A Cost-Effective Solid-State Approach to Synthesize g-C₃N₄ Coated TiO₂ Nanocomposites with Enhanced Visible Light Photocatalytic Activity

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Novel graphitic carbon nitride (g-C₃N₄) coated TiO₂ nanocomposites were prepared by a facile and cost-effective solid-state method by thermal treatment of the mixture of urea and commercial TiO₂. Because the C₃N₄ was dispersed and coated on the TiO₂ nanoparticles, the as-prepared g-C₃N₄/TiO₂ nanocomposites showed enhanced absorption and photocatalytic properties in visible light region. The as-prepared g-C₃N₄ coated TiO₂ nanocomposites under 450°C exhibited efficient visible light photocatalytic activity for degradation of aqueous MB due to the increased visible light absorption and enhanced MB adsorption. The g-C₃N₄ coated TiO₂ nanocomposites would have wide applications in both environmental remediation and solar energy conversion.

1. Introduction

Visible light photocatalysis has attracted the worldwide attention due to its potential application in environmental remediation and solar energy conversion [1–7]. The photocatalyst TiO₂, however, can only utilize the ultraviolet light (about 5% of natural solar light) because of its wide band gap (ca. 3.2 eV for anatase TiO₂). During the past 40 years, many efforts have been devoted to enhance the visible light photocatalytic activity of TiO₂, including metal doping [8–10], nonmetal doping [11–14], surface modification [15], and heterojunction construction [16–19].

In recent years, polymeric g-C₃N₄ materials have attracted much attention because of their similarity to graphene. Zhang et al. reported that the polymeric g-C₃N₄ semiconductors exhibit high photocatalytic performance for water splitting under visible light irradiation [20]. Dong and coworkers reported that polymeric g-C₃N₄ layered materials as novel efficient visible light photocatalyst, which can be synthesized facilely by directly heating urea or thiourea [21, 22].

Very recently, Zhou et al. reported a g-C₃N₄/TiO₂ nanotube array heterojunction with excellent visible light photocatalytic activity [17]. Zhao et al. reported g-C₃N₄/TiO₂ hybrids with wide absorption wavelength and effective photogenerated charge separation [18]. However, the precursors for g-C₃N₄ (dicyandiamide and melamine) are poisonous and detrimental to the environment. The preparation processes were relatively tedious, which may prevent large-scale application [17, 18].

In the present work, g-C₃N₄/TiO₂ nanocomposites were prepared by a facile and cost-effective solid-state method using urea and commercial TiO₂ as precursors. It was interesting to find that g-C₃N₄ was in situ coated on the surface of TiO₂. The precursors (urea and commercial TiO₂) are low cost and easily available. The as-prepared g-C₃N₄ coated TiO₂ nanocomposites exhibited enhanced photocatalytic activity under visible light irradiation.

2. Experimental

2.1. Synthesis. The g-C₃N₄ coated TiO₂ nanocomposites were prepared by a facile and cost-effective solid-state method. In a typical synthesis, 2 g TiO₂ and 6 g urea were immersed in 10 mL H₂O and dried at 60°C to completely remove the water.
The mixtures were put into an alumina crucible with a cover, and then heated to a certain temperature in the range of 400 and 600°C in a muffle furnace for 1 h at a heating rate of 15°C min⁻¹. The final samples were collected for use without further treatment.

2.2. Characterization. The crystal phases of the sample were analyzed by X-ray diffraction with Cu Kα radiation (XRD: model D/max RA, Rigaku Co., Japan). The morphology and structure of the samples were examined by transmission electron microscopy (TEM: JEM-2010, Japan). The UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV-Vis spectrophotometer (UV-Vis DRS: UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly, using BaSO₄ as reflectance sample. The spectra were recorded at room temperature in air range from 250 to 800 nm. X-ray photoelectron spectroscopy with Al Kα X-rays \((hν = 1486.6\text{ eV})\) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties. The shift of the binding energy due to relative surface charging was corrected using the Cls level at 284.8 eV as an internal standard. FT-IR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. The nitrogen adsorption-desorption isotherms were determined by the BET method (BET-BJH: ASAP 2020, USA), from which the surface area, pore volume, and average pore diameter were calculated by using the BJH method. All the samples were degassed at 200°C prior to measurements.

2.3. Evaluation of Photocatalytic Activity. Photocatalytic activity of g-C₃N₄/TiO₂ for MB photodegradation was evaluated in a quartz glass reactor. 0.05 g of N-TiO₂ was dispersed in MB aqueous solution (50 mL, 5 mg/L). The light irradiation system contains a 500 W Xe lamp with a jacket filled with flowing and thermostated aqueous NaNO₂ solution (1 M) between the lamp and the reaction chamber as a filter to block UV light \((λ < 400 \text{ nm})\) and eliminate the temperature effect. The suspension was first allowed to reach adsorption-desorption equilibrium with continuous stirring for 60 min in the dark prior to irradiation. The degradation rate of MB was evaluated using the UV-Vis absorption spectra to measure the peak value of a maximum absorption of MB solution. During the irradiation, 5 mL of suspension was continually taken from the reaction cell at given time intervals for subsequent dye concentration analysis after centrifugation. The MB solution shows a similar pH value at 6.8, which does not affect the light absorption of MB. The maximum absorption of MB is at wavelength of 665 nm. The degradation rate \(\eta\) (%) can be calculated as

\[
\eta\ (%) = \frac{(C₀ - C)}{C₀} \times 100\% ,
\]

where \(C₀\) is the initial concentration of MB considering MB adsorption on the catalyst and \(C\) is the revised concentration after irradiation.

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-prepared g-C₃N₄ coated TiO₂ nanocomposites at different temperatures. The peaks of all the samples can be indexed to the anatase phase of TiO₂ (JCPDS file No. 21-1272). It can be seen that the peak intensity increases gradually under higher treatment temperature, which indicates that the crystal sizes of TiO₂ nanocomposites increase under higher treatment temperature. No typical peaks of g-C₃N₄ can be found for all the samples due to the fact that g-C₃N₄ with layered structures on the surface of TiO₂ is ultrathin (Figure 2) and the crystallinity is low [22].

The morphology of pure TiO₂ and g-C₃N₄/TiO₂ nanocomposites were observed by TEM. As shown in Figure 2, both samples contain a number of monodispersed nanoparticles of TiO₂ with a size of about 11 nm. The intra-aggregation of particles could form the mesoporous structure [23]. It can be seen from Figure 2(b) that the ultrathin g-C₃N₄ with layered structures are dispersed and coated on the surface of TiO₂ particles, which is consistent with absence of the peaks of g-C₃N₄ in XRD (Figure 1).

The FT-IR spectra of pure TiO₂ and g-C₃N₄/TiO₂ nanocomposites are shown in Figure 3(a). The absorption band around 400–800 cm⁻¹ is attributed to Ti–O bonds [23]. Several bands in the range of 1100–1650 cm⁻¹ correspond to the typical stretching vibration of CN heterocycles in g-C₃N₄. The characteristic vibration mode of triazine units can also be found at 801 cm⁻¹ [22]. The peak at 1630 cm⁻¹ is associated with the stretching vibration of water molecules for both samples, including molecular water and hydroxyl groups [23]. The FT-IR spectra further confirm the existence of g-C₃N₄ on the surface of TiO₂.

The TG and DSC thermograms (Figure 3(b)) show that there are several phase transformations during heating. An endothermic peak at 135°C is the melting point of urea. The peak at 242°C indicates the reaction of urea into melamine. The weight loss during the two stages decreases rapidly by 36.1%. The sharp peak at 367°C implies that the thermal
condensation of melamine into g-C$_3$N$_4$ occurred in this temperature range. The weight loss in this stage is about 26.6%. The further weight loss of 4.8% with endothermic peak at 520°C can be attributed to the decomposition of g-C$_3$N$_4$. The TG-DSC result implies that g-C$_3$N$_4$ can be in situ formed on the surface of TiO$_2$, which is consistent with Figure 2(b).

The C1s spectra in Figure 4(a) show that two main carbon species with binding energies of 284.9 and 288.1 eV, corresponding to C–C and C–N–C, respectively. Three binding energies in N1s region (Figure 4(b)) can be observed, which can be indexed to C–N–C (398.8 eV), N–(C)$_3$ (400.1 eV), and N–H groups (401.2 eV), respectively. The binding energy at 529.7 and 533.0 eV can be ascribed to Ti–O, surface hydroxyl groups, and adsorbed molecular water (Figures 4(c) and 4(d)) [22]. The XPS results are consistent with the FT-IR spectra. XPS results also indicate that no peak for Ti–C or Ti–N bond can be observed, which implies that there is no chemical bond connection between g-C$_3$N$_4$ and TiO$_2$.

The nitrogen adsorption-desorption isotherms of pure TiO$_2$ and g-C$_3$N$_4$/TiO$_2$ nanocomposites obtained under 450°C are shown in Figure 5(a). The two samples show a type IV adsorption isotherm with a H$_2$ hysteresis loop in the range ($P/P_0$) of 0.6–1.0, which indicates the presence of mesopores. The surface areas and pore volume of pure TiO$_2$ are 78 m$^2$/g and 0.281 cm$^3$/g, higher than those of g-C$_3$N$_4$/TiO$_2$ nanocomposites (48 m$^2$/g and 0.216 cm$^3$/g). The pore size distribution curve (Figure 5(b)) indicates that the large mesopores of pure TiO$_2$ and g-C$_3$N$_4$/TiO$_2$ nanocomposites are about 37 and 48 nm, respectively. The presence of large mesopores can be ascribed to the aggregation of TiO$_2$ particles. It can be observed that the g-C$_3$N$_4$/TiO$_2$ nanocomposites have small mesopores of around 13.6 nm (inset in Figure 5(b)), which originates from the presence of layered g-C$_3$N$_4$ on the TiO$_2$ surface. The small mesopore is advantageous for enhancing the adsorption for reactant.

Figure 6 shows the UV-Vis DRS spectra of pure TiO$_2$ and the as-prepared g-C$_3$N$_4$/TiO$_2$ nanocomposites. It is clear that the visible light absorption of g-C$_3$N$_4$/TiO$_2$ nanocomposites is enhanced with increased treatment temperatures until 450°C. Then the visible light absorption decreases when the temperature is higher than 450°C. This fact implies
that the as-prepared g-C₃N₄ coated TiO₂ nanocomposites under 450°C may exhibit excellent visible light photocatalytic activity. However, the decrease of visible light absorption intensity of coated TiO₂ nanocomposites under higher treatment temperature can be attributed to the decomposition of g-C₃N₄.

Figure 7 shows the adsorption and photocatalytic activity of pure TiO₂ and g-C₃N₄/TiO₂ nanocomposites for removal of MB. It can be seen that the g-C₃N₄/TiO₂ nanocomposites obtained under 450°C exhibit the highest adsorption capacity, which may be ascribed to presence of layered g-C₃N₄ and small mesopores of the nanocomposites sample. The photocatalytic activities of g-C₃N₄/TiO₂ nanocomposites first increase and then decrease with the increased treatment temperature. Pure TiO₂ shows low visible light activity due to its large band gap. The observed slight visible light activity for the pure TiO₂ sample can be ascribed to the photosensitization effect of the MB as MB can absorb visible light [18]. During the visible light irradiation, the part of MB was self-decomposed due to the photosensitization. When TiO₂ was coated by g-C₃N₄, all the nanocomposite samples show decent visible light activity. Under visible light irradiation, g-C₃N₄ with a band gap of 2.7 eV could be excited and the photogenerated electrons could transfer from the conduction band (CB) of g-C₃N₄ to the CB of TiO₂ [17, 18, 24]. The holes in the valence band (VB) of g-C₃N₄ and electrons on the CB of TiO₂ could initiate the following degradation reactions. The as-prepared g-C₃N₄/TiO₂ nanocomposites under 450°C exhibit the highest photocatalytic activity under visible light irradiation. Considering the fact that the surface area of g-C₃N₄/TiO₂ nanocomposites (48 m²/g) is lower than that of pure TiO₂ (78 m²/g), 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 because of the presence of g-C₃N₄ (Figures 2(b) and 6) and the improved MB adsorption.
because of the small mesopores of the nanocomposites sample (Figure 5(b)). As the precursors (urea and commercial TiO$_2$) are cheap and preparation method is very simple, the as-prepared g-C$_3$N$_4$ coated TiO$_2$ nanocomposites are ready for large-scale applications in environmental pollution control and solar energy conversion [25].

4. Conclusion

The g-C$_3$N$_4$/TiO$_2$ nanocomposites were synthesized by a cost-effective solid-state approach by thermal treatment of the mixture of urea and commercial TiO$_2$. It was found that the surface of TiO$_2$ particles was coated by the in situ formed thin layered g-C$_3$N$_4$ from urea. The adsorption capacity and visible light photocatalytic activity were significantly enhanced. Under the optimized treatment temperature of 450°C, the g-C$_3$N$_4$/TiO$_2$ nanocomposites exhibited highest adsorption capacity and visible light photocatalytic activity toward removal of MB. The enhanced adsorption capacity can be ascribed to the presence of g-C$_3$N$_4$ and small mesopores. The enhanced visible photocatalytic activity originated from the increased visible light adsorption and small mesopores of the nanocomposites sample. The novel
g-C$_3$N$_4$ coated TiO$_2$ nanocomposites prepared by the cost-effective solid-state approach would find wide application in environmental remediation.

**Conflict of Interests**

The authors declare no conflict of interests.

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