Photocatalytic performance of carbon nitride intercalation compound

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Abstract. The carbon nitride intercalation compound photocatalyst was synthesized by a simple molten salt route. The photocatalyst was characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and Fourier transform infrared (FT-IR) spectroscopy. The photocatalytic oxidation ability of the carbon nitride intercalation compound photocatalyst was evaluated by the photocatalytic activity in photo-oxidation of MO. The as-prepared photocatalyst exhibits an improved photocatalytic activity due to the increased surface area.

1. Introduction

Recently, for its potential applications in water splitting for hydrogen or oxygen generation as renewable energy and in the degradation of organic pollutants by using solar energy, photocatalytic technique has attracted considerable interest.[1-3] A good method to improve the photocatalytic activities for degradating organic pollutants under light irradiation is to increase the separation efficiency of photogenerated electron–hole pairs is, such as the use of co-catalysts[4].

A metal-free visible-light responded semiconductor photocatalyst reported by Wang et al for the first time, graphitic carbon nitride (g-C3N4), has attracted vast attention, which is used for hydrogen or oxygen generation from photocatalytic water splitting.[5] However, the photocatalytic performance of g-C3N4 is relatively low, which is induced by the inefficiency in separation and transport of photogenerated carriers[6]. To narrow the band gap such as doping and to enhance the efficiency in separation and transport of photogenerated carriers are to improve the photocatalytic performance of g-C3N4.[7-9] The organic polymer semiconductor material with coordinating alkali metals into the C–N plane of carbon nitride, a carbon nitride intercalation compound has been formed by a simple molten salt route and thus significantly improving the electrical conductivity of g-C3N4 and exhibiting high quantum yield and the prospect for solar energy conversion.[10] Also, it has been well demonstrated that to build g-C3N4-based hybrids photocatalysts with various materials, such as Bi2MoO6, graphene and AgX/g-C3N4 (X = Br, I), can efficiently promote the separation and transfer of the photogenerated carriers.[11-14] In the present study, carbon nitride intercalation compound was prepared via a simple molten salt route and the photocatalytic activity of photodegradation of methyl orange (MO) of carbon nitride intercalation compound under visible light irradiation was studied. The results demonstrated that the carbon nitride intercalation compound photocatalyst showed an improved MO photodegradation activity than bulk g-C3N4.
2. Experimental

2.1. Synthesis of carbon nitride intercalation compound
The carbon nitride intercalation compound was synthesized by a simple molten salt route[10]. Melamine was used as a precursor to synthesize carbon nitride. The eutectic mixture of LiCl·H₂O–KCl–NaCl (1:1:1 weight ratio) with a low melting point of 355 °C was selected as a solvent. With a weight ratio of 15:1 for eutectic salts to melamine, the mixture of eutectic salts and melamine was prepared and finely ground in a mortar. The resulting mixture was transferred into a quartz glass beaker, and then the powder mixtures were heated to 500 °C for 1 h under semiclosed environment. After cooled to room temperature, the obtained yellow powders were washed thoroughly with deionized water, and then the product was collected by centrifugation and dried at 60 °C. In a typical process, the photocatalyst of g-C₃N₄ was prepared by directly heating melamine at 500 °C (heating rate: 20 °C/min) for 2 h, and the further deammoniation treatment was set at 520 °C for 2 h[15], respectively in the semiclosed system to prevent sublimation of melamine.

2.2. Characterization
The specific surface area of the as-prepared powders was obtained on a Micromeritics TriStar 3000 instrument and Brunauer–Emmett–Teller (BET) equation were used to calculate the specific surface area. The morphology and microstructure were observed using a field emission scanning electron microscope (FE-SEM; NOVA230, FEI Ltd.) with accelerating voltage of 15 kV.

2.3. Photocatalysis test
The methyl orange (MO) dye was used to test the photocatalytic activities of as-prepared samples and the photocatalytic reaction was performed in a Pyrex reactor. The catalyst (0.1 g) was dispersed in 100 mL MO aqueous solution (4.2 mg L⁻¹). The light irradiation system contains a 300 W Xe lamp with cut-off filter L42 for visible light and a water filter to remove heating effects. The reaction solutions of the MO photodegradation for all experiments were first stirred in the dark for 1 h to reach the adsorption–desorption equilibrium of MO on catalysts. The MO degradation efficiency was evaluated using the UV-vis absorption spectra to measure the peak value of a maximum absorption of MO solution at wavelength of 463 nm.

3. Results and discussion
The morphology of the carbon nitride intercalation compound sample was characterized by SEM. Figure 1 shows the SEM image of carbon nitride intercalation compound product synthesized through a simple molten salt route. From Figure 1, carbon nitride intercalation compound nanotubes can be observed.

Figure 1. SEM image of carbon nitride intercalation compound photocatalyst.
The morphology and size information of the carbon nitride intercalation compound sample were further characterized by high-resolution SEM. Figure 2 shows the SEM image of carbon nitride intercalation compound product. From Figure 2, the higher magnified SEM image exhibits the size of carbon nitride intercalation compound nanotubes is about 500 nm. The morphology of nanotube leads to the significant difference in BET surface area: 110 m$^2$·g$^{-1}$ for carbon nitride intercalation compound and 8 m$^2$·g$^{-1}$ for bulk g-C$_3$N$_4$.

![Figure 2. High-resolution SEM image of carbon nitride intercalation compound photocatalyst.](image)

In addition, photocatalytic oxidation of MO on the as-prepared carbon nitride intercalation compound sample and bulk g-C$_3$N$_4$ is performed. Figure 3 shows that photocatalytic oxidation of MO by using the above-mentioned carbon nitride intercalation compound sample and bulk g-C$_3$N$_4$ as photocatalysts. From Figure 3, the carbon nitride intercalation compound exhibit much higher activity than bulk g-C$_3$N$_4$, which is ascribed to the more reaction sites produced by relatively higher specific surface area.

![Figure 3. Comparison of MO degradation over different photocatalysts, g-C$_3$N$_4$ (a) and carbon nitride intercalation compound sample (b).](image)

4. Conclusion
In summary, by a simple molten salt route, the carbon nitride intercalation compound samples have been prepared, which exhibit much higher photocatalytic activity in photodegradation of MO compared with bulk g-C$_3$N$_4$ sample. The high photocatalytic activity of the carbon nitride intercalation compound nanotubes is ascribed to high specific surface area with producing the more reaction sites.
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