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Novel Graphene-Gold Hybrid Nanostructures Constructed via Sulfur Modified Graphene: Preparation and Characterization by Surface and Electrochemical Techniques

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ABSTRACT

A novel and uniform graphene nanosheet-gold nanoparticles (GNs-AuNPs) hybrid has been fabricated from sulfur-modified graphene nanosheets (S-GNs) impregnated with $HAuCl_4$ as Au precursor. Physicochemical and morphological characteristics of the GNs-AuNPs hybrids were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), surface Raman spectroscopy (SRS), and high resolution transmission electron microscopy (HRTEM). The results of the XRD and HRTEM demonstrated well dispersed Au nanoparticles on GNs with an average particle size of less than 10 nm and a narrow size distribution of 6 to 8 nm. A film of GNs-AuNPs hybrid was constructed on a glassy carbon electrode (GCE) through layer-by-layer (LBL) assembly of 4-aminothiphenol (ATP) on GCE, and then, transferring the hybrid to the sulfur function of ATP to form GCE-ATP-GNs-AuNPs modified surface. Application of the GNs-AuNPs hybrid in electrochemical biosensing was demonstrated by immobilization of glucose oxidase (GOx) as a model on the surface of GCE-ATP-GNs-AuNPs, and then, using it for sensing of glucose. The biosensor exhibited a wide linear response range, from 1.0 to 12.0 mM and 0.1 to 8.0 mM glucose, with a detection limit of 9.3 and 4.1 μM and high sensitivity, 47.6 $\mu A\, mM^{-1}\, cm^{-2}$ and 45.0 $k\Omega/\log(C_{glucose}/mM)$ obtained by voltammetry and electrochemical impedance spectroscopy (EIS), respectively. According to the results obtained by analysis of the EIS experimental data, the source of enhanced activity was found to be originated from the *synergistic effect* of GNs and AuNPs, the *role of ATP* mediating assembling of GNs-AuNPs hybrid on GCE, and the increase in the *surface roughness*. This work opens up a new and facile way for direct preparation of metal nanoparticles embedded in GNs, which will enable exciting opportunities in advanced applications based on graphene-metal hybrids like electrocatalysis for energy conversion and highly sensitive modifier films for electrochemical sensors and biosensors.

1. Introduction

Graphene nanosheets (GNs), a novel generation of carbon-based nanosheets with a sp^2 hybrid carbon network, has inspired much theoretical and experimental application compared to other carbon materials due to its exceptional electronic, optical, high charge mobility and large surface area properties [1,2–6]. These carbon nanosheets have been exhibited as the foundation for various technologies such as nanoelectronic [7], fuel cell [8], hydrogen storage [9], batteries [10], nanosensors, and nanomeidicine [11,12,13]. The GNs can play an important role in improving the biosensor properties due to its large specific area and excellent electron transfer [14,15,16]. However, due to some inherent disadvantages, such as its chemical inertness and easy aggregation in aqueous solution, the application of GNs has been limited [17,18]. Therefore, the production of a homogeneous suspension of individual GNs in aqueous solution is important in application of GNs [14,19,20]. Chemical modification is one the most common and widely used way to introduce the spacers to GNs and improve their solubility or dispersibility [15,21].

To explore application potential of graphene-based sensors and biosensor, robust methods for producing, modification and functionalization of GNs surface with metal nanoparticles are of great important [22,23], Metal nanoparticle-graphene hybrids have attracted much attention in recent years due to their great promise in various applications [9,24], Among graphene-based hybrid materials, graphene nanosheet-gold nanoparticles (GNs-AuNPs) hybrids are the most interesting studied subjects [25,26]. Attachment of catalytic nanoparticles, such as gold and platinum, could further increase the electrocatalytic activity of these nanosheets [27,28]. In addition, decorating by metal nanoparticles increases the distance

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between the GNs and inhibits adhesion of the resulting GNs in dry state [29]. However, due to hydrophobic nature, pristine GNs do not provide enough anchoring sites for decorating metal nanoparticles.

There are many imaginative methods for decorating metal nanoparticles onto GNs, each offering varying degrees of control of particle size and distribution. However, most of these methods use of organic linker (spacers) [30–32]. Typically, in-situ reduction of gold salt on graphene oxide has been employed to obtain GNs-AuNPs hybrids [33]. Dharuman have used a poly (amidoamine) dendrimer as a linker for adhesion of AuNPs to fabricate label free electrochemical DNA hybridization sensor [34].

Still, there are some significant challenges in synthesis and develop of graphene-based hybrid materials [35–37]. For example: (i) Controlling the uniformity of metal nanoparticle decorating the GNs surface, in particular, the strength of the attachment between the organic and the inorganic nanostructure. (ii) Finding appropriate conditions for modification of the flat and rigid structure of GNs. The harsh conditions, usually used to overcome the high-energy barriers associated with intralayer conjugating and interlayer van der-Waals force, can be destructive for reactants. On contrary, if moderate reaction conditions are used, the yield of the reactions is usually low. (iii) Covalent functionalization generally changes the hybridization of GNs carbon atoms from sp^2 to sp^3 which disrupts the band-to-band transitions of π electrons and causes loss of the desired properties of GNs, such as their high mobility of electron and remarkable mechanical properties [38,39]. Therefore, it is important to modify the surface of GNs by proper techniques, enabling to control distribution and density of the metal nanoparticles on the substrate, and also avoid deterioration of the electronic network of GNs [40].

The GNs surface can be modified by covalent attachment of functional groups or non-covalent adsorption of functional molecules onto the surface. Yang et al. found that non-covalently functionalized CNT surfaces interact strongly with Pt nanoparticles through the formation of Pt-S bonds, resulting in very high Pt nanoparticle loadings, with both good dispersion and a narrow size distribution [41]. Wang et al. have recently shown that elemental sulfur-graphene composites can be prepared through heating a mixture of GNs and elemental sulfur. They used the synthesized composite as cathode for lithium-sulfur batteries [42]. Nazar prepared sulfur-graphene composites with sulfur as high as 87 wt% using a simple one pot, scalable method [43].

Another challenge is a control over orientation and three-dimensional distribution of metal nanoparticle-graphene hybrids, which is a necessity and of prime importance for many applications [36]. To addresses this problem, layer-by-layer (LBL) assembly which is simple, efficient and allowing precise control over the structure and thickness of the films in nanoscale, has been followed [35,44].

Here, we present, for the first time direct thiolation of GNs by physically mixing elemental sulfur with GNs to synthesize highly dispersed AuNPs with narrow size distribution on GNs. The modification is based on sulfur impregnation of GNs from toluene solution followed by a melt-coat step. The AuNPs are supported on the GNs by the wet impregnation-thermal reduction method. Morphological characteristics of GNs-AuNPs hybrids are investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, surface Raman spectroscopy (SRS), X-ray photoelectron spectroscopy (XPS), and high resolution transmission electron microscopy (HRTEM). Then, a simple strategy is proposed for construction of GNs-AuNPs hybrids assembly on glassy carbon electrode (GCE) surface by electrografting process via ATP based on LBL method to get GCE-ATP-GNs-AuNPs.

A combination of analytical methods including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) is used to completely characterize the electrocatalytic properties of GCE-ATP-GNs-AuNPs modified surface for reduction of oxygen, where excellent electrocatalytic activity was observed. To further demonstrate the electrocatalytic efficiency and applicability of the modified surface, the glucose oxidase (GOx) was used as a model, immobilized on the GCE-ATP-GNs-AuNPs and successfully tested for recognition of glucose in the presence oxygen.

2. Experimental

2.1. Material and Reagents

Graphite powder, $HAuCl_4{\cdot}3H_2O$, 4-Aminothiophenol (ATP), elemental sulfur, Glucose oxidase (GOx), (from Aspergillus Niger 20,000 units/g, EC 1.1.3.4) and other chemicals were of analytical grade obtained from commercial sources (Sigma® or Merck®), and used without further purification. All solutions were prepared with double-distilled water. Stoke solutions of glucose (10 mM) were prepared in 0.1 M PBS, pH 7.4, and stored overnight at 4 °C before use. Additionally, about 0.5 mg of GNs-AuNPs hybrid was dispersed in 1 mL ethanol:water mixture (3:7, v:v) and kept at room temperature.

2.2. Synthesis of GNs-AuNPs Hybrid

Graphene oxide (GO) was synthesized by the modified Hummers method (see Supporting Information, Section S1) [45]. The chemical reduction of GO to GNs was accomplished by mixing 70 mL of 0.1 mg/mL GO with 6.8 μL of hydrazine hydrate (25%, v:v) and 140 μL of 29% ammonia solution, shaking vigorously the mixture for 30 min, and then, heating the mixture over an oil bath at 92 °C for 1 h. Finally, the solution was centrifuged, wash with water, and dried at 60 °C in oven under vacuum conditions to separate the GNs [46,47].

The S-GNs with different S/GNs wt. ratio (0.15, 0.3, 0.45 and 0.6) were prepared by a solvent impregnation and melt-coat method. For example; for preparation the S/GNs wt. ratio of 0.45, a 10.8 mg sample of elemental sulfur was ultrasonically dissolved in 3.0 mL toluene solvent and then 24 mg of GNs was added. The mixture was sonicated for 1 h to break aggregates and disperse the GNs. Then, the solvent was evaporated at room temperature and the sample was ground thoroughly in an agate mortar. The mixture was held at 155 °C for 6 h to allow the melted elemental sulfur to diffuse into the GNs.

The S-GNs were impregnated with Au(III) by ultrasonically dispersing the sample in 2 mL methanol solution containing 10 mg $HAuCl_4{\cdot}3H_2O$ to afford 20 wt.% Au on GNs, and then, the solvent was evaporated at room temperature. The resulting mixture was transferred into a quartz tube and heated under a flow of H_2/Ar (10% H_2) to reduce the Au ions and remove the excess of sulfur content. The heating was carried out by ramping the from room temperature to 350 °C (10 °C min^{-1}) and holding at 350 °C for 3 hm [48].

2.3. Preparation of GCE-ATP-GNs-AuNPs

The GCE (0.03 cm^2) was polished with 1, 0.3, and 0.05 μm alumina powder sequentially, and then, washed ultrasonically in ethanol and water for a few minutes, respectively. Mercaptophenyl diazonium cation was generated based on Belanger method with a little modification [49]. The modification of GCE with ATP was conducted with *in-situ* generated aryl diazonium cation based on electrochemical reduction of corresponding aniline function of ATP in acidic media. Typically, 20 μmol of ATP predissolved in methanol, was transferred into 10 mL of 0.5 M HCl solution, and mixed with 20 μmol sodium nitrite ($NaNO_2$) dissolved in 10 mL of double-distilled water. The mixture was degassed with Ar gas and left