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Effects of water environmental factors on the photocatalytic degradation of sulfamethoxazole by AgI/UiO-66 composite under visible light irradiation

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ABSTRACT

It is necessary to find visible light responsive photocatalysts for rapid and simple degradation of organic pollutants in water environment. In this work, a visible light responsive composite photocatalyst AgI/UiO-66 was prepared by an in situ growth method. Sulfamethoxazole (SMZ) antibiotic was selected as the target contaminant to probe the photocatalytic performance of the as-prepared AgI/UiO-66 composite under visible light irradiation. The results showed that the photocatalytic performance of the AgI/UiO-66 composite enhanced significantly compared to pure AgI. The effects of typical environment factors (i.e. pH, inorganic salt ions and common anions) on the degradation of SMZ were evaluated extensively. Results showed that the investigated pH (5.2, 7.0, 9.5) had no apparent effect on the photocatalytic degradation of SMZ except pH 2.5, at which the degradation rate of SMZ decreased significantly. In addition, inorganic salt ions and Cl^-, HCO_3^- and SO_4^{2-} anions in water exhibited no apparent effect on the degradation of SMZ. The effect of water matrix on the degradation of SMZ was also investigated. In the river water, the removal efficiency of SMZ was reduced compared with the cleaner water matrix. The capture experiments of radicals confirmed that superoxide radicals ($\cdot O_2^-$) and hydroxyl radicals ($\cdot OH$) were the main active species for the photocatalytic degradation of SMZ in the present work. Finally, the tentative degradation pathways of SMZ were proposed based on the intermediates analysis.

1. Introduction

The pollution problem of antibiotics in environment has aroused widespread concern in society. Sulfonamide is one type of the most widely used antibiotics in human and veterinary drugs. Each year a large number of sulfonamides enter the environment [1–3]. Sulfonamides are known as trace contaminants in water environment that are difficult to be degraded, thus cause drug resistance for human and environmental organisms. As one of the most widely detected sulfonamides in water, sulfamethoxazole (SMZ) has been investigated in many studies as a sulfonamide antibiotic model for its universality, persistence and toxicity [4,5]. Therefore, it is extremely imperative for human to effectively eliminate SMZ antibiotics.

At present, common methods of removing antibiotics in water include biological treatment [6,7], active carbon adsorption [8], photocatalysis [9,10] and ozone oxidation method [11]. In these water treatment technologies, photocatalytic technology attracts more and more attention. Photocatalysis can quickly and effectively degrade organic pollutants in mild environment without secondary pollution [12,13]. In particular, photocatalytic applications in visible light will be the most attractive, because it can use readily available sunlight [14]. Therefore, it is necessary to develop a semiconductor material with high visible light utilization efficiency.

AgI is a visible light driven photocatalyst and its excellent photocatalytic performance has attracted considerable attention [15–17]. AgI can absorb photons to produce electron-hole pairs under visible light irradiation. But AgI is unstable and is easily reduced to Ag under visible light irradiation [18]. If AgI is dispersed on some carriers, it can maintain stability while preventing the occurrence of photocorrosion because of the fast transferring of

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charges [19]. On the other hand, the metal organic frameworks (MOFs) material has been widely used in the photocatalytic process because of its high specific surface area, adjustable aperture and good stability [20–22]. In particular, UiO-66, a Zr-based MOF has been extensively used for photocatalysis. UiO-66 not only exhibits high structural stability [23], but maintains such stability after the modification of active functional groups or the introduction of missing joint defects [24]. These properties make UiO-66 a particularly prospective candidate for photocatalytic applications in water treatment. This creates a motivation to exploit UiO-66 based photocatalysts for water treatment. Hence, the UiO-66 with high specific surface area was selected as the support to control the growth of AgI.

In this article, AgI nanoparticles were grown in situ on the UiO-66 framework. The phase structures, morphologies and optical properties of the prepared catalysts were detected. Moreover, the effects of water environmental factors (pH value, inorganic salt ions, common anions and water matrix) on the degradation of SMZ were discussed. In addition, the photocatalytic mechanism of SMZ was also investigated, including active substances, oxidation products and degradation pathways.

2. Materials and methods

2.1. Reagent

Zirconium tetrachloride, terephthalic acid, N, *N*-dimethyl formamide, methanol, potassium iodide, argentum nitricum, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride, sodium sulfate, sodium bicarbonate, ferric chloride, calcium chloride, magnesium chloride and potassium chloride were purchased from Sinopharm (China). SMZ was purchased from Aladdin (America). Pure water was acquired from a purification system (Millipore Milli-Q, USA). Acetonitrile and formic acid were supplied by Tedia (America), and they were chromatographic pure reagents. Other reagents were all analytical reagents.

2.2. Preparation of material

2.2.1. Preparation of UiO-66

UiO-66 was synthesized by modified solvothermal method [25]. Zirconium tetrachloride (2.0 mmol) and terephthalic acid (2.0 mmol) were successively dissolved in N, *N*-dimethyl formamide (100 mL) and the solution was transferred into a 200 mL of stainless steel autoclave. The autoclave was sealed and heated in a 120 °C oven for 24 h. After natural cooling, the precipitate was centrifuged and immersed in methanol for three days. Methanol was changed every 24 h. Finally, the white products were dried under vacuum at 60 °C.

2.2.2. Preparation of AgI/UiO-66

Potassium iodide (153 mg) was dissolved in 45.5 mL of pure water. Then, UiO-66 (250 mg, structural formula noted as $Zr_{24}O_{120}C_{192}H_{96}$ [26]) was added into the above solution under vigorous stirring. After stirring for 1 h, 4.61 mL of 0.2 M $AgNO_3$ aqueous solution was added into the above mixture solution and kept stirring at room temperature for 12 h. Next, the products were collected by centrifugation and washed thoroughly with pure water for several times. Ultimately, the obtained samples were dried under vacuum at 60 °C.

2.3. Characterization

The X-ray diffraction patterns of the samples were analyzed by Rigaku's SmartLab diffractometer in the range of 2θ between 5° and 50°. The morphology features of as-prepared samples were observed by transmission electron microscopy (TEM, FEI, TECNAI G20). The optical properties of the samples were researched using UV–Vis diffuse reflectance spectroscopy (Shimadzu, UV3600).

2.4. Photocatalytic experiments

2.4.1. Photocatalytic degradation of SMZ

In this experiment, 25 mg of the as-prepared sample was added to 50 mL of 5 mg/L SMZ aqueous solution and kept in dark conditions for 1 h to achieve adsorption equilibrium. Then the mixture solution was irradiated by a 300 W Xe lamp (Beijing Zhongjiaojinyuan, CEL-HXF300) with a 400 nm cut-off glass filter. After the start of the illumination, 1.5 mL of the solution was taken at regular intervals and filtered with a 0.22 μm syringe filter to remove the suspended solid particle before the detection of the concentration of SMZ. The blank experiment of SMZ photolysis was the same as above procedure except that no catalyst was added. The environmental factor experiment was carried out by the similar procedure.

2.4.2. Trapping experiments of active species

The trapping experiments were carried out under the same reaction conditions except that the capture agent was added into the photocatalytic reaction solution. The active species were •OH, $•O_2^-$ and h^+ which were captured by tert-butanol (5 mmol/L), *p*-benzoquinone (1 mmol/L) and EDTA-2Na (5 mmol/L) respectively.

2.5. Analysis methods

The concentration of SMZ was detected by high performance liquid chromatography (HPLC, Waters e2695) with a UV detector at 270 nm. The chromatographic column was reversed phase C18 column (4.6 mm × 150 mm, 5 μm). The mobile phase was 30% acetonitrile and 70% water (pH = 3) adjusted with phosphoric acid at a flow rate of 1 mL/min. The injection volume was 10 μL and the column temperature was maintained at room temperature during injection analysis.

The intermediates produced during the degradation of SMZ were identified via liquid chromatography-triple quadrupole mass spectrometry (LC-MS, Agilent, 6460 Triple Quad LC/MS series) with a C18 column (2.1 mm × 50 mm, 1.8 μm). The chromatographic conditions of the HPLC were shown as follows: the flow rate was 0.2 mL/min and the column temperature was 25 °C with 5 μL of the injection volume. The mobile phase was aqueous solution A containing 0.1% formic acid and acetonitrile B containing 0.1% formic acid. The gradient elution program was presented as follows: 0–3 min, 10%–20% B, 3–8 min, 20%–35% B, 8–15 min, 35%–60% B, then equilibrated for 6 min. An electrospray ionization source API-ES was used for MS/MS measurements in the positive ion mode and full spectrum scanning. The other parameters were set as follows: the capillary voltage was 3000 V. The atomization pressure and the drying gas temperature were 30 psi and 300 °C, respectively, and the flow rate of dry gas was 10 L/min.

3. Results and discussion

3.1. Characterization

In order to more clearly observe the appearance of the sample, we conducted TEM and HRTEM characterization. It can be seen from Fig. 1(a) that UiO-66 is a regular cube structure. In Fig. 1(b) and (c), several nanometers to dozens of nanometers of small particles adhere to the surface of UiO-66 and grow around UiO-66. In addition, Fig. 1(d) showed that 0.210 nm and 0.225 nm lattice edge spacing correspond to 103 and 110 lattice planes of AgI nanocrystals.