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Hydrothermal preparation of reduced graphene oxide–silver nanocomposite using *Plectranthus amboinicus* leaf extract and its electrochemical performance

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ABSTRACT

Graphene based nanocomposites are receiving increasing attention in many fields such as material chemistry, environmental science and pharmaceutical science. In this study, a facial synthesis of a reduced graphene oxide-silver nanocomposite (RGO-Ag) was carried out from *Plectranthus amboinicus* leaf extract. The synthesized nanocomposite was characterized by using X-ray diffraction, scanning electron microscope, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscope and UV–vis spectroscopy for structural confirmation. The reduction of graphene oxide and silver ions was achieved simultaneously due to the reducibility of the *Plectranthus amboinicus* leaf extract. We further investigated the electrochemical properties of the biosynthesized RGO-Ag nanocomposite. A nonenzymatic H_2O_2 electrochemical sensor was shown to be successfully fabricated by using biosynthesized RGO-Ag nanocomposite. Moreover, the fabricated electrochemical sensor also showed good selectivity.

1. Introduction

Currently biologically assisted synthesis plays a vital role in the fabrication of nanomaterials. The use of environmentally benign materials such as plant extract, fungi and bacteria for generating metal or metal oxide NPs is considered as an eco-friendly approach. For example, Jayaseelan et al. [1] reported the synthesis of ZnO NPs using reproducible bacteria (*Aeromonas hydrophila*), as an eco-friendly reducing and capping agent. Roy et al. demonstrated the synthesis of silver nanoparticles using the extracellular filtrate of the fungal strain, Aspergillus foetidus MTCC8876 [2]. Kannan and Sundrarajan demonstrated the synthesis of yttrium oxide nanoparticles using *Acalypha indica* leaf extract [3]. They also investigated the antibacterial property of biosynthesized Y_2O_3 and showed an increasing rate of antibacterial behavior with pathogens. Moreover, there are many reports on the synthesis of metal, semiconductor, and nanomaterial using aloe vera plant extracts [4–6]. Among them, synthesis of inorganic nanomaterials using a plant mediate reducing agent has been found to be more favorable, due to the low cost and high yield.

Silver nanoparticles have had a substantial impact across a diverse range of fields due to their outstanding electrical, optical, catalytic and antimicrobial properties. There are numerous methods for synthesis of silver nanoparticles; however, those methods always involve utilization of toxic reagents and expensive instruments along with very tedious process control. Thus, the facile synthesis of silver nanoparticles with efficient catalytic activity has significant industrial importance. Many previous researchers have highlighted the facial synthesis of silver nanoparticles. For example, Korbekandi et al. recently proposed a method for biosynthesis of silver nanoparticles using *Quercus brantii* (oak) leaves hydroalcoholic extract [7]. Hassan and co-workers have also synthesized silver nanoparticles using *Althaea officinalis* radix hydroalcoholic extract [8]. Meng et al. demonstrated a biosynthesis of silver nanoparticles using oriental medicinal herb *Gynostemma pentaphyllum* Makino extract [9]. Graphene, a two-dimensional sheet of sp^2 hybridized carbon, have attracted tremendous attention since physicist Geim

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and co-workers isolated in 2004 [10,11]. Graphene-based materials possess extraordinary mechanical strength, large specific surface area and high conductivity. It has showed great promise in improving performance in various electrochemical applications. However, one severe problem that may limit its applications is the hydrophobicity of graphene. Its chemically oxidized form, graphene oxide (GO) is commonly used for as an additive, Incorporation of Ag NPs into graphene sheets is an interesting area to investigate since such systems provide tunable novel properties which can be exploited for different applications. For example, Zhao et al. demonstrated the synthesis of a reduced graphene oxide–silver nanocomposite film for nonenzymatic hydrogen peroxide sensor [12]. Reduced graphene oxide–silver nanoparticle composite was also successfully applied as an effective SERS platform [13]. Very recently, Gurunathan et al. [14] reported the potential anticancer nanotherapy based on the reduced graphene oxide–silver composite, graphene–silver nanocomposite was also applied as catalyst [15] and bactericidal filter [16]. Graphene–Ag nanocomposites are mainly prepared by a deposition and *in situ* synthesis method. In the first method, Ag NPs are deposited on the graphene sheets either by physical adsorption, electrostatic binding or charge transfer interactions. In the second method, nanocomposites are prepared by a single step through the reduction of GO and Ag salts.

Our previous study showed how the leaf extract of *Plectranthus amboinicus* can be successfully used for synthesizing ZnO nanoparticles [17]. In this contribution, we further explored the potential of the nanocomposite using *Plectranthus amboinicus* leaf extract for synthesizing RGO-Ag nanocomposites. *Plectranthus amboinicus* is a tender fleshy perennial plant in the family Lamiaceae with an oregano-like flavor and odor. The plant-synthesized RGO-Ag nanocomposite was subjected to different characterizations, and the electrochemical activity of biosynthesized RGO-Ag nanocomposite was investigated by electrocatalytic detection of H_2O_2.

2. Experimental

2.1. Materials

The preparation of *Plectranthus amboinicus* leaf extract was according to our previous report with small modifications [17]. *Plectranthus amboinicus* plants were purchased from a local nursery of Jiangsu province, China. The plant leaves were cleaned with double distilled water and ethanol. Then, 10 g of *Plectranthus amboinicus* leaves were washed with water and crushed by a shredder. The slurry was then sonicated in 30 mL of water for half hour. The leaf extract was filtered through Whatman No. 1 filter paper and stored in refrigerator for further experiments. $AgNO_3$ and H_2O_2 were purchased from Sigma-Aldrich. Graphene oxide (GO) powder was purchased from JCNANO, INC. Phosphate buffer solution (PBS) was prepared by mixing 0.2 M KH_2PO_4 and K_2HPO_4 solution to appropriate pH. Milli-Q water (18.2 MΩ cm) was used throughout the experiments.

2.2. Biosynthesis of RGO-Ag nanocomposite

An aqueous 50 mg $AgNO_3$ was added into 15 mL GO water dispersion (1 mg/mL). The mixture was kept under continuous stirring for 5 h. Then 15 mL *Plectranthus amboinicus* leaf extract was added to above dispersion. The mixture was transferred into 50 mL steel autoclave. The steel autoclave was sealed, maintained at 120 °C for 12 h and then cooled naturally to the room temperature. The mixture was centrifuged and washed copiously with water for several times and then dried in a vacuum desiccator.

2.3. Characterization of the synthesized RGO-Ag nanocomposite

The crystal phase information of sample was characterized from 10° to 80° in 2θ by a XRD with Cu Kα (λ = 0.1546 nm) radiation (D8-Advanced, Bruker). The optical analysis was obtained by UV–vis spectrophotometer (Perkin Elmer Lambda 950). Raman spectroscopy was performed at room temperature using a Raman Microprobe (Renishaw RM1000) with 514 nm laser light. High-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM-2100 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. The surface functional groups present on the samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet iS5, Thermo Scientific).

2.4. Electrochemical detection of H_2O_2

A glassy carbon electrode (GCE) was polished by 0.3 and 0.05 μm alumina slurry followed by thoroughly rinsing with ethanol and water. For the electrode surface modification, 6 μL of as-prepared RGO-Ag nanocomposite dispersion (1 mg/mL) was dropped onto the GCE surface and dried at room temperature. All electrochemical measurements were performed on a CHI430a electrochemical workstation (USA) at room temperature. A conventional three electrode system containing a modified GCE as working electrode, a platinum wire as auxiliary electrode and an Ag/AgCl (3 M KCl) electrode as reference electrode was used throughout the electrochemical experiments.

3. Results and discussion

The reduction of GO and $AgNO_3$ after hydrothermal treatment can be visually observed. After hydrothermal reaction, the color of GO-$AgNO_3$ dispersion changed from brown-yellow to black. The corresponding UV–vis absorption spectrum of RGO-Ag nanocomposite is recorded in Fig. 1A. In order to confirm the reduction of GO, the spectrum of GO was recorded as well. As shown in Fig. 1A, the spectrum of GO displays a characteristic absorption peak at 233 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the C=C bonds. In contrast, the RGO-Ag nanocomposite shows a peak at 267 nm corresponding to the excitation of π–plasmon of graphitic bond [18]. This red-shift suggests the reduction of GO by *Plectranthus amboinicus* leaf extract under hydrothermal conditions. In addition, an absorption peak located at 391 nm was observed in the spectrum of the RGO-Ag nanocomposite, corresponding to the surface plasmon resonance absorption of Ag nanoparticles. The reduction of GO by *Plectranthus amboinicus* leaf extract was also confirmed by Raman spectroscopy. As shown in Fig. 1B, the spectrum of GO shows two characteristic peaks at 1577 and 1331 cm^{-1}, corresponding to the graphite (G band, first-order scattering of E_{2g} phonons by sp^2 carbon atoms) and diamondoid (D band, breathing mode of κ-point photons of A_{1g} symmetry) bands, respectively [19]. The intensity ratio between two bands (I_D/I_G) increases from 0.89 to 1.08 after reduction by the *Plectranthus amboinicus* leaf extract under hydrothermal conditions, which results in the decreasing of average size of sp^2 domains by reduction of GO [20].The formation process of RGO-Ag nanocomposite using *Plectranthus amboinicus* leaf extract under hydrothermal condition can be described as follows: positively charged Ag ions were firstly adsorbed on the negatively charged GO surface though electrostatic interaction. The nucleation of Ag seeds was then achieved with the addition of *Plectranthus amboinicus* leaf extract. The growth rate of Ag crystal and GO reduction process were accelerated hydrothermally consequently forming a RGO-Ag nanocomposite.