

# Direct Electrodeposition of Gold Nanoparticles onto Indium Tin Oxide Film Coated Glass: Application to the Detection of Arsenic(III)

Xuan DAI and Richard G. COMPTON<sup>†</sup>

*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom*

Gold nanoparticle modified indium tin oxide (ITO) film coated glass electrodes were prepared for the first time through direct electrochemical deposition from 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.1 mM HAuCl<sub>4</sub>. The resulting electrode surfaces were characterized with AFM. Cyclic voltammetry and linear sweep voltammetry (LSV) of arsenic(III) on the modified electrodes were performed. After optimization, a LOD of  $5 \pm 0.2$  ppb was obtained with 60 s deposition at  $-0.6$  V (vs. SCE) in 1 M HNO<sub>3</sub> using LSV.

(Received October 31, 2005; Accepted January 26, 2006)

## Introduction

Arsenic is widely distributed in the earth's crust. Exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects.<sup>1</sup> Contamination of drinking water by arsenic is found in many parts of the world such as Argentina, Bangladesh, Cambodia, Chile, China, Ghana, Hungary, Inner Mongolia, Mexico, Nepal, New Zealand, Philippines, Taiwan, the United States and Vietnam.<sup>2</sup> The World Health Organization has a guideline level of  $10 \mu\text{g L}^{-1}$  for drinking water.<sup>3</sup> Many detection methods have been developed for determination of such levels of arsenic, as summarized in recent reviews.<sup>4-7</sup> These include inductively coupled plasma mass spectrometry (ICP-MS),<sup>8</sup> graphite furnace atomic absorption spectrometry (GFAAS)<sup>9</sup> and high performance liquid chromatography (HPLC) with ICP-MS.<sup>10</sup> However the most reliable techniques are more suitable for laboratory conditions only and are, additionally, time consuming. They cannot thus be used for routine in-field monitoring of a large number of samples. Therefore a sensor needs to be developed to solve these problems. Electrochemical techniques provide a possible means to this end since they are both rapid and portable.

Significant research has been reported about arsenic detection using electrochemical stripping voltammetry methods. Gold was found to be the superior substrate for the working electrode among the substrates considered to date. Using differential pulse anodic stripping voltammetry (DPASV), Forsberg *et al.*<sup>11</sup> found a LOD of 0.02 ppb for As(III) in 1 M perchloric acid with 10 min (sic) pre-deposition. Hua *et al.*<sup>12</sup> determined total arsenic in seawater on a gold ultramicroelectrode (25  $\mu\text{m}$ ) using ASV and achieved a LOD of 0.2 ppb. Hamilton *et al.*<sup>13</sup> used a gold film electrode to determine arsenic and antimony in electrolytic copper samples and obtained a LOD of 0.56 ppb.

Simm *et al.*<sup>14,15</sup> investigated the sonoelectroanalytical arsenic detection on a gold electrode giving a LOD of 0.75 ppb. Using ASV on a gold nanoparticle modified glassy carbon (GC) electrode, a LOD of 0.01 ppb was obtained by this group.<sup>16</sup> More recently, Simm *et al.*<sup>17</sup> compared different types of gold carbon composite electrode for the detection of arsenic. Using micron gold arrays produced in carbon-paste electrodes, a LOD of 0.4 ppb was achieved.

Materials in the nanometer range have shown superior or advantageous functional properties for a wide range of technological applications, including catalysis, optics, microelectronics and chemical/biological sensors. Metal nanoparticles provide four unique advantages over macroelectrodes for electroanalysis: enhancement of mass transport, catalysis, high effective surface area and control over electrode microenvironment conductive.<sup>6,18,19</sup> Several works have been reported using gold nanoparticles. Gold nanoparticles can be made by chemical synthesis,<sup>20,21</sup> UV light or electron-beam irradiation<sup>22</sup> or electrochemical methods.<sup>16,23</sup> The former two methods are either time or cost consuming. In contrast, electrochemical deposition provides an easy and rapid alternative for the preparation of gold nanoparticles electrodes in a short time.

Indium tin oxide (ITO) films are of great interest because of their high optical transparency and good electrical conductivity. Gold nanoparticles were grown onto ITO coated glass mainly through seed-mediated growth<sup>21,24,25</sup> or assembling with polymer.<sup>26-28</sup> Hitherto electrochemical deposition has never been used to fabricate gold nanoparticles on ITO film coated glass. Applications of gold nanoparticle modified ITO glass electrodes include the electrooxidation of nitric oxide,<sup>21</sup> the catalytic reduction of oxygen,<sup>26</sup> the reduction of H<sub>2</sub>O<sub>2</sub>,<sup>25,27</sup> and the electrooxidation of CO.<sup>28</sup> Application of the gold nanoparticle modified ITO glass electrodes to the determination of metal ions has not been reported.

In the present study, gold nanoparticles were directly electrodeposited onto indium tin oxide (ITO) film coated glass electrodes for the first time. The resulting electrode surfaces were characterized using AFM. The application of the gold

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: richard.compton@chem.ox.ac.uk

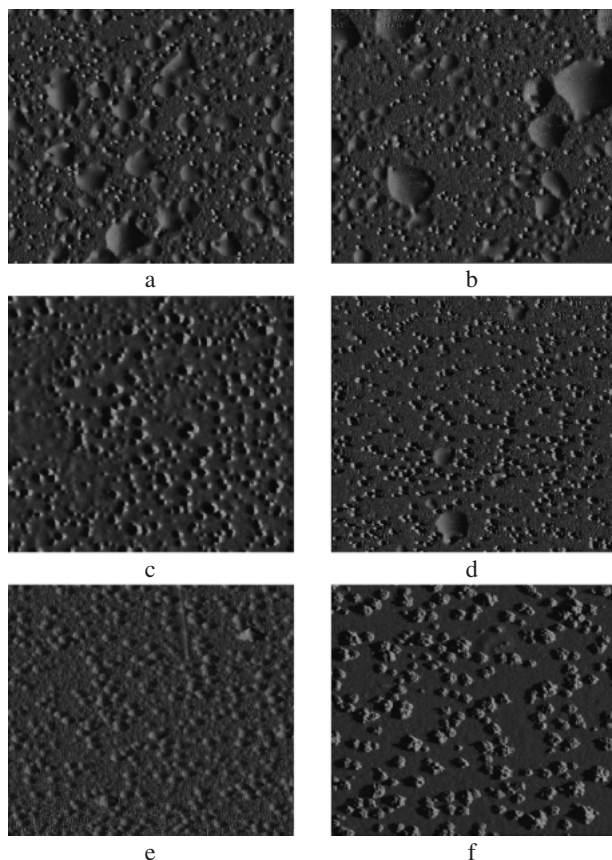


Fig. 1 AFM images (10  $\mu\text{m}$  scale) of gold nanoparticle modified ITO electrodes prepared from a solution of  $\text{AuCl}_4^-$  in 0.5 M  $\text{H}_2\text{SO}_4$  via applying a potential step from +1.055 V to  $-0.045$  V (vs. SCE). The concentration of  $\text{AuCl}_4^-$  and the deposition time were summarized in Table 1.

nanoparticle modified electrodes was investigated for the detection of arsenic(III) with cyclic voltammetry and linear sweep voltammetry. It is possible to use the gold nanoparticle modified ITO electrodes as a disposable material for field analysis.

## Experimental

### Reagents and chemicals

All the reagents were of analytical grade and were used without further purification. Hydrogen tetrachloroaurate(III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.9+%) was from Sigma-Aldrich (Steinheim, Germany). Sodium(*meta*)arsenite ( $\text{NaAsO}_2$ , 99%) was purchased from Fluka (Buchs, Switzerland). All solutions and subsequent dilutions were prepared using deionized water from Vivendi UHQ grade water system (Vivendi, UK) with a resistivity of not less than 18 M $\Omega$  cm. As(III) stock solution (10 mM) was prepared from  $\text{NaAsO}_2$ : 0.013 g  $\text{NaAsO}_2$  was dissolved in 10 mL deionized water.

### Instrumentation

Electrochemical measurements were recorded using an Autolab PGSTAT 30 computer controlled potentiostat (EcoChemie, Netherlands) with a standard three electrode system. A gold nanoparticle modified ITO film coated glass (Sigma-Aldrich, 70–100  $\Omega$  resistance, Steinheim, Germany) electrode (working area  $1 \times 1 \text{ cm}^2$ ) served as a working electrode, a platinum wire was used as a counter electrode with

Table 1 Summary of  $\text{AuCl}_4^-$  concentration, deposition time and total surface area of gold nanoparticles for Fig. 1

Figure	$\text{AuCl}_4^-$ concentration/ mM	Deposition time/s	Total surface area of gold nanoparticles/ $\text{cm}^2$	Sensitivity/ $\text{A cm}^{-2} \text{M}^{-1}$
1a	0.1	50	0.04	24.3
1b	0.1	150	0.09	19.4
1c	0.1	300	0.12	58.8
1d	0.1	20 times of 15 s	0.07	60.7
1e	0.01	300	0.02	33.4
1f	1.0	300	1.08	53.2

a saturated calomel reference electrode (SCE, Radiometer, Copenhagen, Denmark) completing the cell assembly. All experiments were carried at a temperature  $20 \pm 2^\circ\text{C}$ .

The AFM measurements were performed using a Digital Instruments Multimode SPM, operating in *ex situ* tapping mode. A Model “J” scanner was used having a lateral range of  $125 \times 125 \mu\text{m}$  and a vertical range of 5  $\mu\text{m}$ . Standard silicon nitride probes (Type NP, Digital Instruments Multimode SPM), having a force constant of approximately 0.58 N  $\text{m}^{-1}$ , were used.

### Electrode modification

The fabrication of Au/ITO was carried out using electrochemical deposition.<sup>16,22</sup> A sheet of ITO was sonicated in acetone, ethanol and distilled water for 10 min consequently. After cleaning, the glass sheet was immersed into the solution of  $\text{AuCl}_4^-$  in 0.5 M  $\text{H}_2\text{SO}_4$  (see Results and Discussion for details). And a potential step from +1.055 V (vs. SCE) to  $-0.045$  V was applied for a fixed time (15, 50, 150 or 300 s). All solutions were degassed with a  $\text{N}_2$  stream prior to each measurement.

## Results and Discussion

### Gold nanoparticle modified ITO electrodes

Typical AFM images of electrode surfaces formed under different formation conditions (deposition time and  $\text{AuCl}_4^-$  concentration) for the electrodeposition of Au nanoparticles onto ITO film coated glass are shown in Fig. 1. The  $\text{AuCl}_4^-$  concentrations and the deposition times used are summarized in Table 1. In all cases, dispersed gold nanoparticles are found on the substrates. Comparing Figs. 1a, b and c, the  $\text{AuCl}_4^-$  concentration is 0.1 mM and the deposition time is 50, 150, and 300 s, respectively. It can be seen that an increase in the deposition time results in the enhancement of the average particle size of the Au nanoparticles. Comparing Figs. 1e, c and f, the deposition time is 300 s while the concentration is 0.01 mM, 0.1 mM and 1.0 mM, separately. Increasing the concentration of  $\text{AuCl}_4^-$  solution causes an increase of particle size. In Fig. 1f, bigger gold nanoparticles were observed (average diameter about 357.4 nm). For Figs. 1c and d, the concentration is the same of 0.1 mM. In Fig. 1c, a single potential step with 300 s was applied, while 20 cycles of 15 s were used in Fig. 1d. The particle diameter in Fig. 1c is in the range from 70 nm to 309 nm with an average value of 154 nm. The particle diameter in Fig. 1d is in the range from 114 nm to 217 nm with an average value of 165 nm. Applying several cycles of short time potential step results in more uniform nanoparticles. The size variation of the particles in Fig. 1d (standard deviation 30 nm) is smaller than that in Fig. 1c

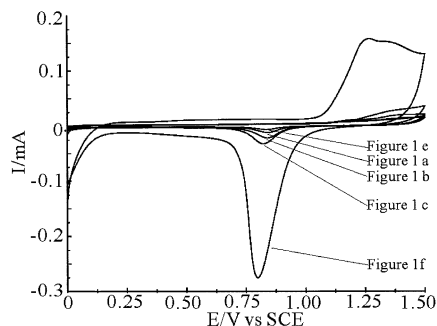


Fig. 2 CV voltammograms of gold nanoparticle modified ITO electrodes in 0.05 M  $\text{H}_2\text{SO}_4$ . Potential scan rate 100  $\text{mV s}^{-1}$ .

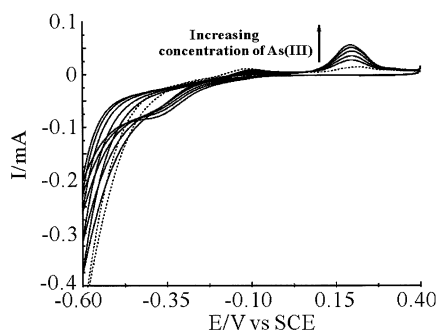


Fig. 3 CV response of As(III) (1 mM each) on a gold nanoparticle modified ITO electrode prepared from 0.1 mM  $\text{AuCl}_4^-$  in 0.5 M  $\text{H}_2\text{SO}_4$  via applying potential step from +1.055 V to  $-0.045$  V (vs. SCE) for 300 s. Potential scan rate 100  $\text{mV s}^{-1}$ .

(standard deviation 68 nm).

In order to get surface information about the electrodeposited Au nanoparticles on ITO film coated glass electrodes, cyclic voltammetric profiles (Fig. 2) of each electrode under various formation conditions were next recorded in 0.05 M  $\text{H}_2\text{SO}_4$  in the potential range from 0 V to 1.5 V (vs. SCE) with the scan rate of 100  $\text{mV s}^{-1}$ . The real surface area of the Au nanoparticles loading on ITO film coated glass electrode can be estimated basing on the amount of charge consumed during the reduction of the Au surface oxide monolayer and a reported value of 400  $\mu\text{C cm}^{-2}$  was used for the calculation.<sup>29,30</sup> The results are presented in Table 1.

#### Electrochemical response of As(III) on gold nanoparticle modified electrodes

Cyclic voltammetry was employed first to examine the electroanalytical performance of gold nanoparticle modified electrodes. Figure 3 illustrates typical cyclic voltammetric responses in the range from  $-0.6$  V to  $+0.4$  V (vs. SCE, 100  $\text{mV s}^{-1}$ ) of a gold nanoparticle modified electrode (stepped from 1.055 V to  $-0.045$  V for 300 s from 0.5 M  $\text{H}_2\text{SO}_4$  containing 0.1 mM  $\text{AuCl}_4^-$ ) in 1 M HCl. It can be seen that no redox processes were registered in the potential range studied in the blank solution (dashed line). With the addition of As(III), new reduction wave emerges at  $-0.35$  V (vs. SCE) upon the addition of 1  $\mu\text{M}$  As(III) and can be attributed to the three electron reduction of As(III) to As(0). On the reversal anodic scan, an oxidation wave at  $+0.25$  V (vs. SCE) was observed. This process is ascribed to the subsequent re-oxidation of As(0) to the parent As(III) species. Both waves were found to increase

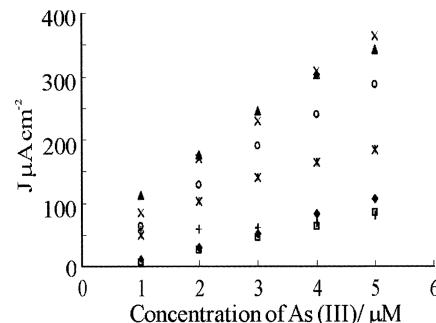


Fig. 4 Plots of current densities vs. concentration of As(III) on gold nanoparticle modified ITO electrode and gold macro electrode. The preparation conditions of gold nanoparticle modified electrode were ( $\text{AuCl}_4^-$  concentration/the deposition time): (◆) 0.1 mM/50 s, (○) 0.1 mM/150 s, (×) 0.1 mM/300 s, (▲) 0.1 mM/20 times of 15 s, (※) 0.01 mM/300 s, (□) 1.0 mM/300 s, (+) macro gold electrode.

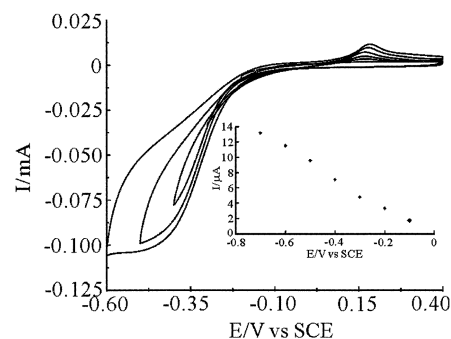


Fig. 5 CV voltammograms of 10  $\mu\text{M}$  As(III) in 1 M HCl at different reverse potential on gold nanoparticle modified ITO electrode prepared from 0.1 mM  $\text{AuCl}_4^-$  in 0.5 M  $\text{H}_2\text{SO}_4$  via applying potential step from +1.055 V to  $-0.045$  V (vs. SCE) for 300 s. Potential scan rate, 100  $\text{mV s}^{-1}$ . Insert: Plots of peak currents vs. reverse potential.

linearly with further additions of As(III).

The plots of current densities vs. concentration of As(III) on different gold nanoparticle modified ITO electrode were present in Fig. 4 and the sensitivities are also summarized in Table 1. The plots of a gold macro electrode were also included as comparison. Increasing the Au deposited on ITO film coated glass by prolonging the deposition time leads to an increase of sensitivity. Increasing the concentration of  $\text{AuCl}_4^-$  from 0.01 mM to 0.1 mM causes the increase of sensitivity, from 33.4 to 58.8  $\text{A cm}^{-2} \text{M}^{-1}$ . However, further increase of the concentration to 1.0 mM results in a decrease of sensitivity to 53.2  $\text{A cm}^{-2} \text{M}^{-1}$ . Although the total surface area of gold nanoparticles is increased, the signal of As(III) on the electrode is not increased significantly compared to the area increasing. When the total deposition time is the same, the sensitivities are nearly the same as well no matter applying one long potential step (60.7  $\text{A cm}^{-2} \text{M}^{-1}$ ) or several cycles of potential step (58.5  $\text{A cm}^{-2} \text{M}^{-1}$ ). All the sensitivities for the gold nanoparticle modified electrodes are better than that for a gold macro electrode (5.9  $\text{A cm}^{-2} \text{M}^{-1}$ ). With the highest sensitivity, 0.1 mM  $\text{AuCl}_4^-$  with 300 s deposition time were selected as the preparation conditions for the gold nanoparticle modified electrodes used in the following experiments.

Different reverse potentials were examined with CV in 1 M HCl containing 10  $\mu\text{M}$  As(III). The resulting voltammograms were shown in Fig. 5. The start potential was kept at  $+0.4$  V

(vs. SCE), while the reverse potential was  $-0.1$  V,  $-0.2$  V,  $-0.3$  V,  $-0.4$  V,  $-0.5$  V,  $-0.6$  V (vs. SCE), respectively. The more negative reverse potential used, the higher the peak current was observed. It can be seen that more negative potential can be used on gold nanoparticle modified ITO electrode, while the most negative potential used on normal gold electrodes is  $-0.3$  V (vs. SCE).

Linear sweep voltammetry was employed next for the determination of As(III). The deposition potential was  $-0.6$  V with 60 s deposition time. 1 M HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> were compared as the supporting electrolytes. In 1 M HCl and H<sub>2</sub>SO<sub>4</sub>, there is another peak appearing at *ca.*  $+0.1$  V which owns to oxygen. In 1 M HNO<sub>3</sub>, the effect of oxygen is minimized. Longer deposition time (120, 180, and 300 s) were also used. But the deposition of oxygen increased significantly with the increase of deposition time. LOD ( $S/N = 3$ )<sup>31</sup> was calculated to be  $5 \pm 0.2$  ppb with deposition at  $-0.6$  V for 60 s in 1 M HNO<sub>3</sub>. Since the World Health Organization's guideline value of arsenic in drinking water is 10 ppb, this method may have practical utility.

## Conclusion

Gold nanoparticle modified ITO film coated glass electrode has been fabricated for the first time *via* direct electrodeposition from 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.1 mM AuCl<sub>4</sub><sup>-</sup>. The resulting electrode surfaces were characterized using AFM. The application of the gold nanoparticle modified ITO electrode to the determination of As(III) was investigated. After optimization, LOD ( $S/N = 3$ ) was  $5 \pm 0.2$  ppb with deposition at  $-0.6$  V for 60 s in 1 M HNO<sub>3</sub>. The electrodes are easily fabricated with low cost and they are stable for several days after the preparation. It is possible to use them as disposable electrodes for in field analysis. In particular we note that gold nanoparticles provide a very sensitive substrate for the detection of arsenic when deposited on glassy carbon.<sup>16</sup> However whilst the latter is excellent for laboratory based work, we believe that ITO offers potential benefits in the context of disposable sensors such as might be required in field analysis where cost is a significant factor.

## Acknowledgements

X. D. thanks the Clarendon Fund of Oxford University and Abington Partners for support.

## References

1. B. K. Mandal and K. T. Suzuki, *Talanta*, **2002**, 58, 201.
2. <http://www.who.int/mediacentre/factsheets/fs210/en/>.
3. <http://www.who.int/int-fs/en/fact210.html>, **1993**.
4. X. C. Le, X. F. Lu, and X. F. Li, *Anal. Chem.*, **2004**, 76, 27A.
5. D. Q. Hung, O. Nekrassova, and R. G. Compton, *Talanta*, **2004**, 64, 269.
6. A. Cavicchioli, M. A. La-Scalea, and I. G. R. Gutz, *Electroanalysis*, **2004**, 16, 697.
7. Kh. Z. Brainina, N. A. Malakhova, and N. Y. Stojko, *Fresenius J. Anal. Chem.*, **2000**, 368, 307.
8. Y. L. Feng, H. Y. Chen, L. C. Tian, and H. Narasaki, *Anal. Chim. Acta*, **1998**, 375, 167.
9. K. Anezaki, I. Nakatsuka, and K. Ohzenki, *Anal. Sci.*, **1999**, 15, 289.
10. P. Thomas and K. Sniatecki, *J. Anal. At. Spectrom.*, **1995**, 10, 615.
11. G. Forsberg, J. W. O'Laughlin, and R. G. Megargle, *Anal. Chem.*, **1975**, 47, 1586.
12. C. Hua, D. Jagner, and L. Renman, *Anal. Chim. Acta*, **1987**, 201, 263.
13. T. W. Hamilton and J. Ellis, *Anal. Chim. Acta*, **1980**, 119, 225.
14. A. O. Simm, C. E. Banks, and R. G. Compton, *Anal. Chem.*, **2004**, 76, 5051.
15. A. O. Simm, C. E. Banks, and R. G. Compton, *Electroanalysis*, **2005**, 17, 335.
16. X. Dai, O. Nekrassova, M. E. Hyde, and R. G. Compton, *Anal. Chem.*, **2004**, 76, 5924.
17. A. O. Simm, C. E. Banks, S. J. Wilkins, N. G. Karousos, J. Davis, and R. G. Compton, *Anal. Bioanal. Chem.*, **2005**, 381, 979.
18. D. Hernandez-Santos, M. B. Gonzalez-Garcia, and A. C. Garcia, *Electroanalysis*, **2002**, 14, 1225.
19. C. E. Welch and R. G. Compton, submitted to *Anal. Bioanal. Chem.*
20. Y. W. Tan, Y. F. Li, and D. B. Zhu, *Langmuir*, **2002**, 18, 3392.
21. J. Zhang and M. Oyama, *Anal. Chim. Acta*, **2005**, 540, 299.
22. M. Fukushima, H. Yanagi, S. Hayashi, N. Suganuma, and Y. Taniguchi, *Thin Solid Films*, **2003**, 438 - 439, 39.
23. M. S. El-Deab, T. Okajima, and T. Ohsaka, *J. Electrochem. Soc.*, **2003**, 150, A851.
24. J. Zhang, M. Kambayashi, and M. Oyama, *Electrochem. Commun.*, **2004**, 6, 683.
25. J. Zhang and M. Oyama, *J. Electroanal. Chem.*, **2005**, 577, 273.
26. M. Huang, Y. Shen, W. Cheng, Y. Shao, X. Shu, B. Liu, and S. Dong, *Anal. Chim. Acta*, **2005**, 535, 15.
27. F. Patolsky, T. Gabriel, and I. Willner, *J. Electroanal. Chem.*, **1999**, 479, 69.
28. T. F. Jaramillo, S. Baeck, B. R. Cuenya, and E. W. McFarland, *J. Am. Chem. Soc.*, **2003**, 125, 7148.
29. H. A. Kozłowska, B. E. Conway, A. Hamelin, and L. Stoicoviciu, *J. Electroanal. Chem.*, **1987**, 228, 429.
30. S. Trasatti and O. A. Petrii, *Pure Appl. Chem.*, **1991**, 63, 711.
31. D. C. Harris, "Quantitative Chemical Analysis", 6th ed., **2003**, W. H. Freeman and Company, New York, 726.