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Research paper

Electrochemical supramolecular recognition of hemin-carbon composites

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ABSTRACT

Hemin-graphite oxide-carbon nanotube (hemin-GO-CNT) and hemin-thermally reduced graphite oxide-carbon nanotube (hemin-TRGO-CNT) composites are synthesized and investigated for the electrochemical supramolecular recognition by electron transfer between biomolecules (dopamine and hydrogen peroxide) and the composite electrodes. Redox reaction mechanisms of two composites with dopamine and hydrogen peroxide are explained in detail by using cyclic voltammetry and differential pulse voltammetry. Hemin-TRGO-CNT displays higher electrochemical detection for dopamine and hydrogen peroxide than that of hemin-GO-CNT, exhibiting enhancement of the electron transfer due to the effective immobilization of redox couple of hemin (Fe^{2+}/Fe^{3+}) on the TRGO-CNT surface.

1. Introduction

Electron transfer process between electrodes and biomolecules in biological systems is one of the leading areas of the biochemical and biophysical sciences. Enzyme-modified electrodes provide a basis for constructing biosensors and biomedical devices, which can obtain valuable information on the mechanisms of biological electron transfer reactions and find potential applications in biotechnology [1].

Hemin, involving the Fe^{3+}/Fe^{2+} redox couple, coordinated in the porphyrinic ring [2,3] and immobilized on an electrode surface is also capable of direct electron transfer from/to biomolecules and excellent as a bioactive material so that it has been used in biosensors widely [4]. The electron transfer between hemin in solution and bare solid electrodes is, however, usually too slow, limiting its performance for the biosensors [5,6]. Effective immobilization of hemin on a host substrate, having high electric conductivity, high thermal stability, and good biocompatibility, as a support material is necessary for the efficient biosensors. Hemin-carbon based electrodes have been intensively investigated because hemin could be immobilized strongly on the carbon electrode [4,7].

Graphite oxide (GO) has been used for the host substrate [8], and GO can be reduced to graphene-like sheets by removing the oxygen-containing groups with the recovery of a conjugated structure [9] in several methods: chemical [10], thermal [11], microwave [12], and photonic [13] methods. The thermal reduction, which has chemical-free and no explosion risk compared to the others, of GO could be good for electrodes of electrochemical devices, such as the biomolecules recognition, because of high surface area, good biocompatibility, nontoxicity, and good hydrophilic property. However, the electric conductivity of thermally reduced GO (TRGO) is still needed to further improve.

Carbon nanotubes (CNTs) have excellent electric conductivity and high aspect ratio, providing a good conductive network or matrix for easy attachment of electrolyte ions in the electrochemical devices [14,15]. Taking account of the advantage of CNT and TRGO, hemin could be immobilized on the TRGO-CNT substrate as the host substrate. GO-CNT composite has been investigated as novel and efficient platform for the immobilization and biosensing of redox enzymes [16]. However, enzymes for the development of biosensors are replaced with Hemin in our report.

Here, hemin was adsorbed onto the surface of the TRGO-CNT substrate through the π-π interaction [3] to form a new electrode facilitating the direct electron transfer between biomolecules (dopamine and hydrogen peroxide) and electrode. The TRGO-CNT composite was characterized for the electrochemical supramolecular detection and compared to the GO-CNT composite as well.

2. Material and methods

Graphite (200 mesh) and multiwalled CNT (20 μm of length, 10 nm of diameter) were purchased from Alfa Aesar and Hanwha Nanotech, respectively. Hemin and biomolecules (dopamine and

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hydrogen peroxide) were purchased from Sigma-Aldrich and used without any pretreatment.

The GO was first synthesized by the modified Brodie method, as described elsewhere [17,18], and then GO of 10 mg was mixed with DI water of 20 mL followed by the sonication for 2 h to form well dispersed GO solution. The GO solution was mixed with CNT (20 mg) and hemin (20 mg) in DI water of 20 mL. The mixture was sonicated for 180 min at room temperature, followed by a vacuum filtration using a cellulose paper. Obtained hemin-GO-CNT composite film was dried at 60 °C in a vacuum oven for overnight and used for the characterization. TRGO was synthesized as follows: GO was heated at 280 °C for 30 min in Ar environment with the ramping rate of 9 °C min^{-1}, and it was cooled down to room temperature for overnight [19]. The same synthesis process of hemin-GO-CNT was then followed to make hemin-TRGO-CNT except for TRGO.

X-ray diffraction (XRD, Rigaku Rotaflex D/MAX System, Rigaku, Japan) at 40 kV with Cu Kα (1.54 Å) was used to characterize the crystal structure of the composites. Thermogravimetric analysis (TGA, TGA Instruments, Q600, Ramp 10 °C min^{-1} to 900 °C, N_2 gas) was performed to measure components and its weight. The surface morphology of the composites was investigated by using scanning electron microscopy (SEM, Ltd., S-4300, JEOL, Japan) at different magnifications. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific, USA) with incident radiation of monochromatic Al K_α (1486.6 eV) was used to evaluate the chemical states of the elements. Brunauer-Emmett-Teller (BET) method was used to inspect surface area of the samples, based on the BET theory at the liquid nitrogen temperature.

Electrochemical properties of the samples were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) by using EC-Lab (Bio-Logic, sp-150, France) in a three-electrode cell. An Ag/AgCl electrode was used as the reference electrode, and a platinum wire was employed as the counter electrode. The working electrode was prepared as follows. Each sample of 0.5 mg was dispersed well in 1 mL of 2-propanol and then the mixture of 10 μg was dropped onto the glassy carbon electrode (GCE) and dried completely. CV was performed at the scanning rate of 50 mV s^{-1}, the frequency from 100 mHz to 100 kHz was applied for the EIS measurement, and DPV was measured in the potential range between −1.0 and 1.0 V, respectively. The pulse amplitude of 2.5 mV, pulse width of 100 ms, and scan rate of 10 mV s^{-1} were applied for DPV measurement. Each biomolecule of 0.25 mL was mixed with 0.1 M phosphate buffer solution (PBS, $[H_2PO_4]^-/[HPO_4]^{2-}$, pH = 7.5) of 10 mL for the supramolecular recognition detection. The EIS measurement is the most common for measuring electrochemical impedance of samples and provides impedances in the frequency region.

3. Results and discussion

Fig. 1 shows the structure of hemin and XRD results of samples. The GO has the typical (0 0 2) peak around 13° [17]. This diffraction peak from GO disappeared and a new broad peak appears near 23° in TRGO due to the removal of considerable oxygen functional groups of GO [20] during the thermal reduction process. CNT has typical peaks at 26 and 13°, corresponding to the first and second order of (0 0 2) diffraction of the graphite structure [21] with interlayer distance of 3.4 Å and 6.8 Å in Fig. 1c. The maghemite Fe_2O_3 phase near 17° was also shown and indicated the existence of metal oxide catalyst used for the synthesis of CNT [22]. The Hemin X-ray diffraction has a broad background between 5 and 25°,

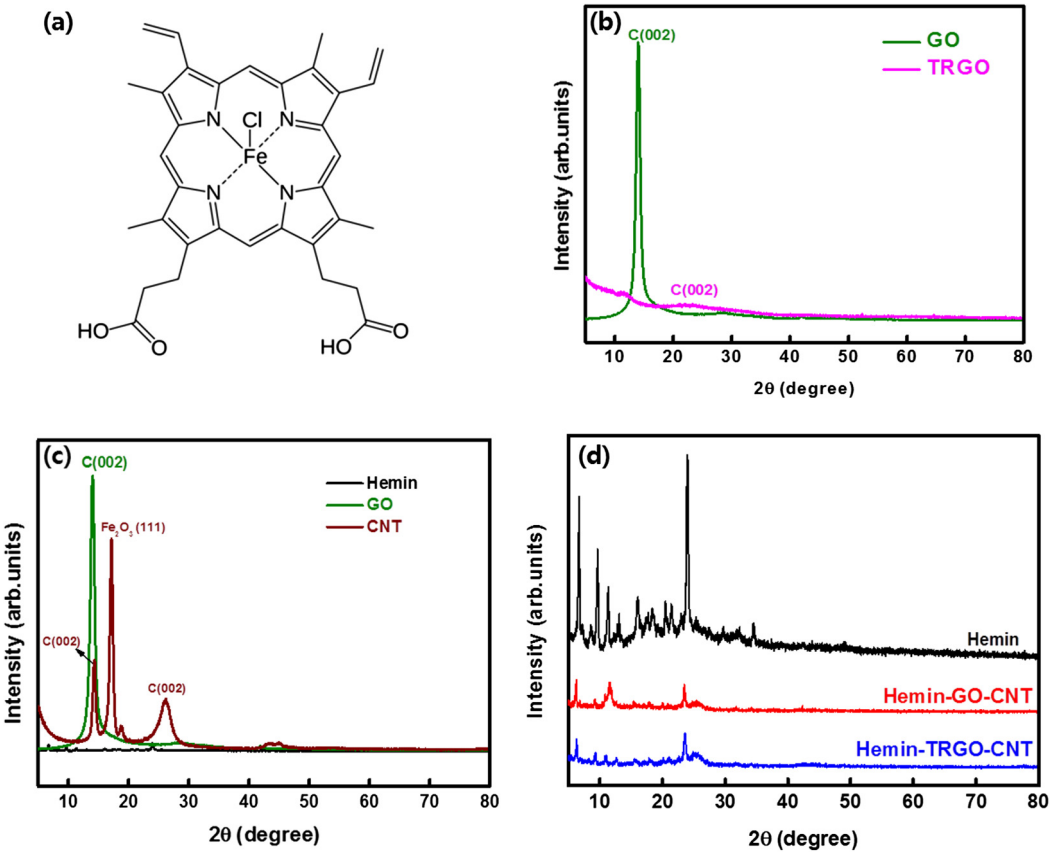

Fig. 1. Structure of hemin (a) and XRD results of the samples (b–d).