



Short communication

A novel strategy for the construction of photoelectrochemical sensors based on quantum dots and electron acceptor: The case of dopamine detection



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ABSTRACT

Most of the current techniques for the photoelectrochemical detection based on the hole oxidation of the reductive substances (acting as electron donor) present in the electrolytes. In this paper, we report a new concept to construct photoelectrochemical sensors based on the interaction between photo-excited electrons of quantum dots (QDs) and electron acceptors. It was found that benzoquinone (BQ) could act as an efficient electron acceptor of the photo-excited CdS QDs, thus blocking the electron transfer of CdS to the indium tin oxide (ITO) electrode, leading to decreased photocurrent. Based on this phenomenon, a novel photoelectrochemical sensor for dopamine (DA) was developed. DA can be oxidized under weakly alkaline (pH 9.0) solution or by electro-deposition in neutral (pH 7.0) solution to form poly-dopamine. Poly-dopamine has abundant benzoquinone (BQ) groups, which acted as electron acceptors of the conduction band electrons of the photo-excited CdS QDs, leading to decreased photocurrent of CdS QDs. The method could detect DA with highly selectivity and sensitivity. This photoelectrochemical strategy based on photo-induced electron transfer between the electron acceptor and QDs opened a new avenue for the design of novel photoelectrochemical sensors.

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1. Introduction

Photoelectrochemical analysis as a newly developed technology has drawn growing interest in analytical chemistry [1–5]. Benefiting from the different form of energy for excitation and detection, photoelectrochemical measurement possesses several advantages such as the reduced undesired background signal, high sensitivity and the cheapness and easy miniaturization of detection devices.

In photoelectrochemical sensing, the interaction between analytes and the illuminated photoelectrochemically active materials leads to photocurrent change of the photoelectrochemically active materials. To date, as an important photoelectrochemically active material, quantum dots (QDs) have attracted much attention due to its unique size- and shape-dependent properties. When QDs are illuminated, an electron–hole pair is generated in the conduction and valence band, respectively [6]. Electrons transfer from the conduction band of the QDs to the electrode with an appropriate energy level and the holes react with the electrolyte at the semiconductor surface, resulting in anodic photocurrent. Reductive substances in electrolyte solution including H₂O₂ [1],

organophosphorus pesticide [3], acetylthiocholine [7] and ascorbic acid [8] were found to act as efficient hole scavengers (or electron donors) and oxidized by holes of QDs directly or indirectly, leading to promoted electron–hole separation and enhanced photocurrent of QDs. Based on the hole oxidation mechanism, different kinds of novel photoelectrochemical sensors were developed [1,3,7,8]. Electrons produced by the illuminated photoelectrochemically active materials are reactive toward electron acceptors such as H⁺ in solution [9], which can be used for H₂ generation. However, little attention was paid on the development of photoelectrochemical sensors based on the interaction between electrons of the photo-excited QDs and electron acceptors in solution. Katz et al. found that the oxidized states of cytochrome c (Cyt C) (a redox protein) could act as an electron acceptor of the photo-excited CdS QDs and the cathodic photocurrent of CdS QDs increased linearly as the concentration of the electron acceptor (Cyt C) increased [10]. However, the exact constituent group of Cyt C acting as electron acceptor of the photo-excited CdS QDs was not demonstrated clearly. Previously we found that Cu⁺/Cu_xS could act as electron–hole recombination centers to decrease the photocurrent of CdS QDs [11]. Riedel et al. found that the cathodic photocurrent (under polarized potential) of CdSe/ZnS was enhanced in the presence of oxygen (acting as an electron acceptor to enhance the separation of charge carriers in the QDs) [12]. Electrons from the conduction band of the QDs can reduce dissolved oxygen in the buffer and holes generated in the valence band can be filled through electron transfer from the electrode.

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Despite the successful detection systems based on hole oxidation, the limited principle in photoelectrochemistry sensing restricts its wide application as a dynamically developing analytical technique. To explore novel photoelectrochemical detection mechanisms is important for the extended design and application of photoelectrochemical sensors. Herein, a novel concept for the construction of photoelectrochemical sensors based on the interaction between photo-excited electrons of quantum dots (QDs) and an electron acceptor was developed. It was found that benzoquinone (BQ) could act as an efficient electron acceptor of the photo-excited CdS QDs, thus blocking the electron transfer of CdS to the indium tin oxide (ITO) electrode, leading to decreased photocurrent. To validate this concept, a novel photoelectrochemical sensor for dopamine (DA) was developed. In weakly alkaline solution, DA was easily oxidized and autopolymerized to form poly-dopamine [11] or DA could be electro-deposited under neutral pH solution on electrode surface to form poly-dopamine [12,13]. Poly-dopamine has abundant benzoquinone (BQ) groups [14], which could efficiently decrease the photocurrent of CdS QDs. Because many enzymes, such as horseradish peroxidase, tyrosinase and laccase, could catalyze the oxidation of phenolic compounds to generate quinones, the detection system may easily be extended to the development of a variety of biosensors such as immunoassay and enzyme sensors. In addition, this study may open the avenue for the development of novel photoelectrochemical sensors based on the interaction between semiconductors and electron acceptors.

2. Experimental section

Thioglycolic acid (TGA)-capped CdS QDs were synthesized in aqueous solution using a modified procedure [17]. 250 μL of TGA was added to 50 mL of 2.0×10^{-2} mol/L CdCl₂ aqueous solution. After that, 1.0 mol/L NaOH was added to adjust the pH of the above solution to 7.0. After 30 min, 5.0 mL of 0.1 mol/L Na₂S was added into the solution. At last, the mixture was reacted at room temperature for another

4 h. The whole reaction process was conducted under highly pure nitrogen atmosphere and under stirring.

The modification of CdS QDs on ITO slices was according to our previously developed methods [8] based on the electrostatic interaction between positively charged poly(diallyldimethylammonium chloride) (PDDA) and negatively charged TGA-capped CdS QDs.

Fluorescence spectra were measured on Cary Eclipse Fluorescence spectrophotometer (Varian Co., LTD, USA). Photoelectrochemical measurements were performed with a homemade photoelectrochemical system at room temperature. 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. CdS QDs modified 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.

DA was detected photoelectrochemically after its oxidation to poly-dopamine. That is, DA was firstly oxidation to poly-dopamine and then the photocurrent of CdS QDs in the presence of poly-dopamine was detected. For the alkaline solution oxidation method [13] to form poly-dopamine, DA was oxidized in 5 mL of 0.1 mol/L PBS (pH 9.0) containing 0.1 mol/L TEA under aerial condition for 15 min, and then the CdS QDs modified ITO electrode was immersed in the above solution for photocurrent measurement. For the formation of poly-dopamine with electro-deposition method [14,15], the CdS QDs modified ITO electrode used as the working electrode was immersed in the solution containing certain concentration of DA and 0.1 mol/L TEA in 5 mL of 0.1 mol/L PBS (pH 7.0), and the electrode was cycled using cyclic voltammograms within the potential range from -1.0 to 0.8 V at $dE/dt = 0.1$ V s⁻¹. After 25 cycles, the modified electrode was used to detect the photocurrent.

3. Results and discussion

In the photoelectrochemical process, the photoactive material (usually a semiconductor) absorbs photons with energies higher than

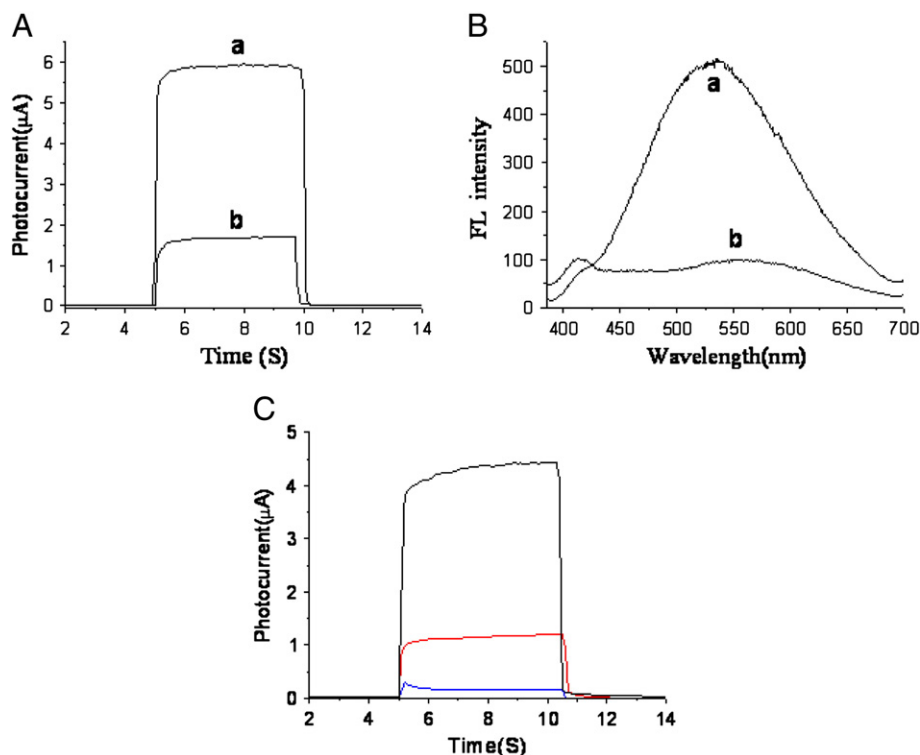


Fig. 1. The photocurrent (A) and fluorescence (B) of CdS QDs in TEA solution before (a) and after (b) the addition of 5.0×10^{-5} mol/L BQ. (C) The photocurrent of CdS QDs modified ITO electrode in 0.1 mol/L TEA and in the absence (black line) and presence of poly-dopamine obtained by alkaline solution oxidation (red line) or electro-deposition (blue line).

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