Preparation of MgO/*g*-C_3N_4 composite and it enhanced photocatalytic activity

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Abstract. Graphitic carbon nitride (*g*-C_3N_4) attracts considerable attention due to its photocatalytic activity with visible light. In this paper, MgO/*g*-C_3N_4 was prepared by self-condensation of NH_4SCN at high temperature under the presence of magnesium acetate, and its photocatalytic performance was measured by photodegradation of methyl orange under simulated solar radiation. According to the results, the photocatalytic activity on MgO/*g*-C_3N_4 is three times as large as that on *g*-C_3N_4.

Introduction

Nowadays a huge energy crisis is coming up and increasing its seriousness. It is estimated that world needs double its energy supply by 2050[1]. How to use solar energy, a kind of renewable energy source widely distributed around the world, attracts much attention. After predicted the structure by Liu and Cohen [2], and found photoreaction ability by Wang [3], graphitic carbon nitride (*g*-C_3N_4) comes into scientists' sight. Different kinds of substances have been used to produce *g*-C_3N_4, such as melamine [3] and ammonium thiocyanate [4]. Yet the photocatalytic performances of these *g*-C_3N_4 materials are below the expectation, therefore, many researchers endeavor to improve the photocatalytic performance of g-C_3N_4. One of the effective routes is to dope metal oxide into g-C_3N_4, and ZnO [5-7], WO_3 [8]and TiO_2 [9] are two good candidates for their photocatalytic activity under UV light. Considering chlorophyll exhibits photocatalytic activity under sunlight and the core of chlorophyll is Mg^{2+}, doping MgO is expected to be an effective route. Although electrochemical intercalation [10] and dispersing *g*-C_3N_4 into saturated solution [11] have been used to modify *g*-C_3N_4, there is no further comparison of the photocatalytic activity between pure and Mg^{2+} doped g-C_3N_4 materials. In the present work, a new method is employed to prepare MgO doped *g*-C_3N_4 material (MgO/*g*-C_3N_4), using ammonium thiocyanate and magnesium acetate as precursors. It is delighted to find that this MgO/*g*-C_3N_4 exhibits a photocatalytic performance much higher than *g*-C_3N_4.

Experimental

Preparation of *g*-C_3N_4. A certain amount of ammonium thiocyanate was put into a crucible with a lid and calcined at 550°C in a muffle furnace for 4 h. The resulting sample was denoted *g*-C_3N_4.

Preparation of MgO/g-C_3N_4. 2 g of magnesium acetate tetrahydrate and 20 g of NH_4SCN were dissolved in ca. 30 mL of water under stirring, and then water was evaporated. The mixture was transferred into a crucible with a lid and calcined at 550 °C in a muffle furnace for 4 h. The resulting sample was denoted MgO/*g*-C_3N_4.

Photodegradation of methyl orange. Photodegradation of methyl orange was performed under irradiation with a 300 W Xenon lamp. 0.1g of catalyst was added into 100 mL of methyl orange (5 mg/L). Before exposed to Xe lamp, the suspension was stirred in the dark for 60 min to ensure the adsorption–desorption equilibrium on the catalyst surface. During the photoreaction, 5 mL of suspension was removed by a syringe every 5 min and immediately filtered. The filtrate was analyzed with a UV-visible spectrophotometer at λ=470nm using pre-constructed calibration curves.

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Results and discussion

G-C_3N_4 prepared by self-condensation of NH_4SCN at high temperature is a yellow powder, which is similar to the *g*-C_3N_4 prepared by self-condensation of melamine. The color of the MgO-doped *g*-C_3N_4 is brown, which indicates that the introduction of MgO affects the appearance of *g*-C_3N_4.

The photocatalytic performance of samples was characterized by studying the photodegradation of methyl orange aqueous solution (5 mg/L) with simulated solar radiation, and the reaction results were listed in Tables 1 and 2. It can be found that the concentrations of methyl orange were approximately equal after stirring in dark for 60 min, indicating that the adsorption abilities of two catalysts were close. After exposed to light, concentration of methyl orange solution with *g*-C_3N_4 dropped from 4.87 $mg \cdot L^{-1}$ to 3.16 $mg \cdot L^{-1}$, 64.9% of initial concentration, in 30 minutes and to 2.07 $mg \cdot L^{-1}$, 42.5% of initial concentration, in 60 minutes. While concentration of solution with MgO/*g*-C_3N_4 diminished sharply, from 4.81 $mg \cdot L^{-1}$ at beginning to 1.29 $mg \cdot L^{-1}$ in 30 minutes and to 0.373 $mg \cdot L^{-1}$ in 60 minutes, indicating 92.2% of methyl orange was degraded in one hour.

As shown in Fig. 1, the photodegradation kinetics of methyl orange on both catalysts can be fitted to a straight line, described as $\ln(C_0/C)=kt$, where C_0 is the initial concentration of methyl orange, C is actual concentration of methyl orange at various irradiation time t, and k is degradation rate constant (min^{-1}). It follows a pseudo-first-order reaction. The photodegradation rate constants obtained from the slopes of the simulated straight lines are 0.043 and 0.014 min^{-1} for MgO/*g*-C_3N_4 and *g*-C_3N_4, respectively. The former is 3 times as high as the latter. It clearly shows that the photocatalytic activity of *g*-C_3N_4 is greatly promoted by introducing MgO.

Table1. Photodegradation result of methyl orange on *g*-C_3N_4

Time（min）	C（$mg \cdot L^{-1}$）	C_0/C	$\ln C_0/C$
Mother solution	5.00	/	/
0	4.87	1.000	0.0000
5	4.40	1.107	0.1017
10	4.09	1.191	0.1748
15	3.85	1.265	0.2351
20	3.61	1.349	0.2994
25	3.30	1.476	0.3894
30	3.16	1.541	0.4324
60	2.07	2.353	0.8557

Table2. Photodegradation result of methyl orange on MgO/*g*-C_3N_4

Time（min）	C（$mg \cdot L^{-1}$）	C_0/C	$\ln C_0/C$
Mother solution	5.00	/	/
0	4.81	1.000	0.0000
5	4.06	1.183	0.1684
10	3.39	1.416	0.3481
15	2.78	1.730	0.5482
20	2.12	2.268	0.8187
25	1.67	2.646	0.9729
30	1.29	3.745	1.3205
60	0.373	12.82	2.5510

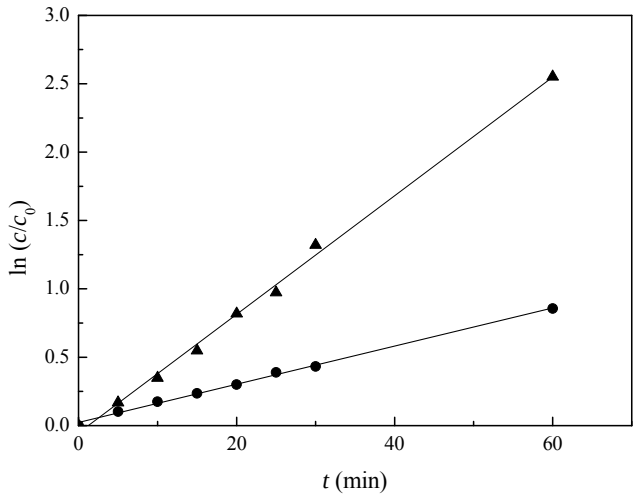

Fig. 1. Photodegradation of methyl orange on MgO/*g*-C_3N_4(▲) and *g*-C_3N_4 (●) under irradiation with a 300 W Xenon lamp.

Summary

Doping MgO can enhance photocatalytic activity of *g*-C_3N_4, and the photodegradation rate constant for MgO/*g*-C_3N_4 is three times as large as that for *g*-C_3N_4. Yet more work is still needed to reveal the change of sample structure.

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