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

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g-C₃N₄/TiO₂ composites with homogeneous well-combined structures 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.

1. Introduction

Titania has been the most popular photocatalyst in photocatalysis since 1972 when Fujishima and Honda discovered the TiO₂ photoelectrode. 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 ions9 and the degradation of organic dyes.10–8 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 elements9,10–14 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.

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, and the improved photocatalytic activity was attributed to the formation of a synergetic heterojunction and the combination of both g-C₃N₄ and doped TiO₂ to absorb visible light more effectively.29 A hybrid g-C₃N₄/TiO₂ has been synthesized by a ball milling method, and the enhanced photocatalytic activities were due to the hybrid structure.30 The growth of g-C₃N₄ on mesoporous TiO₂ spheres with well-controlled structures has been achieved by melt-infiltrating dicyandiamide, and the separation efficiency between photo-generated electrons and holes was enhanced significantly.31 Ma and co-workers prepared g-C₃N₄/TiO₂ via a simple one-step calcination method using...
commercial P25 and melamine as the precursors, and they found the interfacial interaction of g-C3N4 and TiO2 was crucial to the efficiency of NO photocatalytic oxidation.29 Although the prepared g-C3N4/TiO2 composites have performed good photocatalytic activities, there is still a challenge to readily synthesize such a structure with well interconnected g-C3N4 and TiO2 to reduce the migration barrier of charge carriers.

In this work, g-C3N4/TiO2 homogeneous composites have been synthesized by a simple and effective stir-dried method. The TiO2 precursor tetrabutyl orthotitanate (TBOT) and the g-C3N4 precursor dicyandiamide (DICY) were dissolved in ethanol and experienced the stir-drying to form a well-blended mixture. Thus-formed g-C3N4/TiO2 composites were obtained by calcining the mixture in a muffule 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.

2. Materials and methods

2.1 Chemicals

Dicyandiamide (DICY, 99%) was obtained from Adamas, China. Tetrabutyl 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 by evaporation at 65 °C oil bath. The resulting slurry was further dried at 60 °C overnight. The mixture solids were then ground and calcined at 500 °C for 1 h. g-C3N4/TiO2 composites were obtained and marked as CT-0, CT-1, CT-5 and CT-10 when DICY/TBOT mass ratios were of 0 : 1, 1 : 1, 5 : 1 and 10 : 1, respectively. For comparison, pure g-C3N4 was obtained by calcining 2 g of DICY under the same calcination condition.

2.3 Characterizations

The phase structure of the TiO2-based photocatalysts were examined by X-ray diffraction (XRD) using Rigaku Miniflex II with Cu Kα radiation (λ = 0.1542 nm) at 40 kV. Nitrogen adsorption–desorption analysis was conducted using a Micro-meritics ASAP 2020 at 77 K. Each sample was degassed at 120 °C for 120 min previous to analysis. The specific surface areas (S_BET) were calculated by the Brunauer–Emmett–Teller (BET) method. Fourier transform infrared spectra (FTIR) was recorded by a FTIR spectrophotometer (Thermo Electron Nicolet-360, USA) using the KBr wafer technique. The morphology of the samples was observed by scanning electron microscopy (SEM) utilizing a MAGELLAN 400 (FEI, USA) with an operating voltage of 5 kV, and elemental mapping images were obtained by using Energy-Dispersive X-ray Spectroscopy (EDX) on MAGELLAN 400 microscope. X-ray photoelectron spectroscopy (XPS) (AXIS UltraDLD, Japan) was employed to determine surface electronic states. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The UV-Vis diffuse reflectance spectra (DRS) of the samples over a range of 200–800 nm were recorded by UV-2600 (Shimadzu, Japan) spectrophotometer with a BaSO4 reference. Room temperature photoluminescence (PL) spectra was recorded on a spectrofluorometer (FluroMax-4, HORIBA Jobin Yvon) using a Xe lamp as the excitation source.

2.4 Photocatalytic activity test

Methylene blue (MB) was used as a probe dye to evaluate the photocatalytic activity of the g-C3N4/TiO2 composites under a 300 W xenon lamp (CEL-HFX300, light intensity: 83 mW cm−2). To analyze the photocatalytic activity of g-C3N4/TiO2 composites under visible light, a UV cut-off filter (λ > 420 nm) was used. Typically, 40 mg of the as-prepared photocatalyst was dispersed in a 40 mL of MB aqueous solution (10 mg L−1) under constant stirring. Prior to illumination, the solution was kept in dark for 60 min and stirred to reach an adsorption–desorption equilibrium. At given intervals, the supernatant liquid was obtained by filtration with 0.22 μm filter and examined using a UNICO WFZ UV-2802S spectrophotometer at the characteristic wavelength of 664 nm. To evaluate the stability of photocatalyst, the photocatalyst was collected by centrifugation, washing and drying after the photocatalytic reaction for the recycling test. The degradation rates were calculated according to the following equation:

\[ \text{rate} = \frac{C_0 - C_t}{t} \]  

where rate (mg L−1 min−1) is the degradation rate of samples to MB. C_0 (mg L−1) and C_t (mg L−1) stand for the concentrations of dye at initial and time t (min).

3. Results and discussion

3.1 Preparation of g-C3N4/TiO2 composite

XRD patterns of g-C3N4, CT-10, CT-5, CT-1, 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.30 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.43,44 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 TiO₂ crystal.³⁶

FTIR spectra were recorded to show chemical structures of g-C₃N₄, CT-10, CT-5, CT-1 and CT-0. As presented in Fig. 2, characteristic peaks of g-C₃N₄ and pure anatase TiO₂ (CT-0) are consistent to those in literature.³⁷–³⁹ For g-C₃N₄, several adsorption peaks in the region of 1200–1650 cm⁻¹ are attributed to the typical stretching modes of g-C₃N₄ 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 NH₂ group attached to the sp² hybridized carbon and O–H stretching concerning 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-C₃N₄ and anatase TiO₂ appear obviously in CT-10 and CT-5 spectra, demonstrating a successful combination of g-C₃N₄ and TiO₂.⁴⁷ As expected, the spectrum of CT-1 is very similar to that of CT-0 that confirms the low amount of g-C₃N₄ in CT-1.

The morphologies of pristine g-C₃N₄, pure anatase TiO₂ and g-C₃N₄/TiO₂ composites were investigated, and SEM images of g-C₃N₄, CT-0, CT-5 and CT-10 are shown in Fig. 3. Pristine g-C₃N₄ presents a bulk structure composed of sub-micrometer particles, and pure anatase TiO₂ 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 TiO₂ and g-C₃N₄ are interconnected. In order to further prove the homogenous structure of g-C₃N₄/TiO₂ 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-C₃N₄ and TiO₂ 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-C$_3$N$_4$, CT-0 and CT-5 are displayed in Fig. 5. The amount of nitrogen adsorption is very low for g-C$_3$N$_4$ and CT-0. g-C$_3$N$_4$ has a BET surface area of 14 m$^2$ g$^{-1}$ that is similar to the previous reports, indicating the formation of bulk structure of g-C$_3$N$_4$. Pure anatase TiO$_2$ CT-0 also shows a low BET surface area of 14 m$^2$ g$^{-1}$. By incorporation of g-C$_3$N$_4$, CT-1 has a BET surface area of 29 m$^2$ g$^{-1}$. For CT-5, its nitrogen adsorption capacity has a dramatic increase, and its BET surface area increases to 78 m$^2$ g$^{-1}$. Pore size distribution indicates CT-5 has a peak pore size of 3.8 nm (inset displayed in Fig. 5). The amount of nitrogen adsorption is very similar to those of g-C$_3$N$_4$. 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-C$_3$N$_4$ and TiO$_2$. The N 1s spectrum of g-C$_3$N$_4$ 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-C$_3$N$_4$ and TiO$_2$. The Ti 2p spectra of CT-0 and CT-5 are shown in Fig. 6d, two peaks at ca. 458.4 and 464.1 eV for CT-0 sample are assigned to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, suggesting the existence of Ti(IV). For the CT-5 sample, the binding energy of Ti 2p$_{3/2}$ is the same as that of CT-0, and the slight shift for binding energy of Ti 2p$_{1/2}$ is ascribed to the interaction between g-C$_3$N$_4$ and TiO$_2$.

3.2 Photocatalytic performance

The photocatalytic performances of g-C$_3$N$_4$, CT-0, CT-1, CT-5 and CT-10 were investigated by the degradation of MB. CT-5 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-C$_3$N$_4$. The photocactivity of CT-10 is better than that of CT-1. These results demonstrate that g-C$_3$N$_4$/TiO$_2$ composites (CT-1, CT-5 and CT-10) offer much better degradation performance than that of pure g-C$_3$N$_4$ and pure anatase TiO$_2$ CT-0. Pure g-C$_3$N$_4$ 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-C$_3$N$_4$ and TiO$_2$ 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-C$_3$N$_4$/TiO$_2$ composites.

In Fig. 8, the UV-Vis spectra of g-C$_3$N$_4$ and g-C$_3$N$_4$/TiO$_2$ composites show that the main absorption edge of the pure g-C$_3$N$_4$ occurs at ca. 450 nm, comparing with CT-0 in the wavelength of 400–800 nm. The absorption threshold values of the g-C$_3$N$_4$/TiO$_2$ 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.

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 interface 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
synergistic effects between g-C$_3$N$_4$ and TiO$_2$. The electrons accumulated in the CB of TiO$_2$ are believed to reduce the oxygen (O$_2$) to active oxygen radicals (‘$\cdot$O$_2^-$’), and the electron-deficient holes in the VB of g-C$_3$N$_4$ can oxidize the hydroxyl (OH$^-$) to hydroxyl radicals (‘OH’). Both ‘$\cdot$O$_2^-$’ and ‘OH’ are capable to decompose MB effectively.$^{32}$

4. Conclusions

Facile preparation of g-C$_3$N$_4$/TiO$_2$ homogeneous composites with well-combined structures has been achieved by stir-dried evaporation and high temperature calcination. The resulting g-C$_3$N$_4$/TiO$_2$ composites exhibited much higher photocatalytic activity than that of pure g-C$_3$N$_4$ and TiO$_2$ in the degradation of methylene blue under visible light due to the strong synergistic effect between g-C$_3$N$_4$ and TiO$_2$. The CT-5 composite performed the best photocatalytic activity which was nearly 3.8 times to the TiO$_2$ and 2.9 times compared to the pure g-C$_3$N$_4$. 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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