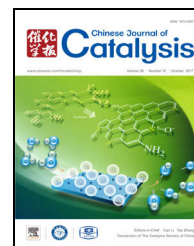


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## Article

# Visible light-responsive carbon-decorated p-type semiconductor $\text{CaFe}_2\text{O}_4$ nanorod photocatalyst for efficient remediation of organic pollutants



Xin Liu, Yuhong Zhang, Yushuai Jia\*, Junzhe Jiang, Yabin Wang, Xiangshu Chen#, Tian Gui

College of Chemistry and Chemical Engineering, Jiangxi Inorganic Membrane Materials Engineering Research Centre, Jiangxi Normal University, Nanchang 330022, JiangXi, China

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## ABSTRACT

We report the fabrication and photocatalytic property of a composite of C/ $\text{CaFe}_2\text{O}_4$  nanorods (NRs) in an effort to reveal the influence of carbon modification. It is demonstrated that the photocatalytic degradation activity is dependent on the mass ratio of C to  $\text{CaFe}_2\text{O}_4$ . The optimal carbon content is determined to be 58 wt% to yield a methylene blue (MB) degradation rate of  $0.0058 \text{ min}^{-1}$ , which is 4.8 times higher than that of the pristine  $\text{CaFe}_2\text{O}_4$  NRs. The decoration of carbon on the surface of  $\text{CaFe}_2\text{O}_4$  NRs improves its adsorption capacity of the MB dye, which is specifically adsorbed on the surface as a monolayer according to the adsorption isotherm analysis. The trapping experiments of the reactive species indicate that superoxide radicals ( $\cdot\text{O}_2^-$ ) are the main active species responsible for the removal of MB under visible-light irradiation. Overall, the unique feature of carbon coating enables the efficient separation and transfer of photogenerated electrons and holes, strengthens the adsorption capacity of MB, and improves the light harvesting capability, hence enhancing the overall photocatalytic degradation of MB.

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## 1. Introduction

As one of the most promising routes for alleviating the environmental pollution and energy crisis, the visible light-driven heterogeneous photocatalysis has attracted extensive attention [1–5]. In recent decades, considerable efforts have been focused on the fabrication of highly efficient semiconductor-based photocatalysts towards the elimination of organic contaminants or hydrogen production through water splitting [6–10]. As a model p-type semiconductor photocatalyst, the nontoxic, inexpensive  $\text{CaFe}_2\text{O}_4$  with a narrow bandgap (about

1.9 eV) has been proven to be capable of photocatalytic decomposition of organic dyes, reduction of carbon dioxide and photoelectrochemical water splitting [11–14]. Nevertheless, owing to its intrinsic problems, such as p-type character with inefficient hole transfer to the surface, high recombination of photoexcited charge carriers and low charge carrier mobility arising from the existence of defects, usually, a low photo-quantum yield is obtained for the  $\text{CaFe}_2\text{O}_4$ -based photocatalysts either in water splitting or the degradation of organic pollutants.

One of the strategies for solving these problems is the con-

\* Corresponding author. E-mail: [ysjia@jxnu.edu.cn](mailto:ysjia@jxnu.edu.cn)# Corresponding author. E-mail: [cxs66cn@jxnu.edu.cn](mailto:cxs66cn@jxnu.edu.cn)

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struction of composite photocatalysts. For example, a series of  $\text{CaFe}_2\text{O}_4$ -based composites, such as  $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$  [15],  $\text{CaFe}_2\text{O}_4/\text{Ag}_3\text{VO}_4$  [16] and  $\text{CaFe}_2\text{O}_4/\text{MgFe}_2\text{O}_4$  [17], have been fabricated and exhibit enhanced photocatalytic activities. Recently, it was found that carbon/inorganic semiconductor composite photocatalysts exhibit promising photocatalytic activities for the removal of the organic pollutants from water [18–20]. For instance, Zhong et al. [21] reported that carbon-deposited  $\text{TiO}_2$  can efficiently degrade Acid Orange 7 and 2,4-dichlorophenol under visible-light irradiation. Chen et al. [22] studied the photocatalytic activity of carbon-coated  $\text{PbMoO}_4$  microspheres for the degradation of rhodamine B (RhB) in an aqueous solution under visible-light irradiation. Li et al. [23] observed that modification with an appropriate amount of carbon could significantly improve the photocatalytic activity of  $\text{Bi}_2\text{WO}_6$  for the degradation of RhB. In general, the major advantages of coupling carbon materials with a semiconductor are as follows: (1) increase of the visible-light absorption of wide bandgap semiconductors, (2) enhancement of electron transport and inhibition of the recombination of photogenerated charge carriers [24,25], (3) high dispersion of semiconductor particles through the wide distribution of hydrophilic groups (such as  $-\text{OH}$  and  $\text{C}=\text{O}$ ), and (4) improvement of the adsorption capacity for organic pollutants. However, most of these are composites of carbon with n-type semiconductors [23,26,27], so would be interesting to determine the carbon coating effect on the photocatalytic performance of p-type semiconductors.

In this work, well-defined  $\text{CaFe}_2\text{O}_4$  nanorod (NR) crystals were prepared by a facile polymerizable complex method in an eutectic mixture of NaCl and KCl molten salts that we have reported earlier [28]. The coating of the carbon layers onto the surface of the  $\text{CaFe}_2\text{O}_4$  NRs was carried out by the impregnation method. Through a comprehensive study of the relationship between the photocatalytic performance and composite structure, carbon loading, methylene blue (MB) adsorption, and oxidant intermediate, the unique effects of carbon coating on a p-type semiconductor are well addressed. This study will serve as a guide for the construction of highly efficient carbon/p-type semiconductor composite photocatalysts.

## 2. Experimental

### 2.1. Materials

Glucose, citric acid, ethylene glycol, NaCl and KCl were purchased from Sinopharm Chemical Reagent Co., Ltd.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and MB were obtained from Aladdin Industrial Corporation. All chemicals were of analytical grade and used as received without any further purification.

### 2.2. Preparation of samples

$\text{CaFe}_2\text{O}_4$  NRs were synthesized according to the procedure reported in our previous paper [28]. Briefly, 8.406 g of citric acid, 4.723 g of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 16.160 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added into 20 mL of distilled water and dissolved com-

pletely under stirring, followed by the addition of ethylene glycol (8 mL) to yield a brown solution. Subsequently, the resulting solution was transferred to an evaporating dish and dried at 130 °C for 20 h to obtain a dry gel. Calcination in air at 500 °C for 2 h yielded the  $\text{CaFe}_2\text{O}_4$  precursor, which was blended and ground with NaCl and KCl in the molar ratios of 1:5:5 for the molten salt crystallization. The mixture was calcined in air at 800 °C for 20 h and washed with boiling water. After drying at 60 °C for 12 h, the  $\text{CaFe}_2\text{O}_4$  NRs product was obtained.

The C/ $\text{CaFe}_2\text{O}_4$  NRs composite material was prepared as follows. 1.440 g of glucose was dissolved in 60 mL of distilled water. The glucose solution was transferred into a 100-mL Teflon-lined stainless-steel autoclave and kept at 180 °C for 24 h, then allowed to cool naturally to room temperature. Then, the reaction solution was centrifuged several times. The resultant yellow aqueous solution containing carbon was obtained for further use. Subsequently,  $\text{CaFe}_2\text{O}_4$  (100 mg) was respectively dispersed into 5, 10, 15, 20, 25, 30 mL of the yellow aqueous solution containing carbon, and sonicated for 10 min. After complete evaporation of the solvent at 60 °C under stirring, the collected products were dried at 60 °C overnight. The carbon contents in the as-prepared composite samples were determined by TG analysis to be 28, 41, 49, 58, 67 and 71 wt%, respectively. Therefore, in the following discussion, the samples are labeled as X wt% C/ $\text{CaFe}_2\text{O}_4$ , where “X” denotes the content of carbon in the composite.

### 2.3. Characterization

To determine the crystal structure of the as-prepared samples, powder X-ray diffraction (XRD) measurements were carried out using a Rigaku RINT-2200 diffractometer with a  $\text{Cu } K_\alpha$  radiation source at 40 kV and 20 mA and a scanning rate of 4°  $\text{min}^{-1}$  ( $2\theta$  from 5° to 90°). TG analysis was performed on a Diamond TG/DTA apparatus in air from room temperature to 1000 °C. The functional groups of the photocatalyst were analyzed by Fourier transform infrared (FTIR) spectroscopy using a Nicolet 6700 spectrometer. The spectra were recorded in the transmission mode ranging from 4000 to 500  $\text{cm}^{-1}$ . The morphology and composition of the photocatalyst were studied by scanning electron microscopy (SEM) on a Hitachi SU-8020 cold field emission source and by an energy-dispersive spectroscopy (EDS) detector attached to the scanning electron microscope, respectively. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was performed on a JASCO V-750 instrument equipped with an integrating sphere. X-ray photoelectron spectroscopy (XPS) was conducted on a VG-ESCALAB 250Xi instrument with a monochromic Al  $K_\alpha$  source at 1486.6 eV (150 W). The peak of C 1s at 284.6 eV was used as the reference to calibrate the binding energy. Nitrogen adsorption-desorption measurements were performed on a BELSORP-mini II analyzer using the Brunauer-Emmett-Teller (BET) method. The photocurrent response was determined using an electrochemical workstation in a three-electrode photoelectrochemical cell. The photocatalyst film coated on fluorine-doped tin oxide conducting glass was used as the working electrode. A platinum foil and a saturated calomel electrode

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