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Facile synthesis of nanorod-type graphitic carbon nitride/Fe_2O_3 composite with enhanced photocatalytic performance

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ABSTRACT

Here we report a facile synthesis of nanorod-type graphitic carbon nitride/Fe_2O_3 composite (Fe_2O_3-g-C_3N_4) by using Fe-melamine supramolecular framework as precursor. The chemical and optical properties of the nanocomposites are well-characterized. The Fe_2O_3-g-C_3N_4 nanocomposite demonstrated excellent photocatalytic activities under visible light due to the efficient utilization of sunlight and the construction of Z-scheme electron transfer pathway. The results indicated that it could be a promising approach for the preparation of efficient g-C_3N_4 nanocomposites photocatalysts by using metal-melamine supramolecular framework as precursors.

1. Introduction

In recent years, much more attentions have been focused on environmental protection and energy conservation [1–6]. Intensive researches on converting solar energy into chemical energy are also stimulated. Semiconductor photocatalysis has emerged as an inherently green, promising technology [7–10]. However, traditional photocatalysts such as TiO_2 and ZnO ca not satisfy practical requirements due to their low utilization of solar energy and the wide band gaps, which can only absorb the UV light [11]. Although different modified TiO_2 photocatalysts have been fabricated, it is still a challenge to design new photocatalysts that are abundant, stable, facile, easy-prepared, as well as having strong visible light response [12–18].

Carbon nitride material has drawn widespread attention duo to its excellent photochemistry stability and attractive electronic structure [19–22]. Its nontoxicity, high stability and low price further make it become a promising catalytic material which is applied in many fields, such as water splitting, pollutants degradation, solar cells, and so on [23–33]. However, it faces three main drawbacks: rapid recombination of photo-generated charge carriers, small specific surface and low visible light utilization efficiency. Therefore it is urgent to synthesize modified **g-C_3N_4** based photocatalysts with high photocatalytic activities [34–44].

Metal-organic supramolecular network, self-assembled from metallic nodes and organic ligands through metal coordination and non-covalent bonds, have emerged as promising precursors for the fabrication of metal oxide/carbon composites or porous carbon materials [45–47]. Recently, we found that **g-C_3N_4** with special structure and defined morphology could be prepared by calcificating preorganized metal-organic supramolecular network at proper thermal condensation conditions [48,49]. Using metal-organic supramolecular network as both sacrificial template and precursor to synthesis **g-C_3N_4** is a promising approach which has several advantages. The structure of metal-organic supramolecular network can be tailored by changing metals and ligands, synthesis conditions (temperature, solvent, molar ratio of metal ions and ligands, etc.) [50–52]. Besides, the formation of metal oxide/g-C_3N_4 nanocomposites leaded by metal coordination and non-covalent bonds can improve the utilization of solar energy. However, for typical synthesis of metal oxide/g-C_3N_4 composites, a two-step depositing of metal oxides on g-C_3N_4 is usually needed. To the best of our knowledge, reports on the synthesis of metal oxide/g-C_3N_4 nanocomposite materials with well-controlled structure by metal-organic supramolecular networks are still scarce.

Herein we report a facile synthesis method for the preparation of nanostructured **Fe_2O_3-g-C_3N_4** composites with enhanced

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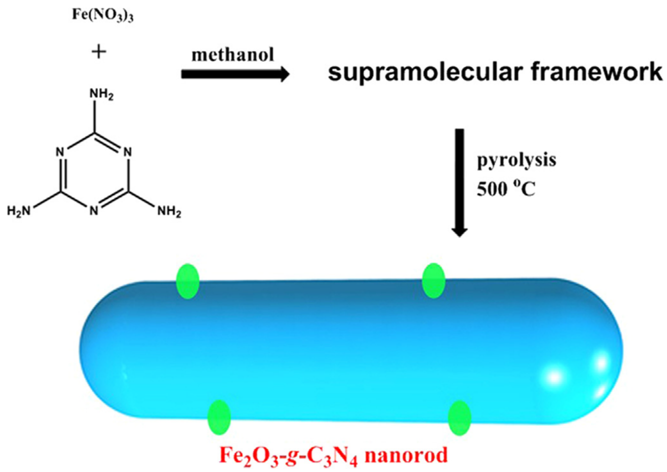

Scheme 1. Preparation of nanorod-like Fe_2O_3-g-C_3N_4 from Fe-melamine supramolecular framework.

photocatalytic properties by using Fe-melamine supramolecular framework as precursor (Scheme 1). The chemical structure, morphology and optical properties of this graphitic carbon nitride/**Fe_2O_3** composite were characterized by XRD, FT-IR, SEM, UV–vis absorption, elemental analysis. The photocatalytic activities were investigated in depth by measuring the degradation of rhodamine B dye under visible light illumination in the presence of the resulting carbon nitrides.

2. Experimental section

2.1. Materials and general methods

All chemicals were purchased from Alfa Aesar, TCI chemical and Aldrich and used without further purification. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu Ka radiation. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min up to 800 °C under N_2 atmosphere. UV–vis absorption spectra were obtained using a Hitachi U-2900 spectrophotometer. Elemental analyses were obtained from a ThermoFinnigan Instruments Flash EA1112 microelemental analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas. The N_2 adsorption-desorption isotherms at 77 K were measured on a Micrometrics ASAP 2010 system to evaluate their pore structures. All the samples were degassed at 120 °C for 2 h before the surface area measurements. The morphologies of the photocatalysts were observed by field emission scanning electron microscopy (FE-SEM, Vltra55, Carl Zeiss) and transmission electron microscopy (TEM, JEM-2100). X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermal Fisher Scientific K-Alpha electron spectrometer. The optical diffuse reflectance spectra were measured on a PerkinElmer Lambda 750 s UV–vis–NIR spectrometer equipped with an integrating sphere. $BaSO_4$ was used as the reference material, and the polycrystalline samples were ground well before the measurement. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function: $\alpha/S=(1-R)2/2R$, in which R is the reflectance at a given wavelength, α is the absorption coefficient, and S is the scattering coefficient.

2.2. Synthesis

2.2.1. Synthesis of photocatalyst

FeMA was synthesized according to literature reported method [53]. $Fe(NO_3)_3\cdot 9H_2O$ (8.0 g, 20 mmol) and melamine (2.5 g, 20 mmol) was added to methanol (200 mL). The mixture was refluxed for 3 h. After cooling down to room temperature, the deep yellow solid was filtered, washed with diethyl ether twice and dried under vacuum. Yield: 8.0 g (72%).

Fe_2O_3-*g*-C_3N_4 was fabricated by heating FeMA framework in furnace at 500 °C for 4 h under Ar with a heating rate of 2 °C/min.

2.3. Photocatalytic experiments

The evaluation of photocatalytic activities of the samples for the visible light photocatalytic degradation of organic dyes was performed at ambient temperature (25 °C). The procedure was as follows: 40 mg of sample was dispersed into 50 mL of rhodamine B (RhB) aqueous solution ($10\ mg\ L^{-1}$), followed by addition of 0.5 mL of hydrogen peroxide solution (H_2O_2 30%). The solution was stirred under dark condition for 60 min to achieve adsorption equilibrium prior to the irradiation. Then, the photocatalytic dye degradation was carried out by irradiating the suspension with a 300 W xenon lamp coupled with a UV cut-off filter ($\lambda > 400$ nm). During the degradation, the mixture was stirred continuously by means of a magnetic stirrer. The samples were withdrawn regularly from the reactor (1 mL), and dispersed powders were removed by centrifugation. At different time intervals, analytical samples were withdrawn and analyzed by UV–vis spectroscopy. The degradation efficiency was determined by dividing C/C_0, where C is the remained RhB concentration and C_0 is the starting RhB concentration. The recycle of photocatalytic degradation of RhB was performed by centrifuging the reaction solution and reusing the catalyst for three times.

3. Results and discussion

The supramolecular framework (**FeMA**) was formed by mixing $Fe(NO_3)_3$ and melamine in methanol, getting a deep yellow solid after refluxing for 3 h. **Fe_2O_3-*g*-C_3N_4** nanocomposite was fabricated by heating **FeMA** at 500 °C for 4 h under argon atmosphere. Bulk ***g*-C_3N_4** was prepared by heating melamine at 500 °C at the same condition. The XRD pattern of **Fe_2O_3-*g*-C_3N_4** is shown in Fig. 1. The peaks at 18.41°, 31.25° and 33.76° could be assigned to the (113), (216) and (109) peaks of typical ***r*-Fe_2O_3** phase. The

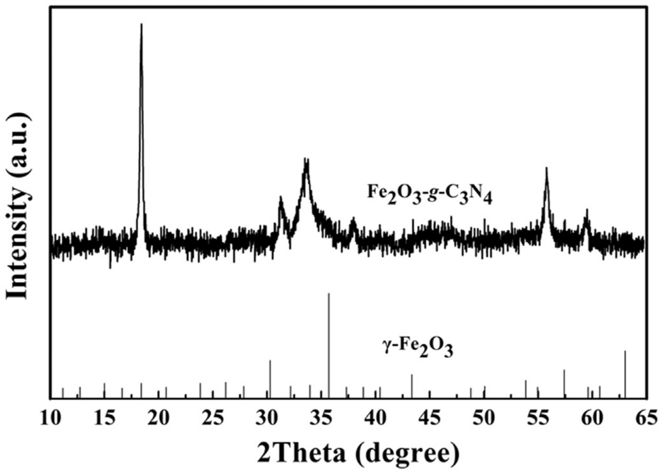

Fig. 1. The powder XRD patterns for **Fe_2O_3-*g*-C_3N_4** and ***g*-C_3N_4**.