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Effect of bismuth tungstate with different hierarchical architectures on photocatalytic degradation of norfloxacin under visible light

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Abstract: The photocatalytic degradation of norfloxacin by bismuth tungstate (Bi_2WO_6) with different hierarchical architectures was investigated under visible light irradiation. Bi_2WO_6 was prepared by hydrothermal method with the reaction solution pH ranging from 4 to11. The relatively ultrathin Bi_2WO_6 nanoflakes prepared at pH 4 showed excellent adsorption and photodegradation efficiency towards norfloxacin. The characterization results showed that Bi_2WO_6 prepared at pH 4 had a larger specific area and faster photo-generated carrier separation rate. The decay rate reached the maximum in weak alkaline reaction solution, which could be attributed to the presence of moderate OH^- anions. The present study demonstrated that the smaller size of Bi_2WO_6 could be an efficient photocatalyst on the degradation of norfloxacin in the aquatic environment.

Key words: norfloxacin; bismuth tungstate; hierarchical architecture; photocatalytic degradation; size effect

1 Introduction

The frequent occurrence of pharmaceuticals in the aquatic environment has become an important issue in past decades [1−3]. Particularly after HIRSCH et al [2] separated antibiotic resistant bacteria from sewage sludge, and NEU [4] reported the crisis in antibiotic resistance of microorganisms, the focus turned to the occurrence of antibiotic drugs in aquatic environment. Most of the antibiotic drugs are not well adsorbed in the subsoil because of their polar structure, and may seep into groundwater aquifers from polluted surface water [5]. Among the antibiotic drugs, fluoroquinolone is synthetic and widely used in human and veterinary medicine. Recently, fluoroquinolone reserved in sewage water, surface water and ground water has been reported to lead to an obviously adverse effect on the aquatic ecosystems [6−11]. Norfloxacin is one of the main fluoroquinolone antibiotics, and 75% of it is excreted from the human body and remain unchanged [12].

In the past decade, researchers have explored the removal of pharmaceutical compounds in aqueous systems by different methods, including adsorption [13], biodegradation [14], ultrasonic [15] and chemical techniques [16]. Carbonaceous absorbents can quickly adsorb antibiotics and heavy metals from water due to their high pore volume and specific surface area [17−20], but there is a potential risk of the “removed” antibiotics and heavy metals being released into aquatic environment if the used sorbent is improperly disposed. Biodegradation method usually takes a long time and depends on many environmental factors such as bacterial counts, salinity, and temperature [21,22]. Among these methods, photocatalysis technique was found to be an effective method with high degradation and mineralization efficiency [23−25]. Since the discovery of the photocatalytic splitting of H_2O on the TiO_2 electrodes by FUJISHIMA et al [26], TiO_2 has been widely used in sterilization, sanitation, and remediation

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applications [27−29], providing a promising method for water treatment. However, the widely used photocatalyst, namely TiO_2, can only be excited by UV light with an irradiation wavelength less than 380 nm, which significantly limits its application. Therefore, it is urgent to develop highly efficient visible-light induced photocatalysts to meet the high requirements in dealing with environmental antibiotic pollution in the future.

Bismuth tungstate is a new kind of photocatalyst, and has been proved to have efficient performance in the solar-light-mediated systems [30]. Our previous work demonstrated that Bi_2WO_6 could efficiently photodegrade norfloxacin under the assistance of surfactant [31]. Bi_2WO_6 can absorb visible light in wider area (λ=400−800 nm) and has a photonic band gap (E_g=2.72 eV) narrower than that of TiO_2. The photocatalytic capability of Bi_2WO_6 is attributed to the band transition from the hybrid orbitals of Bi 6s and O 2p to the W 5d orbitals. Although the potential advantages of Bi_2WO_6 on photocatalysis have been discovered, the study on photocatalytic degradation of antibiotic norfloxacin using the Bi_2WO_6 with different morphologies and hierarchical architectures was rarely reported. The decomposition of organic contaminants in wastewater using the irradiated photocatalyst was explored [32], and the schemes are given as follows:

$$Bi_2WO_6+h\nu \longrightarrow Bi_2WO_6+h^++e \quad (1)$$

$$O_2+e \longrightarrow O_2\bullet^- \quad (2)$$

$$H_2O+h^+ \longrightarrow \bullet OH+H^+ \quad (3)$$

Bi_2WO_6 has different morphologies and hierarchical architectures made up of different sizes of nano-crystals. With the change of crystal size, quantum size effect and good physicochemical property such as high specific area may occur on photocatalyst. They are beneficial to improving the photodegradation of contaminants in the aquatic environment. It is necessary to specifically investigate the effect of different hierarchical architectures of Bi_2WO_6 on photocatalysis of antibiotics, which was seldom studied in the literature. We chose norfloxacin as the target pollutant (shown in Fig. 1).

This work aimed to study the photocatalytic degradation effect of norfloxacin by Bi_2WO_6 with different hierarchical architectures under visible light. Bi_2WO_6 catalysts were synthesized using hydrothermal method with different morphologies by varying the pH values of the reaction solutions. The physicochemical properties of the prepared catalysts were characterized, and their degradation capacities of norfloxacin were investigated. The impacts of different reaction factors on the degradation efficiency of the prepared catalyst were also discussed.

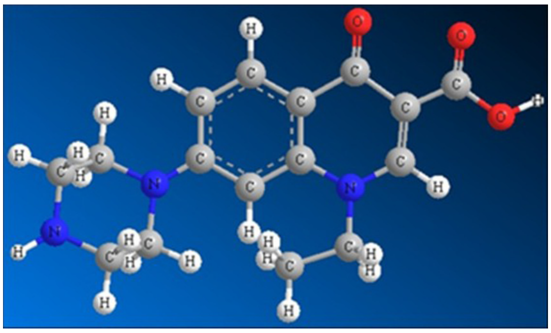

Fig. 1 Molecule structure of norfloxacin

2 Experimental

2.1 Materials

Norfloxacin (purity 99.8%) was purchased from Aladdin Reagent Company, Shanghai, China. All reagents used in the experiment were of analytical reagent grade. Solutions were prepared with high-purity water (18.25 MΩ/cm) from a Milli-Q water purification system.

2.2 Preparation and characterization of photocatalyst Bi_2WO_6

2.2.1 Preparation of photocatalyst Bi_2WO_6

Bi_2WO_6 samples were synthesized using hydrothermal method according to Ref. [33]. In general, 0.97 g of $Bi(NO_3)_3\cdot 5H_2O$ was dissolved into 20 mL of 1.0 mol/L HNO_3. 0.33 g of $Na_2WO_4\cdot 2H_2O$ was dissolved into the same volume of 1.0 mol/L NaOH. Then, the mixed solution was mixed ultrasonically at room temperature for 30 min. The pH value of reaction solution was adjusted to 4, 7, 9, and 11, respectively. Then, the suspension was transferred into a 100 mL Teflon-lined autoclave, and heated at 140 °C for 20 h. The obtained precipitates were washed with water and ethanol several times, and finally dried at 120 °C for 4 h. The obtained samples were denoted as Bi_2WO_6-pH4, Bi_2WO_6-pH7, Bi_2WO_6-pH9 and Bi_2WO_6-pH11, respectively.

2.2.2 Characterization

Crystallographic information of Bi_2WO_6 was obtained by X-ray diffraction (XRD, 43 Rigaku D/MAX-RB, Cu K_α radiation, Japan). The morphology of the prepared samples was observed by a 1530VP scanning electron microscope (SEM, Quanta 200 FEG, FEI Company, America). The specific surface area was measured by a Quantachrome NOVA 2000e sorption analyzer (Quantachrome, America). UV–Vis diffused reflectance spectra (DRS, Shimadzu, UV−3150, Japan) of Bi_2WO_6 were obtained on a Hitachi U−3010 spectrometer, using $BaSO_4$ as the reference.

2.3 Norfloxacin degradation procedures

The degradation experiment was carried out under