Metal-free photocatalyst for degradation of organic pollutants in water

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Introduction

Photocatalysis has been widely employed for production of solar fuels or degradation of pollutants in air or water.[1] Most research endeavors have been engaged in the development of novel photocatalysts, which mainly are metal-based materials, such as TiO_2, ZnO, CdS and $InTaO_4$, etc.[2] The scarcity in nature, high cost, and potential metal leaching by photo-corrosion of metal-based materials have prevented their wide applications. Recently metal-free photocatalysts have attracted extensive attention. Graphitic carbon nitride (g-C_3N_4) as a typical meta-free polymer has demonstrated its effectiveness in photocatalytic hydrogen production from water under visible light irradiations. Due to the large particle size and low specific surface area, the activity was quite low.[3] Graphene is a honeycomb-structured carbon sheet with sp^2 bonding, and has unique electronic properties, large theoretical specific surface area up to 2000 m^2/g, and high transparency. It has been reported that graphene can significantly improve the efficiency of photocatalysts. Recently graphene oxide was shown as an excellent photocatalyst for photocatalytic CO_2 conversion.[4]

In this study, we report that a novel hybrid of graphene-g-C_3N_4 can be prepared by a simple method of thermal polycondensation of melamine with graphene oxide (GO). The metal-free hybrids showed promising activity in degradation of organic pollutants, such as phenol and methylene blue (MB) under different light irradiations.

Materials and Methods

The composites of graphene and g-C_3N_4 were prepared by calcination of 4 g melamine at 550 ^oC for 4 h with 0.1, 0.2, 0.4 and 0.6 g GO, and denoted as G-CN-1, G-CN-2, G-CN-3 and G-CN-4, respectively. Pure g-C_3N_4 was prepared by polycondensation of 4 g melamine in same condition without GO, labelled as CN. The photocatalyst materials were thoroughly investigated by a variety of characterization techniques, such as X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transition electron microscopy (TEM), nitrogen sorption isotherm, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and UV-visible diffuse reflectance spectroscopy (UV-vis). The photocatalytic activities of the G-CN series catalysts were evaluated by photodegradation of MB and phenol under different light irradiations. Initial phenol concentration was 20 ppm, and initial MB concentration was 10 ppm.

Results and Discussion

Characterization showed that the composites of rGO and g-C_3N_4 were successfully prepared. The introduction of rGO to g-C_3N_4 significantly improved the visible light absorption, partially reflected by the color change of CN to G-CN-4 from bright yellow to dark grey. Their photocatalytic activities were investigated. **Figure 1** (A) shows the control experiments in photodegradation of MB and phenol solutions using G-CN-3. In adsorption of MB, sorption equilibrium reaches at about 30 min, showing 23% adsorption of 10 ppm MB. However, adsorption of phenol was not significant and only 4% phenol removal was found within 30 min adsorption. Without a catalyst, only minor MB, 6% in 3 h was degraded by UV-visible light irradiation. **Figure 1** (B) reveals that the metal-free g-C_3N_4 can efficiently degrade MB. After 30 min adsorption and 180 min photocatalysis under visible light, 90% MB was removed. Introduction of rGO would significantly improve the adsorption and photocatalytic ability. Adsorption increases with the increasing rGO amount in the hybrids.[5] G-CN-4 provided 29% MB adsorption at 30 min. G-CN-3 and G-CN-4 showed similar activity, and were able to remove all MB within 180 min. Further studies showed that the metal-free photocatalysts can also effectively decompose phenol under different irradiations. Kinetic studies, such as the effects of catalyst loading, reaction temperature, initial phenol solution on phenol degradation were carried out. The studies suggested that the hybrid catalysts can degrade dyes and phenolics under various light irradiations.

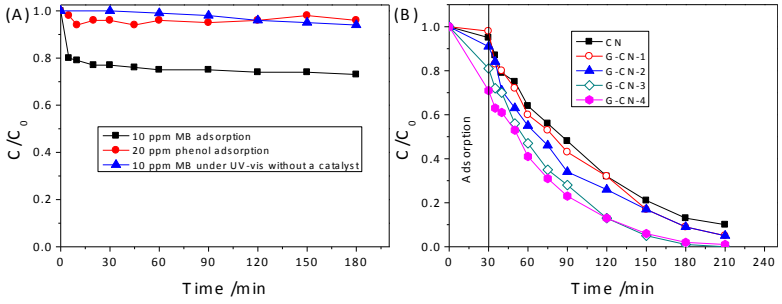

Figure 1. (A) Adsorption and photolysis of MB or phenol, (B) Photodegradation of MB under visible light irradiations ($\lambda > 390$ nm).

Significance

A very simple method was applied to introduce rGO to g-C_3N_4 to significantly improve the adsorption and photodegradation abilities of g-C_3N_4. The metal-free materials demonstrated promising capability to remove dyes or phenolics from water. This study provides a green material for remediation of water pollution with the utilization of solar energy.

References

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