Research Article

Pyrolysis Synthesized g-C₃N₄ for Photocatalytic Degradation of Methylene Blue

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Graphitic carbon nitride (g-C₃N₄) was synthesized at 520°C by the pyrolysis of cyanamide, dicyandiamide, and melamine. The samples were characterized by X-ray diffraction (XRD), UV-visible diffuse reflectance spectra, Fourier transform infrared spectroscopy (FT-IR), and elemental analyzer. The photocatalytic activity of g-C₃N₄ was evaluated by the photodegrading experiments of methylene blue (MB). The results indicated that g-C₃N₄ obtained from dicyandiamide exhibited higher activity, and the higher C/N molar ratio and degree of condensation increase the photocatalytic activity of g-C₃N₄. A photocatalytic mechanism presumed the MB photodegradation over the C₃N₄ photocatalyst is attributed to photogenerated electron impelled multistep reduction of O₂.

1. Introduction

The heterogeneous photocatalysis eliminating an organic pollutant from water or air has numerous potential applications to resolve serious environmental pollution. In recent years, researchers have devoted extensive efforts to prepare semiconductors for the photocatalytic reaction with a suitable band gap, such as metal-containing oxide, sulfide, and oxynitride [1–7]. Very recently, a novel metal-free semiconductor photocatalyst, carbon nitride (C₃N₄), was found to have good performance in the photooxidation of methyl orange (MO), the developed g-C₃N₄ metal including compounds could effectively degrade MO dyes [8, 9]. Wang et al. also reported that g-C₃N₄ with a band gap of 2.7 eV achieved functionality as a stable photocatalyst for H₂ evolution from water under visible light irradiation [10–12]. Covalent carbon nitrides have attracted much attention since the theoretical prediction of their remarkable mechanical and electronic properties of some phases [13, 14], for example, g-C₃N₄ was used as catalyst or carrier due to its excellent stability at an ambient condition [15]. In most cases, g-C₃N₄ powder was prepared by a facile pyrolysis method using amine precursors [16–23]. However, the

obtained g-C₃N₄ from varying amine precursors may present the discrepant photocatalytic properties. To develop a highly efficient photocatalytic system, it is interesting to know the photocatalytic properties of g-C₃N₄ depending on the precursors. The detailed investigation on g-C₃N₄ will provide useful information for its photocatalysis application.

Here, the g-C₃N₄ powder was prepared by heating cyanamide, dicyandiamide, and melamine, respectively, and the photocatalytic activity was evaluated by the photodegradation of methylene blue (MB). The results suggest that the obtained g-C₃N₄ presented the distinct performance of photocatalysis, which depended on the amine precursor.

2. Experimental

2.1. Preparation of g-C₃N₄. The g-C₃N₄ was prepared by heating cyanamide, dicyandiamide, and melamine, respectively. The reaction is performed in an alumina crucible with a cover which can form a semiclosed atmosphere to prevent sublimation of precursors. 3 g of the initial reactant was put into a crucible, heated to reach temperatures of 500°C in a muffle furnace with the heating rate of 20°C/min, kept at this temperature for 4 h, then heated at the rate of

10°C/min to reach temperatures of 520°C, and the further thermal treatment was performed at this temperature for 2 h, at last cooled naturally to room temperature. The obtained yellow polymers were ground into powder, which made from cyanamide, dicyandiamide, and melamine were, respectively, marked as C_3N_4/C , C_3N_4/D , C_3N_4/M .

2.2. Characterization of $g-C_3N_4$. The obtained $g-C_3N_4$ was characterized by X-ray diffraction for phase identification on a DX-2000 diffractometer (Cu $K\alpha 1$ irradiation). The FT-IR spectrum was collected in an Avatar 360 infrared spectrophotometer (Nicolet, USA) with the prepared powders diluted in KBr pellets. The UV-visible diffuse reflection spectrum was recorded using a UV-visible spectrophotometer (UV-500, Japan). The C/N ratios were determined by elemental analysis on an elemental analyzer (vario EL III, Elementar, Germany). The morphology of C_3N_4 was recorded on a transmission electron microscopy (TEM) (Hitachi-800, Japan).

2.3. Photocatalytic Performance of $g-C_3N_4$. Photocatalytic activity of $g-C_3N_4$ for methylene blue (MB) degradation was evaluated in a Pyrex glass cylindrical reactor with the diameter of 50 mm and effective volume of 100 mL, 50 mg of $g-C_3N_4$ was dispersed in MB aqueous solution (50 mL, 50 mg L⁻¹). Photodegradation of MB was performed under a 300 W Xe lamp with a water filter and cutoff filter for visible light (420 nm). At an hour interval, 2 mL suspension was removed, and then the concentration of MB was analyzed using the UV-visible spectrophotometer at 648 nm.

3. Results and Discussion

The results show the typical feather of $g-C_3N_4$ with two peaks resulting from graphite structure and tri-s-triazine units in Figure 1, which is similar to the previous reports [8, 9, 17]. The strongest peak at 27.3° is due to the stacking of the conjugated aromatic system, corresponding to the 002 crystal face and the interplanar distance of aromatic units of 0.326 nm, as well as a peak at 13.2°, resulting from the periodic arrangement of the condensed tri-s-triazine units in the sheets, is indexed as (001), corresponding to interplanar distance of 0.670 nm. This distance is smaller than one tri-s-triazine unit (calculated value is 0.73 nm), presumably owing to the presence of small tilt angularity in the planar structure.

The FT-IR spectrum of $g-C_3N_4$ powder displayed in Figure 2 clearly shows several peaks at the frequency characteristic of vibrational modes related to the chemical bonding between carbon and nitrogen. The absorption peak at 810 cm⁻¹ corresponds to the characteristic breathing mode of the triazine units. Several strong bands in the 1240–1590 cm⁻¹ region can be attributed to the stretching modes of C–N heterocyclics [18–21]. The adsorption peak at about 1336 cm⁻¹ can be attributed to C–N, and at 1641 cm⁻¹ came from the C=N stretching mode [7, 8, 14, 23]. The broad absorption band at 3100–3300 cm⁻¹ can be assigned to the stretching modes of secondary and primary amines and their intermolecular hydrogen-bonding interactions. The broad

FIGURE 1: XRD patterns for $g-C_3N_4$ fabricated from varying precursors.

FIGURE 2: FT-IR spectra for $g-C_3N_4$ powder diluted in a KBr pellet.

FIGURE 3: UV-visible absorption spectra of g-C₃N₄.

band at about 3000 cm⁻¹ may also due to the adsorbed water. Indeed, as reported, the residual hydrogen atoms bind to the edges of the graphene-like C-N sheet in the form of C-NH₂ and 2 C-NH bonds [21].

The optical properties of the samples were investigated by UV-vis diffuse reflectance spectroscopy, and the results are shown in Figure 3. The UV-visible diffuse reflectance spectra showed that the absorption edges of all samples are close to 470 nm, which are 473, 475, and 468 nm for C₃N₄/C, C₃N₄/D, C₃N₄/M. The band gap of samples, which prepared from the various raw materials, was approximate to 2.62 eV. It is worth noting that the weak absorption tails were seen due to the structure defects in the heated samples, which may improve the visible absorption of materials, this probably is attributed to the structure defects formed in samples treated at the high temperature.

A typical TEM image (Figure 4) shows that the surface morphology of g-C₃N₄/D is layered and platelet-like, which is similar to the other samples, indicating that the modification of the polymeric subunits by copolymerization with three precursors does not significantly change the texture of carbon nitride polymer.

The photocatalytic activities of the samples for methylene blue (MB) photodegradation were evaluated under visible light irradiation, as shown in Figure 5. A blank experiment (without catalyst) was also given for comparison. Results showed that 25%, 55%, 66%, 60% MB was photodegraded after 5 h irradiation for the blank, C₃N₄/C, C₃N₄/D, C₃N₄/M. Recycling of the catalyst indicated no obvious deactivation during the entire catalytic reaction, indicating good photochemical stability of g-C₃N₄ photocatalyst for environmental purification. No clearly distinctness was seen for the character of g-C₃N₄ according to the front results, such as the phase and covalent bond of carbon nitride. Whereas, the result of

FIGURE 4: A typical TEM image of g-C₃N₄/D. FIGURE 5: Photodegradation of MB over the g-C₃N₄.

elemental analyses is an exception that proposed the different precursors effected the structural integrity of carbon nitride. The average value of C/N molar ratio is 0.671, 0.685, and 0.676 for C₃N₄/C, C₃N₄/D, C₃N₄/M, for all cases, which are lower than the theoretical value of 0.75, and the surface termination effected by uncondensed amino functions due to the defects, which are in agreement with the FT-IR.

Next, the possible photodegradation mechanism of MB over g-C₃N₄ semiconductor is discussed. The bandgap of the graphitic carbon nitride is estimated to be 2.62 eV from its UV spectrum (Figure 4), showing an intrinsic absorption in the blue region of the visible spectrum. The optical gap is attributed to the transitions between weakly localized states of the π - π^* states that come from the sp² configurations atoms in the network. Indeed, according to Wang, The wavefunction of the valence band is a combination of the HOMO levels of the melem monomer, which are derived from nitrogen p_z orbitals. The conduction band can similarly be connected to the LUMO of the melem monomer, which

consists predominantly of carbon p_z orbitals. Photoexcitation consequently leads to a spatial charge separation between the electron in the conduction band and the hole in the valence band. This suggests that the nitrogen atoms would be the preferred oxidation sites, whereas the carbon atoms provide the reduction sites.

Under light irradiation, some active species, such as the hydroxyl radicals ($\bullet\text{OH}$), the superoxide ($\text{O}_2\bullet$ or $\text{HOO}\bullet$), and the holes, are formed during the photodegradation reaction. The $\bullet\text{OH}$ in aqueous solutions, as the primary oxidant, is generated via the direct hole oxidation or photogenerated electron-induced multistep reduction of O_2 ($\text{O}_2 + e^- = \text{O}_2\bullet$, $\text{O}_2\bullet + e^- + 2\text{H}^+ = \text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2 + e^- = \bullet\text{OH} + \text{OH}^-$). In addition, the photogenerated hole can directly react with organic compounds if the semiconductor photocatalyst has moderate redox potential. For the C_3N_4 , photogenerated hole is not an effective active species during degrading MO over g- C_3N_4 [8]. The oxidation level for water splitting is located slightly above the top of the valence band of C_3N_4 , which would permit transfer of holes, but with a low driving force. This suggests that the low driving force is not beneficial for the hole reactions in aqueous solution system [11].

For the other case, hydroxyl radical reactions are nonselective and will virtually react with almost all the organic compounds by H-atom abstraction, direct electron transfer, or insertion. The $\bullet\text{OH}$ radical is the reactive oxidant to promote the complete mineralization of MB. And that the oxidation potential of hole generated in the C_3N_4 is not high enough to directly oxidize $-\text{OH}$ to hydroxyl radicals, which is generated by the multiple electron (in the conduction band) transfer process in the "oxygen reduction reaction," ORR. In a first step, the moderate oxidant $\bullet\text{O}_2^-$ is produced by the reaction of dissolved O_2 with a first photoinduced electron. $[\text{H}^+]$ is important in the second step, where it helps to transfer a second electron to form H_2O_2 . H_2O_2 can then further be activated to the most reactive $\bullet\text{OH}$ by accepting a third photoinduced electron, a key step which g- C_3N_4 is known to be able to perform, due to its band positions. In our case, it is deduced that the possible photodegradation mechanism of MB over g- C_3N_4 is attributed to photogenerated electron-induced multistep reduction of O_2 .

The C/N molar ratio and the degree of condensation are consistent with the photocatalytic activity. This means that the slightly decreased photocatalytic activity is attributed to the uncompleted condensation [8]. According to Alibart et al., the optical gap is attributed to the transitions between weakly localized states of the π - π^* states that come from the sp^2 configurations atoms in the network. These states form the valence and conduction band edges and control the width of the optical gap. π bonding at Csp^2 sites favours clustering of aromatic rings into graphitic sheets. This clustering dominates the π component of the valence-band edge, in optical absorption, the filled states are excited to empty antibonding states. If the cluster is present, with or without lone pair states at π band, this would give a broader tail. The states may be due to either various clusters of sp^2 sites, which can obviously be either $\text{C}=\text{C}$ or $\text{C}=\text{N}$ bonds, and from "free" (i.e., not saturated with nitrogen atoms) sp^3 sites. This means that

the concentration of the localized states in the gap should increase with increasing amount of sp^2 sites [24]. One can expect that the concentration of localized states in the gap should increase with increasing C/N ratio and the degree of condensation, which make photogenerated electron transfer faster. This means that the slightly increased photocatalytic activity is attributed to the degree of condensation, which increases the photooxidation ability of C_3N_4 . In combination with the elemental analysis results discussed above, it is obvious that the $\text{C}_3\text{N}_4/\text{D}$ obtained from pyrolysis of dicyandiamide with the moderate degrees of condensation and good crystal structure exhibits the best activity in degrading MB. The $\text{C}_3\text{N}_4/\text{D}$ obtained from dicyandiamide has a higher C/N ratio of 0.685, which increase the photocatalytic activity.

4. Conclusions

Three bulk g- C_3N_4 had been synthesized successfully by the self-condensation of cyanamide, dicyandiamide, and melamine in this work. All of the g- C_3N_4 was provided with the analogical properties such as the phase, covalent bond, and the absorption edges under UV-visible light. However, the C/N molar ratio and the structural integrality of carbon nitride are distinct. The average values are 0.671, 0.685, and 0.676 for cyanamide, dicyandiamide, and melamine, respectively. The g- C_3N_4 synthesized from dicyandiamide exhibited the best photodegradation activity. Higher C/N molar ratio and degree of condensation make the photocatalytic activity increase.

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