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Enhancing the photocatalytic activity of bulk g-C_3N_4 by introducing mesoporous structure and hybridizing with graphene

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ABSTRACT

Bulk graphitic carbon nitride (CN) suffers from small surface area and high recombination of charge carriers, which result in low photocatalytic activity. To enhance the activity of g-C_3N_4, the surface area should be enlarged and charge carrier separation should be promoted. In this work, a combined strategy was employed to dramatically enhance the activity of bulk g-C_3N_4 by simultaneously introducing mesoporous structure and hybridizing with graphene/graphene oxide. The mesoporous g-C_3N_4/graphene (MCN-G) and mesoporous g-C_3N_4/graphene oxide (MCN-GO) nanocomposites with enhanced photocatalytic activity (NO removal ratio of 64.9% and 60.7%) were fabricated via a facile sonochemical method. The visible light-harvesting ability of MCN-G and MCN-GO hybrids was enhanced and the conduction band was negatively shifted when 1.0 wt% graphene/graphene oxide was incorporated into the matrix of MCN. As electronic conductive channels, the G/GO sheets could efficiently facilitate the separation of chare carriers. MCN-G and MCN-GO exhibited drastically enhanced visible light photocatalytic activity toward NO removal. The NO removal ratio increased from 16.8% for CN to 64.9% for MCN-G and 60.7% for MCN-GO. This enhanced photocatalytic activity could be attributed to the increased surface area and pore volume, improved visible light utilization, enhanced reduction power of electrons, and promoted separation of charge carriers. This work demonstrates that a combined strategy is extremely effective for the development of active photocatalysts in environmental and energetic applications.

1. Introduction

Visible light-driven semiconductor photocatalytic technology has been the focus of considerable worldwide attention during the past decades because of its great potential in solving current environmental pollution and energy problems [1–5]. To date, the majority of research on photocatalysts is focused on photocatalysts containing metals such as metal oxide, metal sulfide, metal halides, tungstates, niobates, tantalates, and vandates [6–8]. However, the development of efficient, sustainable, and environmental-friendly photocatalysts remains a significant challenge.

Recently, Wang et al. reported that a new kind of conjugated polymer semiconductor, graphitic carbon nitride (g-C_3N_4), can be used as an attractive metal-free organic photocatalyst that can work in visible light [9]. g-C_3N_4 possesses a high thermal and chemical stability as well as appealing electronic and optical properties. As a multifunctional catalyst, g-C_3N_4 has been applied in photosynthesis, energy conversion and storage, contaminants degradation, carbon dioxide storage and reduction, solar cells, and sensing [10,11]. Nevertheless, the photocatalytic efficiency of bulk g-C_3N_4 is limited because of its low surface area and the fast recombination rate of photogenerated electron–hole pairs. To resolve these problems, numerous strategies have been employed to modify the bulk g-C_3N_4, such as texture tuning by templates, band gap modification by heteroatoms doping, post-functionalization, and semiconductor coupling [12–18].

The use of carbonaceous materials, such as fullerenes (C_{60}) [19], carbon nanotubes (CNTs) [20], graphene (G) [21], and graphene oxide (GO) [22], for the enhancements of conductivity and photocatalytic performances of semiconductors has attracted wide research interest because of their special structures and unique electronic properties. Several research groups have developed novel heterojunction photocatalysts by combining g-C_3N_4 with carbonaceous materials. In particular, great interest is focused on combining g-C_3N_4 with graphene-based materials to improve its conductivity and catalytic performance. Graphene, a single two-dimensional π-conjugation nanosheet of sp^2 hybridized carbon, is a zero band gap semiconductor with outstanding mechanical, thermal, and optical properties, massless fermions, ballistic electronic

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transport, and ultrahigh electron mobility [23,24]. Graphene oxide is the oxidative mode of graphene, which possesses two-dimensional π-conjugation structure and superior electric property. Graphene oxide was also employed as an effective electron acceptor, which could efficiently facilitate charge separation [22]. Graphene and graphene oxide have been coupled with g-C_3N_4. Xiang et al. reported that graphene/C_3N_4 composite materials can be synthesized with enhanced visible light photocatalytic H_2 production activity via a combined impregnation-chemical reduction strategy [21]. Liao et al. fabricated graphene oxide-modified g-C_3N_4 with efficient photocatalytic capability under visible light irradiation via a sonochemical approach [22]. These studies showed that graphene/graphene oxide could effectively improve the photocatalytic performance of g-C_3N_4 photocatalysts.

Previously, mesoporous C_3N_4 has been fabricated from the pyrolysis of thiourea by introducing mesoporous structure in g-C_3N_4 via SiO_2 template [18]. Mesoporous C_3N_4 possesses controllable morphology, tunable pore diameter, higher surface areas, and larger number of active sites on the surface compared with the bulk g-C_3N_4. However, the separation of photogenerated electron–hole pairs and the efficiency of charge immigration need further improvement to significantly promote the photocatalytic activity.

In this work, to address the drawbacks of bulk g-C_3N_4 with low surface area and high charge carrier recombination rate, we need to develop a combined strategy which is based on the simultaneous creation of mesoporous structure and hybridization with graphene or graphene oxide. We prepared mesoporous g-C_3N_4/graphene (MCN-G) and mesoporous g-C_3N_4/graphene oxide (MCN-GO) nanocomposites via a facile sonochemical method. The as-prepared MCN-G and MCN-GO were applied to remove NO at 600 ppb level in air under visible-light irradiation. These nanocomposites photocatalysts exhibited highly enhanced performance, which can be ascribed to the increased surface areas, extended visible light absorption range, adjusted band structure, and enhanced separation of charge carriers.

2. Experimental section

2.1. Synthesis of mesoporous carbon nitride

All reagents used in this research were of analytical grade and utilized without further purification. The typical procedure for the synthesis of mesoporous carbon nitride followed the hard-templating method, in which 10 g of dicyandiamide was dispersed into 150 mL of distilled water. About 5 g of commercial SiO_2 with a high surface area (380 m^2/g, see Fig. S1) was then gradually added into the dicyandiamide solution with vigorous stirring for 12 h. The aqueous mixture was dried in an oven at 120 °C for 12 h. The obtained white powder was put into a 50 mL alumina crucible with a cover and heated to 550 °C for 2 h with a heating rate of 15 °C min^{-1}. The released air products during thermal treatment were absorbed by dilute NaOH solution of 0.05 M. After cooling to room temperature, the obtained bright yellow powders were treated in 100 mL of 4 M of ammonium hydrogen difluoride (NH_4HF_2) for 24 h to remove the SiO_2 template. The powders were then subjected to centrifugation and washed with distilled water and ethanol three times. Finally, the product was dried at 80 °C in an oven overnight. The resulting mesoporous sample was denoted as MCN. The bulk C_3N_4 (for simplicity: CN) was also prepared by heating dicyandiamide in a muffle furnace at the same thermal condition without the addition of the SiO_2 template.

2.2. Synthesis of MCN-G and MCN-GO composite photocatalysts

Graphene (G) and graphene oxide (GO) were purchased from Nanjing Xianfeng Chemical Factory. The MCN-G and MCN-GO composite photocatalysts were prepared via a facile sonochemical method. A specific amount of G/GO was added into 50 mL of ethanol followed by consecutive sonication for 60 min at 40 °C. Subsequently, 0.4 g of MCN was added into the G/GO suspension and stirred for 60 min. After which, the dispersion was dried in an oven at 150 °C for 4 h. The weight ratio of G/GO to MCN was controlled at 1.0 wt%. The resultant products were labeled as MCN-G and MCN-GO.

2.3. Characterization

The crystal structures of the samples were investigated using an X-ray diffractometer (XRD: model D/max RA, Japan). FT-IR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets (FT-IR: Nicolet, USA). The morphology and structure of the samples were characterized via transmission electron microscopy (TEM: JEM-2010, Japan) and scanning electron microscopy (SEM: JSM-6490, Japan). The optical absorption properties for the samples were obtained using a scan UV–vis spectrophotometer (UV–vis DRS: Shimadzu UV-2450, Japan) equipped with an integrating sphere assembly, and 100% $BaSO_4$ was used as the reflectance sample. X-ray photoelectron spectroscopy with Al Kα X-rays ($h\nu$ = 1486.6 eV) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties and probe the total density of the state (DOS) distribution in the valence band. The shift of the binding energy caused by relative surface charging was corrected using the C1s level at 284.8 eV as an internal standard. Nitrogen adsorption–desorption isotherms were obtained using a nitrogen adsorption apparatus (BET-BJH: Micromeritics ASAP 2020, USA) with all samples degassed at 150 °C prior to measurements. The photoluminescence spectra (PL) for the samples were obtained using a fluorescence spectrophotometer (PL: FS-2500, Japan) with an Xe lamp with optical filter as the excitation source. Electrochemical impedance spectroscopy (EIS) was conducted using a CHI 660 B electrochemical system (CHI: Chenhua CHI660, China) with a standard three-electrode cell. The working electrode was prepared according to the following process. First, 20 mg of the sample was suspended in 0.5 mL of DMF, which was then dip-coated on a 10 mm × 20 mm indium-tin oxide (ITO) glass electrode. The electrode was then annealed at 350 °C for 1 h at a heating rate 6 °C min^{-1}. EIS was carried out at the open-circuit potential. A sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of $0.05–1 \times 10^5$ Hz.

2.4. Visible light photocatalytic activity

The photocatalytic activities for the obtained products were evaluated by the oxidation of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, which was made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). A 150 W commercial tungsten halogen lamp was vertically placed above the reactor. A UV cutoff filter (420 nm) was adopted to remove UV light in the light beam. 0.1 g of the as-prepared photocatalysts was added into 30 mL of H_2O and sonicated for 10 min, and then the resultant suspension was coated onto two dishes with a diameter of 12.0 cm, respectively. The coated dishes were then pretreated at 70 °C to remove water in the suspension. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 600 ppb by the air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 2.4 L/min by using a mass flow controller. After achieving