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A novel bioelectrochemical sensing platform based on covalently attachment of cobalt phthalocyanine to graphene oxide



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ABSTRACT

Graphene oxide–cobalt phthalocyanine (GO–PcCo) hybrid material as a new electrocatalyst was synthesized and used successfully to fabrication of new biosensor for the electrooxidation of L-cysteine (CSH) in aqueous media. Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM) images revealed that cobalt phthalocyanine is covalently attachment on graphene oxide sheets as single layers GO–PcCo. Cyclic voltammetric studies showed that the GO–PcCo/glassy carbon electrode (GO–PcCo/GCE) improves electrochemical behavior of CSH oxidation, as compared to the GO and PcCo. In addition, the results indicated that GO and PcCo have a synergic effect in the electrooxidation of CSH. The catalytic oxidation responses were studied and the reaction mechanisms were discussed. The electrocatalytic behavior is further developed as a new detection scheme for CSH by chronoamperometry method and under optimized conditions, excellent analytical features, including high sensitivity and selectivity, low detection limit and satisfactory dynamic range, were achieved.

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1. Introduction

Detection of biomolecules at low concentrations is critically important to the early diagnosis and successful treatment of diseases (Claussen et al., 2009; Drummond, 2003; Patolsky et al., 2006). In addition, there have been continuous researches for fabrication of new electrode materials for developing new sensitive and selective electrochemical biosensors for the detection of the trace amounts of biomolecules (Claussen et al., 2009; Drummond, 2003; Patolsky et al., 2006). Cysteine (CSH) is one of the important amino acids and biomolecules that plays an important role in living systems, acting as an active site in biological processes because of the high nucleophilicity of thiol function (Su and Cheng, 2008). Also, CSH has an application in the food, pharmaceutical and medicine industries. Abnormal levels of CSH are related to many diseases, such as slowed growth, Alzheimer's disease and cardiovascular disease (Refsum et al., 1998; Seshadri et al., 2002; Ueland et al., 2004; Wang et al., 2005). Elevated levels of CSH are considered to be associated with cardiovascular disease (van Meurs et al., 2004). Therefore, it is important to develop the simple, rapid and low-cost method for the detection and quantification of CSH in physiological media for academic research and clinic applications. Various chemically modified electrodes (CMEs)

with electrocatalytic properties have been fabricated and applied in the detection of CSH (Chen et al., 2008; Hosseini et al., 2013; Ge et al., 2012; Zhou et al., 2007). The reported CMEs have their advantages and limitations in linear dynamic range, selectivity, sensitivity, detection limit, and other characteristics. So, it is necessary to have further efforts to fabricate simple, low cost, stable, sensitive and selective CMEs that can improve the characteristics of electrocatalytic activity for determination of CSH.

Graphene, the two-dimensional sp^2 -hybridized carbon, is a novel material that has emerged as a rapidly rising star in the field of electrochemistry due to its remarkable physicochemical properties (Chen et al., 2012; Georgakilas et al., 2012). One specific branch of graphene research deals with graphene oxide (GO) and has great potential for providing new approaches and critical improvements in the field of electrochemistry (Chen et al., 2012; Georgakilas et al., 2012). GO-based materials consist of a 2D layered structure with a large surface area and also possess a large number of oxygen-containing functional groups, such as hydroxyl, carboxyl, and epoxy groups. Such properties make it possible to functionalize such GO-based materials using either covalent or noncovalent chemistry in order to modulate the electrode's structural architecture and intrinsic properties (Chen et al., 2012; Georgakilas et al., 2012). These generally exhibit novel, interesting properties and hold promise for design and prepare GO-based electrodes for a wide range of applications in the field of electrochemistry, due to their high electrical conductivity, chemical stability, tunable modification, and multifunctional structures.

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Electrocatalysis lies at the heart of the chemical phenomena that take place at electrochemical interfaces (Markovic, 2013) and represents one of the most important areas for the application of GO-based electrodes in electrochemistry. First of all, GO itself possesses excellent electrocatalytic activities toward some important species (He et al., 2010; Kim, et al., 2010; Lin et al., 2009; Tan et al., 2010; Tang et al., 2009; Wang et al., 2010; Wang et al., 2009a, 2009b; Yang et al., 2010a, 2010b;). Furthermore, the introduction of electrocatalytic centers such as inorganic catalysts to GO may offer GO-based electrodes novel electrocatalytic properties due to the excellent catalytic activities of such GO and electrocatalytic centers. In this case, the GO generally acts as a support for the linking of the inorganic catalysts and it facilitates or mediates the charge/electron transfer between the electroactive species and the electrode surface of the GO supported electrocatalysts and modulates the electrochemical reactions in a controlled fashion. Phthalocyanines (Pc) constitute a remarkably versatile and the best class of compounds with diverse technological applications (Darwent et al., 1982; Leznoff and Lever, 1996). Cobalt phthalocyanines (PcCo) have been used as efficient inorganic electrocatalysts for the construction of new electrode material for the detection of the trace amounts of biologically and environmentally important compounds (Barrera et al., 2006; da Silva et al., 2011). Recently, the graphene modification with the metal phthalocyanines (MPc) has received enormous attention due to their unique properties and few reports were published which describe the synthesis and characterization of metal phthalocyanines (MPc) on graphene. For example, Zhu and co-workers have reported functionalizing the graphene oxide (GO) with zinc phthalocyanine for broadband optical limiting (Zhu et al., 2011). Ragoussi et al. demonstrated that phthalocyanine can be covalently attached to the surface of graphene by photo- and redoxactive linking method (Ragoussi et al., 2012), and Mensing and co-workers prepared graphene-MPc hybrid material by electrolytic exfoliation (Mensing et al., 2012).

Based on the told preface, the covalent attachment of cobalt phthalocyanines (PcCo) to the surface of graphene is a good new strategy used to fabrication of new electrochemical biosensors with unique properties for the detection of biomolecules. Hence, in this work, Graphene oxide-cobalt phthalocyanine hybrid material (GO-PcCo) was synthesized and used successfully as a new electrocatalyst in the fabrication of new electrochemical biosensor for detection of CSH. To the best of our knowledge, this is the first report that the GO covalently with cobalt phthalocyanine (PcCo) was used as a catalyst for the electrooxidation of biomolecules.

2. Materials and methods

2.1. Apparatus and reagents

All chemicals were purchased from Aldrich and used without further purification. FT-IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultra high vacuum. Transmission electron microscopy (TEM) analyzes were performed by a LEO 912AB electron microscope. Ultrasonic bath (EUROSONIC® 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W) was used to disperse materials in solvent. Voltammetric experiments were performed using a μ Autolab Type III electrochemical system. A conventional three-electrode cell consisting of a glassy carbon working electrode (modified and unmodified), a platinum wire counter electrode and a saturated Ag/AgCl reference electrode were used for voltammetric experiments. A digital pH-meter (Ion Analyzer 827, Metrohm) with precision of ± 0.001 was used for pH measurements.

All electrochemical experiments were done at room temperature (25.0 ± 1 °C).

2.2. Preparation of GO

GO was prepared using Hummer's method (Hummers and Offeman, 1958) and is described in Supplementary information.

2.3. Preparation of 2,9,16,23-tetranitro-PcCo

PcCo was synthesized by a template method (Safari et al., 2004; Shaabani, 1998; Shaabani et al., 2007; Shaabani and Rezayan, 2005) and is described in Supplementary information.

2.4. Preparation of 2,9,16,23-tetranitro-PcCo functionalized by 3-(trimethoxysilyl)propane-1-thiol

Under a blanket of nitrogen, 3-(trimethoxysilyl)propane-1-thiol (0.19 g, 1.0 mmol) and PcCo (0.75 g, 1.0 mmol) were dissolved in dry DMSO (5.0 mL). Anhydrous K_2CO_3 (0.20 g, 1.4 mmol) was added to this suspension and the mixture stirred at 80–100 °C. After 48 h the mixture was filtered and dried under vacuum at 25 °C for 24 h (89%). The product was confirmed by FT-IR (Fig. 2S).

2.5. Preparation of GO-PcCo

In a typical run, GO (0.05 g) and DMF (5.0 mL) in a round flask were subjected to ultrasonic pulse for 30 min, and then PcCo functionalized (0.25 g) was added to the solution under nitrogen. The reaction mixture was heated at temperature 80–110 °C for 40 h. For coupling reaction 20 μ L of triethylamine was typically added to the reaction mixture to promote the graft reaction. Then, the mixture was subjected to centrifugation and thoroughly washed with toluene and THF for at least five times. The product was carefully collected and dried under vacuum at 60 °C until constant weight. GO grafted with PcCo was obtained as a black powder and its dispersity in solvents is higher than GO. The procedures for GO-PcCo preparation are shown in Schema 1.

2.6. Preparation of the GO-PcCo/GCE

Prior to the electrode modification process, a glassy carbon electrode (GCE) (2 mm diameter) was washed with deionized water and ethanol after polishing was performed with 0.05 μ m alumina slurry on a polishing cloth. Typically, a stable suspension of GO-PcCo containing 2.0 mg ml^{-1} in DMF using 20 min ultrasonic agitation was prepared. After the electrode surface was air dried, 5.0 μ L of this suspension was cast onto the surface of the pretreated GC electrode with a microsyringe and then it was dried in air. Furthermore, the suspensions of GO and PcCo were prepared and used with the same procedure.

2.7. Analytical procedure

After fabricating each electrode in order to obtain reproducible current-potential curves, cyclic voltammetry was performed at scan rate of 100.0 $mV s^{-1}$ between -0.8 and 1.0 V for 10.0 times in 0.1 M in robinson buffer solution. In addition, the buffer solution was purged with high-purity nitrogen for at least 10.0 min prior to each electrochemical measurement, because CSH can be oxidized by atmospheric oxygen, particularly in basic solutions.

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