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Synergistic combination of cyclodextrin edge-functionalized graphene and multiwall carbon nanotubes as conductive bridges toward enhanced sensing response of supramolecular recognition

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ABSTRACT

Highly conductive 3D interconnected carbon frameworks by synergistically combining β-cyclodextrin (CD) edge-functionalized graphene and multiwall carbon nanotubes (MWCNTs) as conductive bridges have been successfully constructed for rapid and ultrasensitive electrochemical sensing applications. The rationally designed architecture, even though employing trace amounts of CDs firmly located on the edge of graphene, is found to exhibit remarkable stability of structure and sensitive response of bimolecules owing to the incorporation of MWCNTs. Thus, the fabricated electrochemical sensor presents superior simultaneous trace determination of dopamine (DA), uric acid (UA) and tryptophan (Trp) over abundant CDs weakly adsorbed onto graphene surface. Their oxidation peaks could be well separated by cyclic voltammetry and differential pulse voltammetry on the selectively coupled electrode. The oxidation peak currents of DA, UA and Trp display the excellent linear relationships to concentrations, with the detection limits (S/N = 3) of 1.24×10^{-7}, 1.60×10^{-6} and 1.85×10^{-7} M, respectively. For the first time, the enhanced electrochemical performances have been achieved successfully by utilizing trace CDs and relying on synergistic combination of graphene and MWCNTs. Therefore, the synthesis strategy developed here has the more outstanding preponderances than the constantly increasing loading of CDs in controlling electrochemical performance.

1. Introduction

Dopamine (DA), a typical catecholaminergic neurotransmitter, can control mammalian metabolism, cardiovascular system, and central nervous, renal and hormonal functions [1]. Abnormal DA level can be regarded as sensitive indicator of certain pathologic states, e.g., Schizophrenia, Alzheimer and Parkinson's disease, and mental disorders [2,3]. Uric acid (UA) is a primary terminative oxidation product of purine degradation metabolism, which is associated to several diseases such as gout and hyperuricemia. Tryptophan (Trp) is one of the essential amino acids for human and herbivores, and it is also a precursor of the neuro-transmitter serotonin. Usually, these functional biomolecules are coexisted in physiological fluids at different concentration levels. Therefore, it is highly desired to develop sensitive and simultaneous detection approaches for these biomolecules in healthcare, biological analysis, clinical diagnostics and pathological researches.

Compared with spectrophotometric, chromatographic and fluorescence sensing, electroanalytical technique is attracting particular attention owing to its advantages of lower price, rapid response, simplicity, and higher sensitivity [4]. Nevertheless, it is difficult to voltammetrically resolve DA, UA and Trp on conventional bare glassy carbon electrode (GCE) due to their severe overlapping oxidation potential [5,6]. Therefore, the electrode materials must be capable of well separating oxidation peaks of analytes to fulfill the demand of simultaneous determination in early clinical therapeutic diagnosis and neurochemistry research. As a consequence, various sensing materials based on expensive noble metal nanoparticles [7], or carbon nanomaterials [8–11] have recently been designed and applied in electrochemical biosensors [12]. However, noble metal particles have the higher cost, lower stability and possible nanotoxicity in the electrolyte, which severely affect the application and commercialization of the

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biosensors. To develop nonprecious metals or metal-free materials as the biosensors is significant for not destroying the activity of biomolecules.

Carbon nanomaterials, graphene and multi-walls carbon nanotubes (MWCNTs), are mostly used in electrocatalysis owing to their stable physical and chemical properties, large specific surface area, good conductivity, biocompatibility and synergistic effect [7,13]. And, their surface chemistry and functionalization strategies can further provide special impetus and opportunity for developing novel electrode materials [13,14], which prompt us to believe that rational combination of carbon materials as platform with appropriate sensing molecules might generate some novel sensing materials [13].

β-cyclodextrin (CD) is oligosaccharides composed of seven glucose units, which is toroidal in shape with a hydrophobic inner cavity and a hydrophilic exterior. CDs have fascinating supramolecular recognition ability, which can bind selectivity various guest molecules to form stable host-guest complex [15]. Besides, CDs are environmentally friendly, water-soluble, and can improve the solubility and biocompatibility of functional materials [16]. Until now, it has been reported that the composites of CDs and carbon materials (e.g. MWCNTs, graphene) can be formed by van der Waals force, hydrogen-bonding, and hydrophobic interaction, such as CD/MWCNT [17], CD/MWCNT/polyaniline [18], CD/MWCNT/glucose oxidase [19], CD/MWCNT/poly(luminol)/AuNPs [20], CD/MWCNT/poly(N-acetylaniline) [21], CD/graphene [22], CD/graphene/AuNPs [23] and poly-CD/graphene/MWCNT [24]. These electrode materials exhibited good electrochemical response of dopamine in the absence or presence of others biomolecules. It should be noted that these fabricated electrode materials based on weakly noncovalent interactions usually needed employ insulating CDs in large quantity, even accompanying with noble metals. However, much more CDs was embedded into support layers, resulting in decrease of binding sites of CDs, and it is possible that hydrophilic CDs could be detached from hydrophobic surface of carbon materials while washing crude products with various solvents in order to remove hydrazine as reductant. In addition, the conductivity of the reduced graphene prepared from graphene oxide (GO) as precursor is usually lower than pristine graphene theoretically. The introduction of insulating CDs would further decrease the conductivity of the sensing material, which is negative to excellent electrochemical behavior. That is why the sensing materials containing CDs are seldom utilized to simultaneously detect several biomolecules. Until now, the sensing composites with firmly binding trace amounts of CDs are rarely investigated for electrochemical sensing or biosensing applications.

In this work, highly conductive 3D interconnected carbon frameworks by synergistically combining CD edge-functionalized graphene and MWCNTs as conductive bridges have been successfully constructed for rapid and ultrasensitive electrochemical sensing applications. The rationally designed architecture, even though employing trace amounts of CDs firmly located on the edge of graphene, exhibits high stability and superior simultaneous trace determination of DA, UA and Trp in comparison to CD surface-functionalized graphene. The enhanced electrochemical performances strongly demonstrate that highly conductive 3D network has the more outstanding preponderances than the constantly increasing loading of CDs in controlling electrochemical performance. And it should be noted that the simultaneous optimization of the synergetic effects from CDs with host-guest recognition and supports with high conductivity and immobilization is playing a vital role in adjusting electrochemical response. The valuable approach to fabricating extended frameworks would benefit for exploring potential applications in various fields.

2. Experimental

2.1. Materials

NaH_2PO_4 (≥99.0%), Na_2HPO_4 (99%), $K_3Fe(CN)_6$ (≥99.5%), $K_4Fe(CN)_6$ (99%), KCl (99.5%), DA (98%), UA (99%), L-Trp (99%), hydrazine solution (50 wt%), and ammonia solution (25–28 wt%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). DA, UA and Trp solutions were prepared fresh prior to use. Phosphate buffer solutions (PBS) (0.1 M, pH 7.4) were prepared using 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4. Carboxyl-Multi-walled carbon nanotubes (cMWCNTs) were purchased from Boyu High Tech Material Company (Beijing, China). Natural graphite was obtained from Qingdao Zhongtian Company. Nafion solution (5%) was purchased from Alfa Aesar. Other chemicals not mentioned here are of analytical grade and used as received. Doubly distilled

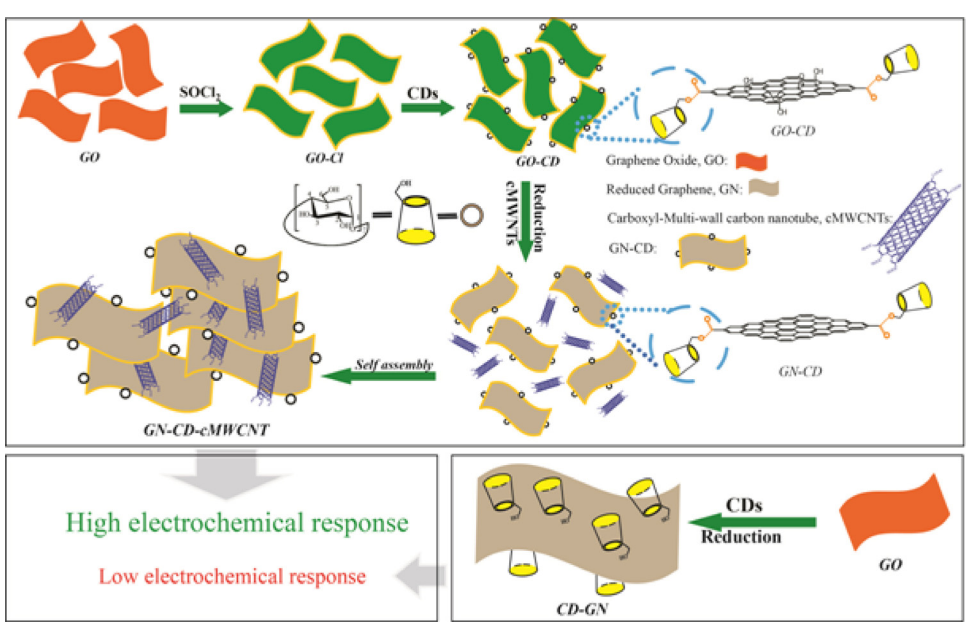

Fig. 1. Illustration of the procedures for fabricating GN-CD-cMWCNT (a) and CD-GN (b).