Modification of Gold Nanoparticles at Carbon Electrodes and the Applications for Arsenic (III) Detections

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Abstract

Modification of carbon, including boron-doped diamond (BDD) and glassy carbon (GC), using gold nanoparticle (AuNP) was developed by self-assembly technique. This technique is based on electrostatic interaction between citrate-capped AuNP to amine terminal groups after surface modification of BDD and GC. The fabricated materials, AuNP-BDD and AuNP-GC, were then utilized as electrodes for As3+ detection using anodic stripping voltammetry (ASV) technique. Anodic stripping voltammograms of both AuNP-BDD and AuNP-GC electrodes showed similar peak potentials of As5+ oxidation at ~0.21 V (vs. Ag/AgCl) in optimum conditions of -500 mV, 180 s, and 100 mV/s for deposition potential, deposition time, and scan rate, respectively. AuNP-BDD shows better performances in the case of wide linear concentration range (0-20 mM) and low limit of detection (0.39 μM or 4.64 ppb), whereas those of AuNP-GC were linear in the concentration range of 0-10 mM with a detection limit of 0.14 μM (13.12 ppb). Excellent reproducibility was shown with RSDs (n=20) of 2.93% and 4.54% at AuNP-BDD and AuNP-GC, respectively. However, decreasing of current responses in 6-consecutive days was found more at AuNP-BDD (~20.1%) than that at AuNP-GC (~2.8%).

Keywords: anodic stripping voltammetry, arsenic, boron-doped diamond, glassy carbon, gold nanoparticles

1. Introduction

Arsenic exists in four oxidation levels, including -3, 0, +3, and +5. As(III) is more toxic than As(V) or organoarsenic compounds. Long term exposure to arsenite increases health risks aranging from conjunctivitis, skin, and internal cancer to diabetes, and vascular, reproductive, neurological effects [1-2]. Maximum contamination level allowed based on World Health Organization (WHO) and U.S. Environmental Protection Agency guide line is about 50-10 mg/mL [3-4].
Many methods have been developed to detect As (III), including graphite furnace atomic absorption spectrometry [5], inductively coupled plasma mass spectrometry (ICPMS) [6], and high performance liquid chromatography coupled by ICPMS [7]. However, those techniques have some disadvantages, such as time consuming analysis, expensive instrument requirement, and impracticable application for in situ analysis [5-7]. On the other hand, electrochemical methods, especially anodic stripping voltammetry (ASV), can provide high accuracy for very low concentration detection of metal ions (in ppb) with fast, inexpensive, simple and easily modified measurements [8-16].

Carbon electrode is generally used in electroanalysis since it is inexpensive, easy to get, inert as well as high conductivity and stability. Moreover, carbon has good biocompatibility [17]. However, carbon is less sensitive to arsen oxidation or reduction [18]. Surface modification, such as metal modification, is generally required to overcome the problem. Modification of carbon surface with metal nanoparticles provides some advantages in electrochemical sensor as it facilitates electron transfer between electrode surface and analyte [18]. Moreover, nano dimension of the modifying metals can theoretically enhance the surface area which means increasing catalytic activity. Some methods to modify carbon with metal nano particles have been developed, such as vacuum vapour deposition, electrochemical deposition and sputtering method [14-16,19]. However, the methods have some disadvantages, especially in the low stability of the deposited metal due to the lack of chemical interaction between metal and carbon [18-19]. Since ASV technique involves 2 steps, including pre-concentration step or deposition of analyte at electrode surface and stripping oxidation step, stable deposited metal particle on the surface is highly required.

In this work, carbon electrodes were modified by -NH₂ functional groups in order to increase the affinity to gold nanoparticles. This technique is known as self-assembly technique since the functional groups can direct the nanoparticle to be placed at the functional group site on carbon surface [20]. Furthermore, high affinity of carbon surface to metal nanoparticle was expected to improve the stability of the deposited nanoparticles [20]. The composite material produced was then utilized as electrodes for As³⁺ detection.

2. Experiment

Materials. Hydrochloric acid, potassium chloride, 1-propanol, ammonium hydroxide and sodium citrate analytical grade were all purchased from Merck. HAuCl₄ and NaBH₄ were supplied by Aldrich. Sodium (meta)-arsenite and α-alumina 0.5 were obtained from Wako. All chemicals were used without further purification. Double distilled water used throughout this study.

Preparation of BDD electrodes. BDD electrodes were deposited on Si (100) wafers in a microwave plasma-assisted chemical vapor deposition (MPCVD) system (ASTeX Corp.) with a plasma power of 3000 W. The deposition time was fixed at 6 hours. Detail of the preparation has been described elsewhere [21-22]. A mixture of acetone and methanol in a ratio of 9:1 (v/v) was used as the carbon source. B₂O₃, used as boron source, was dissolved in the acetone-methanol solution at a concentration of 10⁴ ppm (B/C).

Preparation of colloidal gold nanoparticles. Colloidal gold nanoparticles were prepared by adding 0.5 ml of 0.01 M HAuCl₄ solution into 18.5 ml of water and stirred for 5 min in room temperature. 0.5 ml of 0.1 M sodium citrate was added and stirred for 5 min. Then, 0.5 ml of 0.1 M freshly prepared NaBH₄ solution was added. Characterization was handled by UV-visible spectroscopy at an adsorption band of ~519 nm. TEM was utilized to investigate the nanoparticle dimension.

Modification of GC and BDD electrodes. Glassy carbon (GC) electrode was polished well by aqueous slurries of α-alumina (0.5 μm), whereas no pretreatment was required for the BDD. Both materials were then ultrasonicated in 1-propanol and water, each for 10 min, before drying in room temperature. The materials were then immersed in concentrated NH₄OH solution and irradiated under UV source (λ = 254 nm) for about 6 h. After cleaning and drying process, both materials were immersed in colloidal gold nanoparticles for 20 min followed by drying in 60 °C. The materials were then electrochemically characterized and used as working electrodes.

Electrochemical measurements. A single-compartment cell was used for electrochemical measurements. An Ag/AgCl (saturated KCl) and Pt wire electrode were used as the reference and counter electrodes, respectively. The planar working electrode was mounted on the bottom of the cell by using of a Viton O-ring. The geometric area of the working electrode was estimated to be 0.26 cm². The supporting electrolyte was 0.1 M HCl. All measurements were made at room temperature (23±2 °C) in stirring condition. Stripping voltammograms were recorded using a potentiostat (Hokuto-Denko, Hz-1000).

3. Results and Discussion

HAuCl₄ solution changed from yellow to red ruby after reduction reaction with NaBH₄ and sodium citric, indicating the formation of AuNPs [12].
Characterization of colloidal AuNPs by UV–visible spectrophotometer shows maximum absorption at ~519 nm (Fig. 1). Stability of AuNPs was also examined. The spectra of the first minute to the 7th day showed that the adsorption peak was not significantly changed, indicating good stability of the AuNPs colloid. The stability could be achieved due to the presence of sodium citric as the capping agent. Furthermore, TEM characterization (Fig. 2) shows that the AuNPs formed groups or clusters with an average size of 30 nm.

GC and BDD surface generally provide oxygen termination as the result of oxidation process in air [21,23]. Some reports show that although AuNPs can be deposited at original BDD or GC surface, the stability was very low, especially at BDD [8,19]. The surface of oxygen termination is known to have negative charge due to significant difference in the electronegativity of oxygen and carbon on the surface. This creates an electrostatic barrier to binding of negatively charged AuNPs because in the present work, negatively charged citrate ions are used to stabilize the AuNPs colloid [22]. As the result, the deposited AuNPs could be easily removed from the electrode surface during the measurement or in the cleaning process [21]. On the other hand, nitrogen termination can provide positive charged since H+ adsorbed on the amino groups attached to the BDD surface and facilitated adsorption of negatively charged AuNPs [20]. Therefore, in this work, GC and BDD surface was modified to provide nitrogen termination. Modification was conducted by photochemistry to exchange oxygen with amines (-NH₂) functional group at the surface. The presence of -NH₂ functional group was expected to drive the deposition of AuNPs at the carbon surface. The AuNP-modified GC and BDD electrodes were then named as Au-NP-GC and AuNP-BDD.

Characterization of AuNP-GC and AuNP-BDD was conducted by stripping voltammetry of solution of As⁵⁺ in 0.1 M HCl. Non modified GC and BDD were also examined as control. Theoretically, during deposition process in ASV method, As⁵⁺ is reduced to As⁰ at the surface of gold nanoparticles to form intermetallic Au-As.

Figure 1. UV-vis Spectra of Gold Nanoparticles in Various Time from the 1st Min to the 7th Day after Synthesis

Figure 2. TEM Image of Gold Nanoparticles in 40.000 Times of Magnification

Figure 3. Stripping Voltammograms of 6 μM As⁵⁺ in 0.1 M HCl Solution at (i) Non Modified and (ii) AuNP-modified (a) BDD and (b) GC Electrodes. Potential Deposition, Time Deposition, and Scan Rate of -500 mV, 180 s, and 100 mV/s were Applied, Respectively
As. As° is then reoxidized to As³⁺ in stripping process. Fig. 3 shows plots of the stripping process in ASV. There is no oxidation peak was found at non modified GC and BDD electrodes, whereas well-defined peaks were observed at the potential of ~0.21 V (vs. Ag/AgCl) at AuNP-GC and AuNP-BDD electrodes, indicated that both electrodes have succesfully been modified.

The measurement condition was optimized for deposition potential and time. Deposition potential is the given potential to reduce As³⁺ in the solution to be As° at the electrode surface. The higher the potential, the higher energy supplied to reduce As³⁺. Fig. 4 shows influence of deposition potentials at the oxidation peak currents. Similar trends were observed at both electrodes. The figure shows that peak current increased with the increasing of negative potential and achieved the highest current at the potential of -500 mV. The peak current then decreased significantly at more negative potential due to competition between reduction of As³⁺ and reduction of H⁺ [21]. Consequently, -500 mV was then fixed as the optimum potential deposition. Influence of deposition time to the peak currents was shown in Fig. 5. The longer the deposition time the higher the peak current. However, the peak currents start to be stable at the deposition time of 180 s, indicating that all of As³⁺ was completely reduced to be As° in 180 s. Therefore, 180 s was fixed for optimum deposition time.

In the case of measurements using cyclic or linear sweep voltammetry, current responses produced at GC electrode is generally higher than that at BDD electrode [21]. Sp² configuration of GC causes adsorption controlled mechanism at GC surface, whereas diffusion controlled ocurrs at BDD surface with sp³ configuration [17,21,24]. Adsorption controlled mechanism generally can accumulate more analyte at the surface, resulting in higher current responses [21]. However, it is interesting to see that peak currents of stripping voltammetry at AuNP-BDD is always higher than that at AuNP-GC (Fig. 3). The smaller current at AUNP-GC is probably due to the strong adsorption at GC that caused the stripping step was more difficult. Although the active site of both electrodes is AuNPs, the deposition of As° at the AuNP-GC surface might also block the surface of GC, resulting in slower stripping process. The broad peaks at AuNP-GC (Fig. 3a) confirmed the evidence. Possibility that more amount of AuNP at BDD than that at GC could be negligible since the photochemical reaction of NH₂ formation should be more effective at sp² than at sp³. However, characterization using XPS is required to prove.

Analytical performances of the electrodes were also investigated at the optimum measurement conditions at AuNP-BDD the current responses is linear in the concentration range of 0-20 mM with a detection limit of 0.14 μM (4.64 ppb) (Fig. 6b), whereas at AuNP-GC, linear calibration curve (Fig. 6a) can be achieved in a concentration range of 0–10 μM with a limit detection of 0.39 μM (13.12 ppb), whereas. Better performance
Figure 6. Stripping Voltammograms of Various Concentrations of As$^{3+}$ in 0.1 M HCl Solutions at (a) AuNP-BDD and (b) AuNP-GC Electrodes. Applied Condition was Similar to that of Fig. 3. Insets: Plots of Current Responses vs. Concentrations

of AuNP-BDD caused by its very low background current, resulting in very low limit of detection and wide range of concentration. It is known that BDD has superior low background current among other solid electrodes [21].

Reproducibility of current responses of AuNP-GC and AuNP-BDD was investigated. Figure 7 shows stripping voltammograms of 10 μM As$^{3+}$ in 0.1 M HCl in 20-consecutive measurements. Excellent stability of the electrodes, especially AuNP-BDD was shown by RSDs of 2.93% and 4.56% at AuNP-BDD and AuNP-GC, respectively. AuNP-BDD is considered to be more stable than AuNP-GC due to less adsorptive behavior of BDD than GC as the AuNP-BDD electrode surface remains clean after every measurement, whereas impurity was adsorbed at AuNP-GC surface. In the case of gold nanoparticles, adsorption behavior of the gold particles is minimized due to small dimensions of the particles.

Stability of the electrodes was also examined. Figure 8 shows stripping voltammograms of 10 mM As$^{3+}$ in 0.1 M HCl solution at both electrodes for 6-successive days. Higher decreasing of current observed at AuNP-BDD (~20%) was due to leaching of the gold nanoparticles from electrode surface during storage time between measurements. Leaching at AuNP-BDD could be higher due to the adsorption weakness of BDD surface, indicating that only physical adsorption, in terms of positive negative interaction, occurred between amina functional groups and gold nanoparticles. In the case of GC, although chemical bonds were also not
formed, high adsorption behavior caused advantages to keep AuNPs at the electrode surface as shown by lower current decreasing than AuNP-BDD (~2.8%).

4. Conclusions

Fabrication of AuNP-BDD and AuNP-GC was successfully conducted using self-assembly technique after surface modification of -NH₂ functional groups. The composite material was utilized as electrodes for As(III) detection using anodic stripping voltammetry (ASV) with optimum condition of -500 mV, 180 s and 100 mV/s as deposition potential, deposition time and scan rate, respectively. AuNP-BDD shows better analytical performance than AuNP-GC in terms of current responses, detectable concentration range, low limit of detection, and reproducibility of current responses due to very low adsorption properties of BDD. However, stability of AuNP-BDD electrode is lower than AuNP-GC.

Acknowledgement

This research was partly funded by Hibah Riset Unggulan Universitas Indonesia under contract number 240AP/DRPM-UI/N1.4/2008.

References