



Simultaneous determination of uric acid, xanthine and hypoxanthine based on sulfonic groups functionalized nitrogen-doped graphene

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ABSTRACT

A highly sensitive and selective method was developed for simultaneous detection of uric acid (UA), xanthine (XA) and hypoxanthine (HX) based on a 1,3,6,8-pyrene tetra sulfonic acid sodium salt functionalized nitrogen-doped graphene (PyTS-NG) composite. The material was synthesized by utilizing a facile ultrasonic method via π - π conjugate action between 1,3,6,8-pyrene tetra sulfonic acid sodium salt (PyTS) and nitrogen-doped graphene (NG) molecule. Compared with pristine NG, the material had better dispersivity and conductivity, which might be attributed to a large number of edge-plane-like defective sites on the surface of PyTS-NG that would accelerate electron transfer between electrode and species in solution. The surface morphology was characterized by scanning electron microscopy and transmission electron microscopy. The electrochemical behaviors of UA, XA and HX on the surface of PyTS-NG were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under the optimized condition, the linear ranges for the determination of UA, XA and HX were 9–1000, 8–800 and 8–200 μ M, with the detection limits ($S/N = 3$) of 0.331, 0.0838 and 0.231 μ M, respectively. Furthermore, the practical application of the present method was evidenced by determining UA, XA and HX in human blood serum and urine samples.

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1. Introduction

Uric acid (UA), xanthine (XA) and hypoxanthine (HX) are oxidation products of purine degradation metabolism in human beings and animals [1]. UA is generated by xanthine oxidase from XA and HX, which in turn are produced from purine, and the HX can be oxidized to XA by xanthine oxidase. So XA and HX are intermediates and UA is the ultimate product of purine degradation metabolism [2,3]. It has been proved that excessive accumulation of these metabolites in the body would cause some serious diseases such as xanthinuria, gout, perinatal asphyxia, cerebral ischemia, tumor hyperthermia and preeclampsia. Hence the monitoring of UA, XA and HX is very important in clinical analysis [4].

Up to now, many methods have been reported in the literatures for the determination of UA, XA and HX such as high-performance liquid chromatography (HPLC) [5,6], capillary electrophoresis (CE) [7,8], enzymatic methods [9] and electrochemistry [3,4,10–17]. Among them, electrochemical methods have several advantages such as less cost, more convenient, highly selective and sensitive. In recent years, a few carbon-based materials have been successfully employed to determine UA, XA and HX. For example, Zhang et al. reported a facile one step

electrochemical method to prepare the poly (L-arginine)/graphene composite film modified glass carbon electrode [10]. Amal Raj et al. proposed the electrochemical reduction of graphene oxide attached through 1,6-hexadamine on a glassy carbon electrode [11]. Wang reported a poly(pyrocatechol violet)/carboxyl functionalized multi-walled carbon nanotube composite film modified electrode [14]. Wang et al. prepared a functional single-wall carbon nanotube film electrode [15]. In spite of this, the exploration of novel electrode materials for the simultaneous determination of UA, XA and HX is still a challenge.

Nitrogen-doped graphene (NG), which has better electron transfer efficiency than pristine graphene, also has received a great attentions including in sensors [18–20], biosensors [4], capacitors [21] and oxygen reduction [22]. However, like graphene, NG is hydrophobic and tends to agglomerate irreversibly which limits its further application. In order to overcome its poor processibility, 1,3,6,8-pyrene tetra sulfonic acid sodium salt (PyTS), a bifunctional molecule with an aromatic pyrenyl group and four sulfonic groups, which has been reported that there was a strong π - π stacking interaction between PyTS and graphene [23] was introduced to this work. After functionalizing with PyTS through a facile ultrasonic method, NG exhibited good dispersivity in water. Furthermore, the oxidation responses of UA, XA and HX were enhanced clearly on the surface of PyTS-NG, and the proposed method was applied to simultaneous determination of UA, XA and HX in human blood serum and urine.

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2. Experimental

2.1. Reagents and materials

All chemicals and reagents were of analytical grade and used without further purification. Graphite was purchased from Shanpu Chemical Co., Ltd. (Shanghai, China). Uric acid was purchased from Alfa Aesar Chemical Co., Ltd. (Tianjin, China). Xanthine was purchased from Dibo Chemistry Technology Co., Ltd. (Shanghai, China). Hypoxanthine was purchased from Zhongtai Chemistry Reagent Co. (Shanghai, China). Melamine was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). 1,3,6,8-Pyrene tetra sulfonic acid sodium salt (PyTS) was purchased from Acros Organics. Phosphate buffer solutions (PBS, 0.1 M) with different pH values (4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0) were prepared by mixing the stock solution of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 , the pH was adjusted by 1.0 M KOH or 1.0 M H_3PO_4 . Double distilled water and nitrogen gas (99.999%) were used for all experiments. All experiments were performed at room temperature.

2.2. Instrumentation

Electrochemical experiments and measurements were performed at a CHI660B electrochemical workstation (Shanghai Chenhua Co., China). A conventional three electrode system was used throughout the measurements. A bare or modified glassy carbon electrode (GCE, CHI104, $\Phi = 3$ mm, Gaoss Union Co., Ltd., Wuhan, China) was employed as a working electrode, a platinum column as the counter electrode and an Ag/AgCl electrode (saturated KCl) as the reference. The nitrogen-doped graphene was prepared by a SK-G05123K Tube Furnace (Tianjin Zhonghuan Test Electrical Furnace Co., Ltd., Tianjin, China). The scanning electron microscopy (SEM) image was collected on a JSM-6701F (Japan) at 5.0 kV. The transmission electron microscopy (TEM) image was obtained by a FEI-Tecna G2 TF20 electron microscope (USA) operating at HT200 kV. X-ray photoelectron spectroscopy (XPS) was made based on PHI-5702 (USA). Raman spectra were obtained by inVia Renishaw confocal spectroscopy (Britain) with 514 nm laser excitation. The UV–vis absorption spectra were recorded on a New Century T6 spectrometer (Purkinje General Instrument Co., Ltd., Beijing, China). Electrochemical impedance spectra (EIS) were performed by Princeton Applied Researcher (USA). Impedance measurements were made with the frequencies swept from 10^4 to 0.1 Hz. A Randles equivalent circuit was used to fit the obtained impedance spectra.

2.3. Synthesis of nitrogen-doped graphene

Nitrogen-doped graphene (NG) was prepared by a facile, catalyst-free thermal annealing method with a mixture of graphene oxide (GO) and low-cost industrial material melamine as the nitrogen source [24,25]. The GO was prepared from natural graphite flakes by the improved Hummers' method [26,27]. In a typical procedure, the graphene

oxide and melamine were ground with a weight ratio of 1:10 for 3 h. Then the mixture in a combustion boat was placed in the center of a quartz tube. The annealing temperature was increased at a rate of 5°C min^{-1} to 800°C and maintained for 2 h in an argon atmosphere. After the temperature was cooled down to room temperature, the final product of NG was obtained.

2.4. Synthesis of PyTS–NG

The 1,3,6,8-Pyrene tetra sulfonic acid sodium salt functionalized nitrogen-doped graphene (PyTS–NG) composite was synthesized by a simple and facile ultrasonic method. In a typical experiment, 10.0 mg of PyTS was dissolved in 1.0 mL double distilled water, and 0.5 mg of NG was added. After ultrasonication for 2 h, a black colloidal dispersion with no visible precipitation was formed. Then the solution was centrifuged at 10,000 rpm for 15 min, and the supernatant was poured away. The precipitate was carefully washed with double distilled water 3–5 times till the extra PyTS was removed. At last, the right amount of double distilled water was added in the precipitate to obtain a 0.5 mg mL^{-1} PyTS–NG dispersion solution with the help of ultrasonication. The fabrication procedure is summarized in Fig. 1.

2.5. Preparation of modified electrodes

The bare GCE was polished to a mirror-like surface with 0.3 and $0.05\text{ }\mu\text{m}$ α -alumina slurries, then washed with 1:1 nitric acid, absolute ethanol and water in an ultrasonic bath for 1 min and dried in high-purity nitrogen blow. Then, $4\text{ }\mu\text{L}$ of PyTS–NG dispersion was dropped on the freshly prepared GCE surface, followed by evaporating the solvent in the air. The obtained electrode was noted as PyTS–NG/GCE. By contrast, the NG/GCE (NG dispersed in DMF) was fabricated with a similar procedure.

3. Results and discussion

3.1. Characterization of NG

X-ray photoelectron spectroscopy (XPS) was used to confirm the chemical state of elements, especially the surface nitrogen content and the chemical states of nitrogen. The typical spectra of the NG samples are shown in Fig. 2 and the atomic percentages (at.%) of C, O and N were calculated to be 89.02, 4.09 and 6.89%. As shown in the survey scan spectrum of Fig. 2A, besides the core levels of C1s and O1s at 282.9 and 533.1 eV, the N1s signal was also observed at 399.9 eV clearly. The appearance of the N1s peak in the spectrum indicated that nitrogen was successfully doped into the graphene sheets of the NG [25]. Fig. 2B displays the core levels of the C1s spectra, which could be deconvoluted into three peaks of C=C, C=N and C–N bonds, located at 284.6, 285.8 and 287.6 eV, respectively. However, the peak at 284.6 eV was still the largest one in the C1s spectra, indicating the partial reconstruction of

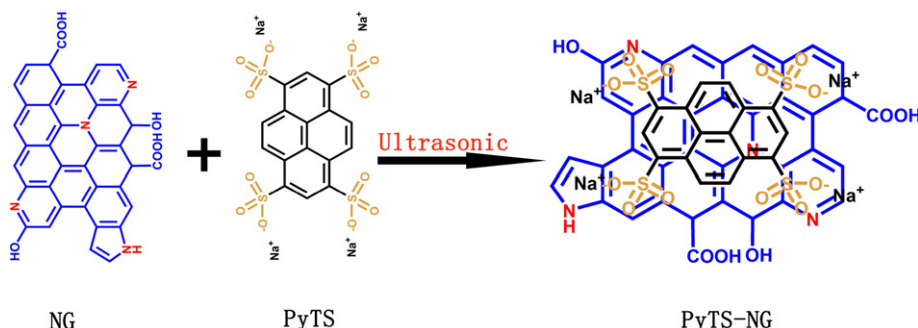


Fig. 1. Schematic diagram of the fabrication procedure of PyTS–NG.

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