SURFACE MORPHOLOGIES OF GOLD NANOPARTICLES ELECTRODEPOSITED ON GLASSY CARBON ELECTRODE AND APPLICABILITY IN DETECTION OF Hg(II) AT TRACE CONCENTRATION

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Abstract

In the present study, we showed the variation of surface morphologies of gold nanoparticles (Au-NPs) on glassy carbon electrode (GCE) obtained by electrochemical method via controlling the electrochemical deposition time and stirring condition. The size in diameter of gold particles was not significantly changed with the variation of these conditions, whereas their surface coverage was strongly dependent. This behavior governed the enhancement of the peak current on the differential pulse voltammograms for reduction of Hg(II) bound to 4-pyridineethanethiolate self-assembled on gold particles through chemical preconcentration. This result clearly proves the applicability of the modified electrode in detection of Hg(II) at trace concentration.

Keywords: Self-assembled monolayers, gold nanoparticles, 4-pyridineethanethiol.

1. INTRODUCTION

Electrochemical deposition of metal nanocrystals onto carbon electrodes has been the subject of large number of investigations for diverse applications, for instant, study of the oxygen reduction kinetics [1, 2], catalytic performance [3, 4], electrocatalytic reduction of oxygen [5], fabrication of phase-separated multi-component SAMs [6], voltammetric determination of methylmercury and inorganic mercury [7]. Of those, some studies have focused on the early stage of electrochemical deposition in an effort to elucidate the nucleation and growth mechanism of the metal phase on the substrate [8, 9]. However, functionalization of the glassy carbon electrodes for designing the surface properties via formation of self-assembled monolayers onto the deposited metal nanocrystals needs supports of the size, structure and distribution of the metal nanocrystal substrate. Ideally, small, well-dispersed gold nanoscrystallites are desired as a foundation for chemical modification. Recently, we found that the GCE surface pretreated by different electrochemical methods can form various surface morphologies of Au-NPs electrodeposited onto the GCE surface [10]. Of those, the surface morphology of Au-NPs formed by the exclusive cathodic polarization with smaller size in diameter and better order arrangement reveals the suitability for assembly of 4-pyridine ethanethiol (PET) monolayer on Au-NPs to coordinate with Hg(II). Thus, our interest in the rational design of chemically modified carbon electrodes has prompted us to consider supported gold nanocrystals as sites for further modification steps.

In this work, our efforts are concentrated towards the variation of morphologies of Au-NPs deposited on GCE and characterizing the signal obtained by differential pulse voltammtery for reduction of Hg(II) coordinated with PET-SAM assembly on Au-NPs. This preliminary work is an initial step toward the fabricating one type of electrochemical sensors used for sensitive determination of Hg(II) at trace concentration.

2. EXPERIMENTAL

2.1. Reagents

4-pyridineethanthiol hydrochloride purchased from Wako Chemicals was used without further purification.$Hg(NO_3)_2$ stock solution (5.0×10^{-3} M) purchased from Merck was used for dilution. More diluted solutions were prepared daily from the stock solution. All other reagent grade chemicals were used without further purification.

2.2. Apparatus

Electrochemical measurements were performed with a home-made potentiostat/galvanostat. A three-electrode configuration was used for measurements, which consists of GCE working electrode, calomel (saturated) reference electrode and Pt counter electrode.

Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 instrument at acceleration voltage of 15-20 kV and a working distance of 4-5 mm.

2.3. Pretreatment of GCE

The GCE was prepared by cutting available plate-shaped glassy carbon (Tokai GC-20 company, NY) into cylinder-shape and mounting into teflon tubes holder so that only a circular area of 0.031 cm^2 was exposed to the electrolyte. GCE was polished with emery paper. Upon polishing, GCE was rinsed and ultra sonicated in distilled water for 3 minutes, rinsed and dried in air. GCE was then electrochemically pretreated as reported in elsewhere [10].

2.4. Preparation of Au-NPs and PET-SAM

Electrochemical deposition of Au-NPs on the GCE surface was carried out at potential of + 0.5 V in 1.0×10^{-3} M $HAuCl_4$ solution for a desired time under stirring rate of 50 rpm.

Preparation of PET-SAM onto Au-NPs electrodeposited on GCE (PET-SAM/Au-NPs/GCE) was carried out in $1.0{\times}10^{-6}$ M ethanolic solution of PET for 3 hours at room temperature.

2.5. Electrochemical measurements

The formation of PET-SAM/GCE was investigated by cyclic voltammetry (CV) for reductive desorption. Measurement was performed in 0.5 M KOH solution, from 0.0 V to -1.1 V at scan rate of 0.1 $V.s^{-1}$.

Detection of Hg^{2+} was performed with two steps. First, Hg(II) was chemically preconcentrated by immersing PET-SAM/Au-NPs/GCE in a 0.1 M KCl + HCl solution, pH 6.7, containing Hg(II) for a desired time under open circuit potential. During the preconcentration, the solution was efficiently stirred at 60 rpm. Second, the reduction of Hg(II) accumulated onto PET-SAM/Au-NPs/GCE was obtained by differential pulse voltammetry (DPV). The voltammogram was recorded in a 0.1 M KCl + HCl solution, pH 3.0; the potential was scanned from +0.7 V to +0.3 V with pulse amplitude 0.050 V; pulse time 0.040 s; voltage step 0.005 V; step time 0.08 s; sweep rate 0.05 $V.s^{-1}$.

All measurements were performed at room temperature.

3. RESULTS AND DISCCUSION

3.1. Variation of morphology of Au-NPs

Figure 1 shows typical SEM photographs of Au-NPs electrodeposited on GCE under different electrodeposition time. A noticeable observation from these images was that Au particles were white dotes or spherical in shape, meanwhile darkareas were attributed to the GCE surface. The formation of Au-NPs from the $HAuCl_4$ solution under the reduction potential was carried out as following [8]:

$$Au^{3+} + 3e^{-} \rightarrow Au^{0}$$

Therefore, the amount of gold particle strongly depends on the electrodepostion time (t_{Au}). As seen in figure 1a÷1c, the total area of white dots increases with increasing t_{Au}, indicating that the amount of gold particles is proportional to t_{Au}. As t_{Au}increased up to 600 s, the surface of GCE was almost completely coated with Au-NPs (figure 1c). Interestingly, the observation of morphology reveals that the increase in the area of Au-NPs is not mainly due to the growth of gold particles, suggesting that the increase in t_{Au} is essential for creating new active nucleis. This is because, generally, the first step of metal deposition is the formation of nuclei of the depositing metal. Subsequently, two competing processes, i.e., the growth and nucleation are take place [11]. Further, the instantaneous adsorption of Cl^- ion on the surface of the Au-NPs at the early stage of electrodeposition (i.e., at the first formed nuclei) results in Au-NPs with a negative charge [12]. This leads to a repulsive interaction among the negatively charged Au-NPs and prevents the further particles growth or coalescence of the neighboring particles. Consequently, elctrodeposition of small particles predominates.

Besides the variation of t_{Au}, a similar effect can also obtained by changing the disturbance of the electrolyte solution, as shown in figures 1c and 1d. In these figures, one can be seen that when the electrolyte solution was not stirred, Au-NPs were not coated completely the GCE surface. This indicates that stirring condition improves the diffusion of Au^{3+} from the bulk solution to the GCE surface for creating Au^0 nucleis. Besides this phenomenon, the significant variation of size of Au-NPs was not observed. Obtained results can be useful because the small size of these particles make

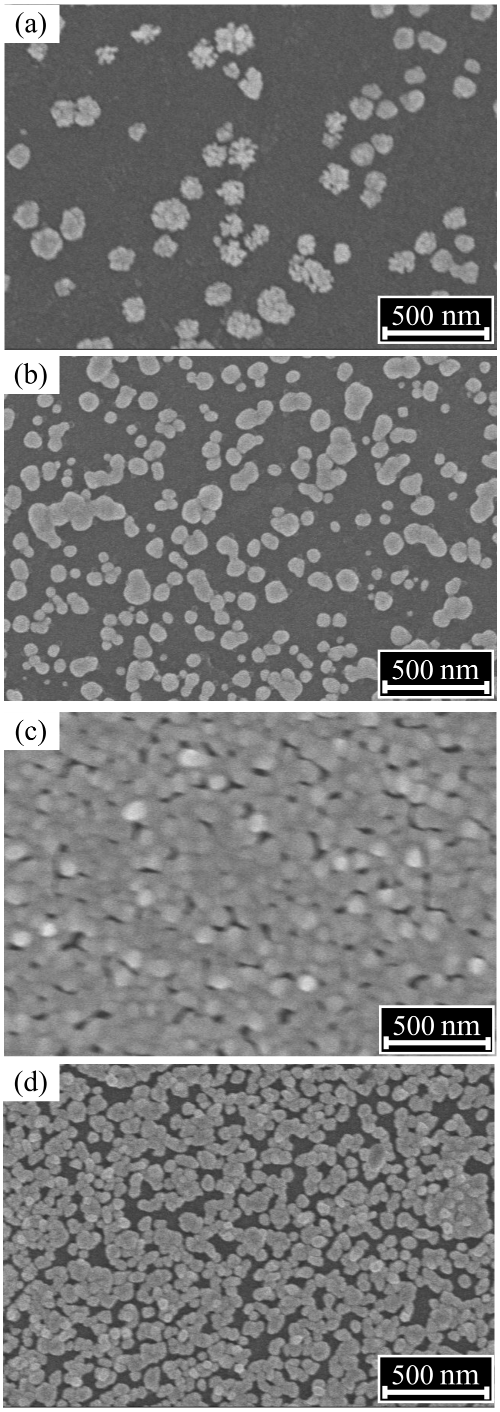

Figure 1: SEM images of Au-NPs on GCE pretreated by cathodic polarization at potential of -1.0 V. Au-NPs was electrodeposited at potential of + 0.5 V in H_2SO_4 solution containing 5.0×10^{-6} M $HAuCl_4$ for 50 s (a), 300 s (b) and 600 s (c) under stirring at 60 rpm, and 600 s without stirring (d)

them ideal catalysts for many chemicals as well as electrochemicalapplications [13]. For instant, being chemically stable but inactive for the catalysis of many reactions, gold catalyst has been developed as small gold particles dispersed on supports of α-Fe_3O_4, Co_3O_4 or NiO oxides by coprecipitation method [14], or can be used to form quantum dots [15].

3.2. Applicability of the modified GCE in detection of Hg(II)

Herein, we report the role of variation of the morphology of Au-NPs electrodeposited on Au-NPs/GCE in detection of Hg(II), which is known as a toxic for human health at low concentration, through coordination with PET-SAM-modified Au-NPs. The presence of PET-SAM on Au-NPs electrodeposition was examined by studying the cyclic voltammetry for reductive desorption of the SAM in N_2-saturated 0.5 M KOH solution, as shown in figure 2. On these voltammograms, two peaks appeared at -0.85 V and -1.2 V can be clearly observed. These peaks correspond to the reduction of alkanethiolate SAM on polycrystalline Au substrates as reported by other authors [16]. As seen, the height of these peaks also increases with prolonging t_{Au}, indicating the amount of PET-SAM also significantly depends on the total areas of Au-NPs on the GCE surface.

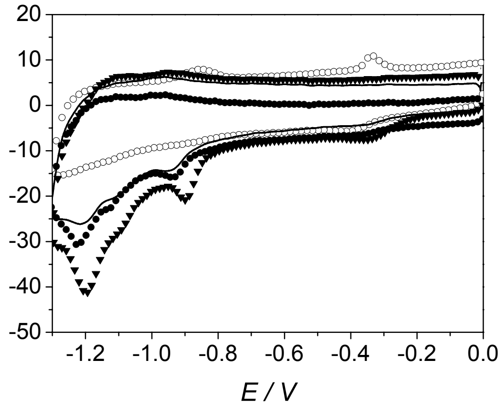

Figure 2: Cyclic voltammograms for reductive desorption of PET-SAM on Au-NPs prepared in different t_{Au}: 50 s (thin line); 300 s (●); 600 s (▼) under stirring at 600 rpm; and for Au-NPs/GCE (○), recorded in 0.5 M KOH solution, v = 0.1 V/s

Though, the applicability of the PET-SAM modified GCE in detection of Hg(II) can be influenced by the morphology of Au-NPs because the assembly of PET molecules inSAM is a key factor for binding with Hg(II) in solution, and that can be affected by the morphology of the substrate. Since, we attempted to investigate the dependence of electrochemical signal obtained in reduction of Hg(II) coordinated with N-donor of the PET-SAM [17], through chemical preconcentration, on the differentmorphologies of Au-NPs. Figure 3 shows DPV for reduction of Hg^{2+} bound to PET-SAM prepared in different t_{Au}. On the voltammogram, the peak appeared at the potential of +0.53 V corresponds to the reduction of Hg(II) → Hg (I) [8, 18]. As seen, the peak raises as increasing t_{Au}, suggesting the amount of Hg(II) preconcentrated onto the PET-SAM is proportional to t_{Au} and depends on the surface morphology of Au-NPs. This is attributed to the prolongation of t_{Au} leading to preferable surface for assembly of PET molecules, promoting the coordination between Hg(II) and the N-donor of the PET-SAM. Particularly, the increase of the area coated by Au-NPs is not the unique factor that governs the enhancement of the reduction peak current, it also includes the ordered arrangement of Au-NPs because it influences significantly the orientation of PET-molecules [8]. Since, the well ordered arrangement of PET molecules in the SAM obtained by our method is also another reason for increasing the reduction peak on the DPV.

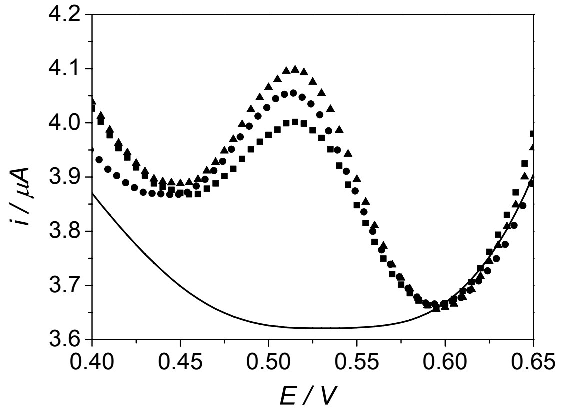

Figure 3: Differential pulse voltammograms for detection of Hg(II) preconcentrated in HCl + KCl solution, pH 6.7 containing 1 ppb Hg(II) onto the PET-SAM/Au-NPs/GCE prepared in different t_{Au}: 50 s (■), 300 s (●), 600 s (▲) and under stirring at 600 rpm. Thin line: recorded for the background curve with same conditions

4. CONCLUSIONS

Modification of GCE with Au-NPs by electrochemical methods has been carried out. Various surface morphologies of gold particles were observed by changing the electrodeposition time as well as the disturbance of the electrolyte solution. Coating Au-NPs with PET-SAM results in coordinationwith Hg(II) ion in the bulk solution to the modified GCE surface during preconcentration. The amount of Hg(II) bound to PET-SAM increases with the total area of Au-NPs, suggesting the suitable surface morphology assembly of adsorbed PET molecules. This is useful for fabricating the electrochemical sensor for determination of Hg(II) at trace concentration.

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