



Research Paper

Fabrication of InVO₄/AgVO₃ heterojunctions with enhanced photocatalytic antifouling efficiency under visible-light



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ABSTRACT

With the increasing of bacterial resistance to available antibiotics and water contamination by poisonous organic dyes, it's necessary to consider how to overcome these concerns. In this paper, novel visible-light-sensitive InVO₄/AgVO₃ photocatalysts with a *p-n* junction were synthesized through an ion exchange and in-situ growth process. The obtained photocatalysts were characterized by X-ray powder diffraction (XRD), Transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectroscopy (UV-DRS) respectively. It can be observed that the AgVO₃ exhibits a rod-shaped structure, while a plentiful of spherical shaped InVO₄ particles are formed on the surface. The rod-shaped structure of AgVO₃ wasn't changed by the addition of InVO₄, but its photocatalytic properties were tremendously improved. The best photocatalyst was 0.5InVO₄/AgVO₃, over which the Rhodamine B (RhB) solution was almost decomposed in 200 min under visible light irradiation. Moreover, about 99.9999% of *P. aeruginosa* (*P. aeruginosa*), *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were killed over 0.5InVO₄/AgVO₃ at 30 min. From these results it can be inferred that 0.5InVO₄/AgVO₃ heterojunctional photocatalyst has an improved efficiency for the separation of the current carriers to enhance the photocatalytic performances. This result provided a valuable design for the novel InVO₄/AgVO₃ heterojunction photocatalysts with excellent photocatalytic properties used in marine antifouling.

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1. Introduction

With the development of marine exploration, there has been a growing attention on the issue of marine biofouling all over the world, which resulted into enormous economic losses and serious security incidents to ocean development [1]. In order to reduce the harm of biofouling, antifouling coating is one of the most effective uses on the surface technology, but this technique triggered serious drug resistance owing to their high biotoxicity [2]. Nowadays, however, resistance to antibiotics and other antibacterial material had been reaching a dangerous level which invalidating the existing antimicrobial drugs. Therefore, it is essential to exploit environmentally friendly antifouling materials to substitute the toxic materials.

In the last few years, a novel and green photocatalytic technology based on semiconductors has been widely concerned, which can harness solar irradiation as a source of energy and show promising applications in the degradation of pollutants, splitting of water and sterilization [3–8]. At the present time, developing visible-light-responsive photocatalysts is the most important matter in this field, because the utilization of visible light, which accounts for more than half of the solar spectrum, is significant. Among all the visible light-driven photocatalysts with narrow band-gap examined so far, metal vanadate photocatalysts (MVO₄ where M = Ag, Bi, Al, Ti, In, Fe, Sr, etc.) have been widely investigated and applied in many fields of sciences and industrial [9–13].

Indium vanadate (InVO₄), with a bandgap of 2.0 eV, is one of these visible-light responsive metal vanadate photocatalysts and has received extensive interest owing to its various applications in many fields, including degradation of air purification, water splitting, organic pollutants, and so on [14–19].

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According to the previous research works [12,20–22], solid phase reaction, hydrothermal and sol–gel synthesis have been applied to synthesizing monoclinic or orthorhombic crystals of InVO_4 . Nevertheless, the performance of InVO_4 photocatalyst is not ideal due to its low efficiency on separating photogenerated electron–hole pairs. In addition, the performance of photocatalytic under visible-light irradiation could be improved by synthesized heterojunction photocatalysts with InVO_4 , such as $\text{TiO}_2/\text{InVO}_4$ [23] and $\text{BiVO}_4/\text{InVO}_4$ [24].

Silver vanadates have attracted increasing attention because of their excellent electrical properties and applications [25–29]. The crystalline phase and stoichiometry of such materials, depend heavily upon reaction conditions, intensively affect the functionalities. Silver vanadate has also been used as an efficient photocatalyst for environment purification [30–32]. This silver vanadate is a cheap, stable material that is abundant and has a controllable surface, so it can be treated as a new material for environmental application.

Therefore, in this study, the novel $\text{InVO}_4/\text{AgVO}_3$ photocatalysts were prepared for the first time by ion exchange and in-situ growth methods. The obtained photocatalysts were characterized by XRD, FESEM, EDS, HRTEM, XPS and UV-DRS respectively. The photocatalytic activities of InVO_4 , AgVO_3 , and $\text{InVO}_4/\text{AgVO}_3$ heterojunctions were presented by the degradation of RhB solution and the antibacterial activity under visible light irradiation. Moreover, the mechanism for the photocatalytic efficiency enhancement of these photocatalysts was proposed by trapping free radicals experiments and calculating energy band.

2. Experimental section

2.1. Preparation of the photocatalysts

All chemicals were analytical reagent (AR) grade and used without extra treatment. In a typical experiment, AgVO_3 photocatalysts were obtained by a facile hydrothermal method [33]. The typical synthesis process is as followings: 1 mmol AgNO_3 and 1 mmol NH_4VO_3 were respectively dissolved in 30 mL distilled water under magnetic stirring to obtain solution A and B. Subsequently, solution B was slowly added dropwise to solution A under stirring to form a final suspension, then the pH value was adjusted to 7.0 with 25 wt% $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 2 mol/L HNO_3 . The suspension was stirred for 1 h in dark, and transferred into a 100 mL Teflon-lined autoclave, and followed by treating it at 180 °C for 24 h. After that, the yellow products were cooled to room temperature naturally, and washed for several times with Milli-Q water and absolute ethanol, respectively. Finally, the samples were dried at 60 °C in air for 6 h to obtain the pure AgVO_3 crystals.

The novel $\text{InVO}_4/\text{AgVO}_3$ photocatalysts were prepared by ion exchange and in-situ growth method as follows: 1.0 mmol AgVO_3 was dispersed in 30 mL distilled water under magnetic stirring. Then, $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.25 g PVP were added to the above solution and then adjusted pH value to 7.0 with 25 wt% $\text{NH}_3 \cdot \text{H}_2\text{O}$. The obtained solid composites were then calcined at 160 °C for 12 h. After cooling to room temperature naturally, the precipitations were collected, washed for several times and then dried in air at 60 °C. According to this method, $\text{InVO}_4/\text{AgVO}_3$ nanocomposites were prepared with various molar ratios of In and Ag, which were denoted as $0.25\text{InVO}_4/\text{AgVO}_3$, $0.5\text{InVO}_4/\text{AgVO}_3$, $0.75\text{InVO}_4/\text{AgVO}_3$, and $1\text{InVO}_4/\text{AgVO}_3$, where the molar ratio of In and Ag was 0.25:1, 0.5:1, 0.75:1 and 1:1, respectively. In addition, the pure InVO_4 and AgVO_3 crystals were also prepared by the same conditions.

2.2. The characterizations of the photocatalysts

The crystalline structures of the samples were characterized by XRD with Rigaku D/max-3C X-ray diffraction operating at 40 kV and 30 mA with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The morphologies were performed by FE-SEM (Hitachi S-4800, Japan) operating at 10 kV. TEM and HRTEM images were implemented on a Tecnai G220 transmission electron microscope at 200 kV acceleration voltage with EDS for elemental analysis. The XPS measurements were measured on Multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI, USA) with total power dissipation of 150 W (15 kV, 10 mA). The UV–vis absorption spectroscopy of the samples were carried out on Hitachi U-4100 UV Spectrometer (Japan) using BaSO_4 as the reference.

2.3. Photocatalytic performance

The photocatalytic activities of the synthesized materials were determined by degradation of RhB under visible light at room temperature. A 800 W xenon lamp was used as the light source, and a cutoff filter was used to remove the wavelength of light less than 420 nm [34]. In those experiments, 25 mg of photocatalysts were dispersed into 50 mL of 50 mg/L RhB solution with quartz tubes respectively. In order to ensure the adsorption/desorption equilibrium, these solution was stirred for 30 min in darkness before irradiation. The photocatalytic degradation ratio was measured by the absorption peak at 553 nm to determine the remnant concentration of RhB at different intervals by the same UV–DRS (UV-2550, Shimadzu, Japan).

Antibacterial response was measured against *E. coli*, *S. aureus* and *P. aeruginosa* which have been pervasively applied to model bacteria in previous research [35–37]. The bacterial stock suspensions concentrations were typically 10^6 cfu/mL. Then, the photocatalytic antifouling experiments were measured by a 800 W xenon lamp with a cutoff filter. In addition, 25 mg of photocatalyst, 49.5 mL of sterilized natural seawater or PBS, and 500 μL of bacterial suspension was added into 50 mL of quartz tubes in sequence. After stirred for 30 min in darkness, the suspensions were exposed to light irradiation for another 30 min. 1 mL of the bacteria suspension was fetched and diluted several multiples with sterilized seawater or PBS every 10 min. Besides, 100 μL of these suspension was immediately coated on LB agar plates and cultured of these bacteria at 37 °C for 24 h to calculate the number of bacteria colony (in cfu). According to the blank control which was disposed without photocatalysts, the antibacterial rate was computed as follows:

$$\text{Antibacteria rate (\%)} = 100 - \left(\frac{N_t}{N_0} \right) \times 100$$

Where, N_0 and N_t are the numbers of bacteria colony in the blank control and the samples with photocatalysts, respectively. Therefore, the anti-microbial rate could be defined as follows:

$$\text{Antimicrobial rate (\%)} = 100 - \text{survial rate}$$

The active free-radicals were trapping by adding scavengers, in which the concentrations of IPA (a scavenger of hydroxyl radical, $\bullet\text{OH}$), of DS (a scavenger of superoxide radical, $\bullet\text{O}_2^-$), and sodium oxalate (a scavenger of holes, h^+) were used in solutions with the addition of 1 mmol of quencher [24,38].

3. Results and discussions

3.1. The structural analysis of the photocatalysts

The X-ray diffraction (XRD) patterns of the as-prepared samples are shown in Fig. 1. For pure InVO_4 , every diffraction peak

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