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An integrated multifunctional photoelectrochemical platform for simultaneous capture, detection, and inactivation of pathogenic bacteria

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ABSTRACT

New approach for the fabrication of the photoelectrochemical (PEC) platform has been firstly demonstrated for simultaneous capture, detection, and inactivation of pathogenic bacteria. The BiOI semiconductor film is selected as photo-electricity conversion unit and visible light driven (VLD) photocatalytic antibacterial unit, gold nanoparticles (AuNPs) are used as link unit and 4-mercaptophenylboronic acid (4-MPBA) is chosen as antibiotic-free capture unit. Based on the reversibly binds between boronic acid group and peptidoglycan of the bacteria cell wall, the integrated PEC platform presents excellent capture performance and high detection sensitivity to *Escherichia coli* (*E. coli*) with a low detection limit of 46 cfu/mL. Moreover, this multifunctional platform shows high antibacterial activity (99.99%) arising from the VLD photocatalytic effect of AuNPs/BiOI. The current work can provide new strategies to construct advanced green PEC platforms for detection of various pathogenic bacteria.

1. Introduction

Bacterial infections and contaminations have always been a major threat to public health and human life [1,2]. Early diagnosis and treatment of bacterial infections are key to improving survival rates [3,4]. Thus, scientists have exploited many methods (*e.g.* flow cytometry [5], fluorescence [6,7], plating and culturing [8], spectroscopic method [9], colorimetric and electrochemical methods [10,11]) for the detection of bacteria. Although these reported methods have presented especially high efficacy, none of them can kill bacteria during the detection process. Consequently, two obstacles severely will be highlighted: (1) the instrument capability is affected by the microbial biofilm forming on the sensitive element surface; (2) the survival of pathogenic bacteria poses a serious health risk to the public. Thus, the integration of capture and sterilize units on a detection platform can be a good solution for overcoming these two drawbacks.

Recently, various sterilize and capture units have been exploited to construct the multifunctional detection platform. For example, Zn-CuO_2 nanoparticles and graphene oxide were used as sterilized unit to construct multifunctional impedance electrode sensor [12]. Concanavalin A functionalized 3D nanowire substrates was also used as capture unit to construct the detection and elimination of multifunctional platform [13]. In our previous work, a multifunctional electrochemical platform was fabricated based on vancomycin-functionalized AgNPs@3D-ZnO nanorod arrays [14]. In this integrated platform, the high antibacterial performance is mainly contributed to the release of Ag^+, which can be easily affected by the change of environment and lead to a gradual decrease in antibacterial activity. Otherwise, vancomycin was used as capture. The overuse of antibiotics can make more antibiotic resistant "superbug". Thus, the construction of an AgNPs and antibiotic free multifunctional platform is still an urgent demand.

As a promising alternative for solar energy utilization, photocatalysis technology based on semiconductors has been extensively used for disinfecting since it not only can kill bacteria but also can degrade toxic substances produced by bacteria. Currently, TiO_2 is the most popular photocatalyst for sterilizing various bacteria owing to its good photocatalytic activity [15,16]. However, UV-only response greatly inhibits its utilization of solar energy and dramatically limits its practical application [17]. Consequently, various visible light driven (VLD) photocatalysts were used for sterilizing bacteria [18–21]. Among of them, BiOI with narrow band has attracted extensive attention recently. Its unique layered structures with the internal static electric field perpendicular to each layer can induce the effective separation of photo-generated electron–hole pairs and exhibit strong VLD

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photoelectrochemical (PEC) signal [22,23]. Thus, BiOI can be used to kill bacteria, degrade pollutants [24], and fabricate PEC sensing platform [25–28]. In our previous work, a high strong BiOI film was constructed on the metal matrix surface and exhibited good VLD catalytic bactericidal activity [29]. As a result, this BiOI filmed metal is expected to be a good photoelectrode for the fabrication of the AgNPs and antibiotic free PEC bacterial sensing multifunctional platform. However, there are several problems need to be solved: (1) a novel antibiotic-free capture unit, (2) stable connection between capture unit and matrix film, and (3) improved performance of VLD photocatalytic antisepsis.

As boronic acids can stable bind with *cis-diols* in the physiological pH range [30,31], boronate affinity materials are widely used for the capture and separation of biomolecules containing *cis-diol* structure (*e.g.* enzymes [32], carbohydrates [33,34] and so on [35–37]). Otherwise, the boronate affinity material (mercaptophenylboronic acid, MPBA) is also used as capture unit for sensing bacteria [38]. Inspired by this unique character, we choose MPBA as bacteria capture unit to design antibiotic-free multifunctional platform. Gold nanoparticles (Au NPs) assembled through Au—S covalent bond have been extensively used as a common link unit for sensing technologies [39,40]. Moreover, they are also used to enhance the semiconductor's photocatalytic activity [41]. Thus, we think that the integrated MPBA/AuNPs/BiOI platform has the prospect of becoming AgNPs and antibiotic free multifunctional detection.

In this work, our goal is to fabricate an integrated multifunctional PEC platform for simultaneous detection, capture, and inactivation of pathogenic bacteria. In this integrated system, the BiOI semiconductor film is selected as photo-electricity conversion unit and VLD photocatalytic antibacterial unit and 4-mercaptophenylboronic acid (4-MPBA) is chosen as antibiotic-free capture unit. The BiOI film was first fabricated on 304-stainless steel (304SS) surface *via* hydrothermal synthesis method. Then, AuNPs were in situ decorated on the BiOI film surface by the ascorbic acid (AA) reducing. After that, bacteria-capturing unit of 4-MPBA was introduced to the AuNPs/BiOI surface *via* covalent binding Au-S bonds (Scheme 1a). Based on the reversibly binds between boronic acid group and peptidoglycan of the bacteria cell wall, *Escherichia coli* (*E. coli*) can be captured on the photoelectrode surface (Scheme 1b), resulting in a decrease of photocurrent due to that the steric hindrance blocks the transfer of electron donor to photoelectrode surface. The decrease of photocurrent is related to the amount of *E. coli* and it can be detected according to the decrease of photocurrent (Scheme 1d). Moreover, bacteria can be killed by the VLD photocatalytic effect (Scheme 1c). This strategy will open a new route for the use of the VLD photocatalytic material-based PEC sensor in public health.

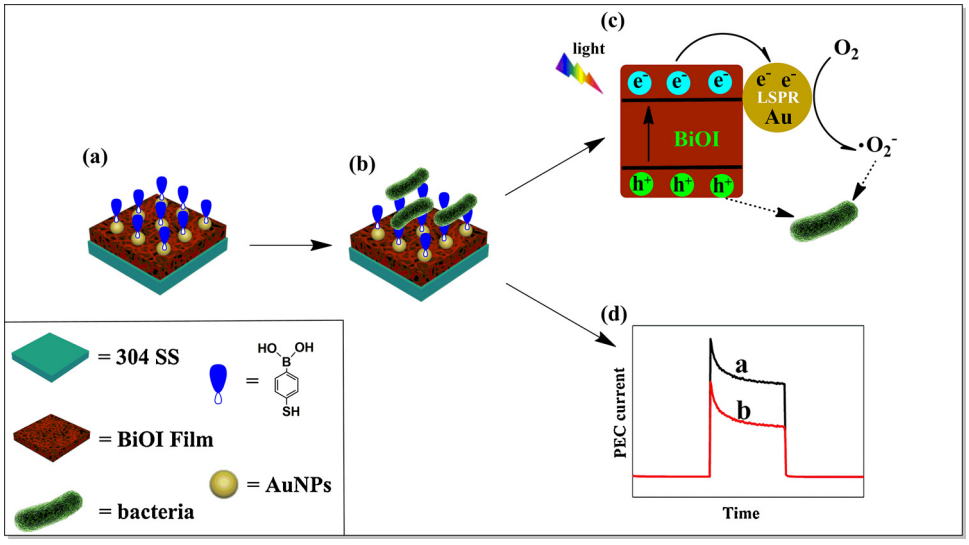
2. Materials and methods

2.1. Reagents and apparatus

The 304SS piece was purchased from Shanghai Xingan Company (China). Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), potassium iodide (KI), polyvinylpyrrolidone (PVP), chloroauric acid ($HAuCl_4$), ethylene glycol (EG) and ethanol absolute were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 4-MPBA was purchased from Sigma-Aldrich Co. (USA). All chemicals were used as received without any further purification. Milli-Q water was used in the experiment (Millipore, USA). *E. coli* provided by the CAS Key Laboratory of Experimental Marine Biology, Chinese Academy of Sciences were chosen as the model pathogenic bacteria.

2.2. Photoelectrode fabrication

The 304SS slice was first polished with 800-gift silicon carbide papers. And then it was cleaned with ethanol absolute and dried in N_2. The photoelectrode was fabricated as shown in Scheme S1 in the electronic supplementary information (ESI). Firstly, the BiOI film was *in-situ* growth fabricated on the 304SS piece *via* hydrothermal synthesis method according to the previous report [29]. In briefly, the 304SS slice was immersed vertically in 80 mL of mixture EG/water solution (the volume ratio of EG to water was maintained at 7:1) containing 0.1 M $Bi(NO_3)_3{\cdot}5H_2O$, 0.1 g of PVP, and 0.1 M KI. Then the mixture solution was heated at 140 °C in 100 mL Teflon-lined autoclave for 4 h. After being cooled down to room temperature naturally, the BiOI film coated slice (noted as BiOI/304SS) was rinsed with ethanol and water in turn and dried at 60 °C for 4 h. To obtain the AuNPs functionalized BiOI, BiOI/304SS was first immersed in $HAuCl_4$ (0.005 g/mL) solution for 30 min. Next, the substrate was rinsed for three time by water to remove the residual $AuCl_4^-$. After further being immersed in the AA solution (20 mM) for 20 min to reduce AuNPs, the AuNPs functionalized BiOI films were obtained and named as AuNPs/BiOI/304SS. Finally, 4-MPBA was modified on the surface of AuNPs by soaking in the 4-MPBA aqueous solution with 10% (V/V) ethanol for 2 h, followed by rinsing with ultrapure water and blowing dry in a stream of N_2, which was named as MPBA/AuNPs/BiOI/304SS. The resultant MPBA/AuNPs/BiOI/304SS is served as photoelectrode in following experiments.



Scheme 1. Schematic representation of the multifunctional PEC platform for capture, detection and inactivation of pathogenic bacteria.