_4$. As the $\text{g-C}_3\text{N}_4$ is a semicrystallized material, it is hard to obtain the clear lattice fringe. However, by comparison of the morphology of $\text{g-C}_3\text{N}_4$ (Figure 6(c)) and TO-M-2.5, it can be concluded that the secondary phase in TO-M-2.5 is $\text{g-C}_3\text{N}_4$. In Figure 6(d), $\text{g-C}_3\text{N}_4/\text{TiO}_2$ (TO-M-2.5) displayed a connection between TiO_2 and $\text{g-C}_3\text{N}_4$, indicating that the formation of heterojunction was possible.

3.7. UV-Vis. Figure 7(a) shows the UV-vis DRS spectra of pure TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{g-C}_3\text{N}_4/\text{TiO}_2$ nanocomposites. Visible light absorption of composites is enhanced by the presence of $\text{g-C}_3\text{N}_4$; however, it cannot be simply concluded that visible light absorption is consistent with photoactivity as many factors influence catalytic activity under visible light [20]. Enhanced activity is due to the presence of the TiO_2 , which can promote effective interfacial electron transfer [21] and conduce efficient space separation of photogenerated electron-hole pairs of $\text{g-C}_3\text{N}_4$. The band gaps of TiO_2 and

$\text{g-C}_3\text{N}_4$ are showed in Figure 7(b), which are 3.2 eV and 2.7 eV, respectively.

3.8. Fluorescence Analysis. Figure 8 shows the photoluminescence spectra of as-prepared samples. Excluding TiO_2 and M-TO-1.5, the as-prepared composites and $\text{g-C}_3\text{N}_4$ exhibit similar profiles with a broad emission band from 350 to 600 nm under an excitation wavelength of 330 nm, with intensity correlated to $\text{g-C}_3\text{N}_4$ content. These spectra imply that PL intensities of as-prepared composites are strongly dependant on recombination of electron-hole pairs in $\text{g-C}_3\text{N}_4$. The PL quenching was observed in $\text{g-C}_3\text{N}_4/\text{TiO}_2$ nanocomposites as the content of TiO_2 increases, probably due to the charge transfer occurring from $\text{g-C}_3\text{N}_4$ to TiO_2 [11, 15].

4. Proposed Photocatalytic Mechanism

The $\text{g-C}_3\text{N}_4$ is formed by sp^2 hybridization between C and N atoms, which depicts the π conjugate structure. Presence of

FIGURE 6: TEM images of pure TiO_2 (a), $\text{g-C}_3\text{N}_4$ (b), and TO-M-2.5 (c, d, and e).

FIGURE 7: UV-vis DRS (a) of $\text{g-C}_3\text{N}_4$, TiO_2 , TO-M-4.5, TO-M-3.5, and TO-M-2.5 and image of band gap of TiO_2 and $\text{g-C}_3\text{N}_4$ (b).

$\text{g-C}_3\text{N}_4$ benefits the dispersion of TiO_2 resulting in increased adsorption capacity. When the as-prepared composite is irradiated with visible light, the electrons get promoted from the valence band (VB) to the conduction band (CB) in $\text{g-C}_3\text{N}_4$ (Figure 9), providing a route for electronic transition. The CB edge potential of $\text{g-C}_3\text{N}_4$ is more negative than that of TiO_2 allowing the excited electron on the surface of $\text{g-C}_3\text{N}_4$ to transfer easily to TiO_2 via the well-built

heterojunction [22, 23] (Figure 6(d)). The recombination of photogenerated charge was inhibited and photocatalytic activities were enhanced effectively [24] for TiO_2 which provides a site for electron translation. The previously mentioned characterization indicates that coupling TiO_2 with $\text{g-C}_3\text{N}_4$ produces a well-contacted solid-solid heterojunction interface between $\text{g-C}_3\text{N}_4$ and TiO_2 semiconductor particles, which promotes the effective interfacial electron transfer

FIGURE 8: PL spectra of samples fabricated with varying ratios of precursors, TiO_2 and $\text{g-C}_3\text{N}_4$.

FIGURE 9: Proposed mechanism of MB photodegradation on the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites under visible light irradiation.

[21, 25] and separation of photogenerated charge carriers, significantly enhancing photocatalytic activity.

5. Conclusions

$\text{g-C}_3\text{N}_4/\text{TiO}_2$ nanocomposite samples were simplistically synthesized by thermal treatment of mixtures of industrial TiO_2 and melamine at different weight ratios. It was observed that TiO_2 particles were distributed on the layered $\text{g-C}_3\text{N}_4$ formed *in situ* from melamine. TO-M-2.5, the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composite fabricated with a precursor ratio ($m_{\text{melamine}} : m_{\text{TO}}$) of 2.5, exhibited the highest visible light catalytic activity. The introduction of $\text{g-C}_3\text{N}_4$ increased visible light adsorption of the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ nanocomposite. The enhanced visible light catalytic activity arises from the heterojunction between $\text{g-C}_3\text{N}_4$ and TiO_2 which effectively enhances separation of

photogenerated electron-hole pairs. The novel $\text{g-C}_3\text{N}_4/\text{TiO}_2$ nanocomposites prepared by this facile approach could have broad application in environmental protection.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This research is financially supported by the Science and Technology Project of CQ CSTC (stc2013yykfb50008, cstc2013jcyjA20018), the Science and Technology Project from Chongqing Education Commission (KJ120713, KJ130725), and the Innovative Research Team Development Program in University of Chongqing (KJTD201314).

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