



Synthesis and characterization of g-C₃N₄/Cu₂O composite catalyst with enhanced photocatalytic activity under visible light irradiation



Biyu Peng^a, Shengsen Zhang^a, Siyuan Yang^a, Hongjuan Wang^a, Hao Yu^a,
Shanqing Zhang^b, Feng Peng^{a,*}

^a School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

^b Centre for Clean Environment and Energy, Griffith School of Environment, Gold Coast Campus, Griffith University, QLD 4222, Australia

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ABSTRACT

To overcome the drawback of low photocatalytic efficiency brought by electron–hole pairs recombination and narrow photo-response range, a novel g-C₃N₄/Cu₂O composite photocatalyst was designed and prepared successfully. Compared with bare Cu₂O and g-C₃N₄, the g-C₃N₄/Cu₂O composite exhibited significantly enhanced photocatalytic activity for acid orange-II (AO-II) degradation under visible light irradiation. Based on energy band positions, the mechanism of enhanced visible-light photocatalytic activity was proposed.

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1. Introduction

Recently, as a metal-free and n-type polymer semiconductor, graphite-like carbon nitride (g-C₃N₄) with its intrinsic characteristic structure [1] has attracted attentions in the photocatalysis field [2–4]. The optical band gap of this polymer semiconductor was determined to be 2.7 eV. The g-C₃N₄ photocatalyst is considered to be stable under light irradiation in water solution as well as in acid or base solution due to the strong covalent bonds between carbon and nitride atoms [1]. These superior properties suggest that the metal-free g-C₃N₄ has promising potential in the photocatalysis field [5–7]. However, the photocatalytic efficiency of pure g-C₃N₄ remains relatively low because of the fast recombination of the photo-generated electron–hole pairs [8]. In order to further advance this promising photocatalytic material, many researchers have coupled g-C₃N₄ with various semiconductors, such as TiO₂ [9], CdS [10], ZnWO₄ [11], BiPO₄ [12] and SmVO₄ [13], to increase the separation efficiency of photogenerated electron–hole pairs, thus to promote the photocatalytic activity.

Cuprous oxide (Cu₂O) is a well-known p-type semiconducting photocatalytic material with small band gap energy of ca. 2.0–2.4 eV [14–16], which is a great advantage in making full use of sunlight, compared with the wide band gap semiconductors.

Furthermore, Cu₂O possesses other advantage intrinsic properties, such as low toxicity, good environmental acceptability, and low price [17]. Therefore, Cu₂O nanocrystals have been widely studied for water splitting and degradation of organic pollutants under visible light irradiation. However, the photocatalytic efficiency still need to be further improved because of the fast recombination of the photogenerated electron–hole pairs [18–20]. At present, Cu₂O has been coupled with various wide-band gap semiconductors, such as TiO₂ [21,22], ZnO [23], and SnO₂ [24], to increase the separation efficiency of photogenerated electron–hole pairs, thus to promote the photocatalytic activity and photostability of Cu₂O nanocrystals [25,26]. However, the coupled Cu₂O with narrow-band-gap semiconductors has rarely been reported. To this end, it is of particular interest to know whether it is possible to further improve photocatalytic activity of Cu₂O by coupling with matching narrow-band-gap semiconductor.

In this work, to facilitate the photocatalytic activity of both p-type Cu₂O and n-type g-C₃N₄ narrow-band-gap semiconductors under the visible light irradiation, a novel g-C₃N₄/Cu₂O photocatalyst was prepared for the first time by an alcohol-aqueous based on chemical precipitation method. The synthesized photocatalysts were characterized in detail. Acid orange-II (AO-II) was used to investigate the activities of g-C₃N₄/Cu₂O photocatalyst under visible-light irradiation ($\lambda > 400$ nm). The results demonstrated that the g-C₃N₄/Cu₂O photocatalyst, compared with the bare Cu₂O and g-C₃N₄, had a remarkably enhanced activity for AO-II photodegradation under visible-light irradiation.

* Corresponding author. Tel.: +86 20 87114916; fax: +86 20 87114916.

E-mail address: cefpeng@scut.edu.cn (F. Peng).

2. Experimental

2.1. Synthesis of $g\text{-C}_3\text{N}_4$ nanoparticles

The $g\text{-C}_3\text{N}_4$ nanoparticles were synthesized based on a general sol–gel process. 50 mL amino cyanide solution was mixed in 50 mL of silica colloidal solution, the mixed solution was magnetic stirring at room temperature for 5 h, and then the homogeneous and viscous solution was then dried at 70 °C for one hour to get a transparent gel. The obtained gel was transferred into a porcelain boat and calcinated at 550 °C for 4 h under N_2 protection. Finally the resulting dark yellow sample was treated with a 4 M NH_4HF_2 solution (400 mL) for a certain amount of hours to remove the silica template and finally yellow powders were harvested by the low-speed centrifugal settling and washed several times with deionized water and ethanol.

2.2. Preparation of $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}$ composites

A typical $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}$ composite was prepared by an alcohol- aqueous based on chemical precipitation method as follows: 0.007 mol $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in 100 mL absolute ethanol to form a deep green solution, and appropriate amount of $g\text{-C}_3\text{N}_4$ was then dispersed in the solution and was sonicated to obtain a uniform suspension. The suspension was subsequently heated to 60 °C in a water bath, 100 mL glucose aqueous solution (0.2 mol/L) was slowly added into the solution as the reducing reagent. Thereafter, 120 mL NaOH solution (0.3 mol/L, the solvent was composed of 70 mL absolute ethanol and 50 mL distilled water) was added in the solution, producing some yellow precipitates after 120 s. Finally, the precipitates were rinsed twice with DI water and collected using a centrifuge, and dried overnight in an oven at 80 °C to yield the products. The as-prepared samples were denoted as $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}\text{-}Y$, where Y corresponds to the weight percentage of $g\text{-C}_3\text{N}_4$ in composites (5, 10, 20, and 30).

2.3. Characterizations of $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}$ composites

X-ray diffraction (XRD) analysis was carried out on an X-ray diffractometer (D/max-III A, Japan) using $\text{CuK}\alpha$ as radiation source, the applied current and voltage were 30 mA and 30 kV, respectively. Scanning electron microscopic (SEM) images were obtained in a LEO 1530 VP microscope equipped with a field emission gun. Fourier transform infrared (FT-IR) measurements were performed using a FT-IR spectrometer (Nicolet 670) only in the mid infrared range of the instrument ($400\text{--}4000\text{ cm}^{-1}$) for samples dispersed in KBr pellets in 1:99 ratios. The chemical nature of Cu was studied

using X-ray photoelectron spectroscopy (XPS) in Krato Axis Ultra DLD spectrometer with $\text{AlK}\alpha$ X-ray ($h\nu = 1486.6\text{ eV}$) at 15 kV and 150 W. The binding energy was referenced to C1s line at 284.6 eV for calibration. The UV–vis diffuse reflection absorption spectra (UV–vis/DR spectra) were recorded by a UV–vis spectrometer (U3010, Hitachi, Japan) equipped with an integrating sphere accessory in the diffuse reflectance mode (R), and referenced by BaSO_4 .

2.4. Photocatalytic reaction

The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in the XPA-II photochemical reactor (Nanjing Xujiang Machine – electronic plant). A 500 W Xe lamp was used as the simulated solar light source (UV–vis light), and a house-made filter was mounted on the lamp to eliminate infrared irradiation. The visible light was obtained using the cut-off filter. The cut-off filter was made up of 1 M sodium nitrite solution, which can absorb the light with wavelength under 400 nm [27]. AO-II with the concentration of 40 mg/L was used as contamination. In order to obtain an optimally dispersed system and reach complete adsorption/desorption equilibration, 20 mg photocatalyst powder was dispersed in 200 mL reaction solutions by ultrasonication for 15 min and then the suspension was magnetically stirred in dark for 2 h and reached complete adsorption/desorption equilibration. During the photocatalytic reaction, air was blown into the reaction medium at a flow rate of 200 mL/min. At regular intervals, 5 mL of the suspension was filtered and then centrifuged. The concentration of the remaining AO-II was measured by its absorbance (A) at 484 nm with a Hitachi UV-3010 spectrophotometer. The decolorization ratio of AO-II could be calculated by $((A^0 - A)/A^0) \times 100\%$. The photocatalytic reusability was also evaluated by AO-II removal. In the end of every experimental run, an appropriate AO-II solution was injected into the reactor to reach the original concentration and volume as the first cycle. After 2 h of adsorption and 3 h photocatalytic process, the next experiment cycle began.

2.5. Photocurrent test

To prepare the working electrodes, 250 mg of the sample was first dispersed into a mixture of 2.0 mL ethanol and 0.1 mL terpinol and sonicated for 30 min to form a slurry, then the resulting slurry was coated on FTO glass (2.3 mm, 15 Ω /square, nippon sheet glass, Japan) using a screen-printing method. The sample film thickness is dependent on the repeating times of the screen printing process. The obtained samples were dried at 80 °C for 24 h in vacuum.

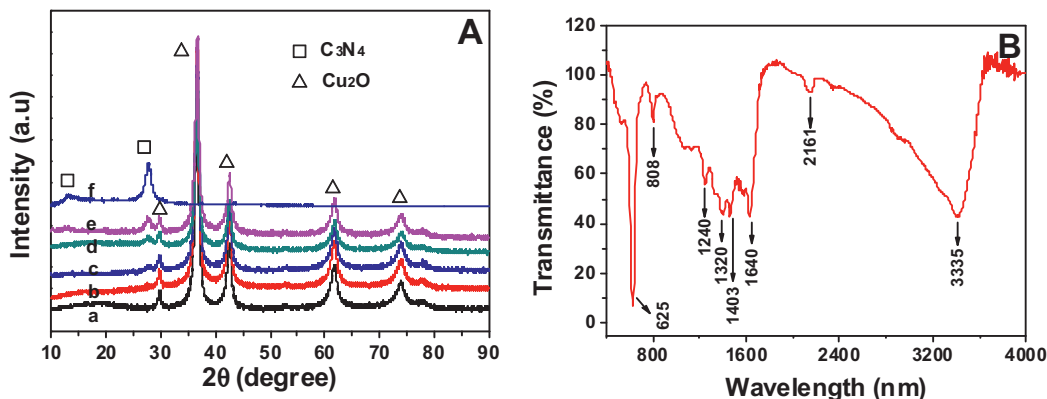


Fig. 1. (A) The XRD patterns of the Cu_2O , $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}$ samples; (B) FT-IR spectrum of the $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}\text{-}10$. a: Cu_2O , b: $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}\text{-}5$, c: $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}\text{-}10$, d: $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}\text{-}20$, e: $g\text{-C}_3\text{N}_4/\text{Cu}_2\text{O}\text{-}30$, $g\text{-C}_3\text{N}_4$.

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