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RESEARCH ARTICLE

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Simple strategy for sensitive detection of dopamine using CdTe QDs modified glassy carbon electrode

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Background: Cellular and brain metabolism of dopamine can be correlated with a number of neurodegenerative disorders, our study was to explore a simple and efficient method to detect dopamine in real samples.

Methods: A new quantum dots (CdTe QDs) could be prepared using the hydrothermal method, the electrochemical biosensor was established by dropping CdTe QDs on the surface of glassy carbon electrode (GCE).

Results: The CdTe QDs/GCE exhibited the excellent electrochemical catalytic activity toward dopamine (DA) with good stability and high sensitivity in presence of interfering substances. The detection limit of DA was calculated by differential pulse voltammetry (DPV) as low as 0.3 μmol L^{-1} with a linear dynamic range of 1 μmol L^{-1} to 400 μmol L^{-1}.

Conclusion: In this paper, the proposed electrochemical biosensor could be effectively used for the direct and rapid detection of DA in human serum and urine samples.

KEYWORDS
dopamine, electrochemical sensor, quantum dots

1 | INTRODUCTION

Dopamine, 3,4-dihydroxyphenyl ethylamine, is a neurotransmitter of great importance for the nervous system of biological organisms,[1] it is involved in motor control, endocrine function, reward, emotion, and cognition.[2] Cellular and brain metabolism of dopamine can be correlated with a number of neurodegenerative disorders such as attention deficit hyperactivity disorder, mood disorders, Parkinson, and Alzheimer.[3,4] The currently available analytical methods for dopamine determination in pharmaceutical samples and biological fluids including spectrophotometry,[5] liquid chromatography,[6] chemiluminescence,[7] capillary electrophoresis,[8] and electrochemical methods.[9] However, aside from electrochemical detection, most of the procedures generally involve a time-consuming sample pretreatment step and long analysis times and are relatively expensive. Therefore, the development of electrochemical biosensor has proven to be an attractive alternative for the determination of DA in the presence of interfering compounds due to their high sensitivity and selectivity, fast detection, low detection limits.

Quantum dots (QDs), are semiconducting nanoparticlesas, that usually consist of group IIB-VIB or IIIB-VB elements and are diameter stable at 2-20 nm, have exhibit excellent optical and electro-optical properties due to their quantum size effect, surface effect, and dielectric confinement effect.[10] As a novel member of carbon family, QDs have been widely used in bioanalytical research,[11,12] however, numerous studies only focus on the optical research of QDs and ignored strong physical adsorption capacity, QDs possess a large number of hydroxyl and amino groups on the surface which can attract the electroactive compound dopamine. In this study, we fabricated a novel DA biosensor which was modified with CdTe QDs, the sensor showed high sensitivity and good reproducibility in determination of DA in human serum and urine samples with a high sensitivity and excellent selectivity.

2 | MATERIALS AND METHODS

2.1 | Reagents

Dopamine ($C_8H_{11}NO_2$), Uric acid ($C_5H_4N_4O_3$, UA) and 3-mercaptopropionic acid (3-MPA) were purchased from Sigma (St. Loius, MO, USA). DA stock solution was prepared with phosphate buffer solution. A phosphate buffer was used to control the pH. Cadmium chloride ($CdCl_2$ $2.5H_2O$), sodium borohydride ($NaBH_4$) and tellurium powder (Te) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Other reagents were of analytical-reagent grade and deionized water purified with Millipore system (Millipore Ltd. China) was used throughout this study. All experiments were conducted at the room temperature of 25°C human serum and urine samples were generously supplied by the first affiliated hospital of the Harbin Medical University. No. 23 Youzheng Street, Harbin, Heilongjiang Province, P. R. China.

2.2 | Apparatus

The cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were performed with a model CHI660C electrochemical workstation (Shanghai Chenhua Instruments Co. Shanghai, China). Electrochemical measurements were performed using a three-electrode system consist of a platinum wire auxiliary electrode, an Ag/AgCl reference electrode and CdTe QDs modified electrode as working electrode (3 mm in diameter), (All from Incole Union Technology Co. Ltd, Tianjin, China). Solution pH was measured on pH meter (from Precision Scientific Instruments Co. Shanghai, China). Images of the CdTe QDs were observed using JEM-2100 transmission electron microscope was purchased from Japan Electron Optics Laboratory Co. (JEOL, Japan). Ultrasonic cleaning machine was purchased from Kunshang. Co. Ltd. (Jiangsu, China).

2.3 | Preparation of CdTe QDs and modified electrode

According to the literature[13,14] the molar ratio of Cd^{2+}/MPA/Te^{-} was optimized for 1:2.5:0.5. Tellurium powder was selected as a source of tellurium to synthetic the tellurium sodium hydride (NaHTe). 435.7 μL MPA solution were piped into 100 mL of 2.0×10^{-2} mol L^{-1} $CdCl_2$ solution, then were sufficiently stirred with a magnetic stirrer, the solution was adjusted with 1 mol L^{-1} NaOH to pH 10.5. The following, the fresh 1 mmol L^{-1} NaHTe solution was slowly poured into it with stirring drastically under N_2 and then heated to reflux at 100°C for 6 hours. Then, the QDs solution was purified by ethanol and separated by centrifugation at a 6700 *g* for three times. Finally, 0.1 g of the precipitate was re-dissolved 50 mL in ultrapure water and preserved at 4°C in dark.

The bare electrode was polished into a mirror with 0.3 and 0.05 μm alumina powder, rinsed with double distilled water, washed ultrasonically for 5 minutes in anhydrous ethanol and double distilled water in turn, then dried in N_2. A 5 μL amount of CdTe QDs was dropped on the bare electrode surface to prepare the CdTe QDs/GCE then were dried in a 4°C N_2 incubator. Finally, unattached CdTe QDs on the modified electrode surface were cleaned before used.

3 | RESULTS

3.1 | Characterization of CdTe QDs

Transmission electron microscopy (TEM) was employed to characterize the morphology of the prepared MPA-capped QDs. Figure 1 shows the TEM micrograph of CdTe QDs dispersed uniformly with spherical shape and the size of the particles ranges between 3-5 nm. CdTe QDs can be preserved for 3 months at 4°C in the dark and exhibit high stability.

Figure 2A shows the cyclic voltammograms of the bare electrode and the CdTe QDs/GCE in 200 μmol L^{-1} DA solution at the scanning rate of 100 mV/s. As it is seen, the anodic peak current of DA on CdTe QDs/GCE is much higher than bare GCE, indicating CdTe QDs/GCE has the excellent electrochemical activity. Figure 2B depicts the electrochemical impedance spectra of bare GCE (a), CdTe QDs/GCE (b) in presence of equimolar 5 mmol L^{-1} $K_3Fe(CN)_6$ + 5 mmol L^{-1} $K_4Fe(CN)_6$ + 0.1 mol L^{-1} KCl. The charge transfer resistance (RCT) values were determined directly from the diameters of the high frequency semicircle. The diameter of the semicircle for CdTe QDs/GCE was larger than that of bare GCE, indicating that the CdTe QDs on the surface of GCE increased the electron transfer rate between the redox probe of the electrode surface and $[Fe(CN)_6]^{3-/4-}$. Plenty of polar and negatively charged oxygen functional groups such as -COOH and -OH prevent $[Fe(CN)_6]^{3-/4-}$ from penetrating the electrode/solution interference.

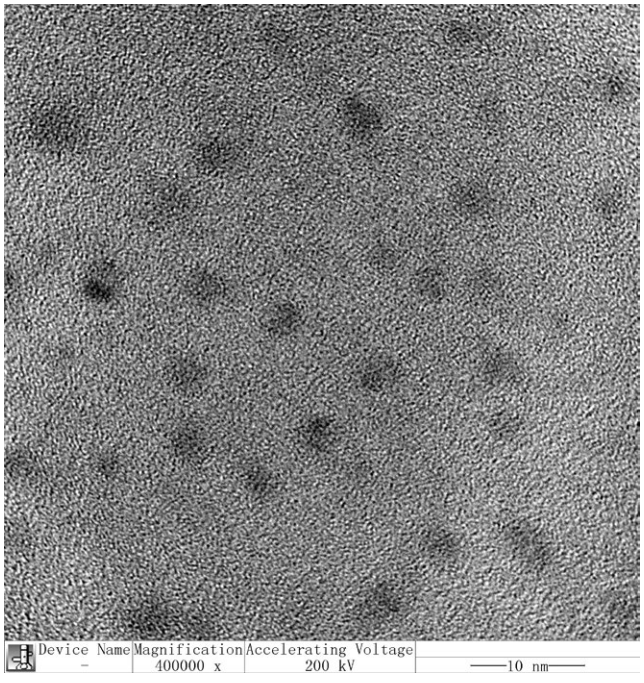

FIGURE 1 TEM image of CdTe QDs

3.2 | Effect of buffer pH

The effect of pH on the electrochemical response of DA attached to CdTe QDs modified electrode were examined by DPV within a pH range of 4.0-9.0 (Figure 3). It is clearly found that the peak currents of DA are pH-dependent, which indicated that protons can participate in the electrochemical reaction of DA. According to the results, the maximum value appeared at pH 7.5 which was selected as optimal pH for the electrochemical detection in all subsequent studies.

3.3 | Electrochemical properties

The mechanism of the proposed CdTe QDs/GCE have higher sensitivity and selectivity for DA detection is that CdTe QDs possess a large number of hydroxyl groups on the surface which can combine the amino on dopamine. Figure 4 A presents DPV response of CdTe QDs/GCE in various of concentrations of DA. The DPV responses of the CdTe QDs/GCE electrode after incubation in a DA solution of concentration ranging from 5 μmol L^{-1} to 200 μmol L^{-1} in a pH = 7.5 buffer shows that the peak current increases as the increase in DA concentration. As shown in Figure 4B, this linear regression equation was described as Ipa(μA) = 0.178C + 0.866, C is concentration, R^2 = 0.992. giving a detection limit of 0.3 μmol L^{-1}, based on signal-to-noise ratio of 3 (S/N = 3). Comparisons of this sensor with other chemically modified electrodes are listed in Table 1. The excellent electro-catalytic ability of the modified electrode is attributed to the large number of carboxylic groups on the surface of CdTe QDs that can effectively interact with DA.

3.4 | Interference

Due to its coexistence with DA, UA in biological samples, herein, we first studied the interference of UA on the detection of 200 μmol L^{-1} DA at the CdTe QDs modified electrode. The oxidation peak currents and potentials of DA was not affected in the presence of UA (Figure 5). Also, we examined the interference of AA and glucose on the detection of 200 μmol L^{-1} DA, the results showed that there is no effect on the determination of DA up to 300 μmol L^{-1} AA and 200 μmol L^{-1} glucose. These results demonstrate that the CdTe QDs modified GCE possesses excellent selectivity.

3.5 | Analysis of DA in real life samples

In order to evaluate the applicability of the proposed sensor, the concentration limit of DA in human serum and urine samples were determined by applying the standard addition method. The serum and urine samples were diluted 15 times with PBS (pH = 7.5) before measurement. The analytical results were showed in Table 2. The recovery was in the range of 99.07%-101.75%. The RSD value is less than 4%, demonstrating that the obtained CdTe QDs modified GCE can be used precisely for DA detection in real samples.

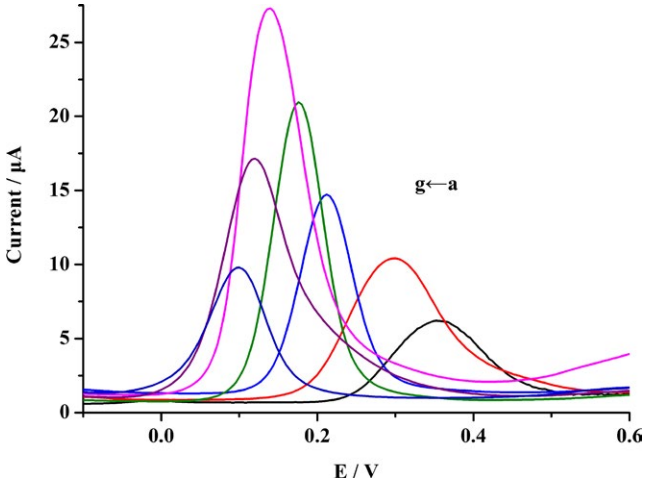

FIGURE 3 Effect of pH on DPV peak current in 0.01 μmol L^{-1} containing 300 μmol L^{-1} DA (pH from a to g: 4, 5, 6, 7, 7.5, 8, 9)

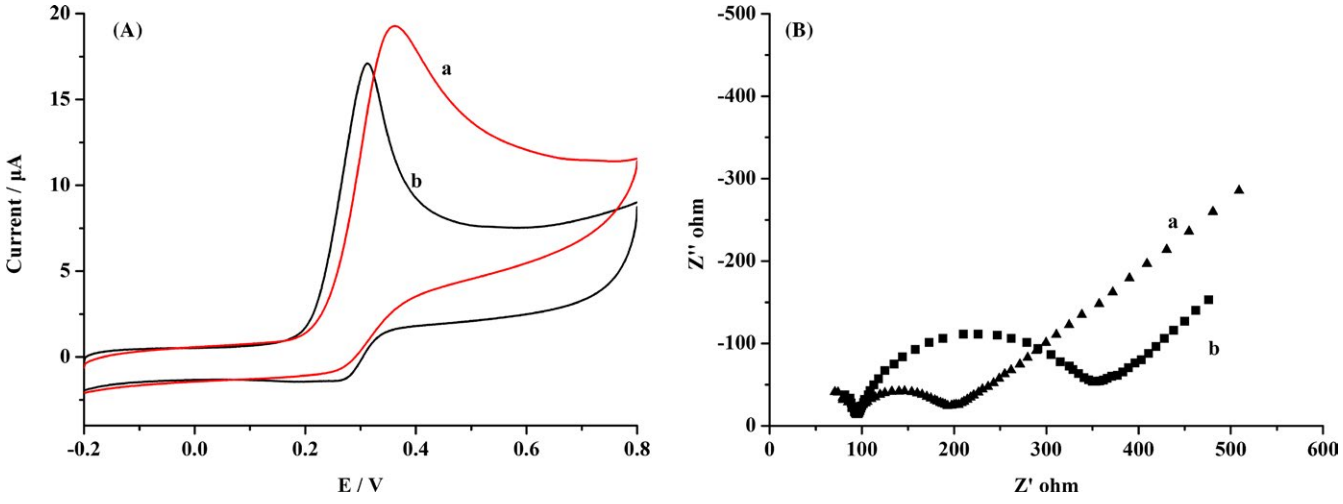

FIGURE 2 (A) shows the cyclic voltammograms of the bare electrode and the CdTe QDs/GCE in 200 μmol L^{-1} DA solution. (B) depicts the electrochemical impedance spectra of bare GCE (a), CdTe QDs/GCE (b)

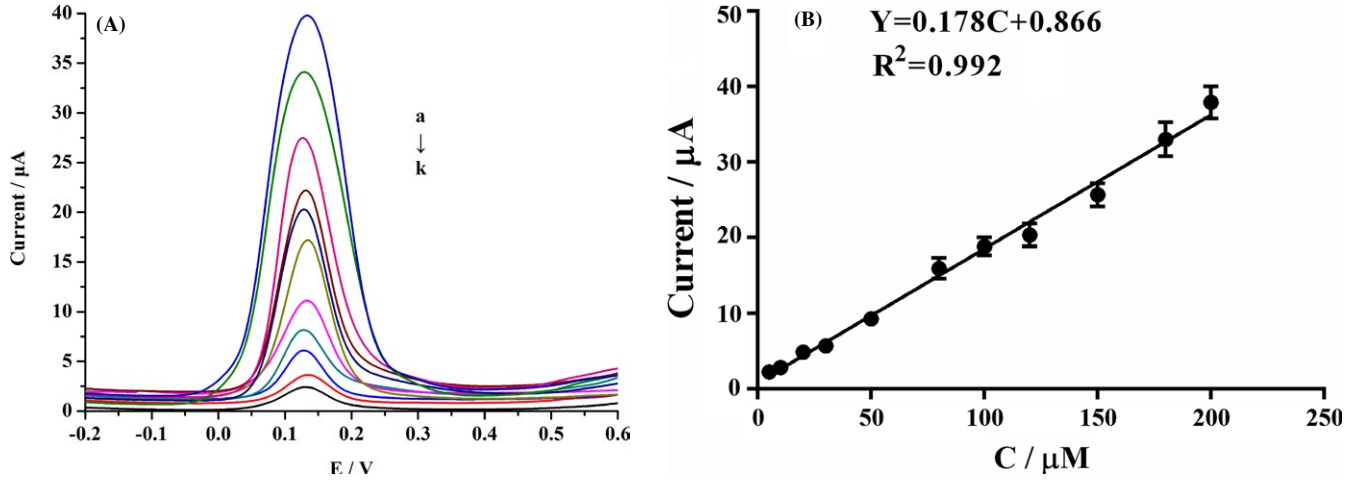

FIGURE 4 (A) DPV response to 200 μmol L^{-1}, 180, 150, 120, 100, 80, 50, 30, 20, 10, 5 μmol L^{-1} of DA (from a to k) and (B) calibration plot of DPV peak current vs target DA concentration

TABLE 1 Comparison of electro analytical parameters for the determination of DA at CdTe QDs modified electrode with other reported modified electrodes

Electro	Detection limit (μmol L^{-1})	Linear range (μmol L^{-1})	Ref.
GR-CS composite	0.0045	0.03-20.06	15
PEDOT/Pd composite	0.5	0.5-1.0	16
PPy-rGOc	1	0.01-10	17
Tyrosinase/NiO/ITO	1.038	2-100	18
AuNP-PAH	0.26	0.49-23.0	3
CdTe	0.3	1-400	This work

3.6 | Reproducibility and stability studies

The reproducibility of the biosensor was investigated by repetitive measurements of DA oxidation peak currents in presence of 200 μmol L^{-1} DA solution in PBS. Five parallel measurements of DA were carried out, the relative standard deviation is 4.3%. indicating that the CdTe QDs modified electrode has good reproducibility. Meanwhile, CdTe QDs/GCE were used intermittently and stored for 2 weeks in order to examine the stability of the modified electrode, the current signals could show a less than 5% decrease relative to the initial response indicating that the obtained CdTe QDs can show an excellent stability of the proposed modified electrode.

4 | CONCLUSIONS

In this paper, the proposed electrochemical biosensor was established by a easy strategy and exhibited good analytical performance in the determination of DA. The promising results obtained in this study suggest that the excellent analytical performance of the proposed method is due to the efficient immobilization of CdTe QDs. With the good selectivity and practicability, the proposed method has been applied to the determination of DA in real samples with satisfactory results. The fabricated sensor may provided a new electrochemical method for clinical diagnosis in the future.

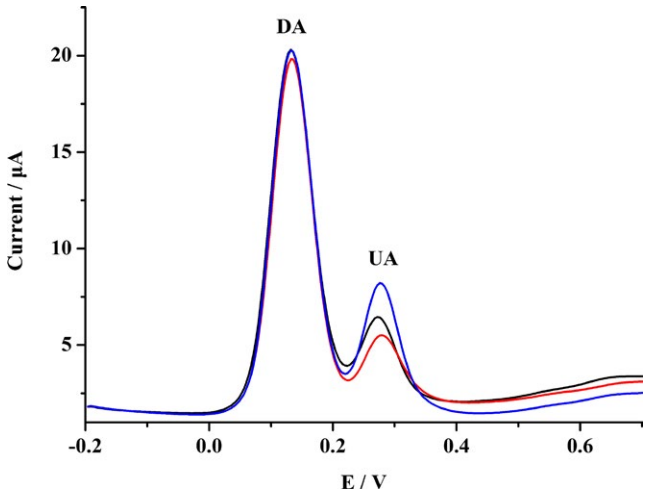

FIGURE 5 DPV profiles at the CdTe QDs modified GCE in PBS buffer (pH 7.5) containing (A) 200 μmol L^{-1} DA and different concentrations of UA (from bottom to top: 100 μmol L^{-1}, 120 μmol L^{-1} and 150 μmol L^{-1} UA)

TABLE 2 Determination of DA in human serum and urine samples at CdTe QDs modified electrode

Sample	Added (μmol L^{-1})	Found (μmol L^{-1})	Recovery (%)	RSD (%)[a]
Serum	100	99.59	99.59	2.53
	150	152.63	101.75	3.88
	200	202.5	101.25	2.86
Urine	100	99.07	99.07	2.61
	150	151.5	101.00	2.18
	200	200.57	100.29	3.63

[a]RSD value reported is for n = 3.

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