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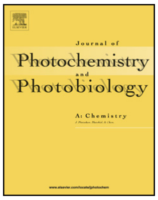

One-pot microwave-assisted synthesis of $Zn_{0.9}Fe_{0.1}S$ photocatalyst and its performance for the removal of bisphenol A

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ABSTRACT

Photocatalysis is an ideal pathway of degradation of emerging contaminants such as endocrine disrupting compounds with least byproducts. This study investigated the synthesis of $Zn_{0.9}Fe_{0.1}S$ nanoparticles with a one-step microwave irradiation method (MIM) and the photocatalytic degradation of Bisphenol A (BPA) under UV-light irradiation. The results showed that the microwave-assisted synthesis changed the morphology of the catalyst, increased its surface area, shortened the preparation time and improved the activity and longevity of the catalyst in comparison to the traditional hydrothermal method (THM). By tracking the quenching of •OH radical, the degradation pathway of BPA by $Zn_{0.9}Fe_{0.1}S$ photocatalysts was proposed. The effects of reaction solution pH, microwave irradiation time, and power on the catalytic activity were discussed, respectively. The stability and reusability of the catalyst were studied through monitoring dissolved ions release from the catalyst.

1. Introduction

Along with the industrialization and development of social economy, a growing number of toxic and harmful organic pollutants are produced, disposed and thus present in the industrial and municipal wastewater. For instance, bisphenol A (BPA), as one of the most important man-made organic compounds with annual production exceeding 3.8 million tons, is widely used in the synthesis of polycarbonates, epoxy resins and thermal paper [1,2]. The toxic BPA is difficult to be fully treated by activated sludge processes, thereby leaving a negative impact on the eco- and environmental systems [3,4]. Moreover, the byproducts of BPA degradation may possess higher endocrine disrupting properties [5]. Thus, a complete transformation of BPA into CO_2 and H_2O is the ideal solution for this pollutant treatment.

Photocatalytic oxidation is considered as an efficient way of degrading persistent organic compounds into H_2O and CO_2 under mild conditions. Recently, sulfide photocatalysts have attracted increasing attention because of their high photocatalytic activity, efficient recycling utilization, and good stability in water purification and wastewater treatment [6–10]. Currently, the usage of sulfide photocatalysts disposing contaminants in artificial water has been reported in abundance. The degraded objects involve phenols, hydrocarbons, dyes, surfactants, polycyclic aromatic hydrocarbons, halogenated aromatic compounds, pesticides, herbicides, other important organic compounds and a small amount of inorganic compounds [11–13]. ZnS exhibited outstanding performance due to its unique energy band structure in the field of degrading refractory poisonous organic pollutants in photocatalytic oxidation. ZnS-based photocatalysts by incorporation of other metals into the structure of ZnS can regulate the band structure, broaden the scope of their optical response and then motivate the photocatalytic activity [14,15]. Several methods can be utilized for the synthesis of sulfide photocatalysts such as ball-milling technique, co-precipitation, aerogel and hydrothermal method [16–18]. However, some methods encounter problems such as the formation of the undesirable phases, the requirement of complicated equipment and the substantial time consumption caused by multiple steps. Therefore, it is important to develop an inexpensive, facile and fast synthesis method for increasing the photocatalytic activity and lowering the cost [19–21].

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In recent years, the microwave technology has achieved a rapid development due to its quicker heating rate, faster kinetics, homogeneity, higher yield, better reproducibility, and energy saving compared with the traditional method [22,23]. Moreover, the microwave system also enables chemical reactions to occur in the temperature-elevating and closed pressurizing system in a short preparation time on the order of minutes rather than days. Due to the excellent microwave absorbing ability, the room temperature ionic liquids (RTILs) combined with microwave heating have been applied in the synthesis of nanomaterials [24–26]. Microwave techniques are therefore used for various types of chemical processes including organic synthesis, materials productions, and catalytic reactions [27–29] by shortening reaction time and improving high product yields in these fields. Microwave-assisted gas-solid heterogeneous catalytic reactions have been introduced in the synthesis of solid catalysts such as zeolites, metals, supported metals, and metal oxides [30–33].

In this work, the $Zn_{0.9}Fe_{0.1}S$ catalysts were synthesized through a one-step microwave irradiation method and the photocatalytic activities of produced catalysts were compared with those prepared by the traditional method using conventional equipment for heating. The BPA degradation efficiencies were investigated with different catalysts. In addition, the role of ·OH formation in the BPA removal was discussed.

2. Experimental

2.1. Materials

BPA (purity 99.5%), was purchased from Tianjin Guangfu Fine Chemical Research Institute. Hydrogen peroxide (30%, v/v), $Zn(CH_3COO)_2{\cdot}2H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Na_2S{\cdot}9H_2O$ were purchased from Tianjin BASF Chemical Co. Ltd. Anhydrous ethanol, terephthalic acid, sulfuric acid and sodium hydroxide were supplied by Aladdin Corporation of China. They were all of analytical grade and used as obtained.

2.2. Synthesis procedure

Microwave irradiation synthesis procedure for preparing the $Zn_{0.9}Fe_{0.1}S$ catalyst was as follows [34–36]. An amount of 50 mL zinc acetate (0.009 mol L^{-1}), 50 mL ferric nitrate (0.001 mol L^{-1}) and 50 mL sodium sulfide (0.01 mol L^{-1}) were mixed into a 250 mL round flask, and pH was adjusted to the appropriate value, which was 3.0, 5.0, 7.0, 9.0 in the different reaction process. Then, the mixed solution was transferred into a microwave oven immediately and microwaved for 10 min under the power of 150 W with magnetic stirring. When the reaction was finished, the mixed solution was placed at room temperature for cooling. Afterwards, the mixture was centrifuged at 2685g for 10 min, and then the supernatant was discarded. The precipitate was washed by ethanol and distilled water for two times, respectively. Finally, the resulting solid was dried in vacuum oven under 60 °C for 5 h, and ground into powders for storage. The synthesis proceeding is exhibited in Fig. S1 in the Supporting information (SI).

The $Zn_{0.9}Fe_{0.1}S$ catalyst was synthesized using a traditional method depending on the reported protocol [14]. Briefly, the zinc acetate and ferric nitrate with the same amount compared with MIM method were dissolved in 100 mL of DI water using a magnetic stirrer. Then, the solution was dropped with 6–8 s/drop of 50 mL sodium sulfide (0.01 mol L^{-1}), and heated to 100 °C for 30 min using a heating jacket. The precipitate was washed by ethanol and distilled water for two times, respectively. Finally, the resulting solid was dried in vacuum oven under 60 °C for 5 h, and ground into powders for storage.

2.3. Photocatalyst characterization

The morphology of the catalysts was determined by a scanning electron microscopy (SEM) (Zeiss Ultra60 microscope). The crystalline structures of the samples were analyzed by an X-ray diffractometer (XRD, Rigaku, DMAX-2500) using Cu $K\alpha$ irradiation under an accelerating voltage of 40 kV and the applied current of 200 mA, respectively. Elemental analysis was performed using both energy-dispersive X-ray spectroscopy (EDS, Zeiss Ultra60 SEM) and inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Optima NexIon^{HM} 300D). The S composition of the photocatalyst was analyzed by Ion Chromatography (IC) on a Dionex AS50 equipped with an ED50 electrochemical detector and an AS9-HC column. The BET surface area was measured through nitrogen adsorption/desorption using a Micromeritics ASAP 2020 Physisorption analyzer.

2.4. Photocatalytic performance

The photocatalytic performance was tested by monitoring the degradation of the endocrine disruptor BPA under UV-light irradiation. A 100 W mercury lamp (dominant wavelength 365 nm) was positioned in the cylindrical quartz cold trap to provide irradiation at an intensity of about 3.4 W cm^{-2} measured by a FZ-A spectroradiometer. The reaction apparatus was made up of a shelter, a power regulator, an illuminant of mercury lamp, a glass reactor,

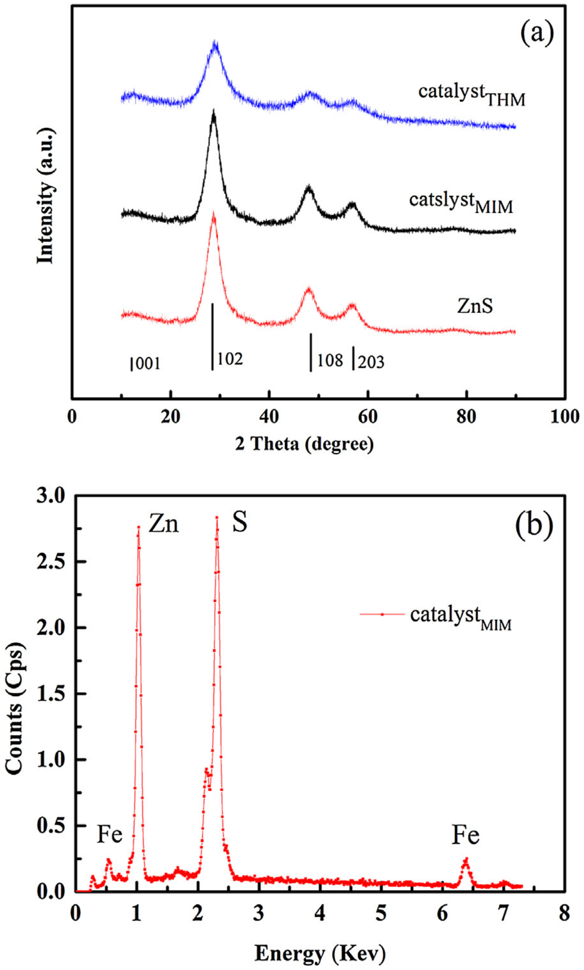

Fig. 1. XRD (a) and EDS (b) patterns of the $Zn_{0.9}Fe_{0.1}S$ catalysts (catalyst$_{MIM}$ and catalyst$_{THM}$ are denoted for catalysts obtained by microwave and traditional methods respectively).

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