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Short communication

Simultaneous voltammetric determination for DA, AA and NO_2^- based on graphene/poly-cyclodextrin/MWCNTs nanocomposite platform

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ABSTRACT

In the present work, graphene sheets (GS) and multiwall carbon nanotubes (MWCNTs) were dispersed in the mixed solution of cyclodextrin (CD) and cyclodextrin prepolymer (pre-CD) and were used as modifier to fabricate chemical modified electrode to simultaneous detect dopamine (DA), ascorbic acid (AA) and nitrite (NO_2^-). CD cross-linked pre-CD (CDP) displays excellent film forming ability, which made the electrode stable. Comparing with CDP–GS, CDP–MWCNTs and CDP–GS–MWCNTs modified electrodes, the CDP–GS–MWCNTs displays higher catalytic activity and selectivity toward the oxidation of DA, AA and NO_2^-, revealing that MWCNTs effectively inhibited the stacking of individual GS and enhanced the utilization of GS based composites. The host–guest chemical reaction ability of CD and π–π stacking interaction between detected molecules and GS–MWCNTs surface were considered as the main reasons of the successfully simultaneous detection of DA, AA and NO_2^-. Cyclic voltammetry (CV), scanning electron microscopy (SEM) and different pulse voltammetry (DPV) were employed to characterize the biosensor. The linear response range for AA, DA and NO_2^- were 5 μM–0.48 mM, 0.15–21.65 μM and 5 μM–6.75 mM, respectively and the detection limits were 1.65 μM, 0.05 μM and 1.65 μM.

1. Introduction

Dopamine (DA) is a neurotransmitter and plays a very important role in the function of central nervous, renal, hormonal and cardiovascular system (Heien et al., 2005). The determination of DA is a subject of great importance for investigating its physiological functions and diagnosing nervous diseases resulting from DA abnormal metabolism, such as epilepsy, senile dementia, Parkinsonism, schizophrenia and HIV infection (Zhou et al., 2010; Ali et al., 2007). However, a major problem of electrochemical detection of DA in real samples is coexistence of many interfering compounds, such as AA and NO_2^-.

Many papers have shown that NO plays a crucial role for intra- and intercellular signally in various tissues. In the central nervous system, NO acts as a neurotransmitter or a neuromodulator (Garthwaite, 1991). Some groups reported that NO enhanced the release of DA, whereas others claimed that NO inhibits DA release (Guevara-Guzmam et al., 1994; Rose et al., 1994). Up to now, the physiological results of NO for DA release in the striatum are controversial. But what is undisputed is that NO can be oxidized to NO_2^- as fast as in a few seconds by reacting with dissolved oxygen in solution and in biological circumstance. From this information we can know that NO_2^- and DA could be coexisted in organisms. AA usually coexists with DA and presents in vivo at concentrations 10^2–10^3 times than DA, and they are oxidized at similar potentials (Alarcon-Angeles et al., 2008). Therefore, it is important to establish simply, rapid and sensitive methods for simultaneous detect DA, AA and NO_2^-. For this purpose, various materials have been employed to modify electrodes, such as nanoparticles, polymers, carbon nanotubes and organic redox mediator (Thiagarajan and Chen, 2007; Nien et al., 2009; Zhang et al., 2005; Palraj Kalimuthu and John, 2009).

Graphene sheets (GS), a two-dimensional (2D) carbon material, have high surface area, superior conductivity and broad potential window (Stankovich et al., 2006; Novoselov et al., 2004; Geim and Novoselov, 2007). Due to its unique properties, graphene has been considered as attractive new material in the design of novel sensors. However, owing to the π–π interaction between individual GS, the GS easily tend to form irreversible agglomerates or even restock to form graphite through Van der waals interactions (Si and Samulski, 2008). Since the aggregated of GS are similar to graphite, the expected performances of GS will lose significantly. In order to improve the solvency and dispersibility of GS, many methods have been reported, such as chemical modification, acid oxidation and non-covalent functionalizations (Sundaram et al., 2008; Bekyarova et al., 2009; Wu et al., 2010). However, these methods are complex, difficult to control or sever which may damage the structure of GS and lose of the intrinsic properties of GS-based materials. Recently, Yang et al. (2010b) reported a new method to reduce the stacking of GS by introducing 1D carbon nanotubes to form a 3D nanohybrid.

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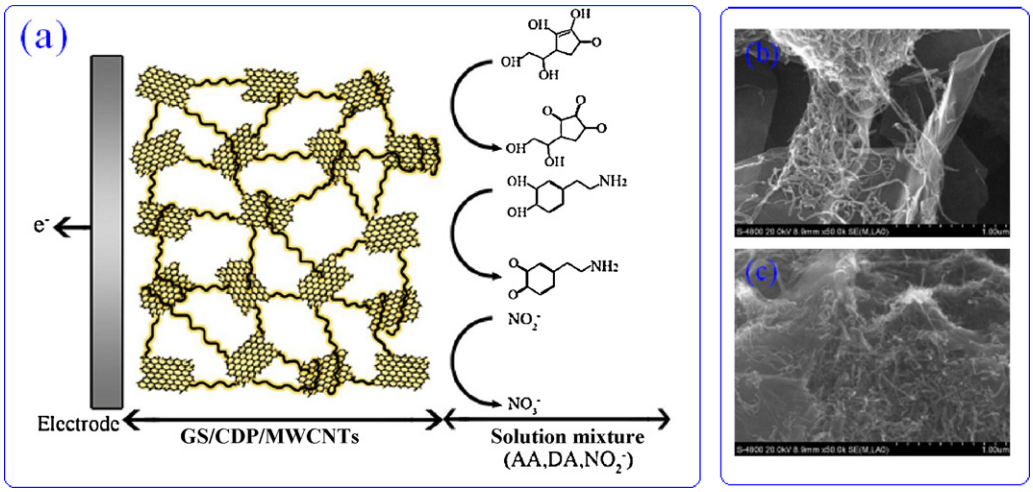

Scheme 1. Schematic representation of the simultaneous electrocatalytic oxidation of AA, DA and NO_2^- by the CDP–GS–MWCNTs modified GCE (a); SEM images of GS/MWCNTs (b) and CDP/GS/MWCNTs (c) nanocomposite.

The long and tortuous MWCNTs bridged adjacent GS and inhibited their aggregation efficiently, which enhanced the utilization of GS-based composites.

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide, consisting of seven glucopyranose unites (Szejtli, 1998). It possesses an electronic and hydrophobic interior microenvironment in its cavity structure, which allows hydrophobic molecules to be easily trapped into its cavity by displacing the water (Breslow and Dong, 1998). And for having a lot of hydroxy groups, the exterior of its cavity is hydrophilic. For these reasons, β-CD has been studied extensively as a model of enzymatic catalysis (Fragoso et al., 2002; Liu et al., 1998), molecular recognition (Ozoemena and Stefan, 2005) and increasing solubility (Badr-Eldin et al., 2008). Alarcon-Angeles et al. (2008) and Tan et al. (2010) have reported using β-CD to detect dopamine (DA) in the presence of ascorbic acid (AA). In their papers, β-CD was adsorbed on the modified electrode physically. Due to the water-solution characteristics of β-CD, these biosensors' stability was not so satisfied. To overcome the problem, water-insoluble polymer is needed. Water-soluble β-CD cross-linked with water-insoluble polymer (pre-CDP) displayed excellent film-forming ability and compared with β-CD modified electrode, the mixture of β-CD and pre-CDP modified electrode more stable (Yang et al., 2010a).

In this work, GS and MWCNTs were dispersed in the mixed solution of β-CD and pre-CDP, and were used as modifiers to fabricate a biosensor to simultaneous detect DA, AA and NO_2^-. The 1D MWCNTs and 2D GS formed a 3D hierarchical structure, and MWCNTs effectively inhibited the stacking of individual GS and enhanced the utilization of GS based composites. β-CD increased the dispersibility and solubility of GS–MWCNTs, and the host–guest recognition of β-CD has high electrochemical sensitivity for the determination of DA and AA. Scheme 1a shows the structure of the modified electrode and explains the electron mediating properties of CDP–GS–MWCNTs nanohybrid film toward the oxidation of AA, DA and NO_2^-.

2. Experimental

2.1. Reagents and materials

MWCNTs (>95% purity) were obtained from Chengdu Organic Chemicals Co. Ltd. of the Chinese Academy of Science and purified by fluxing in concentrated nitric acid for 7 h prior to use. Graphene sheets (GS) were purchased from Chengbo Chemical materials Co. Ltd. (Xian, China). β-Cyclodextrin (β-CD) and epichlorhydrin were obtained from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China). Phosphate buffer solution (PBS) with various pH were prepared by using the stock solution of 0.1 M Na_2HPO_4, 0.1 M NaH_2PO_4, and the supporting electrolyte was 0.1 M KCl. All chemicals used were of analytical grade and were used as received without further purification. Doubly distilled water was used throughout all experiments.

2.2. Apparatus

Electrochemical measurements were carried out using CHI 660D electrochemical workstation (Shanghai CH instruments Co., China). A three-compartment electrochemical cell contained a modified glassy carbon electrode (GCE, Φ = 4 mm) as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The surface morphologies of composites were identified by the scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan). All experiments were carried out at room temperature.

2.3. Preparation of β-CD prepolymer (pre-CDP)

The pre-CDP was prepared according to the literature (Ekberg et al., 1989; Yang et al., 2010b) with slightly modification. Briefly, 10.5 g β-CD was dissolved in 25 mL 35% NaOH, and then 8.5 mL epichlorhydrin was added drop by drop with stirring. The reaction solution was heated to 90 °C for 5 min with stirring. After cooling to room temperature, the pH value was adjusted to 7.0 with 6 mol L^{-1} HCl solution, and then was subjected to dialysis (molecular weight cut-off, 3500). The dialysate was dried at 60 °C under vacuum. Thus the pre-CDP was obtained.

2.4. Fabrication of the biosensor

The GCE was polished subsequently with 0.3 and 0.05 μm alumina slurry, and then sonicated in ethanol and deionized water for several minutes and dried in air. 1 mg GS and 1 mg MWCNTs were dispersed 1 mL of mixed solution of β-CD (1 wt.%) and pre-CD (1 wt.%) by sonicated for 1 h to obtained a stable black suspension. 5 μL of the suspension was dropped on the surface of the GCE to fabricate a biosensor (noted CDP–GS–MWCNTs/GCE). For comparison, CDP–GS/GCE and CDP–MWCNTs/GCE were also prepared by dropping 5 μL CDP–GS and 5 μL CDP–MWCNTs mixed solution on the GCE, and dried in air at room temperature.