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Sodium dodecyl benzene sulfonate functionalized graphene for confined electrochemical growth of metal/oxide nanocomposites for sensing application

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ABSTRACT

The electrochemical fructose sensor attracts considerable attention in the food industry and for clinical applications. Here, a novel fructose biosensor was developed based on immobilization of highly dispersed CuO–Cu nanocomposites on Graphene that was non-covalently functionalized by sodium dodecyl benzene sulfonate (SDBS) (denoted briefly as SDBS/GR/CuO–Cu). The structure and morphology of SDBS/GR/CuO–Cu were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemistry and electrocatalysis were evaluated by cyclic voltammetry (CV). The fructose sensing performances were evaluated by chronoamperometry (i–t). Those properties were also compared with that of CuO–Cu. Results revealed the distinctly enhanced sensing properties of SDBS/GR/CuO–Cu towards fructose, showing significantly lowered overpotential of +0.40 V, ultrafast (< 1 s) and ultra-sensitive current response (932 μA M^{-1} cm^{-2}) in a wide linear range of 3–1000 μM, with satisfactory reproducibility and stability. Those could be ascribed to the good electrical conductivity, large specific surface area, high dispersing ability and chemical stability of GR upon being functionalized non-covalently by SDBS, as well as the outstanding cation anchoring ability of SDBS on GR to resist aggregation among Cu-based nanoparticles during electro-reduction. More importantly, an improved selectivity in fructose detection was achieved. SDBS/GR/CuO–Cu is one of the promising electrode materials for electrochemical detection of fructose.

1. Introduction

Fructose, an insulin-independent monosaccharide, is relatively abundant in nature in fruits, vegetables, soft drinks and diabetic foods [1]. Its determination is extremely important for the food industry as well as in clinical and industrial applications. Several analytical methods like fluorometric [2], infrared spectroscopy [3], gas chromatography [4], and so forth have been applied to quantitatively monitor fructose in samples, and most of them are time-consuming and non-cost effective [5]. Simple and rapid detection methods are therefore required. The electrochemical determination method has recently attracted great attention because of its inherent advantages, including sensitivity, speed and miniaturization [6]. The well-known electrochemical biosensors for fructose determination are enzyme based, in which fructose dehydrogenase (FDH) is immobilized on a supporting electrode [7,8]. Fructose biosensing by FDH exhibits excellent selectivity and high sensitivity. However, like other enzyme based biosensors, the chief drawback is that the immobilized FDH easily lose their activity due to complex immobilization procedures and changeable microenvironment such as pH and temperature [9]. Therefore, detection of fructose using enzymeless sensors may be a more attractive strategy. We pioneered the fabrication of an enzyme-free fructose sensor in a previous report [10]. In this work, cobalt oxide-doped copper oxide composite nanofibers (CCNFs) were utilized as the active electrode material to construct a fructose sensor, which exhibited ultrafast and sensitive current response. Further exploring novel nanostructured electrode materials with high catalytic activity and good selectivity to realize direct and sensitive fructose determination still remains at the forefront of research.

Graphene (GR), an atomically thin 2D aromatic sheet composed of sp^2-bonded carbon atoms, is attracting considerable attention in the fields of batteries [11], super capacitors [12], sensors [13], transistors [14] and so forth [15]. Similar to carbon nanotubes (CNTs), the main challenge in the applications of graphene sheets is aggregation through strong π–π stacking and van der Waals interaction [16]. Dispersed graphene can be

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obtained by covalent and non-covalent functionalization approaches [17,18], in which non-covalent modification by DNA [19], and polymers [20], especially surfactants [21], often results in a stable dispersion of GR or CNT in water. And the damage to structure of the non-covalent modification route is negligible, which meets the challenge well. In this functionalization strategy, the surfactants assist the carbon materials dispersing well in aqueous media, because their charged groups (hydrophilic heads) attract to water and their alkyl chains (hydrophobic tails) adsorb on the surfaces of carbon materials [22]. Compared to other commonly employed surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) is an anionic surfactant that can enhance the stability of carbon materials in water [23,24]. The reason is that π-like stacking of the additional benzene rings in SDBS onto the surface of graphite increases the binding and surface coverage of surfactant molecules to graphite [23]. Zeng et al. recently fabricated stable dispersions of GR by heating the mixture of graphite oxide, hydrazine and SDBS, and no sediments were observed for at least two months [25]. Goak et al. and Wenseleers et al. demonstrated respectively that the intrinsic nature (purity and defect density) of CNT as well as amount of surfactants affected the dispersion of CNT in water [22,26]. Further work on developing stable GR dispersion by SDBS functionalization for catalysis and sensor application are still desirable.

Catalyst support plays an important role in the field of batteries [27], super-capacitors [28], direct alcohol fuel cells [29], electro-catalysis and sensing devices [30]. They are a class of materials utilized to load nano-sized functional materials, such as metals [31] and metal oxides [32], based on their unique properties such as high surface area, good mechanical resistance and chemical stability. Among support materials such as titanate [33], mesoporous silicates [34], metal–organic frameworks [35], and Graphene [36], Graphene possesses not only a large surface area and high chemical stability, but also good electrical conductivity. These unique properties render it a promising candidate for electrochemical sensor application. For example, metal/graphene (Au/GR) and metallic oxides/graphene (Co_3O_4/GR) exhibited excellent electrocatalytic activity toward O_2, H_2O_2, glucose and so forth [37,38]. In this study, a very stable GR dispersion was prepared by using the SDBS non-covalent modification strategy, and no sediments were observed for at least six months. The highly dispersed negative charges on SDBS/GR were further used to anchor functional metal cations on the basis of electrostatic self-assembled strategy. Upon electrochemical reduction, highly dispersed metal/oxide nanocatalysts with high electrochemical activity can be anticipated. Here, a SDBS/GR/CuO–Cu nanocomposite was prepared and attempted as the electrode material for fabrication of enzymeless fructose sensor.

2. Experiments

2.1. Reagents

GR was synthesized according to previously reported work [39]. D-Glucose, ascorbic acid (AA), oxalic acid (OA) and sodium dodecyl benzene sulfonate were obtained from Shanghai Co. Fructose, sucrose, maltose, and sodium hydroxide were purchased from Beijing Chemical Plant. Fructose injection was obtained from the first hospital of Jilin University. All chemicals were used as received without further purification. All solutions were prepared with ultrapure water. Fructose solutions were freshly prepared before each experiment.

2.2. Apparatus

The crystal structures of the samples were determined using an X-ray diffractometer (Siemens D5005, Munich, Germany). The morphologies of samples were viewed by SEM (SHIMADZU SSX-550, Japan). All electrochemical measurements were accomplished on a CHI 660A electrochemical workstation (CH instrument, USA). The SDBS/GR/CuO–Cu modified ITO electrode or CuO–Cu modified ITO electrode was used as the working electrode. A platinum wire electrode was applied as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode.

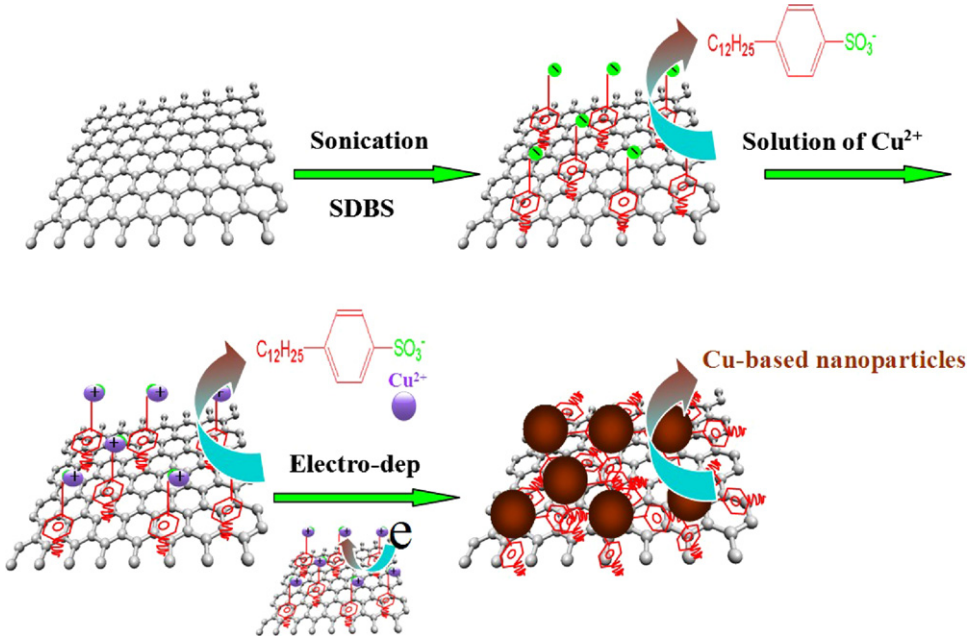

Fig. 1. Schematic representation of the preparation of the SDBS/GR/CuO–Cu nanocomposite film.