

Arsenic Detection by Nanogold/Conducting-Polymer-Modified Glassy Carbon Electrodes

Al-Nakib Chowdhury,¹ Sara Ferdousi,² Md. Mominul Islam,³ Takeyoshi Okajima,³ Takeo Ohsaka³

¹Department of Chemistry, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

²Department of Water Resources Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

³Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Mail Box G1-5, 4259 Nagatsuta, Midori-Ku, Yokohama 226-8502, Japan

Received 1 September 2006; accepted 14 November 2006

DOI 10.1002/app.25785

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article discusses the results for the development of a nanogold-particle/polyaniline-modified glassy carbon electrode for the detection of arsenic(III) in water. A thin polyaniline film was electropolymerized onto a glassy carbon electrode. The gold nanoparticle was then deposited onto the polyaniline-coated glassy carbon electrode via potential step electrolysis from 1.1 to 0 V versus Ag/AgCl/NaCl (saturated) for 45 s from a 0.5M H₂SO₄ solution containing 0.1 mM NaAuCl₄ in the absence and presence of a 0.1 mM KI additive. The surface of the modified electrode was examined with scanning electron microscopy. Cyclic and anodic stripping voltam-

metry of arsenic(III) was performed on the modified electrode. The thus modified nanogold-particle/polyaniline-modified glassy carbon electrode prepared in the presence of the I⁻ (KI) additive showed a high sensitivity in detecting arsenic(III) in water, and with stripping voltammetry, a limit of detection of 0.4 ppb arsenic was obtained, which is much lower than the arsenic guideline limit of the World Health Organization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1306–1311, 2007

Key words: electrochemistry; matrix; nanolayers; polyamines; sensors

INTRODUCTION

Arsenic (As) is an important environmental concern because of its high toxicity to a broad spectrum of living organisms at the level of parts per billion. The contamination of drinking water and groundwater with As has been reported in many parts of the world.¹ In some parts of the contaminated areas, the As level in drinking water is above the World Health Organization guideline value of 10 ppb (10 µg/L).²

As can exist in natural environment in four oxidation states: As⁵⁺, As³⁺ [or As(III)], As⁰ [or As(0)], and As³⁻. The mobility and chemical form of As determine its toxicity.³ The trivalent inorganic forms, such as arsenic trichloride and arsenic trioxide, are highly toxic and are 60 times more poisonous than the metal, its pentavalent salts, or organo-As compounds.⁴ The behavior of As species will change, depending on the biotic and abiotic conditions of the water.

The detection of trace amounts of As appears to be a pressing need as the scale of the As problem for nature and the human life has become clear; it has been emphasized by extensive studies illustrated in a special issue of *Talanta*⁵ entirely dedicated to various aspects of As exposure in nature. Indeed, a number of detection methods have been developed.⁵ Most of them possess limits of detection below the World Health Organization guideline value of 10 ppb. However, some methods for the determination of As at the level of the World Health Organization guideline have also been developed, reported, and reviewed elsewhere.^{6–9} The reliable techniques are suitable for laboratory conditions only. In addition, they are time-consuming and not suitable for the routine analysis of a large number of samples. Therefore, a rapid, portable sensor needs to be developed to overcome these problems. The use of electrochemical methodologies^{5,10–12} for detecting As

Correspondence to: A.-N. Chowdhury (nakib@chem.buet.ac.bd) or T. Ohsaka (ohsaka@echem.titech.ac.jp).

Contract grant sponsor: Tokyo Tech/United Nations Educational, Scientific, and Cultural Organization International Research Program for the Environment (launched in 2004 by the Tokyo Institute of Technology upon commission from the Japanese Ministry of Education, Culture, Sports, Science, and Technology in collaboration with the United Nations Educational, Scientific, and Cultural Organization).

Contract grant sponsor: Japan Student Services Organization (to A.-N.C. through a 2005 Japan Student Services Organization Follow-up Research Fellowship).

Contract grant sponsor: Japanese Ministry of Education, Culture, Sports, Science, and Technology (to S.F. through a Tokyo Institute of Technology/United Nations Educational, Scientific, and Cultural Organization International Research Program Fellowship).

Journal of Applied Polymer Science, Vol. 104, 1306–1311 (2007)
© 2007 Wiley Periodicals, Inc.

has recently come to the forefront of research as a possible means of fulfilling these requirements.

Materials in the nanoscale range have shown superior functional properties for a wide range of technological applications, including catalysis, optics, microelectronics, and chemical/biological sensors. Metal nanoparticles provide three important functions for electrocatalysis: the roughing of the conductive sensing interface, catalytic properties, and conductivity properties.⁷ Several works have been based on gold (Au) nanoparticles. Recently, the detection of As(III) with a Au-nanoparticle-modified glassy carbon (nano-Au/GC) electrode was performed with a limit of detection (LOD) of 0.0096.¹³ In another study,¹⁴ As detection was performed with nano-Au/GC electrodes prepared both in the absence and in the presence of an I⁻ additive, and a superior detection level was attained with the latter electrode.

Polymer-modified electrodes prepared by electropolymerization have received extensive interest in the detection of analytes because of their selectivity, sensitivity, and homogeneity in electrochemical deposition, strong attachment to the electrode surface, and high chemical stability in air.¹⁵ However, the application of a polymer-modified electrode for As detection is, to the best of our knowledge, yet to be reported. This study presents the electrochemical detection of As(III) with a nano-Au/polyaniline-modified glassy carbon (nano-Au/PANI/GC) electrode prepared in the absence and presence of an I⁻ additive. With square-wave voltammetry (SWV), an LOD of 0.4 ppb (0.4 µg/L) was obtained, which is much lower than the As guideline limit of the World Health Organization.

EXPERIMENTAL

All the reagents used in this work were obtained either from Kanto or Wako Chemicals Co. (Tokyo, Japan); they were analytical-grade and hence used without further purification, except for aniline, which was distilled before its use. All the solutions were prepared with deionized water purified by a Milli-Q system. According to the previous work,¹⁶ a stock solution of 8.2 mM As(III) was prepared: 8.1 mg of As₂O₃ was dissolved in a minimal amount of concentrated NaOH (1.0M), and then the solution was acidified with concentrated HCl (1.0M) to adjust the pH to 3 and diluted to a total volume of 10 mL with deionized water.

The procedure for the deposition of the Au nanoparticles onto bare glassy carbon (GC; diameter = 1 mm) was adapted from earlier reports.^{17,18} The GC electrode was polished with alumina powder with decreasing sizes from 1 to 0.06 µm. The electrode was

sonicated for 10 min in deionized water after each stage of polishing. The Au nanoparticle was electrodeposited from an acidic bath of 0.5M H₂SO₄ containing 0.1 mM Na[AuCl₄].2H₂O in the absence and presence of 0.1 mM KI by the stepping of the electrode potential from 1.1 to 0 V for a total deposition of 45 s. Because a longer deposition time would yield a Au film instead of nanoparticles,¹³ the potential stepping in this work was carried out three times; each constituted 15 s of deposition, and thus a total duration of 45 s was achieved for Au-nanoparticle deposition onto the electrode matrices employed. The nano-Au/GC electrodes thus prepared in the absence and presence of KI are termed nano-Au/GC and I⁻-nano-Au/GC electrodes, respectively.

A thin polyaniline (PANI) film was electrodeposited onto the polished, bare GC (diameter = 1 mm) electrode for a pulse width of 500 ms at 1.0 V from an electrolytic solution containing 0.5M aniline and 1.0M HCl. The film thus grown was rinsed several times with deionized water and 0.5M H₂SO₄ before its further use in the experiments. The deposition of Au nanoparticles onto the polyaniline-coated glassy carbon (PANI/GC) electrode was carried out in the same way as that onto the bare GC electrode. Before use, an electrochemical pretreatment of each electrode was carried out to obtain a stable cyclic voltammogram (CV) of the nano-Au-modified electrode (shown later in Fig. 4) by a continuous cycling of the electrode potential from -0.2 to 1.5 V. Such cycling of the electrode potential effectively removed the adsorbed I⁻ from the nano-Au-modified electrodes prepared in the presence of the I⁻ additive. The Au-nanoparticle/PANI-modified GC electrodes thus prepared in the absence and presence of KI are termed nano-Au/PANI/GC and I⁻-nano-Au/PANI/GC electrodes, respectively.

The surface morphology of the modified electrodes was carried out with a model JSM-T220 scanning electron microscope (JEOL Optical Laboratory, Tokyo, Japan) at an acceleration voltage of 15 kV and a working distance of 4–5 mm. All electrochemical measurements were performed with a BAS 50 B/W computer-controlled electrochemical analyzer with a standard three-electrode system. A platinum wire was used as a counter electrode with a silver/silver chloride/saturated sodium chloride [Ag/AgCl/NaCl (saturated)] reference electrode in the cell assembly for all the electrochemical experiments performed. All the measurements were carried out under an N₂ gas atmosphere at 20 ± 2°C.

RESULTS AND DISCUSSION

Chronocoulometry was adopted for the synthesis of thin PANI films on the GC electrode (diameter = 1 mm,

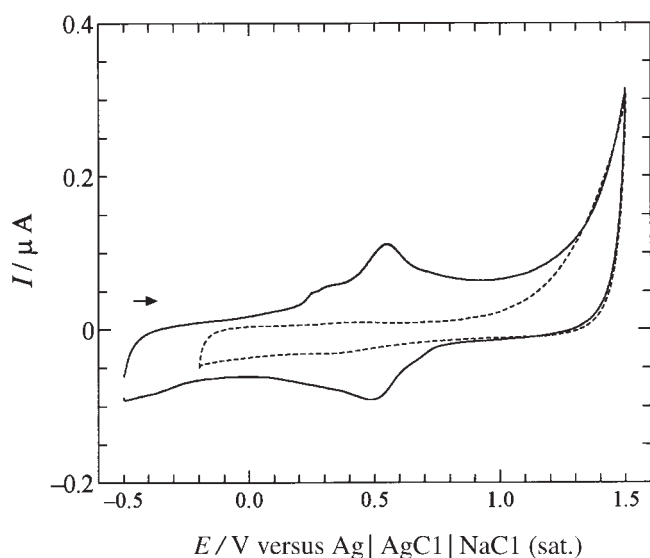
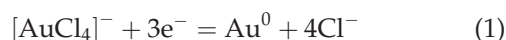


Figure 1 CVs of (---) GC and (—) PANI/GC electrodes in 0.5M H₂SO₄ solutions. *I* and *E* refer to current and potential, respectively. The potential scanning rate was 0.1 V/s.

geometric area = 7.854×10^{-3} cm²). Through the control of the pulse width, the thickness of the films could be controlled. The prepared PANI films with several thicknesses were attempted by the variation of the pulse width from 100 to 1000 ms at 1.0 V. Consequently, a PANI film prepared with a pulse width of 500 ms at 1.0 V was found to be suitable in terms of the formation of a thin film with good adherence to the substrate, reasonable electroactivity, and polymer characteristics in an acidic medium. Figure 1 shows the CVs of the bare GC and PANI/GC electrodes in 0.5M H₂SO₄ at a potential scanning rate of 0.1 V/s. In both cases, the CVs represent those obtained in the third cycle, which appeared to be the stable features of the voltammograms observed. Above 1.0 V, a sharp rise in the anodic current associated with the evolution of oxygen gas was observed for both electrodes. The anodic and cathodic peaks observed at 0.55 and 0.5 V for the PANI/GC electrode correspond to the oxidation (doping) and reduction (dedoping) of the PANI film, respectively, showing the characteristic behaviors of PANI associated with potential sweeping in acidic media.¹⁹

The electrodeposition of Au nanoparticles on the GC and PANI/GC electrodes from an electrolytic solution containing Au(III) was first attempted via the sweeping of the electrode potential between 1.2 and -0.1 V at 0.1 V/s, as shown in Figure 2. The results show the CV responses of both electrodes in a 0.5M H₂SO₄ solution containing 0.1 mM Na[AuCl₄] and 0.1 mM KI. Sharp cathodic peaks of nearly equal magnitudes around 0.5 V were observed for both electrodes employed. Similar results were observed in our previous work,¹⁴ suggesting the deposition of

Au onto the electrode surfaces by the reduction of Au(III) to metallic Au(0) as follows:



To deposit nano-Au particles onto the GC and PANI/GC electrodes, in both the absence and presence of I⁻, the procedure from the previously published reports^{13,18} was adopted. The electrodes were immersed into an electrolytic solution containing Au(III), and a potential step from 1.1 to 0 V was applied for 45 s (the deposition for 45 s was not carried out at once but followed a progressive deposition of 15 s repeated three times; thus, a total of 15 s + 15 s + 15 s = 45 s of deposition was achieved). With the charge-time plots during Au deposition, the surface coverage (Γ) of the nano-Au particles deposited on the electrode surfaces was calculated with the following equation:

$$\Gamma = \frac{Q_{\text{dep}}}{nFA} \quad (2)$$

where Q_{dep} is the amount of the charge that passed during the electrodeposition of Au, n is the number of electrons transferred [shown in eq. (1); in this case, $n = 3$], F is the Faraday constant (96,485 C/mol), and A is the geometric surface area of the GC electrode (7.85×10^{-3} cm²). The surface coverage of Au nanoparticles deposited onto the GC and PANI/GC electrodes was found to be 5.3×10^{-9} and 5.6×10^{-9} mol/cm², respectively, under the experimental conditions employed. In addition, the surface coverage

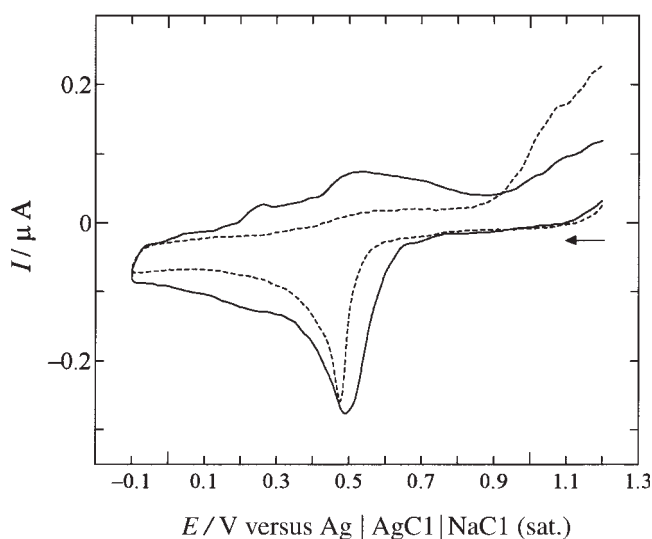


Figure 2 CVs of (---) GC and (—) PANI/GC electrodes in 0.5M H₂SO₄ solutions containing 0.1 mM NaAuCl₄ and 0.1 mM KI solutions. The potential scanning rate was 0.1 V/s.

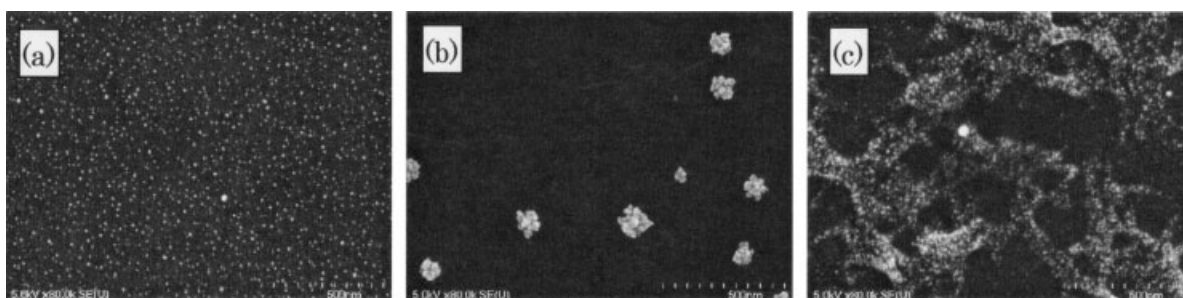


Figure 3 SEM images of nano-Au particles electrodeposited on (a) GC and (b,c) PANI/GC electrodes from 0.5M H₂SO₄ solutions containing 0.1 mM NaAuCl₄ in (a,c) the presence and (b) absence of 0.1 mM KI.

of the nano-Au/GC electrode was found to be 6.0×10^{-9} /mol cm².

Typical scanning electron microscopy (SEM) images of I⁻-nano-Au/GC, nano-Au/GC, and I⁻-nano-Au/PANI/GC electrodes are shown in Figure 3. In the presence of the I⁻ additive, Au particles seemed to be deposited on the substrates on a nanometer scale, typically 20–30 nm, and were dispersed nicely on the substrates [Fig. 3(a,c)], whereas large particles with a dendritic shape were observed to be deposited in the absence of the I⁻ additive [Fig. 3(b)]. The electrodes thus obtained were used for the detection of As(III) in water.

To get surface information about the Au nanoparticles electrodeposited onto the I⁻-nano-Au/GC and I⁻-nano-Au/PANI/GC electrodes, CVs were next recorded in 0.5M H₂SO₄ at a scanning rate of 0.1 V/s. The obtained results are shown in Figure 4. In both cases, a sharp cathodic peak at about 0.9 V could be observed. Analogous voltammetric profiles with a cathodic peak at 0.9 V for a 0.1 mM Au(III) solution were also reported previously and were attributed to the reduction of Au surface oxide.^{17,18} To estimate the real surface area of the Au nanoparticles deposited on the electrodes, the obtained characteristic CV responses, as shown in Figure 4, were used. The real surface areas were evaluated by the calculation of the amount of charge consumed during the reduction of the Au surface oxide monolayer with a reported value of 400 μC/cm².^{20,21} The real surface areas were thus evaluated to be 1.53×10^{-3} and 1.21×10^{-3} cm² for I⁻-nano-Au/GC and I⁻- nano-Au/PANI/GC electrodes, respectively. Similarly, the surface area of the nano-Au/GC electrode was also estimated, and the obtained surface area was higher (1.85×10^{-3} cm²) than those of the electrodes prepared in the absence of the I⁻ additive.

Figure 5(a) shows the electrochemical response of As(III) to the I⁻-nano-Au/PANI/GC electrode at a scanning rate of 0.1 V/s in a 1.0M HCl solution containing 8.2 μM (0.61 ppm) As(III). The reduction wave that emerged around -0.3 V could be attrib-

uted to the three-electron reduction of As(III) to As(0).²² On the reversal anodic scan, an oxidation wave was observed at about 0.25 V. This process was ascribed to the subsequent reoxidation of As(0) to the parent As(III) species. Both the cathodic and anodic waves were found to increase with the addition of As(III) to the 1.0M HCl solution, as depicted in Figure 5(a–e). The observed anodic peak current at 0.3 V for each As(III) concentration gave a linear relationship between them in the low concentration range of As(III) (inset in Fig. 5).

The electrochemical response of As(III) was next examined by SWV because high sensitivity and a large linear range could be achieved with the SWV technique.^{13,14} Also, according to the same report,¹⁴ the SWV parameters of a 75-Hz frequency and 25-mV amplitude were chosen for all the subsequent analysis in this study. The SWV responses of As(III) reduction at -0.3 V for 60 s of predeposition at

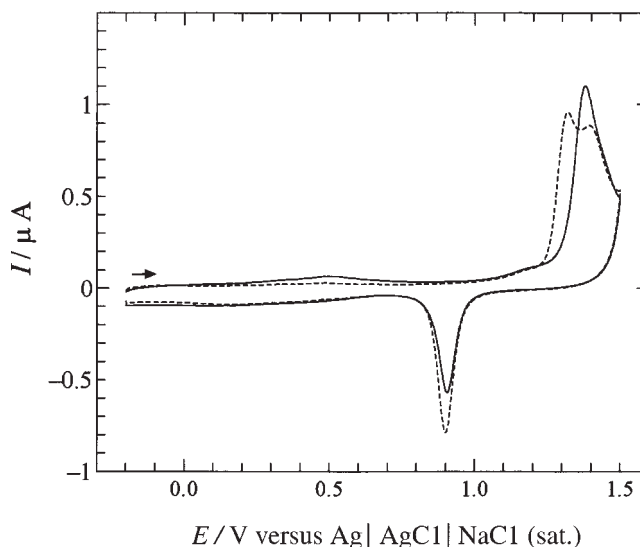


Figure 4 CVs of (- - -) I⁻-nano-Au/GC and (—) I⁻-nano-Au/PANI/GC electrodes in 0.5M H₂SO₄ solutions. The potential scanning rate was 0.1 V/s.

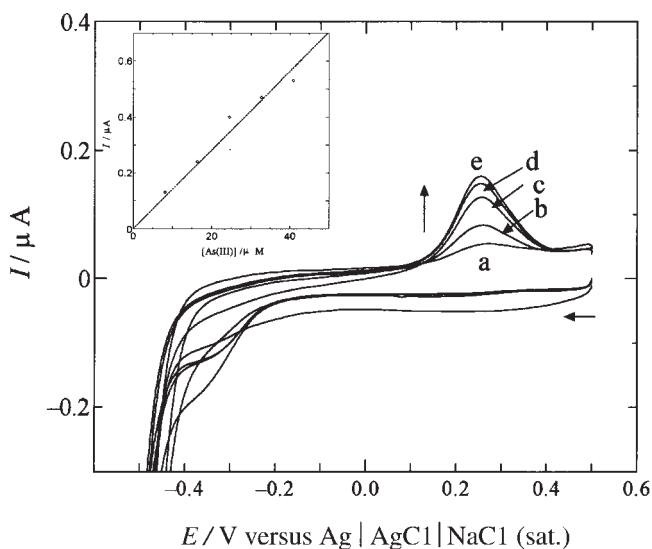


Figure 5 CV response of I^- -nano-Au/PANI/GC electrodes in 1.0M HCl solutions containing various As(III) concentrations of (a) 0.61, (b) 0.61×2 , (c) 0.61×3 , (d) 0.61×4 , and (e) 0.61×5 ppm. The inset shows a plot of the anodic peak current versus the As(III) concentration.

nano-Au/GC, I^- -nano-Au/GC, and I^- -nano-Au/PANI/GC electrodes were examined, and the results are shown in Figure 6. By the subtraction of the background current, the anodic stripping peak currents for the reduction of As(III) in a 1.0M HCl solution containing $8.2 \mu\text{M}$ As(III) were in the following order: nano-Au/GC < I^- -nano-Au/GC

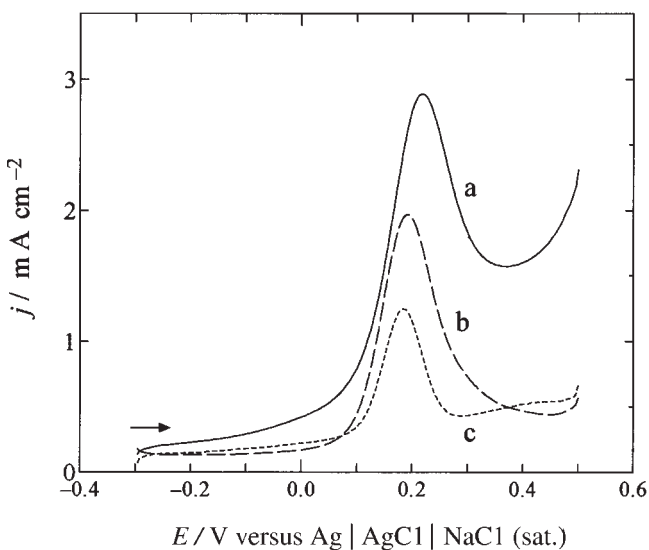


Figure 6 SWV curves for 0.61 ppm As(III) in 1.0M HCl solutions obtained with (a) I^- -nano-Au/PANI/GC, (b) I^- -nano-Au/GC, and (c) nano-Au/GC electrodes. j and E refer to current density and potential, respectively. The SWV parameters were a square-wave amplitude of 25 mV, a square-wave frequency of 75 Hz, and predeposition at -0.3 V for 60 s for each electrode.

< I^- -nano-Au/PANI/GC. The sensitivity of the I^- -nano-Au/PANI/GC electrode toward As(III) analysis in its very low concentration was then examined. Figure 7 shows the SWV curves obtained in 1.0M HCl solutions containing 610 or 0.4 ppb As(III). A sharp anodic peak at 0.21 V with the solution containing 610 ppb As(III) was associated with the As(0) reoxidation, as described previously. Notably, a similar stripping anodic wave was also observed around 0.23 V even in the solution containing as little as 0.4 ppb As(III). At this low As(III) concentration solution, however, the I^- -nano-Au/GC electrode showed no such stripping peak,¹⁴ although it possessed comparable sensitivity in detecting As(III) at concentrations as high as 610 ppb. The origin of the superior detection capacity of the I^- -nano-Au/PANI/GC electrode in the low As(III) concentration was not studied further in this work, but the superior sensitivity may have arisen from the high dispersion of nano-Au particles in the polymer segment, as evidenced by the SEM measurements.

CONCLUSIONS

This study offers considerable simplicity and superior sensitivity for the detection of As (III) on I^- -nano-Au/PANI-modified GC electrodes. A high LOD sensitivity of 0.4 ppb has been achieved and thus provides the possibility of using this electrode for the detection of As(III) in a real matrix, such as As-contaminated natural water.

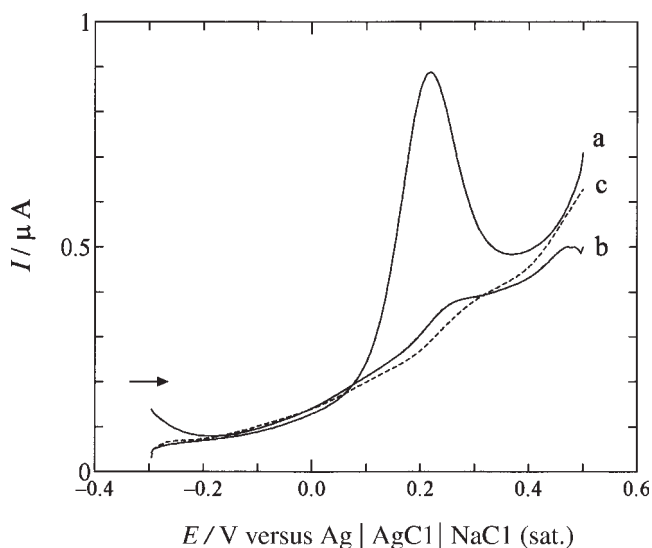


Figure 7 SWV response of (a) 610 and (b) 0.4 ppb As(III) in 1.0M HCl solutions to I^- -nano-Au/PANI/GC electrodes for a predeposition time of 60 s at -0.3 V. Curve c corresponds to the background response (i.e., an As-free 1.0M HCl solution).

References

1. (a) Tseng, W.-P.; Chu, H.-M.; How, S.-W.; Fong, J.-M.; Lin, C.-S.; Yen, S. *J Natl Cancer Inst* 1968, 40, 453; (b) Ray, P. C. *J Forensic Med Toxicol* 1999, 16, 30; (c) Chakraborti, D.; Rahman, M. M.; Raul, K.; Chowdhury, U. K.; Sengupta, M. K.; Lodh, D.; Chanda, C. R.; Saha, K. C.; Mukherjee, S. C. *Talanta* 2002, 58, 3.
2. <http://www.who.int/inf-fs/en/fact210.html> (accessed 1993).
3. Meng, X.; Jing, C.; Korfiatis, G. P. *ACS Symp Ser* 2003, 835, 70.
4. (a) Cullen, W.; Reimer, K. *Chem Rev* 1989, 89, 713; (b) Morita, M. *Pure Appl Chem* 1992, 64, 575.
5. (a) Gong, Z.; Lu, X.; Ma, M.; Watt, C.; Lee, X. C. *Talanta* 2002, 58, 77; (b) Karthikeyan, S.; Hirata, S. *Anal Lett* 2003, 36, 2355; (c) Feeney, R.; Kounaves, S. *Talanta* 2002, 58, 23.
6. Le, X. C.; Lu, X. F.; Li, X. F. *Anal Chem A* 2004, 76, 27.
7. Cavicchioli, A.; La-Scalea, M. A.; Gutz, I. G. R. *Electroanalysis* 2004, 16, 697.
8. Brainina, K. Z.; Malakhova, N. A.; Stojko, N. Y. *Fresenius J Anal Chem* 2000, 368, 307.
9. Hung, D. Q.; Nekrassova, O.; Compton, R. G. *Talanta* 2004, 64, 269.
10. Sadana, R. S. *Anal Chem* 1983, 55, 304.
11. Sun, Y.-C.; Mierzwa, J.; Yang, M.-H. *Talanta* 1997, 44, 1379.
12. Feeney, R.; Kounaves, S. P. *Anal Chem* 2000, 72, 2222.
13. Dai, X.; Nekrassova, O.; Hyde, M. E.; Compton, R. G. *Anal Chem* 2004, 76, 5924.
14. Ferdousi, S.; Ohsaka, T. Tokyo Institute of Technology, UNESCO report, Sept 2005.
15. (a) Ohnuki, Y.; Ohsaka, T.; Matsuda, H.; Oyama, N. *J Electroanal Chem* 1983, 158, 55; (b) Wang, J.; Chen, S. P.; Lin, M. S. *J Electroanal Chem* 1989, 273, 231; (c) Pontie, M.; Gobin, C.; Pauporte, T.; Bedioui, F.; Devynck, J. *Anal Chim Acta* 2000, 411, 175.
16. Forsberg, G.; O'Laughlin, J. W.; Megargle, R. G. *Anal Chem* 1975, 47, 1586.
17. Finot, M. O.; Braybrook, G. D.; McDermott, M. T. *J Electroanal Chem* 1999, 466, 234.
18. (a) El-Deab, M. S.; Okajima, T.; Ohsaka, T. *J Electrochem Soc A* 2003, 150, 851; (b) El-Deab, M. S.; Sotomura, T.; Ohsaka, T. *J Electrochem Soc A* 2005, 152, C1.
19. MacDiarmid, A. G.; Mu, S. L.; Somasiri, N. L. D.; Wu, W. Q. *Mol Cryst Liq Cryst* 1985, 121, 187.
20. Kozłowska, H. A.; Conway, B. E.; Hamelin, A.; Stiocovicu, L. *J Electroanal Chem* 1987, 228, 429.
21. Trasatti, S.; Petrii, O. A. *Pure Appl Chem* 1991, 63, 711.
22. Loucka, T. *J Electroanal Chem* 1973, 47, 103.