Enhanced photocatalytic antifouling efficiency under visible-light by fabrication of composite photocatalysts

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Abstract: In this report, two different novel, efficient and environmentally friendly materials based on green photocatalytic technology to reduce the harm of marine biofouling are studied. Both the Bi_2WO_6/BiOI composite and $InVO_4$/$AgVO_3$ heterojunctions showed enhanced photocatalytic antifouling efficiency, however, the enhancement mechanism is different.

Keywords: Photocatalysis, Antifouling, Visible light

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 develpment[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. In this study, several types of novel composite photocatalysts were prepared and the photocatalytic properties for antibacterial and marine antifouling under visible light irradiation were conducted.

2. Experimental

The photocatalytic antifouling experiments were carried out using a 500 W Xe lamp as the light source with a 420 nm cutoff filter. The illumination power was 0.125 W/cm^2. In order to maintain reaction isothermally, the lamp was put in the cooling tube vertically with a cooling water flow, and a quartz tube jacketed with running water was used as the reaction vessel. Typically, 10 mg of photocatalysts and 9.9 mL of sterilized natural seawater or PBS (0.01 M, pH = 7.4) were added in a 10 mL quartz test tube, followed by adding 100 μL bacterial suspension. Before illumination, the suspension was magnetically stirred for 30 min in dark to establish the adsorption/desorption equilibrium between the photocatalysts and bacterial cells. After that, the suspension was exposed to visible light irradiation under magnetic stirring. At given time intervals, 1 mL of the bacterial suspension was withdrawn and transformed to clean bench and serially diluted with sterilized seawater or PBS. Then, 100 μL of the diluted suspension was dropped on LB agar plates. After incubated at 37 ℃ for 24 h, the number of viable cells (in cfu) was counted. For comparison, the dark control and blank control experiments were done along with photocatalytic experiments. The dark control was carried out with the bacterial suspension in the absence of visible light irradiation, whereas the blank control was conducted with the bacterial suspension in the absence of photocatalysts under visible light irradiation. All the samples using in antifouling experiments were carried out in three parallels and the average values were given. The survival rate was estimated by following formula: Survival rate (%) = $(N_t/N_0) \times 100$, where N_0 and N_t are the numbers of viable cells in the blank control and after photocatalytic reaction with photocatalysts, respectively. The antibacterial rate was defined as follows:

$$\text{Antibacterial rate (\%)} = 100 - \text{Survival rate.}$$

3. Results and Discussions

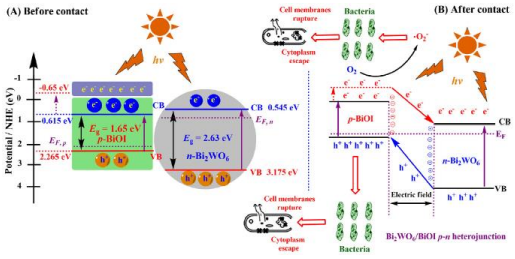

Figure 1. Schematic diagram of photocatalytic antifouling mechanism of the Bi_2WO_6/BiOI p–n heterojunction.

First we want to introduce is the chemical etching preparation of the Bi_2WO_6/BiOI p–n heterojunction with enhanced photocatalytic antifouling activity under visible light irradiation. A novel Bi_2WO_6/BiOI heterojunction photocatalyst was prepared based on a chemical etching method and used in photocatalytic antifouling. The as-prepared Bi_2WO_6/BiOI photocatalyst was composed of Bi_2WO_6 and BiOI, exhibiting a three-dimensional hierarchical microsphere structure. Experimental results indicated that the molar percentage of Bi_2WO_6 to BiOI leaded to different morphologies and photocatalytic activities of Bi_2WO_6/BiOI composites. 30% Bi_2WO_6/BiOI exhibited an improved photocatalytic performance under visible light irradiation compared to pure Bi_2WO_6, pure BiOI, and other Bi_2WO_6/BiOI composites. Almost all (99.99%) of Pseudomonas Aeruginosa (P. aeruginosa), Escherichia Coli (E. coli) and Staphylococcus Aureus (S. aureus) could be killed and the degradation efficiency of methyl blue (MB) could achieve 100% within 60 min in the presence of 30% Bi_2WO_6/BiOI. In addition, after six circulating photocatalytic antifouling experiments, 30% Bi_2WO_6/BiOI exhibited no significant loss of photocatalytic performance, verifying its stability and reusability, which was especially important for its application. Moreover, a possible photocatalytic mechanism was proposed based on active species trapping experiments, demonstrating that the superoxide radicals ($^{\bullet}O_2^-$) and the holes (h^+) were the main reactive species in this system. The obviously enhanced photocatalytic activity of the 30% Bi_2WO_6/BiOI heterojunction photocatalyst could be mainly attributed to the formation of the p–n heterojunction, accelerating the separation of photogenerated charge carriers.

Moreover, we studied the fabrication of $InVO_4/AgVO_3$ heterojunctions with enhanced photocatalytic antifouling efficiency under visible-light. In this section, novel visible-light-sensitive $InVO_4/AgVO_3$ photocatalysts with a *p-n* junction were synthesized through an ion exchange and in-situ growth process. It can be observed that the $AgVO_3$ exhibits a rod-shaped structure, while a plentiful of spherical shaped $InVO_4$ particles are formed on the surface. The rod-shaped structure of $AgVO_3$ wasn't changed by the addition of $InVO_4$, but its photocatalytic properties were tremendously improved. The best photocatalyst was 0.5 $InVO_4/AgVO_3$, over which the Rhodamine B (RhB) solution was almost decomposed in 200 min under visible light irradiation. Moreover, about 99.9999% of P. aeruginosaudomonas aeruginosa (*P. aeruginosa*), Escherichia coli (*E. coli*) and Staphylococcus aureus (*S. aureus*) were killed over 0.5 $InVO_4/AgVO_3$ at 30 min. From these results it can be inferred that 0.5 $InVO_4/AgVO_3$ heterojunctional photocatalyst has an improved efficiency for the separation of the current carriers to enhance the photocatalytic performances. The charge carrier transfer in the present 0.5$InVO_4$/ $AgVO_3$ heterojunction is much different from the previous one. The metal silver would contribute in the separation of electron-hole pairs by the Z-scheme. Metal silver could construct a cross-bonding bridge to connect with two semiconductors. Firstly, the electrons will transfer from CB potential (0.41 eV) of $AgVO_3$ into metal silver through the Schottky battier. Secondly, the electrons in metal silver were shifted tothe VB of $InVO_4$ due to the more negative Fermi level of silver than the VB of $InVO_4$ (1.63 eV), which was faster than the recombination between the electrons in $InVO_4$ or the holes in $AgVO_3$. After that, the Z-scheme mechanism was established.

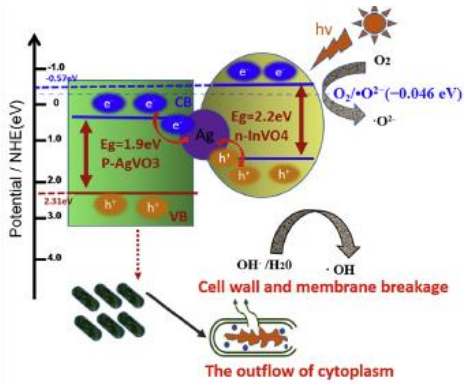

Figure 2. Schematic diagram of the proposed mechanism for photogenerated charge carrier transfer in the 0.5$InVO_4$/ $AgVO_3$ heterojunction under visible-light irradiation.

4. Conclusions

This work provides valuable information for the design of novel heterojunction photocatalyst with excellent photocatalytic properties used in marine antifouling.

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