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Selective Detection of As(V) with High Sensitivity by As-deposited Boron-doped Diamond Electrodes

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Electrochemical selective detection of not only As(III) but also As(V) has been investigated by anodic stripping voltammetry. Here, instead of using modified working electrodes, simple *as-deposited* boron-doped diamond (BDD) electrodes were used with the addition of gold ions in the sample solution as a catalyst for the electrochemical reaction. A *potential-step* technique was performed to minimize the hydrogen evolution effect that occurs at the highly negative potential such as −1.5 V (vs. Ag/AgCl) for the reduction of As(V). The present method realized very high sensitivity with an experimental detection limit of 12 ppb and excellent stability for the detection of both As(III) and As(V) as well as mixed solutions of these forms.

A method for the detection of arsenic in water that is highly sensitive is urgently required, since arsenic can cause a variety of adverse health effects and contamination with arsenic is becoming a serious worldwide threat.[1–3] Typical methods for the monitoring of arsenic in water have generally been based on the use of inductively coupled plasma-atomic emission spectrometry, graphite-furnace atomic adsorption spectrometry, etc. However, such technologies are laboratory-based and are time consuming. In addition, these methods lead to high capital costs for multisample analyses. In contrast, electrochemical methods can provide low-cost, portable, and quick measurements with high sensitivity. Therefore, electrochemical detection is receiving much attention as a promising novel method for overcoming these problems.[4–18] In particular, anodic stripping voltammetry (ASV) is the most popular method due to its low detection limits and ease of operation. However, although both the As(III) and As(V) species (arsenate, $HAsO_4^{2-}$, which is also important to detect) are found in groundwater, reports on direct electrochemical detection methods for As(V) are limited.[9,17,18] It is obvious that the direct electrochemical detection of As(V) with high sensitivity will have an important impact not only in basic electrochemistry but also on the practical application of arsenic-sensing devices.

On the other hand, boron-doped diamond (BDD) electrodes have recently been attracting increasing attention as new electrode materials. These electrodes exhibit superior characteristics over other conventional electrode materials, including a wide potential window in aqueous solution, low background currents, and weak adsorption of polar molecules.[19] These properties have been reported to offer significant advantages for electrochemical sensors that are intended for use with biorelated and environmentally important species.[20,21]

Electrochemical detections of As by gold-modified BDD electrodes were reported by Swain[16] and us.[17] In 2007, Swain et al. reported a detection method of total arsenic (As(III) and As(V)) by a chemical reduction of As(V) to As(III) with Na_2SO_3, followed by the normal ASV determination of As(III).[16] Then, in 2008, we reported an electrochemical selective detection method for As(III) and As(V) without chemical reduction using gold-modified BDD electrodes.[17] In that work,[17] a potential step was applied to minimize the hydrogen evolution effect at the high potentials that need to be applied for the reduction of As(V). Although As(III) could be detected with very high sensitivity (the detection limit was 5 ppb), the detection limit for As(V) was insufficient (100 ppb) for the requirements of "high sensitivity" analysis. Moreover, the stability and reproducibility of gold-modified BDD electrodes were not ideal for practical applications where an electrochemical arsenic sensor was required. It has been suggested that the gold deposited at the BDD surface can easily become detached during the stripping step due to the inert surface of the BDD (sp^3 configuration).[19]

Consequently, in the present work, a highly sensitive, stable, and reproducible detection technique for both As(III) and As(V) using the ASV method is proposed. Here, in order to eliminate the instablility of the modified gold on BDD surface, as-grown BDD electrodes were used, and gold ions (100 ppm) were added into the solutions as catalysts.

Initially, the condition of the solutions was optimized in order to increase sensitivity. First, the pH of the solution was optimized to pH 1 for the reduction of As(III) to As(0), which is consistent with the Pourbaix diagram.[22] Then, in order to enhance the oxidation signal of As(0) to As(III), 2 M NaCl was added to optimise the electrolyte, since chloride ions can control the electron-transfer kinetics of arsenic.[11]

Sodium arsenite ($NaAs^{III}O_2$), sodium arsenate ($Na_2HAs^{V}O_4 \cdot 7H_2O$), and hydrogen tetrachloroaurate trihydrate ($HAu^{III}Cl_4 \cdot 3H_2O$) were supplied by Wako Inc. and used without any purification. Working arsenic sample solutions containing 2 M NaCl, 0.1 M HCl, and 100 ppm $HAuCl_4$ were prepared for the stripping measurements. BDD electrodes were deposited on Si(100) wafers using a microwave plasma-assisted chemical vapor deposition system. Details of these preparation process have been described elsewhere.[19,23] Electrochemical measurements were carried out using a single-component cell equipped with a stirring bar magnet. An Ag/AgCl (saturated KCl) electrode was used as the reference electrode, and Pt wire was used as the counter electrode. The planar working electrode was mounted on the bottom of the cell using a Viton O-ring. The geometric area of the working electrode was estimated at 0.1 cm^2.

Prior to the measurements, pretreatment of the BDD electrodes was undertaken by applying +1.0 V (vs. Ag/AgCl)

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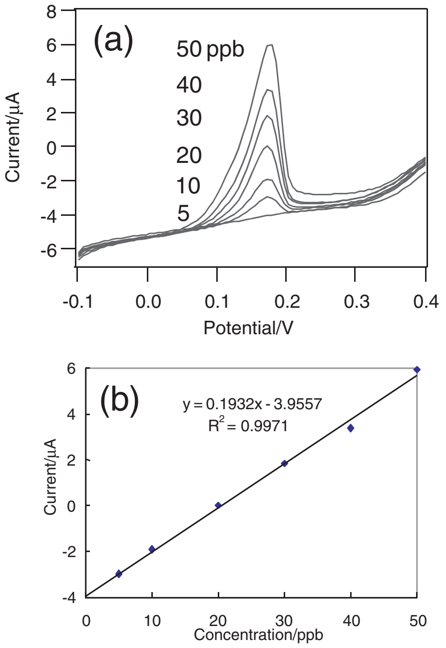

Figure 1. (a) Stripping voltammograms of As(III) in 2 M NaCl solutions at pH 1 in the concentration range 5–50 ppb and (b) calibration curve. Applied parameters were $E_{\text{dep}} = -0.1$ V (vs. Ag/AgCl), $t_{\text{dep}} = 30$ s, potential step of -0.1 V (vs. Ag/AgCl): 30 s, and linear sweep rate: 600 mV s^{-1}.

for 20 s in order to dissolve the adsorbed gold. The removal of the adsorbed species was confirmed by measurement of the background current.

A stripping voltammetry procedure for As(III) was conducted based on the reduction of As(III) to As(0), followed by As(0) oxidation. A deposition potential (E_{dep}) of -0.1 V (vs. Ag/AgCl) was selected, because the reduction potentials of As(III) and Au(III) for a solution at pH 1 were both ca. -0.1 V (vs. Ag/AgCl).[22] The other reaction conditions were also optimized.

The ASV voltammograms of As(III) are shown in Figure 1a. Reduction at -0.1 V (vs. Ag/AgCl) was conducted for 30 s in a stirred solution, followed by 30 s at the same potential without stirring to reduce noise in the recording process. The stripping step was conducted using a range of potentials from -0.1 to 1.0 V (vs. Ag/AgCl) with a sweep rate of 600 mV s^{-1}. A clear peak could be observed at a potential of $+0.17$ V (vs. Ag/AgCl) (Figure 1a), which is attributed to the oxidation of As(0) to As(III).[4,11,13,16] Furthermore, a linear calibration curve could be obtained for the concentration range 5 to 50 ppb (Figure 1b).

It has been suggested that the Au provides a medium in which stable As phases can be formed and subsequently oxidized for highly sensitive detection.[13,16] That is, due to the high affinity of As(0) to Au(0), intermediate As–Au compounds can be formed during the reduction step in the ASV process. In this case, when -0.1 V (vs. Ag/AgCl) was applied, both Au(III) and As(III) were reduced to Au(0) and As(0) and, as a result, were able to form As–Au compounds, which has the general formula, Au_xAs_y, with $x = 1$–3 and $y = 2$–6.[16,24] The As–Au intermetallic compound structure was probed using X-ray diffraction by Tikhomirova et al.[24,25] They mentioned that the compound decomposes to arsenic oxide of the arsenolite type (As_2O_3) and fine-grained gold when exposed to oxidizing potentials.

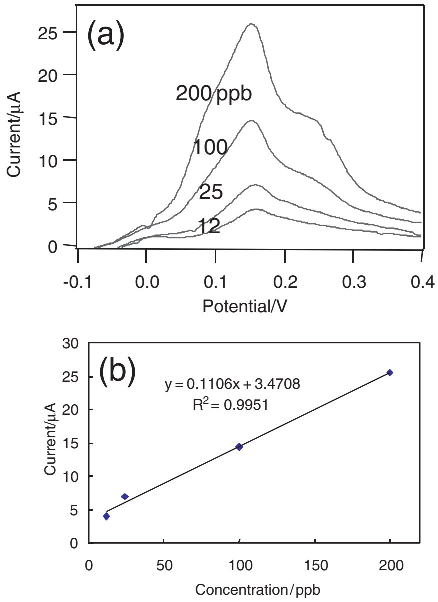

Figure 2. (a) Stripping voltammograms of As(V) in 2 M NaCl solutions at pH 1 in the concentration range between 12–200 ppb and (b) calibration curve. The applied parameters were $E_{\text{dep}} = -1.5$ V (vs. Ag/AgCl), $t_{\text{dep}} = 20$ s, potential step of -0.45 V (vs. Ag/AgCl): 30 s, and linear sweep rate: 600 mV s^{-1}.

Then, in order to realize the detection of As(V), the potential step methods that we proposed previously,[17] were applied (Figure 2a). In the case of As(V) deposition, a highly negative potential was required to overcome the high activation energy for As(V) reduction. On the other hand, the application of a very low potential can generate hydrogen evolution due to water reduction. Although a cell containing a stirrer was used to minimize the adsorption of generated hydrogen, a portion of the hydrogen gas can still be adsorbed at the electrode surface, leading to blocking of As(0) deposition at the electrode surface. Therefore, after the deposition step was carried out at -1.5 V (vs. Ag/AgCl) for 20 s, a potential of -0.45 V was applied for 30 s without stirring followed by the stripping sweep from -0.45 to 1.0 V (vs. Ag/AgCl) at a scan rate of 600 mV s^{-1}.

The current peaks observed at a potential of ca. 0.17 V (vs. Ag/AgCl) definitely correspond to the oxidation of As(0) to As(III) (as shown in Figure 1). The peak current was linear over the concentration range from 12 to 200 ppb of As(V) (Figure 2b). On the other hand, when the stripping sweep was applied soon after the deposition step at -1.5 V (vs. Ag/AgCl) without the step at -0.45 V, no peak characteristic of the oxidation of As(0) was observed. It is highly probable that As(0) accumulated at the electrode surface was detached due to the production of hydrogen gas during the stripping step.

One advantage of this method is the presence of an additional step at -0.45 V for 30 s before the stripping sweep process to remove the gas adsorbed at the electrode surface. It appears that releasing the hydrogen gas that is adsorbed at the electrode surface can overcome the problem of the deposition of

As(0) on the electrode surface. Another advantage is that the gold catalysts are added in solution, not using gold-modified electrodes. This not only enhances the signal due to the catalytic reaction but also provides excellent stability and reproducibility. The long-term stability of the signal at the potential of ca. 0.17 V (vs. Ag/AgCl) was confirmed by measurements every month for 4 months (data not shown). In fact, when gold-modified BDD electrodes were used for the detection, the stability of the deposited gold is low and the gold dissolved/detached by multiple cycling. In the present system, post-treatment of the electrodes by applying +1.0 V (vs. Ag/AgCl) for 20 s can dissolve the adsorbed gold, leaving fresh BDD electrodes that exhibit good reproducibility for the next measurements.

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