



Short communication

Hybrids of gold nanoparticles highly dispersed on graphene for the oxygen reduction reaction

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ABSTRACT

An approach to the synthesis of gold nanoparticles–graphene (AuNPs–GOSH) hybrids via the Au–S bond between the sulfhydryl-functionalized graphene oxide (GOSH) and gold nanoparticles (AuNPs) has been proposed. In this approach, the sulfhydryl groups highly dispersed on the GOSH nanosheets are used to assemble gold nanoparticles, forming the AuNPs–GOSH hybrids. It is found that the AuNPs–rGO hybrids show high electrochemical activity toward the oxygen reduction reaction (ORR) and high stability in alkaline media.

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1. Introduction

Carbon materials have been considered as promising matrix supporting catalysts [1]. Among the allotropes of carbon materials, graphene has been attracting particular interest due to its outstanding conductivity, thermal stability, large surface area, robust mechanical properties and easy surface modification [2–6]. Thus, various methods have been proposed to the synthesis of metal nanoparticles/graphene nanocomposites. All these methods can be divided into two strategies. One is the in situ growth of nanoparticles (NPs) from appropriate metal precursor solutions in the presence of functionalized graphene or pristine graphene nanosheets. This strategy has been widely used in the synthesis of metal NPs/graphene nanocomposites [4,5,7–12]. The main advantage of this approach is simple and cheap with no need for protecting surfactant or extra linker molecules. However, it is difficult to control the size and dispersity of NPs on graphene surface, especially on the inert surfaces of pristine graphene. Ex situ techniques is an alternative strategy for preparing metal NPs/graphene hybrids. In this strategy, metal NPs are synthesized in advance and then linked to the surface of graphene nanosheets via linking reagent by covalent or noncovalent interactions. Modification of the metal NPs or graphene with functional groups is usually required. This method can successfully control the size and distribution of NPs [13]. For example, high quality AuNPs–graphene nanohybrids with well monodispersity was synthesized through the interaction between DNA-functionalized

graphene and AuNPs [14,15]. In these reports, expensive DNA has been used as molecular “glue”, which is not suitable for large-scale synthesis.

In this work, we report an approach to the ex situ synthesis of AuNPs/graphene hybrid. Sulfhydryl-functionalized graphene oxide (GOSH) was synthesized by the condensation reaction between the carboxyl of the graphene oxide surface and the amido of the 2-aminoethanethiol. Directly mixing the aqueous solutions of AuNPs and GOSH resulted in the formation of AuNPs–GO nanohybrids due to Au–S interaction. The resultant AuNPs–rGO nanohybrids showed superior electrochemical activity for the oxygen reduction reaction (ORR) in alkaline media.

2. Experimental section

2.1. Synthesis of AuNPs–GOSH hybrid

Graphene oxide (GO) was synthesized from graphite powder using a modified Hummer's method [16]. To functionalize the GO with sulfhydryl groups, 0.1 g 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC) and excessive 2-aminoethanethiol hydrochloride were added into 20 mL GO suspension ($\sim 1 \text{ mg mL}^{-1}$) and the mixture was refluxed at 35 °C for over 3 days under magnetic stirring. After the condensation reaction, the final GOSH solid was collected by centrifugation at 15000 rpm for 10 min and washed several times with water to remove the remaining reagents, and finally dried at 60 °C for 5 h in a vacuum dryer.

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The AuNPs were synthesized through the NaBH_4 reduction method [17]. Diameter of the nanoparticles is in the range of 3–5 nm. In a typical self-assembly experiment, the aqueous dispersion of AuNPs (10 mg mL^{-1}) was mixed with the aqueous dispersion of GOSH sheets (1 mg mL^{-1}) at a weight ratio of 3:10 under stirring for 2 h. The final AuNPs–GOSH hybrids were obtained by centrifugation at 15000 rpm for 10 min and washed several times, and finally dried at 50°C for 5 h in a vacuum dryer.

2.2. Instruments and measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VERTEX 80v vacuum spectrometer. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 electron microscope at an operating voltage of 200 kV. Scanning electron microscopy (SEM) image was obtained on a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) at an accelerating voltage of 10 kV. Raman spectrum was recorded on a Renishaw micro-Raman spectrometer with an excitation wavelength of 514 nm. All electrochemical experiments were performed on a CHI 900 electrochemical analyzer at room temperature. A standard three-electrode system including a Pt wire counter electrode, an Ag/AgCl reference electrode, and a catalyst modified glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode was used. The rotating disk electrode (RDE) test was performed on a HP-1A system (purchased from Jiangfen Electrochemical Instrument Co. Ltd., China) with a glassy carbon disk (4 mm in diameter). The GCE disk was modified with $5 \mu\text{L}$ of 1 mg mL^{-1} AuNPs–GOSH suspension and on which a thin layer of Nafion was coated. Prior to electrochemical tests, the electrochemical reduction of the AuNPs–GOSH on GCE was performed at -1.5 V in 10 mM pH 5.0 PBS ($\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$) solutions for 500 s in order to reduce the GO completely to graphene [18].

3. Results and discussion

The synthesis of 2-aminoethanethiol functionalized graphene oxide (GOSH) was characterized using FTIR spectroscopy. Fig. 1A shows the FTIR spectra of exfoliated GO and GOSH. The spectrum of GO shows the O–H ($\nu(\text{carboxyl})$) at 1400 cm^{-1} , O–H (broad coupling $\nu(\text{O–H})$) at $\sim 3200 \text{ cm}^{-1}$ originated from carboxylic acid and the band at ca. 3420 cm^{-1} due to the O–H stretching mode of intercalated water, C–O ($\nu(\text{epoxy or alkoxy})$) at $\sim 1059 \text{ cm}^{-1}$, and C=O in carboxylic acid and carbonyl moieties ($\nu(\text{carbonyl})$) at 1720 cm^{-1} ; C=C at $\sim 1620 \text{ cm}^{-1}$ assigns to the skeletal vibrations of unoxidized graphitic domains or contribution from the stretching deformation vibration of intercalated water [19]. After functionalization of the GO with 2-aminoethanethiol, the characteristic absorption band at 1720 cm^{-1} associated with C=O vibration disappears. There appear two characteristic absorption peaks for the formed amide bond near 1629 and 1355 cm^{-1} , respectively associated with amide I and amide III, indicating the formation of O=C–NH bands due

to the chemical grafting of 2-aminoethanethiol to GO surface via a condensation reaction between the amine group of 2-aminoethanethiol and the carboxyl group of GO. This is also supported by the presence of new peaks of deformation band of N–H in C–NH₂ groups at 1080 cm^{-1} .

Fig. 1B shows the Raman spectrum of GO, which exhibits an intense G peak at 1600 cm^{-1} and a highly intense D band at 1356 cm^{-1} . The presence of the intensive D band clearly suggests the existence of many defects in the graphene sheets due to the harsh oxidation process [20]. Whereas there are no significant shifts or line broadening for the GOSH and AuNPs–GOSH, indicating that the structure of graphene is not considerably destroyed during the functionalization processes. With the covalent attachment of AuNPs onto the GOSH via the formation of Au–S bond, the intensity of the D-band relative to the one for the G-band increases. This phenomenon is also observed when other metal nanoparticles are deposited on GO [21]. This result suggests a chemical interaction or bond formation between AuNPs and graphene.

The TEM images of AuNPs–GO (Fig. 2A and C) show that highly dispersed AuNPs are uniformly scattered on the whole surface of the GOSH sheets without any agglomeration. It is worth noting that the distribution density of AuNPs on the GOSH sheet is much higher than the one reported previously [13,14,22–24]. In addition, the particle size of the AuNPs (black dots in Fig. 2C) is in the range of 3–5 nm diameters, which is in good consistency with the AuNPs precursor (Fig. 2D). There are no any free AuNPs on the carbon substrate of the copper meshes, indicating a strong chemical interaction between AuNPs and GOSH. These results demonstrate that the present self-assembly method can easily control the decoration density of AuNPs on graphene surface and preserve the size and morphology of the AuNPs precursors.

The SEM image of the AuNPs–GOSH modified GCE is shown in Fig. 2B, showing a three dimensionally network-like structure. Such structure certainly increases the real surface area and can facilitate the mass transport of reaction molecules, leading to “apparent” catalytic effects as reported previously [25].

Since electrochemical reduction of GO starts at -0.75 V vs. SCE and reaches a maximum at -1.2 V , high quality graphene sheets can be synthesized by electrochemical reduction at -1.5 V [18]. In the present work, the AuNPs–GOSH hybrids was electrochemically reduced at -1.5 V vs. SCE in 10 mM pH 5.0 PBS for 500 s, forming AuNPs-reduced graphene oxide (AuNPs–rGO) hybrids. The electrocatalytic activity of this hybrid for ORR was studied. Fig. 3A shows the cyclic voltammograms of a bare GCE, rGO/GCE, AuNPs/GCE and AuNPs–rGO/GCE in O_2 saturated 0.1 M KOH solution. For the bare GCE, AuNPs/GCE and rGO/GCE, the electrochemical reduction starts at -0.31 V , -0.27 V and -0.15 V , respectively. Whereas, the AuNPs–rGO/GCE exhibits more positive onset potential (-0.10 V) and much larger reduction current for the ORR (Fig. 3A, curve d), demonstrating the superior electrochemical activity of the AuNPs–rGO nanocomposite. Moreover, it is worth noting that the onset potential (-0.10 V) for ORR on AuNPs–rGO is more positive than that (-0.18 V) for the AuNPs/rGO composites prepared in literatures [26], suggesting an improved pathway for activating the adsorbed O_2 on composite surface.

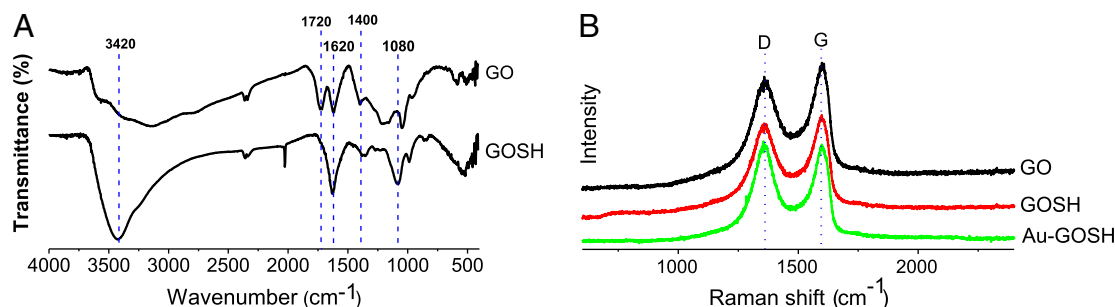


Fig. 1. (A) FT-IR spectra of the GO and GOSH. (B) Raman spectra of GO, GOSH and AuNPs–GOSH.

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