Synthesis and testing of defected g-C$_3$N$_4$ with improved photocatalytic activity

Y Zheng$^{1,3}$, C H Li$^2$ and Y Y Cai$^2$

$^1$Shanxi Institute of Energy, Jinzhong City, Shanxi Province, 030600, China
$^2$Department of Chemical Engineering, Ocean University of China, Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao, 266100, China

E-mail: zhengyu0305@163.com

Abstract. Graphitic carbon nitride samples with defected structure but larger surface areas were synthesized by adding urea as additive to the thermal decomposition (pyrolysis) of melamine. The pyrolysis was carried out at 600°C in ope-air conditions for 2 hours. The as-prepared samples were compared through detailed characterizations such as SEM, BET, XRD, XPS, FTIR and DRS. It was found out that the addition of urea functioned against the perfection of polymerization, and led to defected structure, which were suggested to be g-C$_3$N$_4$ segments in small crystalline domains. As a result, the formation of the defected structure led to blue-shifts in the optical transitions in the UV-Vis spectral range, as well as larger surface areas. In addition, the photocatalytic activities of the samples were measured by degrading Rhodamine B (RhB) with a concentration of 10 mg/L. It was found out that the samples with defected structure exhibited improved improved photocatalytic activity.

1. Introduction

Nowadays, water pollution has become a burning problem worldwide. As an effective solution to this problem, the heterogeneous photocatalysis has induced much attention and endless searching for efficient photocatalysts[1]. A large number of materials such as TiO$_2$[2] have been investigated as possible photocatalysts. However, most of the investigated photocatalysts are not ideal in the ways of either visible-light responded, stable, inexpensive, or nontoxic[3].

Graphitic carbon nitride (g-C$_3$N$_4$), a binary carbon-nitrogen polymeric material, has drawn much attention due to its advantages such as chemical and thermal stability, resistance to wear and biological compatibility[4]. As a photocatalyst, the special electronic property, thanking to its unique tectonic structure motif, endows g-C$_3$N$_4$ a tuneable visible-light-responded band gap (~ 2.7 eV), making it very promising[5,6]. However, pure g-C$_3$N$_4$ has small surface area which leads to unsatisfied adsorption capacity and to poor performance, thus modification is necessary[7].

In this work, pure g-C$_3$N$_4$ was prepared by thermal decomposition of melamine, modification was achieved by adding urea as additive to the precursor. This yielded g-C$_3$N$_4$ samples with defected structure, whose performances were tested by photocatalytic degradation experiment under visible light. In the photo-degradation experiment, RhB was chosen as the target pollutant, since it is a commonly used colorant in textile, food and printing industries, which will cause severe and long-term side effect for the water environment.
2. Experimental

2.1. Preparation of g-C3N4 samples
The g-C3N4 samples were synthesized using the pyrolysis method, with melamine (99.5%, Tianjin Bodi Chemical Reagent Co.) and urea (99.0%, Nanjing Chemical Reagent Co.) as precursors. Samples denoted as 1# to 6# were prepared by varying the weight ratio of urea to precursors as 0, 20, 40, 60, 80, and 100%, respectively. Typically, 10 g of the precursor was placed in a 50 mL crucible with a cover. The crucible was then heated to 600°C for 2 h under atmospheric condition with a 2°C/min heating ratio in a muffle furnace (SX2-4-10, Shandong). After the heating, the crucible was cooled down naturally, then the sample was rinsed three times using ethanol and distilled deionized water and dried at 80°C for 24 h.

2.2. Sample characterization
The crystal structure of the as-prepared samples was investigated through XRD using a Cu–Kα radiation diffractometer working at 40 kV/44 mA, with 2θ scope ranging from 5 to 35°. Sample morphology was revealed by a field emission scanning electron microscope (FESEM), model JSM-7500F (JEOL). The specific surface area was obtained using an automatic adsorption apparatus (Micro metrics, Tri Star 3000). An X-ray photoelectron spectroscopy (XPS, model XSAM-800) was used to analyze the surface chemical states. The transmission spectra of FTIR spectroscopic measurements were taken with an Agilent FTIR (Agilent Technologies, Cary 630). An ultraviolet-visible (UV-Vis) spectrophotometer (Thermo Evolution 300), equipped with a lab sphere diffuse reflectance accessory of 200-800 nm reflectance spectra range, was used to measure the diffuse reflectance spectra (DRS).

2.3. Photo-degradation experiment
The photocatalytic performances of samples were carried out in a slurry reactor placed in a reflective housing unit. Illuminating was powered by a halogen tungsten bulb (300 W, Ushio), with irradiation wavelength higher than 410 nm guaranteed by a UV filter (Kenko Zeta). The reacting temperature was controlled constantly at 25°C by an external cooling jacket. In each test, 0.05 g photocatalyst was added to 200 mL solution containing 10 mg/L reagent-grade RhB. The adsorption-desorption equilibrium between RhB and photocatalyst was first achieved without light for 30 minutes, after which the system was illuminated under constant stirring at 300 rpm for 1 hour. For each test, reacting solution was taken every 10 minutes and centrifuged to get supernatant, which was analyzed using UV-Vis spectrophotometer at a wavelength 554 nm.

3. Results and discussion

3.1. Sample characterization

3.1.1. XRD analysis. The XRD patterns of the as-prepared samples from pure melamine and urea (sample 1# and 6#) are shown in figure 1. These samples display two consistent major peaks at about 13 and 27.5°. The peak at 13° was indicative of an intraplanar motif with a (100) crystal plane, while the peak around 27.5° accords with the stacking of conjugated graphene-like aromatic layers with a (002) crystal plane[8]. However, there is a pronounced difference concerning the intensities of the (002) peak, the sample 6# shows a much weaker one, revealing the presence of smaller crystalline domains. In theory, any deviation from an ideal lattice structure can be seen as defect, thus it is suggested that the samples with smaller crystalline domains are of defected structure. What is more, the (002) peak of sample 6# is shifted towards a larger 2θ position, indicating a denser stacking, also presumably ascribing to the smaller crystalline domains.
3.1.2. SEM analysis. The morphologies of sample 1# and 6# were shown in figure 2, they are of big difference. The sample 1# (figure 2(a)) is primarily comprised of considerable-sized crystal sheets, while sample 6# (figure 2(b)) has a complex morphology and is relatively transparent to electrons. By giving a more detailed look at the redline-circled part, the primary structure motif of sample 6# are stacked lamellar small crystals with smaller porous crystal grains, which are supposedly formed from the self-produced gas during the pyrolysis of urea, which can function as soft template\[9\].

3.1.3. BET analysis. Table 1 summarizes the BET surface areas and final weight of all samples. The surface areas were increased positively with urea contents in the precursor, however the weight were decreased. There were two factors causing these: different intermediates are involved in the pyrolysis of urea, which inevitably leads to thermal-defects\[10\]; the pyrolysis of urea produces large sums of gases such as NH$_3$, H$_2$O and CO$_2$, functioning as soft templates to generate porous structure \[9,10\]. In conclusion, adding urea is beneficial to increasing adsorption capacities of the photocatalysts.

**Table 1.** Surface areas and final weight of sample 1# to 6#.

| Sample | Surface area (m$^2$ g$^{-1}$) | Sample weight (g) |
|--------|-------------------------------|-------------------|
| 1#     | 21.761                        | 6.78              |
| 2#     | 21.909                        | 4.93              |
| 3#     | 31.873                        | 3.95              |
| 4#     | 41.732                        | 3.04              |
| 5#     | 50.077                        | 1.75              |
| 6#     | 56.831                        | 1.32              |

3.1.4. XPS analysis. The spectra from XPS characterizations of sample 1# (figures 3(a) and 3(c)) and 6# (figures 3(b) and 3(d)) were calibrated by C 1s(BE 284.6 eV). As figure 3(a) shows, the C 1s spectrum
has a strong symmetric peak at BE 288.2 eV conforming the C=N bonds. By contrast, the C 1s spectrum of sample 6# shows two more distributions at BEs 286 and 288.5 eV, corresponding to hydroxyl (C-O) and carbonyl groups (C=O). These two oxygen-containing groups are likely the results of surface oxidizing by H₂O produced during the pyrolysis of urea at high temperature. Figure 3(c) and 3d are the deconvolutions of N 1s spectra, and they consistently yield three separate fittings at BEs 398.7, 400.1, and 401.4 eV, which are indicative of “pyridinic” bonds (C=N-C), tertiary nitrogen groups (N-(C)₃), and the pyrrole-like N atoms in amino functions (C-N-H)[11-13]. These three peaks of sample 1# are of optimum ratios, that the intensity of bond N-(C)₃ is four times stronger than that of bond C-N-H, indicating a great number of heptazine units. In sample 6#, however, the fore-mentioned ratios increased, indicating a forming of smaller segments with less heptazine units [14].

3.1.5. FTIR analysis. Figure 4 shows the FTIR results of sample 1# and sample 6#. The sharp peak at ~ 800 cm⁻¹ is supposed to be the breathing mode of s-triazine unit; the bands located at 1310 and 1225 cm⁻¹ and in the region of 1500 - 1700 cm⁻¹ indicate the existence of skeletal stretching modes of aromatic C-N heterocycles[15]. The broad band in the region of 3000 - 3300 cm⁻¹ indicates the existence of the N-H stretching in primary and secondary amide and their intermolecular hydrogen bonds. The addition
of urea tends to shift the -NH/NH2 peak towards higher frequency region, indicating smaller polymer segments contain less heptazine units. This assumption is supported by the increased splitting of the band at 800 cm\(^{-1}\) which can be assigned to individual s-triazine ring.

### 3.1.6. DRS analysis

Figure 5 shows intrinsic absorption patterns of semiconductor in the blue-light region. The absorption edge is blue-shifted towards ultraviolet light regions with the increasing addition of urea. Since the main optical transitions are dominated by the tri-s-triazine core, the blueshift is related to a decreasing degree of polymerization, which eventually leads to a decreased overlap of molecular orbitals. The blue shift can also be explained by quantum size effect, coming from the presence of smaller crystalline domains.

![Figure 5. DRS spectrum of the samples prepared from different precursors.](image)

The \(E_g\) of the samples could be calculated through classic Tauc equation and be estimated by plotting \((\alpha E_{\text{photon}})^{1/2}\) against \(E_{\text{photon}}\), as is shown in figure 5(b)[16]. The \(E_{CB}\) and \(E_{VB}\) can also be calculated empirically[16], the detailed results are listed in table 2. There is a positive correlation between the increase of \(E_g\) and adding urea as additives. The tunable band gap is likely to indicate a quantum size effect coming from the presence of smaller crystalline domains.

#### Table 2. Band potentials of samples prepared from different precursors.

| Sample | 1# | 2# | 3# | 4# | 5# | 6# |
|--------|----|----|----|----|----|----|
| \(E_g\), eV | 2.48 | 2.52 | 2.54 | 2.58 | 2.60 | 2.70 |
| \(E_{VB}\), eV | 1.47 | 1.49 | 1.50 | 1.52 | 1.53 | 1.58 |
| \(E_{CB}\), eV | -1.01 | -1.03 | -1.04 | -1.06 | -1.07 | -1.12 |

### 3.2. Evaluation of photocatalytic activity

The photocatalytic performances of the as-prepared samples were studied by photo-degrading RhB, and the results were plotted in figure 6(a). In the dark adsorption process, the adsorption efficiencies of sample 1# to 6# rose from 7.01±0.032% to 13.70±0.094%, which agrees well with the BET test. The noticeable enhancement in adsorption in turn positively affected photo-degrading of RhB. The pure g-C3N4 (1#) was found to only achieve a degradation efficiency of 31.66±0.057% after 60 minutes, while samples prepared from precursors containing higher contents of urea exhibited better, for after reacting for 60 minutes, samples 2# ~ 6# achieved degradation efficiencies of 49.93±0.018%, 63.26±0.116%, 87.68±0.094%, 99.64±0.111% and 100±0.009%, respectively. To better understand the differences between the photocatalytic degradation processes of different samples, the pseudo first order kinetic model (\(\ln \frac{c_0}{c} = kt\)) was applied (figure 6(b)), where \(k\) is the reaction kinetic constant and \(t\) is the irradiation time. It turns out that the reaction rate constant of the sample 6# is 28.2 times larger than that of the sample 1# (table 3).
Figure 6. Photocatalytic degradation efficiency as a function of time.

Table 3. Pseudo first-order fitting for samples 1# to 6#.

|   | 1#  | 2#  | 3#  | 4#  | 5#  | 6#  |
|---|-----|-----|-----|-----|-----|-----|
| $\kappa$ ($10^{-2}$ min$^{-1}$) | 0.612±0.000 | 1.090±0.000 | 1.598±0.001 | 3.298±0.004 | 9.038±0.005 | 12.729±0.002 |
| $R^2$ | 0.985±0.001 | 0.983±0.008 | 0.994±0.003 | 0.997±0.000 | 0.994±0.002 | 0.988±0.005 |

Figure 7 exhibits a further investigation of the influences on reaction kinetic constant by band gap values and BET surface areas. By plotting $\ln k$ against $E_g$ and $\ln k$ against BET surface areas, positive correlations can be observed. The reaction kinetic constant increased exponentially with increased band gap values and BET surface areas. With the absorption edge blue-shifting towards ultraviolet light regions, the photonic excitations were triggered by photons possessing higher energies, thus led to the formation of photo-generated electron-hole pairs with stronger reducing-oxidizing property, which is crucial to photocatalytic activities. Figure 7 also reveals that the surface area of photocatalysts is the other crucial factor to the photocatalytic activities. With increased surface areas, more adsorption and reacting sites were available. Under the synergistic effects of the increased value of band gap and surface area, the photocatalytic performances of photocatalysts were greatly improved.

Figure 7. Natural Logarithm of $k$ as a function of $E_g$ (a) and BET surface areas (b).

3.3. Mechanism of photocatalytic action

The photocatalytic degradation process of RhB using sample 6# is shown in figure 8(a). The obtained UV-Vis spectra show evident hypsochromic effect caused by de-ethylation. The process begins by adsorbing RhB molecules through diethylamino groups (figure 8(b)), the photo-induced oxygen-containing radicals mainly attack the N-ethyl groups, which are auxochromic groups in RhB molecule[17]. Thus shorter wavelength is expected for the absorption of the less N-ethyl groups intermediate [18]. Furthermore, the step wise de-ethylation process suggests a fast adsorption - desorption equilibrium between RhB/RhB-intermediates and the $g$-$C_3N_4$ surface.
Figure 8. Photo-degradation process of RhB (a) and its adsorption mode (b).

When the photocatalytic degradation process is carried out under visible light irradiation, the visible light assisted RhB-sensitized process should be taken into account, in which the adsorbed RhB molecule absorb visible light and transfer the LUMO electrons of excited RhB (RhB*) to the conduction band of g-C$_3$N$_4$. As a result of the aforementioned electron transfer, active oxygen species were mostly produced on the adsorption site of the RhB molecule. However, there is sites on the surface of g-C$_3$N$_4$ where no RhB molecule is adsorbed. Since g-C$_3$N$_4$ is responsible to visible light, it means that there are active oxygen species being produced directly by g-C$_3$N$_4$ itself, and these active oxygen species will also react with RhB molecule near the surface. To summary, there are most likely two generation mechanisms of the active oxygen species in this system, which can be schematically shown as figure 9. The two mechanisms shown in figure 9 can be expressed as following equations:

Mechanism 1

\[
RhB_{ad} + h\nu \rightarrow RhB^* + e^- \tag{1}
\]

\[
e^- \rightarrow e^-_{CB} \tag{2}
\]

\[
e^- + O_{2ad} \rightarrow \bullet O_2^- \tag{3}
\]
Mechanism 2

\[
P\text{hotocatalyst} + h\nu \rightarrow h_{VB}^+ + e_{CB}^-
\]

\[
h_{VB}^+ + \text{RhB} \rightarrow \text{RhB}^+
\]

\[
o_2 + e_{CB}^- \rightarrow \bullet o_2
\]

4. Conclusions

In this work, graphitic carbon nitride samples with defected structure were synthesized through a pyrolysis method, using precursors in a combination form of melamine and urea. The incorporation of urea in the precursor endowed the sample with defected structure in the form of small crystalline domains. It turns out that the formation of defected structure was beneficial to larger surface areas, which consequently led to advanced photocatalytic performance with regards to the degradation of RhB. At best, a quantity of 200 mL of RhB at a concentration of 10 mgL\(^{-1}\) was completely degraded within 60 minutes using 0.05 g of the as-prepared sample 6#, and the reaction rate constant of which was 28.2 times larger than that of the sample lacking defected structure (1#). The mechanisms of the photocatalytic degradation of RhB under visible light irradiation were also discussed. In conclusion, the addition of urea into the precursor was an efficient way to improve the photocatalytic activity of g-C\(_3\)N\(_4\).

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