



Site-selective immobilization of gold nanoparticles on graphene sheets and its electrochemical properties



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ABSTRACT

The site-selective attachment of metal nanoparticles (NPs) on graphene surface is highly desirable for various applications such as electrochemical sensors and catalysts. Here, we present a simple and effective synthetic approach for the site-selective immobilization of gold NPs (AuNPs) on either basal planes or edges of graphene sheets. The basic principle of this approach is to use cysteamine linker with reactive amine and thiol functional groups at each end, where the amine groups at one end covalently bind to functional groups presented on edges and/or basal planes of chemically synthesized graphene sheets, and the thiol groups at the other end assemble onto pre-synthesized AuNPs through thiol-Au interaction. Due to the difference in the spatial distribution of functional groups presented on graphene oxide (GO) and reduced graphene oxide (rGO) sheets, most of AuNPs are homogeneously immobilized on the basal planes of the cysteamine-functionalized graphene oxide (GO-SH) sheets, whereas AuNPs are selectively attached at the edge parts of the cysteamine-functionalized reduced graphene oxide (rGO-SH) sheets. Raman signals of GO-SH/Au hybrid films with the high content of AuNPs in the hybrids are clearly increased owing to the formation of the charge-transfer complex between AuNPs and GO-SH sheets, exhibiting surface-enhanced Raman scattering (SERS) activity. Furthermore, rGO-SH/Au hybrids enhance the electrochemical activity of modified glassy carbon electrodes owing to the synergetic effects of electrical conduction by the restored aromatic structure of rGO sheets and percolated network of AuNPs along the graphene edges

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1. Introduction

Graphene, a monolayer of aromatic carbon lattice, has attracted tremendous attention in recent years due to its extraordinary electrical, optical, thermal, mechanical properties and huge specific surface area [1–6]. Current methods for preparing graphene sheets include micromechanical exfoliation of graphite, chemical vapor deposition, oxidation/reduction protocol, and epitaxial growth on electrically insulating surface [7–10]. Among these methods, oxidative exfoliation of natural graphite by acid treatment and subsequent chemical reduction has been considered as one of the most efficient methods for the low-cost, large-scale production of graphene sheets. Graphene oxide (GO), an oxidized derivative of graphene generated by this method, has various oxygen-containing functional groups such as epoxide, alcohol, and carboxylic acids

[11], which provides GO with excellent aqueous dispersity and allows further chemical modification using well-developed carbon surface chemistry [12,13]. Owing to such advantages, GO nanosheets have been emerging as promising atomic-scale substrate for the design of new graphene-based hybrid nanomaterials [14]. For example, it has been shown that, when decorated with metal nanoparticles (NPs), the intrinsic properties of graphene can be finely tuned for applying to various applications, such as catalyst, energy generation and storage, optoelectronics, and sensors [15–17].

For the past decades, gold NP (AuNP) has been studied extensively due to its fascinating plasmonic and catalytic properties, which can be tailored by controlling size, shape, surface covering, and assembly of the nanoparticles [18,19]. To date, two main strategies have been proposed for preparing graphene-AuNP hybrid nanostructures: (1) In situ synthesis and assembly of AuNPs on graphene sheets [20,21] and (2) self-assembly of pre-synthesized AuNPs onto functionalized graphene sheets [22,23]. Although the former has been recognized as a simple and efficient method, in situ

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chemical reduction of Au precursors in the presence of GO often results in a lack of fine control of particle size and uniformity [24]. On the other hand, the latter self-assembly method provides an easy control of size, uniformity and density of NPs attached on the graphene plane, wherein chemical linkers such as organic molecules, DNA, or proteins allow binding of AuNPs on the surface of graphene sheets through different driving forces [25–28]. However, only few studies have reported on the ‘self-assembly sites’ of AuNPs on the graphene surface despite its critical importance in controlling the catalytic and electrochemical properties of graphene-AuNP hybrid materials.

In this paper, we present a simple and effective approach for the site-selective immobilization of AuNPs on either basal planes or edges of graphene sheets. The basic principle of this approach is to use cysteamine linker with reactive amine and thiol functional groups at each end, where the amine groups at one end covalently bind to functional groups presented on edges and/or basal planes of chemically synthesized graphene sheets, and the thiol groups at the other end assemble onto the AuNPs through thiol-Au interaction [29]. With this method, we selectively immobilize the pre-synthesized AuNPs onto the basal planes of functionalized graphene oxide sheets and the edges of functionalized reduced graphene oxide (rGO) sheets, which are synthesized by chemical reduction under carefully controlled conditions and subsequent amidation reaction with cysteamine. Furthermore, we demonstrate the enhanced surface-enhanced Raman scattering (SERS) and electrocatalytic activity of graphene-AuNP hybrid materials produced by our site-selective self-assembly method.

2. Experimental

2.1. Synthesis of AuNPs

All reagents were purchased from Sigma Aldrich and were used without further purification. AuNPs were prepared according to the literature [30]. Briefly, 1 mL of 1 wt% HAuCl₄·3H₂O was added to 90 mL of deionized water, and the mixture was stirred for 1 min. Subsequently, 2 mL of 38.8 mM sodium citrate was added, and the reaction mixture was stirred for another minute. Finally, 1 mL of fresh 0.075 wt% NaBH₄ in 38.8 mM sodium citrate was added, and the colloidal solution was stirred for 5 min.

2.2. Synthesis of GO

Graphite flake was oxidized by a modified Hummers method. In the pretreatment step that ensures complete oxidation, potassium persulfate (10 g) and phosphorus pentoxide (10 g) were added in sulfuric acid (50 mL) at 80 °C and stirred until the mixture was dissolved to prepare the oxidation solution. After graphite flake (12 g) was added to the oxidation solution and stirred at 80 °C for 4 h, the solution is diluted with 1.2 L of deionized (DI) water, stirred overnight, and filtered using ester cellulose membrane (Millipore, 0.2 μm pore size). The filtered mixture was washed with water to remove the oxidizing agents and dried in a vacuum oven.

Pretreated graphite (4 g), phosphorus pentoxide (58 g), and potassium manganate (24 g) were added to a solution of sulfuric acid (480 mL) and DI water (80 mL), and then, the mixed solution was stirred slowly for 12 h. After the solution was sonicated in a bath-type sonicator (Hwashin Instrument, Power Sonic 410) for 1 h, 35 wt% hydrogen peroxide (15 mL) and DI water (600 mL) were added to the solution. Thereafter, the mixed solution was stirred vigorously at room temperature and sonicated for 2 h once a day during 1 week. To dissolve nonreacted potassium manganate

solid, 30% hydrogen chloride (300 mL) and ethanol (300 mL) were added to the reaction mixture. The filtered mixture was centrifuged at 4500 rpm for 1 h, and the supernatant was decanted away several times until pH of the supernatant was neutralized. The sediments were dried under vacuum overnight at room temperature.

2.3. Synthesis of rGO

To preserve the dispersity of graphene sheets in water, the hydrazine treated rGO was prepared following the well-described reduction method elsewhere [31]. The 5.0 mL of homogeneous dispersion of GO (1 mg/mL) was mixed with 5.0 mL of water, 5.0 mL of hydrazine solution (35 wt% in water), and 35.0 mL of ammonia solution (28 wt% in water) in a 100 mL three-neck flask. The weight ratio of hydrazine to GO was about 7:10. To control the reduction degree of rGO, the reaction time and temperature were varied from 60 °C to 100 °C and from 10 min to 360 min, respectively, and afterwards the mixture solution was dialyzed for 48 h. Then the dark color suspension of rGO was obtained.

2.4. Synthesis of cysteamine-functionalized GO (GO-SH) and rGO (rGO-SH)

The synthesized GO (100 mg) or rGO (100 mg), 0.5 g of cysteamine hydrochloride (0.004 mol), and 0.5 g of N-ethyl-N’-(3-dimethyl amionpropyl) carbodiimide (EDC) were dissolved in 80 mL of DI water, and the mixed solution was stirred at 30 °C for 12 h. Afterwards, the mixture solution was dialyzed for 48 h to remove EDC and unreacted cysteamine. Then homogeneous GO-SH or rGO-SH suspensions were obtained.

2.5. Immobilization of AuNPs in GO-SH and rGO-SH sheets

The resulting GO-SH or rGO-SH suspension (10 mL, 0.5 mg/mL) was mixed with 10 mL of AuNP aqueous suspension (1:1, v/v ratio vs. GO-SH or rGO-SH, $r_{\text{Au/Graphene}} = 1.0$), followed by stirring at room temperature for 12 h. Then, the resulting mixture was centrifuged and thoroughly washed with ethanol and DI water (3 times) to remove free AuNPs. Finally, the precipitate was redispersed in 5.0 mL of water. In addition, the amount of AuNPs assembled on graphene sheets was controlled by changing the volume ratio ($r_{\text{Au/Graphene}}$) from 1.0 to 2.0 and 3.0 (the corresponding mass ratio of AuNPs to the GO-SH sheets is around 3:7, 5:5 and 7:3; the mass ratio of AuNPs to the rGO-SH sheets is around 2:8, 6:4 and 8:2, respectively).

2.6. Characterization

The chemical structure of the synthesized GO, rGO, GO-SH, and rGO-SH was identified by FT-IR spectrometer (Nicolet iS10, Thermo Scientific). UV-vis spectra of AuNPs were recorded on a Lambda 25 (PerkinElmer) spectrometer. The morphology of the samples was investigated using transmission electron microscopy (JEOL, JEM-1010). Samples dissolved in water were deposited onto carbon-coated copper grids for TEM measurement. The Raman spectra were obtained by using a Jobin Yvon LabRam HR micro-Raman system with 514 nm laser excitation. The GO film and GO-SH/Au films were prepared on Anodisc membrane filter (0.2 μm pore size, 47 mm diameter, Whatman) through vacuum filtration of the GO and GO-SH/Au hybrid suspensions. Electrochemical measurement was performed with a Versa STAT3 potentiostat (Princeton Applied Research). A conventional three-electrode cell was used, including Ag/AgCl electrode as reference electrode, a platinum wire as counter-electrode and a glassy carbon

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