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Biosensors and Bioelectronics

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Enhanced electrochemical sensing of thiols based on cobalt phthalocyanine immobilized on nitrogen-doped graphene

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ARTICLE INFO

Article history:

Received 29 September 2014

Received in revised form

7 November 2014

Accepted 2 December 2014

Available online 3 December 2014

Keywords:

Hybrid electrode

Cobalt phthalocyanine

Nitrogen-doped graphene

Thiol oxidation

ABSTRACT

A hybrid nanocomposite based on cobalt phthalocyanine (CoPc) immobilized on nitrogen-doped graphene (N-G) (N-G/CoPc) has been developed to modify glassy carbon electrode (GCE) for the sensitive detection of thiols. The nanocomposites were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). Cyclic voltammetric studies showed that cobalt phthalocyanine and nitrogen doped graphene have a synergic effect and significantly enhance the electrocatalytic activity of the modified electrode towards thiols oxidation compared with electrodes modified with solely CoPc or N-G. The electrochemical oxidation responses were studied and the reaction mechanisms were discussed. The sensors exhibited a wide linear response range from 1 μM to 16 mM and a low detection limit of 1 μM for the determination of L-cysteine, reduced L-glutathione and 2-mercaptoethanesulfonic acid in alkaline aqueous solution. The proposed N-G/CoPc hybrids contribute to the construction of rapid, convenient and low-cost electrochemical sensors for sensitive detection of thiols.

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1. Introduction

Biological thiols such as L-cysteine, reduced glutathione and 2-mercaptoethane sulfonic acid play crucial roles in many biological processes, including redox homeostasis, cellular growth and catabolism (Chee et al., 2011; Hong et al., 2006; Sies, 1999). As the major intracellular thiols found in mammals, they are indispensable for the structure maintenance of proteins (Obirai and Nyokong, 2007) and can also act as cancer indicator, radioprotective agent, antitoxin, antioxidant and free radical scavenger in the organism (Silva et al., 2013). The detection of thiol-derived substances can be present as contaminants in fuels, used as markers of food deterioration (Griveau et al., 2003), act as indicators of oxidative stress and relevant to clinical diagnosis (Hayes and McLellan, 1999; Pereira-Rodrigues et al., 2007; Stone et al., 2003). Therefore it is significant to develop efficient methods to monitor thiols for clinical applications.

Various analytical methods have been developed for determination of such compounds, such as high-performance liquid chromatography, gas chromatography (GC) and capillary electrophoresis

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(Raouf et al., 2009), with the addition of several detectors, such as fluorescence (Wang et al., 2004), ultraviolet–vis spectroscopy (Katrusiak et al., 2001), mass spectrometry (Tsikas et al., 2000) and electrochemical detector (Inoue and Kirchhoff, 2002). Although the above-mentioned methods can afford thiols detection with high sensitivity and selectivity with little interferences, most of them suffer from difficulties with sample preparation, the necessity of molecules derivatization for GC, limiting their utility in many cases where rapid and accurate determination is required (Chwatko and Bald, 2000; Lima et al., 2008). The instrumental simplicity and portability of electrochemical sensors using chemically modified electrodes could provide sufficient selectivity, high sensitivity and rapid response time (Wang et al., 2011) which benefit from the higher rate of electron transfer from substrates to the electrode. Electrodes modified with graphene oxide (GO) (Yuan et al., 2013b), tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) (Calvo-Marzal et al., 2004), porous nickel oxide (NiO) microflowers (Pang et al., 2012), and ceramic–CNT nanocomposite (CCNNEs) (Gong et al., 2004) have been employed for the determination of thiols. However, many of the reported electrodes showed high overpotential or low detection limit for thiols.

Metal (e.g., Co and Fe) phthalocyanines (MPc), as excellent electrocatalysts, have been extensively employed to electrochemical

oxidation of many important analytes based on their macrocyclic nature including extended π -systems which endowed them the ability to undergo fast redox processes with minimal reorganizational energies (Obirai and Nyokong, 2007; Pereira-Rodrigues et al., 2007; Zagal et al., 2010). For example, electrodes modified with cobalt phthalocyanine (CoPc) complexes by physical adsorption or electropolymerisation have been reported to exhibit a high catalytic activity towards the electro-oxidation of thiols such as L-cysteine, reduced L-glutathione and 2-mercaptoethane sulfonic acid in alkaline aqueous solution (Sehlotho et al., 2008; Silva et al., 2007). Recently, intense efforts have been made to find stable MPC-based materials suitable for thiol detection at lower overpotentials, higher current densities and faster electron transfer rates, and carbon-based electrode materials are good candidates (Hosseini et al., 2014; Porras-Gutiérrez et al., 2013; Silva et al., 2007).

Due to its unique structure and excellent properties, such as large surface area, superior electrical conductivity, ease of functionalization and production, graphene provides an ideal substrate for electronics, electric devices and biosensors. Nitrogen-doped graphene (N-G) can further improve the reactivity and electrocatalytic performance of graphene by forming of a delocalized conjugated system with the sp^2 -hybridized carbon frameworks ascribed to the lone electron pairs of nitrogen atoms. Moreover, N-G provides abundant binding sites for non-covalent functionalization as well as the enhanced biocompatibility and sensitivity in biosensing applications (Qu et al., 2010; Sheng et al., 2011; Tu et al., 2010; Wang et al., 2010). The introduction of organometallic centers such as CoPc to N-G may offer to the electrodes novel electrocatalytic properties due to the excellent catalytic activities of both N-G and CoPc. As a matrix of CoPc molecules, the prominent advantage of N-G is that it could greatly facilitate the electron transfer between the electroactive species and the electrode surface of the N-G supported electrocatalysts.

Herein, we report a facile method to modify glassy carbon (GC) electrode by using unsubstituted cobalt phthalocyanine (CoPc) adsorbed on N-G to fabricate an electrochemical sensor with unique properties for the detection of thiols. The N-G is non-covalently functionalized with CoPc via π - π interaction, and the resulting nanocomposites exhibit the catalytic properties of CoPc without destruction of the electronic properties of N-G (Siswana et al., 2006). TEM, TGA and XPS were employed to confirm the interaction of the two materials. The electrocatalytic activity of N-G/CoPc nanocomposite was evaluated toward the oxidation of three biologically relevant thiols, namely L-cysteine, reduced L-glutathione and 2-mercaptoethane sulfonic acid in alkaline aqueous solution. The proposed hybrid electrodes showed a wide linear range, low detection limit, good reproducibility, and high sensitivity.

2. Material and methods

2.1. Chemicals and solutions

Cobalt phthalocyanine was obtained from Mid-century Chemical Co. (Posen, IL, USA) and used without further purification. Nitrogen doped graphene (3.0–5.0 at% nitrogen), graphene and graphene oxide (99%) were purchased from Nanjing XFNANO Materials Tech Co. (China). Reduced glutathione, L-cysteine and 2-mercaptoethanesulfonic acid were all purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used as received. All other chemicals used were of analytical reagent grade, and the aqueous solutions were prepared with doubly distilled water. 0.1 M NaOH was always employed as the supporting electrolyte, which was deaerated with high purity nitrogen for at least 30 min to remove oxygen prior to the beginning of a series of experiments.

2.2. Instrumentation

Transmission electron microscopy (TEM) measurements were performed on a JEM-2100F transmission electron microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained with a PHI-5000C ESCA system (Perkin Elmer, USA) using 250 W Al K α radiation. Thermogravimetric analysis (TGA) of the sample was performed on a Pyris 1 TGA Instrument (PE, USA). Electrochemical impedance spectroscopic (EIS) measurements were carried out on a PGSTAT 302N system (Metrohm Autolab, Switzerland) in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ over a frequency range of 0.1–10⁵ Hz by applying an AC signal of 5 mV in amplitude throughout the tests. Cyclic voltammetry (CV) and amperometric experiments were performed on a CHI 630B electrochemical workstation (Shanghai, China) with a conventional three-electrode system composed of a modified glassy carbon electrode as a working electrode, a platinum wire as an auxiliary electrode and saturated calomel electrode (SCE) as reference.

2.3. Electrode preparation and modification

Glassy carbon electrodes (GCE) were home made with a diameter of 3.5 mm. The electrode was polished before each experiment with 1, 0.3, and 0.05 μm alumina powder sequentially and then washed ultrasonically in water, ethanol and water for a few minutes, respectively. The cleaned GCE was dried with nitrogen stream for the next modification. To prepare N-G/CoPc composite, NG (5 mg) which was highly dispersed in dimethylformamide (DMF) (5 mL) was successively added to CoPc in DMF (1 mL, 1 mg/mL) and the resulting suspension was ultrasonically dispersed for 1 h. A drop of the suspension of N-G/CoPc in DMF (2.5 μL , 1 mg/mL) was deposited on the top of GCE surface and dried at room temperature to obtain the N-G/CoPc-modified electrode. Similarly, a GO/CoPc-modified GCE and G/CoPc-modified GCE were prepared for comparison. The CoPc-modified GCE and N-G-modified GCE was prepared by casting 2.5 μL of N-G (1 mg/mL) or CoPc (1 mg/mL) suspension which contains the same mass of N-G or CoPc in DMF as the suspension of N-G/CoPc on the GCE surface and dried at room temperature. The experimental parameters above for preparing N-G/CoPc, GO/CoPc, G/CoPc, CoPc, N-G-modified electrodes were all optimized by AC impedance experiments in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl (data not shown) Scheme 1.

3. Results and discussion

3.1. Characterization of N-G/CoPc hybrid nanocomposites

Transmission electron microscopy was employed to characterize the hybrid nanocomposite of CoPc onto N-G. Fig. 1A shows the TEM image of pristine N-G without anchoring. After immobilization (Figs. 1B and S1), CoPc islands with diameters ranged from several to tens of nanometers are distributed on the N-G surface without obvious large-scale aggregation of CoPc, indicating that CoPc molecules are homogeneously dispersed onto the surfaces of N-G.

In order to investigate π - π interactions between CoPc and N-G, and thermal stability of N-G/CoPc complex, TGA was performed under air atmosphere. As shown in Fig. S2, the onset pyrolysis temperature (502.7 °C) of the N-G/CoPc complex is remarkably lower than that of the N-G (610.1 °C). The lower decomposition temperature indicates that the stability of the CoPc molecules anchored on N-G is lower than that of the N-G, that is to say, the internal energy of the N-G increases because of its π - π interactions with the adsorbed CoPc (Wang et al., 2002).

XPS was further employed to determine the elemental composition and bonding character of the N-G/CoPc composite. Fig. 2A

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