Photocatalytic activity enhancement of modified g-C₃N₄ by ionothermal copolymerization

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Abstract

The chemical structure and morphology of g-C₃N₄ were controlled. Dicyandiamide and barbituric acid were used as a co-precursor to graft aromatic groups in the tri-s-triazine structure unit and form the delocalized π-conjugate system. Meanwhile, lithium chloride and potassium chloride were used as heating media to restrain the agglomeration and keep the layered structure of the products. The results show that the as-prepared photocatalysts have a (C₃N₄)x(C₇N₇)y structure. According to the images by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) a clearly lamellar structure of the photocatalysts appears when the amount of barbituric acid is <0.86 g. The specific surface area can be increased by the ionothermal copolymerization synthesis method. Compared to g-C₃N₄-550, BA-CN₄ has a greater photocatalytic ability. The as-prepared photocatalyst has a good degradation ratio after 4-run degradation of RhB dye recycle experiment.

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Keywords: Carbon nitride; Copolymerization; Ionothermal; Photocatalysis

1. Introduction

Two-dimensional (2D) materials have attracted more attentions recently. As a graphite-like layered material, carbon nitride (C₃N₄) is used as a promising candidate for hydrogen evolution and environment purification under visible irradiation [1–4]. C₃N₄ has a broad application prospect for photocatalysis due to its unique semiconductor band structure, excellent chemical stability, high temperature stability and cheap raw materials [5–7]. However, some disadvantages like a high recombination rate of its photo-generated electron–hole pairs, low absorption intensity of visible light (λ > 450 nm) and aggregated structure restrict the application of C₃N₄ [8–10]. In order to overcome these disadvantages, C₃N₄ was modified with metallic elements (Fe, Ag, Co, Mn) [11–14], doped with non-metallic elements (B, S, P, F) [2,15–17] or composited with semiconductor (TiO₂, ZnO, CdS, Bi₂WO₆) [18–21] to improve the photocatalytic performance. Meanwhile, in some work [22–24], hard and soft templates were used to prepare nano-, meso- and micro-pore g-C₃N₄ and increase the specific surface area.

Zhang et al. [25] selected barbituric acid and dicyandiamide as a co-precursor to prepare the modified C₃N₄ polymer self-doped with carbon, resulting in a mixed C₃N₄–C₇N₇ structure. It was indicated that there is an enormous promotion of visible-light absorption region (up to 750 nm), which is realized by substituting the ring nitrogen with carbon, forming an extended delocalization π-conjugated system and changing the intrinsic semiconductor properties. Also, the more barbituric acid, the less the hydrogen evolution would be. This was
since the excessive doping could spoil the indirect character of the semiconductor and offer some potential recombination sites.

Considering the special delocalization $\pi$-conjugated system and excellent visible-light absorption activity, we believe that it could be an outstanding photocatalyst to degrade organic pollutants. A preliminary work showed that the bulk $\text{g-C}_3\text{N}_4$ prepared by only dicyandiamide had a better photocatalytic activity than those photocatalysts prepared by copolymerization of dicyandiamide and barbituric acid. The degradation rate of those photocatalysts prepared by copolymerization was decreased when the mass of barbituric acid was increased, which was similar to the hydrogen evolution study above. It is suggested that the recombination of electron–hole pair could be accelerated due to the formation of agglomeration in the copolymerization process. As a consequence, it could be possible to improve the photocatalytic activity of $\text{g-C}_3\text{N}_4$ by designing a delocalization $\pi$-conjugated system and inhibiting the agglomeration of products simultaneously.

A crystalline, condensed and 2D carbon nitride was synthesized by an ionothermal method, which simply heated monomer with lithium chloride/bromide and potassium chloride/bromide [26–28]. Lithium chloride and potassium chloride are used as solvents due to their high-temperature stability, non-corrosive properties and melting point below the polycondensation point of s-heptazine. Noted that the condensation network could be facilitated by the solvation of the small molecular precursors and subsequent aggregation of higher molecular mass [27]. Therefore, a co-monomer was calcined by an ionothermal method to obtain the high visible-light absorption intensity and less agglomeration of carbon-nitrogen network for the enhancement of photocatalytic activity.

2. Experimental

2.1. Synthesis of photocatalysts

All the chemicals were used without further purification. The samples were treated via thermal treatment of completely mixed powders composed of 2 g dicyandiamide, 4.5 g lithium chloride ($\text{LiCl}$), 5.5 g potassium chloride ($\text{KCl}$) and different amounts of barbituric acid ($0, 0.15, 0.27, 0.37, 0.52$ and $0.86$ g) in a tube furnace under $\text{N}_2$ atmosphere. The mixed powders were heated to 400 °C for 6 h, and then heated to 570 °C for 12 h with a heating rate of 7 °C/min. The resultant products were ground and then washed with distilled water for 3 times to remove residual salt, then ultrasonicated for 1 h and centrifuged at 10,000 rpm for 5 min before drying at 80 °C. The final products were obtained and denoted as $\text{BA-CN}_0, \text{BA-CN}_1, \text{BA-CN}_2, \text{BA-CN}_3, \text{BA-CN}_4$ and $\text{BA-CN}_5$, respectively (see Table 1). The bulk $\text{g-C}_3\text{N}_4$ was prepared by the same procedure above without $\text{LiCl}$ and $\text{KCl}$, denoted as $\text{g-C}_3\text{N}_4-570$. Meanwhile, to compare to the photocatalytic ability of bulk $\text{g-C}_3\text{N}_4$ prepared at a lower temperature, 2 g dicyandiamide was heated to 400 °C for 6 h, and then heated to 550 °C for 12 h with a heating rate of 7 °C/min under the $\text{N}_2$ atmosphere. The product was denoted as $\text{g-C}_3\text{N}_4-550$.

<table>
<thead>
<tr>
<th>Dicyandiamide/g</th>
<th>LiCl/g</th>
<th>KCl/g</th>
<th>Barbituric acid/g</th>
<th>Temperature/°C</th>
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<tr>
<td>$\text{g-C}_3\text{N}_4$-550</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>550</td>
</tr>
<tr>
<td>$\text{g-C}_3\text{N}_4$-570</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>570</td>
</tr>
<tr>
<td>$\text{BA-CN}_0$</td>
<td>2</td>
<td>4.5</td>
<td>5.5</td>
<td>570</td>
</tr>
<tr>
<td>$\text{BA-CN}_1$</td>
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<td>4.5</td>
<td>5.5 0.15</td>
<td>570</td>
</tr>
<tr>
<td>$\text{BA-CN}_2$</td>
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<td>4.5</td>
<td>5.5 0.27</td>
<td>570</td>
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<tr>
<td>$\text{BA-CN}_3$</td>
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<td>4.5</td>
<td>5.5 0.37</td>
<td>570</td>
</tr>
<tr>
<td>$\text{BA-CN}_4$</td>
<td>2</td>
<td>4.5</td>
<td>5.5 0.52</td>
<td>570</td>
</tr>
<tr>
<td>$\text{BA-CN}_5$</td>
<td>2</td>
<td>4.5</td>
<td>5.5 0.86</td>
<td>570</td>
</tr>
</tbody>
</table>

2.2. Characterization

The samples were characterized on a model Rigaku D/max2500 X-ray diffractometer for monochromatized Cu Kα ($\lambda = 1.5406$ Å) radiation. The XRD data were collected with a scanning speed of 5°/min in the 20 range from 10° to 80°. The transmission electron microscopy (TEM) images were obtained by a model JEM-2100 (JEOL) transmission electron microscope. The microcrystalline structure and surface characteristics of the photocatalysts were observed by a model JSM-7001F field-emission scanning electron microscope (FE-SEM). The Fourier transformed infrared (FTIR) spectra were obtained using a model MX-1E (Nicolet) spectrometer at 600—4000 cm$^{-1}$. The diffuse reflection spectra (DRS) were obtained on a model Shimadzu UV-2450 spectrophotometer using $\text{BaSO}_4$ as a reference. The specific surface areas and pore structures were probed via the measurement of volumetric $\text{N}_2$ adsorption—desorption isotherms at liquid nitrogen temperature, using a NOVA 2000e instrument (Quantachrome, USA). The samples were degassed under vacuum at 120 °C for 8 h before measurements. The elemental analysis was performed on a model EA-1112 to obtain the mass ratio of carbon, nitrogen and hydrogen elements. The lithium quantification was performed by inductively coupled plasma mass spectrometry (ICP-MS) on an XSeries spectrometer.

2.3. Photocatalytic activity

The photocatalytic activities of the photocatalysts were determined in the degradation reaction of RhB aqueous solution (5 mg/L) under irradiation of a 125 W xenon light lamp with a 420 nm cutoff filter providing visible light irradiation. 100 mg of catalyst powder was added into 100 mL of the RhB solution in a quartz tube. Prior to irradiation, the suspension was magnetically stirred in dark for 50 min to establish an adsorption—desorption equilibrium between RhB and the catalyst. At the irradiation time intervals of 10 min, 5 mL suspension was collected and centrifuged to remove the particles. The RhB concentration was monitored at 553 nm during the photodegradation process using a UV—vis spectrophotometer.
3. Results and discussion

Fig. 1 shows the XRD patterns of g-C₃N₄-570 and BA-CNₓ. Two peaks appear at 12.8° and 27.3° of the pure g-C₃N₄, which can be indexed to the (100) and (002) diffraction planes, due to the inter-planer packing and the characteristic inter-layer structural stacking peaks of the aromatic systems [5], respectively. The BA-CNₓ sample has two main peaks at 12.8° and 27.3°, showing the formation of CₓNₓ. The differences of diffraction angle and intensity between g-C₃N₄-570 and other samples indicate that the co-effects related to the molten salts and the quantity of barbituric acid can be described as follows: the diffraction angle is mainly affected by molten salts when the amount of barbituric acid is very small, but it will be mainly affected by barbituric acid at a certain amount. For instance, the molten salts lead to a smaller diffraction angle than 12.8° when the amount of barbituric acid is less than 0.15 g (i.e., BA-CNₓ and BA-CN₁). When the amount of barbituric acid is more than 0.27 g, it is interesting that the weight of barbituric acid has some effects on the two main peaks. The diffraction angle of 27.3° decreases, but the diffraction angle of 12.8° increases with increasing the amount of barbituric acid. This can be explained by the distortion of the tri-s-triazine unit due to the barbituric acid aromatic ring grafted in it, which occurred in plane instead of inter plane. The decreased quantity of hydrogen band, demonstrated by the decreased diffraction angle of 12.8° and inter-plane moves to 3380 cm⁻¹ (see Fig. 4), indicating the presence of –NH₂ and –NH but the absence of hydrogen bond in the polymer network prepared by ionothermal copolymerization [30]. In addition, the band at 2163 cm⁻¹ is attributed to the C≡N band stretching vibration modes [31], which can be found in the samples except g-C₃N₄-570. The reason for this is probably because of the deformation of CN heterocycles induced by the high temperature treatment and the existence of LiCl/KCl.

Fig. 2 shows the SEM images of the as-synthesized g-C₃N₄-570, BA-CN₀, BA-CN₁, and BA-CN₅, respectively. In Fig. 2(a), the morphology of g-C₃N₄ is bulk with a lamellar structure at the edges [29]. In Fig. 2(b), BA-CN₀ clearly shows large sheets composed of some irregular but micro-fragments with the sizes of 10–50 nm. According to Bojdys et al. [27], the hexagonal prisms were not generated because the samples were not prepared at a high temperature (i.e., 600 °C) and airtight condition. BA-CN₁ is composed of some micro-fragments, which is similar to BA-CN₀, except for the obviously agglomerated products induced by the addition of barbituric acid. In Fig. 2(d), the overweight of barbituric acid can decrease the features of platelike and microcrystalline [25].

Fig. 4 shows the FT-IR spectra of the as-prepared photocatalysts in the wavelength range of 500–3500 cm⁻¹. The band at 810 cm⁻¹ is a characteristic of tri-s-triazine. The bands located in the range of 1242–1637 cm⁻¹ are contributed to the typical stretching modes of CN heterocycles, which shift slightly due to the addition of the barbituric acid and LiCl/KCl. The board peak at 3163 cm⁻¹ of bulk g-C₃N₄ corresponding to the N–H band involving with hydrogen bond in and inter-plane moves to 3380 cm⁻¹ (see Fig. 4), indicating the presence of –NH₂ and –NH but the absence of hydrogen bond in the polymer network prepared by ionothermal copolymerization [30]. In addition, the band at 2163 cm⁻¹ is attributed to the C≡N band stretching vibration modes [31], which can be found in the samples except g-C₃N₄-570. The reason for this is probably because of the deformation of CN heterocycles induced by the high temperature treatment and the existence of LiCl/KCl.

Fig. 5 shows the UV–vis absorption spectra for the as-prepared samples. Clearly, there is an obvious red shift and the light absorption intensity in the range of visible light wavelength increases when barbituric acid content increases, compared to that from g-C₃N₄-570 [25]. The red shift of the absorption wavelength favors the photocatalysts to generate more electron–hole pairs under sunlight irradiation, resulting in enhanced photocatalytic properties. Fig. 5 also shows an unobvious regular pattern of light absorption, which may be due to the complicated chemical structure developed in the copolymerization with molten salts. It is speculated that the molten salts inhibit the diffusion of barbituric acid molecules. As a consequence, CₓNₓ and CₓN₇ units are unregularly distributed in the network, leading to the differences of delocalized π-conjugate system among these samples. BA-CN₀ shows a blue shift of the optical absorption, which could be ascribed to the changed electronic structure induced by the Li⁺ or other ions. The existence of Li element is determined by ICP-MS.

The elemental analysis was further used to determine the mole ratio of carbon to nitrogen (C:N) in the products. The C:N value of g-C₃N₄-570, BA-CN₀, BA-CN₁, BA-CN₂, BA-CN₃, and BA-CN₅ is 0.658, 0.679, 0.766, 0.783, 0.809, 0.844 and 0.908, respectively. It means that the aromatic ring is indeed grafted in tri-s-triazine unit and the CₓN₇ structure is formed, resulting in an increased content of carbon element and the formation of delocalized π-conjugate system.
Fig. 2. SEM images of the as-prepared samples: (a) g-C3N4-570, (b) BA-CN0, (c) BA-CN3, (d) BA-CN5.

Fig. 3. TEM images of the as-prepared samples: (a) g-C3N4-570, (b) BA-CN0, (c) BA-CN3, (d) BA-CN5.
which can change the intrinsic semiconductor properties. It is assumed that the basic structural unit of BA-CN3 should be \((C_3N_4)x\)\(^e\)(C7N7)\(^y\). When the mole ratio of C:N is 0.809, the value of \(x:y\) is 5.67. Table 2 shows the calculated results of others. We attributed the deviation of C:N with stoichiometry of C3N4 to the structure defects, such as the \(\text{NH}\), \(\text{NH}_2\) and \(\text{C}^\text{N}\) groups.

Fig. 6 shows the N\(_2\) sorption isotherms and pore size distribution curves (BJH) of BA-CN\(_0\), BA-CN\(_1\), BA-CN\(_2\), BA-CN\(_3\), BA-CN\(_4\), and g-C\(_3\)N\(_4\)-570, respectively. The corresponding pore size distribution curves are determined from the desorption branches using Barret-Joyner-Halender method (see the inset in Fig. 6). In Table 2, the specific surface area of BA-CN\(_x\) increases greatly by ionothermal copolymerization synthesis method. The sample BA-CN\(_3\) has the greatest specific surface area, explaining the clearly adsorption of RhB in the dark (see Fig. 7). The excessive doping of barbituric acid decreases the specific surface area.

Fig. 7 shows (a) the photocatalytic degradation of RhB as a function of irradiation time for g-C\(_3\)N\(_4\)-570, BA-CN\(_0\), BA-CN\(_1\), BA-CN\(_2\), BA-CN\(_3\), BA-CN\(_4\), and g-C\(_3\)N\(_4\)-570 samples under visible light irradiation, (b) the photocatalytic activity of g-C\(_3\)N\(_4\)-570, g-C\(_3\)N\(_4\)-570 and BA-CN\(_x\), and (c) the relationship between the RhB degradation efficiency and the light irradiation time, respectively. In Fig. 7(a), the photocatalytic activity of photocatalysts increases by increasing the content of barbituric acid to 0.86 g, due to that the excessive doping spoils the indirect character of the semiconductor and offers potential recombination sites [25]. The sample BA-CN\(_3\) exhibits a more intense adsorption to RhB dye rather than the other samples, which is improved using an appropriate amount of barbituric acid.

The photocatalytic ability of g-C\(_3\)N\(_4\) is related with the synthesis temperature [2]. It is necessary to distinguish the contribution of two factors, which are the synthesis temperature and ionothermal copolymerization process. In Fig. 7(b), a higher synthesis temperature for g-C\(_3\)N\(_4\)-550 leads to a better photocatalytic ability, compared to g-C\(_3\)N\(_4\)-570 [2]. Also, the ionothermal copolymerization can improve the photocatalytic ability of BA-CN\(_x\), compared to g-C\(_3\)N\(_4\)-570. The ratio of degrading RhB increases from 41.5% (g-C\(_3\)N\(_4\)-550) to 83.8% (BA-CN\(_x\)) after irradiating under visible light for 90 min, which is calculated according to the formula as \(\eta \left(\frac{C_1 - C}{C}\right)\) (where \(C_1\) and \(C\) are the relative concentrations of RhB at 0 and 90 min, respectively), indicating the increase of the photocatalytic activity by ionothermally copolymerized at a high temperature.

The kinetics of RhB photodecomposition on the catalyst surface can be described by the first-order equation

\[
\ln\left(\frac{C_0}{C}\right) = kt
\]

where \(k\) is the rate constant (min\(^{-1}\)), \(C_0\) is the initial concentration of target dye, and \(C\) is the actual concentration of target dye at light irradiation time \(t\). In Fig. 7(c), the \(k\) value increases gradually with increasing the amount of barbituric acid until 0.86 g, which is because the excessive doping of aromatic groups spoils the indirect character of the semiconductor and offers potential recombination sites. The sample BA-CN\(_4\) shows the maximal \(k\) value of 0.02031 min\(^{-1}\) because it has the best (C\(_3\)N\(_4\))\(^e\)(C7N7)\(^y\) equilibrium and no severe agglomeration. The sample BA-CN\(_0\) shows the lowest degradation ratio because the excessive ions existed in the polymer network changed its energy band structure, thus decreasing its visible light absorption activity (see Fig. 5).

Fig. 8 shows the recycled experimental results of the photodegradation of RhB catalyzed by BA-CN\(_4\). Clearly, the photocatalytic activity of BA-CN\(_4\) has no apparent deactivation (the degradation ratio is 80%) after 4 recycles for the degradation of RhB under visible light irradiation, revealing that the photocatalyst possesses a good stability. Moreover, Fig. 9 shows the XRD pattern of BA-CN\(_4\) after 4-run recycles. The sample BA-CN\(_4\) still has a good degradation ratio although the diffraction peaks decrease in the XRD pattern.

4. Conclusions

Carbon nitride contained (C\(_3\)N\(_4\))\(^e\)(C7N7)\(^y\) unit was synthesized by heating dicyandiamide and barbituric acid as the
co-precursor in lithium chloride and potassium chloride as media. Based on the analysis by X-ray diffraction, the structure characteristic of the as-prepared photocatalysts was similar to that of bulk g-C₃N₄. In the SEM and TEM images, an obvious layered structure of BA-CNₓ occurred. In the FT-IR spectra, BA-CNₓ had the similar groups as bulk g-C₃N₄. The UV–vis spectra indicated that BA-CNₓ had an obvious red shift and an increased light absorption intensity, compared to bulk g-C₃N₄. The specific surface area of BA-CNₓ could be increased by the ionothermal copolymerization synthesis method. The photocatalytic degradation of RhB under visible light showed the optimum photocatalytic ability of BA-CNₓ when the weight of barbituric acid was 0.52 g, because it had the best \((\text{C}_3\text{N}_4)_x-(\text{C}_7\text{N}_7)_y\) equilibrium and no severe

<table>
<thead>
<tr>
<th>Experimental C/N mole ratio</th>
<th>g-C₃N₄-570</th>
<th>BA-CN₀</th>
<th>BA-CN₁</th>
<th>BA-CN₂</th>
<th>BA-CN₃</th>
<th>BA-CN₄</th>
<th>BA-CN₅</th>
</tr>
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<tbody>
<tr>
<td>Value of x:y</td>
<td>0.658</td>
<td>0.679</td>
<td>0.766</td>
<td>0.783</td>
<td>0.809</td>
<td>0.844</td>
<td>0.908</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>20.848</td>
<td>137.585</td>
<td>149.089</td>
<td>171.463</td>
<td>246.066</td>
<td>175.380</td>
<td>164.209</td>
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Fig. 6. N₂ sorption isotherms and pore size distribution curves (BJH): (a) BA-CN₀, (b) BA-CN₁, (c) BA-CN₂, (d) BA-CN₃, (e) BA-CN₄, (f) BA-CN₅, (g) g-C₃N₄-570.
The photocatalytic property was also stable after 4-run recycles.

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