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# Charge recombination suppression-based photoelectrochemical strategy for detection of dopamine

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ABSTRACT

A new photoelectrochemical strategy based on charge recombination suppression is designed for the selective detection of dopamine. The photoelectrochemical platform was fabricated by simply coating the surface-unpassivated CdTe quantum dots (QDs) on the fluorine-doped tin oxide (FTO). When QDs were excited by light with the wavelength of 405 nm, the charge separations were generated, and then some electrons transformed to $O_2$ to produce $O_2^{-}\bullet$, leading to the photocurrent. Electron donors, whose energy level lies between the conduction band and valance band of QDs, could inhibit the charge recombination so that the photoelectric conversion efficiency is enhanced. Based on the recombination suppression, a new photoelectrochemical strategy was developed for the selective detection of dopamine. The photoelectrochemical system shows a good performance with the 5-order wide linear range of $4.0\times10^{-7}$ M to $1.0\times10^{-2}$ M, and a detection limit of $1.7\times10^{-7}$ M. This recombination suppression-based photoelectrochemical strategy could be extensively used in other donors-semiconductor material systems.

## 1. Introduction

Photoelectrochemical measurement as a promising analytical technology has drawn growing attention in various areas such as solar cells, environmental monitoring, and bioanalysis [1–8]. Owing to the separation of excitation signal and detection signal, photoelectrochemical strategy has plenty of advantages such as low background, low potential different from electrochemiluminescence, which lead to a good analytical performance. Thus, the photoelectrochemical platforms have been designed for the detection of pesticide [1], glutathione [2], DNA [3], $Cu^{2+}$ ion [4], glucose [5] and $H_2O_2$ [7]. The above photoelectrochemical strategies are usually based on the enhancement of photocurrent via holes oxidation [1], dye-sensitization [2], energy transfer [3], and the inhibition of photocurrent via the decomposition of quantum dots (QDs) [4], consumption of coreactant [5], and blocking of electron transfer [8].

On the other hand, when photoelectrochemical materials are excited by light and generated electron–hole pairs, charge recombination could be occurred, which obviously restrict the photoelectric conversion efficiency [9,10]. The presence of electron donors, whose energy level is suitable, can enhance photocurrent via the scavenging holes [11,12]. In this work, a new photoelectrochemical strategy based on charge recombination suppression is presented (Fig. 1). Under light irradiation, electrons transform from the valence band (VB) to conduction band (CB) of QDs, and generated electron–hole pairs. Then some electrons are excited to CB transformed to $O_2$ to produce $O_2^{-}\bullet$, resulting in photocurrent. In the presence of electron donor, the holes are scavenged. Thus the process of charge recombination is inhibited, and improves the photocurrent intensity. Using surface-unpassivated CdTe QDs as photoelectrochemical materials, this strategy was successfully applied in the detection of dopamine (DA). This photoelectrochemical strategy shows a good performance with a 5-order wide dynamic range, and can be applied in many other electron donor systems.

## 2. Experimental

### 2.1. Chemicals

Meso-2,3-dimercaptosuccinic acid (DMSA), cadmium chloride ($CdCl_2\cdot2.5H_2O$) and dopamine hydrochloride were purchased from Alfa Aesar China Ltd. (China). Tellurium rod (4 mm in diameter) was purchased from Leshan Kayada Photoelectricity Co. (China). All other chemicals were of analytical grade. Aqueous solutions were prepared with ultrapure water from a Millipore water purification system (≥18 MΩ, Milli-Q, Millipore). 0.01 M pH 7.0 phosphate buffer saline (PBS) was employed as supporting electrolyte. High purity nitrogen was used for synthesis of QDs.

### 2.2. Apparatus

Ultra-violet-visible absorption spectra were recorded using a UV-3600 spectrometer (Shimdzu, Japan). The synthesis of DMSA capped

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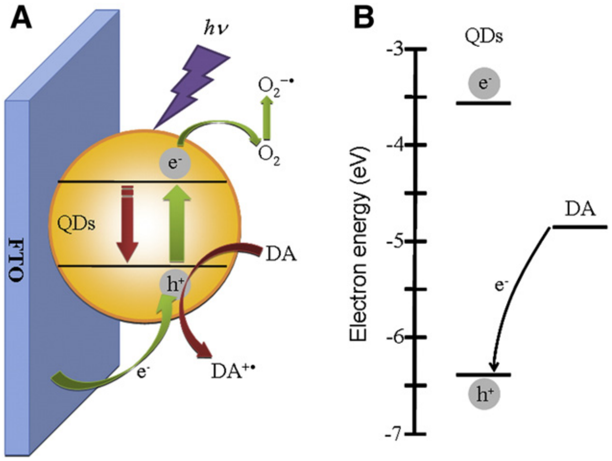

**Fig. 1.** Schematic illustration of charge recombination suppression-based photoelectrochemical strategy for detection of dopamine at CdTe/FTO electrode.

CdTe QDs and cyclic voltammetric experiments were performed on a CHI 660D electrochemical workstation (CH Instruments Inc., USA). Photoelectrochemical detection was performed on Zahner intensity modulated photo spectrometer (Zahner, German) with a LW405 LED light as the accessory light source. All experiments were carried out at room temperature using a conventional three-electrode system with a modified fluorine-doped tin oxide (FTO) electrode (0.5 cm in diameter), as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode.

### 2.3. Synthesis of DMSA-CdTe QDs

According to our electrolysis method [13], the DMSA-CdTe QDs were synthesized by applying a constant potential of −1.0 V (*vs* Ag/AgCl/saturated KCl) on Te work electrode. The resulting QDs have plenty of surface traps to enhance the photoelectrochemical activity.

### 2.4. Fabrication of the electrode and photoelectrochemical detection

900 μL of as-prepared QDs solution was mixed with 900 μL of isopropyl alcohol, and centrifuged at 8000 rmp min$^{-1}$ for 5 min. After washed with a 1:1 mixture of isopropyl alcohol and water, the precipitation was redissolved in 180 μL of water. Then 5 μL of QDs was cast onto FTO electrode, and dried at 37 °C for 20 min to obtain the QDs modified electrode. The photocurrent signals were detected in pH 7.0 PBS under the light irritation with the wavelength of 405 nm, and 50 W m$^{-2}$ light intensity at applying potential of −0.2 V.

## 3. Results and discussion

### 3.1. Photoelectrochemical mechanism

The photoelectrochemical strategy based on charge recombination-suppression is shown in Fig. 1A. Under light irradiation, electrons transformed from VB to CB of QDs, and generated electron–hole pairs. Then electrons transformed from CB of QDs to $O_2$ to produce $O_2^{-}$•, realizing the electron circuit. However, some parts of electrons are back to VB and result in the charge recombinations of electron–hole pairs, which decrease the photoelectric conversion efficiency. Electron donor whose energy level lies between the CB and VB of photoelectrochemical materials, could scavenge the holes. Therefore, the process of charge recombination is inhibited, and more electrons occupied on CB of QDs, which is a determining step for the enhancement of photocurrent [14]. These procedures lead to more electrons transforming from CB to surrounding solution, and improve photocurrent. Based on the charge recombination suppression, an enhanced photocurrent strategy is established for the sensitive detection of the donor.

In order to fully understand the transforming process of electron in this strategy, cyclic voltammetry (CV) was carried out to determine the energy levels of QDs and DA, and absorption spectra were recorded to determine the band gap of QDs (Fig. 2). The formal potential of the redox couple (at −0.92 V and −1.32 V) was determined to be −1.12 V (Fig. 2A), so the CB level of QDs (−3.62 eV) was calculated based on the vacuum energy of SCE (−4.74 eV) [15,16]. Since the energy gap of the QDs (2.67 eV) can be taken as the energy of the lowest exciton absorption peak at 465 nm (Fig. 2C), the VB energy of QDs was calculated to be −6.29 eV [12]. Similarly, the energy level of DA was calculated to be −4.91 eV according to the formal redox couple at 0.399 and −0.057 V, and the vacuum energy of SCE (Fig. 2B). Therefore, the energy level of DA lies between the CB and VB of the as-prepared QDs (Fig. 1B), which provides a possibility for a new photoelectrochemical strategy based on charge recombination-suppression.

### 3.2. Detection of DA

The wavelength is an important factor that is relevant to the photocurrent response. The photocurrent increment decreased at the applied potential of −0.2 V as the exciting wavelength increased from

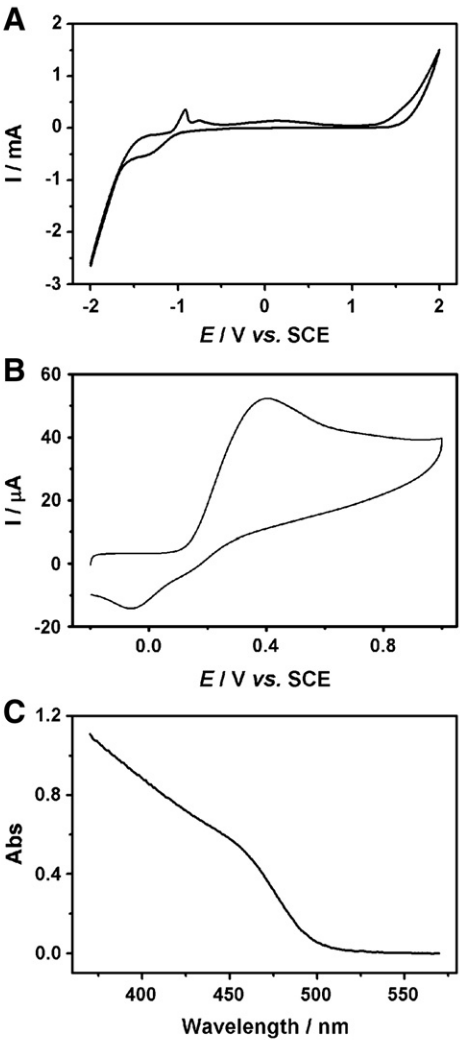

**Fig. 2.** Cyclic voltammetries in (A) PBS at CdTe/FTO electrode, and (B) PBS containing $1\times10^{-5}$ M dopamine at FTO electrode. Scan rate: 100 mV s$^{-1}$. (C) is UV–vis absorption of CdTe QDs.

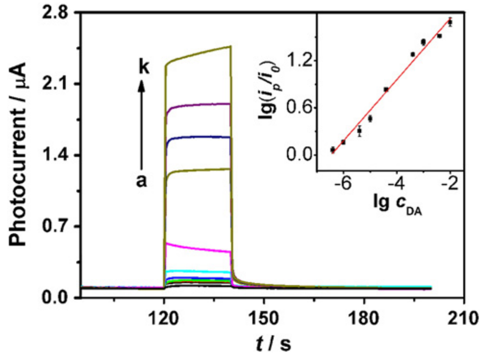

**Fig. 3.** Photocurrent responses of as-prepared electrode in the presence of 0, 0.4, 1, 4, 10, 40 and 400 μM, and 1, 4, 10 mM dopamine (from curve b to k, 0.01 M air-saturated PBS pH 7.0; $t_{\text{light}} = 20$ s; $E = -0.2$ V *vs* SCE), curve a is photocurrent response in $N_2$-saturated PBS. Inset: calibration curve.

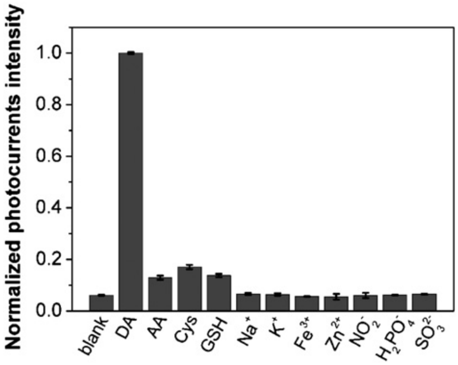

**Fig. 4.** Normalized photocurrent intensities of CdTe QDs modified FTO in the presence of 0.1 mM the individual interference under the same conditions (n = 3).

395 to 435 nm. The photocurrent intensity at 405 nm was 95% of that at 395 nm, showing enough sensitivity for photoelectrochemical detection of DA. Thus, 405 nm was chosen for the photoelectrochemical biosensing of DA.

The pH of electrolyte is other significant factor relevant to the photocurrent response. To investigate the pH influence, the photocurrent was measured at different pH in the range of 6–8.7. The photocurrent intensity decreased with the increasing pH value from 7.0 to 8.7. When the pH value is too acidic, the QDs are easily decomposed. Thus, 0.01 M pH 7.0 PBS was employed throughout the following experiments.

The photocurrent–time curve of QDs modified ITO electrode clearly illustrates the rapid response to DA at an applied potential of −0.2 V (Fig. 3). In the absence of $O_2$, no obvious photocurrent was observed (Fig. 3, curve a). Under the optimal conditions in air-saturated PBS, the logarithm of the ratio of the photocurrent with DA ($i_p$) to the photocurrent without DA ($i_o$) showed a good linear relationship to logarithm of the molar concentration value of DA (Fig. 3, inset). The linear range was from 0.4 μM to 10 mM, with a detection limit of $1.7 \times 10^{-7}$ M at signal-to-noise of 3. The linear response range was much wider than those of the electrochemical strategy (5 μM–200 μM) [17], and electrogenerated chemiluminescence of Au nanoclusters (2.5–47.5 μM) [18]. The stability of the biosensor was investigated by ten continuous photoelectrochemical measurements in pH 7.0 PBS with relative standard deviation (RSD) of 6.4%. At DA concentrations of 0.01 and 1 mM, the RSDs of the photoelectrochemical biosensor are 8.0% and 2.7%, respectively, which confirm the acceptable accuracy of this method.

### 3.3. Interferences

To evaluate the selectivity of the present sensing system, the interferences of 4 cations, 3 anions and 3 small biomolecules were tested at the same experimental conditions (Fig. 4). The cations and anions showed no obvious interference for the detection. Although the energy level of ascorbic Acid (AA) lies between CB and VB of QDs, the photocurrents of AA was about one time than that of the blank. However, the ratio of the photocurrent of DA and blank was nearly 16:1, since the presence of oxidized dopamine-quinone functioning as an electron acceptor enhanced the photocurrent response [19]. Thus, the photoelectrochemical strategy showed good selectivity in the detection of DA.

## 4. Conclusions

A new photoelectrochemical strategy based on charge recombination suppression was developed for the selective detection of dopamine. Substances like dopamine, whose energy level lies between CB and VB of QDs, could inhibit charge recombination of electron–hole pairs. The recombination suppression effect leads to large improvement of photocurrent, and thus provides a new photoelectrochemical method in analytical chemistry. The resulting photoelectrochemical biosensor shows good performance with much wide linear range, low potential, high sensitivity, and acceptable accuracy. This photoelectrochemical strategy based on charge recombination suppression provides a robust tool to detect electron donors in practice.

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