Decoration of electro-reduced graphene oxide with uniform gold nanoparticles based on in situ diazonium chemistry and their application in methanol oxidation

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ABSTRACT

Decorating graphene with high destiny and uniform size of noble metal nanoparticles is very important for a number of applications including sensing and electrocatalysis. Herein, a novel approach based on in situ diazonium chemistry was reported to design gold nanoparticles/graphene hybrid materials (Au-NPs/G). Graphene oxide was firstly electro-reduced on the glassy carbon electrode, and then this modified electrode was grafted by aminophenyl diazonium cations, generated in situ from p-phenylenediamine. Subsequently, gold nanoparticles (Au-NPs) were deposited on the p-phenylenediamine grafted electrode by a potentiostatic method. X-ray photoelectron spectroscopy, scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy were used to characterize the Au-NPs/G. The results demonstrated that the Au-NPs with high destiny and uniform size were dispersed on the electro-reduced graphene oxide. In addition, the obtained Au-NPs/G was utilized in electrocatalysis toward the oxidation of methanol showing excellent catalytic activity.

1. Introduction

Catalyst assemblies based on noble metal nanoparticles (Au, Pt, and Pd, etc.) and graphene have attracted an enormous level of interest throughout the scientific community, owing to its promising applications in biosensors [1–3], fuel cells [4–7], capacitors [8–10] and storage batteries [11–13]. Composites of graphene-metal nanocomposites possess practically indispensable properties, which include extremely large surface areas [14], high carrier mobility [15], good thermal/chemical resistivity [4,16], and so forth. Although many works were explored in this field, two important points should be paid attention to: (a) the difficulty in maintaining metal nanoparticles and graphene firm connection and (b) ensuring wide uniform dispersal of metal nanoparticles on the graphene sheets.

At present, several groups have been developed to construct graphene-metal nanocomposites for sensing and electrocatalysis. Wang’s group [17] have decorated graphene with Pt nanoparticles for electro-catalytic oxidation of methanol. However, due to the poor dispersibility of graphene, most resulting graphene–metal nanocomposites were not stable and easy to aggregate after a long time. Anchoring metal nanoparticles to graphene oxide (GO) was explored by several groups due to its good dispersibility in aqueous solution [5,18–21]. However, GO was insulating in contrast to the unique transport properties of graphene. Randomly distributed oxygen functionalities on the surface of GO could result in non-homogenous GO-based composites. Self-assembly was an important and effective strategy for fabricating metal–graphene hybrid materials, where certain linkers, such as organic molecules [22,23], DNA [24] and proteins [25] self-assembled onto the graphene surface by various driving forces, and could bind metallic nanoparticles to graphene sheets. Unfortunately, in situ anchoring of metal nanoparticles to GO or graphene often lacked fine control over the size, the uniformity and the density of nanoparticles on the sheets in the reaction process.

In this work, we have developed a new strategy to design gold nanoparticles/graphene hybrid materials (Au-NPs/G) based on in situ diazonium chemistry. GO was firstly electro-reduced on the glassy carbon electrode (GCE-ERGO), and then ERGO were grafted with Aminophenyl diazonium cations, generated in situ from p-phenylenediamine, DNA-phenylenediamine (PD-NH2). Subsequently, gold nanoparticles (Au-NPs) were deposited on the PD-NH2 grafted ERGO by a potentiostatic method. PD-NH2 was used as a bifunctional linker. On one hand, it could firmly connect graphene by C–C covalent bonds [26,27]; on the other hand, it could offer amine groups for gold deposition. Characterizations by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and electro-chemical techniques demonstrated that Au-NPs were loaded on ERGO. In addition, the obtained Au-NPs/G was utilized in electrocatalysis toward the oxidation of methanol showing excellent catalytic activity.

Keywords: Electro-reduced graphene oxide, Aryl diazonium salts, Gold nanoparticles, Methanol oxidation

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2. Experimental

2.1. Reagents and instruments

Graphite Powders (320 meshes) were of spectroscopically pure reagent and obtained from Shanghai Chemicals, China. GO was synthesized from natural graphite powder by a modified Hummers’ method as originally presented by Kovtyukhova et al. [28]. Hydrogen tetrachloroaurate (HAuCl4, 99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. p-phenylenediamine (PD-NH2, 97%) was obtained from Alfa. Sodium nitrite (NaNO2), methanol, potassium ferricyanide (K3Fe(CN)6), potassium ferrocyanide (K4Fe(CN)6), potassium chloride (KCl) were analytical grade and used as received. All aqueous solutions were prepared with purified water (>18 MΩ) from a Milli-Q Plus system (Millipore). Phosphate buffer solution (PBS) used in this work contained 0.05 M KCl and 0.05 M Na2HPO4/NaH2PO4 adjusted to pH 9.18 with NaOH solution. All the measurement solutions were deoxygenated by bubbling at least 15 min with high-purity nitrogen.

SEM images were recorded with a XL30 environmental scanning electron microscope (ESEM, Philips Electron Optics) with finite element model and 20 kV accelerating voltage. XPS analysis was carried out on an ESCALAB MKII X-ray photoelectron spectrometer with Al Kα X-ray radiation for excitation. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Solartron 1255B Frequency Response Analyzer (Solartron Inc., UK). All electrochemical experiments were performed using a CHI660A Electrochemical Workstation (CHI) and a conventional three-electrode system, comprising a glass carbon (GCE, d = 3 mm) or modified glass carbon working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. All potentials were reported versus SCE reference electrode at room temperature.

2.2. Electrode preparation and modification

The process of modified electrode is outlined by Fig. 1. Before use, GCEs were carefully polished to a mirror finish with 1.0, 0.3, and 0.05 μm alumina slurries, successively. GCE was first casted 10 μL of a 0.5 mg mL−1 GO and dried in a vacuum desiccator, then the electrochemical reduction of GO was carried out by scanning in a potential range between 0 to −1.5 V versus SCE in PBS for 40 cycles at 100 mV s−1. Secondly, amine groups on the GCE-ERGO were introduced by electrochemical reduction of the aryldiazonium cation generated in situ from PD-NH2. Briefly, 1 mM (final concentration) NaNO2 was added to a 0.5 M acidic aqueous solution (HCl) of the aryl amine (1 mM) to generate the aryldiazonium cation. The solution was kept in complete darkness in an ice bath and allowed to reaction for 15 min under a nitrogen stream and stirring. Surface derivatization was carried out using electrochemical reduction by scanning the working electrode from 0.6 to −1.0 V versus SCE at a rate of 100 mV s−1 for 2 cycles in the aryldiazonium cation-generating solution. The resulting modified electrodes (GCE-ERGO/PD-NH2) were removed and rinsed with large amount of water and dried under a stream of nitrogen. At last, the GCE-ERGO/PD-NH2 was then immersed into 0.1 M HClO4 solution containing 1.5 mM HAuCl4 for several minutes. After being rinsed with 0.1 M HClO4, the AuCl4− adsorbed GCE-ERGO/PD-NH2 was transferred to a 0.1 M HCl blank solution and Au-NPs were grown on the GCE-ERGO/PD-NH2 by a pulsed potentiostatic method. The potential was stepped from 700 to 0 mV versus SCE for 120 ms. This modified electrode was designated as GCE-ERGO/PD-NH/Au-NPs. As a control, GCE-ERGO/Au-NPs were designed as the same condition without grafting PD-NH2.

2.3. Electrochemical measurement

EIS measurements were carried out between 10−1 to 105 Hz using a signal amplitude of 10 mV in mixed solution of 1 mM [Fe(CN)6]3−/4 and 0.1 KCl aqueous solution adjusted to pH 11 with NaOH or HCl solution. The electrocatalytic activity of GCE-ERGO/PD-NH/Au-NPs was checked by cyclic voltammetrys (CVs), in which 0.1 M KCl containing 1 M CH3OH was used as the electrolyte solution.

3. Results and discussion

3.1. Fabrication of GCE-ERGO/PD-NH/Au-NPs

3.1.1. Electro-reduced GO

With respect to chemical reduction of GO, electrochemical reduction of GO is a new strategy [29,30]. Because this method is green and nontoxic, one can easily deposit graphene to conductive
substrate without protective agents, which is convenient to be covalently modified by organic molecular. Fig. 2A showed the CVs of electro-reductive GO. It demonstrated that GO started to reduce at $-0.75$ V and at $-1.2$ V with a large cathodic peak current. This large reduction current should derive from the reduction of the surface oxygen groups of GO since the reduction of water to hydrogen occurs at more negative potentials (e.g., $-1.5$ V). In the second cycle, the cathodic peak current was sharply decreased, manifesting that the surface-oxygenated species of GO were irreversibly reduced. After several scans, the reductive current at the negative potential almost disappeared. In order to reduce GO thoroughly, forty consecutive cycles were chosen.

3.1.2. Grafted GCE-ERGO with PD-NH₂

The obtained ERGO provided large areas for grafting aryl diazonium cations. CVs of in situ generated diazonium cations of PD-NH₂ at an ERGO modified electrode were shown in Fig. 2B. The first cycle presented two irreversible reduction peaks at $0.38$ V and $-0.25$ V, which were attributed to the formation of the 4-aminophenyl radical from the diazonium derivative with concomitant release of nitrogen and formation of a covalent bond between ERGO and the 4-aminophenyl moiety. This electrochemical response was analogous to the ones obtained for the electrochemical reduction of substituted aryl diazonium cations on single walled carbon nanotubes modified electrode [31]. During the second cycle, these redox waves were suppressed. CVs only exhibited a very small current at a lower potential, which suggested the presence of the grafted layer [31,32]. The lower current obtained in the second cycle was evidence of surface saturation and suggested that a layer of covalently bond molecules was formed, which afforded much active position for depositing Au-NPs.

3.1.3. Deposition of Au-NPs on GCE-ERGO/PD-NH₂

Amine groups grafted ERGO were protonated in 0.1 M HClO₄ because the pKₐ of GCE-ERGO/PD-NH₂ should be close to that of surface bound p-aminothiophenol and to that of aniline adsorbed on gold pKₐ = 4.6 [33]. When GCE-ERGO/PD-NH₂ were dropped in 0.1 M HClO₄ solution containing 1.5 mM HAuCl₄, AuCl₄⁻ anions were adsorbed on the GCE-ERGO/PD-NH₂ through electrostatic interaction, then AuCl₄⁻ anions were electro-reduced to Au atom and formed a special size of Au-NPs. Fig. 2C(b) shows a typical current–time transient seen AuCl₄⁻ anions on GCE-ERGO/PD-NH₂ in the 0.1 M HCl dilute solution. Compared to Fig. 2C(a) which had no AuCl₄⁻ anions adsorbed on a GCE-ERGO/PD-NH₂, Fig. 2C(b) had much larger current indicating that AuCl₄⁻ anions were successfully adsorbed on GCE-ERGO/PD-NH₂ and then were reduced.

3.2. Characterizations of ERGO/PD-NH/Au-NPs

The detailed compositional analysis of ERGO/PD-NH/Au-NPs was characterized and compared with GO by XPS. As shown in Fig. 3A, the intensity of O peak on the ERGO/PD-NH/Au-NPs was extensively decreased in contrast to GO (Fig. 3B) suggesting that the GO had been well deoxygenated to form RGO. A new peak at 399.4 eV in the ERGO/PD-NH/Au-NPs corresponded to the N1s formed by the PD-NH₂ treatment [34]. The high-resolution spectrum in Fig. 3A (inset) represented the signature of the Au4f doublet (4f7/2 and 4f5/2). The Au4f7/2 and Au4f5/2 peaks at 84.25 eV and 87.9 eV were consistent with the Au⁰ state [35]. The appearance of the Au4f signature further confirmed the grafting of Au-NPs to the ERGO/PD-NH₂. The above results demonstrated that ERGO/PD-NH/Au-NPs was successful designed.

The surface morphology and distribution of Au-NPs on the ERGO/PD-NH₂ support surfaces can be explored by SEM. As shown...
in Fig. 4B, Au-NPs with a diameter of about 30 nm were clearly observed and well distributed on the surface of ERGO/PD-NH2. The Au-NPs showed no tendency to aggregate at defects of the graphene surface. Previous attempts to prepare metal nanoparticles on graphene surface or other carbon substrate did not often obtain size-similar and highly dispersed metal nanoparticles [17,36]. One of the reasons was that metal nanoparticles were easily formed at the defects on the surface of graphene[37], which were also observed on the ERGO without grafting PD-NH2 in Fig. 4A. Therefore, to obtain monodispersity Au-NPs, we projected graphene surfaces with PD-NH2 molecular. Covalent bonding of a two-dimensional PD-NH2 monolayer on graphene surfaces provided a uniform surface with positively charged sites, which not only prevented the non-uniform deposition of Au-NPs, but also served as a charge bridge for binding AuCl4− anions, so Au-NPs showed no tendency to aggregate at steps or defects on the surface of graphene.

3.3. Electrochemical properties of GCE-ERGO/PD-NH/Au-NPs

Potassium ferrocyanide solution was used to evaluate the electrochemical behavior of GCE-ERGO/PD-NH/Au-NPs composite modified electrodes. The CVs of GCE and modified GCEs in 1 mM Fe(CN)63−/4− with 0.1 M KCl (pH 11) were shown in Fig. 5A. A larger redox wave were observed at ERGO-GC than that of GCE due to the increased electrochemical active sites by ERGO surface modification, which was in agreement with the results of Chen [38] and Xia [29]. However, after ERGO being grafted with PD-NH2, the redox wave was sharply decreased and even disappeared, indicating that a compact layer was formed. This compact layer blocked the behavior for oxidation and reduction reactions of the Fe(CN)63−/4− redox system [39]. When Au-NPs were deposited on GCE-ERGO/PD-NH2, it showed higher redox current than that of the other three electrodes, indicating that the modified electrodes had enhanced electro-catalytic activity. The reason is that the conductive graphene sheets connected individual Au-NPs and improved the charge transfer between the modifying layer and GCE substrate. Therefore, the results demonstrated that GCE-ERGO/PD-NH/Au-NPs with excellent electro-catalytic prosperities were designed.

The EIS is an important technique to provide significant information on the effect of solution resistance, double layer charging and charge transfer process occurring at the modified electrode surfaces. The Nyquist plots in Fig. 5B were obtained for GCE and modified electrodes in 1 mM Fe(CN)63−/4− with 0.1 M KCl (pH 11). The charge-transfer resistance (Rct) of GCE-ERGO/ PD-NH2, estimated from the diameter of the semicircle of the Nyquist plot is 7103 Ω cm², which is higher than that of other three electrodes revealing a stronger barrier effect for the others. After Au-NPs being deposited on the GCE-ERGO/PD-NH2, the Rct of GCE-ERGO/ PD-NH/Au-NPs was sharply decreasing (45.16 Ω cm²) and even smaller than that of GCE-ERGO (200.50 Ω cm²). The results suggested that uniform gold nanoparticles decorated on GO could promote electronic transfer, which made the GCE-ERGO/PD-NH/Au-NPs obtain high electro-catalytic activity.

3.4. Electrocatalytic oxidation of methanol

Fig. 6 shows the typical CVs in KOH solution at GCE/ERGO/PD-NH/Au-NPs and GCE/ERGO/Au-NPs electrodes with and without 1 M methanol. In the methanol-free KOH solution, the redox peaks
at both electrodes are attributed to formation of gold oxides and subsequently the oxides reduction, respectively [40]. When 1 M methanol was added, the anodic peak for the oxidation of methanol on the GCE/ERGO/PD-NH/Au-NPs occurred at 0.28 V whereas it occurred at 0.31 V on the GCE/ERGO/Au-NPs. Both are more negative than gold dendrite electrode and bare gold electrode [41]. Moreover, the peak current density for oxidation of methanol at GCE/ERGO/PD-NH/Au-NPs (131.94 μA/cm²) is about nine times than that at GCE/ERGO/Au-NPs (14.25 μA/cm²). The less positive potential and higher peak current indicated that GCE/ERGO/PD-NH/Au-NPs exhibited high electrocatalytic ability towards oxidation of methanol. The high catalytic activity can be explained by considering the surface morphology and dispersibility of the gold nanoparticles. With the assistant of PD-NH₂, small size and uniform of gold nanoparticles were decorated on the ERGO (shown in Fig. 4B). Therefore, ERGO/PD-NH/Au-NPs obtain much specific area and active sites, which can accelerate the electronic transfer (shown EIS in Fig. 5B) and promote oxidation of methanol.

Since the stability of catalyst is a key factor for the oxidation of methanol, the stability of GCE/ERGO/PD-NH/Au-NPs for electrocatalytic of methanol in 0.1 M KOH solution was evaluated. After 1000 CVs cycle (Fig. 7), the catalytic activity was declined to 80.5%, which is higher than that of bare gold electrode (76.1%). It demonstrated that the GCE/ERGO/PD-NH/Au-NPs had high stability toward methanol oxidation. The high stability was proposed to attribute to less poisoning intermediates, which were not formed on the GCE/ERGO/PD-NH/Au-NPs in the process of methanol oxidation [42]. On the basis of the electrochemical results described above, one can conclude that the high electrocatalytic activity and stability of GCE/ERGO/PD-NH/Au-NPs have great potential in direct methanol fuel cells.

4. Conclusions

In summary, a novel method was introduced to design Au-NPs/G based on in situ diazonium chemistry. With respect to ERGO, PD-NH₂ grafted ERGO has proved to provide more deposited active sites, on which high-density and uniform size Au-NPs were decorated. The prepared Au-NPs/G was applied in the catalytic oxidation of methanol, showing a high catalytic activity and a well-performing anti-poisoning property. Although only Au-NPs were used in this study to form composites with ERGO, this study suggested the possibility for fabrication of hybrid other noble metal nanoparticles with ERGO for the application of sensors and energy conversion devices.

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References