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#### Short communication

# High-sensitive detection of dopamine using graphitic carbon nitride by electrochemical method



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#### 1. Introduction

Dopamine (DA), one of the most significant catecholamines that belongs to the family of excitatory chemical neurotransmitters, is extensively distributed in the mammalian central nerve system [1,2]. For instance, low levels of DA concentration would bring about Parkinson's disease [3]. In biological systems, the normal concentration range of DA is from  $10^{-8}$  to  $10^{-6}$  M [4,5]. It is reported that abnormal production of DA in the brain is related to the severity and progression of neurological and neurodegenerative disorders such as attention-deficit hyperactivity disorder (ADHD) and Huntington's disease [6,7]. Therefore, DA has been given tremendous attention in biomedical and analytical investigations and there is an urgent necessity to establish a sensitive, selective, and reliable method for the direct detection of DA.

Different methods have been developed for the determination of DA such as high performance liquid chromatography [8], fluorescence method [9], spectrophotometry [10] and electrochemical method [11]. Among these analytical methods, electrochemical method has a number of advantages, including simple, cost effective and high sensitivity. Because DA is an electroactive compound that can be easily oxidized on the electrode, electroanalysis of DA based on its electro-oxidation had been received

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#### ABSTRACT

A simple electrochemical biosensor was developed based on graphitic carbon nitride polymers (g-CN) modified glass carbon electrode (g-CN/GCE). The modified electrode displayed the electrochemical sensitive to dopamine (DA) and showed a good linear and broad response to detect of DA. The inorganic ions had no effect on detecting of DA as well. The decreasing of electrochemical activity was only about 10% after exposure in PBS solution for 15 days which showed excellent stability and reproducibility. It is suggested that the g-CN biosensors have promising application for DA analysis.

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much attention due to its considerably high sensitivity, rapid response, low cost and ease of operation [12,13]. Based on the inherent redox activity of DA and excellent characteristics of electrochemical methods, many materials including metal oxide nanoparticles [14], conducting polymer [15], carbon based materials [16], nanocomposites [17], etc., have been used for the direct electrochemical determination of DA. However, the analytical performance (such as detection limit, stability and selectivity) of these modified electrodes are not entirely satisfactory to the practical application in biological samples.

Graphitic carbon nitride (g-CN) is a class of polymeric materials consisting mainly of carbon and nitrogen [18]. They can be obtained from carbon materials, through substitution of the carbon atoms by nitrogen, and become appealing candidates for a variety of applications. The framework topology previously identified in g-CN is in fact presumably a defect-rich, N-bridged "poly(tris-s-triazine)". As the s-triazine ring (C<sub>3</sub>N<sub>4</sub>) is aromatic, it is expected that a conjugated, two-dimensional polymer of s-triazine would tend to form a  $\pi$ -conjugated planar layers like that of graphite, which has been proben by wide-angle X-ray diffraction (XRD) patterns and SEM and TEM observations [19]. The tris-striazine ring structure and the high degree of condensation makes the polymer possess highly stable with respect to thermal (up to 600 °C in air) and chemical attack (for example, acid, base, and organic solvents) and an appealing electronic structure, being a medium-bandgap, indirect semiconductor [20]. This allows its direct use in sustainable chemistry as a multifunctional heterogeneous metal-free catalyst. It has been reported that g-CN is a



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promising catalyst for various reactions, including oxidation of hydrocarbons [21–24], water splitting [25], CO<sub>2</sub> activation [26,27], transesterification [28], oxygen reduction [29,30], hydrogen production [31,32], photodegradation of dyes [33], etc. Several reviews reporting the catalytic performances of g-CN in a variety of reactions can be found elsewhere [33–37].

Because of the fact that nitrogen has one more electron than carbon, g-CN has rich surface properties. The g-CN exhibit many advantages, such as low cytoxicity, high chemical stability, easy preparation, and environmental friendliness [3]. More and more attentions have been paid to these emerging carbon nanomaterials, including their syntheses, property studies, and applications [17]. In our previous work [38], N-doped carbon quantum dots (NCQDs) can efficiently induce charge delocalization and tune the work function of carbon because the doping of N atoms. In this work, g-CN has be synthesized by directly heating melamine [39]. Then, g-CN were loaded on the bare glassy carbon electrode by Nafion solution to form g-CN modified glass carbon electrode (g-CN/GCE). The as-prepared modified electrode has been used as a biosensor to detect DA by an electrochemical method.

#### 2. Experimental

#### 2.1. Materials

Melamine and other reagents were supplied by Aladdin Reagent Co., Ltd. Milli-Q water was utilized through the whole experiment. The graphitic carbon nitride polymers (denoted as g-CN) was prepared according to previous method [39].

#### 2.2. Characterization of g-CN

Dynamic light scattering (DLS) measurements were performed in aqueous solution using a HORIBA Zetasizer LB-550 V apparatus at 25 °C. JEM-2100 TEM operated at an accelerating voltage of 200 kV, whereby a small drop of solution was deposited onto a copper EM grid and dried at 40°C under atmospheric pressure, was utilized to study transmission election microscopy (TEM). X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 spectrometer (Thermo-VG Scientific Co., Waltham, MA) with an ultrahigh vacuum generator. A CHI 660D electrochemical workstation was employed to accomplish the electrochemical experiments with platinum electrode as an auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode and a glassy carbon electrode as the working electrode. Microstructures of the as-prepared samples were analyzed with a SIEMENS Diffraktometer D5000 X-ray diffractometer using Cu K $\alpha$  radiation source at 35 KV, with a scan rate of  $0.02^{\circ} \text{ S}^{-1}$  in the  $2\theta$  range of  $10-80^{\circ}$ .

#### 2.3. Calculation of LOD

The limit of detection (LOD) were calculated using the following equations:

$$LOD = \frac{3\sigma}{R}$$

where  $\sigma$  is the standard deviation of the peak current of the lowest concentration of the linearity ran, *R* is slope of the fitted curve.



Fig. 1. The TEM image (A), HR-TEM (B), Zeta potential (C) and XRD pattern (D) of g-CN.

Specific figures were as follows:

 $\sigma = 1.74 \times 10^{-8}, R = 42.85, \text{LOD} = 1.0 \times 10^{-9} \text{M}$ 

#### 3. Results and discussions

The morphological structure of as-synthesized material was investigated by TEM measurement. Typical TEM images of the bulk g-CN is shown in Fig. 1. The bulk g-CN displays a large layer structure (Fig. 1A), and its edge area consists of several sheets, which exhibits a relatively dark brightness (Fig. 1B). g-CN mainly shows a flaky structure with bubble-like or irregular morphology. which looks more transparent in its edge regions (Fig. 1B). The zeta potential of g-CN is -15.25 mV (Fig. 1C). It indicates the negative charge nature for the surface of g-CN. The typical X-ray diffraction (XRD) pattern of the as-prepared g-CN is shown in Fig. 1D. The strongest peak at 27.5° is a characteristic interplanar stacking peak of aromatic system, indexed for the (002) peak of graphitic materials. A stacking distance of the aromatic units of d = 0.326 nm can be calculated. This stacking is significantly more tight than the packing in carbon with graphene units (d = 0.353 nm) and even 3% more dense than the packing in crystalline graphite, which exhibits d = 0.335 nm [40]. The higher packing density perpendicular to the layers for aromatic systems with heteroatom substitution is well understood and can be attributed to the localization of the electrons and stronger binding between the layers. This peak position is also in agreement with previous reports on high quality melon materials. A pronounced additional peak is found at  $13.2^{\circ}$ , corresponding to a distance d = 0.675 nm. Also this peak is typical of more oriented melons [41,42], but is rather differently interpreted by various authors. Based on the electron microscopy evidence reported above, the  $13.2^{\circ}$  small angle peak presumably related to an in-plane structural packing motif, such as the hole-tohole distance of the nitride pores in the crystal. This distance is only slightly below the size of one *tris*-s-triazine unit (ca. 0.73 nm), indicative of the already discussed buckling. Komatsu [43] has indexed the  $13.2^{\circ}$  and  $27.3^{\circ}$  peaks in a more complicated fashion.

X-ray photoelectron spectrum (XPS) was utilized to confirm the effective incorporation of nitrogen and surface chemical properties of the obtained g-CN. As shown in Fig. 2A, XPS spectrum for g-CN contains three prominent peaks with C, N and O at percentage of 48.38%, 48.94% and 2.68%, respectively. The The C1s spectrum of g-CN contains three components and the main peak at 284.33 eV corresponds to graphitic sp<sup>2</sup> C. It indicates that most of the carbon atoms are arranged in a conjugated lattice. The peak 287.68 eV peak corresponds to N-sp<sup>3</sup> C bonds (Fig. 2B) [17]. The N1s peak has three components, indicating that N is present in three different bonding characters, as shown in Fig. 2C. The peaks at 399.32 eV can be assigned as the presence of "pyrrolic" N. Therefore, N is present in a  $\pi$ -conjugated system where two p-electrons are present in the system. A peak at 400.68 eV corresponds to graphitic N [44]. The high-resolution O spectrum of the g-CN display two peaks at



Fig. 2. XPS spectrum of g-CN (A) and high-resolution XPS spectra of C (B) and N (C) and O (D) over g-CN.

532.69 and 533.88 eV, which are attributed to the C=O and C—OH (Fig. 2D). Further high-resolution analysis demonstrates that the binding energies for C1s and N1s are exactly the same for all three different geometrical materials with the same for all three different geometrical materials with the same carbon nitride composition.

The g-CN/GCE electrode was prepared using a simple drop casting method by casting a g-CN-Nafion solution onto the surface of a glassy carbon electrode and dried under room temperature in the air. Fig. 3A shows the typical cyclic voltammograms (CV) curves in 0.1 M PBS solution with the potential range from -1.2 to 1.2 V. As expected, the CV curves exhibit well-defined redox peaks with the scan rate range from 20 to 350 mV/s. The peak currents are increased gradually with increasing of scan rate. Fig. 3B shows the relationship between the peak current and scan rate obtained from the experimental data in Fig. 3A. The anodic and cathodic peak currents show a linear dependence on the square root of the scan rate as following:  $I_{PC} = 0.5007 + 0.1043$  V<sup>1/2</sup>,  $R^2 = 0.9972$ ;  $I_{PA} = 0.0447 - 0.0947$  V<sup>1/2</sup>,  $R^2 = 0.9939$ .

Electrochemical impedance spectroscopy (EIS) is an effective method to characterize the interfacial electrical property of modified electrode. In EIS, the semicircle diameter of the impedance is equal to the electron transfer resistance, which controls the electron transfer kinetics of the redox probe at the electrode surface [45]. Fig. 3C shows the results of impedance spectroscopy of bare glassy carbon electrode (curve a) and g-CN/GCE in 0.5 M KNO<sub>3</sub> and 5.0 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> (curve b). The bare

GCE shows a small semicircle with a charge transfer resistance ( $R_{ct}$ ) of about 300  $\Omega$  at high frequencies. However, after casting of g-CN onto the surface of GCE, the Nyquist plots consisted of a semicircle at high frequency and a straight line at low frequency with  $R_{ct}$  value increased to 4688  $\Omega$  dramatically. It is attributed to the formation of g-CN layer that embracing the electron transfer. The middle frequency semicircle is attributed to charge transfer. It implies that the g-CN/GCE is an excellent electrical conducting material.

On the basis of the excellent electrochemical properties of g-CN, it would be applied to detect electroactive molecules. To verify the recognition capabilities of g-CN, an electroactive molecule, dopamine (DA), has been chosen as the guest molecule. Fig. 3D shows the CV curve obtained with the scan rate at 50 mV/s in 0.1 M PBS (pH 7.4) and the concentration of DA at 0.02 mM. Compared with the oxidation peak with absence of DA, higher electrochemical response toward DA molecules can be observed. And the potential of oxidiation peak increased from 0.55 V to 0.60 V. The peak potential difference of  $\Delta E_P = 0.05V$  suggests that dopamine is undergoing two-electron oxidation [46].

The pH of the electrolyte can affect the stability of g-CN/GCE, as reported previously [47]. The DPV curves of g-CN/GCE in 0.1 M PBS obtained at various pH values are shown in Fig. 4A. No significant differences are founded, which indicates the excellent stability of g-CN/GCE against different pH environments. DPV curves for detection of DA using g-CN/GCE electrode under different pH conditions are shown in Fig. 4A. The oxidation peak currents of DA on the g-CN/GCE



**Fig. 3.** Cyclic voltammetry curves of g-CN in 0.1 M PBS obtained at different scan rates (A), linear relation between peak current and the square root of the scan rate (B), Nyquist plots of bare glassy carbon electrode (a), and g-CN/GCE (b) in 0.5 M KNO<sub>3</sub> and 5.0 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> (C), CV curves of g-CN/GCE at a scan rate of 50 mV/s in 0.1 M PBS (pH 7.4) with or without of DA (D).



Fig. 4. Effect of pH on the differential pulse voltammogramps of g-CN/GCE in 0.5 mM DA and 0.1 M PBS (A), relation between peak current and different pH (B), DPV responses of g-CN/GCE with the different concentrations of DA (C), the related linear relationship between currents and the concentrations of DA using g-CN/GCE as electrode (D).

are decreased from pH 6.4–8.4. The optimal pH value is 7.4 that close to the normal physiological environment, which has been selected for evaluating the detection performance of DA on g-CN/GCE. The potentials of oxidation peaks versus the value of pH are shown in Fig. 4B. A linear relationship with potentials and pH can be obtained with the correlation coefficient at 0.9908. It indicates that protons participate in the oxidation of DA. According to the Nernst equation, the relation between  $E_p$  and pH is  $E_p = (-0.0592m/n)$  pH + b (where *n* is the electron transfer number and *m* is the number of protons participating in the electrochemical oxidation reaction, respectively). The equation can be defined as:  $E_p = 0.76 - 0.019$  pH. The slope of this equation is 19 pH/mV. It is demonstrated that the ratio between protons transferred from DA to g-CN/GCE and electronics participating in the reaction is close to 1:1, which proves that the redox process of DA on g-CN/GCE is a two-step process with two electrons and two protons [46]. When the pH < 7.0, most of the amino group on dopamine are in the dopamine cationic protonated form. Firstly, protonated dopamine cations lose two electrons to form dopaquinone. Then, dopaquinones lose electrons until intramolecular cyclization completed [46]. Since acidity promotes the intramolecular cyclization, the oxidation peak currents of DA on the g-CN/GCE are decreased from pH 6.4 to 8.4.

g-CN/GCE is applied to detect DA by different pulse voltammetry (DPV). As shown in Fig. 4C, upon increasing the concentration of DA in PBS, the oxidation peak current improves significantly which suggests that g-CN/GCE could be applied to the quantitative determination of DA. The anodic peak current of DA shows a good linear relationship with DA concentration in the range from 0.005 to 0.6 mM (Fig. 4C). The linear regression equation is defined as  $I_p = 1.76 + 40.27c$  with  $R^2 = 0.9923$  (Fig. 4D), and lowest detection

#### Table 1

Comparison of some characteristics of different novel electrodes for the determination of DA.

Electrode	Electrolyte	Detection limit (µM)	Linear range (µM)	Reference
RGO/Pd-NPS/GCE	рН 7.0	0.233	1-150	[1]
Au-NPs/PANI/GCE	pH 4.0	0.8	3–115	[2]
Pd/CNF/carbon paste electrode	pH 7.0	0.2	0.5-160	[3]
Au/PE/PS/BDDa	pH 7.2	0.8	5-100	[4]
PANI/Au nanoelectrode	pH 6.8	0.1	0.3-200	[5]
Ag-Pt/pCNFs/GCE	pH 7.0	0.11	10-500	[6]
g-CN/GCE	pH 7.4	0.001	5-600	This work

Gold nanoparticles and polyelectrolyte (PE) on polystyrene (PS)-modified boron-doped diamond (BDD) electrode.



Fig. 5. The changes of g-CN/GCE activity as different ions added into the solution when detected DA(A), the changes of g-CN/GCE activity as it preserved in PBS (pH 7.4) solution (B).

limit is evaluated to be  $1 \times 10^{-9}$  M (signal-to-noise (S/N) = 3), which is better than some previous reports (shown in Table 1) [1–6]. Since the normal concentration range of DA in human body is from  $10^{-8}$ to  $10^{-6}$  M [5]. The linear functions suggests that dopamine is undergoing a diffusion-controlled process [47]. It is evident that this g-CN/GCE has excellent electrochemical activity and can be a promising sensor for DA clinical determination.

The effect of ions on the g-CN/GCE electrochemical activity is also investigated. When the relative error is lower 5%, substances are considered as no interference for DA detection. As shown in Fig. 5A, it is found that 6.0 M concentration of Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, 2.0 M concentration of Mg<sup>2+</sup> and Ca<sup>2+</sup> caused negligible influence for peak current of DA. The results demonstrated that these ions have no interference for DA detecting using g-CN/GCE.

The stability and reproducibility are the important considerations for the practical application of electrochemical sensors. To evaluate the working stability of g-CN/GCE, the sensor without renewing the electrode surface subjected to determine of 0.5 mM DA in 0.1 M PBS (pH 7.0) with 30 min intervals. After 360 min, the modified electrodes retained 95.0% of their initial activity (Fig. 5B). When the measurements are completed, the modified electrode is stored in the PBS. After 15 days, the current response on the g-CN/ GCE still remained about 85.5% (Fig. 5B), indicating excellent stability and reproducibility.

#### 4. Conclusion

The graphitic carbon nitride polymers (g-CN) have been prepared by simple pyrolysis of melamine. The prepared g-CN was utilized for modification of glassy carbon electrode to detect DA selectively. CV and EIS measurements confirmed that g-CN/GCE has been effectively absorbed onto the surface of bare glassy carbon electrode. The g-CN modified electrode displays higher electrochemical response to DA. Especially, the as-prepared biosensor exhibit an excellent electrochemical performance for DA with broad linear range and low detection limit at a signal-tonoise ratio of 3. The inorganic ions had no effect on detecting of DA as well. The decreasing of electrochemical activity was only about 10% after exposure in PBS solution for 15 days which showed excellent stability and reproducibility.

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