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Biomolecule-assisted synthesis of Ag/reduced graphene oxide nanocomposite with excellent electrocatalytic and antibacterial performance

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ABSTRACT

In this work, an environmentally friendly method was applied for the synthesis of aqueous suspension of L-cysteine modified Ag nanoparticles (NPs)-decorated reduced graphene oxide (rGO) nanocomposite. L-cysteine played a triple role as reducing agent, stabilizer and linker of Ag NPs onto the surface of rGO. The resultant nanocomposite was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction studies (XRD), zeta potential, Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDX). Meanwhile, minimum inhibitory concentration (MIC), minimum bacterial concentration (MBC), agar well diffusion and cyclic voltammetry (CV) techniques were used for the investigation of antibacterial and electrocatalytic behaviors of the nanocomposite, respectively. The obtained nanocomposite showed not only enhanced electrocatalytic activity for glucose but also excellent antibacterial activity against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*).

1. Introduction

Recently, numerous efforts have been made in the synthesis of graphene nanocomposites with inorganic nanoparticles (NPs), especially noble metal NPs [1]. Graphene, a single-atom-tick two-dimensional graphitic carbon, has attracted significance due to its electronic, electrical, mechanical properties, high compatibility with living cells and various applications [1,2]. In general, graphene-nanoparticles composites can exist into two types either the nanoparticles decorated on graphene sheets or nanoparticles surface coated with graphene [2,3]. These nanocomposites mainly can be prepared by combining graphene or its derivatives (graphene oxide (GO) and reduced graphene oxide (rGO)) with nanoparticles [3,4].

Among noble metal NPs, Ag NPs have attracted attention due to their potential applications in antibacterial, electronic equipment's, sensors and biosensors [5–7]. These nanoparticles have been particularly interesting because of their unique and unusual properties such as high biocompatibility, electrical, antibacterial and optical properties [8].

The recent studies have demonstrated that the combination of Ag NPs with graphene show additional unique physicochemical properties compared to individual use of materials [4]. These nanocomposites not only display the individual properties of the Ag NPs and GO but also exhibit additional advantages and synergistic properties. For instance, by the loading of Ag NPs on graphene surfaces, the electronic conduction enhanced through the modification of the local electronic structure and resulted nanocomposite showed improved performance as catalyst [9,10]. Because of the synergistic effect between Ag NPs and graphene and the enhanced properties, Ag NPs based graphene nanocomposites offer high potential for various applications including sensors, biosensors, antibacterial and use in biomedical fields and pharmaceuticals [11,12]. Ag-graphene nanocomposites are usually synthesized through in situ reduction of silver salts on reduced graphene oxide (rGO) or loading of synthesized Ag NPs on the surface of rGO [13]. In the preparation of Ag-graphene nanocomposites, toxic reducing agents such as hydrazine (N_2H_4) and sodium borohydride ($NaBH_4$) are commonly used [13]. But, resent studies have showed that green methods using plants extracts or biomolecules (e.g. amino acids) as reducing and stabilizing agent are simple, fast and environmental friendly methods [14–18]. In green method, the use and generation of hazardous materials are minimized and high temperature or harsh reducing agents are not used [15,19]. Resultant nanocomposites based on green methods make them attractive in biological applications such as antibacterial activity, surface enhanced Raman spectroscopy (SERS), cell viability and electrochemical activity [14,19–21].

Amino acids having functional groups can act as modifier and reducing agent in the preparation of metal-graphene oxide nanocomposites. Yang and coworkers synthesized silver-graphene oxide

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nanocomposites through a green one-pot method in the presence of tryptophan as a reducing and stabilizing agent [21]. The synthesized Ag-GO nanocomposites showed excellent surface-enhanced Raman scattering (SERS) activity in detection of crystal violet in aqueous media [21]. Our research group also synthesized a suspension of rGO/Ag nanocomposite based on glycine modified Ag NPs via an environmentally, mild method and then investigated its electroactivity [22].

Among the amino acids, L-cysteine (Cys) has attracted attention because of its multifunctional groups (—SH, —NH_2, and —COO^-), which can interact with Ag NPs surface via the formation of covalent Ag—S, Ag—N, Ag—O bonds and increase the colloidal stability of resultant nanoparticles [23–26]. Podstawka and coworkers synthesized Ag NPs in the presence Cys molecules and proved that interaction of Cys with the Ag NPs is via the —NH_2, —CS and carboxylate groups [24]. Ravindrance et al. showed the sensor application of Cys modified Ag NPs to recognize Cr^{2+} ion [25]. Jiang et al. demonstrated a two–photon sensing strategy for detection of mercury ions with Cys functionalized Ag [26]. Cys having SH and NH_2 groups can reduce and modify GO sheets. Muralikrishna and coworkers synthesized reduced and modified GO (rMGO) in the presence of Cys and then used it for simultaneous electrochemical determination of some ions [27]. Zhang and coworkers prepared CuS/rGO nanocomposites with enhanced photocatalytic performance in the presence of Cys [28]. Furthermore, thiol-functions of Cys could react with the outer cell surface and improve absorptive endocytosis [29], as well as could increase the electroactivity of graphene sheets [30]. To the best of our knowledge, there is a gap in scientific literatures regarding the synthesis of metal-graphene nanocomposites in the presence of cysteine. Therefore, in this research, rGO/Ag nanocomposite was synthesized based on Cys modified Ag (MAg) NPs; which Cys played a triple role including: stabilizer of Ag NPs, modifier and reducer of GO. rGO/MAg biocompatible nanocomposite with high colloidal stability was synthesized in room temperature without using any further reducer and then characterized by UV–vis, XRD, Raman, Zeta potential and SEM-EDX. Meanwhile, antibacterial and electrocatalytic behaviors of resulted nanocomposite were investigated by the minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC), agar well diffusion and cyclic voltammetry (CV) methods, respectively.

2. Experimental

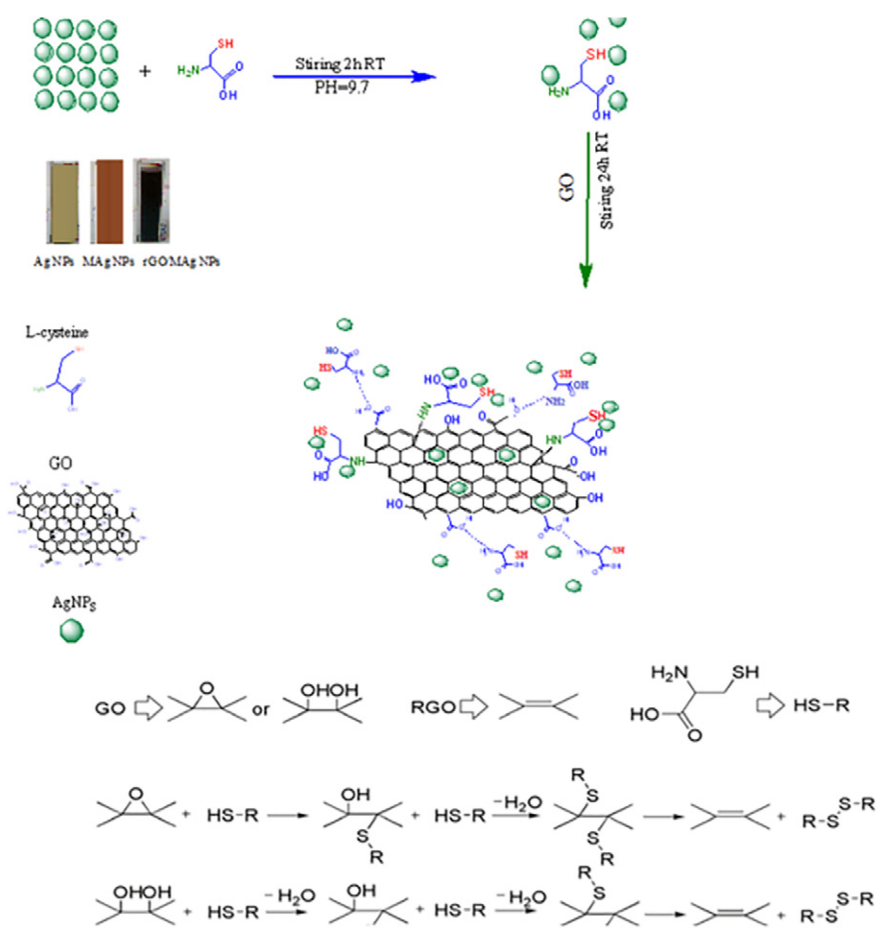
2.1. Materials

Silver nitrate ($AgNO_3$), trisodium citrate, graphite, L-cysteine (Cys), potassium permanganate ($KMnO_4$, 98%), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl), phosphoric acid (H_3PO_4, 98%), hydrogen peroxide (H_2O_2, 30%) and glucose were obtained from Merck Chemical Co. All chemicals used in this experimental were of analytical grade, and used as received. Deionized water was used during the sample preparation.

2.2. Experimental procedures

2.2.1. Synthesis of Cys modified Ag NPs (MAg NPs)

The citrate-stabilized Ag NPs were prepared according to the Zhou's method [31]. In brief, $AgNO_3$ solution (20 ml, 1 mM) was heated to boiling point and then sodium citrate solution (20 ml, 5 mM) was added drop wise to the mixture reaction (Ag:citrate molar ratio was 1:5).



Scheme 1. Schematic diagram of the preparation of the rGO/MAg nanocomposite.