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A new approach to light up the application of semiconductor nanomaterials for photoelectrochemical biosensors: Using self-operating photocathode as a highly selective enzyme sensor

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ABSTRACT

Due to the intrinsic hole oxidation reaction occurred on the photoanode surface, currently developed photoelectrochemical biosensors suffer from the interference from coexisting reductive species (acting as electron donor) and a novel design strategy of photoelectrode for photoelectrochemical detection is urgently required. In this paper, a self-operating photocathode based on CdS quantum dots sensitized three-dimensional (3D) nanoporous NiO was designed and created, which showed highly selective and reversible response to dissolved oxygen (acting as electron acceptor) in the electrolyte solution. Using glucose oxidase (GOD) as a biocatalyst, a novel photoelectrochemical sensor for glucose was developed. The commonly encountered interferents such as H₂O₂, ascorbic acid (AA), cysteine (Cys), dopamine (DA), etc., almost had no effect for the cathodic photocurrent of the 3D NiO/CdS electrode, though these substances were proved to greatly influence the photocurrent of photoanodes, which indicated greatly improved selectivity of the method. The method was applied to detect glucose in real samples including serum and glucose injections with satisfactory results. This study could provide a new train of thought on designing of self-operating photocathode in photoelectrochemical sensing, promoting the application of semiconductor nanomaterials in photoelectrochemistry.

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1. Introduction

As a newly developed and promising analytical technique, photoelectrochemical measurement has attracted considerable attention because it possesses several advantages such as the reduced undesired background signal, high sensitivity and the cheapness and easy miniaturization of detection devices (Gill et al., 2008; Haddour et al., 2006; Long et al., 2011; Wang et al., 2009a, 2009b). This method has promising analytical applications for portable, rapid, and high-throughput assays on paper-based analytical devices for point-of care diagnosis (Wang et al., 2013). The principle of the photoelectrochemical detection was based on analytes induced photocurrent change of the photoelectrochemically active species modified electrode. Thus, the photoelectrochemically active materials were crucial for the performance of the as developed photoelectrochemical sensors. Semiconductor nanocrystals have unique photoelectric features, which receive

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considerable attention in photoelectrochemical sensing. To the best of our knowledge, almost all the current photoelectrochemical detection systems focused on photoanode made up of n-type semiconductors or sensitized n-type semiconductors such as TiO₂ (Zhu et al., 2009; An et al., 2010), CdSe_xTe_{1-x}/TiO₂ (Kang et al., 2010), CdSe/ZnS (Schubert et al., 2010), CdS (Wang et al., 2009a, 2009b; Tu et al., 2012; Wang et al., 2013), etc. Upon illumination with photons having energy equal or larger than the band gap of the semiconductor, electron–hole pairs are generated. Fast hole transfer towards the electrolyte than that of electrons results into anodic photocurrent (photoanode) for n-type semiconductors. It was found that many reductive agents such as H₂O₂ (An et al., 2010; Tu et al., 2012; Wang et al., 2013), nicotinamide adenine dinucleotide (NADH) (Schubert et al., 2010), ascorbic acid (Wang et al., 2009a, 2009b), triethanolamine (Vered et al., 2008), and thio compounds (Long et al., 2011; Zhao et al., 2012a, 2012b) could act as hole scavengers through oxidation by holes, leading to improved charge separation and enhanced photocurrent of the photoanodes. Based on the interaction between holes and reductive species, a variety of photoelectrochemical biosensors were developed. For example, photoelectrochemical immunosensors were constructed based on the formation of immunocomplex

with enhanced steric hindrance, thus blocking the electron/mass transfer between the semiconductors and the hole scavengers (Wang et al., 2009a, 2009b; Kang et al., 2010). Another route to conduct photoelectrochemical immunoassay was by the generation of hole scavengers catalyzed by an enzyme labelled to a secondary antibody (Zhao et al., 2012a, 2012b).

Despite these extensive investigations, how to improve the selectivity of photoelectrochemical biosensors to realize accurate detection for real samples is still highly challenging. As known, the components of biological substrates are very complex (Zachariou and Hearn, 2000) and there are many reductive agents such as ascorbic acid, dopamine, thio-compounds coexisting in biological fluids (Qian et al., 2012; Kaya and Volkan, 2012) that could affect the photocurrent of the photoanode. The interference from the competitive reactions of these reductive species has become the main drawback of the currently developed photoanode-based biosensors. Due to the intrinsic hole oxidation reaction occurred at the photoanode/electrolyte interface, this problem is difficult to resolve by facile change of the composition of photoanode itself and a novel design strategy of photoelectrode for photoelectrochemical detection is greatly required.

Besides the widely reported photoanodes, there is another type of photoelectrode–photocathode, which has a different photoelectric property from that of photoanode (Choudhary et al., 2012). Lindquist and co-workers published the first true self-operating photocathode based on a p-type nickel oxide electrode sensitized by a freebase porphyrin or by erythrosine B, whose photocurrent was delivered when the photocathode was not biased with an external potentiostat to collect the injected holes (He et al., 1999). This pioneering work has generated renewed interest in solar cells in recent years (Odobel et al., 2010; Walter et al., 2010). Considering the different charge generation and charge transfer properties of photocathode from that of photoanode, it may be expected that self-operating photocathode based on p-type semiconductors will open a new avenue for photoelectrochemical sensing.

To validate this concept, herein, we report the first application of self-operating photocathode in photoelectrochemical sensing. CdS quantum dots (QDs) sensitized p-type NiO photocathode with a three-dimensional (3D) nanoporous structure was designed and prepared. Cathodic photocurrent of the CdS QDs sensitized NiO was observed when no biased external potential even positive potentials were applied. The cathodic photocurrent of the NiO/CdS was sensitively, selectively and reversibly enhanced/decreased by the on/off state of dissolved oxygen in the electrolyte solution, indicating that oxygen acted as an efficient electron acceptor of the photo-generated electrons of the photocathode. Different from the feature that the anodic photocurrent of photoanode is sensitive to the presence of a variety of hole scavengers (i.e. electron donors), the photocurrent of CdS sensitized photocathode was independent of the electron donors (such as H₂O₂, ascorbic acid, dopamine, cysteine, etc.), indicating its excellent anti-interference ability from reductive agents coexisting in biological samples. Considering the significance of sensing glucose because glucose played an important role in both energy metabolism and biosynthesis in the cells of most mammals (Cárdenas et al., 1998; Dörr et al., 2003; Nishimasu et al., 2006) and glucose could potentially be used in cancer therapy to restrict cancer-cell growth (Kaadige et al., 2009), based on the as-obtained photocathode, a novel photoelectrochemical enzyme sensor was developed using glucose oxidase as a model. This methodology not only overcame the selectivity shortcomings of the previously developed photoelectrochemical sensors for glucose (Tanne et al., 2011; Zheng et al., 2011; Wang et al., 2012), but also opened up a new type of photoelectrode for photoelectrochemical sensing. We hope that this study may serve as a foundation for the design and application of self-operating

photocathode for more exciting photoelectrochemical sensors and bioelectrochemical devices.

2. Experimental

2.1. Chemicals and materials

CdCl₂·2.5H₂O, Ni(NO₃)₂·6H₂O, thioglycolic acid (TGA), hexamethylene tetramine (C₆H₁₂N₄), Tris(hydroxymethyl)aminomethane (Tris), ascorbic acid (AA), L-Cysteine (Cys), dopamine (DA), D-(+)-Glucose were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Na₂S·9H₂O was purchased from Shanghai TongYa Chemical Reagent Co., Ltd. (Shanghai, China). Glucose oxidase (GOD, G2133-10 KU), PDDA (20%, w/w in water, molecular weight=200,000–350,000) was obtained from Sigma-Aldrich (USA). All other chemicals used were of analytical grade. A 0.1 mol/L Tris–HCl buffer solution was prepared and used as the supporting electrolyte for photocurrent measurements. GOD was dissolved in phosphate-buffered saline solution (PBS, 10 mM, pH 7.4) to obtain a solution (2.0 mg mL⁻¹) and was stored at 4 °C. All solutions were prepared with ultrapure water (18.2 MΩ cm⁻¹) obtained from a Healforce water purification system.

2.2. Instrumentation

Photoelectrochemical measurements were performed with a homemade photoelectrochemical system. A 500 W Xe lamp equipped with an ultraviolet cutoff filter ($\lambda \geq 400$ nm) was used as the irradiation source. Photocurrent was measured on a CHI 800C electrochemical workstation. NiO/CdS modified indium tin oxide (ITO) electrode with an area of 0.25 cm² was employed as the working electrode. A Pt wire was used as the counter-electrode and a saturated Ag/AgCl as the reference electrode. The photocurrent measurements were performed at a constant potential of 0 V (vs saturated Ag/AgCl). A 0.1 mol/L Tris–HCl (pH 7.0) was used as the supporting electrolyte for photocurrent measurements. Scanning electron microscopy (SEM) images were acquired on a Hitachi S-4800 High resolution scanning electron microscope (Hitachi, Japan). The X-ray powder diffraction (XRD) was obtained using an X'Pert Philips Materials Research Diffractometer using Cu K_α radiation and employing a scanning speed of 0.02° s⁻¹ in the 2θ range of 10° to 90°. The X-ray photoelectron spectra (XPS) were gained by an AXIS Ultra^{DL} X-ray Photoelectron Spectroscopy (Shimadzu-Kratos, Japan). The pH of the Tris–HCl was measured with a glass electrode connected to a PHS-25 pH meter (Shanghai, China).

2.3. Synthesis of CdS QDs

TGA-capped CdS QDs were synthesized in aqueous solution using our previously reported work (Wang et al., 2009a, 2009b). Typically, 250 μL TGA was added to 50 mL of 0.01 mol/L CdCl₂ aqueous solution in a round bottomed flask. The pH of the solution was adjusted to about 7.0 by dropwise addition of 1.0 mol/L NaOH. Then, 5.0 mL of 0.1 mol/L Na₂S aqueous solution was injected and the reaction was continued at room temperature for 4 h to obtain TGA-capped water-soluble CdS QDs. All the above process was conducted under magnetic stirring and high purity N₂ atmosphere. The finally obtained TGA-capped CdS QDs was stored in a refrigerator at 4 °C for future use.

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