Preparation of g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites and their enhanced visible-light photocatalytic performance

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Abstract. g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites were prepared successfully by liquid phase reduction-precipitation method with melamine, anhydrous copper sulfate, ferric chloride as the main raw material. The morphology and structure of the composites were characterized by SEM, IR and XRD. Using reactive brilliant red X-3B solution (X-3B) as a model pollutant, the visible-light photocatalytic performance of the composites was compared with pure Cu$_2$O and g-C$_3$N$_4$/Fe$_3$O$_4$. The results showed that Cu$_2$O was inlaid in honeycomb-like g-C$_3$N$_4$ matrix embedded with Fe$_3$O$_4$ nanoparticles, and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites had good magnetically separable performance. Compared with pure Cu$_2$O and g-C$_3$N$_4$/Fe$_3$O$_4$, g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites exhibited enhanced efficiency for photocatalytic degradation of X-3B under visible light irradiation.

Introduction

The semiconductor composites have been regarded as promising materials applied in dealing with energy shortages and environmental pollution [1,2]. As an old p-type semiconductor, cuprous oxide (Cu$_2$O) has received much attention due to its narrow band gap, low toxicity and low production cost [3,4]. However, the photocatalytic activity of pure Cu$_2$O is relatively low because of the easy recombination between photo-generated electrons and holes. In recent years, a novel metal-free polymeric material, graphitic carbon nitride (g-C$_3$N$_4$) as a n-type semiconductor photocatalyst was reported extensively owing to its chemical stability and narrow band gap energy of 2.7eV [5,6]. The p-n heterojunction structure in the semiconductor composites can improve separation efficiency of photogenerated charge carriers and enhancing the photocatalytic activity and stability of composites [4]. In addition, magnetically separable photocatalysts could be easily separated and collected with magnetic field, which is important from the perspective of reusability, it is also important to avoid the adverse biological effects of the semiconductor nanoparticles [7,8]. Herein, we prepared g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites through reduction-precipitation method. The microstructure characteristics were determined. The visible-light photocatalytic performance of the prepared composites was studied through the photocatalytic decolorization of reactive brilliant red X-3B (X-3B) dye.

Experimental

Materials. The dye, reactive brilliant red X-3B (X-3B) was purchased from ShunKe Chemical Dyestuff Co., Ltd. (Shanghai, China). Other chemical reagents were analytical grade and used without further purification.

Preparation of photocatalysts. g-C$_3$N$_4$ was synthesized by thermal polycondensation of melamine[9], and then treated in concentrated sulfuric acid. g-C$_3$N$_4$/Fe$_3$O$_4$ composites (the mass ratio of g-C$_3$N$_4$ and Fe$_3$O$_4$ is 3:2) were in situ prepared by the reduction-precipitation method described in our previous report [8]. The g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites (g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O) were synthesized via one-step process as follows: 1.68 g as-prepared g-C$_3$N$_4$/Fe$_3$O$_4$ were dispersed in 50 ml 0.2 mol/L CuSO$_4$·5H$_2$O

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solution. The obtained mixture was then kept in water bath at 54 °C with magnetic stirring and pH value was adjusted to about 10 using 40 mL 1 mol/L sodium hydroxide solution. The blue precipitate suspension appeared soon. Then reducer glucose (0.01 mol) were added into above suspension solution under continuous stirring, and the color gradually changed into reddish brown. Finally, the reddish-brown products were collected with the aid of an adscitious magnet and washed with distilled water and absolute ethanol for several times, respectively, then dried in vacuum oven at 60 °C. For comparison, pure Cu$_2$O powders were also prepared using the same conditions and method mentioned above.

**Analysis instruments.** The SEM images were taken with a SU8010 high resolution field emission scanning electron microscopy (Hitachi, Japan). The XRD patterns of the samples were recorded by an X’Pert Pro X-ray diffractometer (PANalytical, Holland) with Cu Kα radiation ($\lambda = 1.5406$ Å) at a scanning rate of 0.026°/s from 10° to 80° (2θ). The FT-IR spectra were obtained on a Tensor 27 infrared spectrometer (Bruker, German) with a KBr pellet in the range of 4000-400 cm$^{-1}$.

**Photocatalytic decolorization experiments.** The photocatalytic performance of samples was evaluated using X-3B degradation in aqueous solution under visible-light irradiation. Experiments were carried out in a quartz reactor. Typically, 60 mg of as-prepared photocatalyst was dispersed in 100 mL of 10 mg/L dye X-3B solution (pH=5.6) with gently stirring for 30 min to ensure adsorption/desorption equilibrium, and then the suspension was exposed to a 500 W tungsten-halogen lamp ($\lambda_d=584$ nm) which was located at a distance of 150 mm above the surface of the solution. At given irradiation time intervals, about 4mL supernatant was extracted and separated by an external magnetic field, and the absorbance of the supernatant was measured by TU-1810 UV-vis spectrophotometer at 538 nm in order to determine the concentration of X-3B.

The photocatalytic decolorization rate ($D/\%$) was calculated by the following Eq. (1):

$$D(\%) = \frac{c_0 - c_t}{c_0} \times 100$$  (1)

Where $c_0$ is initial X-3B concentration (mg/L), $c_t$ is the X-3B concentration at time $t$ minutes (mg/L).

**Results and Discussion**

**XRD analysis.** Fig. 1 shows the XRD patterns of g-C$_3$N$_4$, g-C$_3$N$_4$/Fe$_3$O$_4$ and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O. It can be seen in curve a that there was a distinct peak 2θ = 27.8° corresponding to interlayer stacking of aromatic segments of (002) plane for graphitic materials. After coupling g-C$_3$N$_4$ with Fe$_3$O$_4$, the peak decreased and meanwhile, five clear diffraction peaks assigned to a face-centered cubic Fe$_3$O$_4$ structure were observed in curve b, indicating the successful sedimentation of Fe$_3$O$_4$ onto the surface of g-C$_3$N$_4$ and...
the well-crystallization of Fe$_3$O$_4$ particles. In the XRD pattern of g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O (curve c), besides typical peaks of g-C$_3$N$_4$ and Fe$_3$O$_4$, there were six clear peaks corresponding to the crystal planes of (110), (111), (200), (220), (311) and (222) of cubic-structured Cu$_2$O, respectively. These results revealed that Cu$_2$O particles were in situ formed in g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O and the crystal structures of Fe$_3$O$_4$ and Cu$_2$O were kept unchanged in the composites.

**FTIR analysis.** The FTIR spectra of g-C$_3$N$_4$, g-C$_3$N$_4$/Fe$_3$O$_4$ and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O were applied as shown in Fig. 2. Three characteristic absorption regions of g-C$_3$N$_4$ at 3428 cm$^{-1}$, 1242–1642 cm$^{-1}$ and 806 cm$^{-1}$ are observed in Fig. 2a. Similarly, these absorption regions were also observed in the spectrogram of g-C$_3$N$_4$/Fe$_3$O$_4$ (curve b) and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O (curve c). Meanwhile, the characteristic adsorption peak at 601 cm$^{-1}$ corresponding to the Fe-O bond vibration of Fe$_3$O$_4$ appeared in the spectrum of g-C$_3$N$_4$/Fe$_3$O$_4$ (curve b), and the characteristic adsorption peak at 618 cm$^{-1}$ corresponding to the Cu-O bond vibration of Cu$_2$O appeared in the spectrum of g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O (curve c). These results showed the successful formation of g-C$_3$N$_4$/Fe$_3$O$_4$ and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites.

**Morphological analysis.** The morphology and surface of g-C$_3$N$_4$, g-C$_3$N$_4$/Fe$_3$O$_4$ and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O was studied by SEM, as shown in Fig. 3. It could be seen from Fig. 3a that g-C$_3$N$_4$ presented honeycomb-like shape and smooth surface. In contrast, g-C$_3$N$_4$ in Fig. 3b had rough surface because Fe$_3$O$_4$ nanoparticles were formed successfully on the surface of honeycomb-like g-C$_3$N$_4$. From Fig. 3c, we could find that Cu$_2$O was inlaid in g-C$_3$N$_4$ matrix embedded with Fe$_3$O$_4$ nanoparticles, further indicating the successful formation g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O composites.

**Magnetic and photocatalytic performance.** The magnetic and enhanced visible-light photocatalytic performance of g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O were illustrated in Fig. 4. As seen in Fig. 4, after 60 min visible-light

![Fig.3 SEM images of g-C$_3$N$_4$ (a), g-C$_3$N$_4$/Fe$_3$O$_4$ (b) and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O (c)](image)

![Fig.4 The photocatalytic decolorization curves of X-3B dye using g-C$_3$N$_4$ (a), g-C$_3$N$_4$/Fe$_3$O$_4$ (b) and g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O (c) as catalyst under visible light irradiation. Inset shows the photographs of g-C$_3$N$_4$/Fe$_3$O$_4$/Cu$_2$O attracted to the place near the magnet outside the vessel.](image)
irradiation, under constant dye initial concentration (10mg/L) and catalyst amount (0.6g/L), the photocatalytic degradation rate of X-3B over the g-C₃N₄/Fe₃O₄/Cu_2O composites could reach about 70%, much higher than that over pure Cu_2O and g-C₃N₄/Fe₃O₄. Moreover, inset in Fig. 4 shows the photograph of g-C₃N₄/Fe₃O₄/Cu_2O attracted to the place near the magnet in aqueous solution by applying a magnet outside the vessel. The results above suggested that g-C₃N₄/Fe₃O₄/Cu_2O composites presented good magnetically separable and enhanced visible-light photocatalytic performance.

Conclusions

Novel g-C₃N₄/Fe₃O₄/Cu_2O composites were constructed via a facile and low-temperature liquid phase reduction-precipitation process. The g-C₃N₄/Fe₃O₄/Cu_2O composites had enhanced visible-light photocatalytic activity as well as good magnetically separable performance through combining the advantages of p-type Cu_2O photocatalysts, n-type semiconductor g-C₃N₄ and Fe₃O₄ magnetic particles.

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