Modification of gold nanoparticles through allyl mercaptan bridge at boron-doped diamond electrode for an arsen (V) sensor

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Abstract. A simple, cheap and fast analytical procedure for arsen (V) detection was developed by applying the BDD (boron-doped diamond) modified by gold nanoparticles (AuNPs-BDD). The gold nanoparticles (AuNPs) with an average particle size of 10 nm was synthesized through reduction reaction of gold ions by NaBH4 in the presence of allyl mercaptan. These nanoparticles could be successfully deposited on the surface of boron-doped diamond (BDD) by an immersion process under the exposure of UV light (λ = 254 nm) for 6 h. An Au/C ratio of around 1:56 was observed at the prepared AuNPs-BDD. Preliminary study for arsen (V) detection by using anodic stripping voltammetry (ASV) technique using this electrode in a solution of 0.1 M HCl containing of NaBH4 showed a good linearity (R² = 0.99) of the current flow in the concentration range of 0–100 μM with a limit detection of 0.105 μM.

Keywords: Boron-doped diamond, gold nanoparticles, allyl mercaptan, surface modification, arsenic detection

1. Introduction

Inorganic arsenic contamination in drinking water has attracted a lot of attentions since several million people in various parts of the world are at a risk of arsenic contamination. This contamination can cause health problems, such as chronic diseases or even death [1, 2]. Although arsenic level in natural water are usually low in some area with different geographic, World Health Organization (WHO) established that limit groundwater content level should be no more than 10 μgL⁻¹ to reduce carcinogenic effects in humans [1].

The methods of determining inorganic arsenic have been carried out in various ways, such as AAS (Atomic Absorption Spectrometry), AES (Emission Spectrometry), GFAAS (Graphite Furnace Atomic Absorption Spectrometry), HPLC (High Pressure Liquid Chromatography), (ICP-MS) Inductively Coupled Plasma-Mass Spectrometry [3, 4]. Some of methods mentioned above have some drawbacks including the requirement of high operational costs, expensive equipment and complicated sample preparation processes. Another method, ASV (Anodic Stripping Voltammetry) is one of the popular methods used in electrochemistry due to its low detection limit and easy operation [5, 6]. This method was performed by a pre-concentration step of the analyte on the electrode surface followed by a stripping step of the pre-concentrated analyte [6]. Various electrodes, such as mercury, platinum and gold, were
reported to be employed for ASV method [5]. Among these electrodes, gold-based electrodes are the most popular used to measure arsen [7].

Meanwhile, BDD (boron-doped diamond) has been reported as an electrode substance with many advantages due to its high chemical, mechanical, and biological inertness, which affect its wide working potential and low blank current [7-9]. However, since BDD has less electrochemical sensitivity to arsen, surface modification with gold is necessary [5, 7]. In the previous work, the BDD surface was modified with allyl mercaptan-capped gold nanoparticles (AuNPs) [10]. Under a UV light irradiation, the double bonds in allyl mercaptan was expected to break and form chemical bonds to the BDD surface, while the sulfur sites bind with gold. This AuNP-modified BDD was stable enough for application as \( \text{As}^{3+} \) detection [10]. In this work, an application for \( \text{As}^{5+} \) detection was studied by using the same electrodes.

2. Materials and method

2.1. Materials
Hydrogen tetrachloroaurat (III) tetrahydrate (HAuCl\(_4\).4H\(_2\)O), sodium arsenite (NaAsO\(_2\)), sodium arsenate (Na\(_2\)HAsO\(_4\).7H\(_2\)O), allyl mercaptan (2-propene thiol), and sodium borohydrate (NaBH\(_4\)) were obtained from Sigma Aldrich, while hydrochloric acid (HCl), 2-propanol and ethanol were supplied from Merck. BDD (Boron-doped diamond) films were laboratory made in Keio University, Japan.

2.2. Synthesis of AuNPs (gold nanoparticles)
AuNPs was prepared by mixing 5 mL of 0.01 % (v/v) HAuCl\(_4\).4H\(_2\)O in 50 % ethanol solution. Then, 2.5 mL of 0.002 % allyl mercaptan in ethanol solution was added [10]. After 5 min of mixing, 0.5 mL of 0.1 M NaBH\(_4\) solution was added and mixed for 10 min. The nanoparticles was determined by using UV-VIS Spectroscopy, TEM, and PSA.

2.3. Modification of AuNPs-BDD electrodes
AuNPs-BDD was prepared by immersing BDD in the prepared colloidal AuNPs and irradiated under UV light (\( \lambda = 254 \text{ nm} \)) for 6 h. The surface was identified by using SEM.

2.4. Electrochemical study of AuNPs-BDD as arsenic sensor
Electrochemical study was performed by using cyclic voltammetry (CV) and anodic stripping voltammogram (ASV) for standard solutions of arsenic (III) and (V) using a potentiostat (Dropsens) in an electrochemical cell with 3 electrodes. The prepared AuNPs-BDD was applied as the working electrode, while Ag/AgCl system and Pt wire were used as the reference and counter electrode, respectively. Planar working electrode (estimated geometric area of \( \sim 0.26 \text{ cm}^2 \)) was placed at the bottom of the cell using the Vitton O-ring. The supporting electrolyte was 0.1 M HCl containing of 0.1 M NaBH\(_4\).

3. Results and discussion

3.1. Synthesis of AuNPs (gold nanoparticles)
AuNPs was prepared by reduction reaction using NaBH\(_4\) as the reducing agent and allyl mercaptan 0.002 % as the capping agent. The change in color of solution from yellow to red purplish indicating the formation of AuNPs with the change of Au\(^{3+}\) to Au\(^0\) [11]. The presence of allyl mercaptan (C\(_3\)H\(_6\)S) was expected to be around gold nanoparticle as a high affinity of the SH-group performed hydrogen interactions with gold as shown in figure 1 [11]. The interaction between gold and allyl mercaptan was proposed as the complex formation between the ligand and its central metal with gold as the central
metal and allyl mercaptan as the ligand [11]. The -SH group on allyl mercaptan has a good affinity with Au based on the nature of the Hard Soft Acid Base.

The initial characterization was performed using UV-Visible Spectrophotometer (UV-VIS), showing the maximum absorption peak at a wavelength of 545 nm (figure 2). In general, AuNPs provides a strong surface plasmon absorption peak in the range 510–580 nm [10].

The stability of this peak was examined for 3 days. The absorbance spectrum for 3 days showed that the peak was relatively stable for 2 days before decreased at the 3rd day. This result indicates the low stability of AuNPs colloids. This is reasonable as the lack of the charge in C=C groups in allyl mercaptan structure did not provide a repulsion effect between the nanoparticles. However, in fact, the stable period of the nanoparticles for several hours was enough to be modified on the BDD surface.

Furthermore, investigation by using Transmission Electron Microscopy (TEM) (figure 3) was performed. The nanosphere shape was obtained from the synthesis of gold using allyl mercaptan [11]. Further confirmation by using Particle Size-Analyzer characterization (PSA) (figure 4) showed that the average particle size was 10 ± 2 nm.

3.2. Modification of AuNPs-BDD electrodes

The prepared AuNPs was expected to be firmly attached to the BDD electrode under photochemical reaction between thiol (-SH) functional groups of the nanoparticles and the surface of BDD (figure 5). Previously, it was reported that covalent bonds between AuNPs and -SH was probably formed under UV irradiation [10, 11]. Confirmation with SEM (figure 6) showed that the nanoparticles were successfully distributed on the BDD surface. Further observation using EDS showed that Au/C ratio of 1:56 was observed (table 1). The modified BDD electrode was then named as AuNPs-BDD electrodes.

![Figure 1. Interaction of Au with capping agent of allyl mercaptan.](image1)

![Figure 2. UV-VIS AuNPs spectrum at various times for 3 days after synthesis.](image2)

![Figure 3. TEM image of AuNP](image3)

![Figure 4. Size distribution of AuNP with PSA.](image4)
Electrochemical investigation was conducted in an electrochemical cell with 3 electrodes. CV (Cyclic voltammetry) was performed in 0.1 M HCl to confirm the existence of gold nanoparticles on BDD surface. The voltammograms comparison in the potential range from -0.8 to +2.0 V (vs. Ag/AgCl) at BDD, gold plate and AuNPs-BDD is displayed in figure 7. There was no peak observed on the BDD surface, which confirmed that there was no active species on the BDD surface. On the contrary, the specific gold oxidation peak at around +1.5 V and the reduction peak at around +0.4 V were observed at gold plate electrode. In the case of AuNps-BDD, the oxidation and reduction peaks were found at around +1.33 V and +0.1 V, respectively. These shifts were probably due to the kinetic different between gold plate and AuNPs-BDD surface. Since the surface modification of BDD involved not only gold particles but also allyl mercaptan as the capping agent, the surface different might also influence the kinetics of arsenic ions. However, the different of CVs on the BDD and the AuNPs-BDD surface indicates that the modification has successfully performed.

3.3. Electrochemical study of AuNPs-BDD as arsenic (V) sensor

AuNPs-BDD was then electrochemically examined for arsenic (V) sensors as the working electrode. ASV technique was set up following the previous research at the potential deposition of -500 mV for 120 s [11]. Then, stripping step was performed in the potential range from -0.4 V to +0.8 V (vs. Ag/AgCl). A pretreatment using 0.1 M NaBH₄ was applied to reduce As⁵⁺ to be As³⁺ to perform...
Figure 7. CV (Cyclic voltammograms) results of 0.1 M HCL solution vs Ag/AgCl on (a) BDD, (b) Gold plate, and (c) AuNPs BDD electrodes.

Figure 8. Stripping voltammograms of 0.1 M HCl containing various concentrations of (a) As$^{3+}$ and (b) As$^{5+}$ and 0.1 M NaBH$_4$ together with the related linear calibration curves. The potential deposition of -500 mV for 120 s was applied at AuNPs-BDD as the working electrode.

the measurements at low potential. Figure 8 shows the comparison of voltammograms at AuNPs-BDD between various concentrations of As$^{3+}$ and As$^{5+}$ by using ASV technique in 0.1 M HCl.
Linear calibration curves for As$^{3+}$ and As$^{5+}$ concentrations of 100-500 μm were obtained at $y = -0.0164x + 8.522$ ($R^2 = 0.91$) and $y = -0.0081x + 5.546$ ($R^2 = 0.97$) (figure 8). The calibration curve results show that the prepared AuNPs-BDD has the possibility to be applied as arsenic sensors. Similar peak potentials at around +0.2 V were observed at both species. However, lower sensitivity was found in As$^{5+}$ measurements, probably because not all As$^{5+}$ could be reduced to be As$^{3+}$. Further, more convincing techniques and methods are required to specify the detection for a mixture of As$^{3+}$ and As$^{5+}$ [9].

4. Conclusion
Gold nanoparticles have been successfully synthesized using allyl mercaptan as a capping agent and deposited on the surface of BDD. TEM (Transmission Electron Microscopy) and PSA (Particle Size Analyzer) showed an average size of AuNPs at 10 ± 2 nm. Characterization by using SEM-EDS confirmed that AuNPs-BDD electrodes had an Au:C ratio of 1:56. Application of this material as the working electrode in As$^{3+}$ and As$^{5+}$ sensors using the ASV technique showed a good sensitivity for the detection.

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