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Layer-by-layer chitosan-decorated pristine graphene on screen-printed electrodes by one-step electrodeposition for non-enzymatic hydrogen peroxide sensor

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ABSTRACT

Layer-by-layer chitosan-decorated pristine graphene on screen-printed electrodes was achieved by one-step electrodeposition method and an enzyme-free hydrogen peroxide electrochemical biosensor was fabricated for its application. Negatively charged pristine graphene absorbed with positively charged chitosan by electrostatic interactions was electrodeposited on the electrodes. The successful immobilization of pristine graphene was confirmed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and electrochemical characterizations. The graphene-chitosan volume ratio and cyclic voltammetry scan cycles during the electrodeposition process were optimized. The resulting hydrogen peroxide biosensors showed a 178 times improved sensitivity and exhibited two wide linear detection ranges from 20 μM to 20 mM and from 20 mM to 60 mM. The biosensors also showed a good reproducibility, stability, selectivity and could be used in real samples detection. The superior electrochemical performance of graphene-chitosan was attributed to the preservation of excellent properties of pristine graphene, and the formation of layer-by-layer structure with high surface area. The proposed strategy of direct immobilization of pristine graphene can be extended for the immobilization of other nanomaterials and biomolecules.

1. Introduction

Graphene, one-atom-thick two-dimensional honeycomb crystal lattice of carbon atoms with an sp^2 hybridized structure [1], has been widely used in the fields of electrochemistry, biosensors, fuel cell, supercapacitors and so on, due to its ease of functionalization, fast electron transfer capabilities, large specific surface area, excellent electrical and thermal conductivities. Pristine graphene possesses uniform pi-electron distribution and few defect, showing high conductivity, excellent electron transfer and strong adsorption capacity, thus proved itself a good catalyst support [2]. However, it is difficult to uniformly and effectively immobilize graphene because graphene sheets tend to restack together due to van der Waals [3–5] and strong π-π interaction, thus forming a densely packed layered structure, accompanied by the loss of many unique properties.

The most common technique to immobilize graphene is via the oxidation of graphite to yield graphene oxide (GO) suspension, followed by the reduction of GO to obtain reduced graphene oxide (RGO) through chemical [6], thermal [7] or electrochemical [8] reduction method, and the immobilization of RGO was achieved at the same time. Nevertheless, the unique properties of pristine graphene could not fully restore after the reduction due to the retention of oxidation in RGO [9], although intrinsic defect and electrical insulation of GO have been improved by the reduction to some extent [10]. The conductivity of reduced GO monolayers is approximately 3 orders of magnitude lower than pristine graphene [10]. Hence the effective immobilization method of pristine graphene with preservation of its intrinsic extraordinary conductivity is of great demand.

Chitosan (CS) is a polysaccharide widely used as the matrix for entrapment of biomolecules and nanomaterials due to its excellent film forming ability [11], good adhesion, nontoxicity and biocompatibility. When protonated in slightly acidic solution and positively charged with

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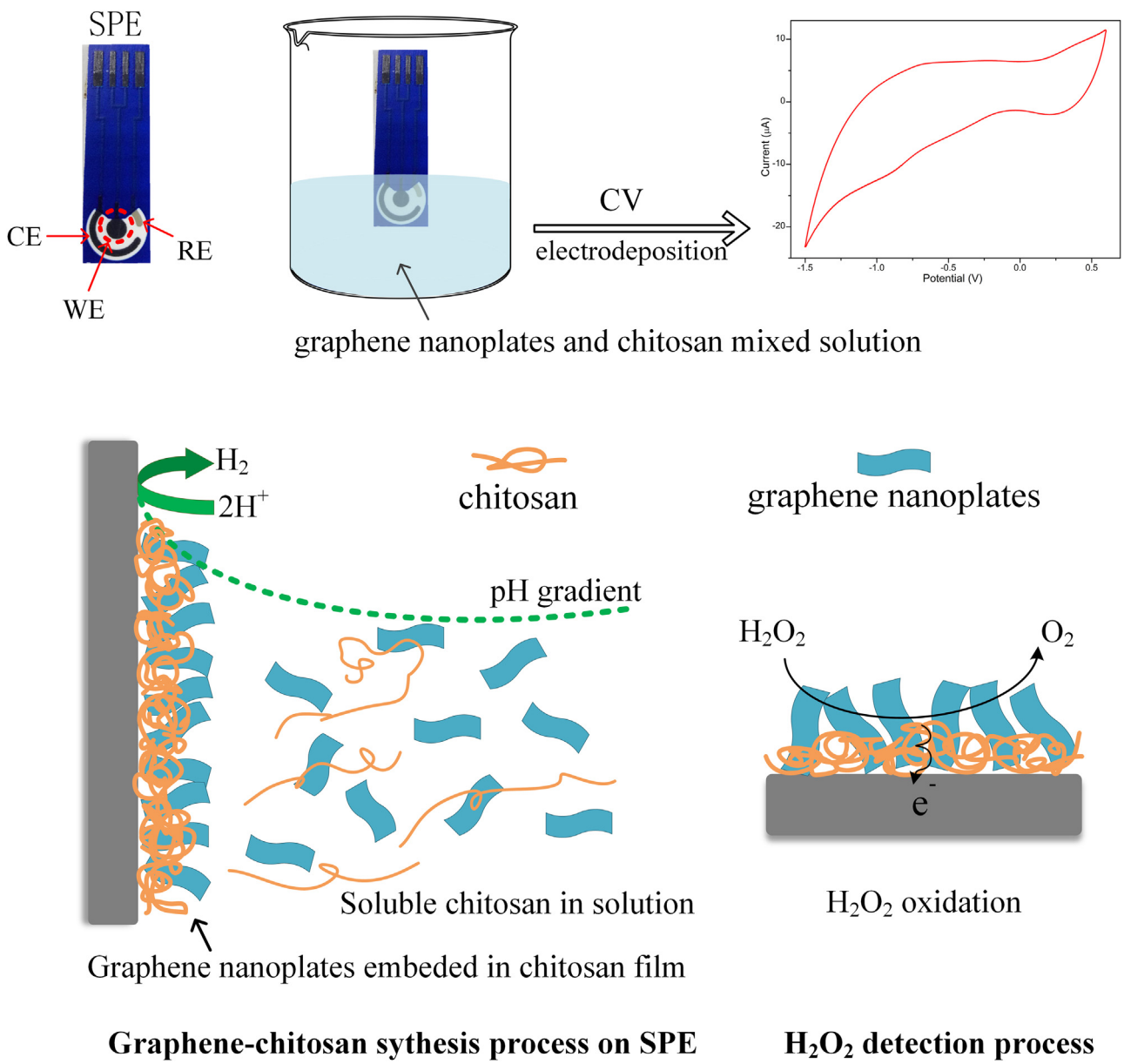

Scheme 1. Schematic illustration of pristine graphene immobilization procedure via one-step cyclic voltammetry electrodeposition method.

-NH3$^+$ groups, chitosan can adhere to negatively charged materials [12] to prevent the aggregation [13] and immobilize them onto the surface of the electrodes. Therefore, a variety of researches [14–16] have integrated chitosan with such materials for the fabrication of electrochemical biosensors to improve biosensor characteristics. However, in these applications, chitosan-containing mixed solution was casting or dropping onto the electrode surfaces. Thus, the thickness of the hybrid film was hardly controllable, leading to a loss of active surface area [17], and the reproducibility of the sensors could not be guaranteed. The electrodeposition method for sensor fabrication has been proved to be an effective solution for such problem as reported previously [18,19].

Compared with traditional fabrication techniques, electrodeposition method has the advantage of convenient operation, reproducibility and controllable thickness of obtained films by altering electrochemical experiment conditions. When the pH does not exceed pK_a of 6.3, many amino groups of CS are protonated, and CS is soluble. Successful electrodeposition of the CS sol-gel film has been achieved through H^+ consuming at the cathode, thus locally pH gradient established and the solubility of CS decreased, eventually resulting in a reproducible and stable CS film on the electrodes [18,20]. Other materials such as carbon nanotubes [21] and Pt nanoparticles [22] can also be immobilized onto the electrode along with CS films during the electrodeposition at the same time. However, studies about one-step co-electrodeposition of pristine graphene nanoplates and chitosan by CV method has not been explored thus far.

Screen-printed electrodes have been extensively used for biosensors owing to its properties, such as low cost, reproducibility, portability and mass production [23–25]. Here, a low-cost, facile and effective method for the direct immobilization of pristine graphene nanoplates on screen-printed electrodes has been proposed for the first time via one-step co-electrodeposition in the graphene and chitosan mixed solution, as depicted in Scheme 1. In order to explore the electrochemical sensor applications of the graphene-chitosan, enzyme-free hydrogen peroxide biosensor was fabricated. The presence of pristine graphene nanoplates provide the excellent catalytic activity for hydrogen peroxide, and positively charged chitosan acts as effective cross-linkage to immobilize negatively charged pristine graphene nanoplates via electrostatic

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