



# One step electrosynthesis of polyacrylamide crosslinked by reduced graphene oxide and its application in the simultaneous determination of dopamine and uric acid



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## ABSTRACT

Polyacrylamide (PAM)/reduced graphene oxide (rGO) nanocomposite (PAM/rGO) with rGO nanosheets as cross-linkers were synthesized via electropolymerizing acrylamide in an aqueous suspension of GO containing sodium nitrate and potassium persulfate. The PAM/rGO was characterized with X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). XRD patterns of the PAM/rGO indicated that rGO was fully exfoliated into individual sheets in the polymer matrix. SEM study exhibits the highly uniform coverage of PAM/rGO membrane on the GCE and its fibrous nanostructure. The electrochemical characteristics of the PAM/rGO modified glassy carbon electrode (GCE) were investigated with cyclic voltammetry (CV), suggesting the extraordinary electrocatalytic effect of PAM/rGO/GCE towards the electro-oxidation of UA and DA. The PAM/rGO/GCE behaved linearly to DA and UA in the concentration range of  $3 \times 10^{-7}$  to  $5 \times 10^{-5}$  M and  $1 \times 10^{-6}$  to  $5 \times 10^{-5}$  M with a detection limit of  $1 \times 10^{-7}$  M and  $5 \times 10^{-7}$  M, respectively. The proposed method was successfully utilized for simultaneous determination of UA and DA in real samples.

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## 1. Introduction

Graphene, a unique 2D nanocarbon material, has stimulated great interest due to the extraordinary electrical, mechanical and thermal properties [1–3]. Graphene oxide (GO) acts as an important precursor for graphene-based structure. It has also received considerable attentions especially from chemists because of its hydrophilic nature and solution processability [4]. GO can be easily exfoliated into monolayer sheets stably dispersed in water, mainly due to the hydroxyl, epoxide and carboxyl groups on its surface [5]. These groups also enable GO to be functionalized through covalent or non-covalent approaches [6]. Many applications of GO have been proposed and are currently being explored. Recently, GO has drawn increasing attention as a reinforcing nanofiller or cross-linker for polymers [7–12]. When incorporated into polymer, GO can greatly increase the mechanical and thermal properties of the polymer hosts. Moreover, GO is also used in such applications as nanoelectronic devices, gas sensors, super capacitors, and drug delivery systems [13,14].

Polyacrylamide (PAM) is an important type of water-soluble molecule due to its amino bond, which can easily form hydrogen bonds. PAM has many special properties and is well known for its hydrophilicity, permanent biocompatibility, good stability and resistance to degradation which make it a suitable candidate for applications in drug delivery [15,16], biosensing as molecularly imprinted polymers (MIPs) [17,18], etc. Electropolymerization has been regarded as a promising polymerization method in respect that the polymers are adherent to the electrode surface and their thickness can be easily controlled [19]. There are many cases of electrosynthesis of polyacrylamide cross-linked by organic cross-linkers [20–23]. However, the electropolymerization of acrylamide (AM) with rGO as cross-linker has never been reported.

Dopamine (DA), existing in the tissues and body fluids in the form of cations, is one of the most important neurotransmitters in the central nervous system of the mammals [24]. Uric acid (UA) and other oxypurines are the principal final products of purine metabolism in the human body [25]. Abnormal levels of UA cause symptoms of several diseases, including gout, hyperuricemia and Lesch-Nyan disease [26]. DA and UA coexist in biological fluids such as blood and urine. Due to their crucial role in neurochemistry, many methods have been developed for their simultaneous determination. Among these, electrochemical methods have more advantage over the others because of their simplicity, feasibility

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and high sensitivity [27,28]. In the past, several modified electrodes have been used for the simultaneous determination of UA and DA. For electrochemical analysis, UA and AA were simultaneously determined with electrodes modified with gold nanoparticles (NPs) [29], MWNT/poly(neutral red)/GCE [30], poly(eriochrome black T)/GCE [31], tetrabromo-p-benzoquinone/CPE [32], silver hexacyanoferrate/MWNT/GCE [33], Fe<sub>3</sub>O<sub>4</sub> NPs/reduced graphene oxide (rGO)/GCE [34], palladium NP-loaded carbon nanofibers/CPE [35], graphene/poly-cyclodextrin/MWNT/GCE [36], and iron(III)-porphyrin/MWNT/GCE [37]. The major limitation for the electrochemical analysis of UA and DA is the overlapping of oxidation potentials of DA and UA and hence often suffers from a pronounced fouling effect that results in rather poor selectivity and reproducibility. Although various materials have been utilized to modify electrodes in order to resolve the above problem, developing a facile and sensitive method to simultaneously determine DA and UA is still a challenge.

In the present work, a novel polyacrylamide (PAM) nanocomposite was synthesized by electropolymerization of acrylamide (AM) in the presence of rGO nanosheets without adding any organic cross-linkers. The obtained PAM/rGO modified GCE was employed in the determination of uric acid (UA) and dopamine (DA), which exhibited electrocatalytic capability for the oxidation of DA and UA by lowering the overpotential and greatly enhanced the current response. The PAM/rGO modified GCE was further applied in the analysis of DA and UA in real biological samples.

## 2. Experimental

All chemical reagents were of analytical grade and used as received. AM and UA were purchased from Sinopharm Chemical Reagent Co., Ltd in Shanghai, China. Uric acid (UA) was purchased from Sigma Chemical Co. (St. Louis, MO, USA). All the chemicals were of analytical grade. Phosphate buffer solutions (0.1 M pH8.0) served as the supporting electrolyte and were prepared using 0.1 M Na<sub>2</sub>HPO<sub>4</sub> and 0.1 M NaH<sub>2</sub>PO<sub>4</sub>. Twice-distilled water was used throughout the experiment. In a typical synthesis, graphene oxide (GO) powders were initially prepared by a modified Hummers' method [38].

The electrolytic solution was prepared by the following steps: First, 30 mg GO was dispersed in 10 mL pH 8.0 PB solution under ultrasonic agitation for 2 hours. Then 225 mg AM, 100 mg sodium nitrate and 12 mg potassium persulfate were dissolved in the GO aqueous dispersion under magnetic stirring. Finally, the solution was purged with high purity nitrogen for at least 30 minutes. To obtain mirror-like surface, the GCE was polished successively with 0.3 and 0.05 μm alumina slurry. Then, it was rinsed with doubly distilled water and ethanol in ultrasonic bath to remove the physically absorbed substance. After that, the GCE was allowed to dry at room temperature. The PAM/rGO/GCE was prepared by cycling the GCE in the electrolytic solution at 20 mV s<sup>-1</sup> between -0.4 and -1.2 V for 10 cycles.

The rGO modified GCE (rGO/GCE) was prepared by cycling the potential (20 mV s<sup>-1</sup>) between -0.4 and -1.2 V for 10 cycles in 10 mL aqueous solution containing only 30 mg GO and 100 mg sodium nitrate [39]. The rGO and PAM/rGO films were peeled off from GCE substrate very carefully and used for XRD and FT-IR characterizations.

A GCE (Φ = 3 mm) was used as the working electrode, a saturated calomel electrode (SCE) and a platinum foil as the reference and counter electrode, respectively. All potentials were reported with respect to SCE. All the pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution everyday. The scanning electron microscopy (SEM) was performed with a Quanta 200 scanning electron microscope (SEM;

FEI Company, Holland). The X-ray diffraction (XRD) patterns are obtained by Shimadzu XRD-6000 diffractometer with a Ni filter and Cu Kα radiation (λ = 0.154056 nm).

Except as otherwise stated, 0.1 M phosphate buffer solutions (pH7.0) was used as supporting electrolyte for DA and UA determination. Stock solutions of 0.01 M DA and 0.01 M UA were firstly prepared, and then aliquots were diluted to the appropriate concentration with 0.1 M phosphate buffer solutions (pH7.0) before commencing the voltammetric scan. Voltammograms were obtained by scanning the potential from 0 to 1.25 V (vs. SCE). The quantitative determination of DA and UA was achieved by measuring the oxidation peak currents after background subtraction using differential pulse voltammetry (DPV).

## 3. Results and Discussion

With AM as the functional monomer, rGO as the crosslinking agent, NaNO<sub>3</sub> as the supporting electrolyte and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the initiator, respectively, the resulting polymer PAM/rGO was assembled on the electrode surface during the electropolymerization process. Cyclic voltammetry experiments were used to verify the formation of the PAM/rGO membrane on the GCE. Curve a in Fig. 1 shows the cyclic voltammogram of the bare GCE in the presence of 5 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>]. A pair of typical redox peaks corresponding to the redox couple K<sub>4</sub>[Fe(CN)<sub>6</sub>]/K<sub>3</sub>[Fe(CN)<sub>6</sub>] can be found. Curve b and curve c shows the cyclic voltammograms of the rGO/GCE and PAM/rGO/GCE under the same condition. It is well-known that the introduction of reduced graphene (rGO) onto the electrode surface may cause significant increase of the double layer capacitance [38]. As shown in curve b and curve c of Fig. 1, fairly rectangular CV curves are exhibited, which is indicative of capacitive behavior, a well-known characteristics of the rGO or rGO composite modified electrode [38]. In comparison with those on bare GCE, the redox peak currents on rGO/GCE significantly decreased while the separation between anodic and cathodic peaks remains the same (Fig. 1, curve b). However, it was found out that the redox peak currents on PAM/rGO/GCE is slightly lower than those on bare GCE while the peak-to-peak separation was conspicuously diminished (Fig. 1, curve c).

Wu, et al. synthesized PAM with N, N'-methylenebisacrylamide as crosslinker and AM as monomer by electropolymerization on GCE [18]. The CV curves of bare GCE and PAM modified GCE electrode (PAM/GCE) in K<sub>3</sub>[Fe(CN)<sub>6</sub>] aqueous solution were recorded [18]. The total disappearance of the redox peaks on PAM/GCE were due to the formation of non-conducting PAM

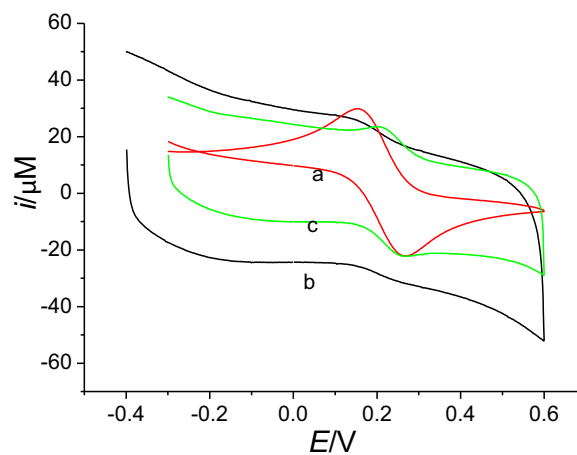


Fig. 1. Cyclic voltammograms for bare GCE (curve a), PAM/rGO/GCE (curve b) and rGO/GCE (curve c) in 5 mM potassium ferrocyanide solution containing 0.1 M KCl. Scan rate: 100 mV s<sup>-1</sup>.

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