Journal of Colloid and Interface Science 512 (2018) 272–281

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

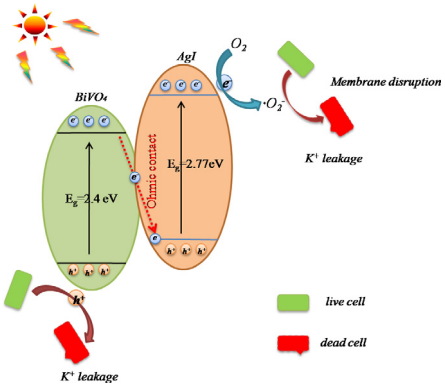
Enhanced *Escherichia coli* inactivation and oxytetracycline hydrochloride degradation by a Z-scheme silver iodide decorated bismuth vanadate nanocomposite under visible light irradiation

Dan-Lin Guan, Cheng-Gang Niu *, Xiao-Ju Wen, Hai Guo, Can-Hui Deng, Guang-Ming Zeng *

College of Environmental Science Engineering, Key Laboratory of Environmental Biology Pollution Control, Ministry of Education, Hunan University, Changsha 410082, China

GRAPHICAL ABSTRACT

Schematic diagram for the antibacterial in the direct Z-scheme silver iodide decorated bismuth vanadate photocatalyst.



ARTICLE INFO

Article history:
Received 1 August 2017
Revised 15 October 2017
Accepted 16 October 2017
Available online 17 October 2017

Keywords:
$AgI/BiVO_4$
Z-scheme
Heterojunction semiconductors
E. coil antibacterial
Inorganic anions

ABSTRACT

Novel Z-scheme $AgI/BiVO_4$ photocatalysts were fabricated by a chemical deposition-precipitation approach. The photocatalytic activities of the obtained catalysts were evaluated by disinfection of *Escherichia coli* (*E. coli*) and degradation of oxytetracycline hydrochloride (OTC-HCl) under visible-light irradiation. The BA3 (contained 9.09% of AgI) exhibited the highest photocatalytic activity and maintained good stability. It could completely inactivate 7.0×10^7 CFU/mL of *E. coli* in 50 min and degrade 80% of OTC-HCl in 60 min. The enhanced photocatalytic activity of $AgI/BiVO_4$ composites could be ascribed to the lower recombination rate of electron-hole pairs. Meanwhile, radical trapping experiments revealed that the superoxide radical ($\cdot O_2^-$) and holes (h^+) were the dominant reactive species in photo-disinfection process. Furthermore, the effects of bacterial initial concentration and inorganic anions were also investigated to optimize the photocatalyst for practical application. This study will give a new insight to construct the effective Z-scheme system for bacterial inactivation and organic pollutants degradation.

1. Introduction

Escherichia coli, as one kind of pathogenic microorganisms, is found ubiquitously in the intestines of warm-blooded vertebrates

* Corresponding authors.
E-mail addresses: cgniu@hnu.edu.cn, cgniu@hotmail.com (C.-G. Niu), zgming@hnu.edu.cn (G.-M. Zeng).

https://doi.org/10.1016/j.jcis.2017.10.068
0021-9797/

[1–3]. It can enter the aquatic environment easily, and then may cause many enteric diseases, such as peritonitis, cholecystitis, cystitis, diarrhea and so on [4,5]. More importantly, *E. coli* can threaten the public health and ecological stability even at low concentration. In order to disinfect wastewater, many approaches including ozonation, ultraviolet radiation, chlorination and advanced filtration have been widely used [6–8]. Among them, photocatalysis has attracted extensive attention due to its "zero" waste scheme and being economical for wastewater purification [9–14].

As is known to all, varieties of photocatalysts have been investigated and applied in the field of bacterial inactivation and organic pollution decomposition [15]. Amid these materials, bismuth vanadate ($BiVO_4$) is frequently employed for its characteristics of low cost, easy fabrication, high chemical stability and excellent biocompatibility [16]. $BiVO_4$ has a narrow band gap about 2.4 eV and possesses an excellent capacity of absorbing visible-light [17–19]. However, the charge pairs induced by light in $BiVO_4$ can easily recombine, which directly resulted in weak photocatalytic performance and photon efficiency. These defects severely restrict its practical applications [20]. Therefore, in order to weaken the fast recombination rate of electron-hole pairs, it is necessary to modify $BiVO_4$ with other semiconducting materials, which has been proved to be a good strategy [21,22].

By far, various semiconducting materials coupled with $BiVO_4$ have been successfully prepared to enhance the photocatalytic activity, such as $CuO/BiVO_4$ [23], $WO_3/BiVO_4$ [24], $BiVO_4$-Ru/$SrTiO_3$ [25], Ag@AgCl/$BiVO_4$ [26], etc. These composites showed higher photocatalytic efficiency than single $BiVO_4$ in degrading organic pollutants, however, seldom of them have been investigated in inactivating bacteria. Thus to further broaden the applications of $BiVO_4$ in photocatalysis, it is expected to design novel $BiVO_4$-based photocatalysts.

In recent years, silver halides (AgX, X = Cl, Br, I) have been reported as a class of efficient promising photosensitizers [27,28]. As one member of the silver halides, AgI has been served as an active component to modify other semiconductor photocatalysts thanks to its suitable energy-band position. For instance, Hu et al. have investigated that TiO_2 decorated with AgI exhibited superior photocatalytic efficiency than that of pure TiO_2 in *E. coli* and Staphylococcus aureus inactivation [29]. Liang also demonstrated that 3.0×10^7 CFU/mL of *E. coli* could be completely inactivated by $AgI/AgBr/BiOBr_{0.75}I_{0.25}$ composite under visible light irradiation owing to the effective separation of electron and holes [30]. In view of the above analysis, $BiVO_4$ modified with AgI nanoparticles (NPs) is likely to be a reliable candidate of catalyst. Furthermore, owing to the suitable band structures between AgI and $BiVO_4$ [31], combining them together could form a heterojunction system and contribute to an excellent photocatalytic activity.

Herein, the AgI/$BiVO_4$ composites were fabricated through a simple chemical deposition-precipitation method. The crystal phase, morphology structure and surface chemical state of the obtained photocatalysts were fully characterized. *E. coli* and oxytetracycline hydrochloride (OTC-HCl) were selected as probe reactions to investigate the photocatalytic performance of AgI/$BiVO_4$ composites. Taking the practical application into consideration, the effects of initial *E. coli* concentration and inorganic anions were also investigated. Moreover, a possible Z-scheme mechanism was proposed on the basis of photocatalytic experiments.

2. Material and method

2.1. Bacteria strain and chemicals

The *E. coli* ATCC 25922 was employed as bacteria strain and purchased from the China Center for Type Culture Collection (Beijing, China). The bacteria strain was stock on a Luria-Bertani (LB) medium at 4 °C and all cultures were saved on a cupboard [32]. Oxytetracycline hydrochloride, bismuth nitrate pentahydrate, ammonium metavanadate, silver nitrate, potassium iodide, sodium hydroxide, nitric acid, sodium oxalate, isopropyl alcohol, ferrous chloride, nitrogen were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and utilized without any further purification. Deionized (DI) water was used throughout the experiments.

2.2. The preparation of photocatalysts and cells

2.2.1. The synthesis of pure $BiVO_4$ sample

The pure $BiVO_4$ was fabricated by a hydrothermal method. In detail, 4.85 g bismuth nitrate pentahydrate was first dissolved in 5 mL of nitric acid, and then 35 mL of deionized water was added into the mixed solution. Subsequently, 80 mL of ammonium metavanadate solution (0.125 M) was added into the suspension drop by drop under magnetically stirring. Before being further stirred for 30 min, the pH value of the mixed solution was adjusted to 8.0 by adding NaOH (2 M) or HCl (2 M). Then, the suspension was transferred into a 200 mL stainless steel autoclave and heated at 180 °C for 12 h. After naturally cooling down to ambient temperature, the bright yellow powder was collected by filtration, washed with deionized water and ethanol thoroughly, and dried at 55 °C overnight.

2.2.2. The synthesis of AgI/$BiVO_4$ composites

The AgI/$BiVO_4$ was fabricated via a deposition-precipitation procedure [33]. Briefly, 300 mg of the as-prepared $BiVO_4$ and 30 mg $AgNO_3$ were dispersed into 50 mL deionized water. Then, the suspension was sonicated for 15 min and stirred for 1 h to form a homogeneous solution. Subsequently, an excessive amount of KI was slowly dropped into the mixed solution with vigorous stirring. After continuously stirring for 3 h, the products were filtrated, washed with deionized water and ethanol, and then dried at 55 °C overnight. The obtained catalyst was labeled as the BA3. Similarly, samples BA1, BA2, BA4 were synthesized by changing the amount of $AgNO_3$ to be 6, 15, and 45 mg, respectively. Additionally, pristine AgI was also prepared through the same procedures in the absence of $BiVO_4$.

2.2.3. The preparation of *E. coli* cells suspension

Typically, the *E. coli* cells suspension was obtained from the treated *E. coli* strain. The *E. coli* strain was cultivated in a LB medium at 37 °C on a shaker (~120 rpm) for 24 h. Then, some residue in *E. coli* strain suspension was removed by centrifugation, washing and re-suspending. After that, the *E. coli* cells suspension was preliminary achieved. To get a stable concentration of *E. coli* cells about 7×10^9 colony forming unit per milliliter (CFU/mL), the *E. coli* cells suspension was diluted several times with sterile DI water [34]. In addition, prior to each inactivation experiment, all glass apparatuses were sterilized at 121 °C for 20 min with autoclave.

2.3. Characterization

The crystal phase of obtained catalysts was characterized by an X-ray diffraction pattern (XRD, a Bruker D8 diffractometer with monochromatic Cu Kα radiation). The morphology of catalysts was carried out by a scanning electron microscope (SEM, Hitachi S4800, Japan) with energy-dispersive X-ray spectroscopy (EDX). Meanwhile, the transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were applied to further examine the microstructure and elementary composition of samples. The X-ray photoelectron spectroscopy