Synthesis of carbon-doped g-C₃N₄ composites with enhanced visible-light photocatalytic activity

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Abstract

Novel visible-light-active carbon-doped graphitic carbon nitride composites (C/g-C₃N₄) were prepared by hydrothermal treatment of the mixture of g-C₃N₄ and glucose solution. The products were characterized by X-ray diffraction, transmission electron microscopy (XRD), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–vis), and photocurrent–time measurement (PT). Compared to g-C₃N₄, the C/g-C₃N₄ showed enhanced visible-light absorption, adsorptivity and improved photocurrent response. C/g-C₃N₄ composites also showed enhanced performance for Methylene Blue (MB) photodegradation. The enhanced activity of the C/g-C₃N₄ composites is attributed to the synergistic effect between the doped carbon and g-C₃N₄.

1. Introduction

Graphitic carbon nitride (g-C₃N₄), with narrow band gap and chemical stability, is considered to be a promising visible light active candidate for degradation of pollutants, production of H₂ and O₂ from water and photocatalytic conversion of CO₂ [1–4]. However, the high recombination rate of photo-generated electrons and holes limits its large scale application in environmental and energy fields. Several efforts have been developed to improve the photocatalytic performance of g-C₃N₄ in terms of introducing heteroatoms [2,3], coupling with semiconductors [4,5], insulators [6,7], and controlling morphology [8].

Besides, doping g-C₃N₄ with carbon elements has received much attention. g-C₃N₄ has been doped with carbon elements such as graphene [9], oxide graphene [10], MWNTs [11] and fullerene [12], etc. glucose is a green and economical carbon agent in the synthesis process [13]. The prepared products were characterized by XRD, TEM, XPS, UV–vis and PT. The photocatalytic activities were investigated by degradation of MB under visible light. The synergistic effects of carbon doping with g-C₃N₄ were investigated.

2. Experimental details

All reagents were of analytical grade and were used without further purification. g-C₃N₄ powder was prepared by direct heating dicyandiamide at 550 °C in a muffle furnace for 4 h at a heating rate of 20 °C min⁻¹. The synthesis of C/g-C₃N₄ composite was as follows: 0.4 g g-C₃N₄ and 0.0025 g glucose was added to 20 ml distilled water and stirred for 2 h; the suspension was then transferred to an autoclave, heated to 180 °C and maintained for 4 h. The suspension was subsequently dried at 90 °C for 12 h. The carbon-doped g-C₃N₄ composite was obtained and named as C1/g-C₃N₄. The composites with different amounts of glucose (0.005 g, 0.01 g, 0.02 g and 0.03 g) added were prepared in the similar procedure and named as C2/g-C₃N₄, C3/g-C₃N₄, C4/g-C₃N₄ and C5/g-C₃N₄, respectively.

In this work, novel visible-light-active C/g-C₃N₄ composites were prepared by hydrothermal treatment of a mixture of g-C₃N₄ and glucose solution. Different from previous expensive carbon precursors (graphene [9], MWNTs [11] and fullerene [12], etc.), glucose is a green and economical carbon agent in the synthesis process [13]. The prepared products were characterized by XRD, TEM, XPS, UV–vis and PT. The photocatalytic activities were investigated by degradation of MB under visible light. The synergistic effects of carbon doping with g-C₃N₄ were investigated.
measured using a UV–vis spectrophotometer (Shimadzu UV-2450, Japan). BaSO4 was used as the reflectance standard material. Photocurrent measurements were performed on an electrochemical analyzer (CHI660D, CHI Shanghai, Inc.) and the photocatalytic activity test was determined by MB degradation (see Supporting information).

3. Results and discussion

The crystal structure and phase of the as prepared samples were analyzed by their XRD patterns. As presented in Fig. 1, in the case of all samples, two characteristic peaks at 13.1° and 27.4° are indexed as the (100) and (002) planes, corresponding to the interlayer structural packing and the characteristic interplanar staking peaks of aromatic systems, respectively [8], suggesting the major structure of g-C3N4 was not subjected to any change after the addition of carbon. Whereas, in the case of C/g-C3N4 composites, no diffraction peaks corresponding to carbon are observed in Fig. 1. This may be due to the amorphous nature of carbon and/or due to the small amount of carbon used.

The morphology and microstructures of pure g-C3N4 and C/g-C3N4 composites were studied by TEM. As shown in Fig. 2, both the g-C3N4 (Fig. 2A) and the C2/g-C3N4 composite (Fig. 2B) were made up of irregular shaped sheets, indicating that the addition of carbon had minimal influence on the g-C3N4 microstructures. Combined with the XRD analysis, it can be known that the doping carbon combined with g-C3N4 tightly and evenly.

XPS measurements were performed to explicate the chemical states of g-C3N4 and C2/g-C3N4 composite. The high resolution XPS spectra of C1s and N1s are provided in Fig. 3A and B. In the case of g-C3N4, the C1s spectrum has two peaks at 288.1 eV and 284.6 eV (Fig. 3A), which are attributed to the existence of C–N–C coordination and surface adventitious carbon, respectively [14]. Similarly, the N1s spectrum of g-C3N4 has a main peak at 398.6 eV (Fig. 3B), which corresponds to sp2 N atoms involved in triazine rings [7]. However, in the case of C2/g-C3N4 composite, both the C1s and N1s peaks show a slight positive shift with respect to that of g-C3N4, suggesting that there are some interactions between carbon and g-C3N4. The C/N ratio of C2/g-C3N4 composite calculated using XPS is 0.803, a little higher in comparison with the value 0.743 in g-C3N4, which proves that C2/g-C3N4 composite has a high concentration of C.

The absorbance measurement of the C/g-C3N4 composite was investigated by using UV–vis absorption spectroscopy. As presented in Fig. 3C, all samples have the absorption edge at about 460 nm, which is assigned to g-C3N4 intrinsic band gap absorption (∼2.7 eV) [4]. A comparison of the absorption spectrum of pure g-C3N4 with those obtained C/g-C3N4 composites shows that the latter exhibit a broad background absorption in the visible-light region near 800 nm, which is attributed to the presence of doped carbon in the C/g-C3N4 composites. Meanwhile, the composite samples show stronger broad background absorption with increasing carbon content, which is in agreement with the color changing from yellow to brown (inset in Fig. 3C). Critical observation of the results obtained from XPS and UV–vis analysis revealed that the carbon was well doped into g-C3N4.

The transient photocurrent responses of g-C3N4 and C2/g-C3N4 composite were investigated to further illuminate the interaction between carbon and g-C3N4. As shown in Fig. 3D, the photocurrent decreases to zero as soon as the lamp turns off and the photocurrent comes back to stable values when the lamp is turned on. This phenomenon indicates that the photogenerated electrons migrate to the ITO substrates to produce photocurrent under visible light irradiation [10]. In addition, compared to g-C3N4, C2/g-C3N4 composite shows much stronger photocurrent response, indicating a lower rate of recombination and more efficient separation of photogenerated electron–hole pairs at the interface between carbon and g-C3N4. In C/g-C3N4 composites the efficient separation may be ascribed to the doped carbon, which becomes the separation center of the photogenerated electrons and holes.
And carbon are considered to be a good electron-acceptor material to effectively hinder the electron–hole pairs recombination due to its two-dimensional π-conjugation structure [11,15].

An adsorption experiment was performed to evaluate the adsorption ability of g-C₃N₄ and the Cₓ/g-C₃N₄ composites in the dark. After equilibration in the dark for 60 min, 35%, 44%, 52%, 55%, 61% and 58% MB were removed from the solution with g-C₃N₄ and Cₓ/g-C₃N₄ (x = 1, 2, 3, 4, 5) composites, respectively. Compared with g-C₃N₄, the adsorption of MB in Cₓ/g-C₃N₄ composite increased. The result can be attributed to two aspects: (i) both the doped carbon and g-C₃N₄ on the surface of Cₓ/g-C₃N₄ composites with π-conjugation structure (ii) the π–π stacking exists between Cₓ/g-C₃N₄ composite and MB [5]. As a result, the enhanced adsorptivity supports a good supplement for the high photocatalytic activity of the Cₓ/g-C₃N₄ composites.

The photocatalytic activity of Cₓ/g-C₃N₄ composites was evaluated by decomposing MB under visible-light irradiation (λ > 400 nm). Fig. 4 shows the photocatalytic activity of the Cₓ/g-C₃N₄ composites with different carbon contents. As can be seen in Fig. 4, without catalysts the absorbency of MB solution displays little difference, indicating that the photolysis is negligible. By increasing the weight of precursor glucose from 0.0025 g to 0.005 g, the photocatalytic activity of Cₓ/g-C₃N₄ composites increased. The optimum sample C2/g-C₃N₄ composite induced MB 97% degradation within 2.0 h under visible light irradiation. The result is much higher than that of g-C₃N₄ (73%). However, further increasing the weight of glucose, the photocatalytic activity of Cₓ/g-C₃N₄ composite decreased. The decrease in the activity of samples with a heavy loading of carbon is likely due to the shading effect, which can block the absorption of the incident light by g-C₃N₄. Just as our previously reported bentonite/g-C₃N₄, the excess loading of bentonite prevent g-C₃N₄ from absorbing the visible light and then lead a decreasing of
photocatalytic activity [7]. Therefore, excess loading of carbon is not favorable for the improving photocatalytic activity.

4. Conclusion

C/g-C$_3$N$_4$ composites were successfully synthesized by hydrothermal treatment with a mixture of g-C$_3$N$_4$ and glucose solution. Carbon doping by glucose is an efficient way to improve the photocatalytic performance of g-C$_3$N$_4$. The enhanced activity of the C/g-C$_3$N$_4$ composite is attributed to the synergistic effect between carbon and g-C$_3$N$_4$: increased visible-light absorption, enhanced adsorptivity and improved photoinduced electron–hole separation efficiency. Carbon doping by glucose may provide an efficient, economical and green strategy to improve the photocatalytic property of g-C$_3$N$_4$.

Acknowledgments

The authors genuinely appreciate the financial support from the National Natural Science Foundation of China (Nos. 21406094, 21177050 and 21175061) and the Foundation of Jiangsu University (04JDG048).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.08.142.

References