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Facile ultrasonic synthesis of graphene/SnO_2 nanocomposite and its application to the simultaneous electrochemical determination of dopamine, ascorbic acid, and uric acid

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ABSTRACT

One-step facile ultrasonic method was developed to fabricate graphene/SnO_2 (GS) nanocomposite in acidic solution. Graphite oxides were reduced by $SnCl_2$ to graphene sheets in the presence of HCl. The reducing process was accompanied by generation of SnO_2 nanoparticles. This work report the detailed study on the GS nanocomposite modified glass carbon electrode. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were used for the detection of dopamine (DA), ascorbic acid (AA), and uric acid (UA). In AA, DA, and UA ternary mixture, three well-defined peaks located at about 180 mV, 420 mV and 600 mV vs. SCE were obtained. Comparing with either pristine SnO_2 or graphene, the prepared graphene/SnO_2 nanocomposite shows superior electrocatalytic activity.

1. Introduction

Dopamine (DA) is one of the most important neurotransmitters in the central nervous system of the mammals, which exist in the tissues and body fluids (in mammalian central nervous system found in high amounts 50 nmol/g in a region of the brain known as the "caudate nucleus") [1] in the form of cations for controlling the nervous system [2]. Ascorbic acid (AA) being a constituent of the cell has momentous biological functions and is an analyte of great importance. It is found in fruits, vegetables and in beverages especially those derived from fruit juices [3], which mainly act as a preventer of respiratory viral infections [4]. Uric acid (UA) and other oxypurines are the principal final products of purine metabolism in the human body [5]. Urate is present in a concentration range of 4.1 ± 8.8 mg/100 mL in serum for normal, healthy humans [6]. Abnormal levels of UA cause symptoms of several diseases, including gout, hyperuricemia and Lesch–Nyhan disease [7]. However, DA, AA, and UA usually coexist together and considered as important molecules for physiological processes in human metabolism. DA, AA and UA deficiencies results in several diseases and disorders [8–11]. Determination of these species exhibits overlapping oxidation peaks at solid electrodes. Thus, simultaneous determinations of these species take a special keen interest in biosensors. There has been a considerable interest in the determination of DA in the presence of AA and UA in biological samples by voltammetric methods. It is generally believed that direct redox reactions of these species at the bare electrodes are irreversible, and can cause electrode fouling. Electrode fouling is a common issue during electrochemical analysis of phenolic compounds, and has been revealed in Yang's paper [12,13], where a powerful model was presented for deep understanding of the mechanism of electrode fouling. For this purpose the electrode was modified with various films [14]. The modified electrode can lower the overpotential, increase the reaction rate and sensitivity, and improve the selectivity. In electrode materials, the graphene exhibited a superior biosensing performance for sensing DA [15–17].

Many methods have been developed to produce grapheme [18–20]. In 2004, Geim and coworkers [21] first reported graphene sheets prepared by mechanical exfoliation (repeated peeling) of highly oriented pyrolytic graphite. However, it is not suitable for mass production. The other method for producing defect-free/defect-less graphene is the mild exfoliation of graphite [22–25], but the yield so far is very low [22]. Graphene has also been prepared by thermal decomposition of SiC wafer under ultrahigh vacuum (UHV) conditions [26–29] or by CVD growth on metal substrates (ruthenium [30], Ni [31,32], and Cu [33]) or by substratefree CVD [34]. This is a potential mass-production method with the aim of

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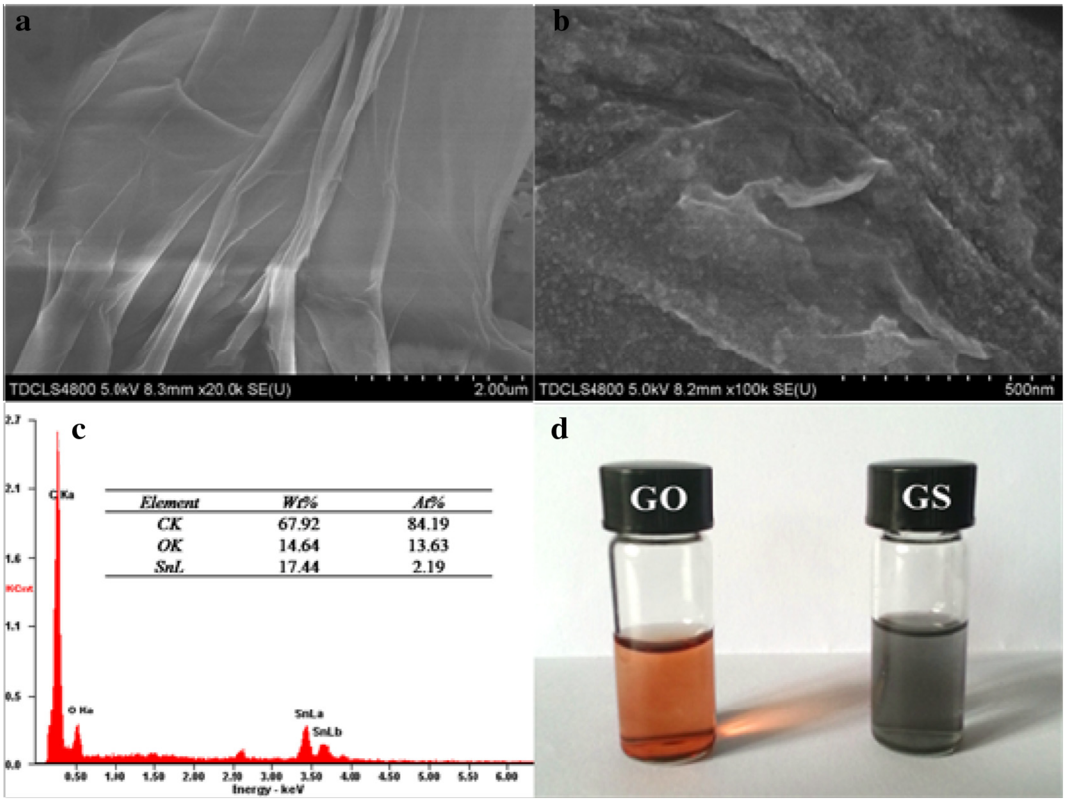

Element	*Wt%*	*At%*
CK	67.92	84.19
OK	14.64	13.63
SnL	17.44	2.19

Fig. 1. (a and b) FE-SEM images of the GO, and GS nanocomposite, (c) EDS spectrum of the GS nanocomposite, (d) photograph of the GO and GS solution.

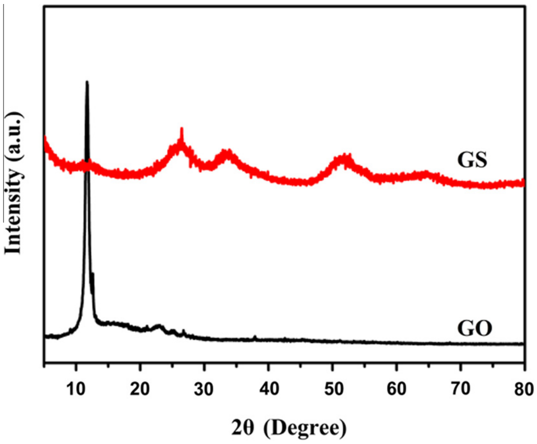

Fig. 2. XRD patterns of GO and GS.

producing graphene for electronics applications [35,36]. Another mass-production method is chemical [37–40] or thermal reduction [41] of graphite oxide (GO). It is also considered to be the most economical way to produce graphene [19,42]. Most of graphene used in electrochemistry are produced with the last method of GO reduction. Graphene from GO reduction, which is also called functionalized graphene sheets or chemically reduced graphene oxide, usually has abundant structural defects [19,41] and functional groups [37] which are advantageous for electrochemical applications [20,43–46].

In this work, we present the facile rapid synthesis of graphene, and their utility for simultaneous electrochemical determination of DA, AA, and UA. We reduced GO by $SnCl_2$ in the presence of HCl to fabricate graphene/SnO_2 (GS) nanocomposite using an ultrasonic method. The GS nanocomposite is modified on electrode surface to study by means of cyclic voltammetry, SEM, XRD, and differential pulse voltammetry. The surface morphology and electrochemical property of GS film are observed and compared with bare glassy carbon (GC) electrode. Electrocatalytic reactions including simultaneously electrocatalytic oxidation for DA, AA, and UA by GS nanocomposite are also examined and discussed.

2. Experimental

GO were synthesized from natural graphite powder by a modified Hummers method as originally presented by Kovtyukhova et al. [47]. Then GO were subjected to dialysis for 3–4 days to completely remove metal ions and acids. Finally, the product was dried in air at room temperature.

Dried GO (10 mg) were exfoliated in distilled water (20 ml) with ultrasonic treatment to form a colloidal suspension. Subsequently, 0.15 ml of HCl (36–38%,), 0.22 g of $SnCl_2{\cdot}2H_2O$ (98.0%) were added, then the mixture was continually ultrasonic for 3 h. The product was rinsed completely with distilled water and dried at room temperature under vacuum.

DA, AA, and UA were obtained from Sigma. Sulfuric acid (H_2SO_4), NaCl, KCl, KH_2PO_4 and Na_2HPO_4 were of analytical-reagent grade and used without further purification. Phosphate buffer solution (PBS, 0.05 M, pH 6.8) was prepared with KH_2PO_4 and Na_2HPO_4. All the aqueous solutions were prepared with double-distilled water.

Field-emission scanning electron microscopy (FE-SEM) images were obtained from a Hitachi S4800 scanning electron microscope operating at 20 kV. The composites were characterized by a powder X-ray diffraction (XRD) on Rigaku D/MAX-2500 X-ray diffractometer with Cu Kα irradiation ($\lambda = 0.15406$ nm). Cyclic voltammetry and different pulse voltammetry measurements were