



Application of N-doped graphene modified carbon ionic liquid electrode for direct electrochemistry of hemoglobin



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ARTICLE INFO

Article history:

Received 16 October 2013

Received in revised form 15 January 2014

Accepted 17 February 2014

Available online 24 February 2014

Keywords:

N-doped graphene

Hemoglobin

Carbon ionic liquid electrode

Direct electrochemistry

ABSTRACT

Nitrogen-doped graphene (NG) was synthesized and used for the investigation on direct electrochemistry of hemoglobin (Hb) with a carbon ionic liquid electrode as the substrate electrode. Due to specific characteristics of NG such as excellent electrocatalytic property and large surface area, direct electron transfer of Hb was realized with enhanced electrochemical responses appearing. Electrochemical behaviors of Hb on the NG modified electrode were carefully investigated with the electrochemical parameters calculated. The Hb modified electrode exhibited excellent electrocatalytic reduction activity toward different substrates, such as trichloroacetic acid and H₂O₂, with wider dynamic range and lower detection limit. These findings show that NG can be used for the preparation of chemically modified electrodes with improved performance and has potential applications in electrochemical sensing.

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1. Introduction

As a 2D carbon nanomaterial with specific physical and chemical properties such as high thermal conductivity, large surface area and fast charged carrier mobility, graphene (GR) has been widely used in the fields of electrochemistry and electrochemical sensors [1,2]. By decorating GR with different kinds of modifiers, functionalized GR had also been investigated due to its unique structures or multi-functions [3]. Among them chemical doping with heteroatoms is an effective method to modify materials with new properties appearing. Nitrogen is an excellent candidate for chemical doping. The presence of nitrogen dopant in the carbon structure can influence the spin density and charge distribution of carbon atoms with the improvement of the electrocatalytic activity. For example, Gong et al. reported that nitrogen-doped carbon nanotube (CNT) arrays exhibited high electrocatalytic activity for the oxygen reduction reaction (ORR) [4]. Tang et al. investigated the electrocatalytic activity of nitrogen-doped CNT cups as the catalyst in ORR and electroanalysis [5]. The presence of nitrogen atoms in the carbon nanostructures can result in the conjugation between the nitrogen lone-pair electrons with the π -system of GR, which exhibit many tailored electronic and mechanical properties [6]. Also the nitrogen doping can enhance the biocompatibility and sensitivity of CNT in the field of biosensors [7]. Recently nitrogen-doped graphene (NG) was

synthesized by different methods [8,9] and used in various fields such as lithium ion battery [10] and superior capacitive energy storage [11]. The intrinsic modification of nitrogen atom in the carbon lattice of GR can modulate the electronic properties of GR, decorate the GR planar sheet and open the band gap of GR. So the presence of nitrogen dopant plays an important role in regulating the electronic properties, results in the enhanced electrocatalytic ability, and improves the electrical/thermal conductivities with enrichment of free charge-carrier density. Wang et al. reviewed the progresses on synthesis, characterization and potential applications of NG [12]. Xin et al. prepared NG by microwave heating and further used it as the supporting materials for fuel cell catalyst [13]. Wang et al. applied an NG modified electrode for the electrochemical sensing of glucose [14]. Shao et al. investigated the electrochemical applications of NG, which exhibited higher electrocatalytic activity toward the reduction of oxygen and H₂O₂ with higher durability and selectivity [15]. Li et al. developed an electrochemical immunosensor with NG modified electrode for label-free detection of the breast cancer biomarker CA 15-3 [16]. Choi et al. found that NG derived catalyst exhibited an enhanced electrochemical ORR ability than the graphite or CNT derived catalyst [17].

Direct electrochemistry of redox proteins has been widely investigated due to its importance in studying the structures and functions of proteins, as well as the fabrication of electrochemical sensors or electronic devices [18]. Due to deep burying of redox active centers in the protein structure, direct electron transfer of redox proteins on commonly used working electrodes is difficult to be realized. So protein film electrodes with various kinds of modifiers or promoters have been devised to accelerate the electron transfer rate [19]. Among them

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nanomaterials with different morphologies have been used due to their specific properties. Nanomaterials have been exhibiting specific properties such as big surface area, tunable porosity, excellent conductivity and high chemical stability, which can shorten the distance between the electroactive centers of redox proteins and accelerate the electron transfer rate. As a commercially available redox protein with clearly reported structure, hemoglobin (Hb) has been widely used as the model protein for the investigation on the direct electron transfer with electrode. Also Hb based electrochemical sensors had been reported for the electrocatalytic detection of different substrates [20,21]. Due to the specific properties of GR, such as high electrochemical conductivity, large surface area, and excellent electrocatalytic ability, GR has been used in the protein electrochemistry. Xu et al. realized the direct electrochemistry of Hb in the GR and the chitosan film [22]. However GR nanosheets are not stable in aqueous solution and easy to aggregate due to the π - π interaction, which limit the real applications. To further extend the usage of GR, various GR related nanomaterials had been synthesized and used for the protein electrochemistry. Liu et al. investigated the direct electrochemistry of Hb based on poly(diallyldimethylammonium chloride) functionalized GR/room temperature ionic liquid composite film [23]. He et al. applied a magnetite-GR for the direct electrochemistry of Hb and its biosensing application [24]. Xu et al. studied the direct electrochemistry and enhanced electrocatalytic activity of Hb entrapped in GR and ZnO nanosphere composite film [25]. Our groups also prepared various GR based composites such as GR-Ag [26], GR-TiO₂ [27], and GR-LDH [28] for the realization of direct electron transfer of Hb. Due to the contribution of GR and other components, the synergistic effects with multiple functionalities could be achieved and the direct electron transfer of redox proteins with electrode could be greatly enhanced.

However, there are seldom reports about the usage of NG in the realization of direct electrochemistry of Hb. Because the nitrogen dopant in GR structure can influence the spin density and charge distribution of carbon atom, the presence of nitrogen in the carbon network can result in some activation region on the GR surface. So NG has potential application in protein electrochemistry. In this paper NG was synthesized by a solvothermal method and used to realize the direct electrochemistry of Hb with a carbon ionic liquid electrode (CILE) as the basic electrode. CILE is prepared by using ionic liquid as the modifier and the binder in the carbon paste electrode, which has been proven to exhibit excellent electrochemical performance than traditional carbon electrodes [29]. Direct electrochemistry of Hb on the NG modified CILE could be directly realized with a pair of well-defined redox peaks appearing, which indicated that NG exhibited unique properties due to the presence of nitrogen atom in the GR structure. Electrocatalysis of the modified electrode to different substrates was further achieved with satisfactory results.

2. Experimental

2.1. Reagents and apparatus

Graphite powder (particle size 30 μm , Shanghai Colloid Chem. Co., China), 1-hexylpyridinium hexafluorophosphate (HPPF₆, Lanzhou Greenchem. ILS. LICP. CAS., China), hemoglobin (Hb, MW. 64500, Tianjin Chuanye Biochem. Co., China), chitosan (CTS, Dalian Xindie Chem. Co., China) and trichloroacetic acid (TCA, Tianjin Kemiou Chem. Co. Ltd., China) were used as received without further purification. Phosphate buffer solutions (PBS; 0.1 mol L⁻¹) with various pH values were used as supporting electrolyte, which were deoxygenated by bubbling highly pure nitrogen thoroughly for at least 30 min before the experiments. All the chemicals were of analytical grade and doubly distilled water was used throughout.

Electrochemical experiments were performed on a CHI 750B electrochemical workstation (Shanghai Chenhua Instrument, China). A three-electrode system was used with a saturated calomel electrode

(SCE) as reference electrode, a platinum wire electrode as auxiliary electrode and an Hb modified CILE as working electrode. Ultraviolet-visible (UV-vis) absorption and Fourier transform infrared (FT-IR) spectrum were obtained on a Cary 50 probe spectrophotometer (Varian, Australia) and Tensor 27 FT-IR spectrophotometer (Bruker, Germany). The morphology and graphitization of NG were characterized by JEM-2100 transmission electron microscopy (TEM, JEOL, Japan) and Renishaw in Via-Reflex Raman confocal microscopy.

2.2. Synthesis of NG

Based on our recent reported procedure [30], NG was synthesized by the reaction of tetrachloromethane (CCl₄, 2.0 mL) and lithium nitride (Li₃N, 1.0 g), which was sealed in a stainless steel autoclave (50 mL) that was filled with argon and heated at 200 °C for 20 h. Prior to being dried at 100 °C for 12 h, the product was filtered and washed by water for several times to remove reactant residual.

2.3. Preparation of the modified electrode

Based on reference [31], CILE was fabricated by using HPPF₆ as the binder and the modifier, which was mixed homogeneously with graphite powder and the mixture was inserted into a glass tube ($\Phi = 4.2$ mm) with a copper wire as the electrical contact. The surface of CILE was polished on a weighing paper just before use.

The modifier was prepared by mixing 1.0 mg mL⁻¹ NG, 12.0 mg mL⁻¹ Hb and 0.5 mg mL⁻¹ CTS (in 1.0% HAc) and vigorously stirring for 30 min to get a uniform solution. Then 7.0 μL of the mixture was pipetted onto the surface of CILE and dried to get the modified electrode, which was denoted as CTS-NG-Hb/CILE.

3. Result and discussion

3.1. Characteristics of NG and electrochemical behaviors of NG modified CILE

NG was synthesized by a solvothermal method with the typical TEM image shown in Fig. 1A. It can be seen that NG nanosheets rippled together to form clusters with a dimension of circa 100 nm. The content and bonding status of nitrogen could be analyzed by X-ray diffraction (XPS), which was reported in our previous work [32]. The amount of nitrogen dopant was determined to be 10.5%. Also three types of bonding configurations of nitrogen atoms existed within carbon structures, which were pyridinic, pyrrolic, and quaternary nitrogen. The Raman spectrum of NG was further recorded with the result shown in Fig. 1B. The G band is associated with the doubly degenerated E_{2g} phonon mode at the Brillouin zone center due to the in-plane vibration of the sp² carbon atoms, and the 2D band originates from the second order scattering process [33]. The G band at 1580 cm⁻¹ and the 2D band at 2700 cm⁻¹ were the most prominent features in the Raman spectrum of monolayer GR. In addition, the D band at around 1350 cm⁻¹ was associated with the presence of disorders in atomic arrangement or the edge effect of GR. In contrast to pure GR significant enhancement in the D band for NG can be attributed to defects inside the GR network and functional edges of GR sheets, as well as the incorporation of nitrogen atoms. More information about the synthesis of NG by this solvothermal process could be found in our recent report [30] and the detailed explanations about the formation mechanism were discussed.

Fig. 1C showed cyclic voltammograms of CILE (curve a) and NG/CILE (curve b) in the ferricyanide solution, which was commonly used as the probe for the evaluation of the performances of the modified electrode. On CILE (curve a) a pair of well-defined redox peaks appeared, indicating the good electrochemical performances of CILE. While on NG/CILE (curve b) the redox peak currents greatly increased with the decrease of the peak-to-peak separation (ΔE_p), indicating that better

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