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CuI-BiOI/Cu film for enhanced photo-induced charge separation and visible-light antibacterial activity

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ABSTRACT

CuI-BiOI/Cu film with effective photocatalytic inactivation of E. coli under visible-light-driven (VLD) were prepared on copper sheet and were characterized by TEM, SEM, XRD, XPS and DRS. The photocatalytic inactivation of E. coli of CuI, BiOI, CuI-BiOI and CuI-BiOI/Cu film were investigated. The results showed that CuI-BiOI/Cu film exhibit the most excellent bacteria disinfection activity, and the quantity of viable bacteria could almost inactivate after being illuminated for 2 h. The Laser Scanning Confocal Microscopy (LSCM) observation exhibits that the morphology of bacteria changed a lot after visible light irradiation, and the UV spectra confirm the leakage of bacterial protein. The antibacterial mechanism was studied by employing photoelectrochemical techniques and scavengers of different reactive species, which reveals that the effect of reactive species on the antibacterial activity decrease in order $h^+ > e^- > H_2O_2 > \cdot HO > \cdot O_2^-$. The CuI and Cu play the important role in the separation of h^+ and e^-. During the photocatalytic process, the CuI act as a hole-transport channel and the Cu act as electron transfer for CuI-BiOI heterostructure, which promotes the separation of photo-generated charges and enhances the photocatalytic antibacterial activity of the as-prepared samples.

1. Introduction

Water is an essential element for human daily life. However, microbial contamination in water has been a constant threat to human health all over the world. Millions of people die of diseases and disabilities caused by pathogenic microorganisms each year [1,2]. Hence, rapid and efficient disinfection methods for drinking water are urgently required. However, traditional water treatment technology, such as UV disinfection, chlorination and filtration techniques, unavoidably append noxious disinfection by products (DBPs). Solar energy is an attractive renewable-energy resource and can be used for water disinfection via the solar disinfection of drinking water. Recently, photocatalytic disinfection, an economical, effective and environmentally friendly photooxidation process, has attracted more and more attention from the perspective of using abundant solar energy and low toxicity [3–5].

Bismuth oxyhalides BiOX (X = Cl, Br, I), a category of Bi-based semiconductors with outstanding optical and electrical properties, have exhibited great potential in water disinfection and attractive photocatalytic activity on the degradation of organic pollutant because of its low toxicity, chemical stability, and inexpensiveness [6–12]. BiOI is one of the most suitable visible light photocatalyst due to its narrow band gap (1.8 eV), which enables it to be applied in treatment of Microorganisms in water under visible light. However, the small band–gap leads to the high recombination efficiency of photo-generated e^--h^+ pairs that limits its photocatalytic disinfection efficiency. In general, the photocatalytic disinfection efficiency mainly relies on the e^- which can directly attract bacterial and on oxygen species (ROS) such as $\cdot O^{2-}$ and $\cdot OH$ that were generated by photo-exited electron and hole, respectively [3]. In fact, most of the photo-excited electrons and holes rapidly recombine and only few of them can transfer to photocatalyst surface and participate in the disinfection process. Hence, to many efforts, including the fabrication of heterojunction structure orfabrication of heterojunction structure or developing modified BiOI, have been conducted to suppress the recombination of photogenerated electron–hole pairs of BiOI, and then enhance their visible light driven (VLD) [11].

The Cuprous iodide (CuI), a P-type semiconductor material, which steadily exists as γ crystalline phase when temperatures below 350 °C, has attracted great attention due to its particular features, especially its active layers for hole transportation. Some studies have reported that

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CuI exhibit high mobility of hole and improve the photoelectrocatalytic activity of CuI-BiOI heterojunction [13]. If the fascinating optical properties of BiOI combined with CuI, the CuI could be used as a hole-transport channel for CuI-BiOI heterostructure and charger separation might be improved. Hence, in this work, we prepared CuI-BiOI on copper sheet by water bath method. The photocatalytic antibacterial activity and stability of CuI-BiOI/Cu film were assessed by using E. coli K – 12 as model bacterium. To compare, the antibacterial activity of BiOI, CuI and CuI-BiOI were investigated under the same condition. By further detecting the generation of reactive oxygen species (ROS), the reasonable mechanism of photocatalytic antibacterial activity of CuI-BiOI/Cu film was discussed. It is hoped that our work offered a possibility to achieve more efficient water disinfection method.

2. Experimental

2.1. Materials

The copper sheets were purchased by Tianjin Fuchen Chemical Reagents Factory, bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, AR), potassium iodide (KI, AR), silver nitrate ($AgNO_3$, AR), ethylene glycol (AR), Polyvinyl Pyrrolidone (PVP, AR), Polyethylene Glycol (PEG, AR), Hydroiodic Acid (HI, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., China without any further purification, the human serum albumin (HSA) was purchased by CSL Behring L.L.C., U.S.A. The bacterial cells were cultured in ueller hinton broth solution at 37 °C for 18 h and immediately diluted. The concentration of cell density is $10^{6.5}$ cfu (colony forming unit)/ml. Deionized water was also used in all the experiments. All glass apparatuses used were washed with deionized water, and then autoclaved at 121 °C for 20 min.

2.2. Synthesis of BiOI

4 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was added into 40 ml of mixture solution of EG/water (the volume ratio of EG to water was maintained at 7:1) containing 4 mmol KI with 50 mg PVP. After stirring for 2 h, the mixture solution was transferred into a 100 ml Teflon–lined stainless autoclave. The autoclave was heated at 140 °C for 4 h under autogenous pressure, and then it was cooled to room temperature naturally. The resulting products of BiOI were gathered and rinsed with deionized water and ethyl alcohol thoroughly, and finally dried at 60 °C.

2.3. Fabrication of CuI-BiOI film on copper sheet

The copper sheets were first cleaned with acetone and ethanol, and water subsequently. Afterward, the cleaned copper sheets were immersed in 0.1 M HCl solution for 15 min to clear the surface oxidization layer and then were dried at 60 °C. Then the obtained BiOI sample was added into 50 ml solution containing 10 g PEG. The treated copper sheets with a lateral size of 35 mm × 35 mm were immersed in mixture solution immediately. After stirring in a 70 °C water bath for 24 h, then the obtained CuI-BiOI/Cu film were dried at 60 °C overnight.

2.4. Characterization

Crystal structure identification was performed using Bruker D8 X–ray diffractometer (XRD) with Cu Kα radiation operating at 40 kV and 40 mA. The morphologies of CuI-BiOI were observed by a scanning electron microscopy (SEM, ZEISS SUPRA 55), transmission electron microscopy (TEM, Tecnai F20) and elemental mapping patterns were investigated using OXFORD EDX 6767. The morphology of bacteria was observed by a Laser Scanning Confocal Microscopy (LSCM, Leica DMI4000 CS) Diffuse reflection spectra (DRS) of the samples were recorded on a Varian Cary–500 spectrophotometer, using $BaSO_4$ as the reference. The X-ray photoelectron spectroscopy (XPS) measurements of the samples were carried out on a ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 3.0×10^{-10} mbar with monochromatic Al Kα radiation (E = 1486.2 eV). UV–vis spectroscopy (Shimadzu, UV-1780) was used to detect the leakage of bacterial cell contents. Photoelectrochemical characterization was conducted on a ZENNIUM electrochemical workstation (Zahner, Germany) with a standard three-electrode system. The prepared samples served as the working electrode with an active area of ca. 0.25 cm^2. The counter and reference electrodes were Pt plate and Ag/AgCl electrode and 0.2 M Na_2SO_4 (pH = 6.8) was used as electrolyte. The electrochemical impedance spectroscopy (EIS) measurement was measured *via* an EIS spectrometer (CHI-660D workstation, CH Instrument) in the three-electrode cell in the presence of 0.5 M KCl solution containing 5.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ by applying an AC voltage with 5 mV amplitude in a frequency range from 1 Hz to 100 kHz under open circuit potential conditions. The cyclic voltammograms (CV) were measured in the same solution in the three electrode cell as that of the EIS measurement on the BAS Epsilon workstation. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 5 mV s^{-1}.

2.5. Photocatalytic disinfection performance

E. coli K – 12 was used as a model bacterium to investigate the antimicrobial activity of CuI film and CuI-BiOI. The bacterial cells were cultured in nutrient broth at 37 °C. During each test, 40 ml bacterial PBS solution ($1 \times 10^{6.5}$ cfu/ml) was poured into a pyrex glass reactor which contained a 1 cm × 1 cm CuI or CuI-BiOI. These *E. coli* solutions were then irradiated with a Xe lamp equipped with a long–pass cut–off filter VL (300 W, $\lambda \geq 400$ nm). Aliquots (0.5 ml) of photo-treated *E. coli* solutions were withdrawn at regular time intervals, diluted and spread on freshly prepared agar plates and incubated at 37 °C for 24 h.

2.6. Laser scanning confocal microscopy (LSCM) observation of bacteria

Bacterial LSCM was used to visualize the changes of cell morphologies. The phototreated bacteria at different irradiation time intervals (0, 1 and 2 h) were uniformly dispersed on the glass bottom cell culture dishes for LSCM.

2.7. The UV absorption of the bacterial protein

The UV absorption was used to confirm the leakage of the bacterial protein after visible light irradiation. Then the photo-treated bacteria at different irradiation time intervals (0, 1 and 2 h) were diluted with PBS solution, the prepared bacterial fluid was used for UV test.

3. Results and discussion

3.1. Properties of CuI-BiOI

Fig. 1 shows X–ray diffraction (XRD) images of CuI-BiOI, pure BiOI and CuI in the range of $15° < 2\theta < 80°$. The BiOI peaks appeared at 24.3° (101), 29.7° (102), 31.7° (110) and 49.9° (005) which could be well-indexed to the standard tetragonal phase of BiOI (JCPDS Card No.10–0445). The typical diffraction peaks of CuI appeared at 25.5° (111), 42.2° (220) and 49.9° (311), which could be attributed to γ crystalline phase of CuI (JCPDS Card No. 06–0246). In addition, two sets of diffraction peaks of BiOI and CuI can be seen in the XRD patterns of CuI-BiOI indicating that CuI-BiOI have high crystallinity. However, the XRD peaks corresponding to BiOI in the patterns of CuI-BiOI became weaker and broader than that of pure BiOI, suggesting that the growth of BiOI has been suppressed by CuI in the preparing process.

The typical SEM and TEM images of CuI-BiOI were shown in Fig. 2. As can be seen from Fig. 2a, CuI-BiOI exhibits flower-like network hierarchical microstructures, which are assembled by a large number of BiOI nanosheets and irregular CuI particles. As shown in Fig. 2c, the