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Multifunctional poly(dopamine)-assisted synthesis of silver nano particles/carbon nanotubes nanocomposite: Toward electrochemical sensing of hydrogen peroxide with enhanced sensitivity

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ABSTRACT

This study describes a facile and effective polymer-assisted route to synthesis of structurally uniform and electrochemically active single-walled carbon nanotubes–poly(dopamine)–silver particles nanocomposite (SWCNTs–PDA–AgNPs). Poly(dopamine) used here serves as a multifunctional molecule for: (1) dispersing SWCNTs into an aqueous system, tethering Ag^+ precursor onto SWCNT surfaces, then (2) reducing Ag^+ to Ag to eventually on-spot grow AgNPs nanoparticles onto SWCNT, and (3) promoting the nanocomposite adhesion ability. The synthetic nanocomposite was found to possess a good electrocatalytic activity toward H_2O_2 reduction by remarkably enhancing the current response and decreasing H_2O_2 reduction over potential at −0.23 V vs. Ag/AgCl, which is positive than most other electrocatalysts for H_2O_2 reduction. The excellent performance of H_2O_2 sensor can be ascribed to the synergy effects of the large surface-to-volume ratio and excellent electrocatalytic properties of SWCNTs and AgNPs, as well as the dispersing ability, reductive properties together with excellent adhesive of PDA.

1. Introduction

Hydrogen peroxide (H_2O_2) is a reactive oxygen species (ROS) from several oxidative metabolic pathways [1–3], and plays an important role in regulating diverse biological processes [4]. Therefore, sensitive and reliable determination of H_2O_2 is highly demanded. Many traditional methods for the determination of H_2O_2 such as chemiluminescence, spectrophotometry etc. [5–7] are complex and time-consuming, while enzyme-based H_2O_2 biosensors require harsh determination environment and expensive preparation and thus limiting its further applicability [8–10]. Hence, the development of nonenzymatic sensors recently has drawn more attention due to their fast response, low-cost and high sensitivity [11,12].

Metal nanoparticles (NPs) have become excellent substitutes of enzymes to catalyze the H_2O_2 as well they have good biocompatibility, high stability and conductivity [13–16]. For instance, silver nanoparticles (AgNPs) have drawn much attention in electrochemical H_2O_2 sensors due to their good biocompatibility and excellent chemical, electrical, and electrocatalytic properties [17,18]. However, the performance of the H_2O_2 sensor depended strongly on the size, shape, matrix and distribution of AgNPs [19,20]. In addition, carbon nanotubes (CNTs) have become attractive over the past years for biosensors fabrication due to their fast electron transfer rate, strong adsorptive ability, high chemical stability, and excellent biocompatibility [21,22]. Especially, the large surface area and high electric conductivity of CNT endow it excellent property to load metal NPs, such as silver NPs to form nano composite with high catalytic activity [23,24]. However, the intrinsic van der Waals interactions between the pristine CNTs make them easily into bundles and limit its further loading ability to metal NPs [25]. Several approaches including noncovalent interactions and covalent sidewall coupling reactions have been developed to disperse CNTs [26,27]. Nevertheless, there is still a challenge to develop CNTs based composite with simplified method, good catalytic activity and high stability.

Poly(dopamine) (PDA), a kind of environment friendly biopolymer, could be adhered on nearly any inorganic and organic surfaces through the formation of strong covalent and noncovalent bonds with surfaces [28]. The good hydrophilicity of PDA make it could effectively improve dispersibility of hydrophobic matrix such as SWCNTs in aqueous solution. Moreover, the most characteristic property of PDA is that it can be used as a versatile platform for secondary reactions [29,30]. For instance, the catechol and

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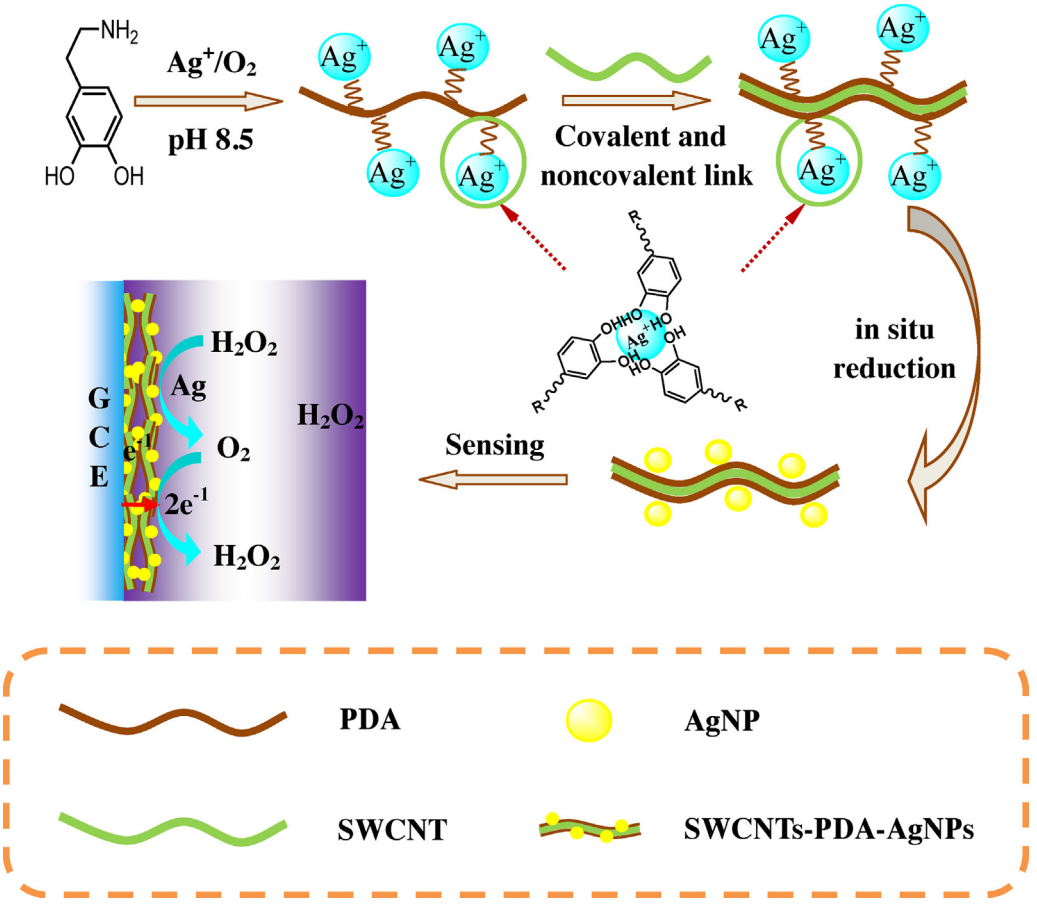

Scheme 1. Schematic illustration of the proposed mechanism of composite growth and catalytic process involved multi-step reactions to hydrogen peroxide reduction.

nitrogen-containing groups in PDA could be exploited to absorb silver ions by metal-binding ability, and the weak reducibility of PDA could reduce silver ions into silver nanoparticles [31]. In such a way, PDA could perform like a binder to integrate SWCNTs and AgNPs tightly and stably, forming a three-in-one nanocomposite with excellent dispersion.

In this work, a novel nonenzymatic sensor with high sensitivity was developed by utilizing PDA as multifunctional intermediate for depositing AgNPs onto SWCNTs. Compared to the non-hybrid SWCNTs or PDA–AgNPs, the as-obtained SWCNTs–PDA–AgNPs exhibited higher electrocatalytic performance toward the electroreduction of H_2O_2. The advantages of the hydrogen peroxide sensor could be ascribed as: (1) SWCNTs can work as effective matrix for AgNPs loading due to large surface area, and improve the conductivity of nanocomposite; (2) AgNPs are uniformly immobilized onto SWCNTs through in situ chemical reduction by PDA, in such a way surface active site for electrochemical catalysis are improved; (3) PDA is a simple, versatile, and effective strategy to disperse SWCNTs and promote nanocomposite adhesion ability.

2. Experimental

2.1. Reagents

The single-walled carbon nanotubes (SWCNTs) used (diameter: 5–20 nm, length: 5–30 μm) were obtained from Dekedaojin Technology Co. Ltd. (Beijing, China). Sodium ascorbate, glucose (GLU), dopamine (DA) hydrochloride, uric acid (UA), 5-hydroxytryptamine (5-HT), tris(hydroxymethyl)aminomethane (Tris) and silver nitrate were all purchased from Sigma and used as supplied. Hydrogen peroxide solution (30 wt%) was purchased from Beijing Chemical Company (Beijing, China). Stock solution of hydrogen peroxide (5 mM) was prepared just before use. Other chemicals were of at least analytical reagent and were used as received. All aqueous solutions were prepared with double distilled water.

2.2. Apparatus and electrodes

The surface morphology and energy Dispersive X-Ray Spectroscopy (EDX) of SWCNTs–PDA–AgNPs nanocomposite was characterized by FE-SEM (SU8010, Hitachi, Japan). FT-IR spectra (Fourier Transform Infrared Spectroscopy) of SWCNTs–PDA and SWCNTs–PDA–AgNPs were performed by (EQUINOX 55, BRUKER, Germany). Electrochemical measurements were carried out with a computer-controlled electrochemical analyzer (CHI 600E, Chenhua, China) and a computer-controlled advanced electrochemical system (Princeton Applied Research (PARSTAT 2273)) in a two-compartment electrochemical cell with a bare or modified GCE (3 mm in diameter) as working electrode, a platinum wire as counter electrode, and an Ag/AgCl electrode (KCl-saturated) as reference electrode. All the electrochemistry experiments were performed at room temperature.

2.3. Preparation of SWCNTs–PDA–AgNPs nanocomposite

The nanocomposite was obtained by quickly mix 0.5 mL of the DA (0.1 mg mL^{-1}, 10 mM Tris, pH 8.5) solution with 0.5 mL of $AgNO_3$ solution (2 mg mL^{-1}), then disperse 2 mg of SWNTs into the mixture by the term of sequentially ultrasonicating the mixture for 10 min. For the SEM characterization, the SWCNTs–PDA–AgNPs