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Enhanced photoelectrocatalytic degradation of norfloxacin by an $Ag_3PO_4/BiVO_4$ electrode with low bias

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ABSTRACT

In this work, an Ag_3PO_4-modified $BiVO_4$ electrode was prepared on an FTO substrate and used as a photoanode for photoelectrocatalytic degradation of organic contaminants. The photocurrent generated from the synthesized $Ag_3PO_4/BiVO_4$ photoelectrode under visible light irradiation was more than twice that from pure the $BiVO_4$ electrode, which could be attributed to the lower recombination rate of the photogenerated electron–hole pairs of the $Ag_3PO_4/BiVO_4$ photoanode, as proved by the electrochemical impedance spectroscopy and photoluminescence spectra. The $Ag_3PO_4/BiVO_4$ electrode was effective for the oxidation of organic pollutants in photoelectrocatalysis systems at relatively low bias potentials. A higher photoelectrocatalytic activity for norfloxacin degradation was observed when the $Ag_3PO_4/BiVO_4$ electrode was than with the $BiVO_4$ electrode, where norfloxacin with an initial concentration of 5 mg/L could be degraded within 90 min. The apparent rate constants of norfloxacin degradation using a $BiVO_4$ electrode and $Ag_3PO_4/BiVO_4$ are estimated to be 2.83×10^{-4} min^{-1} ($R^2 = 0.994$) and 7.94×10^{-4} min^{-1} ($R^2 = 0.996$), respectively. Analysis of the degradation intermediates indicated that the piperazine ring and the carboxyl group of the norfloxacin were attacked during the degradation process. The $Ag_3PO_4/BiVO_4$ photoanode was also proved to be effective for the degradation of two other antibiotics, sulfamethoxazole and oxytetracycline.

1. Introduction

With the increasing demand for clean energy and the growing problem of water pollution, the photoelectrocatalytic process that can be used for the generation of electricity [1] or the degradation of organic pollutants [2] has undergone rapid development in recent years. The most investigated photoanode material is TiO_2. It can utilize ultraviolet light to achieve efficient degradation of various organic pollutants [3–5]. To make the most of the solar light, more visible-light-responsive semiconductors such as WO_3 [6], $BiVO_4$ [7–9], and Fe_2O_3 [10] have been developed.

Monoclinic $BiVO_4$ is one of the most promising photoanode materials. It is an n-type metal oxide semiconductor, which has shown high performance in photoelectrochemical applications such as water splitting [11,12] and oxidation of organic pollutants [13]. Monoclinic $BiVO_4$ has a band gap of ca. 2.4 eV, and it can absorb visible light up to 525 nm [14]. $BiVO_4$ film electrodes have been synthesized successfully using various methods. Kim and Choi synthesized nanoporous $BiVO_4$ electrodes with a diameter of about 70 nm using an electrodeposition–annealing method [15]. The synthesized electrode showed high activity for photoelectrochemical water splitting. Kuang et al. have synthesized a semitransparent $BiVO_4$ electrode, which further extends the applications of $BiVO_4$ electrodes [16].

However, one of the problems with $BiVO_4$ electrodes is still the low separation efficiency of photogenerated electron–hole pairs. To address this problem, various methods such as doping [17,18], constructing heterojunctions [1,19], and chemical treatment [20] have been tried to increase the separation efficiency of the photogenerated charge carriers. A W–Mo co-doped $BiVO_4$ electrode was successfully synthesized by Park et al. [21]. The doping of W and Mo has significantly improved the separation of the charge carriers; compared with pure $BiVO_4$ electrodes, a more than 10 times increase in water oxidation activity was observed after W–Mo doping. The formation of heterojunctions is also widely investigated, and various heterojunction structures such as $WO_3/BiVO_4$ [22], $CdS/BiVO_4$ [23], and $Cu_2O/BiVO_4$ [24] that have good photocatalytic performance have been constructed successfully.

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Ag_3PO_4 is a visible-light-responsive semiconductor and has shown high activity for the photocatalytic degradation of various pollutants [25,26]. The preparation of $Ag_3PO_4/BiVO_4$ heterojunction photocatalysts has been studied and the $Ag_3PO_4/BiVO_4$ heterojunctions possess higher photocatalytic activity than singular Ag_3PO_4 or $BiVO_4$ photocatalysts [11,27,28]. However, to the best of our knowledge, the synthesis of $Ag_3PO_4/BiVO_4$ electrodes has not been reported yet, and their performance in a photoelectrocatalysis system has not been studied.

In this work, an $Ag_3PO_4/BiVO_4$ electrode was synthesized onto a fluorine-doped tin oxide (FTO) substrate. $BiVO_4$ electrodes using FTO glass substrate were prepared using an electrodeposition-based method, and then Ag_3PO_4 particles were grown in situ on the $BiVO_4$ film. The formation of $Ag_3PO_4/BiVO_4$ electrodes significantly promoted the separation of the photogenerated electron–hole pairs. Norfloxacin, one of the most widely used quinolone antibiotics, was used as a model pollutant in this study. The removal of oxytetracycline and sulfamethazole, which are the most used tetracyclines and sulfanilamides, were also studied. High activity for the degradation of the antibiotics was demonstrated. The enhanced mechanism was proposed.

2. Experimental

2.1. Materials

Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), potassium iodide (KI), *p*-benzoquinone, vanadylacetylacetonate ($VO(acac)_2$), and dimethyl sulfoxide were purchased from Sinopharm Chemical Reagent Co. and were used as received without further purification. Transparent FTO conductive glasses ($5 \times 2.5 \times 2.2$ mm, 6 Ω) were purchased from South China Xiang Science & Technology Co. Milli-Q water (18.2 MΩ·cm) were used throughout this study.

2.2. Preparation of $BiVO_4$ electrodes

$BiVO_4$ electrodes were prepared by electrodeposition reported by as Kim and Choi [15]. In brief, $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in a 0.4 M KI solution of 50 mL (pH was adjusted to 1.7 with HNO_3) to achieve a $Bi(NO_3)_3{\cdot}5H_2O$ concentration of 0.04 M. A 0.23 M *p*-benzoquinone solution of 20 mL was prepared by dissolving *p*-benzoquinone in absolute ethanol. The two solutions were mixed and stirred for 2 min before electrodeposition. A three-electrode system was used for the deposition of BiOI. The working electrode was a pretreated FTO glass, the counter electrode was a Pt wire, and the reference electrode was a saturated calomel electrode (SCE). All potentials used were demonstrated vs. SCE in this work. The electrodeposition process was conducted at −0.15 V for 5 min. Then a drop of DMSO containing 0.2 M $VO(acac)_2$ was cast onto the BiOI and the electrode was heated in a muffle furnace at 450 °C for 2 h. Excessive V_2O_5 was removed by immersing the electrode in 0.1 M NaOH for 30 min and then washing it with plenty of water. The $BiVO_4$ electrode was dried before use.

2.3. Preparation of $Ag_3PO_4/BiVO_4$ composite electrodes

The $Ag_3PO_4/BiVO_4$ composite electrodes were prepared by the in situ growth of Ag_3PO_4 on $BiVO_4$ electrodes. The $BiVO_4$ electrodes were immersed in $AgNO_3$ solutions at different concentrations (3, 6, 15, 30 mM). Then K_2HPO_4 was added to the solution to achieve Ag_3PO_4 concentration of 1, 2, 5, and 10 mM. The solution was slowly stirred under darkness for 4 h. The electrodes were dried in an oven and washed with water several times afterward to remove excessive NO_3^-, HPO_4^{2-}, and the loosely bonded Ag_3PO_4 particles. The electrodes were denoted as $Ag_3PO_4/BiVO_4$-1, $Ag_3PO_4/BiVO_4$-2, $Ag_3PO_4/BiVO_4$-5, and $Ag_3PO_4/BiVO_4$-10, respectively.

2.4. Characterization techniques

The morphology of the electrodes was observed with a field emission scanning electron microscope (FESEM, HITACHI SU8020, Japan) equipped with an energy-dispersive X-ray spectroscopy system (EDX). The XRD patterns of the electrodes were measured on a diffractometer (Panalytical X'Pert Pro, Netherlands) with Cu Kα radiation (λ = 1.5418 Å). Raman spectra were obtained from a Raman spectrometer (Horiba Scientific HR800, France). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Perkin–Elmer PHI-5300 ESCA spectrometer with Al*K*α source. UV–visible diffuse reflectance spectra (UV-DRS) were obtained with a Shimazu S 2600 UV spectrophotometer. The content of Ag_3PO_4 and $BiVO_4$ in the electrode was measured by dissolving the electrode with 1 M HNO_3 and measuring the concentrations of Ag, Bi, and V by inductively coupled plasma optical emission spectrometry (ICP-OES) (for details see Text 1 in the Supporting Information).

2.5. Photoelectrochemical tests

The photoelectrochemical tests were performed in a 0.1 M $NaClO_4$ solution using a three-electrode system, where the prepared $Ag_3PO_4/BiVO_4$ electrodes, Pt wire, and SCE were used as working electrode, counter electrode, and reference electrode, respectively. The electrodes were back-illuminated with a 300 W Xe lamp equipped with a 420 nm cutoff filter. The effective area of the electrode is 6.25 cm^2 and films were illuminated from the back of the FTO. Linear sweep voltammetry (LSV) measurements were conducted at a sweep rate of 50 mV/s, and $i-t$ measurements were performed by applying a constant potential. All measurements are reported vs. the SCE. Electrochemical impedance spectroscopy (EIS) measurements were conducted from 0.1 to 100 000 Hz at open circuit potential (OCP).

2.6. Degradation experiments

The degradation experiments were also conducted using the above-mentioned three-electrode system. The electrolyte was 10 mM $NaClO_4$. The concentration of the antibiotics was measured by high-performance liquid chromatography (HPLC, Shimadzu LC-20AD, Japan) with an Agilent TC-C18 column (150×4.6 mm). The specific measuring methods are listed in Table S1 in the Supporting Information. The leaching of Ag, V, and Bi was measured by inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Characterization of $BiVO_4$ and $Ag_3PO_4/BiVO_4$ electrodes

Fig. 1 shows the SEM images of the as-prepared pure $BiVO_4$ and composite $Ag_3PO_4/BiVO_4$ electrodes. It can be seen from Fig. 1A that the pure $BiVO_4$ electrode shows a 3D nanoporous structure and the diameters of the $BiVO_4$ nanoparticles are about 80 nm. Fig. 1B–E show the composite $Ag_3PO_4/BiVO_4$ electrodes with different Ag_3PO_4 amounts. Ag_3PO_4 nanoparticles with different morphologies were observed when Ag_3PO_4 concentration increased from 1 to 10 mM during the preparation process. For $Ag_3PO_4/BiVO_4$-1, only large Ag_3PO_4 nanoparticles were observed. It can be observed that composite $Ag_3PO_4/BiVO_4$-2 and $Ag_3PO_4/BiVO_4$-5 electrodes were covered with ordered Ag_3PO_4 nanoparticles, whereas $Ag_3PO_4/BiVO_4$-5 showed a 3D nanoporous structure with the most ordered morphology and the smallest diameter of Ag_3PO_4