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Determination of ascorbic acid, dopamine, and uric acid by a novel electrochemical sensor based on pristine graphene

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ABSTRACT

In this article, a novel electrochemical sensor based on pristine graphene (PG) is successfully constructed to detect ascorbic acid (AA), dopamine (DA), and uric acid (UA). The PG is obtained by liquid-phase exfoliation of graphite and characterized by transmission electron microscopy and X-ray photoelectron spectroscopy. The sensor based on PG prepared by this method to realize simultaneous determination of AA, DA, and UA is firstly reported. The linear detection ranges for AA, DA, and UA are 9.00–2314 μM, 5.00–710 μM, and 6.00–1330 μM, respectively, with detection limits of 6.45, 2.00, and 4.82 μM. This PG based sensor exhibits excellent performance for detection of AA, DA, and UA, which is much better than those electrochemical sensors based on chemical converted graphene.

1. Introduction

The discovery of graphene has drawn great public attention since 2004 [1]. Due to its remarkable and excellent properties, graphene has already been applied in many devices, including biosensor, fuel cell, and supercapacitor. To date, there are three basic methods to prepare graphene: mechanical cleavage method [1], Hummers method [2], and liquid phase exfoliation method [3,4]. While mechanical cleavage method is effective for some scientific research, it is too low in output. The Hummers method is the most popular strategy owing to its stable great yield. However, the graphene prepared by this method need to be treated with strong acid and then reduced by some chemicals and is therefore often called chemical converted graphene (CCG). The chemical processes definitely cause the irreversible structure destruction of CCG and result in a decline in its conductivity [5,6]. Recently, high quality pristine graphene (PG) based on liquid phase exfoliation method (high throughput) [7] has become a hot topic.

Ascorbic acid (AA), dopamine (DA), and uric acid (UA) are of grave importance to physiology of living organism. AA, a water-soluble antioxidant, can protect living organisms from oxidative stress [8]. DA is an important neurotransmitter for message transfer [9]. UA is also a vital biomolecule which consists in urine and blood [10]. The imbalance of their contents is likely to cause some diseases, such as cancer [11], Parkinson's disease [12], and cardiovascular disease [13]. Therefore, detection of AA, DA, and UA is crucial for diagnoses and monitoring. Lately, a variety of CCGs, including water-soluble sulfonated graphene (s-GR) [14], chitosan-graphene [15], chemically reduced graphene oxide (CR-GO) [16], and electrochemically reduced graphene oxide (ER-GO) [17], have been used to fabricate electrochemical sensors to detect these three species. However, compared with CCG, although PG has defect-free structure and much better electrical property [18], it has been seldom reported to construct electrochemical sensors [19] for determination of AA, DA, and UA, which may be due to the lower yield of PG production.

In our recent work, Du et al. [20,21] reported a very simple organic salt-assisted exfoliation method to produce PG with high yield. It is found thus prepared PG has conductivity as high as 13000 S m^{-1}, which is much higher than those of CCGs (s-GR:1250 S m^{-1} [22], thermally reduced graphene oxide: 600 S m^{-1} [23], CR-GO: 405 S m^{-1} [24]). Inspired by the high conductivity, in this article, the PG obtained by the organic salt-assisted exfoliation method is used to fabricate an electrochemical sensor for the simultaneous determination of AA, DA, and UA. Since among those reported CCGs, s-GR has both higher conductivity and higher solubility [22], and recently has been reported to fabricate a sensor [14] of DA with very high sensitivity and low detection limit, it is therefore selected to perform comparative experiments and

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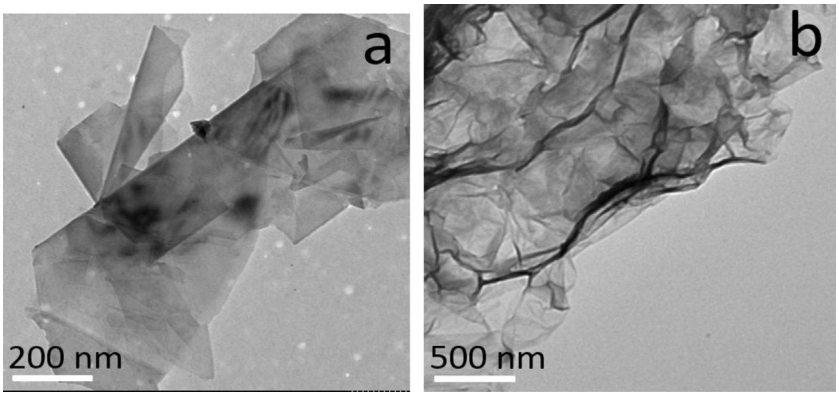

Fig. 1. TEM images of PG (a) and s-GR (b).

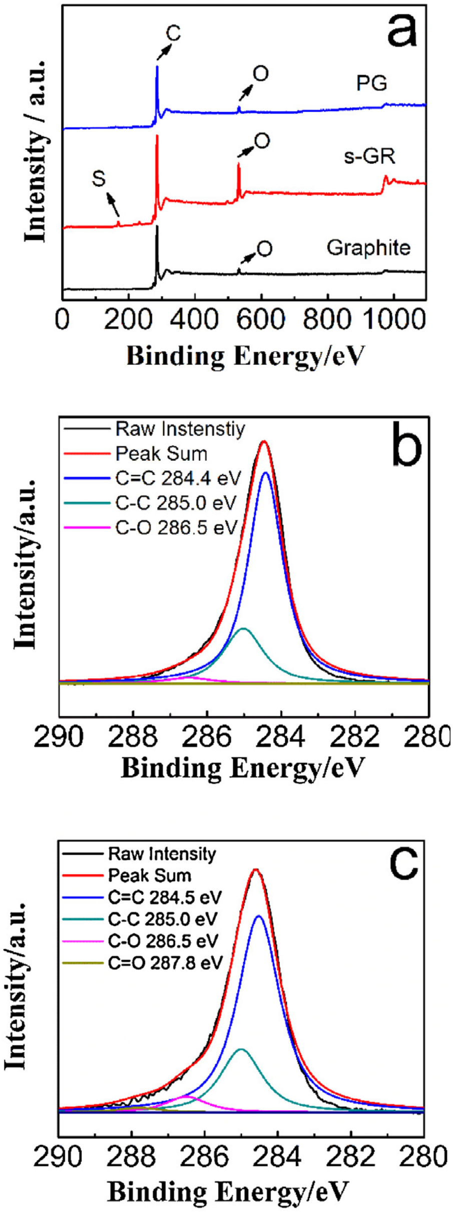

Fig. 2. XPS spectra of PG, s-GR and graphite (a). The C 1s peaks of PG (b) and s-GR (c).

contrast to PG. The results prove that the PG based sensor shows outstanding features which are better than CCG based sensors.

2. Experimental

2.1. Chemicals

Graphite powder (particle size ≤30 μm), dimethyl sulfoxide (DMSO), ethanol, sodium bicarbonate ($NaHCO_3$), sodium citrate ($Na_3C_6H_5O_7·2H_2O$), sodium nitrite ($NaNO_2$), potassium ferricyanide ($K_3Fe(CN)_6$), and potassium ferrocyanide ($K_4Fe(CN)_6$) were purchased from Shanghai Chemical Reagent Co. Ltd. ρ-Aminobenzene sulfonic acid was bought from Shanghai SSS Reagent Co. Ltd. AA, sodium borohydride ($NaBH_4$), and hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Co. Ltd. DA and UA were bought from Aladdin and Sigma–Aldrich, respectively. Phosphate buffer solution (PBS, pH 7.0, 0.1 M ($mol\,L^{-1}$)) was prepared by potassium dihydrogen phosphate (KH_2PO_4) and sodium hydroxide (NaOH). Ultrapure water (resistivity of 18.25 MΩ cm) was used throughout the work.

2.2. Apparatus

Transmission electron microscopy (TEM) (Hitachi-7650, 80 kV) and XPS (PHI-5000 Versaprobe X-ray photoelectron spectrometer) were utilized to characterize morphologies of samples. All electrochemical measurements were carried out on a CHI660c electrochemical workstation (Shanghai CH Instruments Co. Ltd, China) with a traditional three-electrode configuration which had a PG or s-GR modified glassy carbon working electrode (GCE, diameter: 3 mm), an Ag/AgCl (saturated KCl) reference electrode and a platinum wire counter electrode. The electrical conductivity of graphene film on a glass slide was measured by four-point probe method using a resistivity meter (Loresta GP MCP-T610, Mitsubishi Chemical Corp.) after being dried at 70 °C for 2 hours.

2.3. Methods

(1) Preparation of PG

PG dispersion was synthesized according to our previous work [21] by sonicating original graphite in DMSO with aid of organic salt. Typically, graphite powder (1 g) and $Na_3C_6H_5O_7·2H_2O$ (2 g) were added in 50 mL DMSO. The resulting mixture was then placed in an ultrasonic bath with a frequency of 40 KHz for 3 hours at room temperature. The sonicated dispersion was then centrifuged (5000 rpm for 30 minutes) using a UNIVERSAL 320 centrifuge. The supernatant was transferred out discreetly using a pipette, followed by aggregating the dispersion through adding some inorganic salt. The aggregate was then washed in succession with