



Simultaneous determination of dopamine, ascorbic acid and uric acid at electrochemically reduced graphene oxide modified electrode



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ABSTRACT

A facile electrochemical method was applied to prepare electrochemically reduced graphene oxide (ERGO). The morphology and structure of ERGO were characterized by scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray diffraction (XRD). Compared with the bare glassy carbon electrode (GCE), ERGO modified GCE (ERGO/GCE) exhibits much higher electrocatalytic activities toward the oxidation of dopamine (DA), ascorbic acid (AA) and uric acid (UA) with increasing of peak currents and decreasing of oxidation overpotentials. Differential pulse voltammetry results show that DA, AA and UA could be detected selectively and sensitively at ERGO/GCE with peak-to-peak separation of 240 mV and 130 mV for AA–DA and DA–UA, respectively. The linear ranges for AA, UA and DA are 500–2000 μM , 0.5–60 μM and 0.5–60 μM , respectively. Meanwhile, due to the negligible response to physiological level of AA (0.1 mM), ERGO/GCE could be used for the determination of DA in biological sample with high sensitivity and good selectivity. In addition, the presented method was successfully applied for the simultaneous determination of DA, AA and UA in urine sample with reliable recovery. This work provides a simple and green route to construct graphene-based electrochemical sensor, which is promising for the simultaneous determination of DA, AA and UA.

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1. Introduction

Ascorbic acid (AA) is a common anti-oxidant, which plays a great role in the metabolic process of human bodies. It influences essential physiological processes, such as cell division, gene expression and activation of biological defence mechanisms [1]. Dopamine (DA) is an important neurotransmitter in the mammalian central nervous system. Low levels of DA may cause neurological disorders, such as Parkinson's disease and schizophrenia [2]. Uric acid (UA) is the primary product of purine metabolism. Its abnormal concentration levels may lead to several diseases, such as hyperuricemia, gout and pneumonia [3]. DA, AA and UA usually coexist in biological samples. Since the basal DA concentration is very low (0.01–1 μM), while the concentration of AA is generally much higher (about 0.1 mM) [4], it is essential to develop selective and sensitive methods for their simultaneous determination both in analytical application and diagnostic research.

Since DA, AA and UA are highly electrochemically active, electrochemical methods for their simultaneous determination possess

the merits of convenience, rapidity and high sensitivity. However, overlapping of the oxidation peaks of these three species at traditional electrodes makes their simultaneous determination highly difficult. To overcome this problem, various chemically modified electrodes have been developed [5–7]. Due to its wide potential window, relatively inert electrochemistry and high electrocatalytic activity for a variety of redox reactions [8], carbon-based nanomaterials, such as carbon nanofiber, multi-walled carbon nanotube and hollow nitrogen-doped carbon microspheres, have been widely utilized for the simultaneous determination of DA, AA and UA [9–11].

As a kind of new carbon material, graphene has attracted tremendous attentions from scientific communities in recent years. Owing to its unique structural and electronic properties, graphene has been widely used for the construction of electrochemical sensors [12–14]. Presently, graphene used in electrochemical sensors are mostly prepared by chemical reduction method. This method generally employs toxicity reducing agents result in bringing impurities. Furthermore, partial removal of oxygenated species by chemical reduction method will degrade the electronic properties and weaken the electrochemical performance of graphene [15]. Therefore, a novel green and convenient electrochemical reducing method was proposed by Xia's group to

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prepare electrochemically reduced graphene oxide (ERGO). The obtained ERGO showed improved electrochemical performance compared with chemically reduced graphene oxide (CRGO) [16]. Recently, various strategies have been developed to fabricate ERGO film modified electrodes. Kim's group developed a polypyrrole and ERGO composite film modified electrode by an electrochemical polymerization process. The modified electrode realized the selective determination of DA in presence of AA and UA [17]. Raj et al. fabricated a 1,6-hexanediamine/ERGO (HDA/ERGO) film modified electrode by a self-assembly method [18]. Despite the HDA/ERGO film modified electrode realized the separation of the oxidation peaks of DA, AA and UA, the toxicity agent HDA may have adverse effects on the performance of the modified electrode.

In this work, we fabricated an ERGO film modified electrode via drop-casting of graphene oxide (GO) dispersion on the surface of GCE followed by an electrochemical reduction process, which is more convenient than the electrochemical polymerization and self-assembly method. The as-prepared ERGO was characterized with unique structural features and electrochemical properties, which provided it excellent performance as a promising electrode material. Compared with the bare GCE, ERGO modified GCE (ERGO/GCE) exhibited much higher electrocatalytic activities toward the oxidation of DA, AA and UA. Hence, the ERGO-based electrochemical sensor was used for the simultaneous determination of DA, AA and UA with good selectivity and high sensitivity.

2. Experimental

2.1. Apparatus

Atomic force microscopy (AFM) images were obtained by using a SPI3800N microscope (Seiko Instruments, Inc.) in tapping mode under ambient conditions. The surface morphologies of GO and ERGO were evaluated by scanning electron microscopy (SEM, PHILIPSLX-30ESEM) at an accelerating voltage of 15 kV. Raman spectra were recorded on a Renishaw Raman microscope (model RM2000) with laser excitation wavelength of 514.5 nm. X-ray diffraction (XRD) patterns were obtained using a D8 ADVANCE (Bruker AXS, Germany) X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 X-ray photoelectron spectrometer (VG Scientific, UK). Electrochemical experiments were performed with a CHI 832 electrochemical workstation (China). A conventional three-electrode system was used for all electrochemical experiments, which consisted of an Ag/AgCl/saturated KCl as reference electrode, a platinum wire as auxiliary electrode, and a bare GCE (2 mm in diameter) or ERGO modified GCE as working electrode.

2.2. Chemicals

Natural graphite flake, DA and UA were obtained from Alfa Aesar. AA was obtained from Chemical Reagent Company of Shanghai (China). All other chemicals used were of analytical grade. Double distilled water was used throughout the experiments.

2.3. Preparation of ERGO

Graphite oxide was synthesized from natural graphite flake by the modified Hummers method [19]. Then, the as-synthesized graphite oxide was subjected to ultrasonication for 40 min (200 W). Finally, a homogeneous graphene oxide (GO) dispersion was obtained. GO modified GCE (GO/GCE) was prepared by casting 3 μL GO dispersion onto the pretreated GCE surface and allowed to dry at room temperature. Then, an electrochemical reduction process

was applied to obtain ERGO/GCE by immersing GO/GCE into 0.1 M pH 7.0 PBS solution with cyclic sweeping in the potential range from 0.0 to -1.4 V at a scan rate of 20 mV/s for 5 cycles. All experiments were conducted at room temperature.

3. Results and discussion

3.1. Morphological characterization

Graphite oxide synthesized by the modified Hummers method was exfoliated into single layer graphene oxide, which is confirmed by AFM analysis. As shown in Fig. 1, GO existed as flat sheets with a lateral dimension of about $1 \mu\text{m}$ (Fig. 1a), and a thickness of 0.9 nm (Fig. 1b), which matches well with the thickness of an individual layer of GO [20]. The cyclic voltammetry (CV) curves recorded during the reduction process are shown in Fig. S1. There is a large reduction peak at -1.3 V with an onset potential of -0.75 V , which can be attributed to the reduction of surface oxygen groups of GO. The reduction current decrease remarkably and disappear after several cycles later, indicating the reduction process was quick and irreversible. The surface morphologies of GO and ERGO were investigated by SEM. GO displays a relative smooth surface (Fig. 1c). After being electrochemically reduced, ERGO exhibits rough surface with random wrinkles (Fig. 1d). This unique morphology is highly beneficial in maintaining large electroactive area on the electrode surface.

3.2. Structural characterization

The structure of ERGO was characterized by XPS, XRD and Raman spectra. As shown in Fig. 2, compared with the C1s spectrum of GO, the intensities of C1s peaks assigned to carbon atoms bound to oxygen in ERGO decreased obviously, indicating that most of the oxygen-containing groups were removed after electrochemical reduction. XRD patterns in Fig. 3a show that the sharp diffraction peak in graphite ($2\theta = 26.6^\circ$, $d = 0.34 \text{ nm}$) disappeared after oxidation and a new one ($2\theta = 10.8^\circ$, $d = 0.87 \text{ nm}$) appeared in GO, indicating the complete oxidation of graphite [21]. Accordingly, the diffraction peak at $2\theta = 26.6^\circ$ does not reappear in ERGO, which means that either all stacking of graphene layers in ERGO is lost, or any remaining stacking is disordered [22]. To further insight into the ordered and disordered crystal structures of carbon in graphite, GO and ERGO, Raman spectra were investigated (Fig. 3b). Graphite displays a strong G band at 1578 cm^{-1} , which is assigned to the E_{2g} phonon of sp^2 carbon atoms. While a prominent D band at 1350 cm^{-1} appeared in GO, which corresponds to the breathing mode of κ -point phonons of A_{1g} symmetry. The emergence of D band indicates the existence of defects in GO caused by oxidation [23]. When GO was electrochemically reduced to ERGO, the D/G intensity ratio increases obviously, suggesting a decrease in the average size of sp^2 domains [24].

3.3. Electrochemical characterization

We choose $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Fe}^{3+/2+}$ as probe molecules to investigate the electrochemical properties of ERGO. In case of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, a similar redox peak potential difference (ΔE_p) was obtained at GCE and ERGO/GCE, indicating that both electrodes can realize the fast electron transfer (Fig. S2a). For $\text{Fe}(\text{CN})_6^{3-/4-}$, a probe molecule which is sensitive to the surface state, especially the C sp^2 edge plane defects [25], ERGO/GCE shows smaller ΔE_p with response current 1.8 times higher than that at GCE (Fig. S2b), implying that ERGO has more edge plane defects and larger electroactive surface area. As an "oxide-sensitive" probe of $\text{Fe}^{3+/2+}$, GCE exhibits a sluggish response, while ERGO/GCE presents a well-defined CV response (Fig. S2c),

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