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Direct electrolytic exfoliation of graphite with hemin and single-walled carbon nanotube: Creating functional hybrid nanomaterial for hydrogen peroxide detection

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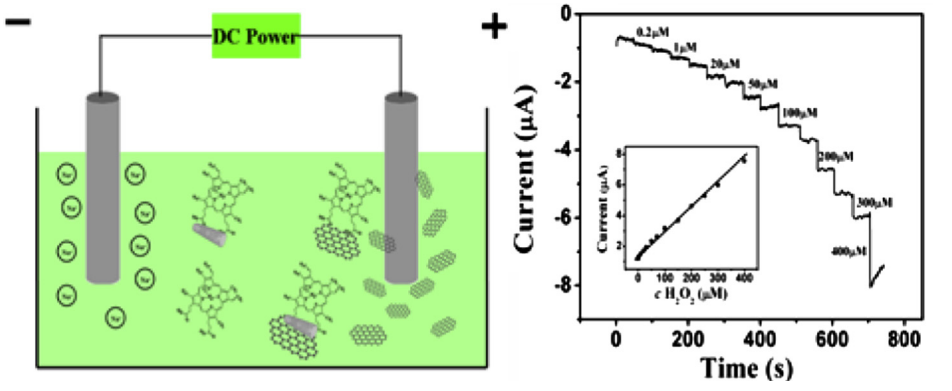
HIGHLIGHTS

- GN–HN–SWCNT hybrid nanomaterials were prepared by a simple and efficient method.
- The hybrid nanomaterials integrate excellent properties of GN, HN and SWCNT.
- The hybrid nanomaterials possessed excellent electrocatalysis properties to H_2O_2.
- The as-prepared biosensor displayed a wide linear range and a low detection limit.
- The developed biosensor was successfully applied for real samples.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a new, facile and efficient method to prepare functional graphene (GN) hybrid nanomaterials using direct electrolytic exfoliation of graphite robs in hemin (HN) and single-walled carbon nanotube (SWCNT) solution. During the exfoliation process, HN and SWCNT were simultaneously adsorbed on the surface of GN nanosheets through noncovalent π–π interaction, and then 3D GN–HN–SWCNT hybrid nanomaterials were formed. Due to the synergic effect among GN, HN, and SWCNT, these hybrid nanomaterials possessed excellent electrocatalysis properties and were used to construct novel electrochemical biosensor for H_2O_2 determination. The results displayed a wide linear range of 0.2 μM–0.4 mM and a low detection limit of 0.05 μM. Moreover, the developed sensor was successfully applied for real samples, such as beverages, and showed great promise in routine sensing applications.

1. Introduction

Carbon-based materials, especially carbon nanotubes and graphene (GN) show the hot topics of materials research. Carbon nanotubes as nanoscale building blocks have been employed for various potential applications, especially biosensors [1]. In comparison with well-known carbon nanotubes, GN is a rapidly rising star on the horizon of materials science and has been applied in many fields due to its unique structure and fascinating electronic properties [2–5]. With the widespread applications of GN-based materials, various fabrication techniques, such as micromechanical cleavage, epitaxial growth, solution-based reduction of graphene oxide, chemical vapor deposition and electrolytic exfoliation have

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been performed to obtain GN nanosheets [6–10]. Among these methods, electrolytic exfoliation, usually in the presence of functionalizing agents, is particularly promising for its simple, economic, and environmentally friend operates at ambient temperature and pressure [11,12]. Moreover, it is a one-step method that does not involve the destructive oxidations of graphite. Therefore, it is more desirable to prepare GN nanosheets directly from graphite, and at the same time to functionalize the surface of GN.

Hemin (HN), the active center of the HN-protein family, is protoporphyrin IX containing a ferric iron ion and a chloride ligand. It has the peroxidase-like activity similar to the peroxidase enzyme [13]. It also can be well used as electron media based on the reversible redox of Fe(III)/Fe(II), and exhibits good electrocatalysis to many small molecules related to life process, such as NO, neurotransmitters, hydrogen peroxide, nitrite, and dissolved oxygen [14]. However, the hydrophobic nature of porphyrin ring leads to the low solubility of HN, and then HN dimerization occurs which reduce the catalytic activity and limit the direct application [15]. An efficient method for solving this problem is to load HN on some supporting materials that can provide suitable micro-environments to prevent HN dimerization.

In this work, we used GN and single-walled carbon nanotube (SWCNT) as building blocks to load HN and concomitant non-covalent functionalization of GN by HN and SWCNT. The hybrid nanomaterials have been prepared by direct electrolytic exfoliation of graphite robs in $NaNO_3$ solution containing HN and SWCNT via sonication. For its flat and planar aromatic structure, HN can be adsorbed on the surface of GN and the sidewalls of SWCNT through π-π stacking [13,16]. Noncovalent functionalization makes GN and SWCNT as perfect substrates to support HN for the improvements in catalytic activity and stability. At the same time, the presence of SWCNT and HN guarantees to exfoliate graphite to yield single or few layer GN, and to non-covalently functionalize/dope GN. Moreover, one-dimensional (1D) SWCNT can combine with 2D GN to form a 3D nanohybrid. Coupled with high electrocatalysis of HN and excellent properties of GN and SWCNT, the new resulting hybrid nanomaterials modified electrodes exhibit highly efficient electrocatalytic activity for the reduction of hydrogen peroxide (H_2O_2), and highly sensitive amperometric biosensors for H_2O_2 have also been developed.

2. Experimental

2.1. Reagents

High purity graphite rods (Φ 6 mm, 99.999%) were supplied from Aldrich. SWCNT (>95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd. and purified by refluxing in concentrated nitric acid for 7 h prior to use. H_2O_2 (30 wt% in H_2O), $NaNO_3$ were obtained from Beijing Chemical Reagent Company. HN (ferriprotoporphyrin IX chloride, 98 wt%), glucose, ascorbic acid, sucrose and citric acid were obtained from Sigma. All other chemical were of analytical grade and used as received without further purification in experiments. H_2O_2 solutions were freshly prepared before used. Phosphate buffer solution (PBS) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4. All aqueous solutions were prepared with ultrapure water from a Milli-Q Plus system (Millipore).

2.2. Instruments

UV–vis absorption spectra were carried out with a UV-2150 spectrophotometer (Shimadzu, Japan). Fourier transform infrared spectroscopy (FT-IR) experiments were performed on a Tensor 27 FT-IR spectrometer (Bruker, Germany). Electrochemical measurements were recorded on a CHI 840C electrochemical analyzer (Shanghai Chenhua Instruments, China) with a three-electrodes system composed of platinum wire as an auxiliary electrode, Ag/AgCl electrode as a reference electrode, and the modified glassy carbon electrode (GCE, 3 mm in diameter) as a working electrode. The transmission electron microscopic (TEM) images were acquired with a JEOL mode 2000 instrument operated at 200 kV (JEOL Ltd., Japan). Resonance Raman spectra were measured on a LabRAM HR 800 Raman spectrophotometer (Jobin Yvon, France).

2.3. Preparation of GN–HN–SWCNT hybrid nanomaterials

The GN–HN–SWCNT hybrid nanomaterials were synthesized by direct electrolytic exfoliation of graphite robs in $NaNO_3$ solution containing HN and SWCNT via sonication. Briefly, an amount of SWCNT was dissolved in 10 mL HN DMF solution under sonication, then the suspension was mixed with 90 mL $NaNO_3$ solution and the resulting mixture was used as electrolyte. Two high-purity graphite rods used as electrode were inserted into the electrolyte and paralleled with a distance of 4.0 cm. The constant potential between the two electrodes was set at 10 V (DC voltage) and the whole electrolytic experiment was carried out under sonication. Under these conditions, the anode graphite rod was corroded and a lot of black precipitate or sludge gradually appeared at the bottom of the reactor. Then, the precipitate was taken out of the reactor after 8 h and centrifuged at 3000 rpm to remove the heavy particles. Subsequently, the obtained product was centrifuged again at 10,000 rpm and the precipitate was extracted. Finally, the precipitate was dispersed in ultrapure water and used for further experiment. The experimental setup for electrolytic exfoliation is schematically shown in Fig. 1.

2.4. Fabrication of GN–HN–SWCNT hybrid nanomaterials modified electrode

Prior to experiment, GCE was carefully polished with 1.0, 0.3 and 0.05 μm alumina powder separately until a mirror like surface was obtained. Then, GCE was sonicated in alcohol and water successively and dried in nitrogen. After that, 5 μL of GN–HN–SWCNT suspension was coated onto the surface of GCE and dried in air. For comparison, GN–HN/GCE and SWCNT–HN/GCE were also prepared by a similar procedure.

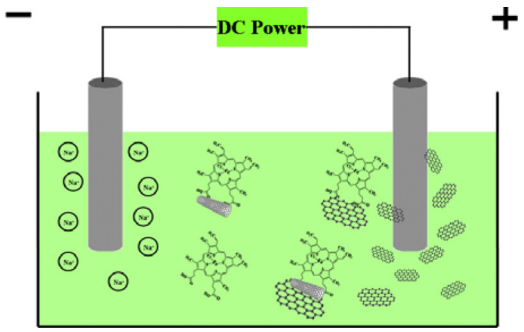

Fig. 1. Schematic illustration of the synthesis of GN–HN–SWCNT hybrid nanomaterials via electrolytic exfoliation of graphite robs.