

Enhanced voltammetric determination of dopamine using a glassy carbon electrode modified with ionic liquid-functionalized graphene and carbon dots

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Abstract The authors describe a dopamine (DA) sensor based on a glassy carbon electrode modified with a composite film composed of carbon dots (C-dots) and graphene functionalized with an ionic liquid. The C-dots were functionalized with carboxy groups whose negative charge promotes electrostatic attraction to the protonated amino groups in DA. The presence of an imidazole cation in the IL facilitates interaction with the C-dots and DA via electrostatic interactions and π -stacking forces. Under optimal conditions, the modified GCE display improved electrochemical response to DA compared to a bare GCE, or a GCE modified with C-dots or IL-graphene only. The oxidation current, measured best at a potential of 0.22 V (vs. Ag/AgCl) is linearly related to the DA concentration in the 0.1 to 600 μ M range, with a 30 nM detection limit at a signal-to-noise ratio of 3. Ascorbic acid does not interfere even in large excess, and the sensor is stable for at least a month. The modified GCE was applied to the determination of DA in spiked fetal bovine serum and gave satisfactory results.

Keywords Dopamine · Ionic liquid · Graphene · Carbon dot

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Introduction

Dopamine (DA) behaves as a vital neurotransmitter in the human brain playing a significant role in the renal, cardiovascular, central nervous and hormonal systems [1, 2]. When an occurrence of an anomaly pertaining to the dopamine concentration presents itself, it is most likely linked to several neurological disorders such as parkinsonism, epilepsy and schizophrenia [3]. In addition, DA is available as an intravenous medication that acts on the sympathetic nervous system. It can produce noticeable effects by increasing heart rate and blood pressure [4]. Therefore, detection and quantification of DA in vivo/vitro is a subject of great importance in medical practice. Various methods, such as liquid chromatography [5], spectroscopy [6], fluorescence [7] and electrochemical analysis [8, 9] have been implemented for the assay of DA. Among them, electrochemical analysis has received great interest due to its considerably high sensitivity, rapid response, low cost and ease of operation. Many attempts have been made to develop chemically modified electrodes with a variety of materials for the selective determination of DA; the most commonly used materials are carbon nanomaterials and metal oxides due to their internal excellent catalytic properties, such as carbon nanotubes [10], graphene [11], graphene oxide (GO) [12], MnO₂ [13], Cu₂O [14], TiO₂ [15], and Fe₃O₄ [16].

Being a two-dimensional carbon material, graphene has demonstrated a myriad of beneficial characteristics [17]. For instance, graphene has been shown to display unique physical and chemical properties in bioelectronics and biosensing [18]. Graphene has exceptional thermal, chemical, and mechanical properties [19], as well as high specific surface area and excellent electrical conductivity [20]. These unique properties hold great promise for potential applications in technological fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors and hydrogen storage [21]. One

important issue concerning its application is molecular aggregation, in which graphene sheets tend to form agglomerates via *van der Waals* interactions [22]. Aggregation can be reduced by covalent or non-covalent attachment of other molecules or polymers onto the sheets. It is imperative to introduce desirable substances to graphene in order to elucidate novel properties. Due to their wide solubility and introduction of a surface charge, ionic liquid-functionalized graphene (IL-graphene) sheets with good dispersibility and long-term stability in various solvents have been synthesized by the Niu group [23]. In addition, IL-graphene based electrochemical sensors and biosensors have also been extensively reported in literature for direct electron transfer of various redox enzymes and the detection of various types of compounds, such as p53 gene [24], bovine serum albumin [25], bovine hemoglobin [26], and rutin [27].

Traditional semiconductor quantum dots (such as CdSe, CdTe ect.) are commonly synthesized with the use of toxic heavy metals, limiting their widespread use in biological applications [28]. These heavy metals are hazardous to the environment and pose long term toxicity concerns. Compared with conventional semiconductor quantum dots or metal quantum dots, carbon dots (C-dots) are a new class of carbon nanomaterials that are superior due to their low cytotoxicity, excellent biocompatibility, facile synthesis, cost-effective, remarkable conductivity, high aqueous solubility, and favorable optical properties. The C-dots can provide an abundant source of carboxyl groups and/or amino groups at the surface that can significantly enhance the redox response of dopamine [29].

Herein, a kind of compound consisting of carbon dots and IL-graphene was fabricated. It can be implemented for detection of DA and it also shows a wide linear range, higher sensitivity, lower detection limit, better reproducibility, and better stability. In addition, the sensor also has a strong anti-interference ability for potential interference substances. Under optimal conditions, differential pulse voltammetry (DPV) peak current and the concentration of DA in the range from 0.1 to 600 μM and its detection limit is 30 nM.

Experimental section

Reagents and instrumentations

GO was purchased from Nanjing XFNano Materials Technology Company (Nanjing, China, <http://www.xfnano.com>). Ascorbic acid (AA), DA, 1-methylimidazole and 2-bromoethylamine hydrobromide were obtained from Sigma (Shanghai, China, <http://www.sigmaaldrich.com/china-mainland.html>). All reagents were analytical grade reagents. Nanopure deionized and distilled water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used throughout all experiments.

Electrochemical studies were performed with a CHI 660D instrument (Chenhua Instruments, Shanghai, China). A modified glassy carbon electrode (GCE) served as the working electrode, an Ag/AgCl (saturated KCl solution) was used as the reference electrode, and a Pt wire was employed as an auxiliary electrode. The UV-visible absorption was registered on a Thermo Scientific NanoDrop 2000/2000C spectrophotometer. Scanning electron microscopy (SEM) was performed on a S-4800 electron microscope (Hitachi, Ltd., Japan). Transmission electron microscopy (TEM) was performed on a JEM-2100F electron microscope (JEOL, Ltd., Japan) at 300 kV. All experiments were conducted at room temperature.

Synthesis of C-dots/IL-graphene

IL-graphene was prepared according to Niu's method [23] and the C-dots were prepared according to Francesca Arcudi's method [30]. A typical procedure to synthesis C-dots/IL-graphene is as follows: 1 mg IL-graphene was added to 10 mL C-dots solution (2.0 mg mL^{-1}). Subsequently, the composite was placed into a Teflon-lined stainless steel autoclave for 4 h at 90°C , and then C-dots/IL-graphene was obtained.

Electrode preparation

First, the GCE was polished to a mirror-like surface using $0.3 \mu\text{m}$ and $0.05 \mu\text{m}$ γ -alumina slurry. The GCE was successively washed by water, ethanol and distilled water in an ultrasonic bath and dried in air before use. The obtained C-dots/IL-graphene nanocomposite solution of $5 \mu\text{L}$ was dropped

Scheme 1 Schematic illustration of the enhanced electrochemical detection strategy for DA based on C-dots/IL-graphene composites modified on the GCE

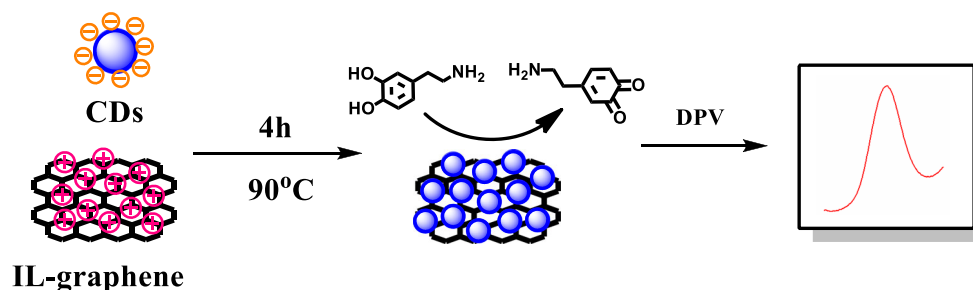
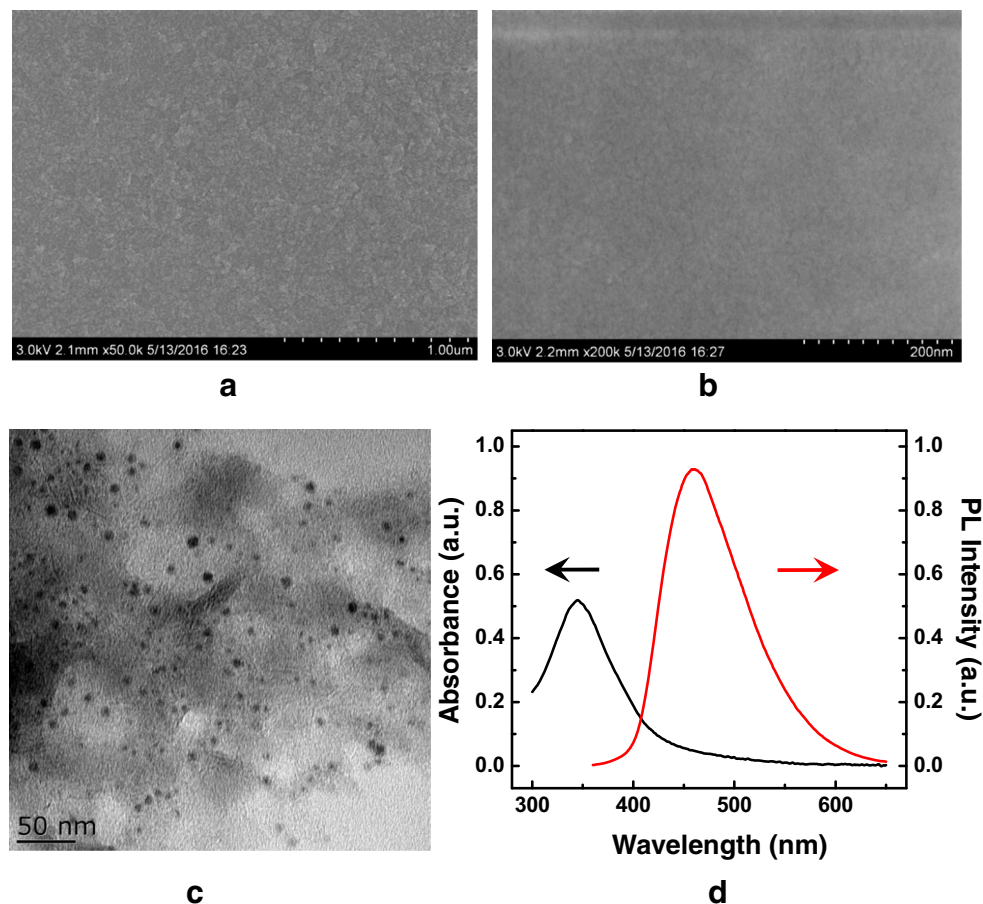


Fig. 1 **a** SEM image of IL-graphene. **b** SEM image of C-dots/IL-graphene. **c** TEM image of C-dots/IL-graphene. **d** UV-vis absorption and fluorescence emission spectra of C-dots intensity



onto the surface of the GCE and slowly dried in ambient conditions to form C-dots/IL-graphene modified GCE (C-dots/IL-graphene/GCE). Subsequently, it was rinsed with water to physically remove adsorbed species before use. The sensing strategy for DA is illustrated in Scheme 1. Cyclic voltammetry (CV) was performed to characterize the different modified electrodes in the pH 6.5 phosphate buffer containing different concentrations at a scan rate of 0.1 V s^{-1} . Finally, the DPV signals were recorded in the range of -0.2 V to $+0.6 \text{ V}$.

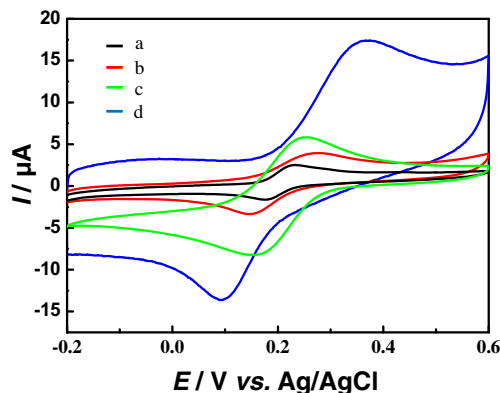


Fig. 2 CV of 0.10 mM DA recorded on bare GCE (a), C-dots/GCE (b), IL-graphene/GCE (c), and C-dots/IL-graphene/GCE (d) in the pH 6.5 phosphate buffer (scan rate: 0.1 V s^{-1})

Results and discussion

Characterization of IL-graphene, C-dots, and C-dots/IL-graphene/GCE

The morphology of IL-graphene (Fig. 1a) and C-dots/IL-graphene (Fig. 1b) were characterized via SEM, the typically crumpled and wrinkled structure of IL-graphene and C-dots/IL-graphene were observed. As presented in Fig. 1c, the C-dots/IL-graphene composite was characterized via TEM with sizes ranging from 5 to 10 nm of C-dots Fig. 1d depicts the UV-Visible absorption spectra and the fluorescent emission peak of C-dots. C-dots exhibited a well-defined absorption and emission peak at 340 and 460 nm, respectively.

CV behavior of DA on the C-dots/IL-graphene/GCE

CV measurements were tested on the different working electrodes of 10 mM DA including a bare GCE, a C-dots/GCE, an IL-graphene/GCE and a C-dots/IL-graphene/GCE in a pH 6.5 phosphate buffer. As depicted in Fig. 2, the cyclic voltammogram measured of bare GCE shows an oxidation peak current at $2.506 \mu\text{A}$ and a reduction peak at $-1.651 \mu\text{A}$. C-dots were immobilized on the same electrode in which the oxidation

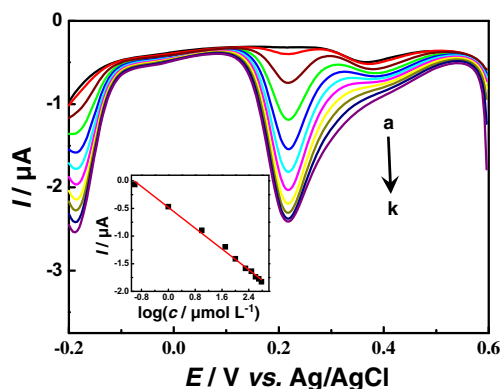


Fig. 3 DPV of DA recorded on C-dots/IL-graphene/GCE with increasing concentration (from a to k: 0, 0.10, 1.0, 10.0, 50.0, 100.0, 200.0, 300.0, 400.0, 500.0, and 600.0 μM , respectively)

current and the reduction current were observed to have increased by 131.4 % and 400.8 %, respectively. On the IL-graphene/GCE, the oxidation current and the reduction current were observed to have increased by 56.6 % and 102.5 %, respectively. However, the oxidation and reduction currents are further increased by 591.9 % and 728.0 % at C-dots/IL-graphene/GCE. Many scientists have discussed the possible reaction mechanism of C-dots/IL-graphene/GCE with DA. The C-dots provide a more conductive electrode surface. C-dots have not only increased the stability, but also promoted interactions with amino groups in DA via electrostatic interactions to increase recognition DA with high specificity. [31].

The effect of pH

The electrochemical redox behavior of DA with C-dots/IL-graphene/GCE in buffer systems of varying pH values ranging from 3.0 to 8.0 was investigated by CV; results are shown Fig. S1. With an increase of pH value, results show the oxidation peak potential negatively shifted that indicates protons are being involved in the electrode reaction. A good linear relationship between E_{pa} and pH was constructed with linear regression equation as $E_{\text{pa}} (\text{V}) = -(0.0610 \pm 0.0003) \text{pH} +$

(0.740 ± 0.005) ($n = 3$, $R^2 = 0.9967$). The slope value of -61.0 mV/pH shows that the electron transfer was accompanied by an equal number of protons. At the same time, when the pH is 6.5, the oxidation peak current (I_{pa}) of DA was the largest. Therefore, by taking into account the sensitive determination for DA, the phosphate buffer of pH = 6.5 was chosen as the optimal pH acidity in this experiment.

Effects of scan rate

In order to investigate the reaction kinetics, CV measurements were performed of 10 mM DA at C-dots/IL-graphene/GCE at varying scan rates, as shown in Fig. S2. As scan rate increases, the redox peak current increased correspondingly. Moreover, both the cathodic and anodic peak currents increased with an increase in scan rate from 0.01 to 0.5 V s^{-1} . Results indicate that the electro-redox of DA on C-dots/IL-graphene/GCE behaves as a typical diffusion-controlled process [32]. In addition, at higher scan rates, the anode (E_{pa}) and cathode (E_{pc}) peak potential have a linear relationship with the logarithm of scan rate ($\log v$). The regression equations were: $E_{\text{pa}} (\text{V}) = (0.0744 \pm 0.0002) \log v (\text{V s}^{-1}) + (0.394 \pm 0.004)$ ($n = 3$, $R^2 = 0.9917$) and $E_{\text{pc}} (\text{V}) = -(0.0351 \pm 0.0003) \log v (\text{V s}^{-1}) + (0.0819 \pm 0.0005)$ ($n = 3$, $R^2 = 0.9910$), respectively. According to the equations by Laviron [33], the relationship between the potential and scan rate can be described and made computations for the electron transfer coefficient ($\alpha = 0.58$) and the number of transfer electron ($n = 1.97$).

Interference effect

It is well established in literature that the oxidation peak potentials for AA and DA are essentially identical and thus it is difficult to separate these compounds due to their overlapping signals on a bare GCE [31]. This problem can be resolved via electrostatic attractions. The C-dots possess carboxyl groups of a negative charge, preventing anionic AA from reaching the electrode surface. Hence, C-dots/IL-graphene is a anionic

Table 1 Comparing the electrocatalytic performance with other DA electrochemical sensors for the determination of DA

Sensors	Method	Linear range (μM)	Detection limit (μM)	References
Pd-NC ^a /rGO ^b	Amperometry	20 - 220	7.02	[2]
rGO/Ni	DPV	0.05–50	0.01	[3]
GNS-CNTs ^c /MoS ₂	DPV	0.1–100	0.05	[9]
[Ni(phen) ₂] ²⁺ /SWCNTs ^d	DPV	1–780	1	[10]
MoS ₂ /rGO	DPV	5–545	0.05	[12]
GO-MWCNT/MnO ₂ /AuNP ^e	Amperometry	0.5–2500	0.17	[13]
pCu ₂ O NS ^f -rGO	DPV	0.05–109	0.015	[14]
C-dots/IL-graphene	DPV	0.1–600	0.03	This study

^a palladium nanocubes, ^b reduced graphene oxide, ^c graphene nanosheets and multiwalled carbon nanotubes, ^d the nickel(II)-bis(1,10-phenanthroline) complex and single-walled carbon nanotubes, ^e gold nanoparticles, ^f porous Cu₂O nanospheres

Table 2 Method recoveries for the determination of DA in the fetal bovine serum ($n = 5$)

Spiked (μM)	Found (μM)	Recovery (%)	RSD (%)
0.50	0.504	100.7	1.6
5.0	4.98	99.5	2.0
50	50.2	100.4	1.2
150	149.1	99.1	2.7

exchanger at the GCE surface selectively attracting cationic DA and allowing them to pass through to the electrode surface, while preventing anionic AA from reaching the electrode surface; as a result, AA did not exchange electrons with the electrode. Fig. S3 showed that AA does not interfere.

Furthermore, other influences from common co-existing substances were investigated. When the relative error (E_r) exceeded 5 %, the tested matter was considered to be an interfering agent. The common interferences in vivo and chemicals similar to DA, such as epinephrine, 3-methoxyphenol, quercetin, vanillin, serotonin, tyramine, and dopa, were tested the disturbance to the detection of DA as shown in Fig. S4. The results revealed these interferences did not response at the C-dots/IL-graphene/GCE. It was found that most ions and common substances at high concentration caused negligible change: Na^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-} (>300 fold); Ca^{2+} , Zn^{2+} , Mg^{2+} (150 fold); uric acid, lysine, cysteine and glucose (100 fold). Results indicate that the C-dots/IL-graphene/GCE exhibited enhanced selectivity for DA detection.

Detection of dopamine

The more sensitive DPV was implemented as the detection method for the C-dots/IL-graphene/GCE device. Under the optimal conditions, the oxidation peak current (I_{pa}) of DA increased with its concentration in the range from 0.1 μM to 600.0 μM . The DPV shown in Fig. 3 was equated by the linear regression equations of I_{pa} (μA) = $-(0.4706 \pm 0.0001) \lg c$ (μM) - (0.4809 ± 0.0003) ($n = 3$, $R^2 = 0.9939$); the detection limit was calculated to be 30 nM ($S/N = 3$). It was lower than some previous reports [34, 35], illustrating C-dots/IL-graphene/GCE possesses improved sensitivity and a wide linear range. Table 1 showed a comparison of the methods, linear ranges, and detection limits by Pd, Ni, and other nanomaterials used for electrochemically determining dopamine in a phosphate buffer media.

The repeatability of the sensors was examined by analysis of the same concentration of DA (0.5 mM) using five equally prepared electrodes. The five sensors exhibited similar response and the relative standard deviation (RSD) was 2.8 % (less than 5 %). When the sensors were stored at 4 °C after a week, it remained 92.6 % of its initial response. These results indicated the sensors represented excellent repeatability and stability.

Application of the probe

The utilization of the method in real sample analysis was also investigated by direct analysis of DA in the fetal bovine serum. The ability in DPV determination of DA concentration in the fetal bovine serum based on the repeated DPV responses ($n = 5$) of the diluted analytes was measured. The samples were spiked with a specified concentration of DA and, using the standard addition method, measurements were made of the DA concentration in the pharmaceutical preparations and of the recovery rate of the spiked samples; the results are listed in Table 2.

Conclusions

A DA sensor based on the C-dots/IL-graphene/GCE electrode with high sensitivity, improved specificity and adequate stability was developed and characterized. Under optimal conditions, selective detection of DA in a linear concentration range of 0.1–600.0 μM was obtained at a tolerance limit of 30 nM. Furthermore, C-dots/IL-graphene/GCE exhibited enhanced ability to suppress the background current from large excess AA. Additionally, the C-dots/IL-graphene/GCE was applied to the detection of DA with satisfactory results. Therefore, a C-dots/IL-graphene/GCE is a promising analytical platform for the detection of DA.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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