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Facile fabrication of a direct Z-scheme Ag_2CrO_4/g-C_3N_4 photocatalyst with enhanced visible light photocatalytic activity

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ABSTRACT

Graphite-like carbon nitride (g-C_3N_4) and silver-based compounds have attracted considerable attentions due to their excellent optical characteristic and photocatalytic performance. In this work, Z-scheme silver chromate-g-C_3N_4 nanosheets photocatalysts were prepared by binding growth of Ag_2CrO_4 nanoparticles on the surface of g-C_3N_4 nanosheets (g-C_3N_4-N) via a facile precipitation method. The morphologies, structure, specific surface area and optical property of the prepared photocatalysts were characterized by X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), high resolution-transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectra (UV-vis DRS) and photoluminescence (PL) spectra. The photocatalytic performances of the prepared Ag_2CrO_4/g-C_3N_4-N were evaluated by photodegradation of methyl orange (MO) and rhodamine B (RhB) under visible light irradiation ($\lambda > 400$ nm). The experiment results indicated that Ag_2CrO_4/g-C_3N_4-N composites presented enhanced photocatalytic activity and stability in the degradation of the dye contaminants in aqueous solution. The optimal composites with the mass ratio of Ag_2CrO_4 to g-C_3N_4-N as 50% (CNA-50) showed the highest photocatalytic activity for MO degradation, which is 5.9 and 10.8 times than those of pure Ag_2CrO_4 and pure g-C_3N_4-N, respectively. The formation of Ag_2CrO_4/g-C_3N_4-N Z-scheme heterojunction contributed to the improved photodegradation efficiency, which can not only promote the separation and transportation efficiencies of the photogenerated electron-hole pairs, but also present strong redox ability. And meanwhile the excellent transportation efficiency of the photogenerated electrons from Ag_2CrO_4 to g-C_3N_4-N greatly hindered the photocorrosion of Ag_2CrO_4 nanoparticles. This work provides a new understanding into the mechanism of the g-C_3N_4-N based composite and gives a new insight into the design and fabrication of Z-scheme photocatalysts.

1. Introduction

In recent years, photocatalytic degradation based on semiconductor materials has attracted great attentions, which was regarded as a green and environmental friendly strategy and employed in the decomposition of the organic pollutants into harmless or non-hazardous compounds under light irradiation [1–4]. It is known that TiO_2 is the most widely used photocatalyst and owns excellent photocatalytic activity and stability, but its practical applications have been broadly limited due to its wide band gap and high recombination rate of photo-generated electron-hole pairs [5–7]. Therefore, it is necessary to design novel and efficient visible-light-active photocatalysts. Recently, many new types of visible-light active photocatalysts have been developed, such Fe_2O_3 [8,9], Bi_2WO_6 [10,11], $BiVO_4$ [12,13], Cu_2O [14] and WO_3 [15,16]. Among these photocatalysts, silver-based compounds have attracted great attentions due to their high utilization efficiencies of visible light [17,18]. For example, Zhao et al. reported the simple in-situ synthesis of Ag/$AgVO_3$ one-dimensional hybrid nanoribbons and their potential application in the degradation of organic contaminants [19]. Ma et al. reported a facile method for the synthesis of Ag_3PO_4 nanoparticles and present high degradation efficiency of RhB under visible light [20]. Besides, it was reported that Ag_2CO_3 nanorods with porous structure performed enhanced photocatalytic activity [21]. Other silver compounds, such as silver halides or their hybrid

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composites were also reported for photodegradation application [22–24]. Notably, among various silver-based photocatalysts, silver chromate (Ag_2CrO_4) is regarded as a promising candidate for the efficient photocatalysts due to its unique crystal structure and electronic structure, and with a narrow band gap of ~1.80 eV [25–27]. Unfortunately, similar to most of the silver-based composites, the photocorrosion for Ag_2CrO_4 is a thorny problem, which greatly hinders their photocatalytic performance. Therefore, it is important to find and design an effectively Ag_2CrO_4 based photocatalysts with better stability and higher activity. Ag_2CrO_4-GO composites were reported to improve the photocatalytic activity and stability of Ag_2CrO_4 [25]. However, there still exists a lot of work to be done to develop more efficient photocatalysts.

Recently, graphite-like carbon nitride (g-C_3N_4), a kind of polymeric metal-free semiconductor materials with a narrow band gap of 2.7 eV, used in the photocatalytic water splitting and photodegradation field, has attracted much attention due to its excellent optical characteristic and photocatalytic performance [28–30]. However, the photocatalytic performance of pure g-C_3N_4 is still limited due to the high recombination rate of its photogenerated electron-hole pairs and low specific surface areas [31]. Thus, a variety of g-C_3N_4 based photocatalysts, such as Co_3O_4/g-C_3N_4 [32], Cu_2O/g-C_3N_4 [33], AuPt/g-C_3N_4 [34], $CuFe_2O_4$/g-C_3N_4, [35] TiO_2–In_2O_3/g-C_3N_4 [36], and Ag_2CO_3 [37] have been developed. However, as a kind of photocatalysts, the lower specific surface area of g-C_3N_4 is still not satisfying enough for high photocatalytic performance. To further enhance the photocatalytic activity of g-C_3N_4, many researchers have focused their attentions on the preparation of bulk g-C_3N_4 into 2D ultrathin g-C_3N_4 nanosheets, since the structure of nanosheets possesses large specific surface area for giving quantities of reactive sites and short photogenerated carrier diffusion length for reducing their recombination efficiency [38,39]. Additionally, it is certified that g-C_3N_4 can also act as an efficient photocatalyst for hydrogen production in the water splitting system due to its negative conduction band position [40–42]. Thus, it is possible to form a Z-scheme Ag_2CrO_4/g-C_3N_4-N photocatalyst with excellent stability and enhanced photocatalytic activity by the combination of Ag_2CrO_4 nanoparticles and g-C_3N_4 nanosheets.

Herein, g-C_3N_4 nanosheets obtained from the bulk g-C_3N_4 through a thermal exploitation method was used as an excellent substrate, and Ag_2CrO_4 nanoparticles were loaded on the surface of g-C_3N_4 nanosheets (g-C_3N_4-N) to prepare a Z-scheme Ag_2CrO_4/g-C_3N_4-N composite photocatalyst for the first time. The as-obtained Ag_2CrO_4/g-C_3N_4 composites showed distinctly enhanced photocatalytic activity than that of pure Ag_2CrO_4 nanoparticles on the degradation of dyes under visible light irradiation. Notably, the photocorrosion of Ag_2CrO_4 was efficiently hindered due to the synergistic effect between Ag_2CrO_4 and g-C_3N_4. Moreover, a Z-scheme mechanism was proposed in Ag_2CrO_4/g-C_3N_4-N based photocatalytic reaction system. The existence of the Z-scheme mechanism means strong redox ability and high transfer efficiency of photogenerated electron-hole pairs. This research will broaden the studies of g-C_3N_4-based photocatalysts with excellent photocorrosion inhibition ability and high photocatalytic activity.

2. Experimental

2.1. .Materials

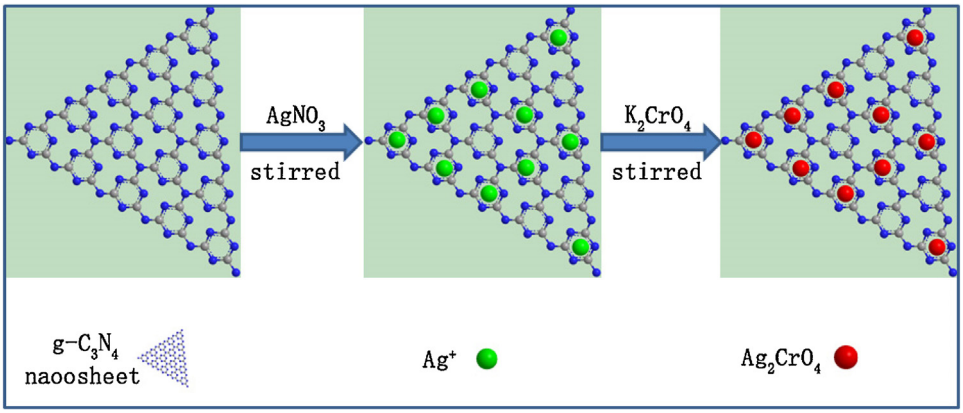
All the reagents and materials were of analytical reagent grade and obtained commercially from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification. Ultra-pure water (18.25 MΩ cm^{-1}) from a Milli-pore Q water purification system was used in all experiments.

2.1. Preparation of g-C_3N_4 nanosheets

The g-C_3N_4 nanosheets were prepared by two stage thermal treatment process according to a previous literature [38,43]. In the first thermal treatment, 5 g of melamine was put into a ceramic crucible with a cover, and then heated at 500 °C for 2 h at a rate of 2 °C/min, and followed by heating at 520 °C for another 2 h at the same heating rate. After cooling down to room temperature naturally, the obtained product was milled into powder in a mortar and used for the second thermal exploitation treatment. In the second thermal exploitation process, 1 g of the bulk g-C_3N_4 was placed in an open ceramic crucible and heated at 520 °C at a heating rate of 2 °C/min and then kept at this temperature for 4 h. A light yellow powder of g-C_3N_4 nanosheets were obtained and used in the following experiments. For a more convenient narrative, the obtained g-C_3N_4 nanosheets were denoted as g-C_3N_4-N in the following description unless otherwise stated.

2.2. Preparation of Ag_2CrO_4/g-C_3N_4-N composites

The Ag_2CrO_4/g-C_3N_4-N photocatalysts were prepared by a self-assembly precipitation method. Typically, 100 mg of the as-prepared g-C_3N_4 nanosheets was dispersed in 100 mL of ultrapure water and sonicated for 6 h to obtain a suspension of g-C_3N_4-N. Then a certain amount of $AgNO_3$ solution (0.06 mol/L) was added into the above suspension and stirred for 1 h to reach complete adsorption of Ag^+ on the surface of g-C_3N_4-N under dark condition. After that, the same amount of K_2CrO_4 solution (0.03 mol/L) was added dropwise into the above Ag^+-g-C_3N_4-N suspension. After stirring for another 4 h, the precipitate was collected by centrifugation and washed with ethanol and water for several times, and dried



Scheme 1. Schematic diagram of the preparation of Ag_2CrO_4 doped g-C_3N_4 nanosheets composites.