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Full Length Article

Construction of RGO/$CdIn_2S_4$/g-C_3N_4 ternary hybrid with enhanced photocatalytic activity for the degradation of tetracycline hydrochloride

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ABSTRACT

Although RGO shows great advantage in promoting charge separation and transfer of semiconductor, construction of an efficient RGO-incorporated photocatalyst is still challenging. Herein, RGO was employed to construct novel RGO/$CdIn_2S_4$/g-C_3N_4 (donated as RGO/CIS/CN) ternary photocatalyst by a facile hydrothermal method for the degradation of tetracycline hydrochloride (TC). The RGO/CIS/CN ternary photocatalyst showed significantly enhanced photocatalytic activity towards the degradation of TC as compared to the binary CIS/CN, CIS/CN, and CN/RGO. The photoluminescence and photocurrent response results indicate that this enhanced photocatalytic activity can be mainly ascribed to the improved charge separation and transfer efficiency. Based on the radical trapping and electron spin resonance results, the superoxide radicals and holes are proposed to play an important role in the degradation of TC over RGO/CIS/CN ternary photocatalyst. This work paves new opportunities for the synthesis of RGO-incorporated ternary photocatalyst as an efficient photocatalyst for the degradation of organic contaminant.

1. Introduction

Semiconductor-based photocatalysis has emerged as a promising technology for pollution abatement and energy production [1–3]. In recent years, graphite carbon nitride (g-C_3N_4, denoted as CN) has attracted wide attention in photocatalysis [4–9]. However, high recombination rate and insufficient photon absorption are two factors that restrict the photocatalytic efficiency of CN [10,11]. In order to solve these problems and improve the photocatalytic degradation performance of CN, a large number of methods were explored, for example, morphology control [12–16], doping [17–19], and coupling with metal, graphene, and semiconductor [20–29]. In particular, the construction of composite photocatalytic system is an important strategy to promote the separation of the photogenerated electron–hole pairs and subsequently to enhance the photocatalytic activity [30,31]. Particularly, CN/metal sulfide nanocomposites have been investigated as the photocatalyst for the degradation of organic pollutant and hydrogen production [32–36]. Despite these advance, the photocatalytic activity of these binary hybrid photocatalysts are still not sufficient because of the sluggish charge transfer dynamic. Therefore, it is imperative to introduce another material to remit this issue and therefore to achieve efficient photocatalytic activity for practical application.

It has been widely recognized that the carbonaceous materials can effectively enhance the photocatalytic activity of the binary composites [37–39]. As an outstanding carbonaceous material, reduced graphene oxide (RGO) shows good ability in the enhancing the photocatalytic acidity of the binary systems, since it could can act as an electron shuttle which promotes photogenerated electron transfer at the interface between the neighboring semiconductors [40–55]. For example, Liu and co-workers synthesized Cu_2O/RGO/In_2O_3 hybrid with abundant oxygen vacancies [56]. The hybrid Cu_2O/RGO/In_2O_3 photocatalyst displayed improved photocatalytic activity in water oxidation and degradation of environmental pollutants compared with bare In_2O_3 and Cu_2O materials. Motivated by these ternary systems, it can be anticipated that favorable charge separation and transfer would be realized by using the RGO as the conducting platform for the binary nanocomposite system. Up to now, there is no report on the construction of ternary nanocomposites based on the integration of CN with RGO and $CdIn_2S_4$ for the degradation of organic pollutant.

In the present study, novel RGO/$CdIn_2S_4$/g-C_3N_4 (donated as RGO/CIS/CN) ternary hybrid was constructed by a facile hydrothermal method for the degradation of tetracycline hydrochloride (TC).

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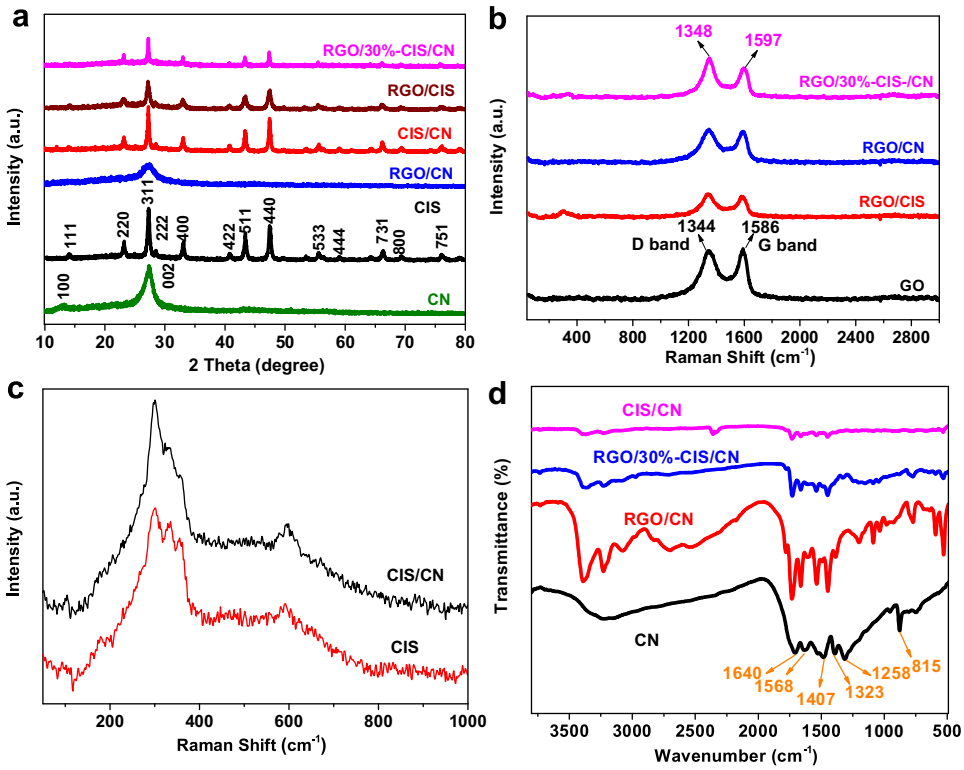

Fig. 1. (a) XRD patterns, (b,c) Raman spectra, and (d) FTIR spectra of the as-prepared samples.

It is demonstrated that the RGO/CIS/CN ternary hybrid shows the significantly enhanced photocatalytic activity towards the degradation of TC under visible light as compared to the binary CIS/CN, CIS/CN, and CN/RGO. A possible enhancement mechanism of the photocatalytic activity of the RGO/CIS/CN ternary hybrid was also investigated. This enhanced photocatalytic activity can be mainly ascribed to the improved charge separation and transfer efficiency. This work demonstrates an effective strategy to enhance photocatalytic activity by constructing ternary photocatalysts by incorporation with graphene.

2. Experimental section

2.1. Preparation of catalyst composites

Graphite oxide (GO) was prepared by a modified Hummers method [49]. CN nanosheets were synthesized from the urea according to our previous method [24]. For the hydrothermal synthesis of RGO/CIS/CN ternary hybrid, CN powder (73.5 mg) and GO (14.5 mg) were dissolved in 15 mL of distilled water by ultrasonic for 1 h. Subsequently, $Cd(NO_3)_2{\cdot}4H_2O$ (27.3 mg) and $In(NO_3)_3{\cdot}4.5H_2O$ (78.4 mg) as indium source and cadmium source were then added into the above solution and stirred for 30 min. Then, 16.3 mL of thioglycolic acid (0.2 mol/L) and 3.25 mL of sodium sulfide (0.2 mol/L) were added into the mixture and stirred for 1 h. The above mixture was placed in an autoclave for hydrothermal treatment and held at 180 °C for 12 h. Afterward, the reaction mixture was centrifuged and washed, and dried in an oven at 60 °C. The content of CIS in the RGO/CIS/CN ternary hybrid is 30 wt%, which is denoted as RGO/30%-CIS/CN. In addition, the content of RGO in this ternary hybrid is 10 wt%. By means of changing the addition of raw material, RGO/CIS/CN ternary hybrids with various CIS contents, CIS, RGO/CIS, CIS/CN were also synthesized by the similar method.

2.2. Characterization

The phase purity of the as-prepared photocatalysts were measured by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer) with Cu-Kα radiation (λ = 1.5406 Å). FT-IR spectrum was obtained with a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation). Surface composition analysis of the as-prepared photocatalysts was conducted by X-ray photoelectron spectroscopy (XPS) on ESCA PHI500 spectrometer. Transmission electron microscopy (TEM) was conducted by a JEOL JEM-2010 (HT). High-resolution TEM (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) were measured on a JEOL JEM-2100F transmission electron microscope. The surface areas of the photocatalysts were measured by a TriStar II 3020-BET/BJH Surface Area. UV–vis diffuse reflectance spectra (DRS) were tested on a Shimadzu UV-2450 spectrophotometer. The photoluminescence (PL) spectra of the samples were measured on a Varian Cary Eclipse spectrometer. The electron spin resonance (ESR) signals of spin-trapped radicals were conducted on a Bruker model ESR JES-FA200 spectrometer using spin-trap reagent DMPO in water and methanol, respectively.

2.3. Photocatalytic activity

The photocatalytic activities of the photocatalysts were tested in the degradation reaction of TC aqueous solution (10 mg/L) under irradiation of a 500 W tungsten light lamp. For a typical photocatalytic degradation experiment: 60 mg of photocatalysts powder was added into 60 mL of TC solution in a reaction bottle. The mixed solution was kept stirring 1 h in the dark condition to ensure the TC could reach the absorption-desorption equilibrium on the photocatalysts surface. 4 mL of suspension was sampled and centrifuged to remove the photocatalyst in a certain time intervals. For the sake of eliminating the deviation of light temperature, the reaction