Arsenic and arsenate detection with anodic stripping voltammetry technique using boron-doped diamond modified by platinum

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Abstract. High homogeneity and stability of platinum particles modified at boron-doped diamond (BDD) electrode was successfully performed using chemical seeding, followed by electrodeposition technique. The platinum particles on the surface of BDD characterized using Scanning Electron Microscopy- Energy Dispersive X-Ray Spectroscopy (SEM-EDS) showed that the coverage of Pt particles was 1.54 % on the BDD surface. These modified electrodes were used for As\textsuperscript{3+} and As\textsuperscript{5+} sensors using the anodic stripping voltammetry technique in 0.1 M phosphate buffer solution pH 6. Prior to the detection, pretreatment was required by the addition of 0.1 M NaBH\textsubscript{4} to change As\textsuperscript{3+} to As\textsuperscript{5+}. The optimum parameters were at a deposition potential of -500 mV, a deposition time of 150 s, and a scan rate of 200 mV/s. The voltammograms were linear for As\textsuperscript{5+} and As\textsuperscript{3+} (R = 0.9797 and 0.9903, respectively) in the concentration range of 0 to 100 ppb. Estimated detection limits of 16.50 and 8.19 ppb for As\textsuperscript{3+} and As\textsuperscript{5+} were achieved, respectively, suggesting that the method is promising for the specification detection of As\textsuperscript{3+} and As\textsuperscript{5+}.

Keywords: arsenic, arsenate, anodic stripping voltammetry, boron-doped diamond, platinum

1. Introduction
Arsenic contamination in water has become a serious problem for human health and the ecosystem. Arsenic, mainly accumulated in sewage and industrial waste, is a hazardous substance [1]. It is poisoning and can cause death in high doses [2]. It is also carcinogenic [3] and easily distributed in the environment [4], therefore, a detection method to monitor its contamination in the environment is necessary.

Various methods and techniques were generally employed in the detection of arsenic, such as hydride generation atomic fluorescence spectrometry, chemiluminescence, inductively coupled plasma atomic emission spectrometry, and inductively coupled plasma mass spectrometry [5]. However, these methods require relatively complex procedures and expensive instrumentations as well [6]. On the opposite, electrochemistry method offers the same efficiency with cheaper instrument. It can also develop to be portable, therefore, making it an ideal method for field analysis. Various types of working electrodes can be used, including gold [7], iridium [8], silver and platinum [9]. However, their high background currents make their modification on the surface of less conductivity substrates to be interesting [10]. Stripping voltammetry technique particularly has an advantage in pre-concentration step, which can provide high concentration of analyte on the surface [6]. Boron-doped diamond (BDD), popular with its low background current and wide potential window, is one of the interesting materials for substrates, but it is not very easy to be modified due to high stability of its sp\textsuperscript{3} configuration [11–12].
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Know the coverage of Pt on the surface of BDD. Table 1 displays the summary of atomic comparison larger and distributed more were deposited.

Figure 1. SEM image of (a) Bare BDD (b) after wet seeding and (c) after electrodeposition step.

In this work, BDD electrodes were modified with platinum for an application as arsenic and arsenate detection. The modification was performed by amperometry with an addition step, i.e. wet chemical seeding, to provide a better distribution of the deposited particles. High homogeneity and stability of Pt particles could be achieved, which increased the sensitivity and stability of measurements.

2. Materials and methods

2.1. Apparatus and chemicals

All apparatus and chemicals used in this research were BDD (supplied by Einaga’s laboratory, Keio University, Japan), an electrochemical cell made from Telfon® completed with magnetic stirrer, platinum and Ag/AgCl (saturated KCl) electrodes, NaAsO₂, Na₅H₅AsO₆.7H₂O, H₂PtCl₆.6H₂O, KH₂PO₄, KH₂PO₃, and NaBH₄, were supplied from Wako, Japan.

2.2. Modification of the BDD with Pt

Modification using wet chemical seeding was performed by dropping subsequently NaBH₄ and H₂PtCl₆ solutions on the BDD surface, then washed and dried after 24 h. This treatment was modified from Gao et al. [12] and repeated three times. Next, the electrodeposition was conducted at a potential of -0.2 V for 15 minutes using H₂PtCl₆ solution. After calcinated the electrode at 700 °C in N₂ atmosphere for 5 minutes, the materials were resulted by using Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and then used as working electrode to detect arsenic trace.

2.3. Detection procedure of As⁵⁻ and As³⁻

Examination of the Pt-BDD for arsenic sensor was performed in phosphate buffer solution (PBS) pH 6 containing various concentrations of As⁵⁻ and As³⁻. Parameters of anodic stripping voltammetry (ASV) were fixed at a deposition potential of -500 mV and deposition time of 150 s with a stripping rate of 200 mV/s. For As⁵⁻ detection, 0.1 M NaBH₄, that added before was stirred for 1 min to reduce As⁵⁻ to As³⁻ before ASV technique was performed. For the detection of As³⁻ and As⁵⁻ mixture, initially ASV was conducted to determine As³⁻ concentration, then 0.1 M NaBH₄, that added before, was stirred for 1 min before the second ASV technique was performed.

3. Results and discussion

3.1. Modification of the BDD with Pt

Modification of the BDD surface was performed by combining the wet seeding to grow the crystal nuclei of Pt on the BD surface and electrodeposition to grow the Pt crystal on the BDD surface [12]. Figure 1 shows the SEM images of the BDD before and after modification with Pt with magnification of 2000 × (figure 1a) and 10000 × (figure 1b and figure 1c). After wet seeding step, smaller particles were deposited on the surface of the BDD, while after electrodeposition step the particles were grown larger and distributed more homogeneously.

Characterization was also performed by using Energy Dispersive X-Ray Spectroscopy (EDS) to know the coverage of Pt on the surface of BDD. Table 1 displays the summary of atomic comparison

Figure 1. SEM image of (a) Bare BDD (b) after wet seeding and (c) after electrodeposition step.
Table 1. Summary of EDS measurements of the Pt-modified BDD after the wet seeding and electrodeposition steps

| Element | Surface composition of BDD after wet seeding step | Surface composition of BDD after electrodeposition step |
|---------|--------------------------------------------------|--------------------------------------------------------|
| Carbon  | 96.74                                            | 94.91                                                  |
| Oxygen  | 02.32                                            | 02.74                                                  |
| Platinum| 00.94                                            | 01.54                                                  |

Figure 2. (a) Stripping voltammogram of various concentrations of As³⁺ together with (b) the current plots at the potentials +0.15 V vs. As³⁺ concentrations. The stripping voltammetry parameters were at deposition potential of -0.5 V for 150 s and scan rate of 200 mV/s.

on the modified BDD surface, showing that after wet seeding step 0.94 % surface was covered. This amount increased to be 1.54 % after the electrodeposition step. On the surface of BDD, oxygen was also observed, which probably due to the oxygen sites of the BDD grown when it was prepared and stored [7,11]. The Pt sites on the surface will be used for arsenic detection to increase the interaction between As and Pt particles ASV measurements. Therefore, platinum distribution on the BDD surface has a prominent effect on the sensitivity of the electrode towards arsenic.

3.2. As⁵⁺ detection
The detection of As⁵⁺ using Pt-modified BDD was conducted in the concentration range of 0 ppb to 500 ppb as shown in figure 3. In this detection, it is necessary to add NaBH₄ as a chemical reducing agent as to reduce As⁵⁺ needs a very negative potential that can cause a competition with hydrogen evolution. As the results, the reduction As⁵⁺ on the surface of electrode was imperfect. Figure 3a shows that the oxidation peak observed at the same potential at around 0.15 V (A), confirmed that the peak belongs to
Figure 3. (a) Stripping voltammogram of various concentrations of As\(^{5+}\) together with (b) the current plots at the potentials +0.15 V vs. As\(^{3+}\) concentrations. Stripping voltammetry parameters were the same as in figure 2.

Figure 4. Stripping voltammograms of 100 ppb (a) As\(^{3+}\) solutions with the addition of various concentrations of As\(^{5+}\) (b) As\(^{5+}\) solutions with various concentrations of As\(^{3+}\) together with (c) and (d) which showed the plots of the related currents at the potentials +0.15 V of (a) and (b) respectively. The stripping voltammetry parameters were the same as figure 2.
the oxidation of As$^+$ to As$^{5+}$. Other peak at around 0.05 V was not detected due to less formation of the hydrogen using this procedure. The plots of current responses vs. As$^{3+}$ concentrations in figure 3b show the linearity from 40–100 ppb.

3.4. As$^{3+}$ and As$^{5+}$ mixture detection

Next, the detection of As$^{3+}$ and As$^{5+}$ mixture solution was conducted using ASV in two steps. First, ASV was performed to determine As$^{3+}$. Then, the same solution was added with NaBH$_4$, before the ASV measurement to measure the total arsenic concentration of As$^{3+}$ and As$^{5+}$. The concentration of As$^{3+}$ can be determined by subtracting As$^{5+}$ from the total arsenic concentration. Two series of testing was examined. In the first one, solution of 100 ppb of As$^{3+}$ was used with the addition of various concentrations of As$^{5+}$ from 100 to 400 ppb, whereas in the second one, 100 ppb As$^{3+}$ solution was used as the constant variable with addition of 100 to 400 ppb As$^{5+}$. The voltammograms of the first and the second series are shown in figure 4a and figure 4b, respectively. In both figures, the increase of current responses was observed with the increase of As$^{3+}$ (figure 4a) and As$^{5+}$ (figure 4b) concentrations. The linear calibration curves are shown in figure 4c and 4d, respectively, for As$^{3+}$ and As$^{5+}$ with a correlation value (R) of 0.98 and 0.979, indicating that the method can be applied for real applications. Furthermore, the stability of the Pt-modified BDD was examined during the detection of As$^{3+}$ and As$^{5+}$ in five consecutive days. The % RSD of under 3 % was observed for both, suggesting that the Pt-modified BDD was stable enough to be employed for the detection of both As$^{3+}$ and As$^{5+}$ species.

4. Conclusions

Modification of BDD with Pt particles has been successfully examined using combination of the wet seeding and electrodeposition process, resulting in 1.54 % coverage of Pt on the surface of BDD. Applications of the modified BDD as the working electrode to detect As$^{3+}$ and As$^{5+}$ using anodic stripping voltammetry showed a good linearity in the measurements of individual solutions of As$^{3+}$ and As$^{5+}$ as well as of the mixture solution of As$^{3+}$ and As$^{5+}$ with good linearity and stability.

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