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Synthesis of $ZnWO_4$ Electrode with tailored facets: Deactivating the Microorganisms through Photoelectrocatalytic methods

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ABSTRACT

The exotic invasive species from the ballast water in the ship will bring about serious damages to ecosystem. Photocatalyst films have been widely studied for sterilization. In this study, $ZnWO_4$ with different exposed facets was synthesized by hydrothermal method, and $ZnWO_4$ film electrodes have been applied in ballast water treatment through the electro-assisted photocatalytic system. Then the samples were investigated by X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), Field emission on scanning electron microcopy (FE-SEM), Transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy (DRS), BET specific surface area analysis, Fourier transform infrared (FT-IR) and Electrochemical impedance spectra (EIS). $ZnWO_4$ with an appropriate exposure of (0 1 1) facets ratio exhibited the best photocatalytic and photoelectrocatalytic activities. The microorganisms deactivated completely in 10 min by $ZnWO_4$ films with 3 V bias. The mechanisms of (0 1 1) facets enhanced the photocatalytic and photoelectrocatalytic activities which were deduced based on the calculated result from the first principles. Simultaneously, appropriate exposed facets and applied bias could reduce the recombination of the photogenerated electron-hole pairs, and improve the photocatalytic activities of $ZnWO_4$.

1. Introduction

The ballast waters need to be injected and discharged in order to provide needed stability and maneuverability when the ships are moving. Current data shows that 3–5 billion tons of ballast water is transferred from ships yearly [1]. The organisms in ballast water can spread to a new environment, becoming invasive species. These external species will seriously threaten the ecosystem and human activities [2]. Therefore, the International Maritime Organization (IMO) prescribes that all cargo ships must have a system for treating ballast water aimed at preventing or reducing these problems [3]. In those studies, some works indicate that the hydroxyl radical (•OH) with high oxidation potential has an excellent bactericidal effect, which is a sound way to treat ballast water [4,5].

For our best knowledge, hydroxyl radical (•OH) will be generated easily in photocatalytic reaction systems, which may be used in the process of ballast water discharge [6–10]. Researchers found that some of these photocatalysts are active for deactivation of bacteria [11,12]. $ZnWO_4$ as a photocatalytic material has a wide application prospect in bactericidal effects due to its high oxygen evolution potential [13,14]. Hydroxyl radical (•OH) generated by $ZnWO_4$ has a stronger oxidation ability than TiO_2 [15]. So far, the applications of $ZnWO_4$ in the photocatalysis have been greatly limited due to the low efficiencies resulted from the easy recombination of photogenerated charge carriers. Many researchers do a lot of works to improve the separation efficiency of hole and electron.

According to our update, there are four methods to enhance photocatalytic activities of $ZnWO_4$. (1) Forming heterojunction, such as: $BiOBr/ZnWO_4$ [16], $In_2S_3/ZnWO_4$ etc. [17]; (2) Ions doping: Er^{3+} [18], Sn^{2+} [19]; (3) Exposed different crystal facets [20,21]; (4) Electro-assisted photocatalytic activity [22,23]. For the photocatalytic activities test, $ZnWO_4$ can achieve great effects on organic decomposition: Methyl Orange [24,25], Phenol [26], Methylene Blue [27,28], 4-nitrophenol, 4-methoxybenzyl alcohol [29], Auramine O [30], 4-Chlorophenol [31] and AR18 [32]. Despite this progress, the efficiencies are still inadequate and the mechanisms for enhanced $ZnWO_4$ activity in the theoretical calculations need to be further discussed. For all we know, there are few reports on deactivated microorganism by $ZnWO_4$.

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In this work, $ZnWO_4$ photocatalyst film electrodes have been applied in ballast water treatment. The detailed process, in which exposed crystal facets and photoelectrocatalytic methods were integrated, was designed to improve the efficiencies. $ZnWO_4$ photocatalysts with different exposed facets were synthesized by the hydrothermal method at different pH value condition. Microorganisms (chlorella) were employed as the probe reaction to test the photocatalytic and photoelectrocatalytic activity of the $ZnWO_4$ films. $ZnWO_4$ with an appropriate exposure ratio of (0 1 1) facets exhibited greatly enhanced activity in the photocatalytic and photoelectrocatalytic sterilization (chlorella). Then the mechanisms are investigated from the first principles calculations.

2. Experimental

2.1. Preparation of $ZnWO_4$

$Zn(NO_3)_2{\cdot}6H_2O$ and $Na_2WO_4{\cdot}2H_2O$ (molar ratio of $Zn(NO_3)_2{\cdot}6H_2O$–$Na_2WO_4{\cdot}2H_2O$ 1:1) were mixed in 80 mL deionized water. Adjusting the pH value to a specific condition using HNO_3 or $NH_3{\cdot}H_2O$ solution. The mixture was transferred into a reaction kettle after ultrasonication for 30 min. The reactors were heated at 180 °C for 24 h. Then the obtained samples were washed by distilled water three times. Finally the collected samples were further dried in an oven at 80 °C for 4 h.

2.2. Preparation of the $ZnWO_4$ film electrodes

The $ZnWO_4$/ITO (indium-tin oxide glass) film electrodes were prepared using the coating method. First, 0.1 g $ZnWO_4$ and 1 mg XC-72 were dissolved in 1000 μL methanol, 7000 μL distilled water and 3000 μL polytetrafluoroethylene (PTFE). The slurry was mixed by ultrasonication for 10 min. Then, 600 μL slurry was applied onto ITO glass (60 × 20 mm). Finally the ITO glasses were dried at 60 °C for 2 h in air. The carbon black, XC-72, used only as conductive material can improve the electrical conductivity of the $ZnWO_4$ films electrode. PTFE acts as the film former agent [26].

2.3. Experiment of photocatalytic and photoelectrocatalytic activities

The photocatalytic and the photoelectrocatalytic activities were evaluated by deactivating the chlorella in seawater. The conventional three-electrode cell system connected with the working electrodes ($ZnWO_4$ film, active area of 3 cm^2), the counter electrode (Ti, 30 mm in length and 10 mm in width) and the reference electrodes (calomel electrode). The working electrodes were irradiated under UV light irradiation (12 W, 254 nm). Raw and treated ballast water (150 mL) with an initial chlorella concentration of 1×10^4 cell/mL was sampled in triplicate at certain time intervals to numerate the concentration of the chlorella [33]. The concentrations of the microorganisms were enumerated using a total count method under a biological microscope [34].

To investigate the photogenerated holes and electrons separation efficiency, electrochemical impedance spectra (EIS) were tested in seawater solution by an electrochemical workstation (VMP3 Princeton Research). The reference electrodes was calomel electrode and the counter electrodes was titanium. $ZnWO_4$ films were used as working electrodes. The 12 W Ultraviolet lamp with 254 nm wavelength was used as light source [35,36].

2.4. Characterization

The crystalline structures were characterized by X-ray diffraction (XRD) with CuKα radiation on Rigaku DMAX$^-$ Ultima$^+$ diffractometer. The chemical composition of the film electrodes were studied by X-ray photoelectron spectroscopy (XPS) measurements with AlKα radiation on Thermo Escalab250 XPS system. The morphology was characterized by the field emission on scanning electron microscope (FE-SEM) on SUPRA 55 SAPPHIRE. The crystal structures were investigated by transmission electron microscopy (TEM) on JEOL JEM-2100 instrument. The photo properties of the samples were studied by UV–vis diffuse reflectance spectroscopy (DRS) on TU-1901 UV–vis spectrophotometer. $BaSO_4$ was used as the reflectance standard. The N_2 adsorption and desorption of catalysts were monitored by WBL 810. The hydrogen-related defects were examined by FT-IR spectrometer (PerkinElmer Frontier).

3. Results and discussion

Total count method was used to evaluate the deactivation ratio of chlorella by the $ZnWO_4$ film electrodes under different experimental conditions. Fig. 1(a) shows the data for deactivation ratio of chlorella under UV light irradiation. pH value had a significant effect on the photocatalytic activities. The deactivation ratio were 12%, 43%, 100% and 65%, respectively in 30 min, for the samples prepared at pH 4, 6, 9 and 12. The photocatalytic activities of $ZnWO_4$ films were enhanced with the pH value increase when the pH value was below 9. $ZnWO_4$ prepared at pH 9 showed the highest deactivation efficiency. However, as the pH value further increased, the activity decreased.

Fig. 1(b) exhibits the deactivation ratio of the photoelectrocatalytic deactivation of chlorella at different bias: 1, 2, 3 and 4 V. The efficiency of deactivation increased as the bias potential increased. At the potential of 3 and 4 V, the deactivation ratio can reach 100% in 10 min. Therefore, 3 V bias potential was the best experiment condition to fulfill the consideration energy efficiency.

The photoelectrocatalytic sterilization at 3 V bias potential for all samples has shown in Fig. 1(c). The activities have been significantly improved for all samples in comparison of photocatalytic activities. The deactivation ratio can reach 100% in 10 min by the $ZnWO_4$ films obtained at pH 9, which increase to 3 times as a photocatalytic process. As a consequence, a suitable pH value could not only improve the photocatalytic activities but also enhance the photoelectrocatalytic activities. The effect of pH value for activities will be discussed subsequently.

Electrochemical impedance spectra Nyquist tests have been applied widely in demonstrating the separation efficiency of electrons and holes of photocatalysts [37]. EIS data under different bias potential were illustrated in Fig. 1(d)–(f). When the pH value below 9, the radius of the arc decreased gradually as the pH value increased. $ZnWO_4$ obtained at pH 9 shows the smallest arc radius for both photocatalytic and photoelectrocatalytic process. The smaller radius of the circular arc means the lower resistance of the interfacial which will cause the higher separation efficiency of the electron-hole pairs [38]. As we can see from Fig. 1(d), there was one radius on the EIS Nyquist plot, which indicated that the process of photocatalytic deactivation of chlorella was an electrode reaction process [39]. EIS Nyquist plots of photoelectrocatalytic process (pH 9) were shown in Fig. 1(e). As the voltage of applied bias increased the radius of the arc decreased gradually. This result indicated the bias potential can accelerate the rate of charge transfer. Fig. 1(f) shows that $ZnWO_4$ film (pH 9) exhibited a smaller radius than the other samples under UV light and 3 V bias potential. Compared with Fig. 1(d), it has been found that the arc shape was different. This denotes that the separation of electron-hole pairs was very efficient. Furthermore, the diffusion of reactants to the electrode interface is another factor determining the reaction rate. For this work, the charge in $ZnWO_4$ (pH 9) would be quickly moved to the Ti electrode through the solid/liquid interface, which would inhibit charge recombination [40].

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