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Novel biochar@$CoFe_2O_4$/Ag_3PO_4 photocatalysts for highly efficient degradation of bisphenol a under visible-light irradiation

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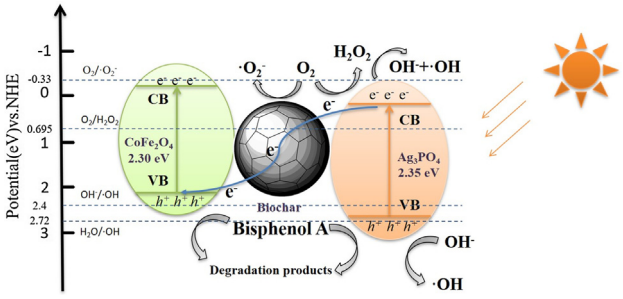
GRAPHICAL ABSTRACT



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ABSTRACT

In the study, a series of novel Z-scheme biochar@$CoFe_2O_4$/Ag_3PO_4 photocatalysts were synthesized and employed to degrade bisphenol A under visible light irradiation ($\lambda \geq 420$ nm). The structural morphology, optical properties and physicochemical properties of composites were characterized by means of TEM, XRD, FT-IR, XPS, UV–Vis, BET, EIS and VSM analysis. The photocatalytic performances of the photocatalysts were evaluated systematically. The MBA-3 photocatalyst exhibited the highest photocatalytic and mineralization ability within 60 min among all photocatalysts, 91.12% and 80.23%, respectively. After four cycles, the degradation of BPA still kept the photocatalytic activity of 73.94%, and the removal rate of TOC remained 58.96%. Moreover, the active species in the photocatalytic process were evaluated, and we proposed the Z-scheme photocatalytic mechanism for highly efficient degradation of BPA. According to the GC-MS results, the photodegradation pathway of BPA is also suggested. The present study has provided a valuable way of using the magnetic biochar in the design of new and efficient system for the degradation of organic pollutions in waste water.

1. Introduction

In recent years, bisphenol A (BPA), one of the most typical endocrine disrupting chemicals (EDCs), has been proven to be a huge threat to human health and the environment even at trace levels (less than 1 ng/L) [1]. BPA can be detected in most water environments, and its concentration considerably varies (from ng/L to μg/L) [2,3]. According to recent research, long-term exposure to such environments not only affects thyroid hormone production and DNA transmission [4], but also causes dysplasia of the reproductive system [5] and a certain risk of carcinogenicity and teratogenicity [6,7]. Therefore, highly efficient and stable methods are urgently needed to remove BPA from water environments.

Silver (Ag)-based semiconductors have become increasingly popular for the degradation of organic pollution [8–13]. Generally, such semiconductors exhibit good photocatalytic activity by

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forming heterojunctions, thereby removing organic pollution well. Among these semiconductors, silver phosphate (Ag_3PO_4), a new type of visible light-responsive photocatalyst, shows higher quantum efficiency (90%) compared with other semiconductors and is favored for the construction of highly efficient photocatalysts [14]. However, Ag_3PO_4 has several drawbacks, thus considerably limiting its further application. One such drawback is photocorrosion caused by Ag^+ reduction [15,16]. Extensive effort has been exerted to solve this problem by constructing heterojunctions with other semiconductors, such as Ag_3PO_4/BiOX [17–19], AgX/Ag_3PO_4 [20], Ag_3PO_4/GO [21], Ag_3PO_4/WO_3 [22], Ag_3PO_4/TiO_2 [23,24], which all improved photocatalytic performance better than unstructured heterojunctions. Meanwhile, the photocatalytic efficiency of the Z-scheme is much higher than other heterojunction photocatalysts [22]. Another vital issue that limits the practical application of Ag_3PO_4 is the desired recycling of photocatalysts. In this line, the introduction of magnetic materials is believed to be effective in material separation. Therefore, finding a semiconductor that can perform magnetic separation and form a heterostructure with Ag_3PO_4 is crucial. $CoFe_2O_4$, a narrow bandgap semiconductor, has excellent magnetic separation properties and good visible light responsiveness; it has been proven to form a heterojunction with Ag_3PO_4 [25].

Biochar, a type of charcoal, has been receiving widespread attention because of its unique superiority over similar carbon materials. It has a large specific surface area that can provide more active sites for photocatalysis [26]. Zhou et al. [27] found that persistent free radicals (PFRs) in biochar can induce oxygen to produce $\cdot O_2^-$. Moreover, studies have shown that biochar can be used as a conduction medium for the Z-scheme system to promote a highly efficient separation of photogenerated electron holes [28,29].

On this basis, this study proposes a novel Z-scheme mechanism visible-light photocatalyst based on biochar@$CoFe_2O_4$/Ag_3PO_4 composites. Biochar@$CoFe_2O_4$/Ag_3PO_4 is synthesized by in-situ precipitation. The structural morphology, optical properties, and physicochemical properties of the composites were characterized. In addition, the photocatalytic performance of the as-prepared materials and the active species in the photocatalytic process were systematically evaluated. Results demonstrate that the MBA-m composites exhibit higher photocatalytic activity compared with Ag_3PO_4. The Z-scheme photocatalytic mechanism and degradation intermediates are discussed in detail.

2. Experimental

2.1. Materials

Pine pollen was purchased from Yunnan dekot biological engineering co. LTD. Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), iron nitrate hydrate ($Fe(NO_3)_3{\cdot}9H_2O$), silver nitrate ($AgNO_3$) and sodium hydroxide (NaOH) were purchased from Xilong chemical co. LTD. Disodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$), ethylene glycol ($C_2H_6O_2$), ethylenediamine tetraacetic acid disodium (EDTA-2Na), isopropanol (IPA) and phenylhydrazine (BZQ) were purchased from Tianjin guangfu technology development co. LTD. The BPA used in the photocatalytic experiments was purchased from Aladdin reagent co. LTD. All the reagents used in the experiment except methanol (chromatographic grade) are of analytical grade and can be used without further purification.

2.2. Synthesis of the photocatalysts

2.2.1. Synthesis of biochar@$CoFe_2O_4$ (MB)

The preparation of magnetic biochar was synthesized via a one-pot method. First, a certain amount of pine pollen was mixed in a mixture of $Fe(NO_3)_3{\cdot}9H_2O$ (0.1 mol/L) and $Co(NO_3)_2{\cdot}6H_2O$ (0.1 mol/L) and kept stirred overnight. Adjust pH = 12 with NaOH (2 mol/L) and stir another 1 h. Transfer above solution into a Teflon-lined autoclave and keep heated at 180 °C for 12 h. Subsequently, the obtained powder was calcined at 500 °C for 2 h in a tube furnace at a rate of 5 °C/min under an atmosphere of N_2. Magnetic biochar (biochar@$CoFe_2O_4$) was finally obtained and denoted as MB.

2.2.2. Synthesis of biochar@$CoFe_2O_4$/Ag_3PO_4 (MBA)

The facile in-situ precipitation method was used to synthesize biochar@$CoFe_2O_4$/Ag_3PO_4 with different ratios. In a typical process, a series of different qualities MB were added to 100 mL $C_2H_6O_2$ and sonicated for 30 min. Afterwards, 50 mL $AgNO_3$ (0.129 mol) was added and kept stirred for 12 h to make Ag^+ combine with MB sufficiently. Subsequently, another 50 mL $Na_2HPO_4{\cdot}12H_2O$ (0.043 mol) was added dropwise to the above mixed solution and then maintained with stirring for 1 h. The above mixture was washed several times with ultrapure water, and then collected for use. The synthesized biochar@$CoFe_2O_4$/Ag_3PO_4 with different ratios were denoted as MBA-m, and m represents the mass ratio of MB in the MBA-m composite. For example, MBA-1 means that the content of MB in the composite was 10 wt%.

2.3. Characterization

Transmission electron microscopy (TEM) image was observed by JEOL JEM2100 microscopy at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were analyzed by Rigaku D/max 2500 diffractometer equipped with Cu Kα radiation in the range of 10–90°. Fourier transform infrared spectroscopy (FT-IR) was used to investigate the bonding of surface elements of different materials. The chemical composition of the photocatalysts was analyzed by X-ray photoelectron spectroscopy (XPS). In order to study the optical absorption properties of the photocatalysts, the UV–vis spectroscopy were recorded on UV2550 spectrometer (Shimadzu) within the range of 200–800 nm. An adsorption instrument (TriStar II 3020, Micromeritics Company, USA) was used to evaluate the specific surface areas and pore structures of photocatalysts. Electrochemical impedance spectroscopy (EIS) was taken by 760E electrochemical workstation. The magnetic hysteresis loop was measured on a MPMS-XL-7 vibrating sample magnetometer.

2.4. Photocatalytic activity experiments

The photocatalytic activities of MBA-m photocatalysts with BPA as target pollution were evaluated under visible-light irradiation. A 300 W Xe lamp (Xi'an Bilang Biotechnology Co. Ltd) furnished with a cutoff filter ($\lambda \geq 420$ nm) was used as a visible light source. In a typical process, adding a certain amount (25 mg) of catalyst to a quartz tube containing 50 mL of BPA solution (20 mg/L). After the adsorption equilibrium was reached, and the lamp was turned on for photocatalytic reaction. Approximate 5 mL of the samples were withdrawn at given time intervals and treated with a 0.45 um water membrane. The concentrations of the BPA solution and TOC were quantified by HPLC (Agilent 1260) equipped with a UV–vis detector and TOC analyzer, respectively. The possible intermediates of BPA were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 7890-5977B).

3. Results and discussion

3.1. TEM analysis

Fig. 1 shows the TEM and EDX mapping of MBA-3. It could be observed that $CoFe_2O_4$ and biochar were randomly loaded on the