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Rapid synthesis of Ag/AgCl@ZIF-8 as a highly efficient photocatalyst for degradation of acetaminophen under visible light

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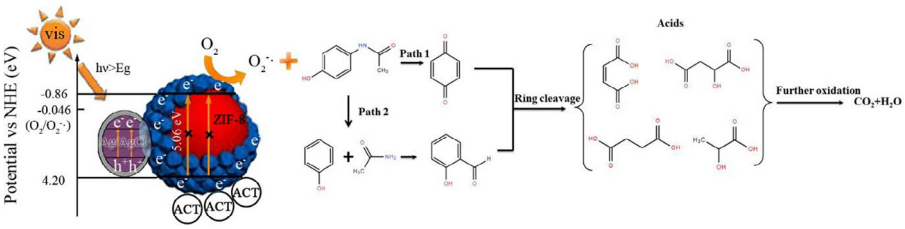
HIGHLIGHTS

- A visible-light-driven Ag-doped MOFs photocatalyst was synthesized to photodegrade PPCPs.
- Different factors on the degradation efficiency of ACT were investigated.
- Kinetics in the photodegradation process of ACT were studied.
- Intermediates, photocatalytic path and mechanisms were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of acetaminophen (ACT) used for painkillers has attracted great attention in the world, which have potentially adverse effects on aquatic lives and human beings. Advanced oxidation technology applied to water repair has received increasing concerns in recent years. In this study, photodegradation ACT in aqueous solution over Ag/AgCl@ZIF-8 synthesised by a simple stirring method was investigated under visible light irradiation. The prepared photocatalyst was characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (SEM) and UV-visible diffuse reflectance spectra (UV-vis). The degradation rates of ACT under different parameters were studied to get the optimal operating conditions in water. Results showed that the photodegradation process fitted pseudo-first order model well. 99% ACT degradation achieved when Ag/AgCl@ZIF-8 was delivered to the solution compared with ZIF-8 and Ag/AgCl with the maximum value of constant (k_{app}). The degradation rate obviously slowed down when the initial concentration of ACT increased to 2 mg/L while it increased with the increasing of dosage of photocatalyst. In contrast, pH has little effect on the degradation of ACT over Ag/AgCl@ZIF-8. The Ag/AgCl@ZIF-8 showed high efficiency for degradation after three repeated cycles which demonstrated the prepared photocatalyst has high stability. The $O_2^{-\cdot}$ turned out to be the main active group during the photodegradation process responsible for the disappearance of ACT. Intermediate products analysis results by LC-MS showed that photolysis was the first step of photocatalytic degradation for ACT followed by a ring cleavage.

1. Introduction

In the past decades, pharmaceutical and personal care products (PPCPs) as kinds of the major sources of pollution have attracted great attention, which are generally discharged into surface water and soil with the wastewater from hospitals, domestic sewage systems and

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industries [1,2]. Acetaminophen (ACT), a typical PPCPs, as one of the most widely used drugs [3] is used for painkiller and found about 58–68% excreting from the body during therapeutic process [4]. ACT has been detected in sewers, sewage plants and even in drinking water due to its large usage [5,6]. In China, ACT also is one of the largest drug products to moderate pain relief and the quality of discharge water from domestic normal ACT manufacturers cannot meet the discharge standards by local government. The concentration of ACT in natural water can reach 6–10 μg/L [7,8]. It presents threats to the environment and health even at low concentrations. So, it's urgent to find an economic and reasonable method to remove ACT from the water.

So far, there have been many techniques for the treatment of PPCPs to produce high quality water, such as hybrid technologies, combinations of conventional and advanced treatments and so on [9]. Among them, photocatalytic decomposition as one of the most efficient and environmentally friendly remediation techniques has attracted a lot of attention. Photocatalytic technology has been used to destroy and mineralize some recalcitrant organics in wastewater because it can produce highly reactive chemical species which are able to non-selectively oxidize organic pollutants [10]. Unfortunately, the low surface area and wide band gap of conventional photocatalysts limit the application of photocatalytic technology in water treatment. Unmodified catalysts have very low utilization of visible light because of their wide band gap [11].

As an important multi-functional material, silver-based semiconductor photocatalysts mostly has suitable band gap which can make full use of the energy of sunlight both visible-light and UV-light [12]. Therefore, Ag plays an important role in the field of photocatalysis. To date, many silver-containing materials such as Ag_2O [13], AgX (Cl, Br, I) [14], Ag_2CO_3 [15], Ag_2PO_4 [16] are considered to be good light-driven photocatalysts. Wang et al. [17] found that Ag_2O showed good photocatalytic performance for the photocatalytic decolorization of an MO solution. However, Ag compounds are rarely used alone as catalysts due to the poor adsorption capacity and high electron-hole fast recombination of photo-generated charges [14]. Ag compounds are often used as a modified material for the synthesis of supported silver-based catalysts [18,19] or heterostructures [16]. In addition, Ag is one of the trace elements in human tissues, so a trace amount of silver is harmless to the human health. According to the “Guidelines for Drinking-Water Quality” (fourth edition) by the World Health Organization guidelines in 2017, drinking water with level of silver up to 0.1 mg/L can be tolerant without risk to human health. The maximum concentration of silver in public water supplies is also 0.1 mg/L, which is regulated by US Environmental Protection Agency (EPA).

Metal-organic frameworks (MOFs) are a kind of porous nanocomposites with periodic multidimensional network structure formed by self-assembly of organic ligands such as metal ions and aromatic polyacids by coordination action. They have a large surface area, high porosity, good thermal stability, physical and chemical properties easy to control etc. [20,21]. Recently, they have been widely applied to separation, adsorption, catalysis, gas storage, sensors, batteries and many other areas [22,23]. However, the photocatalytic performance of them is not so good result from their low efficiency in exciton generation. Integrate MOFs with light-harvesting semiconductor materials to form heterostructures is proven to be a good method to improve the catalysts' photocatalytic activity. So far, MOFs photocatalysis is mainly used for the degradation of dyes. Few studies focused on MOFs photocatalytic elimination of PPCPs in aqueous solutions. ZIF-8 is a kind of MOFs with zinc ion as the central atom, whose thermal and chemical stability is higher than other MOFs [24–26]. Therefore, taking advantage of its high adsorption capacity is expected to make it a good support photocatalyst in the future. This work aims to investigate the photocatalytic properties of a novel heterostructures integrating MOFs with light-harvesting semiconductor materials for ACT degradation under visible light and to get the optimal parameters for ACT degradation in water solution. A facile route was employed to large-scale synthesis of Ag/AgCl@ZIF-8 through a stirring method. The effects of ACT initial concentration, MOFs dosage and initial pH on the photodegradation of ACT were investigated. What's more, the photogenerated reactive species and the photodegradation intermediates of ACT generated during the reaction were identified and the potential photocatalytic path and mechanism were proposed.

2. Experimental

2.1. Reagents

ACT and 2-methylimidazole were obtained from Aladdin Reagent Co., Ltd. $Zn(NO_3)_2{\cdot}6H_2O$, methanol, sodium chloride, ethanol and silver nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals for the synthesis of nanomaterials were used as received without any further purification.

2.2. Synthesis of nanomaterials

The nanomaterials used in this study were synthesized via stirring methods mainly according to Gao et al. [27].

2.2.1. Synthesis of ZIF-8 nanocrystals

In a typical synthesis, 2.348 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 5.192 g 2-methylimidazole were dissolved in 160 mL methanol to form solution A and solution B, respectively. Then, solution A was rapidly poured into solution B under magnetic stirring. The mixture was vigorously stirred at room temperature for 2 h. After 2 h, the resulting solid was harvested by centrifugation and was washed three times with absolute ethanol. Finally, the white crystalline product was obtained after being kept at 70 °C for 12 h.

2.2.2. Synthesis of Ag/AgCl@ZIF-8 photocatalyst

ZIF-8 with 0.2 g ground was dispersed in 14 mL of 53.7 mM $AgNO_3$ water-ethanol (v/v = 1: 6) mixture under magnetic stirring for 3 h. Then, the solution was added dropwise into 98 mL of 10.48 mM NaCl water–ethanol (v/v = 1: 6) mixture within 20 min and stirred at room temperature for 10 h. The solution was changed from white to light blue. Then, the products were recovered by centrifugation, washed with deionized water for three times, and finally dried at 70 °C for 12 h.

2.2.3. Synthesis of Ag/AgCl

For comparison, Ag/AgCl was synthesized by a precipitation method. 0.17 g $AgNO_3$ was firstly dissolved in 25 mL deionized water under stirring. The solution was added dropwise into 23 mL of 40 mM NaCl water solution within 20 min and kept stirring for ten hours at room temperature. After reaction, the resultant was collected by centrifugation, washing with deionized water three times for the removal of excess sodium chloride. The samples were dried at 70 °C in air for 12 h. The black Ag/AgCl powder was finally obtained.

2.3. Characterization

The X-ray diffraction (XRD) patterns were identified by X-ray diffractometry using Cu Kα radiation (λ = 0.15418 nm) at a scanning speed of 20°/min, in the 2θ range of 5–70°. UV–visible (UV-vis) diffuse reflection spectra was obtained using a UV-vis spectrophotometer (Perkin-Elmer, Lambda950, USA) with $BaSO_4$ as a reflectance standard. The morphologies of the samples were observed by scanning electron microscope (SEM) (Hitachi, S-4800, Japan), Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEOL, 2100F, Japan), respectively. Brunauer-Emmett-Teller (BET) surface areas were measured by nitrogen adsorption isotherm measurements on a surface area and porosity analyzer (Micromeritics, ASAP2020 HD88, USA) at liquid nitrogen temperature (77 K). Prior to the experiment the samples were degassed for 10 h at 423 K under vacuum. X-ray photoelectron