



Short communication

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

Tengteng Jiang^a, Guohua Jiang^{a,b,c,*}, Qin Huang^a, Huijie Zhou^d^a Department of Materials Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, PR China^b National Engineering Laboratory for Textile Fiber Materials and Processing Technology (Zhejiang), Hangzhou 310018, PR China^c Key Laboratory of Advanced Textile Materials and Manufacturing Technology (ATMT), Ministry of Education, Hangzhou 310018, PR China^d Qixin Honour School, Zhejiang Sci Tech University, Hangzhou 310018, PR China

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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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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

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_3N_4) is aromatic, it is expected that a conjugated, two-dimensional polymer of *s*-triazine would tend to form a π -conjugated planar layers like that of graphite, which has been proven by wide-angle X-ray diffraction (XRD) patterns and SEM and TEM observations [19]. The *tris-s*-triazine 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

* Corresponding author at: Department of Materials Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, PR China.

E-mail address: ghjiang_cn@zstu.edu.cn (G. Jiang).

promising catalyst for various reactions, including oxidation of hydrocarbons [21–24], water splitting [25], CO₂ 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 cytotoxicity, high chemical stability, easy preparation, and environmental friendliness [3]. More and more attentions have been paid to these emerging carbon nano-materials, 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 been 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-550V 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 electron 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 α radiation source at 35 KV, with a scan rate of 0.02° S⁻¹ in the 2 θ range of 10–80°.

2.3. Calculation of LOD

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

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

where σ is the standard deviation of the peak current of the lowest concentration of the linearity ran, R is slope of the fitted curve.

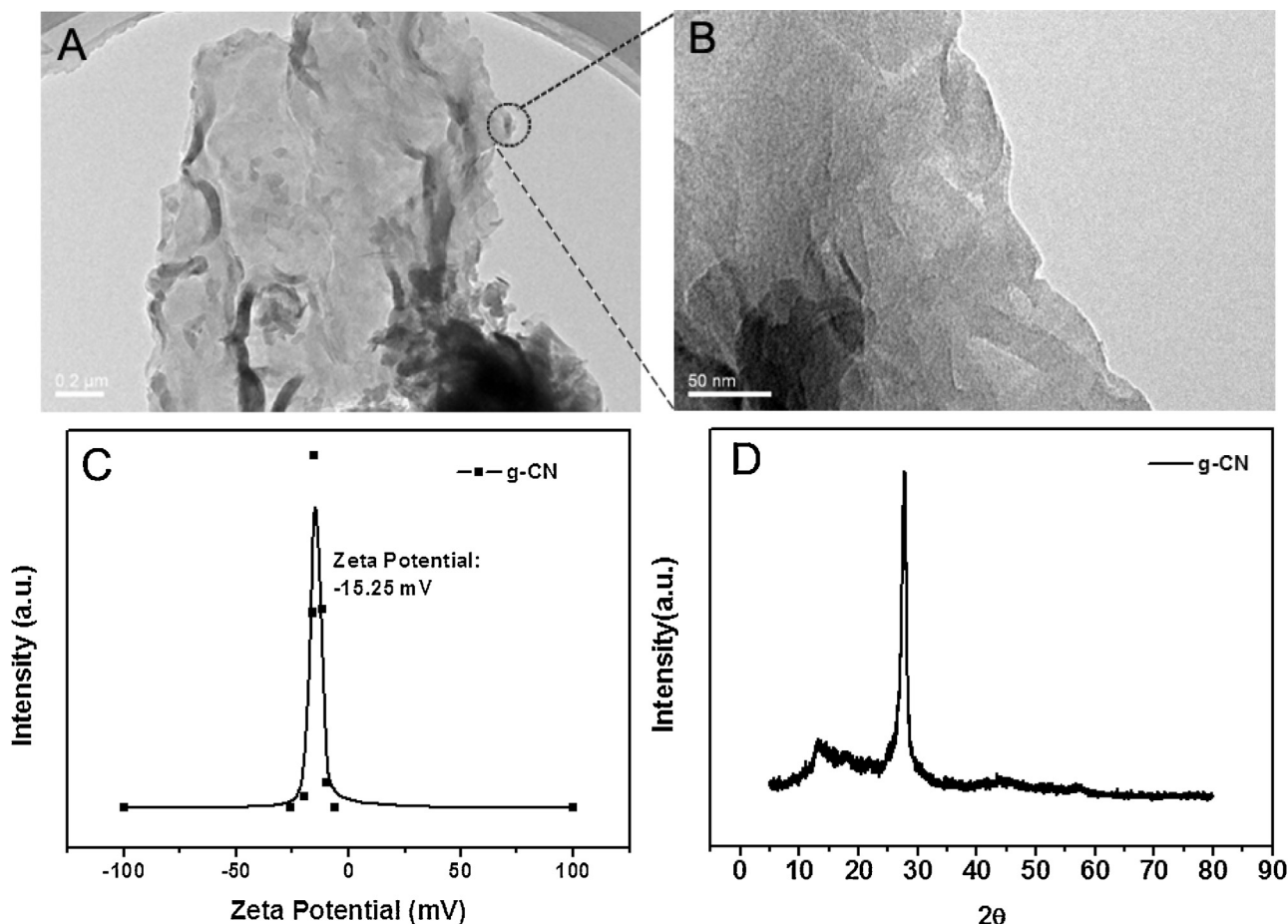


Fig. 1. The TEM image (A), HR-TEM (B), Zeta potential (C) and XRD pattern (D) of g-CN.

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