Effect of Nanostructures of Au Electrodes on the Electrochemical Detection of As

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ABSTRACT
The development of simple methods for As detection has received great attention because As is a toxic chemical element causing environmental and health-related issues. In this work, the effect of nanostructures of Au electrodes on their electroanalytical performance during As detection was investigated. Different Au nanostructures with various surface morphologies such as nanoplate Au, nanospike Au, and dendritic Au structures were prepared, and their electrochemical behaviors toward square-wave anodic stripping voltammetric As detection were examined. The difference in intrinsic efficiency for As detection between nanostructured and flat Au electrodes was explained based on the crystallographic orientations of Au surfaces, as examined by the underpotential deposition of Pb. The most efficient As detection performance was obtained with nanoplate Au electrodes, and the effects of the pre-deposition time and interference on As detection of the nanoplate Au electrodes were also investigated.

Keywords: Au Nanostructures, Nanoplate Au, Electrochemical Detection, Arsenic

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1. Introduction
Arsenic (As) is a toxic chemical element naturally existing in the form of inorganic and organic compounds incorporated in groundwater and soil [1,2]. Two predominant forms of As are arsenite (As(III)) and arsenate (As(V)), among which As(III) is more toxic than As(V), which is electrochemically inactive under normal conditions [3-6]. Prolonged exposure to trace amounts of As causes adverse health effects such as cancers and hyperkeratosis, as seen in many countries where the As level in drinking water is above the WHO standards (i.e. 10 µg L⁻¹) [2,5,7-10]. Therefore, it is important to develop an As detection method which is sensitive, simple, and low-cost as well as portable for use in both laboratories and on-site analysis.

Several analytical methods have been developed to monitor low-levels of As, including hydride generation atomic fluorescence spectrometry, inductively coupled plasma atomic emission mass spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), fluorescence spectrophotometry, atomic absorption spectrometry (AAS), and high-performance liquid chromatography coupled with ICP-MS [5,6,9-11]. Even though these techniques are successful in detecting low concentration levels of As, they require expensive instrumentation and highly skilled expertise.

In contrast, electrochemical methods provide an easy, less expensive and portable option for monitoring As. In particular, anodic stripping voltammetry (ASV) has excellent sensitivity and accuracy, the ability to distinguish between metal ions, and a shorter analysis time than conventional methods [10,12,13]. ASV consists of a two-step process for As detection: pre-deposition of As ions in the form of As(0) and oxidative stripping of the As(0) to As(III) [12]. There have been several investigations of the experimental factors affecting the performance of ASV detection of As, such as the electrode materials, solution pH, and chloride ion concentration in the electrolyte solution [5,14].

Au-based electrode materials have been extensively examined for the detection of As(III) with
ASV and are known to provide excellent sensitivity and limits of detection (LOD) [4,15]. Several types of electrode materials, such as Au and Pt wires fused into glass tubes, Au fiber electrodes, Au disc electrodes, and Au modified glassy carbon (GC) electrodes, have been used in combination with various supporting electrolytes such as HClO₄, H₂SO₄, and HCl for the determination of As(III) [16-20]. The effects of the crystallographic orientation of Au electrodes on As detection have been investigated. Polycrystalline (111)-like Au electrodes were shown to be effective for the selective detection of As(III) [21]. A comparative investigation of Au nanoparticles with different surface orientations toward the detection of As showed that the Au(111) surface exhibited greater sensitivity compared to the Au(100) and Au(110) surfaces [22,23].

In the present work, we investigated the effects of Au nanostructures with different morphologies on the performance of ASV detection of As. Different Au nanostructures such as nanoplate Au, nanospike Au, and dendritic Au structures were prepared and their electrochemical detection performances were compared. The relationships between crystallographic orientations of Au nanostructures and the As detection performance were examined. For the Au nanostructures with best As detection performances, the experimental parameters were optimized and the interference effect was examined.

2. Experimental

All solutions were prepared using ion-free water purified by a filtration system (Milli-Q). Pb(CH₃COO)₂, Pb(NO₃)₂, and As₂O₃ (99.995%) were purchased from Sigma Aldrich. KAu(CN)₄, HAuCl₄, and NaOH were purchased from Alfa-Aesar. A non-cyanide, sulfite-based commercial electrolyte (Techni Gold 25ES) was purchased from Technic Inc. (Cranston, RI). A stock solution (5 mM) was prepared from 4.946 mg of As₂O₃ dissolved in minimum concentrated NaOH, the pH was adjusted to 3.0, and the solution was diluted with water [19]. Electrochemical measurements were conducted using a CHI 750E system (CH Instruments, Inc. U.S.A) with three electrodes. Pt wires and Ag/AgCl electrodes (3 M NaCl) were used as counter and reference electrodes, respectively. Commercial Au rod electrodes (d = 2 mm, CH Instruments) were used as working electrodes. The Au rod electrodes were polished with alumina powders (1 µm and 0.05 µm) and electrochemically cleaned using cyclic voltammetric scanning in 0.1 M H₂SO₄ between -0.2 V and 1.5 V. The electrolyte solutions were purged with N₂ before electrochemical measurements.

Nanostructured Au electrodes were prepared using electrochemical deposition of Au on Au rod electrodes, as reported in previous investigations. Nano-plate Au structures were electrodeposited at a deposition potential of -1.1 V from a solution containing 15 mM KAu(CN)₄ and 0.25 M Na₂CO₃ [24]. Dendritic Au structures were electrodeposited at -0.83 V from a solution containing 36 mM Au(I) ions complexed with sulfite anions [25,26]. Nanospike Au surfaces were electrodeposited at 0.05 V from a solution containing 6.9 mM HAuCl₄ and 0.5 mM Pb(CH₃COO)₂ [27]. Electrochemical detection of As(III) was conducted using square-wave ASV (SWASV) in 1 M HCl electrolyte solutions, which have been widely used in previous works because of the reproducible and sensitive stripping peaks in these electrolytes. Typical parameters for ASV were a deposition potential of -0.2 V and deposition time of 150 s. The parameters for square-wave voltammetry were increment E = 0.004 V, amplitude = 25 mV, and frequency = 15 Hz.

3. Results and Discussion

Fig. 1 shows the SWASV of flat Au and nanostructured Au surfaces obtained in the presence of 3 µM As(III) in 1 M HCl after pre-deposition at -0.2 V for 150 s. The insets in Fig. 1 show SEM images of the typical Au nanostructures used for As detection in the present work. Fig. 1a shows that the As stripping peak on flat Au electrodes was observed at ca. 0.07 V with a stripping current of 10 µA. On nanoplate Au electrodes, the stripping peaks were observed at 0.03 V, and the overall stripping currents significantly increased compared to those observed on flat Au electrodes (Fig. 1b). The electrochemical surface area (ESA) of the nanoplate Au increased as the deposition charge for the preparation of nanoplate Au was increased (Table S1). As a result, the stripping current on nanoplate Au increased when the deposition charge was increased from 0.01 C to 0.019 C. However, the stripping current decreased when the deposition charge was further increased to 0.028 C, which
indicates that the increase in ESA of the nanoplate Au electrodes does not necessarily result in increased stripping currents for As detection.

On dendritic Au electrodes, the stripping peaks appeared at 0.05 V, and the overall stripping currents became smaller than those observed on nanoplate Au electrodes (Fig. 1c). The ESA of the dendritic Au electrodes increased as the deposition charge was increased (Table S1), and the stripping currents also increased. The stripping currents decreased slightly when the deposition charge was increased from 0.014 C to 0.025 C. In the case of nanospike Au electrodes (Fig. 1d), the position and currents of the stripping peaks are similar to those observed on dendritic Au electrodes. Greater stripping currents were observed for the nanospike Au electrodes obtained at a higher deposition charge due to the increased ESA (Table S1). The stripping peaks for nanostructured Au electrodes are narrower than those of flat Au electrodes. In particular, the nanoplate Au electrodes exhibited significantly sharper peaks than other Au electrodes, because of the well-defined surface orientation of the nanoplate Au surfaces (vide infra for detailed discussion).

The results shown above indicate that the efficiency of SWASV for As detection is best on nanoplate Au surfaces. However, as the ESA of the Au electrodes depends on the types of nanostructures and the deposition charge used during the preparation procedures, the ESA of each Au electrode should be considered for close examination of the detection efficiency during SWASV. The intrinsic surface properties of Au nanostructures for the detection of As are compared in Fig. 2 using the normalized peak currents of each surface evaluated by dividing the As oxidation peak currents by the ESA. Fig. 2 shows that nanoplate Au electrodes exhibited greater normalized peak current than dendritic Au and nanospike Au electrodes. The nanoplate Au electrode prepared with 0.019 C showed the maximum efficiency for electrochemical detection of As. For dendritic Au and nanospike Au electrodes, there was a gradual decrease in normalized peak currents as the deposition charge for the nanostructures was increased. The normalized peak current of the flat Au electrode (dotted line) is in between those of the nanospike Au and dendritic Au electrodes. The intrinsic efficiencies of SWASV for As detection for nanoplate Au and nanospike Au electrodes are better than that of the flat Au electrodes, whereas the dendritic Au electrodes exhibited worse efficiency than...
To examine the origin of the high efficiency of the nanoplate Au electrodes toward electrochemical As detection, we performed underpotential deposition (UPD) of Pb on the Au electrodes. It has been reported that Pb UPD is an effective technique to examine the crystallographic surface structures of Au electrodes [28,29]. Fig. 3 shows a comparison of the voltammetric profiles of Pb UPD obtained on nanostructured Au and flat Au electrodes. Two sets of redox waves consisting of cathodic deposition and anodic stripping of Pb appear in the Pb UPD profiles. The redox waves observed in more negative potential regions between -0.55 V and -0.65 V correspond to Pb UPD occurring on the (111) facets of the Au electrode surfaces. The redox waves in the less positive regions correspond to Pb UPD on Au facets with higher surface energy such as (100) and (110). Fig. 3 reveals that each Au electrode surface has a different ratio of Au facets between (111) and (100)/(110). In particular, the (111) facets are dominant on the nanoplate Au electrode surfaces. In contrast, the (100)/(110) facets are more dominant than (111) facets on the dendritic Au electrode surfaces. The relative ratio of (111) and (100)/(110) Au facets can be evaluated from the ratio of the charges consumed during the anodic stripping of UPD Pb (Table S2) [30,31]. The nanoplate Au electrode exhibited the greatest relative ratio (3.09), whereas the dendritic Au showed the smallest one (0.49). The ratio of (111) facets of the Au electrode surface increases in this order: dendritic Au < flat Au < nanospike Au < nanoplate Au. This trend is in agreement with the trend of efficiency for electrochemical As detection observed between Au electrode surfaces (Fig. 2). It has been reported that Au(111) facets are more efficient than Au(100) and Au(110) facets [22,23]; thus, the high efficiency of nanoplate Au electrodes for As detection can be attributed to the large amount of (111) facets on the Au surfaces. For the dendritic Au electrodes, the (100) and (110) facets are dominant on the Au surfaces which results in high electrocatalytic activity in oxygen reduction and glucose oxidation reactions [25]. In contrast, the dendritic Au electrodes did not exhibit good activity for As detection in spite of their large ESAs, as shown in Fig. 1.

We further obtained calibration plots for As detection on flat Au and nanostructured Au electrodes prepared with different deposition charges. The SWASV responses on various Au electrode surfaces were obtained for increasing As concentrations (Fig. 4 and Fig. S1, S2, and S3), from which calibration plots for each electrode were constructed. All of the Au electrodes showed reasonable calibration plots for As detection, as shown in Fig. 4. Nanostructured Au electrodes exhibited greater sensitivities for As detection compared to the flat Au electrodes. As expected from the results presented above, the nanoplate Au
electrodes showed greater sensitivity than the other nanostructured Au electrodes. The peak potential of As stripping on nanoplate Au was less positive than on other Au electrodes, indicating easy desorption of As on nanoplate Au surfaces. The best electroanalytical performance for As detection was achieved on nanoplate Au electrodes prepared with 0.019 C of deposition charge; these electrodes were utilized for further investigation of their analytical performance for As detection, as discussed below.

The effect of pre-deposition potential, which causes the accumulation of As ions in the form of As (0), on the peak current of the As stripping was examined on the nanoplate Au electrodes (Fig. S4). The stripping current increased when the pre-deposition potential was increased from -0.1 V to -0.2 V. At more negative pre-deposition potentials, the stripping currents decreased. In particular, the stripping current decreased sharply at a pre-deposition potential of -0.4 V because of the hydrogen evolution reaction rather than the deposition of As. Therefore, the optimal pre-deposition potential was chosen as -0.2 V, which has been used throughout the present investigation.

Fig. 5 shows the relationship between As stripping peak current and pre-deposition time. As the pre-deposition time was increased, the resulting stripping current increased on both flat and nanoplate Au electrodes. On flat Au electrodes, the stripping currents increased with pre-deposition time up to 150 s, after which the current did not increase significantly. A pre-deposition time of 150 s is enough for As detection for flat Au electrodes. In contrast, the stripping currents on nanoplate Au electrodes increased with pre-deposition time up to 400 s and reached a plateau. It has been reported that pre-deposited As(0) on Au surfaces forms insulating layers [20]. When the active sites on Au surfaces are fully covered with
As(0) layers, then further deposition of As(0) is prohibited and saturation of the stripping currents occurs. The stripping currents on nanoplate Au electrodes became greater at longer pre-deposition times compared to those on the flat Au electrodes, indicating that the active Au sites for pre-deposition of As are more abundant on nanoplate Au than on the flat Au electrodes. This result suggests that greater stripping currents can be obtained at longer pre-deposition times on the nanoplate Au electrodes compared to those on the flat Au electrodes.

To investigate the electroanalytical efficiency for As detection at different pre-deposition times, SWASV responses of flat Au and nanoplate Au electrodes were obtained (Fig. S5 and Fig. S6). Fig. 6 shows a comparison of the calibration plots for As detection obtained from flat Au and nanoplate Au electrodes with different pre-deposition times. The nanoplate Au electrodes exhibited greater sensitivities for As detection than the flat Au electrode regardless of the pre-deposition times. However, the degree of sensitivity enhancement between flat and nanoplate Au differs depending on the pre-deposition time. The sensitivity ratio between nanoplate and flat Au at 50 s of pre-deposition time was 4.79 (Table S3). The sensitivity ratio increased to 6.21 and 7.97 as the pre-deposition time was increased to 150 s and 400 s, respectively. These results indicate that the electroanalytical efficiency for As detection on the nanoplate Au electrodes was further improved compared to that on the flat Au electrodes by increasing the pre-deposition time. For flat Au electrodes, 150 s of pre-deposition time is enough for As detection, whereas the nanoplate Au electrodes exhibited improved electroanalytical efficiency for As detection with a pre-deposition time of 400 s.

Interference effects during the SWASV detection of As on the nanoplate Au electrodes were examined using Cu(II) as a representative interfering ion. Fig. 7 shows the SWASV responses of the nanoplate Au electrode for As detection in the absence and presence of 3 µM Cu(II). The stripping peaks of Cu on the nanoplate Au electrodes are clearly separated from those of As. The sensitivity of the nanoplate Au electrode in the absence of Cu(II) was found to be 23.3 µA µM⁻¹. In the presence of 3 µM Cu(II), the sensitivity was measured at 21.2 µA µM⁻¹, which is slightly smaller than that measured in the presence of Cu(II) ions. It has been reported that the interference
effect of Cu during the detection of As arises from the formation of Cu-As intermetallic compounds, which depends on the structure of the Au electrode surfaces [3,9,32]. The nanoplate Au electrodes do not suffer from interference by Cu during the SWASV detection of As, presumably due to their unique nanoplate Au structures. The LOD of nanoplate Au electrodes for As detection was measured being 0.01 µM (Fig. S7), which is lower than the WHO standard guideline for As in water.

4. Conclusions

We investigated the effect of Au nanostructures on the electroanalytical performance of Au electrodes for As detection. Different Au nanostructures, such as nanoplate Au, nanospike Au, and dendritic Au structures, were prepared by electrochemical deposition, and their electroanalytical As detection properties were compared. The crystallographic orientations of the Au nanostructures were investigated by Pb UPD measurements to address the difference in intrinsic efficiency for As detection between nanostructured and flat Au electrodes. The nanoplate Au electrodes showed the best efficiency for electrochemical detection of As, which can be ascribed to the predominant (111) facets on the nanoplate Au surfaces. The efficiency of As detection on the nanoplate Au electrodes compared to that on the flat Au electrodes can be improved by applying a longer pre-deposition time. The interference effect of Cu was not significant toward the electrochemical detection of As. The results of the present study provide insight into the preparation of efficient electrochemical sensors for As detection.

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Supporting Information

Additional electrochemical data and tables. This material is available from the author upon request.

References


