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Research paper

Synthesis and Characterization of a Silver Nanoparticles-Reduced Graphene Oxide Nanohybrid by using 'Zingiber Officinale' Extract as a Reducing and Stabilizing Agent

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Abstract

An eco-friendly solution-based chemical approach has been used to prepare silver nanoparticles-reduced graphene oxide (AgNPs-rGO) nanohybrid using *Zingiber officinale* extract as a reducing and stabilizing agent. The products form a stable aqueous solution without any surfactant stabilizers and hence makes it possible to produce AgNPs-rGO nanohybrid on a large scale using low-cost solution processing technique. The nanohybrid was monitored at different concentration of GO solution (0.1 mg/ml, 0.5 mg/ml and 1.0 mg/ml) and characterized using UV- visible (UV-Vis) absorption spectrum, transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy analyses. From the UV-Vis analysis, the formation of silver nanoparticles (AgNPs) was confirmed and showed a surface plasmon resonance (SPR) absorption band at 420 nm for nanohybrids with GO concentration of 0.5 mg/ml. Raman spectra shows an increase in I_D/I_G ratio for rGO with values of 1.007 corresponding to the concentration of GO (0.5mg/ml) as compared to GO (0.88). Completely spherical Ag nanoparticles (NPs) were found at a nanohybrid with 0.5 mg/ml of GO with an average particle size of 20 nm. The AgNPs-rGO(0.5) nanohybrid exhibit fast electron-transfer kinetics for electrochemical reaction of Fe $(CN)_6^{3-/4-}$ redox couple, suggesting the potential applications for electrocatalysis and electrochemical sensor.

Keywords: *Use about five key words or phrases in alphabetical order, Separated by Semicolon.*

1. Introduction

Graphene is known as a thin layer of pure carbon in the structure of a plane of sp^2 bonded into a two-dimensional honeycomb lattice. Graphene has unique properties such as large surface area (~2600m^2/g), high thermal conductivity (3000Wm/K), excellent charge carrier mobility (10,000cm^2/Vs) and great mechanical properties (1 TPa) [1]. Graphene oxide (GO), an oxygenated, hydrophilic layered carbon material, has also received a great deal of attention amongst researchers due to its light-weight, large surface area, easy availability in bulk quantity, low cost preparation, good water-dispersibility and readily functionalized by chemical reaction for many applications [2]. GO can also be used to stabilize the growth of metal nanoparticles and inhibits their aggregation. However, in some cases, the use of GO is challenging due to its tendency to aggregate and processing difficulty [3]. Therefore, an efficient approach to the production of surface-functionalized graphene sheets in large quantities has been a major focus of numerous researchers, with the goal of exploiting the most frequently proposed application of graphene in the areas of sensor application [4].

Most widely used metal in nanotechnology are silver (Ag), gold (Au) and platinum (Pt) [5]. Silver are exceptionally preferred because of their affordability, low cost and superior electrochemical properties such as greater chemical stability, large specific surface area, strong adsorption ability, good electrical conductivity, ease of functionalization and good biocompatibility [6]. Silver nanoparticles (AgNPs) has been greatly used in antimicrobial applications, nanomedicine, biosensor materials, composite fibers, cryogenic superconducting materials, cosmetic products, and electronic components [7,8]. The deposition of AgNPs on a graphene surface is possible because a graphene derivative sheet is a highly versatile two-dimensional conducting support material and possesses excellent physicochemical properties such as large theoretical surface area with high conductivity at room temperature, and a wide electrochemical window. Due to the presence of surface functional groups and high conductivity with huge surface area, graphene derivative serves as a support material for growing AgNPs which is highly beneficial for high performance electrocatalytic applications [9]. Additionally, AgNPs can be utilized as catalysts in various oxidation reactions. Therefore, incorporation of AgNPs in graphene for synthesis of nanohybrids provides strategies for manufacturing innovative materials that combine the merits of silver and graphene in a synergistic effect [10]. The synthesis and stabilized process of metal-graphene nanohybrid is usually done via physical and chemical approach: the chemical approach includes chemical reduction and electrochemical techniques. Today there is developing need to create an ecology friendly process of synthesis of nanoparticles that does not utilize any toxic and harmful chemicals. It is a novelty to use plants instead of chemicals in synthesis of nanoparticles which provides advancement over chemical and physical method as it is low cost, environmentally friendly, easily scaled up for large scale synthesis and in this method, there is no need to use high pressure, energy, temperature and toxic chemicals [11]. This green approach has opened up a new era of safe nanotechnology by using biological resources such as lemon juice [12], honey [13], Salacia chinensis [14] and jatropha curcas [15]. Herein, is reported an eco-friendly approach for high conductivity silver nanoparticles-

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reduced graphene oxide (AgNPs-rGO) nanohybrid by using ginger extract. The ginger extract served as reducing and capping agents for the formation of AgNPs. TEM image of AgNPs-rGO nanohybrid revealed the uniform distribution of AgNPs on rGO sheets with an average size of 20 nm.

2. Experimental Section

2.1. Materials

Graphite flakes (3061, Asbury Graphite Mill Inc.), silver nitrate ($AgNO_3$) (98%), potassium permanganate ($KMnO_4$) (98%) and sodium nitrite ($NaNO_2$) were purchased from R&M Chemicals. Ammonia solution ($NH_3.H_2O$, 25%) was received from Riedel-de Haen (www.riedeldehaen.com). Monosodium phosphate (NaH_2PO_4), disodium phosphate (Na_2HPO_4), sulphuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2, 30%) were obtained from Systerm (www.haiou saintifik.com). All the chemicals were used as received without further purification.

2.2 Preparation of Ginger Extract

The fresh ginger (*Zingiber Officinale*) was peeled and rinsed with deionized water to remove dirt. 5 g of ginger was cut into small pieces and pulverized with a mortar and pestle. Then, the mashed ginger was homogenized in 50 ml distilled water and was left for 30 minutes. The extract was then squeezed in a muslin cloth and filtered using the Whatman filter paper to isolate the solid ginger pieces. The liquid part was centrifuged at 10000 rpm for 10 minutes and was stored at 4℃ for further use.

2.3 Synthesis of Ag-rGO Nanohybrid

GO was prepared by following a simplified Hummer's method [16]. The AgNPs-rGO nanohybrid was synthesized as follows. The aqueous solutions of GO (0.1, 0.5, 1.0 mg/ml), ginger extract and $[Ag(NH_3)_2]^+$ solution were mixed together and were exposed to sunlight for 3 hours. First, the 0.1 M of $[Ag(NH_3)_2]^+$ solution was prepared by mixing 100 ml of 0.1 M of $AgNO_3$ solution with 200 mL of 0.1 M aqueous NH_3 solution. For the synthesis of AgNPs-rGO nanohybrid, 1 ml of GO (0.1mg/ml) and 20 ml of 0.1 M $[Ag(NH_3)_2]^+$ solutions were mixed together in a beaker and stirred for a few minutes. Then, 2 ml of ginger extract was added under stirring to the mixture. The same procedures were repeated to prepare the nanohybrid with different concentrations of GO (0.1, 0.5 and 1.0 mg/ml). Finally, the solution was centrifuged at 14000 rpm for 15 min and the precipitate was washed for five times with distilled water. The final product was dispersed in 50 ml of deionized water and used for further studies. The AgNPs-rGO nanohybrid prepared with (0.1, 0.5 and 1.0 mg/ml) concentrations of GO are presented as AgNPs-rGO (0.1), AgNPs-rGO (0.5) and AgNPs-rGO (1.0).

2.4 Characterization techniques

UV–visible absorption spectrum of AgNPs-rGO nanohybrid was recorded on a Thermo scientific Evolution 300 instrument. Fourier transform infrared spectra (FTIR) of the nanohybrid was recorded on a Perkin-Elmer FTIR spectroscopy model 1725X and the Raman spectra was measured using a Reinshaw in Via Raman microscope with green laser excitation (532 nm line of a He–Ne laser as the excitation source). X-ray diffraction (XRD) pattern was obtained with a D5000, Siemens instrument using copper Kα radiation (λ=1.5418 Å) at a scan rate of 0.02° s^{-1}. Transmission electron microscopy (TEM) analysis was performed with a JEOL JEM-2100F instrument operated at 200 kV. Electrochemical characterization was carried out using a PAR-Versa STAT- 3 Electrochemical Workstation.

3. Results and Discussion

3.1. UV-Visible Spectroscopy Analysis

The formation of AgNPs on the rGO sheet was primarily confirmed by UV–vis absorption spectroscopy (Figure 1). The GO solution displayed a maximum absorption peak at 230 nm (Figure 1(inset)) which was due to the π-π* transition of the atomic C-C bonds and a small shoulder peak at 300 nm is attributed to n- π* transitions of the C-O group in sp^2 hybrid region of GO [17]. The sample of AgNPs-rGO (0.5) nanohybrid showed a surface plasmon resonance (SPR) absorption band of Ag NPs at 256 nm and 420 nm. The peak at 256 nm is due to restoration of π conjugated networks whereas the peak at 420 nm is the SPR absorption band of Ag-NPs which indicates the formation of AgNPs [18]. The SPR band of AgNPs-rGO (1.0) nanohybrid showed a peak at 436 nm. Meanwhile, at a concentration 0.1 mg/ml of GO, the nanohybrid displayed a slightly flat and broad absorption band of AgNPs with two peaks at around 343 nm and 466 nm, which indicates that the formation of AgNPs have a different shape other than spherical particles. This broad absorption may have been due to the formation of poly-dispersed and/or aggregated Ag NPs. At a concentration of GO of 0.1 mg/ml, the reduction of GO does not occur. This may be caused by insufficient GO that has interacted with the reduction agent and $[Ag(NH_3)_2]^+$ complex. The $[Ag(NH_3)_2]^+$ complex easily interacted with GO surface through physisorption and electrostatic binding. The initial formation of $[Ag(NH_3)_2]^+$ complex protected the fast reduction of silver ions and thereby, controlled the growth of AgNPs. It is known that neutral nucleophiles and neutral stabilizing polymers have strong influence on the SPR band of Ag and/or metal nanoparticles and donate the electron density to the particles via lone pairs of electrons. Visible color changes in the nanohybrids at different concentration of GO solution indicate changes in the aggregation state or size and the shape of the AgNPs. The above phenomena confirmed the reduction of GO along with the formation of Ag nanoparticles.

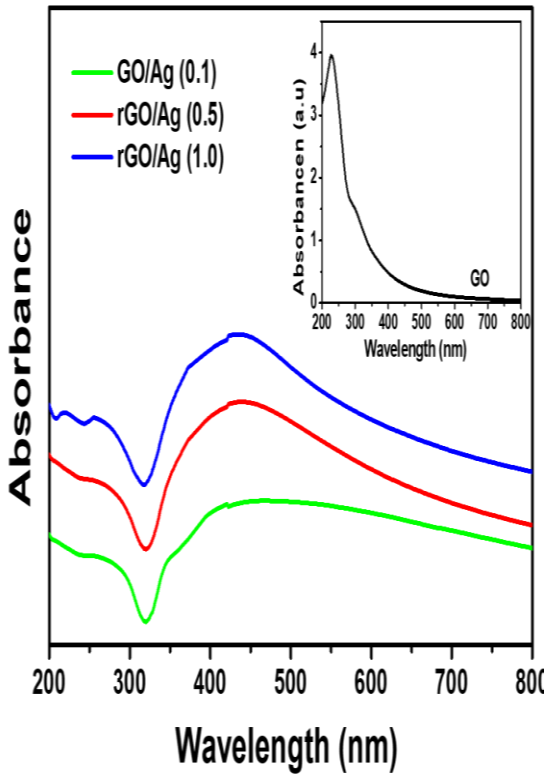

Fig. 1: UV-visible absorption spectra obtained for Ag-rGO and Ag-GO nanohybrid solution prepared with different concentration of GO (a: 1.0 mg/ml, b: 0.5mg/ml and c: 0.1/mg/ml). Inset shows a UV- visible absorption spectrum of GO solution.

3.2. X-Ray Diffraction (XRD) Analysis

AgNPs-rGO nanohybrid prepared with different concentrations of GO were studied using XRD analysis (Figure 2). The XRD pattern of the GO showed a characteristic diffraction peak of C (0 0 1) at 10.5° (inset of Figure 2) [19]. The diffraction peak of C (0 0 2) appeared at 26.6° indicates the reduction of GO. The three diffraction peaks corresponding to the (1 1 1), (2 0 0) and (2 2 0) crystalline planes of Ag are present at 37.78°, 44.22° and 64.38° respectively [20]. The increase in intensity of AgNPs diffraction peak at Ag (1 1 1) plane could be credited to the increase in the concentration of the nanoparticles over the rGO. The peak intensity increased with respect to the concentration of GO, which suggested an increased reduction of GO with increasing concentration of GO. As can be seen in Figure 2, no obvious diffraction peaks corresponding to the planes of Ag for nanohybrid that was using concentration of GO 0.1 mg/ml were observed. The reason may be the content of graphene oxide is relatively lower.

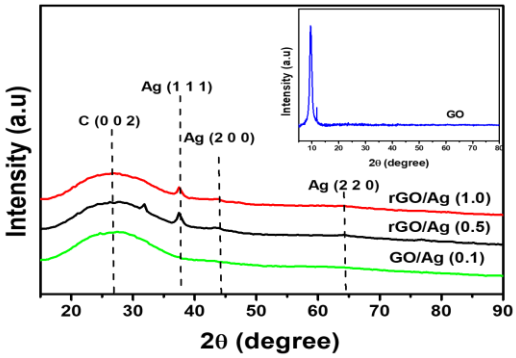

Fig. 2: XRD patterns of GO (a) and Ag-rGO nanohybrids prepared with different concentration of GO (0.1, 0.5, and 1.0). Inset: XRD pattern of GO sheet.

3.3. Raman Spectrum Analysis

The reduction of GO could be indicated from the typical peaks of GO in the Raman spectra analysis (Figure 3). The two prominent peaks observed in Raman spectrum of GO displayed a G band at around 1600 cm^{-1} and a D band at around 1350^{-1}, corresponding to the E_{2g} phonon of C sp^2 atoms and a breathing mode of k-point phonons of A_{1g} symmetry respectively. The intensity ratio of the D and G bands (I_D/I_G) is related to the amount of disorder or the size of the sp^2 domains due to reduction. In most reports, there is an increase in I_D/I_G ratio for rGO as compared to GO [18]. According to Figure 3, the value of I_D/I_G is about 0.895 for GO. During the formation of the AgNPs-rGO nanohybrid, the G and D bands of GO changed in band intensity with the intensity ratios (I_D/I_G) of 0.983, 1.003 and 1.007 corresponding to the concentration of GO (0.1, 0.5 and 1.0) respectively. Ag-rGO (1.0) recorded the highest value of (I_D/I_G) which is 1.007. The increase in the ID/IG intensity with increase in concentration of GO suggested the decreased size of in-plane sp^2 domains during the reduction of GO to rGO.

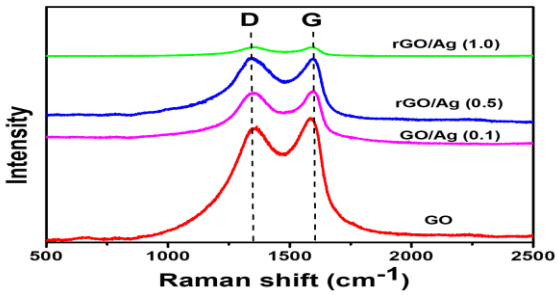

Fig. 3: Raman spectra of GO and Ag-rGO nanohybrid with different concentration of GO.

3.4. Transmission Electron Microscopy Analysis

The morphology of the AgNPs deposited on rGO sheets for AgNPs-rGO (0.5) nanohybrid was analysed by TEM studies. From the images, it can be seen that the AgNPs are deposited on rGO sheet and they are uniformly distributed (Figure 4). Almost all the NPs are seen on the rGO surface and it shows that the AgNPs-rGO (0.5) nanohybrid was facilely formed by the proposed synthetic method. The shape of Ag NPs is spherical (inset of Figure 4) with an average size of 20 nm.

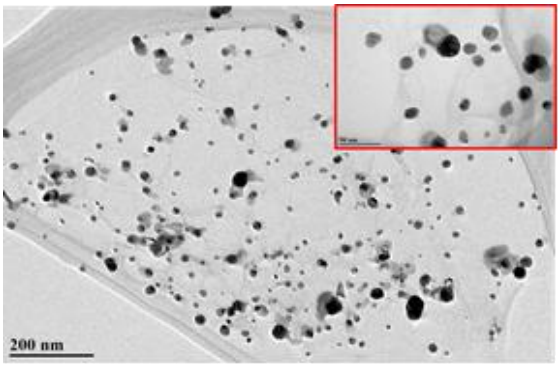

Fig. 4: TEM image of GO–Ag nanohybrid. Inset: Image at higher magnification.

3.5. Electrochemical behavior of AgNPs-rGO nanohybrid -modified electrode

The redox behavior of the $[Fe(CN)_6]^{3-/4-}$ couple was used to study the kinetic barrier of the modified electrode solution interface. The bare GCE showed reversible voltammetric characteristic of one electron redox process of $[Fe(CN)_6]^{3-/4-}$ couple with a peak-to-peak separation of 65 mV (Figure 5 (a)). After modification with GO, the GCE lost its reversible voltammetric behavior because of the non-conducting nature of the GO matrix (Fig. 5(b)). However, the reversibility was retained after modification with the rGO-Ag nanochybrid because of the high conductivity of Ag and the presence of rGO (Fig. 5(c–e)). The AgNPs-rGO (0.5) nanohybrid showed higher redox peak currents compared to the AgNPs-rGO (0.1 and 1.0) nanohybrid. This observation indicates that the AgNPs-rGO (0.5) nanohybrid acted as a new surface on the GCE and exhibited good electrical contact with the underlying electrode surface.

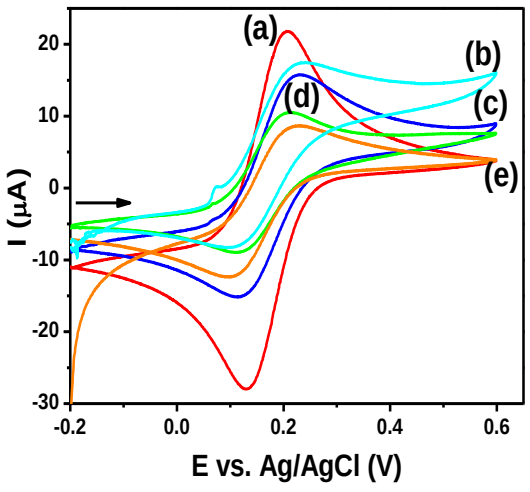

Fig. 5: Cyclic voltammograms obtained for bare GCE (a), GO (b), AgNPs-rGO (0.1 mg/ml) (c), AgNPs-rGO (0.5 mg/ml) (d) and AgNPs-rGO (1.0 mg/ml) (e) nanohybrid for 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at a scan rate of 50 mV s^{-1}.

4. Conclusion

An eco-friendly synthetic method was proposed for the preparation of AgNPs-rGO nanohybrid using ginger extract and sunlight irradiation. The nanohybrid was successfully characterized by UV–vis absorption spectroscopy, TEM, XRD, FTIR and Raman analyses. From the UV-Vis analysis, the formation of AgNPs was confirmed and showed a surface plasmon resonance (SPR) absorption band at 420 nm for nanohybrids with GO concentration of 0.5 mg/ml. Completely spherical AgNPs were found for nanohybrid with 0.5 mg/ml of GO with an average particle size of 20 nm.

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