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Green synthesized Co nanoparticles doped amino-graphene modified electrode and its application towards determination of baicalin

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A B S T R A C T

The present paper reported an one-pot synthesis of Co nanoparticles doped amino-graphene nanocomposites (Co-amino-Gr), involving *in situ* generation of Co nanoparticles (NPs). The simultaneous reduction of graphene oxide (GO) and Co^{2+} to produce Co-amino-Gr had been achieved under mild reaction conditions using an environmentally benign reducing agent, glycine. By combining the merits of amino-Gr and the Co NPs, a highly sensitive electrochemical sensor was erected to detect baicalin based on the Co-amino-Gr nanocomposites. Under optimum conditions, the response peak currents were linear related with baicalin concentrations in the range of 1.0×10^{-8}–8.0×10^{-7} mol L^{-1} with a lower detection limit of 5.0×10^{-9} mol L^{-1} (S/N=3). Additionally, the proposed method was used to detect baicalin in the medicinal capsules with satisfactory results.

1. Introduction

Graphene (Gr) has emerged as an enhanced material for constructing high-performance electrochemical sensors and biosensors [1,2], owing to its extremely large specific surface area, excellent electronic conductivity, outstanding intrinsic mechanical strength, reasonable chemical stability and superior thermal conductivity [3,4]. However, the hydrophobic character of Gr makes it easy to form irreversible aggregation or even restack due to strong π-π stacking interaction and Van der Waals forces [5]. To further improve its applicability, the problem can be resolved by covalent reaction between some amino acids and Gr to produce amino-Gr [6], such as arginine [7], lysine [8] and glycine [9]. In present work, glycine was used as reducing agent for effective reduction of graphene oxide (GO) to Gr [10] and simultaneously as functionalized reagent to avoid the aggregation of Gr.

The morphological and physicochemical features of amino-Gr could further be improved by forming its nanocomposites with different metal nanoparticles (NPs). Among the different metal NPs (Fe, Co and Ni) [11–14], Co NPs is economical and electrically conducting and largely used in electro catalysis. It is also expected to result in increasing its specific surface area besides enhancing the surface reactivity [15] and catalytic activity [16]. Here, Co^{2+} was reduced as Co NPs by glycine and uniformly dispersed on the amino-Gr surface. Co-amino-Gr nanocomposites were synthesized for the first time under environmental benign conditions and used in preparation of electrochemical sensor.

Baicalin (Fig. 7), belonging to the flavonoids, is an important anti-inflammatory and anticancer drug. It has been demonstrated to possess a series of biological effects, including anti-allergy, free radical scavenging, inhibit the proliferation of cancer cells or induce apoptosis in breast and prostatic cell lines [17–19]. Therefore, establishment of suitable analytical method for the determination of baicalin is of great significance in clinic and pharmaceutics. So far, several methods such as thin layer chromatography [20], capillary electrophoresis [21], high performance liquid chromatography (HPLC) [22,23], fluorimetry [24], and liquid chromatography-mass spectrometry (LC-MS) [25] have been developed for the analysis of baicalin. These methods have advantages of sensitivity and accuracy, but require high cost and complicated operation. Electrochemical detection is an attractive alternative to these techniques because of high sensitivity, instrument simplicity, fast response, low cost, and feasibility of miniaturization. By now, some voltammetric methods have been application for determination of baicalin [26–30]. However, one or more disadvantage was presented in each strategy, either low detection sensitivity or complicated synthesis process of modified materials. This challenge presented an opportunity to develop a more sensitive baicalin sensor.

Herein, we reported an environmentally friendly one-pot method to fabricate Co-amino-Gr nanocomposites under mild condition. Co NPs anchored on the well-dispersed amino-Gr sheets. The proposed modified glass carbon electrode (Co-amino-Gr/GCE) exhibited high specific voltammetric response to baicalin. Meanwhile, the electrochemical properties of baicalin were investigated in detail and a sensitive

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determination method was estiblished synchronously.

2. Experimental

2.1. Instruments and reagents

UV–vis absorption spectra were acquired on a Shimadzu UV-2550s Spectrophotometer. Infrared spectrogram were recorded on Infrared Spectrometer (Thermo Nicolet Coporation, Santa Clara, California, USA). Transmission electron microscope (TEM) images were obtained on TECNAIG^{2}F20-S-TWIN (USA) with a 200 kV accelerating voltage. X-ray diffractiometer (XRD, Shimadzu) study was conducted by Cu Ka radiation source (λ=1.54056 Å). High performance liquid chromatography (HPLC) was performed on 1260 Infinity Quaternary LC System (Agilent Technologies Inc., Santa Clara, California, USA). All electrochemical experiments were carried out using a RST5000 electrochemical workstation (Zhengzhou Shiruisi Instrument Technology Co. Ltd., Zhengzhou, China). A three-electrode system was employed, consisting of a bare GCE (4 mm diameter) or modified GCE working electrode, a platinum wire counter electrode (0.5 mm diameter) and a saturated calomel reference electrode, respectively. All the pH measurements were made with a PHS-3C precision pH meter (Leici Devices Factory, Shanghai, China), which was calibrated with a standard buffer solution at 25 ± 0.1 °C every day.

Baicalin (HPLC≥98%) was purchased from Shanghai Yuanye Biological Technology Co., Ltd. (Shanghai, China). A standard solution of Baicalin (1×10^{-3} mol L^{-1}) was prepared with dimethylformamide (DMF) and kept darkly under 4 °C. Glycine and $Co(NO_3)_2\cdot6H_2O$ were purchased from Aladdin Co. Ltd. (Shanghai, China). Baicalin capsules were purchased from local drugstore (Zhengzhou, China). Phosphate buffer solution (PBS, 0.1 mol L^{-1}) were prepared using the mixture of the stock solutions (0.1 mol L^{-1} NaH_2PO_4 and Na_2HPO_4). The lower pH value of PBS was adjusted with 0.1 mol L^{-1} H_3PO_4. Working solutions were prepared daily by diluting the stock solution of baicalin in 0.1 mol L^{-1} PBS. All reagents were of analytical grade and all solutions used in this work were prepared with double distilled water. All experiments were performed at room temperature.

2.2. Synthesis of Co-amino-Gr nanocomposites

Graphene oxide (GO) was synthesized by exfoliation of graphite according to the well-established Hummers method [31]. GO (10 mg) was dispersed into 10 mL of double distilled water under ultrasonication for 2 h to obtain a uniformly yellow-brown dispersions. Then 200 mg of glycine were added to above dispersions with stirring. The pH was adjusted to 10 by dropwise addition of NaOH (0.1 M). Subsequently, $Co(NO_3)_2\cdot6H_2O$ (100 mg) was added slowly. After being stirred for 1 h, the reaction mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 100 °C for 3 h. Finally, the autoclave was cooled down to room temperature naturally. The product was centrifuged and washed with ethanol and water for several times to obtain the Co-amino-Gr nanocomposites. For comparison purposes, amino-Gr was hydrothermally treated at the same condition without the addition of $Co(NO_3)_2\cdot6H_2O$.

2.3. Preparation of modified electrode

The prepared Co-amino-Gr nanocomposites were dispersed in double water with ultrasonication for 1 h to get a homogenous suspension (0.5 mg mL^{-1}). Prior to the modification, the bare GCE was polished to a mirror-like surface with 0.3 and 0.05 µm alumina slurry in turn, and sequentially sonicated in absolute alcohol and double distilled water, respectively. The Co-amino-Gr/GCE was fabricated by depositing Co-amino-Gr (10 µL) on a fresh GCE surface using a micro-injector, and then dried naturally. The amino-Gr/GCE was also prepared similarly for comparison.

2.4. Analytical procedure

Prior to use, the prepared Co-amino-Gr/GCE was scanned between 0.1 V and 0.7 V with a scan rate of 0.1 V s^{-1} in 0.1 mol L^{-1} PBS (pH 4.0), until a steady voltammogram was obtained. Then a certain amount of standard stock solution of baicalin was added to the electrochemical cell. Subsequently, an accumulation step was performed under open-circuit conditions along with solution agitation for 180 s (The effect of accumulation time was studied and shown in supplementary information). The square wave voltammetry (SWV) technique was used to establish the analytical method and the current-potential curve was recorded in a potential window of between 0.1 V and 0.6 V. After each determination, the electrode was immersed in 0.1 mol L^{-1} PBS (pH 8.0) for two cyclic scans to get a regenerated electrode surface.

2.5. Sample solution preparation

The powder was poured out from medicinal baicalin capsules. Exact weight of 0.2g powder was put in beaker and dissolved with 10 mL DMF. After ultrasonication for 30 min, the solution was centrifuged for 10 min at 5000 rpm. This step was repeated several times for ensuring extraction completely. All supernatants were transferred into a 25 mL volumetric flask and diluted up to this volume with DMF for analysis. SWV was conducted with the parameters of quiet time 3 s; square wave amplitude 0.025 V; square wave period 40 ms and sample width 5 ms. Before each measurement, the sample solution (10 µL) was mixed with 10 mL 0.1 mol L^{-1} PBS (pH 4.0).

3. Results and discussion

3.1. Characterization of Co-amino-Gr nanocomposites

The morphology and structure features of amino-Gr and Co-amino-Gr were observed by TEM analysis (Fig. 1). Fig. 1A indicated that the amino-Gr sheet exhibited flake-like structure with wrinkled edges. Co-amino-Gr nanocomposites (Fig. 1B) showed a uniform dispersion of Co nanoparticles on the Gr sheets with the average size of 20 nm. EDX (Fig. 1C) spectra of the sample clearly showed the presence of C, O, N and Co in the case of Co-amino-Gr. The images confirmed that glycine successfully reduced GO to Gr and the formation of Co nanoparticles well dispersed on the amino-Gr sheets surface.

UV–vis spectroscopy was also utilized to characterize the Co-amino-Gr. In Fig. 2A, the UV–vis spectrum of GO (curve a) exhibited a band at 230 nm and a shoulder at 300 nm, while for the Co-amino-Gr (curve b), the absorption peak was red shifted to 268 nm. This phenomenon indicated that the GO was reduced using the simple and green method [32].

Fig. 2B showed the IR spectra taken from GO (curve a) and Co-amino-Gr (curve b). The various prominent vibrational bands of GO were observed at 3441 cm^{-1}, 2925 cm^{-1}, 2853 cm^{-1}, 1730 cm^{-1}, 1629 cm^{-1}, 1382 cm^{-1}, 1221 cm^{-1} and 1054 cm^{-1}, which were attributed to –OH stretching, symmetrical and unsymmetrical –C–H stretching, C=O (carboxylic), C=C, C–OH (stretching/deformation), C–O–C (epoxy) and C–O (alkoxy) oxygen functionalities, respectively [33]. In contrast, the obvious decrease of these characteristic absorption peaks of Co-amino-Gr confirmed the reduction of most oxygen functionalities in the GO. Furthermore, a new broad peak of 1580 cm^{-1} was likely to arise from the co-contribution of both aromatic C=C and –N–H bending. Apart from this, a strong and sharp peak was also observed at 1340 cm^{-1}, which was assigned to C–N stretching [34]. These data verified glycine not only had the high efficiency in reducing GO to Gr but also functionalized graphene.

XRD patterns of the GO and Co-amino-Gr were acquired and shown in Fig. 2C. As depicted in curve a, a characteristic diffraction peak of GO was observed at around 2θ=10°, corresponding to the (002)

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