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# BiOI/$BiVO_4$ *p–n* heterojunction with enhanced photocatalytic activity under visible-light irradiation

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ABSTRACT

A novel visible-light-sensitive BiOI/$BiVO_4$ photocatalyst with a *p–n* heterojunction structure was synthesized through a facile coprecipitation method. The physical and chemical properties of as-synthesized BiOI/$BiVO_4$ composites were characterized by XRD, XPS, BET, SEM, EDS, HRTEM, photoluminescence spectrum and UV–DRS respectively. The photocatalytic activity of the prepared photocatalysts was evaluated by photodegrading methylene blue and killing of *Pseudomonas aeruginosa* (*P. aeruginosa*) under visible light irradiation. The results showed that the 30%BiOI/$BiVO_4$ (molar ratio of I:V = 3:7) exhibits the higher photocatalytic activity than the pristine BiOI and $BiVO_4$. Moreover, the sterilization mechanism involved in the photocatalytic disinfection process was studied by captive species trapping experiments. The result revealed that hydroxyl radical ($^{\bullet}OH$) and holes ($h^+$) are the main reactive species for killing of *P. aeruginosa* under visible light irradiation. In addition, after five recycles for killing of *P. aeruginosa* under visible light irradiation, 30%BiOI/$BiVO_4$ does not exhibit significant loss of photocatalytic activity. The results confirm that the synthesized 30%BiOI/$BiVO_4$ photocatalyst has long-time reusability and good photocatalytic stability. The photocatalyst shows potential application in marine antifouling.

## Introduction

Marine biofouling is one of the most serious problems in marine systems all over the world. It arises from the adhesion of marine organisms (bacteria, algae, mollusc, etc.) and their secretion [1]. Marine biofouling can lead to many serious economical and safety problems, including the acceleration of metal corrosion, the service lifetime of marine engineering installations, and the reduction of the quantity and quality of aquaculture industry. Traditionally, in order to reduce the harm caused by biofouling, antifouling coatings are used on the surface of marine installations and has obtained reasonably good antifouling results, while they give rise to serious marine biological hazard owing to their high biotoxicity. Meanwhile, the new European and international regulations on chemical products will limit the coatings with biocides uses for environmental application [2]. Hence, it is urgent and essential to develop novel, efficient, and environmentally friendly marine antifouling materials to replace traditional ones [3,4].

In recent years, a novel and green technique based on semiconductor materials (known as photocatalysis technology) has been widely concerned, which can use solar energy to degrade organic pollutants and disinfection [5–8]. Moreover, photocatalysis technology is not only a cost-effective technology, but also an efficient method to decompose organisms completely into common harmless compounds ($CO_2$ and $H_2O$). Since the application of $TiO_2$ in photocatalytic disinfection was firstly reported by Matsunaga et al. [8], many scholars are committed to evaluate the photocatalytic bactericidal activity of $TiO_2$ [9–12]. Until now, due to its good photocatalytic activity, high catalytic stability and non-toxicity, $TiO_2$ has been widely used in the field of photocatalytic disinfection [9,10,13]. However, the intrinsic large band gap of $TiO_2$ leads to its response poor under visible light irradiation (only making use of 4% of sunlight) [14]. In order to harness solar energy

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effectively, a number of novel and visible-light-driven photocatalyse materials have been developed [15–17]. Among these photocatalyse materials, due to their subtle electron properties and physical properties and excellent light absorption properties, bismuth-based materials have been regarded as very promising photocatalysts.

Among these bismuth-based materials, bismuth vanadate ($BiVO_4$) is a new *n*-type semiconductor with a narrow band-gap (about 2.4 eV). It has good prospect in organic pollutants decomposing and photocatalytic disinfection [18]. The photocatalytic activity of $BiVO_4$ is to a great extent dependent on its crystal phase. It is reported that $BiVO_4$ has three main types of crystal phases: monoclinic scheelite, tetragonal scheelite and tetragonal zircon. The monoclinic scheelite $BiVO_4$ (m-$BiVO_4$) was regarded as a promising visible-light-responsive photocatalyst due to its relatively narrow band-gap [19–22]. Nevertheless, the higher photo-generated electron–hole pairs recombination rates and adsorptive performance, limit wide application of $BiVO_4$ [23,24].

Another bismuth-based semiconductor material, *p*-type semiconductor BiOI, has attracted increasing interest owing to its narrow band gap (about 1.8 eV) in recent years [25–32]. BiOI exhibits excellent visible-light absorption ability, making it a promising photocatalyst in water purification and disinfection [33]. Nevertheless, the photocatalytic activity of BiOI is also far from efficient for practical applications due to rapid recombination of photo-generated electron–hole pairs. Therefore, it is indispensable to boost the photocatalytic efficiency. Numerous efforts have been taken to promote the photocatalytic activity of BiOI. Among these approaches, the choice of transition other semiconductors is an easy and effective way, such as BiOI/$TiO_2$ [34], BiOI/AgI [35], BiOI/$Bi_2MoO_6$ [36], BiOI/$(BiO)_2CO_3$ [37], etc.

In the present study, we reported a novel BiOI/$BiVO_4$ heterojunction with a flower like structure synthesized by a facile coprecipitation method firstly. The photocatalytic activity of the BiOI/$BiVO_4$ heterojunction was evaluated by decomposing methylene blue (a model of organic contaminant) and killing *Pseudomonas aeruginosa* (a model of biofouling microorganism) under visible light irradiation for the first time. The results showed that the 30%BiOI/$BiVO_4$ (molar ratio of I:V = 3:7) can remove organic pollutants and kill waterborne bacteria efficiently. Moreover, we proposed the enhanced photocatalytic sterilization mechanism of BiOI/$BiVO_4$ heterojunction based on trapping experiments and calculated energy bands in detail. Therefore, the combination of $BiVO_4$ and BiOI in theory has the potential to improve the catalytic efficiency of BiOI.

There have been few similar studies done lately [38,39], but the morphology shapes and photocatalytic activities differs between our work and previous works. And the preparation method of BiOI/$BiVO_4$ composite is operated easily and controllable, which make it applicable for industrial production. Benefitting from easy operation, low cost and high stability, BiOI/$BiVO_4$ composite have great potential for further applications as photocatalyst in the marine biofouling and environment purification.

## Experimental

### *Materials*

$NH_4VO_3$, $Bi(NO_3)_3 \cdot 5H_2O$, KI, methyl blue (MB), isopropanol (IPA), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), sodium oxalate, glutaraldehyde, nutrient agar, tryptone, and other chemicals were all of analytical grade and provided by Sinopharm Chemical Reagent Co., Ltd. (China) except that analytical reagent grade yeast extract was purchased from Oxoid, Basingstoke, Hampshire (England). All reagents were used as received without any further purification. Milli-Q water (Millipore, USA) was used throughout this study. *P. aeruginosa* was obtained from the Key Laboratory of Experimental Marine Biology, Institute of Oceanology, Chinese Academy of Sciences (Qingdao, China). Natural seawater used after sterilization by autoclaving for 20 min at 121 °C at 0.1 MPa was collected from Huiquan Bay (Huanghai Sea, Qingdao, China) and filtered through a membrane filter (0.22 μm pore-size) before usage.

### *Preparation of photocatalysts*

The BiOI/$BiVO_4$ heterostructure was prepared by a facile coprecipitation method with different molar ratio of I:V. In a typical synthesis, 0.0332 g (0.0002 mol) of KI and 0.2106 g (0.0018 mol) $NH_4VO_3$ were dispersed in 40 mL of 50% ethanol and stirred for 30 min (marked as solution A). Simultaneously, 0.97 g (0.002 mol) of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 40 mL of 50% ethanol and stirred for 30 min (marked as solution B). Subsequently, adding solution B dropwise into solution A under stirring to obtain a suspension. The suspension was stirred for another 60 min, then transferred into a 100 mL Teflon-lined autoclave, heated at 180 °C for 24 h. After being cooled down to room temperature naturally, the resulting 10%BiOI/$BiVO_4$ nanocomposite (molar ratio of I:V = 1:9) was collected by filtration and washed by absolute ethanol and distilled water for three times, then dried at 60 °C in air for 2 h. By changing the amount of KI and $NH_4VO_3$, pure BiOI, pure $BiVO_4$ and BiOI/$BiVO_4$ composites with different I:V molar ratios were obtained. In addition, the sample (molar ratio of I:V = 3:7) was also prepared via physical mixing method, denoted as m-30%BiOI/$BiVO_4$.

### *Characterization*

The X-ray diffraction (XRD) patterns of the samples were recorded by Ultima IV diffractometer using Cu $K_\alpha$ radiation ($\lambda = 0.15418$ nm) with the $2\theta$ ranging from 10° to 80°. The morphology and structure of the products were observed on Hitachi S-4800 field-emission scanning electron microscopy (FESEM). Energy-dispersive X-ray spectroscopy (EDS) was following on FESEM image captured. TEM images, high resolution transmission electron microscopy (HRTEM) image, and selected area electron diffraction (SAED) pattern of the samples were taken on JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV. A Thermo Scientific ESCALAB 250Xi with monochromatized Al Ka radiation was used for the X-ray photoelectron spectroscopy (XPS) analysis and the binding energy positions were calibrated against the C 1s at 284.8 eV. The specific surface area was estimated based on nitrogen adsorption–desorption isotherm at 77 K according to the Brunauer–Emmett–Teller model. The photoluminescence spectrum was conducted on a Horiba Jobin Yvon FluoroMax-4 fluorescence spectrophotometer using a 150 W Xe lamp. The UV–visible diffuse reflectance spectra (UV–DRS) were obtained using an UV-visible spectrophotometer (Hitachi U-4100) with $BaSO_4$ as reference.

### *Photocatalytic experiments*

MB was chosen as a model of organic contaminant to determine the photocatalytic activities of the samples. A 500 W Xe lamp with a 420 nm cutoff filter was chosen as the light source. Experiments were carried out as follows: 0.01 g of photocatalyst and 10 mL of 20 mg/L MB solution were added into a quartz tube respectively. Prior to illumination, the reaction system was magnetically stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium of MB on the photocatalyst surface. Then the reaction system was exposed to light irradiation under continuous stirring. At given time intervals, 3 mL suspension were withdrawn and