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LETTER

An easy method for manufacture of gold nanoparticles on a glassy carbon surface

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Introduction

Cycloaddition reactions are powerful and widely used reactions for C–C bond formation. In addition to the cycloaddition reactions in the solution phase, this reaction can also occur between the C=C bonds of alkenes molecules and the dimers of the solid surface such as Si (100) and diamond (100) to form [2 + 2] cycloaddition products [1–3]. The surface of glassy carbon (GC) is the sp^2-bonded carbon and thus the [2 + 2] cycloaddition reaction is expected to occur on its surface.

On the other hand, the assembly of ordered metal nanoparticles, especially gold nanoparticles (AuNPs), on electrodes surfaces has attracted increasing interest due to its great application potentials in electroanalysis and electrocatalysis [4–8]. Characteristics of AuNPs such as high surface-to-volume ratio, high surface energy, and ability as electron-conducting pathways between redox molecules and electrode surfaces, have been claimed as reasons for the high electrocatalytic activity of redox processes [9, 10]. In many instances, the bifunctional molecules (e.g., dithiols and diisocyanides), which act as coupling agents for linking to substrates such as gold or platinum, have been used for the assembly of AuNPs on electrode surfaces [11, 12]. A chemical reaction of an aryldiazonium salt with sulfhydryl group was described the ability to extend the range of binding AuNPs to carbon-based materials [13]. However, the diazonium reaction suffers from the critical condition, and as a result, the applications of this method are limited. NH_3 plasma treatment was also reported to generate amino groups for the immobilization of AuNPs, while surface coverage of the amino groups was low [14]. Therefore, the search for simple and reliable methods of the AuNP assembly on the carbon-based materials is still interesting.

Keeping this aim in view, a photochemical reaction between the vinyl groups of allylamine molecules and GC surface was designed to modify the GC surface, producing a layer of amino groups. The resultant amino groups were further used to immobilize the AuNPs on the GC surface, and the electrochemistry of AuNPs-modified GC electrode was investigated.

Experimental

All the chemicals were all analytical reagent grades and were used as received. All solutions were made with deionized water (>18 MΩ cm) from a Millipore Milli Q system. The gold colloidal solution was prepared according to Frens method [15].

The AuNPs-modified GC surfaces were fabricated in three steps. First, GC surfaces were polished with 4.0, 1.0, and 0.05 μm alumina powder in succession, rinsed thoroughly with deionized water between each polishing step, and then sonicated in acetone and deionized water in succession. Second, 20 μL of allylamine was placed onto the

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fresh GC surface ($A = 1\ \mathrm{cm}^2$) in a N_2 purged Teflon reaction chamber covered with a quartz window and was irradiated with ultraviolet (UV) lamp (254 nm, 20 W) for 12 h at room temperature. The GC surfaces were ultrasonically cleaned in 2-propanol for 10 min to remove the adsorbed or polymerized molecules of allylamine. Finally, the above resulting GC surfaces were immersed into the gold colloid solution (pH 4.0) for 24 h.

Morphology of the AuNPs was evaluated by transmission electron microscopy (TEM, JEM-200 CX Electron Microscope). The TEM sample was prepared by dropping 20 μL gold colloidal solution onto a copper grid (3 mm, 300 mesh) coated with carbon film, and then was dried up by airing. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCA Lab 220I-XL photoelectron spectrometer system, with a monochromatized Al $K\alpha$ source (1486.6 eV). Scanning electron microscope (SEM) images were obtained with a Hitachi Ultra-high-Resolution S-4300 SEM at an acceleration voltage of 10 kV. Cyclic voltammetric measurements were performed with a Potentiostat/Galvanostat (Princeton 263A) in a three-electrode cell system. The cell system consisted of a GC working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE).

Results and discussion

A photochemical reaction of the fresh GC surface and the vinyl group of allylamine was shown in Fig. 1. XPS was performed to analyze the chemical composition of the GC surfaces before and after the photochemical modification, as depicted in Fig. 2. For the fresh GC surface, the expected bands in the C1s and O1s XPS peaks located at 532.1 and 284.6 eV were detected, respectively. After photochemical modification, a band of N1s shows a peak centered at 399.8 eV from the N atom of the amino group, and the N1s band achieved to ~4% of the area of the bulk carbon peak for or more than 12 h irradiation. Thus, the allylamine molecules have been covalently attached the fresh GC surface via the 254 nm UV rays and the GC surface was partially converted into an amine-terminated surface. The photochemical reaction was supposed to perform by the [2 + 2] cycloaddition reaction between the vinyl groups of allylamine and the sp^2 carbon of GC surface.

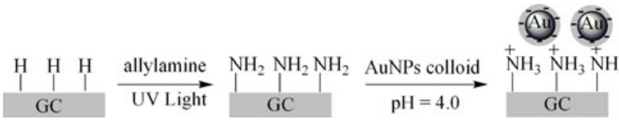

Fig. 1 Illustration of photochemical modification of GC surface and subsequent attachment of AuNPs onto the GC surface

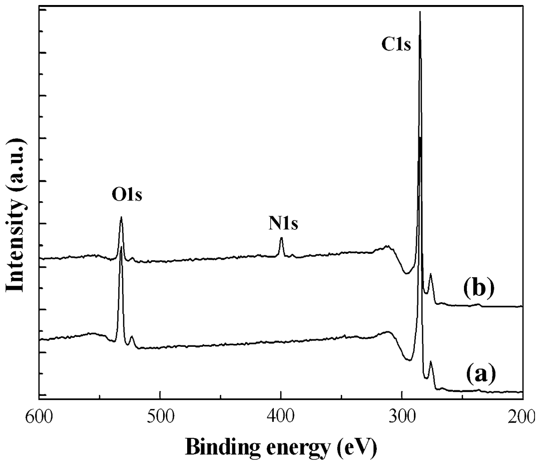

Fig. 2 XPS spectra of GC surfaces *a* before and *b* after photochemical reaction with allylamine

To further verify the above results, the amino groups on the GC surface were used as binding sites for the immobilization of AuNPs. As shown in the inset of Fig. 3, the spherical AuNPs prepared according to Frens [15] method with the size of 15 ± 2.0 nm diameter were obtained. It is worth mentioning that the AuNPs are negatively charged species as a result of the absorption of citrate in the preparation process. In Fig. 1, treatment of the amine-terminated GC surface with the gold colloidal solution was carried out by an assembly process. The pH dependence of AuNPs assembly was investigated in the pH range from 2.0 to 6.0. The best, high density, and homogenous AuNPs on the amine-terminated GC surfaces was obtained at $pH = 4.0$ solution after 24 h, as shown in Fig. 3a and b. As the pH decreases ($2.0 < pH < 4.0$), the AuNPs would be less negatively charged, which results in the weakening of inter-repulsion between adjacent AuNPs and aggregation occurred. On the other hand, the increase of pH ($4.0 < pH < 6.0$) decreased the protonation of amine, and then hindered the AuNPs assembly. Thus, the citrate-capped negatively charged AuNPs have been successfully immobilized on the positively charged amino groups of the GC surface via electrostatic interaction at $pH = 4.0$ solution. Figure 3c also shows the assembly result on fresh GC surface, and as expected, just sparse AuNPs were adsorbed. Compared with the reported methods including electrochemical deposition, vacuum evaporation, sputtering, and etching, the present method is simple and inexpensive [16–19]. Importantly, the uniform AuNPs could be obtained and the AuNPs on the GC surface could retain 95% after 5 min sonication.

The assembly of ordered AuNPs on the GC surface is expected to have electrocatalytic activity. $[Fe(CN)_6]^{3-/4-}$,

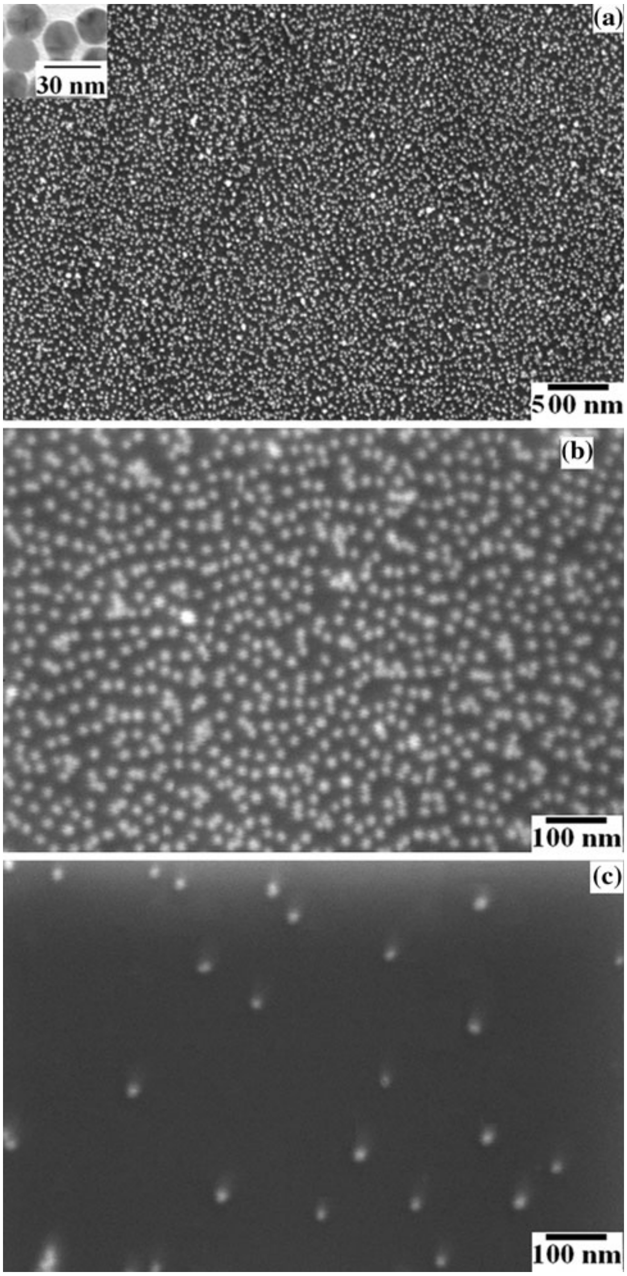

Fig. 3 SEM images of the amine-terminated GC surfaces with AuNPs immobilized on the surfaces at **a** low and **b** high resolution. **c** SEM image of the fresh GC surface with AuNPs adsorbed on the surface and TEM image of AuNPs (*inset*)

as an electrochemical probe, was used to investigate the electrochemical properties of these prepared electrodes. Figure 4 compares the cyclic voltammograms (CVs) of $[Fe(CN)_6]^{3-/4-}$ at the fresh, amine-terminated, and AuNPs-modified GC electrodes. Well-defined CV curves of $[Fe(CN)_6]^{3-/4-}$ were obtained, indicating nearly reversible or quasi-reversible electron-transfer kinetics for electrode interfaces. In contrast to the fresh GC electrode, the decrease in the cathodic and anodic current responses and the increase in the separation of peak to peak (ΔE_p) at the amine-terminated electrode were observed ascribed to the characteristic of barriers with the coverage of amine layer. For AuNPs-modified GC electrode, there was an increase in the current responses and nearly equivalent ΔE_p compared to those of the fresh GC electrode. The results demonstrate that the AuNPs on the GC electrode have a marked influence on the interface property of the modified electrode and accelerate the electron transfer between the electrode and the $[Fe(CN)_6]^{3-/4-}$ molecules. The repeatability and stability of the AuNPs-modified GC electrodes were also investigated. The relative standard deviation (RSD) for the response to 0.5 mM $[Fe(CN)_6]^{3-/4-}$ is 2.3% for nine successive assays, and about 95% surface coverage could be obtained after the above CV measurements. Thus, the AuNPs-modified GC electrode should have the potential in the fabrication of electrochemical sensors or biosensors due to the electrocatalytic ability and biocompatibility.

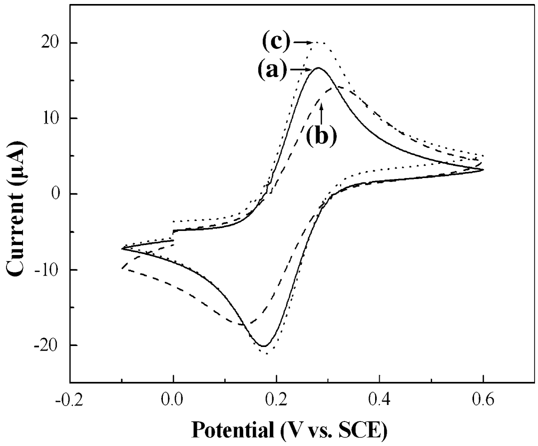

Fig. 4 CVs of 0.5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M phosphate buffer solution (pH 7.0) at the *a* fresh, *b* amine-terminated, and *c* AuNPs-modified GC electrodes. Scan rate is 50 mV s^{-1}

Conclusion

In summary, this study has introduced a novel and simple method for activating the GC surfaces with amino groups. AuNPs were further immobilized on the amine-terminated GC surfaces by electrostatic interaction, and the AuNPs on the GC electrode were proved to facilitate the electron exchange between the electrode and the redox molecules in aqueous solution. This fabrication strategy was expected to extend to the other sp^2-bonded carbon materials such as graphite, carbon paste, carbon nanotubes, and carbon nanofibers, opening up potential applications in the area of electroanalysis and electrocatalysis because of its convenient preparation and good properties.

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