Facile stir-dried preparation of g-C₃N₄/TiO₂ homogeneous composites with enhanced photocatalytic activity

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Polymeric graphitic carbon nitride (g-C₃N₄) is the most stable material of all the carbon nitride allotropes under ambient conditions.¹⁹,²⁰ Besides, unlike the photocatalysts of sulphide and oxynitride semiconductor, the g-C₃N₄ is stable under light irradiation in water solution as well as strong acid or base solutions.²¹,²² Furthermore, its band gap energy is only 2.58–2.89 eV.²³ The above-mentioned advantages make g-C₃N₄ a promising photocatalyst under visible light in various solutions. Some reports have focused on the applications of g-C₃N₄ in water splitting²⁴–²⁶ and organic pollutant degradation.²⁷,²⁸ Nonetheless, the high recombination rate of photo-generated electron–hole pairs results in a low photocatalytic activity of g-C₃N₄. To overcome this problem, coupling with TiO₂ is a feasible method because the interfacial connection between g-C₃N₄ and TiO₂ can make the electrons transfer easily from g-C₃N₄ to TiO₂. However, the biggest drawback of TiO₂ is its large band gap (3.2 and 3.0 eV for anatase and rutile, respectively) and thus can only harvest UV light, which makes up merely 3–5% of solar light, thereby restricting practical applications of titania.⁷ Therefore, much effort has been devoted to make TiO₂ absorb visible light. In recent years, various methods for TiO₂ modification have been attempted, including doping non-metal elements³–⁸,¹⁰ and constructing composites with other semiconductors.¹¹–¹³ Besides these modifications, metal deposition¹⁴–¹⁶ has also been extensively explored, and plasmonic metals, such as Au, Ag, and Cu which absorb visible light owing to their surface plasmon resonance effect, are employed as a sink of photo-induced electrons to enhance charge separation efficiency.¹⁷,¹⁸ Though progress has been made, the cost of the metals is expensive and their enhancing efficiency is still in question.

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1. Introduction

Titania has been the most popular photocatalyst in photocatalysis since 1972 when Fujishima and Honda discovered the TiO₂ photoelectrode.¹ It has been widely used in generating H₂ from water and in controlling water pollution discharged from industry, such as the reduction of heavy metal ions³–⁵ and the degradation of organic dyes.⁴–⁶ However, the biggest drawback of TiO₂ is its large band gap (3.2 and 3.0 eV for anatase and rutile, respectively) and thus can only harvest UV light, which makes up merely 3–5% of solar light, thereby restricting practical applications of titania.⁷ Therefore, much effort has been devoted to make TiO₂ absorb visible light. In recent years, various methods for TiO₂ modification have been attempted, including doping non-metal elements³–⁸,¹⁰ and constructing composites with other semiconductors.¹¹–¹³ Besides these modifications, metal deposition¹⁴–¹⁶ has also been extensively explored, and plasmonic metals, such as Au, Ag, and Cu which absorb visible light owing to their surface plasmon resonance effect, are employed as a sink of photo-induced electrons to enhance charge separation efficiency.¹⁷,¹⁸ Though progress has been made, the cost of the metals is expensive and their enhancing efficiency is still in question.

To further enhance the photocatalytic activity of TiO₂, the concept of hybridization has been proposed.¹⁴–¹⁶,¹⁸–⁲⁰ Hybridization can improve the separation efficiency of photo-generated electrons and holes, which can significantly enhance the photocatalytic activity of TiO₂. For example, the TiO₂/SiO₂ composite has been synthesized by sol–gel method.²¹ Furthermore, the TiO₂/SiO₂ composite exhibits a larger band gap than pure TiO₂, which results in a larger light absorption range.²² Moreover, the TiO₂/SiO₂ composite has a higher photocatalytic activity than pure TiO₂, which is due to the enhanced separation efficiency of photo-generated electrons and holes.²³ However, the TiO₂/SiO₂ composite still has some problems, such as the low stability and the high cost of TiO₂. Therefore, the fabrication of a simple and effective method for the preparation of TiO₂-based photocatalysts with enhanced photocatalytic activity is still in demand.

To overcome these problems, coupling with g-C₃N₄ is a feasible method because the interfacial connection between g-C₃N₄ and TiO₂ can make the electrons transfer easily from g-C₃N₄ to TiO₂. However, the biggest drawback of TiO₂ is its large band gap (3.2 and 3.0 eV for anatase and rutile, respectively) and thus can only harvest UV light, which makes up merely 3–5% of solar light, thereby restricting practical applications of titania. Therefore, much effort has been devoted to make TiO₂ absorb visible light. In recent years, various methods for TiO₂ modification have been attempted, including doping non-metal elements and constructing composites with other semiconductors. Besides these modifications, metal deposition has also been extensively explored, and plasmonic metals, such as Au, Ag, and Cu which absorb visible light owing to their surface plasmon resonance effect, are employed as a sink of photo-induced electrons to enhance charge separation efficiency. Though progress has been made, the cost of the metals is expensive and their enhancing efficiency is still in question.

To further enhance the photocatalytic activity of TiO₂, the concept of hybridization has been proposed. For example, the TiO₂/SiO₂ composite has been synthesized by sol–gel method. Furthermore, the TiO₂/SiO₂ composite has a larger band gap than pure TiO₂, which results in a larger light absorption range. Moreover, the TiO₂/SiO₂ composite has a higher photocatalytic activity than pure TiO₂, which is due to the enhanced separation efficiency of photo-generated electrons and holes. However, the TiO₂/SiO₂ composite still has some problems, such as the low stability and the high cost of TiO₂. Therefore, the fabrication of a simple and effective method for the preparation of TiO₂-based photocatalysts with enhanced photocatalytic activity is still in demand.

In this study, g-C₃N₄/TiO₂ homogeneous composites with enhanced photocatalytic activity were prepared by a simple stir-dried method, using dicyandiamide (DICY) and tetrabutyl orthotitanate (TBOT) as the precursors, followed by high-temperature calcination. Various characterization techniques including XRD, FTIR, nitrogen adsorption–desorption, SEM and XPS confirm the formation of an interconnected structure between g-C₃N₄ and TiO₂ in the composites. g-C₃N₄/TiO₂ composites exhibit much higher photocatalytic activity than that of pure g-C₃N₄ and TiO₂ in the degradation of methylene blue under visible light. In particular, the CT-5 composite prepared with DICY/TBOT at a mass ratio of 5 : 1, exhibited a photodegradation activity that is about 3.8 times that of TiO₂ and 2.9 times that of pure g-C₃N₄. The homogeneous g-C₃N₄/TiO₂ composite CT-5 can be repetitively used without significant loss of activity. The strong synergistic effect between g-C₃N₄ and TiO₂ achieved by this preparation method greatly improves the separation efficiency of photo-generated electrons and holes, thus offering enhanced photocatalytic performances.
2. Materials and methods

2.1 Chemicals

Dicyandiamide (DICY, 99%) was obtained from Adamas, China. Tetraetyl orthotitanate (TBOT) was purchased from Shanghai Lingfeng Chemical, China. Methylene Blue (MB) was obtained from Acros, New Jersey, USA. Anhydrous ethanol was purchased from Sinopharm Chemical, China. All chemicals were used as received without further treatment.

2.2 Preparation of homogeneous g-C3N4/TiO2

A series of g-C3N4/TiO2 mixtures were prepared. In a typical synthesis, 0.2–2 g of TBOT was dissolved in 50 mL of anhydrous ethanol and stirred for 10 min. 2 g of DICY was added into the TBOT solution and ultrasonicated for 10 min, and then stirred for another 2 h to ensure their thorough dissolving and mixing. The mixture solution was undergone alcoholysis and stir-dried for another 2 h to ensure their thorough dissolving and mixing. Thus-formed g-C3N4/TiO2 composites were obtained by calcining the mixture in a muffle furnace. Moreover, g-C3N4/TiO2 composites with different DICY/TBOT mass ratios were studied systematically, and the resulting composites exhibited higher photoactivity than that of the pure g-C3N4 and TiO2 for the degradation of methylene blue under visible light.

3. Results and discussion

3.1 Preparation of g-C3N4/TiO2 composite

XRD patterns of g-C3N4, CT-10, CT-5, CT-0 are shown in Fig. 1. The diffraction peak of pure g-C3N4 at 2θ 27.4° represents the conjugated aromatic system, which is indexed to (002) graphitic material. An obvious g-C3N4 characteristic peak is shown in CT-10. A relatively weak peak of g-C3N4 is observed in CT-5 (inset in Fig. 1), showing that the presence of g-C3N4. However, no obvious diffraction peak of g-C3N4 is found in CT-1, probably due to the very small amount of DICY used. CT-0 shows several characteristic peaks at 2θ 25.3°, 37.8°, 48.0°, 53.9° and 55.0°, which are attributed to (101), (004), (200), (105) and (211) crystal planes of anatase TiO2, respectively. For CT-1, CT-5 and CT-10, TiO2 characteristic peaks are found in all samples. It is worthy to note the diffraction peak of the (101) face shifts toward lower angles (25.1°) for sample CT-5 and CT-10, and the d-spacing of (101) face changes from 0.3520 to
0.3548 nm according to the Bragg equation, probably because some N ions are doped into TiO$_2$ crystal.$^{36}$

FTIR spectra were recorded to show chemical structures of g-C$_3$N$_4$, CT-10, CT-5, CT-1 and CT-0. As presented in Fig. 2, characteristic peaks of g-C$_3$N$_4$ and pure anatase TiO$_2$ (CT-0) are consistent to those in literature.$^{37-39}$ For g-C$_3$N$_4$, several adsorption peaks in the region of 1200–1650 cm$^{-1}$ are attributed to the typical stretching modes of g-C$_3$N$_4$ heterocycles. Among them, the adsorption peaks at 1255, 1328, 1417, 1544 cm$^{-1}$ are assigned to aromatic C–N stretching, and the peaks at 1635 cm$^{-1}$ are ascribed to C–N stretching.$^{40,41}$ In addition, the peak at 808 cm$^{-1}$ is ascribed to characteristic breathing mode of triazine units.$^{42}$ A wide adsorption region of 3000–3600 cm$^{-1}$ (e.g. 3184, 3444 cm$^{-1}$) are assigned to N–H stretching vibration of remainder NH$_2$ group attached to the sp$^2$ hybridized carbon and O–H stretching concerned with the adsorbed water.$^{43,44}$ In the spectrum of CT-0, a wide band from 400 to 800 cm$^{-1}$ is ascribed to Ti–O–Ti stretching vibration mode.$^{45,46}$ All characteristic adsorption peaks of g-C$_3$N$_4$ and anatase TiO$_2$ appear obviously in CT-10 and CT-5 spectra, demonstrating a successful combination of g-C$_3$N$_4$ and TiO$_2$. As expected, the spectrum of CT-1 is very similar to that of CT-0 that confirms the low amount of g-C$_3$N$_4$ in CT-1.

The morphologies of pristine g-C$_3$N$_4$, pure anatase TiO$_2$ and g-C$_3$N$_4$/TiO$_2$ composites were investigated, and SEM images of g-C$_3$N$_4$, CT-0, CT-5 and CT-10 are shown in Fig. 3. Pristine g-C$_3$N$_4$ presents a bulk structure composed of sub-micrometer particles, and pure anatase TiO$_2$ CT-0 shows spherical-like particles with sizes of 20–200 nm. CT-5 and CT-10 also show a bulk structure, whereas no spherical-like particles were observed. Such structures could partially confirm that TiO$_2$ and g-C$_3$N$_4$ are interconnected. In order to further prove the homogenous structure of g-C$_3$N$_4$/TiO$_2$ composites, CT-5 was selected to conduct the EDX mapping with the results give in Fig. 4, which shows that the sample CT-5 contains elements of N, O and Ti. It is clearly shown that element N, O and Ti are well dispersed in the sample, indicating g-C$_3$N$_4$ and TiO$_2$ form a homogeneous structure. The homogeneous structure is
beneficial to efficient charge carrier separation in photocatalysis.

BET surface areas and pore volumes of the samples were tested by nitrogen adsorption–desorption, and the nitrogen adsorption–desorption isotherms of g-C₃N₄, CT-0 and CT-5 are displayed in Fig. 5. The amount of nitrogen adsorption is very low for g-C₃N₄ and CT-0. g-C₃N₄ has a BET surface area of 14 m² g⁻¹ that is similar to the previous reports, indicating the formation of bulk structure of g-C₃N₄. Pure anatase TiO₂ CT-0 also shows a low BET surface area of 14 m² g⁻¹. By incorporation of g-C₃N₄, CT-1 has a BET surface area of 29 m² g⁻¹. For CT-5, its nitrogen adsorption capacity has a dramatic increase, and its BET surface area increases to 78 m² g⁻¹. Pore size distribution indicates CT-5 has a peak pore size of 3.8 nm (inset in Fig. 5), which should arise from the intraparticle voids. The pore volume of CT-5 increases to 0.147 cm³ g⁻¹ that is higher than those of g-C₃N₄ and CT-0 (0.026–0.034 cm³ g⁻¹). It is believed that the suitable amount of g-C₃N₄ favors a good dispersion of g-C₃N₄ and TiO₂ to form a homogeneous structure. However, excess amount of g-C₃N₄ in CT-10 tends to self-aggregation, leading to a low surface area (49 m² g⁻¹) and a low pore volume (0.098 cm³ g⁻¹). A high surface area and pore volume benefit the enhancement of photocatalytic performance.

XPS analyses were carried out to investigate the surface chemical compositions of the samples and the oxidation state of key elements of C, N, and Ti. XPS survey spectra of g-C₃N₄, CT-0 and CT-5 are shown in Fig. 6a, showing the element C, N, Ti and O are observed. The common C 1s signal about 284.8 eV is set for calibration. N and Ti elements are obviously observed in CT-5, implying the presence of g-C₃N₄ and TiO₂ in the composite, which is in accordance with the results demonstrated by the XRD patterns and the FTIR spectra. Fig. 6b–d show the high-resolution XPS spectra of C 1s, N 1s and Ti 2p. In the C 1s XPS spectrum of g-C₃N₄, there are two peaks (Fig. 6b). The peak at about 284.8 eV is ascribed to the adventitious carbon, and the peak at about 288.2 eV is ascribed to C–N or C–(N)₃ groups. For the CT-5 sample, the C 1s peaks are similar to those of g-C₃N₄. However, the peaks of C–N or C–(N)₃ groups shift 0.4 eV towards the higher binding energy, probably due to the hybridization of g-C₃N₄ and TiO₂. The N 1s spectrum of g-C₃N₄ and CT-5 are shown in Fig. 6c and two peaks can be seen. Peaks at about 398.5 and 403.9 eV are attributed to the C–N=C groups and charging effects. By comparison, the two peaks of CT-5 in the N 1s spectrum shift 0.3 and 0.2, respectively, which is due to the chemical environment change arising from the close interaction between g-C₃N₄ and TiO₂. The Ti 2p spectra of CT-0 and CT-5 are shown in Fig. 6d, two peaks at ca. 458.4 and 461.4 eV for CT-0 sample are assigned to Ti 2p₃/₂ and Ti 2p₁/₂, suggesting the existence of Ti(IV). For the CT-5 sample, the binding energy of Ti 2p₃/₂ is the same as that of CT-0, and the slight shift for binding energy of Ti 2p₁/₂ is ascribed to the interaction between g-C₃N₄ and TiO₂.

3.2 Photocatalytic performance

The photocatalytic performances of g-C₃N₄, CT-0, CT-1, CT-5 and CT-10 were investigated by the degradation of MB. CT-10 exhibits the best photocatalytic performance under visible light irradiation as compared to other photocatalysts (Fig. 7a), about 3.8 times higher as to CT-0 and 2.9 times to the pure g-C₃N₄. The photoactivity of CT-10 is better than that of CT-1. These results demonstrate that g-C₃N₄/TiO₂ composites (CT-1, CT-5 and CT-10) offer much better degradation performance than that of pure g-C₃N₄ and pure anatase TiO₂ CT-0. Pure g-C₃N₄ shows a little higher photocatalytic activity than CT-0, owing to its small band gap, but the high recombination rate of photo electrons and holes limits its photocatalytic activity. The above results demonstrate that the combination of g-C₃N₄ and TiO₂ not only enormously improves light harvest, but also increases the survival time of photo-induced electrons. The photodegradation efficiency of CT-5 under Xe light without UV cut-off filter is shown in Fig. 7b, in which CT-5 could degrade 94% of MB in 2.5 h, but only 67% of MB could be decomposed under visible light irradiation in 3 h, demonstrating the generality of the synthetic effect of g-C₃N₄/TiO₂ composites. In Fig. 8, the UV-Vis spectra of g-C₃N₄ and g-C₃N₄/TiO₂ composites show that the main absorption edge of the pure g-C₃N₄ occurs at ca. 450 nm, comparing with CT-0 in the wavelength of 400–800 nm. The absorption threshold values of the g-C₃N₄/TiO₂ composites are extended up to the visible light region.
(500 nm) obviously, which confirms that more visible light can be harvested by g-C₃N₄/TiO₂ composites.

Photoluminescence (PL) spectra of the photocatalysts is shown in Fig. 9. The PL intensity of CT-5 and CT-10 are significantly reduced in comparison with pure g-C₃N₄, indicating that the electron–hole recombination on the surface of these photocatalysts is largely inhibited, to generate more photo-induced electrons and holes to participate in the photocatalytic reaction. At the same time, the survival time of photoelectrons is increased greatly, which is crucial to the photocatalytic efficiency. This is because the interfacial interaction between g-C₃N₄ and TiO₂ can prevent the recombination of photo-generated charge effectively. The strong intensity of CT-1 is probably due to small amount of g-C₃N₄ in TiO₂, leading to poor interfacial interaction between g-C₃N₄ and TiO₂. Therefore, the above results, including BET surface areas, UV-Vis diffuse reflection spectra and PL spectra, are consistent to their photodegradation performance of MB.

To evaluate the reusability of CT-5, the experiments were carried out on MB degradation under visible light irradiation for three times at the same conditions. The photocatalysts were recycled by centrifugation, washed with water three times and then dried. To make sure the amount of recycled catalysts was equal to that of the first-time use, several batches of reactions were carried out under equal conditions and then combined the recycled photocatalysts together. The experimental results are shown in Fig. 10, no significant decrease of activity is observed.

The slight decrease should relate to the intermediates that were strongly adsorbed on the surface of the as-prepared photocatalysts, which might decline the electron transfer velocity and the adsorption capacity. The reusability test indicates that CT-5 has good stability in MB photodegradation under visible light irradiation.

3.3 Photocatalytic mechanism of homogeneous g-C₃N₄/TiO₂

The above-mentioned results have confirmed that g-C₃N₄/TiO₂ composite CT-5 exhibits much better photocatalytic efficiency than the pure g-C₃N₄ and TiO₂ (CT-0). The better photocatalytic performance is mainly associated with two factors: (1) the capacity of harvesting light and (2) the separation efficiency of the photoelectrons and holes. For the first factor of light absorption, TiO₂ has little adsorption of visible light; on the contrary, g-C₃N₄ shows a wide adsorption edge (Fig. 8). Therefore, the composite CT-5 could harvest the visible light greatly since the two substances combined together. For the second factor of charger separation, as shown in Scheme 1, when the visible light irradiates, photo-generated electrons (e⁻) transfer from the valence band (VB) to the conduction band (CB) of g-C₃N₄, leaving the holes (h⁺) in the VB. The different energy levels of g-C₃N₄ and TiO₂ drive the electrons transfer from the CB of g-C₃N₄ to that of TiO₂, thus increasing the survival time of the electrons and separating electrons and holes effectively. The homogeneously interconnected interfacial structure between g-C₃N₄ and TiO₂ provides a closely-matched path for the free transfer of electrons, compared with the physical mixture of g-C₃N₄ and TiO₂. The discussions above are called the

![Scheme 1 Proposed mechanism of charge transfer at the interface between g-C₃N₄ and TiO₂.](image_url)
synergistic effects between g-C3N4 and TiO2. The electrons accumulated in the CB of TiO2 are believed to reduce the oxygen (O2) to active oxygen radicals (’O2•−), and the electron-deficient holes in the VB of g-C3N4 can oxidize the hydroxyl (OH−) to hydroxyl radicals (’OH). Both ’O2•− and ’OH are capable to decompose MB effectively.32

4. Conclusions
Facile preparation of g-C3N4/TiO2 homogeneous composites with well-combined structures has been achieved by stir-dried evaporation and high temperature calcination. The resulting g-C3N4/TiO2 composites exhibited much higher photocatalytic activity than that of pure g-C3N4 and TiO2 in the degradation of methylene blue under visible light due to the strong synergistic effect between g-C3N4 and TiO2. The CT-5 composite performed the best photocatalytic activity which was nearly 3.8 times to the TiO2 and 2.9 times compared to the pure g-C3N4. In addition, the CT-5 composite showed outstanding photocatalytic activity under Xe light, good stability and recyclability. Overall, this work provides a simple and effective path to prepare photocatalysts with fine hybrid structures and may inspire peers to design novel photocatalytic nanomaterials to enhance the efficiency of solar energy utilization for such as environmental remediation and clean chemicals synthesis.

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