



The electrocatalytic oxidation of glucose on the bimetallic Au-Ag particles-modified reduced graphene oxide electrodes in alkaline solutions



Qiaofang Shi, Guowang Diao, Shaolin Mu*

College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, P. R. China

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ABSTRACT

A given amount of Au and Ag is electrodeposited on the reduced graphene oxide (RGO)/glassy carbon (GC) electrodes to form the Au/Ag/RGO/GC and Ag/Au/RGO/GC electrodes. The electrodeposition potential of Au or Ag is set at -0.30 V (vs. SCE). The electrochemical oxidation of glucose is carried out in NaOH solutions. The experimental results indicate that Ag in the bimetallic Au-Ag electrodes plays an important role in the electrocatalytic oxidation of glucose; the electrochemical behavior of glucose oxidation is very sensitive to the ratio of Ag to Au loading density in the bimetallic composition. The electrocatalytic activity and stability of the bimetallic Au-Ag electrodes are assessed by cyclic voltammetry. The peak current density of the bimetallic Au-Ag electrodes at about 0.24 V is about 4.5 times as large as the gold nanoparticles deposited on the GC electrode reported previously. Enhancing current density is due to the synergetic catalytic effect of Au and Ag. The Ag/Au/RGO/GC electrode lost only 26.2% of its original activity after 500 cycles in a solution consisting of 10.0 mM glucose and 0.10 M NaOH, which is better than that of the Au/Ag/RGO/GC electrode, Ag/Au/GC and Au/Ag/GC electrodes. The reason for this is caused by the electrode structure and RGO used in this work.

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1. Introduction

The electrocatalytic oxidation of glucose in alkaline solutions is an attractive research field for applications in glucose-oxygen fuel cells [1–4], which is generally investigated using metallic electrodes including noble metals (Pt, Pd, Rh, and Au) [5–11] and transition metallic oxides (CuO, NiO, and CoO) [12,13]. The peak potential and the peak current density of glucose oxidation at the nanostructured gold electrode in a solution containing 0.1 M KOH and 10 mM glucose are -0.7 V (vs. SHE) and $ca. 3.5$ mA cm⁻² [14]. The potentials of glucose oxidation at Cu, Ni and Fe electrodes are more positive than that of Au electrode in alkaline media by $ca. 0.6$ – 0.7 V (vs. Ag/AgCl) [15]. The peak potential and the peak current density of glucose oxidation are 0.65 V and 2.9 mA cm⁻² at the Cu/SAMs (self-assembled monolayers) [16]. Therefore, Au shows higher catalytic activity towards glucose oxidation in alkaline media among metal electrodes [17]. In addition, Pt-M (M = Ag, Au, Co, Cu, Ni, Rh, and Ru) alloy electrodes were also used to investigate glucose oxidation in alkaline media [18–22]. The peak potential and the effective peak

current density of glucose oxidation are 0.5 V and $ca. 1$ mA cm⁻² at the Ni electrode and 0.48 V (vs. SCE) and 2.1 mA cm⁻² at the Ni-Cr (80:20) electrode in a solution containing 10 mM glucose and 0.1 M NaOH [23]. The oxidation peak potentials of glucose oxidation are $ca. 0.48$ V at the NiO_x/GC electrode and 0.52 V at MnO_x/NiO_x/GC electrode (vs. Ag/AgCl with sat. KCl solution), in 0.5 M NaOH solution containing glucose [24]. The peak of glucose oxidation at the gold-silver alloy electrode shifts towards negative potentials by $ca. 0.1$ V compared to that at Au nanoparticle modified electrode in 0.1 M NaOH solution [18] and just as it does for silver modified gold film electrode [22]. And the peak potential of glucose oxidation at the silver-UPD (under potential deposition) single crystal gold electrode occurs at -0.44 V (vs. Ag/AgCl) in 0.1 M NaOH solution [25], such low oxidation potential is conducive to raising open-circuit voltage of the glucose-oxygen fuel cell. The highly catalytic performance of the gold-silver to glucose oxidation is attributed to the electrocatalytic activity of silver to glucose oxidation [26]. On the basis of the oxidation peak potential and the peak current density of glucose oxidation on the different electrodes, therefore, the gold-silver alloy electrode shows the effective electrocatalytic oxidation towards glucose oxidation among alloy electrodes in alkaline media. In spite of a great deal of research effect, the peak current density of glucose oxidation on the metal and metal alloy electrodes

* Corresponding author. Tel.: +86 514 87975520; fax: +86 514 87975244.
E-mail address: slmu@yzu.edu.cn (S. Mu).

as described above is evidently lower than that of methanol oxidation at gold nanoparticle electrodes in acid solutions, the latter is about 60 mA cm^{-2} at a scan rate of 50 mVs^{-1} [27,28]. Clearly, there is a long way to go for the practical application in the glucose-oxygen fuel cells, which therefore provides a great chance of further studying glucose oxidation in the alkaline media and also is a severe challenge, i.e.; how to raise greatly the electrocatalytic activity of the metallic catalysts to glucose oxidation in the alkaline media.

Graphene exhibits a unique structure of two-dimensional sheets composed of sp^2 -bonded carbon atoms with one-atom thickness and possesses high conductivity and large specific surface area (the theoretical value of $2630 \text{ m}^2 \text{ g}^{-1}$) [29,30], thus which is a suitable supporting material for loading metal particles [31–33]. Graphene contains the abundant surface groups ($-\text{OH}$, $\text{C}-\text{O}-\text{C}$, and $-\text{COOH}$) that can provide reactive sites for the nucleation and growth of noble metal nanoparticles [34–39], increases the metal dispersion and prevents agglomeration of deposited metal particles [28], and improves the catalytic activity and stability of deposited metal nanoparticles [32]. In addition, graphene containing free radicals can electrocatalyze redox of some species [40–42]. In fact, graphene has been used to fabricate Pt-Ni nanoparticle-graphene electrode for highly selective nonenzymatic glucose detection [21].

In this paper, RGO was used for a supporting material. Au and Ag were electrodeposited on the RGO sheets to form the electrodes, which were used to investigate the electrochemical oxidation of glucose in NaOH solutions. It was found that bimetallic Au-Ag nanoparticles deposited on the RGO sheets exhibit higher electrocatalytic activity to glucose oxidation. The peak current density of the bimetallic Au-Ag electrodes on the cyclic voltammograms is higher than that of Au nanoparticles deposited on the RGO sheets. The electrochemical behavior of glucose oxidation on the bimetallic Au-Ag electrodes is different from that on Au nanoparticles [14] and Ag-Au alloy electrodes [18], which will be discussed in detail.

2. Experimental

Glucose and other chemicals used were purchased from Sinopharm Chemical Reagent Co., in Shanghai, which are of analytical reagent grade. Doubly distilled water was used to prepare all aqueous solutions. A GC disk electrode (3 mm diameter) was polished with alumina slurry of $0.5 \mu\text{m}$ diameter on a polishing cloth and then sonicated in a distilled water bath for 15 min before use.

Graphene oxide (GO) nanosheets were prepared from natural graphite powders by a modified Hummer's method [43]. Aqueous dispersion of pristine GO sheets (0.05 wt. %) was prepared by sonicating for 40 min. A $5 \mu\text{L}$ aqueous dispersion of GO sheets was dropped on a GC disk that was then allowed to dry at 40°C to form a GO/GC electrode. The GO/GC electrode was reduced at -1.0 V for 30 min in a 0.30 M phosphate buffer of pH 4.1 to form a RGO/GC electrode [42,44]. A traditional three-electrode system, consisting of a RGO/GC working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE), was used for the electrochemical experiments that were performed on a CHI 407 workstation. In addition, the electrodeposition of gold and silver was carried out on a PAR Model 173 potentiostat-galvanostat with a Model 179 digital coulometer that can accurately record charges during the electrodeposition process.

A solution of 1.0 mM HAuCl_4 with pH 2.8 and a solution consisting of 5.0 mM AgNO_3 and 0.10 M NaNO_3 (pH 5.5) were used for the electrodeposition of Au and Ag, respectively, which were carried out at a constant potential of -0.30 V . The amount of Au or Ag deposited on the RGO/GC electrodes was controlled and

determined by total charges consumed during the electrolytic process, assuming a 100% current efficiency.

$$W_{\text{Au}} = \frac{QM_{\text{Au}}}{nF}$$

Where n is the number of electrons for the reduction of HAuCl_4 to Au, which is taken as 3; the number of electrons for the reduction of AgNO_3 to Ag is taken as 1. The other symbols have their usual meanings. The total charges of $-2.6 \times 10^{-2} \text{ C}$ was used to deposit Au on the electrodes; the corresponding Au loading is $250 \mu\text{g cm}^{-2}$. The total charges of $-1.2 \times 10^{-3} \text{ C}$, $-2.4 \times 10^{-3} \text{ C}$, and $-3.6 \times 10^{-3} \text{ C}$ were used to deposited Ag on the RGO/GC electrodes, which correspond to Ag loading of 19, 38, and $57 \mu\text{g cm}^{-2}$, respectively.

Two kinds of the bimetallic electrodes are used in this work, one is Au/Ag/RGO/GC electrode, i.e.; Ag was first electrodeposited on the RGO/GC electrode followed by the electrodeposition of Au; other one is Ag/Au/RGO/GC electrode, i.e.; Au was first electrodeposited on the RGO/GC electrode followed by the electrodeposition of Ag. All electrochemical experiments were performed at 25°C .

The images of Au, Ag, and bimetallic Ag-Au particles electrodeposited on RGO/GC and GC electrodes were observed by a field emission scanning electron microscope (SEM) S-4800 II FE-SEM. X-ray photoelectron spectroscopy (XPS) spectra of the bimetallic Au-Ag particles deposited on RGO/GC electrodes were collected on a Thermo ESCALAB 250 spectrometer with an Al $K\alpha$ X-ray source (1486.6 eV). All binding energies were referenced to C1s neutral carbon peak at 284.6 eV.

3. Results and Discussion

3.1. Images of metal particles deposited on the RGO/GC and GC electrodes

Fig. 1A shows the image of RGO dispersed on the GC disk electrode surface, which is composed of multilayer sheets and its surface is rather rough because of the enough amount of GO dispersed on the GC disk electrode as described in the experimental section. Fig. 1B is the image of Ag particles deposited on the RGO/GC electrode with Ag loading of $38 \mu\text{g cm}^{-2}$. It is clearly, some of the small Ag particles are aggregated together to form larger particles, which are loosely dispersed on the electrode surface because only a small amount of Ag were deposited on the electrode surface. And it was found that the colloidal material around the cathodic electrode was formed during the electrolytic process. The morphology of Ag particles in Fig. 1B is slightly similar to that of Ag nanoparticle-graphene composite prepared from the precursor silver phosphate-graphene oxide nanocomposite [45], but quite different from that of silver nanoparticles deposited on platinum sheet prepared with electrochemical synthesis under protection of poly(*N*-vinylpyrrolidone) [46], in which its morphology shows spherical silver nanoparticles. The difference in morphology of silver particles described above is relative to its preparation method, substrate materials and protective agents used. Fig. 1 C and D show the images of the Au/Ag/GC and Ag/Au/GC electrodes with Au loading of $250 \mu\text{g cm}^{-2}$ and Ag loading of $57 \mu\text{g cm}^{-2}$ on each electrode, respectively. Clearly, the sizes of particles in Fig. 1 C are larger than those in Fig. 1D, and the space between particles in Fig. 1 C is looser than that in Fig. 1D. This is because Ag particles electrodeposited on the electrode surface also exhibits loose structure with largely aggregated particles, in this case, followed by Au electrodeposition, which results in the formation of loose and large Au-Ag particles on the Au/Ag/GC electrode. The image of the Ag/GC electrode is similar to that of Ag/RGO/GC electrode in Fig. 1B, which is omitted here.

Fig. 2A shows the image of Au particles deposited on the RGO/GC electrode with Au loading of $250 \mu\text{g cm}^{-2}$, in which Au

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