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Enhanced photocatalytic activity of a double conductive $C/Fe_3O_4/Bi_2O_3$ composite photocatalyst based on biomass

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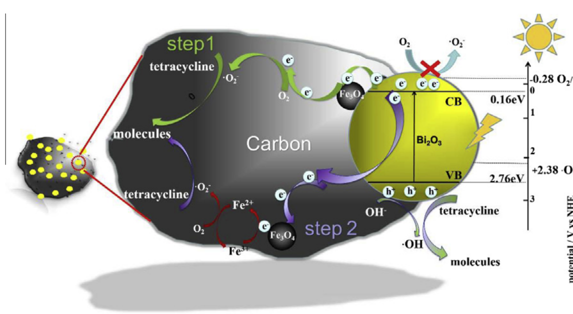
HIGHLIGHTS

- The $C/Fe_3O_4/Bi_2O_3$ has double conductivity which enhanced the photocatalytic activity greatly.
- Using biomass as carbon source realized the rational utilization of waste.
- C/Fe_3O_4 was obtained by one-step method and showed good magnetic property.
- The C/Fe_3O_4 is conductive and it can receive and transport electrons.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to realize the rational utilization of waste, C/Fe_3O_4 was obtained by using biomass as the carbon source and prepared via one-step method, afterwards, a double conductive $C/Fe_3O_4/Bi_2O_3$ composite photocatalyst was further synthesized via solvothermal method. Due to the good double conductivity, the electrons in Bi_2O_3 could be transported to C/Fe_3O_4, which greatly inhibited the recombination of electron-hole pairs, it is worth noting that the double conductivity effectively blocked the reverse transfer of electrons to Bi_2O_3. Consequently, the photodegradation rate of $C/Fe_3O_4/Bi_2O_3$ composite photocatalyst reached 91%, which was much higher than that of pure Bi_2O_3. In addition, the mechanism exploration experiment showed that h^+ was the main activity specie, meanwhile, the photocatalytic electron transfer mechanism was also investigated.

1. Introduction

Environmental pollution and energy crisis coexist in human society which are closely related to life. Accordingly, it is an important task to seek a suitable method to solve above problems. Photocatalysis has been regarded as one of most efficient strategies to solve the environmental pollution [1,2]. TiO_2, as the most used photocatalyst, possesses its unique performance [3,4], such as high efficiency and good stability [5]. Nevertheless, the large bandgap and the narrow range of light absorption greatly hinder the practical application of TiO_2, therefore, finding a suitable visible light responsive material is very critical.

Bi_2O_3, a kind of Bi-based material with a smaller band gap [6], is widely used in environment in virtue of its nontoxic and good visible photocatalytic performance [7], whereas the pragmatic photocatalytic efficiency of Bi_2O_3 is still at a low state because of the fast recombination of electron-hole pairs [8]. Some modification

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methods [9–14] are proved to be important strategies to ameliorate these shortcomings by constructing a composite structure to improve the separation of photogenerated electron-hole pairs [15]. However, the electrons transport between simple composite structures is insufficient and a part of electrons would be returned to the photocatalyst and caused the decrease of photocatalytic performance. Numerous researches have been down to overcome the shortcoming, previous literatures [16–20] have attested that the combination of carbon and photocatalyst can enhance the photocatalytic degradation rate by improving the electron transfer rate and blocking the recombination of electron-hole pairs, the degree of electrons transferred back to photocatalyst can be reduced [21]. Therefore, it is convinced that the photocatalytic performance of Bi_2O_3 can be improved by combining with carbon material.

However, the carbon source used in mentioned above researches were organic compound which makes the cost higher, it will be more reasonable that if they had fully consideration of the economic efficiency and environment pollution. Using biomass as carbon source not only controls the waste of agricultural wastes [22] to relieve the environment pollution as well as energy crisis [23] but also increases the activity of photocatalyst. Up to now there are few reports about the application of biomass carbon on photocatalytic.

Biomass is a kind of renewable feedstock [24] which is widely distributed in our country, the biomass resources, such as corn cobs, straw and rice husk are defined as agricultural waste. Hitherto many researches have been carried out to study the conductivity of carbon which derived from biomass [25–27], open up new avenues for the reuse of agricultural waste. Carbon, fabricated from biomass by calcination or hydrothermal method, can be used as supporter to let the metal particles grow on surface in dispersed state to increase the stability [28], meanwhile, it often acts as adsorbent to absorb pollutants toward to the photocatalyst, furthermore, the excited electrons will be transferred away by carbon rather than aggregated on the photocatalyst, therefore, the recombination probability of the holes and electrons on the photocatalyst will be impeded and the lifetime of photogenerated electrons will be prolong [29].

Nevertheless, the recycle of the composite photocatalyst is so hard that the cost becomes higher, in order to further realize the low carbon idea, Fe_3O_4, being introduced into the composite photocatalyst, is regarded as an ideal magnetic material, the combination of Fe_3O_4 and semiconductor to form a composite structure has been frequently investigated [29,30], the addition of Fe_3O_4 makes the photocatayst become more easily recovered from the solution [31], from another point of view, the Fe_3O_4 is conductive which can facilitate the separation of the electron-hole pairs effectively [32] and achieve the purpose of increasing the photocatalytic activity ultimately.

In this work, we demonstrate a method to synthesis the $C/Fe_3O_4/Bi_2O_3$ composite photocatalyst, tetracycline is selected as the target pollutant, and corn cobs are used as biomass carbon raw materials, the obtained carbon is used for the matrix material. Herein, a series of factors such as different proportion of C/Fe_3O_4 and different matrix materials are put forward, aimed at studying the role of carbon in the reaction of photocatalytic. The main active species during the process of photocatalytic are evaluated through mechanism explore experiment, the photocatalytic electron transfer mechanism will be discussed in this paper.

2. Experimental section

2.1. Materials

$Bi(NO_3)_3·5H_2O$ (98.0%), ethylene glycol (EG, 98.0%) were all supported by Aladdin Chemistry Co., Ltd. ethanol (C_2H_5OH, 95.0%), $Fe(NO_3)_3·9H_2O$ (98.0%), activated carbon, tetracycline were purchased from Sinopharm Chemical Reagent Co., Ltd. Corn cobs were obtained from Zhenjiang, Jiangsu Province, China. Tetracycline was analytical pure and used without further purification, distilled water was used in the whole experiments.

2.2. Sample preparation

2.2.1. Synthesis of C/Fe_3O_4 materials

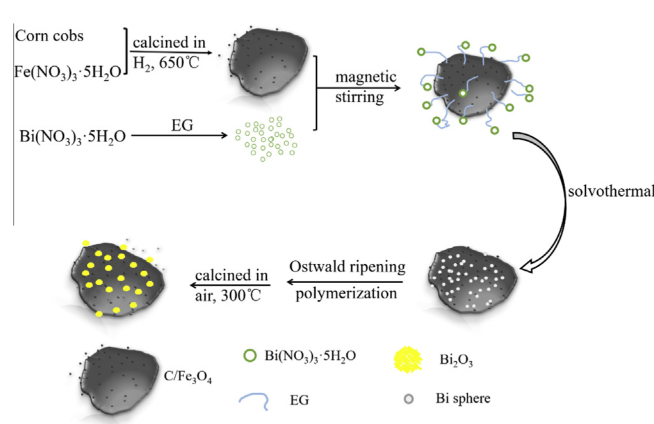
All reagents were of analytical grade and used without further purification. Corn cob powder (5 g) and $Fe(NO_3)_3·9H_2O$ (5 g) were dissolved in 100 mL ethanol, the mixed materials were stirred by a magnetic stirrer under room temperature for one hour, and then the suspension was filtered and dried in an oven at 80 °C overnight. Put the dried powder into tube furnace, calcined at 650 °C for 3 h under H_2 atmosphere. The carbon was synthesized by the same way in addition to $Fe(NO_3)_3·9H_2O$ at the beginning. Put some $Fe(NO_3)_3·9H_2O$ powders into porcelain boat, calcined in tube furnace to form Fe_3O_4 by the same condition.

2.2.2. Synthesis of $C/Fe_3O_4/Bi_2O_3$ composite materials

The as-prepared C/Fe_3O_4 (0.04 g) was dispersed into ethylene glycol (35 mL), ultrasonicated for 1 h, afterwards, $Bi(NO_3)_3·5H_2O$ (0.73 g, 1.5 mmol) was dissolved in the mixed solution, ultrasound for 1 h and then magnetic stirred for 2 h, the mixture was poured into a Teflon-lined stainless-steel autoclave, sealed and maintained at 160 °C for 15 h. After the reaction was completed, the resulting precipitates were collected by magnetic, washed several times with deionized water and ethanol, dried in an oven at 80 °C. Finally the product was calcined in tube furnace under air at 300 °C for 1 h. Samples synthesized with C/Fe_3O_4 content 2.5 wt.%, 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% were denoted as $C/Fe_3O_4/Bi_2O_3$-2.5, $C/Fe_3O_4/Bi_2O_3$-5, $C/Fe_3O_4/Bi_2O_3$-10, $C/Fe_3O_4/Bi_2O_3$-15 and $C/Fe_3O_4/Bi_2O_3$-20, respectively. For comparison, the pure Bi_2O_3, C/Bi_2O_3 and Fe_3O_4/Bi_2O_3 were synthesized by the method mentioned above. The preparation process of $C/Fe_3O_4/Bi_2O_3$ is shown in Scheme 1.

2.3. Characterization

The type and phase structure of the as-prepared product was detected using powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer using Cu Kα = 1.5406 Å), Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were taken to observe and analyze the morphology, structure and chemical element composition of product. Transmission electron microscopy (TEM) was used to observe the inner microcosmic



Scheme 1. Illustration of the possible formation process of $C/Fe_3O_4/Bi_2O_3$ composite photocatalyst.