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Electrochemical Detection of Trichloroethylene with an Electrodeposited Pb-Modified Electrode

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The amperometric sensing of trichloroethylene (TCE) in the organic phase by using modified Pb electrode was described. The influence of pretreatment, electrodeposition current density, electrodeposition time, and electrodeposition temperature for preparation of the working electrode were discussed. The optimal conditions for preparation of modified Pb electrode were obtained as 0.1 M HNO₃ pretreatment, 20 mA/cm² electrodeposition current density, and 30°C electrodeposition temperature. Additionally, the optimal sensing conditions such as -2.10 V sensing potential [*vs.* Ag/Ag⁺ with 0.1 M tetrabutylammonium perchlorate in acetonitrile (AN) solution], 155 rpm agitation rate, and at room temperature with 0.01 M tetrabutylammonium tetrafluoroborate electrolyte concentration in AN solution were obtained in this system. Under the optimal sensing conditions, the results indicated that the response time was 20 s (90% response time) and the correlation of sensing response current, i_d , and TCE concentration, C_L , is $i_d = 1.060 C_L$ in the range from 100 to 700 ppm. Furthermore, the rate constant of TCE mass transfer, *k*, was also obtained to be 7.217×10^{-4} /cm s.

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Trichloroethylene (TCE) is a generally used chemical material in industries such as electronic manufacturing,¹ plastics production,² textile process³ and organic synthesis.⁴ At the same time, TCE is also an organic chemical that has been used in dry cleaning, for metal degreasing, and as a solvent for oils and resins.⁵⁻⁷ Besides, the waste solution is also a contaminant in the soil or groundwater around environment.⁸ Furthermore, TCE was confirmed to be a carcinogenic material in many medical investigations.⁹⁻¹¹ Therefore, to detect and monitor TCE concentration in order to protect people health is very important in the working environment.

At present, the monitoring of TCE relies principally on gas chromatography, which provides good sensitivity and selectivity.¹² However, this method is not well suited for use as a simple, portable measuring devices.¹³ Besides, other analytical techniques such as electrochemical method,^{14,15} spectroscopic method,^{16,17} photocatalytic oxidation method,^{18,19} and biochemical method²⁰⁻²² have been applied to detect the concentration of TCE. However, all these methods had some disadvantages, for example, complicated operation, high cost, poor stability, and long measurement time. Furthermore, all these mentioned analytical instruments cannot, minimization in production and *in situ*, apply in the field for automatic monitoring of TCE concentration.

Sensors may be the most practical monitor setup because of their convenience, accuracy, easy minimization, and automation-*in situ* measurement. Several TCE sensors have been developed such as fiber-optic-based TCE sensor,²³ microbial TCE sensor,²⁴ and flow injection TCE sensor.²⁵ However, these sensors may have some disadvantages also, for example, unstable, expensive and long response time. Therefore, it is necessary to develop a new TCE sensor with good performance, simple structure, and lower cost.

In this work, an electrodeposited Pb-modified electrode was used to sense TCE because this configuration has been shown to give good sensitivities.²⁶ Furthermore, the characteristics of this developed TCE sensor such as amperometric response current and response time were also explored.

Experimental

Chemicals and instrumentation.—The electrodeposition solution components of Pb were purchased from several sources: lead(II) tetrafluoroborate [Pb(BF₄)₂, Alfa Aesar, USA], tetrafluoroboric acid (HBF₄, Rieded-de Haen, Germany), boric acid (H₃BO₃, Alfa Aesar, USA), and polyethylene glycol (PEG 300, Hayashi, Japan). The tetrabutylammonium tetrafluoroborate (TBAT) and tetrabutylammonium perchlorate (TBAP) are all GC grades of TCI (Japan). The acetonitrile (AN) and TCE are high performance liquid chromatography and gas chromatography grades of Tedia (USA) and Aldrich (USA), respectively. All aqueous solutions were prepared with deionized (DI) water purified to a resistivity of a least 18.3 M Ω cm by a water purification system (Milli-RO 60, Japan). Additionally, the surface structure of the prepared electrode was characterized with scanning electron microscopy (SEM, FE-S 4200, Hitachi, Japan), X-ray diffraction (XRD, D/max 3. V, Rigaku, Japan), and electron spectroscopy for chemical analysis (ESCA, VG/ESCA 210, U.K.).

Preparation of working electrode.—The Pb foil $(6 \times 1 \times 0.01 \text{ cm}, \text{Alfa Aesar, USA})$ attached to an alumina plate $(5 \times 1.5 \times 0.1 \text{ cm}, \text{Lei Ke}, \text{Taiwan})$, then the sensing area 1 cm^2 was controlled by Teflon tape. The working electrode was ultrasonically cleaned in 0.1 M HNO₃ aqueous solution, then washing with DI water thoroughly. After, the Pb foil substrate was immersed in electrodeposited Pb aqueous solution containing 0.63 M Pb(BF₄)₂, 0.68 M HBF₄, 0.43 M H₃BO₃, and 0.0006 M PEG 300. Then, the electrodeposition of Pb for preparation of the working electrode was carried out at 30 rpm agitation rate. Electrodeposition current density, time, and temperature were adjusted, respectively, to control the electrodeposition process.

Sensing procedures.—All electrochemical measurements were carried out in a conventional three-electrode electrochemical cell with a 263A electrochemical analysis system (EG&G, USA). The modified Pb electrode was used as working electrode. A platinum plate and Ag/Ag^+ (with 0.1 M TBAP in AN solution) were used as auxiliary and reference electrodes, respectively. After, the sensing potential was set in the limiting current region. Then, the steady state amperometric signals were obtained, *i.e.*, the background current. Immediately, a desired concentration of TCE was added into the sensing system, then the amperometric current of the working electrode was also attained, *i.e.*, the measured current. The response current is equal to the measured current minus the background current.

Analysis and identification of products.—The GC-mass analysis was performed on a Hewlett-Packard 5890 gas chromatograph (GC) connected to an ion trap detector, for separating the volatile material and then into a VG 70–250S mass spectrometer. The GC was equipped with a 30 m Rtx-5 capillary column. The column temperature was held at an initial temperature of 100°C for 2 min and then increased at 6°C/min to 190°C where it was held for 20 min. High

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Figure 1. The SEM morphologies of Pb surface at different pretreatments for preparation of working electrode. (A) without treatment by 0.1 M HNO_3 aqueous solution (B) with treatment by 0.1 M HNO_3 aqueous solution. Pretreating conditions: 0.1 M pretreating HNO₃ aqueous solution concentration and 1 h pretreating time.

purity helium (99.99%) was used as carrier gas at a flow rate of 36 mL/min. Electron impact mass spectroscopy was used at the ionization energy of 70 eV.

Results and Discussion

Surface morphology of the electrode.—Comparison of the pretreatment time on the electrode surface morphologies is shown in Fig. 1. In Fig. 1A, the electrode without treatment by a 0.1 M HNO₃ aqueous solution, the smooth surface of electrode was obtained. On the other hand, in the Fig. 1B, the Pb electrode with treatment by a 0.1 M HNO₃ aqueous solution, the electrode surface showed large roughness more than that without treatment by a 0.1 M HNO₃ aqueous solution. These data clearly indicated that increasing the size of the voids increased the amount of deposited Pb. Consequently, the 1 h pretreatment time by a 0.1 M HNO₃ aqueous solution was chosen as the pretreatment condition for preparation of the working electrode.

Determination of the amperometric potential window.—The current/potential curves at different concentrations of TCE by using electrodeposited Pb-modified electrode were shown in Fig. 2A. The results show that increasing the concentration of TCE from 0 to 500 ppm, increased the measured current for TCE reduction. This is understandable, because in the electrochemical reaction, the reduction current increased with the increase of the TCE concentration.



Figure 2. (A) The current/potential curves at different concentration of TCE by using an electrodeposited Pb modified electrode. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: 0.63 M Pb(BF₄)₂, 0.68 M HBF₄, 0.43 M H₃BO₃, and 0.0006 M poly(ethylene glycol) 300 aqueous solution, 20 mA/cm² deposition current density, and 30 rpm agitation rate, at 30°C and 2 h. Sensing conditions: 0.01 M TBAT in AN solution, Ag/Ag⁺ (with 0.1 M TBAP in AN solution) as reference electrode, 155 rpm agitation rate, at room temperature and 1 cm² working electrode surface area. (B) The current/potential curve of 500 ppm TCE reduction by using an electrodeposited Pb modified electrode. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A.

Moreover, the limiting current region at the concentration of 500 ppm TCE was shown in Fig. 2B. In Fig. 2B, the response current is equal to the measured current (500 ppm) minus the background current (0 ppm TCE). The result showed that increasing the driving force from -1.98 to -2.06 V (vs. Ag/Ag⁺ with 0.1 M TBAP in AN solution) increased the current of reduction. The result showed that the response current was controlled by both kinetic and masstransfer mechanisms in this potential range. Further increasing the potential from -2.06 to -2.14 V (vs. Ag/Ag⁺ with 0.1 M TBAP in AN solution), the current reached a constant, thus the reaction was only controlled by mass transfer in that potential range. And then, the current rapidly increased when the potential increased from -2.14 to -2.28 V (vs. Ag/Ag⁺ with 0.1 M TBAP in AN solution); the response current increased due to the decomposition of electrolyte. In Fig. 2B, the main reduction of TCE took place between the potential from -2.06 to -2.14 V (vs. Ag/Ag⁺ with 0.1 M in AN

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Figure 3. Effect of pretreatment time on the sensitivity of TCE sensor. Pretreatment condition: 0.1 M HNO₃ aqueous solution. Electrodeposition conditions: same as Fig. 2A. Sensing conditions: 0.01 M TBAT in AN solution, -2.10 V (*vs.* Ag/Ag⁺ with 0.1 M TBAP in AN solution), 155 rpm agitation rate, at room temperature and 1 cm² working electrode surface area.

solution). Because -2.10 V (*vs.* Ag/Ag⁺ with 0.1 TBAP in AN solution) is within this constant current region, its sensing reaction is mass-transfer controlled. Conclusively, the reasonable and suitable applied potential for TCE sensing in this system was chosen to be -2.10 V (*vs.* Ag/Ag⁺ with 0.1 M TBAP in AN solution).

Effect of pretreatment time with 0.1 M HNO₃.—Effect of pretreatment time with 0.1 M HNO₃ aqueous solution on the sensitivity is shown in Fig. 3. The result shows that increasing the pretreatment time with 0.1 M HNO₃ aqueous solution from 0 to 60 min, increased the sensitivity from 0.28 to 1.06 μ A/cm² ppm. Apparently, the untreated Pb foil by 0.1 M HNO₃ aqueous solution exhibited bad performance for TCE sensing. It can be explained that the void fraction and coarseness increased with pretreatment time in the 0.1 M HNO₃ aqueous solution. Consequently, the optimal pretreating condition is 60 min pretreatment time.



Figure 4. Effect of electrodeposition current density for preparing the working electrode on the sensitivity of TCE sensor. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: $0.63 \text{ M Pb}(BF_4)_2$, 0.68 M HBF_4 , 0.43 M H_3BO_3 , and 0.0006 M PEG 300 aqueous solution, 30 rpm agitation rate, at 30°C and 2 h. Sensing conditions: same as Fig. 3.



000010 15.0kV X100 180/m



Figure 5. The SEM morphologies for preparation of working electrode at different electrodeposition current densities: (A) 5 mA/cm², (B) 10 mA/cm², and (C) 20 mA/cm². Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 4.

Effect of electrodeposition current density.—Effect of electrodeposition current density on the sensitivity for sensing of TCE is shown in Fig. 4. The result shows that increasing the electrodeposition current density from 0 (*i.e.*, original Pb foil) to 20 mA/cm² for preparing the modified Pb electrode, decreases the sensing sensitivity from 1.813 to 1.060 mA/cm² ppm. The surface morphologies of modified Pb electrode at different electrodeposition current densities for preparing the modified Pb electrode are shown in Fig. 5. These data clearly suggest that the working electrode surface was not electroplated completely under 5 and 10 mA/cm² electrodeposition current densities, respectively, which induced the different sensitivity



Figure 6. Amperometric response of TCE by using a modified Pb electrode prepared at different electrodeposition current densities: (A) 0 mA/cm^2 , (B) 5 mA/cm^2 , (C) 10 mA/cm^2 , and (D) 20 mA/cm^2 . Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 3. Sensing conditions: same as Fig. 4.

TCE by using these electrodes. However, the unstable and nonlinear response current was apparently found during the sensing reaction when the electrodeposition current density for preparing the working electrode was smaller than 20 mA/cm² as shown in Fig. 6. It may have been due to the formation of unstable material with negatively charged metal particles on the Pb electrode surface²⁷ which induced to the failure of the sensing reaction. Additionally, the XRD patterns and ESCA spectra of naked and electrodeposited Pb electrodes are shown in Fig. 7 and Table I, respectively. Comparison of the data of Fig. 7A and B clearly suggest that the crystal structure was transformed from a face centered cubic structure²⁸ to a tetragonal structure between the general Pb metal and the electrodeposited Pb. Additionally, comparison of Tables IA and B show that the B, F elements were only indwelled on the surface of electrodeposited Pb-modified electrode. Comparison of Fig. 7B and Table IB suggests that surface derivatives of electrodeposited Pb-modified electrode can be confirmed as BF3 and PbF2. Therefore, the BF3 and PbF2 were doped into the Pb foil electrode surface which had a positive effect on the sensitivity of TCE by using this electrode. Consequently, the 20 mA/cm² electrodeposition current density for preparing the working electrode was chosen for further development of the TCE sensor.

Table I. (A) ESCA spectra for Pb foil electrode. Pretreating conditions: same as Fig. 1. (B) ESCA spectra for electrodeposited Pb-modified electrode. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A.

A	Pinding operate	Aroo
Component	(eV)	(%)
O (1s)	532.07	29.20
C (1s)	284.98	50.70
Pb (4f7)	138.05	20.20
В		
Component	Binding energy (eV)	Area (%)
Component F (1s)	Binding energy (eV) 684.42	Area (%) 27.80
Component F (1s) O (1s)	Binding energy (eV) 684.42 532.62	Area (%) 27.80 23.60
Component F (1s) O (1s) C (1s)	Binding energy (eV) 684.42 532.62 285.02	Area (%) 27.80 23.60 15.40
Component F (1s) O (1s) C (1s) B (1s)	Binding energy (eV) 684.42 532.62 285.02 193.02	Area (%) 27.80 23.60 15.40 10.40
Component F (1s) O (1s) C (1s) B (1s) Pb (4f7)	Binding energy (eV) 684.42 532.62 285.02 193.02 139.42	Area (%) 27.80 23.60 15.40 10.40 22.90



Figure 7. (A) The XRD patterns for preparation of working electrode: (A) Pb foil electrode and (B) modified Pb electrode. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A. (B) The XRD patterns for preparation of working electrode: (A) Pb foil electrode and (B) modified Pb electrode. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A.

Effect of electrodeposition time.—The sensitivity of the sensing of TCE was investigated as a function of electrodeposition time for preparing the modified Pb electrode as shown in Fig. 8. The result indicated that increasing the electrodeposition time from 1 to 2 h deceased the sensing sensitivity of TCE from 1.910 to 1.060 μ A/cm² ppm. Then, the sensitivity increased slightly from 1.060 to 1.280 μ A/cm² ppm when the electrodeposition time increased from 2 to 4 h. However, an unstable and nonlinear response current was obtained also, when the electrodeposition time for preparing the working electrode was 1 h. Additionally, Fig. 8 clearly suggests that the Pb film thickness and deposition time are insignificant factors on the sensitivity of the TCE sensor. Comparing the energy consumption and small enlargement effect of sensitivity, the 2 h electrodeposition time was chosen to prepare the working electrode.

Effect of electrodeposition temperature.—The effect of temperature for preparing the electrode on the sensitivity of the TCE sensor was shown in Fig. 9. The result shows that increasing the electrodeposition temperature slightly increased the sensitivity. For example, increasing the electrodeposition temperature for preparing the working electrode from 25 to 40°C slightly increased the sensitivity of TCE sensing from 0.854 to 1.210 μ A/cm² ppm. The active



Figure 8. Effect of electrodeposition time for preparing the working electrode on the sensitivity of TCE sensor. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: $0.63 \text{ M Pb}(BF_4)_2$, 0.68 M HBF_4 , 0.43 M H₃BO₃, and 0.0006 M poly(ethylene glycol) 300 aqueous solution, 20 mA/cm² deposition current density, 30 rpm agitation rate and 30°C. Sensing conditions: same as Fig. 3.

surface area increased slightly by SEM morphology with increasing temperature results in an insignificant increase of sensitivity. However, the electrodeposition temperature for preparing the electrode showed a positive effect on the sensitivity. However, in this system, the temperature was over 40°C which allowed the formation of hydrofluoric acid as shown in Eq. 1²⁹

$$4HF + H_3BO_3 \rightleftharpoons HBF_4 + 3H_2O$$
[1]

In order to prevent the vent of HF gas, the 30°C electrodeposition temperature was chosen as temperature for preparing the electrode.

Amperometric measurement of TCE.—Under previously selected optimal conditions for preparation of working electrode, the typical amperometric response curves at single and different TCE addition concentration for detection of TCE by using an electrodeposited Pb-modified electrode are shown in Fig. 10. Curve A of Fig. 10



Figure 9. Effect of electrodeposition temperature for preparing the working electrode on the sensitivity of TCE sensor. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: 0.63 M Pb(BF₄)₂, 0.68 M HBF₄, 0.43 M H₃BO₃, and 0.0006 M poly(ethylene glycol) 300 aqueous solution, 20 mA/cm² deposition current density, 30 rpm agitation rate, and 2 h. Sensing conditions: same as Fig. 3.



Figure 10. Amperometric response of electrodeposited Pb-modified electrode to the addition of TCE (A) signal concentration increasing TCE concentration after each addition, (B) different concentration increasing TCE concentration after each addition. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A. Sensing conditions: same as Fig. 3.

shows that one 100 ppm concentration of TCE was injected into the electrochemical cell for each sensing step, and that the response current increased rapidly and reached a steady state. Additionally, curve B was obtained by different injection concentration of each sensing step. Comparison of the curves A and B in Fig. 10 shows that a similar amperometric response current curve and identical sensitivity were obtained. These data clearly show that TCE sensing has good reliability on the sensitivity and reproducibility. Additionally, response currents are plotted against the TCE concentration resulting in a straight line in the range from 100 to 700 ppm of TCE concentrations as shown in Fig. 11. The equation of linear fitting is i = 1.060[TCE] + 9.167, where the slope of the straight line is $1.060 \text{ }\mu\text{A/cm}^2$ ppm which is the sensing sensitivity and the R^2 is over 0.998.

Reaction mechanism.—Figure 12 shows that the peak for gas chromatography-mass spectroscopy of the main product locates at 60 of molecular weight. Hence, the product of electrolysis was acetylene chloride. Furthermore, after electrolysis, an AgNO₃



Figure 11. Typical calibration plot in sensing TCE by using modified Pb electrode. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A. Sensing conditions: same as Fig. 3.



Figure 12. GC-Mass spectroscopy of electrolysis product. Pretreating conditions: same as Fig. 1. Electrodeposition conditions: same as Fig. 2A. Electrolysis conditions: 0.01 M TBAT in AN solution, electrodeposited Pb-modified electrode as cathode, Pt plate as anode, Ag/Ag^+ (with 0.1 M TBAP in AN solution) as reference electrode, 155 rpm agitation rate, and at room temperature.

aqueous solution was added to the catholyte and the white AgCl was found. It can be confirmed that chlorine ion presents in the catholyte. Moreover, the pH of catholyte decreased from 7.0 to 1.0 during the electrolysis. All results show that hydrogen ion is generated in the catholyte after electrolysis. The acetylene chloride not only has stronger acidity than TCE but also dissociated to acetylene chloride anion in the solution. The electrochemical reduction mechanism for TCE by using electrodeposited Pb-modified electrode as working electrode is proposed as shown in Eq. 2



Comparison of the experimental results and the theoretical ones.—The sensing reaction was mass-transfer controlled and the TCE concentration was less than 700 ppm, the relationship of diffusion current, i_d , and the concentration of TCE in the solution, C_L , can be described as shown in Eq. 3

$$i_{\rm d} = ZFAkC_{\rm L}$$
[3]

where Z is the number of electron transfer, F is the Faraday constant, A is the sensing area of electrode, and k is the rate constant of mass transfer control. Equation 3 implies a linear relationship between TCE concentration and cathodic current. The relationship of i_d and C_L at the desired sensing conditions was obtained from the data of Fig. 11 resulting in Eq. 4

$$i_{\rm d} = 1.060C_{\rm L}$$
 [4]

Comparing Eq. 3 and 4 and substituting the number of electron transfer, Z, which is 2,²⁶ and A, which is 1.0 cm², k can be obtained to be 7.217×10^{-4} /cm s.

Conclusions

Electrodeposition of Pb has been shown to be a suitable metal catalyst as sensing electrode for amperometric TCE sensor. The SEM morphologies of prepared working electrode show that the substrate surface has the larger roughness by pretreating electrode with 0.1 M HNO₃ aqueous solution. Additionally, the XRD pattern also showed the modified Pb electrode containing some derivatives after the electrodeposition which enhanced the stability of the TCE sensor. The optimal conditions for preparation working electrode were obtained as 0.1 M HNO₃ pretreatment, 20 mA/cm² electrodeposition current density, and 30°C electrodeposition temperature. Under the optimal sensing conditions, a linear response, *i* = 1.060[TCE] + 9.167, was obtained under TCE concentration range from 100 to 700 ppm. Additionally, *k* is 7.217 10^{-4} /cm s. Therefore, the electrochemical TCE sensor by using modified Pb electrode showed promising features for commercial application.

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References

- 1. K. H. Kilburn, Arch. Environ, Health, 57, 113 (2002).
- T. H. Ma, C. Xu, S. Liao, H. McConnell, B. S. Jeong, and C. D. Won, *Mutat. Res.*, 359, 39 (1996).
- 3. Y. Ku, C. M. Ma, and Y. S. Shen, Appl. Catal., B, 34, 181 (2001).
- 4. D. Bogdal and J. Pielichowski, Bull. Soc. Chim. Fr., 132, 1127 (1995).
- P. Kumar, A. K. Prasad, and K. K. Dutta, *Hum. Exp. Toxicol.*, **19**, 117 (2000).
 D. Wartenberg, D. Reyner, and C. S. Scott, *Environ. Health Perspect.*, **108**, 161
- D. watcholeg, D. Keyner, and C. S. Scott, *Environ. Teaun Perspect.*, 106, 101 (2000).
 A. Ojajarvi, T. Partanen, A. Ahlbom, P. Boffetta, T. Hakulinen, N. Jourenkova, T
- A. Ojajarvi, T. Partanen, A. Ahlbom, P. Boffetta, T. Hakulinen, N. Jourenkova, T. Kauppinen, M. Kogevinas, H. Vainio, E. Weiderpass, and C. Wesseling, *Am. J. Epidemiol.*, **153**, 841 (2001).
- S. Hanada, T. Shigematsu, K. Shibuya, M. Eguchi, T. Hasegawa, F. Suda, Y. Kamagata, T. Kanagawa, and R. Kurane, J. Ferment. Bioeng., 86, 539 (1998).
- T. L. Jacobs, J. M. Warmerdam, M. A. Medina, and W. T. Piver, *Environ. Health Perspect.*, 104, 866 (1996).
- E. A. Maull, V. J. Cogliano, C. S. Scott, H. A. Barton, J. W. Fisher, M. Greenberg, L. Rhomberg, and S. P. Sorgen, *Drug Chem. Toxicol.*, 20, 427 (1997).
- 11. T. Kaneko, P. Y. Wang, and A. Sato, Ind. Health, 35, 301 (1997).
- 12. J. Xie, F. Hui, and R. Rosset, Analusis, 24, 214 (1996).
- 13. L. R. Jordan and P. C. Hauser, Anal. Chem., 69, 2669 (1997).
- 14. J. Farrell, N. Melitas, M. Kason, and T. Li, Environ. Sci. Technol., 34, 2549 (2000).
- 15. T. Li and J. Farrell, Environ. Sci. Technol., 35, 3560 (2001).
- 16. J. F. Fan and J. T. Yates, J. Am. Chem. Soc., 118, 4686 (1996).
- M. D. Driessen, T. M. Miller, and V. H. Grassian, J. Mol. Catal. A: Chem., 131, 149 (1998).
- D. Chatterjee and C. Bhattacharya, Indian J. Chem. Section A-Inorganic Bio-Inorganic Physical Theoretical Anal. Chem., 38, 1256 (1999).
- L. H. Zhao, S. Ozaki, K. Itoh, and M. Murabayashi, *Electrochemistry (Tokyo, Jpn.)*, 70, 8 (2002).
- 20. L. Yang, Y. F. Chang, and M. S. Chou, J. Haz. Mater, 69, 111 (1999).
- R. E. Parales, J. L. Ditty, and C. S. Harwood, *Appl. Environ. Microbiol.*, 66, 4098 (2000).
- 22. E. Hourbron, S. Escoffier, and B. Capdeville, Water Sci. Technol., 42, 395 (2000).
- 23. F. Hoffman, D. Ronen, H. Rosin, and F. Milanovich, Talanta, 43, 681 (1996).
- T. S. Han, Y. C. Kim, S. Sasaki, K. Yano, K. Ikebukuro, A. Kitayama, T. Nagamune, and I. Karube, *Anal. Chim. Acta*, 431, 225 (2001).
- T. S. Han, S. Sasaki, K. Yano, K. Ikebukuro, A. Kitayama, T. Nagamune, and I. Karube, *Talanta*, 57, 271 (2002).
- 26. M. H. Chen, T. Y. Lin, and T. C. Chou, J. Electrochem. Soc., 149, H87 (2002)
- 27. J. Simonet, Y. Astier, and C. Dano, J. Electroanal. Chem., 451, 5 (1998)
- C. Kittel, Introduction to Solid State Physics, 7th ed., p. 23, John Wiley & Sons, New York (1996).
- F. A. Lowenheim, *Method Electroplating*, 3rd ed., p. 268, John Wiley & Sons, New York (1974).