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Electrochemical Detection of Arsenic on a Gold Nanoparticle Array¹

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Abstract—The detection of As(III) was investigated on a gold nanoparticle array. At the first stage, gold nanoparticles were synthesized on glassy carbon microspheres. The resulting hybrid material was characterized by SEM and the sizes of the nanoparticles were found to be in the range 20–200 nm. At the second stage, glassy carbon microspheres decorated with Au nanoparticles were abrasively attached to the surface of a basal-plane pyrolytic electrode. The resulting gold nanoarray was characterized by the reduction of surface gold oxides. Furthermore, it was found to have good characteristics for the sensing of arsenic via anodic stripping voltammetry with a limit of detection of 0.8 μ M and a sensitivity of 0.91 C M⁻¹.

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INTRODUCTION

In recent years, metal and semiconductor nanoparticles have attracted great interest due to their superior characteristics and possible application in numerous technological areas such as catalysis, optics, microelectronics, and chemical/biological sensors. Therefore, much research has been done into their synthesis and characterization.

Metal nanoparticles have been widely used in electrochemistry, both in electrocatalysis [1, 2] and bioelectroanalysis [3–5] for the detection of different electroactive analytes. Nanoparticles exhibit unique advantages over macroelectrodes when used for electroanalysis such as enhancement of mass transport, catalysis, high effective surface area, and control over electrode microenvironment.

Metallic gold is characterized by chemical inertness and good thermal and electrical conductivity. Bulk gold electrodes have been employed for electrochemical detection of metal ions such as chromium [6, 7] and arsenic [8], as well as amino acids [9] and other organic compounds [10]. Gold has also been used in the detection of hydrogen peroxide [11]. Although gold in its bulk form has shown poor electrocatalytic activity for the reduction and oxidation of hydrogen peroxide, gold nanoparticles have exhibited good catalytic activity due to their high surface area-to-volume ratio and their interface-dominated properties [12]. Gold nanoparticles have also shown excellent catalytic activity for the oxidation of carbon monoxide [13].

Arsenic is a naturally occurring element widely distributed in the earth's crust. However, exposure to arsenic can cause a variety of serious health problems, such as dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic maladies. The contamination of groundwater and soil in various parts of the world with arsenic has been widely reported [14–18]. In Bangladesh alone, an estimated 50 million people are at risk, a threat regarded by the WHO as world's worst mass human poisoning disaster [19–21].

In this paper, we for the first time present the synthesis of gold nanoparticles on glassy carbon microspheres by electroless deposition and provide a characterization of the resulting material via microscopic and electrochemical techniques. Next, the detection of arsenic was explored on a gold nanoparticle–glassy carbon-powder-decorated basal-plane pyrolytic electrode. The modified electrode was found to provide good determination of arsenic.

EXPERIMENTAL

Reagents and materials. Sodium(meta)arsenite (NaAsO₂, 99%) was supplied by Fluka and used without further purification. A stock solution of As(III) (4 mM) was prepared from NaAsO₂ by dissolving 5.19 mg of NaAsO₂ in 10 cm³ of deionized water. Gold (I) sodium thiosulfate (AuNa(S₂O₃)₂ · H₂O, 99.9%) and glassy carbon spherical powder (10–20 µm, type 1) were purchased from Alfa Aesar (Heysham, UK). L-ascorbic acid (C₆H₈O₆, 99.7%) and sulfuric acid (H₂SO₄) were purchased from BDH and used as received.

All solutions were prepared using deionized water with a resistivity not less than 18.2 M Ω cm at 25°C (Vivendi Water Systems, UK).

Electrochemical measurements. The electrochemical cell was a standard three-electrode cell. The refer-

¹The text was submitted by the authors in English.



Scheme. Schematic representation of the surface of a BBPG electrode with abrasively attached glassy carbon microspheres decorated with gold nanoparticles (AuNPs-GC).

ence electrode was an aqueous saturated calomel electrode (SCE, Radiometer Analytical), and the auxiliary electrode was a carbon graphite rod. The working macrodisc electrode was a 5-mm diameter basal-plane pyrolytic graphite electrode (BPPG, Le Carbone Ltd., Sussex, UK). The working electrode was used immediately after carrying out a voltammetric scan in the background solution (1 M H₂SO₄) at 0.1 V s⁻¹ between 0 and +1.5 V vs. SCE. All experiments were performed at 20°C under a nitrogen atmosphere. The electrochemical investigations were performed using an Eco Chemie μ Autolab potentiostat monitored by a PC.

Electroless deposition of metal nanoparticles onto glassy carbon microspheres. Gold nanoparticles were synthesized on glassy carbon spherical powder by an electroless deposition technique. The procedure involved stirring 0.2 g of GC spherical powder in 100 cm^3 of AuNa(S₂O₃)₂ solution (0.150 g) with 0.090 g of L-ascorbic acid being added as a reducing agent slowly at the beginning of the reaction. The pH of the reaction mixture was adjusted to 5.2 by adding sodium hydroxide. The reaction mixture was then mixed for 24 h at room temperature. After the reaction was finished, the reaction mixture was filtered and rinsed with water to remove any unreacted species. The resulting powder was left to dry in the air.

Abrasive attachment of carbon microspheres on a basal-plane pyrolytic graphite electrode. The abrasive attachment of glassy carbon microspheres decorated by Au nanoparticles (AuNPs-GC) on a basal-plane pyrolytic graphite electrode was performed by gently rubbing the electrode surface on a thin layer of microsphere powder lying on a filter paper (Scheme). The excess of non-attached microspheres on the electrode surface was then removed by rubbing the electrode surface with a wet cotton cloth. Moreover, after modification of the electrode, its surface was immersed in the solution for 15 min before starting measurements in order to minimize any AuNPs-GC loss during the measurements. The electrode surface can be renewed by pressing cellotape on the electrode surface and removing it along with several surface layers of graphite.

Electron microscopy and elemental analysis. Scanning electron microscopy (SEM) imaging of the electrode surfaces was carried out using a JEOL JMS model 6500F scanning electron microscope.

Calculation limits of detection. The given value corresponds to the limit of detection obtained with the standard addition method consisting of six additions of



Fig. 1. SEM image of glassy carbon microspheres (a) and Au nanoparticles supported on glassy carbon microspheres (b).

 $2 \mu M$ of arsenic to the sample. The limit of detection was evaluated from the data using the 3-sigma method.

RESULTS AND DISCUSSION

Characterization of Metal Nanoparticle-Modified Glassy Carbon Spheres

Glassy carbon powder modified with gold nanoparticles via the electroless deposition technique reported above was characterized using both spectroscopic and electrochemical techniques.

First, the unmodified GC powder was examined using scanning electron microscopy. The SEM image of the unmodified GC powder verified that it consisted of spheres 10–20 μ m in diameter according to supplier's specification (Fig. 1a). In addition, some particles of smaller diameter arising from the manufacturing process were observed. Next, GC powder modified with gold was examined by SEM. The obtained SEM images of modified GC spheres (Fig. 1b) showed that randomly distributed metal nanoparticles were formed on GC spheres. It was found that gold nanoparticles were 20–200 nm in size.

Glassy carbon powder modified via the electroless deposition procedure was next characterized using cyclic voltammetry. The modified glassy carbon powder was abrasively attached to a basal-plane pyrolytic graphite electrode as described in Section 2.4 and subsequently qualitatively and quantitatively characterized.

Cyclic voltammograms of the AuNPS-GC modified BPPG electrode were run in 0.5 M H_2SO_4 solution from 0 to +1.5 V vs. SCE at a scan rate of 0.2 V s⁻¹. A broad peak could be observed on the cathodic scan at ca. +0.8 V vs. SCE (Fig. 2). This peak potential was reported as a value characteristic for the reduction of surface oxides of gold [22, 23], confirming that metal gold was synthesized on GC spheres by the electroless deposition method reported above.

The electroactive surface area of the metal formed on GC powder and abrasively attached to the BPPG electrode could be evaluated from the area under the surface-metal reduction peak using the literature values for charge passed per unit area on the surface of metal [23].

As(III) Detection on a Gold Nanoparticle-Modified Electrode

Next we examined the detection of As(III) on a BPPG electrode with abrasively attached gold nanoparticles—modified GC powder. Note that the abrasive attachment of metal nanoparticles—modified microspheres—is a very quick and efficient way to create a metal array. In addition, it is believed that this procedure reduces the formation of nanoparticle agglomer-



Fig. 2. Cyclic voltammetry at a 5-mm-diameter BBPG electrode modified by the abrasive attachment of AuNPs-GC in 1 M H_2SO_4 at scan rate of 0.1 V s⁻¹.

ates. The AuNPs-GC-BPPG electrode was electrochemically characterized prior to the investigation of As(III) detection. The total surface area of gold on the electrode was evaluated from the metal-oxide reduction peak area using the literature value of 390 μ C cm⁻² [23] for charge passed per unit area on the surface of the metal; it was found to be 0.40 cm².

Detection of As(III) on the AuNPs-GC modified BPPG electrode was investigated in a 1-M H_2SO_4 solution scanning at 0.1 V s⁻¹ between 0 and 0.5 V vs. SCE after holding the potential at ~0.4 V for 40 s. No peak could be observed in the examined potential range in a blank solution without any As(III) added. However, the cyclic voltammogram run after adding 0.1 mM As(III) was characterized with a clear peak at ca. +0.2 V vs. SCE. The peak current was found to increase with 5 μ M As(III) additions.

The limit of detection of As(III) on the AuNPs-GC-BPPG electrode was determined using the standard addition method. Figure 3 shows the voltammetric response of the AuNPs-GC-BPPG electrode obtained for successive 2 µM As(III) additions. Again, a clear peak corresponding to the oxidation of As(III) could be seen, which increased with increasing the As(III) concentration. The correlation of the peak area for six successive additions was found to be linear with As(III) concentration; the limit of detection for As(III) equal to 0.8 µM was calculated based on the peak area vs. As(III) concentration plot using the 3-sigma method. Sensitivity was evaluated from the same set of data and found to be 0.90875 C M⁻¹. With optimization, further improvement is likely possible-the limit of detection can be lowered by applying longer deposition time and using more sensitive electrochemical techniques. This is the first time that metal nanoparticles have been abrasively attached to the electrode surface without the use of any binding substances such as nafion. This simple and quick method of modifying the electrode surface with metal nanoparticles also provides good contact



Fig. 3. Cyclic voltammetry at a 5-mm-diameter BPPG electrode modified by abrasive attachment of AuNPs-GC at 0.1 V s⁻¹, after holding the potential at -0.4 V for 40 s in 1 M H₂SO₄ and upon the additions of As (III); (a) $a=0, b=5, c=10, d=15, e=20, f=25, g=30 \,\mu\text{M}$; (b) $a=0, b=2, c=4, d=6, e=8, f=10, \text{ and } g=12 \,\mu\text{M}$; (c, d) are the corresponding calibration curves.

between the electrode and metal nanoparticles, as is evidenced by the obtained oxidation peak.

CONCLUSIONS

The synthesis of gold nanoparticles on glassy carbon microspheres via electroless deposition has been presented, and the formed hybrid material characterized using both spectroscopic and electrochemical techniques evidencing that gold nanoparticles of 20 to 200 nm in diameter were prepared. The glassy carbon microspheres decorated with Au nanoparticles were abrasively attached on the surface of a basal-plane pyrolytic electrode, and the detection of As(III) was investigated on a gold nanoparticle array. The resulting gold nanoarray showed good characteristics for the sensing of arsenic with a limit of detection of 0.8 μ M, which can be further optimized.

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