



Application of graphene–copper sulfide nanocomposite modified electrode for electrochemistry and electrocatalysis of hemoglobin



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ABSTRACT

In this paper a graphene (GR) and copper sulfide (CuS) nanocomposite was synthesized by hydrothermal method and used for the electrode modification with a N-butylpyridinium hexafluorophosphate based carbon ionic liquid electrode (CILE) as the substrate electrode. Hemoglobin (Hb) was immobilized on the modified electrode to get a biocompatible sensing platform. UV–vis absorption spectroscopic results confirmed that Hb retained its native secondary structure in the composite. Direct electron transfer of Hb incorporated into the nanocomposite was investigated with a pair of well-defined redox waves appeared on cyclic voltammogram, indicating the realization of direct electrochemistry of Hb on the modified electrode. The results can be ascribed to the presence of GR–CuS nanocomposite on the electrode surface that facilitates the electron transfer rate between the electroactive center of Hb and the electrode. The Hb modified electrode showed excellent electrocatalytic activity to the reduction of trichloroacetic acid in the concentration range from 3.0 to 64.0 mmol L⁻¹ with the detection limit of 0.20 mmol L⁻¹ (3σ). The fabricated biosensor displayed the advantages such as high sensitivity, good reproducibility and long-term stability.

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1. Introduction

Investigation on direct electron transfer (DET) of the redox proteins has attracted much interest in recent years (Armstrong et al., 1988). However, the process is difficult to be realized due to the deeply embedment of the electroactive centers within the protein structures, and the partially denaturalization or the unfavorable orientation of proteins on the surface of electrode (Rusling, 1998; Armstrong and Wilson, 2000). Therefore different kinds of mediators have been used to facilitate the direct electron transfer of redox proteins with the underlying electrode. As a well-characterized redox protein with commercial availability and moderate cost, hemoglobin (Hb) has been extensively studied as the model for the DET of redox proteins. Hb is a heme protein that consists of four polypeptide chains with one heme group at each chain, which can store and transport oxygen in the red blood cells. Direct electrochemistry of Hb have been realized on different kinds of chemically modified electrodes such as biopolymers, surfactants, membranes and nanocomposites (Nadzhafova et al., 2007; Feng et al., 2007; Shi et al., 2007; Ma and Tian, 2010; Sun et al., 2012, 2013a, 2013b).

As a two-dimensional single-atom-thick carbon network, graphene (GR) has been the research focus due to its unique structure and physicochemical properties (Novoselov et al., 2004). GR has exhibited the specific characteristics including extremely electric conductivity, large specific surface area, unusual electronic structure, and upstanding thermal conductivity (Pumera, 2010). Electrochemical applications of GR and its related materials had been reviewed for their excellent electrochemical properties (Chen et al., 2010). Due to the easily aggregation of GR nanosheets by π – π stacking interaction and Van der Waals, various GR composites have been investigated, which can prevent the aggregation of GR nanosheets and exhibit the synergistic effects (Singh et al., 2011). Huang et al. (2012b) reviewed the recent developments of GR based composites and their applications in different fields such as Li-ion batteries, supercapacitors, fuel cells and photovoltaic devices. Among the GR based composite, there are seldom reports about GR–CuS composite. CuS is an important p-type semiconductor with excellent optical, electronic, catalytic and other physicochemical properties, which has been extensively studied for various applications such as photocatalysis, solar cells, electrochemistry, catalyst, super ionic materials and Li-ion batteries (Chung and Sohn, 2002; Wang et al., 2003; Martinson et al., 2009; Zhuge et al., 2009; Basu et al., 2010). Various attempts have been proposed for the synthesis of CuS with different morphologies, such as flower, microsphere and nanotube (Wang et al., 2007; Li et al., 2007; Thongtem et al., 2009). Recently Goel et al. (2014)

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reviewed the synthesis and biomedical applications of CuS nanoparticles from sensors to theranostics. CuS has been proven to exhibit interesting properties including metal-like electrical conductivity, which may have potential application in electrochemical sensors (Mane and Lokhande, 2000; Zhang et al., 2008b). Liu and Xue (2011) prepared a CuS nanotube modified glassy carbon electrode (GCE) for the electrocatalytic oxidation of glucose. Zou et al. (2014) applied a CuS nanocrystal modified GCE for the electrochemical detection of hydroquinone. Yang et al. (2014) fabricated a CuS nanoflower modified GCE for the electrocatalytic sensing of hydrogen peroxide and glucose. Bo et al. (2010) applied a CuS nanoparticles decorated ordered mesoporous carbon modified GCE for the electrocatalytic detection of hydrogen peroxide. By combining GR with CuS to get a composite, GR–CuS nanocomposite has exhibited synergistic effects with intriguing properties. For example, Qian et al. (2014) prepared a CuS nanocrystal/reduced graphene oxide (GO) composite by a one-pot solvothermal reaction and applied to the catalytic investigation on hydrogen peroxide. Park et al. (2013) prepared a CuS–GO/TiO₂ composite for the high photonic effect and photocatalytic activity under visible light. Zhang et al. (2012) developed an environmental friendly strategy toward one-pot synthesis of CuS nanoparticles decorated reduced GO nanocomposite with enhanced photocatalytic performance. However, no references about the application of GR–CuS composite for the protein electrochemistry have been reported until now. The combination of GR with CuS nanomaterials can result in the synergetic effects of two components and exhibit the enhanced performance. GO with high surface area can act as a good matrix for the growth of CuS nanoparticles with excellent dispersion. Also the presence of CuS can prevent the aggregation of single-layer GR nanosheet. The GR–CuS nanocomposite with rough interface can provide sufficient spaces for the immobilization of redox proteins with close interconnection. The higher conductive GR and the excellent electrocatalytic activity of CuS can provide a favorable microenvironment for electrochemical communication, which is suitable for the electrochemical application with fast electron transfer. Therefore the GR–CuS nanocomposite is investigated to elucidate its potential application in direct electrochemistry of redox proteins.

In the paper direct electrochemistry of Hb on GR–CuS nanocomposite modified electrode was realized and investigated in detail by using carbon ionic liquid electrode (CILE) as the substrate electrode. CILE is prepared by using ionic liquid (IL) as the modifier in the traditional carbon paste electrode (CPE). Due to the specific electrochemical characteristics of IL, such as higher ionic conductivity, wider electrochemical windows and lower background, CILE exhibits the advantage including good resistance towards electrode fouling, high electron transfer rate and the inherent catalytic activity (Sun et al., 2007a; Opallo and Lesniewski, 2011). The synergistic effects of CILE and GR–CuS nanocomposite were benefit for the realization of direct electrochemistry of Hb with a pair of well-defined redox peaks appeared. The as-prepared CTS/Hb/GR–CuS/CILE demonstrated excellent electrocatalytic ability to the reduction of trichloroacetic acid (TCA) with wider dynamic range and lower detection limit. Therefore, the GR–CuS nanocomposite modified electrode can be served as a promising platform for the development of electrochemical biosensor with high-efficiency.

2. Experimental

2.1. Reagents

Bovine hemoglobin (Hb, MW. 64500, Sinopharm Chemical Reagent Co., China), 1-butylpyridinium hexafluorophosphate

(BPPF₆, Lanzhou Greenchem ILS. LIPC. CAS., China), graphite powder (particle size 30 μm, Shanghai Colloid Chem. Co., China), chitosan (CTS, Dalian Xindie Ltd. Co., China), trichloroacetic acid (TCA, Tianjin Kemiou Chemical Ltd. Co., China) and graphene oxide (GO, Taiyuan Tanmei Co., China) were used as received. 0.1 mol L⁻¹ phosphate buffer solutions (PBS) with various pH values were used as the supporting electrolyte. All the other chemicals used were of analytical reagent grade and doubly distilled water was used in the experiments.

2.2. Apparatus

All the electrochemical measurements were executed on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument, China). A conventional three-electrode system was used with an Hb modified electrode as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. FT-IR spectra and UV–vis absorption spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA) and a TU-1901 double beam UV–visible spectrophotometer (Beijing General Instrument Ltd. Co., China). Scanning electron microscopy (SEM) was recorded on a JSM-7100F scanning electron microscope (Japan Electron Company, Japan). Raman spectroscopy was performed using a Renishaw InVia Raman microspectrometer (Renishaw Plc., UK) using 514 nm lasers.

2.3. Synthesis of the GR–CuS nanocomposite

1.0 mL of GO suspension (1.0 mg mL⁻¹) and 40.0 mL of ethylene glycol were mixed together, followed by stirring for 30 min. Then 0.001 mol of Cu(NO₃)₂ and 0.001 mol of thiourea were added into as-prepared GO solution with stirring. After being stirred for about 30 min, the reaction solution was transferred to a Teflon-lined stainless-steel autoclave (50 mL capacity) and heated at 120 °C for 4.0 h in an electric oven. After the reaction, the autoclave was allowed to cool to room temperature. The final products were centrifuged, washed with deionized water and absolute ethanol, and then dried at 70 °C for 10 h in air to get the GR–CuS nanocomposite.

2.4. Preparation of the modified electrode

CILE was fabricated according to a reported procedure (Sun et al., 2007b). In brief 3.0 g graphite powder and 1.0 g BPPF₆ were mixed thoroughly in an agate mortar and the homogeneous paste was packed into a cavity of a glass tube (∅=4.0 mm). A copper wire was inserted through the opposite end to establish an electrical contact. Prior to use the electrode was polished on a weighing paper to get a mirror-like surface.

6.0 μL of 0.05 mg mL⁻¹ GR–CuS suspension was directly applied on the CILE surface and left to dry at room temperature. Then 8.0 μL of 15.0 mg mL⁻¹ Hb was cast on the surface of GR–CuS/CILE and dried to get Hb/GR–CuS/CILE. Finally, 5.0 μL of 1.0 mg mL⁻¹ CTS (in 1.0% HAC) solution was spread evenly onto the surface of Hb/GR–CuS/CILE to get the modified electrode as CTS/Hb/GR–CuS/CILE. Other kinds of modified electrodes including CTS/Hb/CILE, CTS/GR–CuS/CILE, CTS/CILE etc. were prepared by the similar procedure and used for comparison.

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