Effect of the sp²/sp³ Ratio in a Hybrid Nanocarbon Thin Film Electrode for Anodic Stripping Voltammetry Fabricated by Unbalanced Magnetron Sputtering Equipment

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The effect of the sp²/sp³ ratio in an unbalanced magnetron sputtered nanocarbon film electrode was studied for determining Cd²⁺ and Pb²⁺ by anodic stripping voltammetry (ASV). The signal-to-noise ratio in the ASV measurement improved as the sp³ concentration in the carbon film increased because the noise current decreased with the increasing sp³ concentration. The detection limits with a carbon film containing 50% sp³ were 0.25 and 1.0 μg L⁻¹ for Cd²⁺ and Pb²⁺ with high repeatability (Cd: 4.6% and Pb: 6.4%, n = 3). For a real sample measurement, a pretreatment system combining a photooxidation reactor and a cation exchange column was used to eliminate the interference from EDTA and Cu²⁺, which forms a stable complex or alloy with Cd²⁺ and Pb²⁺. More than 99% of the interference was eliminated, and accurate signal currents for Cd²⁺ and Pb²⁺ were successfully obtained with the pretreatment system.

Keywords Carbon film electrode, anodic stripping voltammetry, unbalanced magnetron sputtering, heavy metal ion

(Received February 27, 2015; Accepted April 9, 2015; Published July 10, 2015)

Introduction

The presence of the heavy metal ions Cd²⁺ and Pb²⁺ in water must be monitored because of the teratogenic and carcinogenic risks they pose for human health and safety.¹ Environmental pollution is growing worse in developing countries because of work in the mining and manufacturing industries.¹ The World Health Organization (WHO) strictly regulates heavy metal concentrations in drinking water and sewage. Atomic absorption spectroscopy (AAS) and inductively coupled plasma–mass spectrometry (ICP-MS) have been used as standard analytical methods for detecting heavy metal ions, because they have a wide dynamic range and a low detection limit. AAS and ICP-MS techniques provide accurate and reliable analytical results; however, the equipment is expensive, time consuming to operate, and unsuitable for on-site measurements.

The anodic stripping voltammetry (ASV) measurement technique is inexpensive, and suitable for on-site monitoring, and so meets the requirements of developing countries. An Hg electrode has been used as a working electrode for ASV;²,³ however, Hg has been avoided in recent years because of its toxicity. Therefore, alternative metal electrodes, such as Ir,⁴,⁵ Au,⁶,⁷ Ag⁸ and Bi,⁹ have been investigated. Unfortunately, they did not perform as well as the Hg electrode. More recently, various carbon electrodes, such as glassy carbon (GC),¹¹,¹³ screen-printed carbon,¹⁴ carbon nanotube¹⁵ and boron doped diamond (BDD)¹⁶–²¹ electrodes, have been employed for ASV. Table 1 summarizes their performance as regards sensitivity, background current and detection limit. sp² dominant carbon electrodes, such as graphite,²⁶ carbon nanotubes¹⁵ and GC,¹³ tend to exhibit a large signal current in ASV. However, these electrodes also have a high background current, which degrades

Table 1 Experimental parameters, namely sensitivity, background current and detection limit, at various carbon electrodes for ASV analysis of Cd²⁺

| Electrode          | sp²:sp³ | Sensitivity/ Backgrou Background/ Detection | μA cm⁻² | Background current | limit/ limit/ L⁻¹ | μA cm⁻² | L⁻¹ |
|-------------------|---------|---------------------------------------------|---------|--------------------|------------------|---------|-----|
| Graphite²⁶         | 100:0   | 11.0                                        | 663.4   | 10                 |
| Carbon nanotube¹⁵ | 100:0   | 0.8                                         | 198.1   | 1.1                |
| Glassy carbon³³,³⁵| 100:0   | 2.7                                         | 160     | 5                  |
| ECR-nanocarbon³³  | 60:40   | 1.0                                         | 5.3     | 0.3                |
| UBM-nanocarbon³³  | 50:50   | 0.47                                        | 20      | 0.5                |
| DLC (N-dope)²³    | —       | —                                           | —       | about 12           |
| BDD (Renault)²¹   | 0:100   | 0.0042                                      | 0.012   | 0.05               |
| BDD (Swain)²²     | 0:100   | 0.074                                       | 2.7     | 1                  |

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the signal-to-noise ratio ($S/N$). In contrast, an $sp^3$ dominant BDD electrode was reported to achieve a low detection limit due to its low noise current. Diamond-like carbon (DLC) and nitrogen doped DLC were also used as an electrode for ASV; however, the ASV performance of DLC is reported to be poorer than that of BDD. This is because DLC is generally amorphous and not electrochemically active, and so cannot efficiently preconcentrate metal ions on a DLC surface.

We previously reported a nanocarbon film electrode formed by an electron cyclotron resonance (ECR) sputtering method. A low detection limit for Cd$^{2+}$ (0.3 μg L$^{-1}$) in ASV was achieved with the ECR nanocarbon film because of a low noise current while maintaining high electrode activity. We have also reported a nanocarbon film electrode fabricated with unbalanced magnetron (UBM) sputtering equipment, and the UBM-sputtered carbon film has equivalent electrochemical characteristics to those of ECR nanocarbon films. The advantages of UBM sputtering compared with ECR sputtering are that it is inexpensive and has a high throughput. By using the UBM nanocarbon film, we also achieved a relatively low detection limit for Cd$^{2+}$ (0.5 μg L$^{-1}$), which is comparable to that of ECR nanocarbon. One of the features of the UBM sputtering method is that the $sp^3/sp^4$ ratio in a carbon film is controllable by tuning the ion irradiation energy between a substrate and a carbon target. We assume that it is important to study the effect of the $sp^3/sp^4$ ratio to improve the ASV performance. In fact, there have been no reports about the ASV performance when the $sp^3/sp^4$ ratio is varied in a carbon electrode.

To fit the ASV performance to environmental samples, any pretreatment is also important because many researchers have reported that the ASV performance is degraded by interference when measuring real samples. For example, a chelating agent, such as EDTA, degrades the ASV response of the Cd$^{2+}$ and Pb$^{2+}$ because of the formation of a stable complex. Also, Cu$^{2+}$ is widely distributed in the environment and forms an alloy with Cd$^{2+}$ and Pb$^{2+}$, and therefore an accurate ASV peak cannot be obtained in the presence of Cu$^{2+}$.

In this study, we fabricated nanocarbon films with various $sp^3/sp^4$ ratios, and applied them to the ASV measurement of Cd$^{2+}$ and Pb$^{2+}$ in order to investigate the effect of the $sp^3/sp^4$ ratio on the sensitivity, noise current, detection limit and repeatability. We also investigated the effect of the interference of EDTA and Cu$^{2+}$ on the ASV measurement and the elimination efficiency by employing pretreatment with a photooxidation reactor and a cation-exchange column.

**Experimental**

**Materials**

Potassium ferricyanide, trisodium citrate dihydrate, sodium acetate and an AAS-grade standard solution 0.100 g L$^{-1}$ Pb$^{2+}$ were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). An AAS-grade standard solution 1.00 g L$^{-1}$ Cd$^{2+}$ was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Potassium chloride was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Ethylenediaminetetraacetic acid copper(II) disodium salt tetrahydrate was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Hexaammineruthenium(III) chloride was purchased from Aldrich (WI, USA). The GC (20-SS) electrode was purchased from Tokai Carbon Co., Ltd. (Tokyo, Japan). Ultrapure water (Milli-Q) was used in all of the experiments.

**Electrode preparation**

A nanocarbon film electrode was deposited on a boron-doped silicon (100) substrate with UBM sputtering equipment (USP330, Universal Systems Co., Ltd., Tokyo, Japan) at room temperature. Sintered carbon was used as a target. During the sputter deposition, the argon gas pressure was 6.0 × 10$^{-1}$ Pa and the substrate target power ranged from 100 to 400 W. The substrate bias voltages were 20, 75 and 100 V; these UBM nanocarbon electrodes are abbreviated as UBM (80:20), (64:36) and (50:50), respectively. The $sp^3/(sp^3+sp^4)$ ratio of the nanocarbon film was confirmed from the X-ray photoelectron spectra (Kratos Axis Ultra, Shimadzu Corp., Kyoto, Japan) by comparing the magnitudes of the peaks observed at 284.5 eV (sp$^3$) and 285.5 eV (sp$^4$) (Fig. S1, Supporting Information).

**Electrochemical property of carbon electrode**

Electrochemical measurements were performed using a potentiostat (Model CHI 660C, CH Instruments, Austin, TX). We used a three-electrode configuration throughout the experiments. We employed carbon materials including UBM nanocarbon films (2 mm diameter), and a conventional GC (2 mm diameter) as a working electrode, a platinum counter electrode and an Ag/AgCl (saturated KCl) reference electrode. The potential window is defined as the potential range between current limits that do not exceed ±500 μA cm$^{-2}$, as previously reported by Granger et al.

**Electrochemical measurement of Cd$^{2+}$ and Pb$^{2+}$**

Cd$^{2+}$ and Pb$^{2+}$ were analyzed by the ASV method as follows. The potential of a carbon working electrode was held at −1.3 V vs. Ag/AgCl for 240 s to preconcentrate each metal on the carbon electrode surface under stirring at 450 rpm with a magnetic stirrer (Model FS-05, TGK, Tokyo, Japan). We stopped stirring and carried out square wave voltammetry from −1.3 V to 0.6 V using the following parameters (step height, 8 or 14 mV; amplitude, 0.025 V; frequency, 50 Hz).

**Photooxidation reactor to remove any organic substance**

We employed a photooxidation reactor previously reported by one of the authors to remove organic substances in artificial environmental samples containing one of the target ions and interfering substances (100 μg L$^{-1}$ Cu$^{2+}$ and 0.1 mM EDTA). The system consisted of quartz tubing and an Hg lamp. The photooxidation reactor was fabricated with a power output of 40 W. The sample solution was pumped through the quartz tubing at a flow rate of 0.2 mL min$^{-1}$. In the tubing, the sample solution was irradiated with ultraviolet light to decompose the EDTA.

**Cation-exchange method to remove interfering metal ions**

Zero-point five grams of Chelex 100 cation exchange resin (200 – 400 dry mesh, Bio-Rad Laboratories, Inc., Hercules, CA) was packed into an Econo Column (cross sectional area 1.77 cm$^2$, Bio-Rad Laboratories, Inc.) The resin was washed with about 5 mL of 0.1 M HCl and conditioned with 0.1 M acetate buffer pH 2.0 (for Cd$^{2+}$) or 0.1 M citrate buffer pH 2.0 (for Pb$^{2+}$) before use. Then, 9.0 mL of the UV treated solution was mixed with 1.0 mL of a 1.0 M acetate buffer (pH 2.0) or 1.0 M citrate buffer (pH 2.0). The solution was introduced into the cation- exchange column to remove Cu$^{2+}$ at a flow rate of 0.4 mL min$^{-1}$. With Cd$^{2+}$, 9.0 mL of analyte elution was mixed with 1.0 mL of 1.0 M acetate buffer (pH 5.0) to control the pH.
Table 2: Surface properties of different sp²/sp³ UBM nanocarbon film electrodes and GC electrode

| Carbon electrode | sp³/(sp²+sp³)  | O/C ratio | Ra (nm) |
|-----------------|----------------|-----------|---------|
| GC              | 0              | 0.09      | 0.42    |
| UBM-20          | 0.20           | 0.03      | 0.32    |
| UBM-75          | 0.36           | 0.03      | 0.11    |
| UBM-100         | 0.50           | 0.02      | 0.12    |

a. The number after "UBM" indicates the acceleration voltage. b. O/C ratios were obtained from XPS analysis. c. Ra values were obtained from AFM measurements.

Table 3: Comparison of electron transfer rate constant (k⁰) and potential window of two kinds of measurement solutions at different electrodes

| Carbon electrode | pH 5.0 for Cd²⁺ | pH 2.0 for Pb²⁺ | k⁰/10⁷ cm s⁻¹ |
|-----------------|------------------|------------------|---------------|
| UBM-100         | –1.49 – 1.77     | –1.02 – 1.86     | 2.54          |
| UBM (80:20)     | –1.50 – 1.98     | –1.33 – 2.00     | 2.00          |
| (64:36)         | –1.79 – 1.84     | –1.37 – 1.87     | 0.83          |
| UBM (50:50)     | –1.94 – 1.97     | –1.51 – 2.00     | 0.43          |

This is because an edge plane contributes more to the reduction of the target metals than a basal plane in ASV measurements. The electron transfer rate constant (k⁰) on UBM (50:50) was about 4.5-times smaller than that of UBM (80:20) (Table 3). This implies that the content of the edge plane in a UBM electrode becomes smaller as the sp³ content increases.

Effect of interfering substances and a pretreatment for the ASV measurement

The ASV measurement is affected by chelating agents and Cu²⁺ in an environmental sample. Therefore, it is necessary to remove them before performing an ASV measurement. We tested a way to remove EDTA and Cu²⁺ with a photooxidation reactor and a cation-exchange column. Figure 2 shows the effect of the pretreatment to voltammograms of 50 μL L⁻¹ Cd²⁺ and Pb²⁺ in the presence of 0.1 mM EDTA and 100 μL L⁻¹ Cu²⁺, before and after the pretreatment techniques were employed. Signal currents were observed without the pretreatment when the sample solution contained EDTA (gray broken line). After the photooxidation treatment, signal peaks appeared (black broken line) in spite of the EDTA contamination. Three ASV peaks, which were derived from Cd²⁺, Cd-Cu alloy and Cu²⁺, can be observed in Fig. 2(a).

However, no ASV peak derived from Pb²⁺ can be observed in
Calibration curves for (a) Cd$^{2+}$ in acetate (pH 5.0) and (b) Pb$^{2+}$ in citrate (pH 2.0). (●), UBM (50:50); (▲), UBM (64:36); (■), UBM (80:20) and (□), GC electrode (100:0). Error bars represent one standard deviation for 3 measurements. (c) and (d) show signal and noise currents of Cd$^{2+}$ and Pb$^{2+}$ (50 μg L$^{-1}$), respectively.

### Table 4

|                        | ASV method (sp$^3$/sp$^3$)$^a$ | AAS | ICP-MS |
|------------------------|---------------------------------|-----|--------|
|                        | GC (100:0)  | UBM (80:20) | UBM (64:36) | UBM (50:50) |       |
| Cd$^{2+}$              |                      |     |     |         |       |
| Detection limits/μg L$^{-1}$ | 1.0              | 0.50 | 0.50 | 0.25 | 0.1 | 0.003 |
| Repeatability, %$^b$   | 31.0              | 25.6 | 8.9  | 4.6  | <5% | 3.2% |
| Pb$^{2+}$              |                      |     |     |         |       |
| Detection limits/μg L$^{-1}$ | 5.0              | 5.0  | 1.0  | 1.0  | 0.5 | 0.005 |
| Repeatability, %$^b$   | 33.1              | 20.6 | 14.7 | 6.4  | <12%| 2.6% |

$^a$ ( ) shows sp$^3$/sp$^3$ ratio, $^b$ Repeatability at 1.0 μg L$^{-1}$ ($n = 3$).

### Table 5

| Carbon electrode (sp$^3$/sp$^3$) | Cd$^{2+}$ | Pb$^{2+}$ |
|----------------------------------|-----------|-----------|
|                                  | GC (100:0) | UBM (80:20) | UBM (64:36) | UBM (50:50) | GC (100:0) | UBM (80:20) | UBM (64:36) | UBM (50:50) |
| Sensitivity/μA cm$^{-2}$ (μg L$^{-1}$)$^{-1}$ | 10.5 | 7.4 | 3.8 | 2.0 | 7.1 | 4.6 | 2.0 | 0.71 |
| Noise Current/μA cm$^{-3}$       | 317 | 170 | 80 | 22 | 710 | 512 | 151 | 73 |
| Background current/μA cm$^{-2}$  | 26.4 | 21.4 | 9.1 | 7.2 | 7.3 | 6.7 | 6.9 | 5.9 |
| S/N ratio (×10$^3$ at 50 μg L$^{-1}$) | 1.6 | 2.1 | 2.4 | 4.6 | 0.48 | 0.43 | 0.78 | 0.50 |
Fig. 2(b). This is because Pb^{2+} easily forms the Pb-Cu alloy, i.e., all Pb^{2+} was deposited as the Pb-Cu alloy on an electrode under an excess Cu^{2+} concentration. The mineralization efficiency of organic carbon of 0.1 mM EDTA in the presence of 100 μg L^{-1} Cu^{2+} was 97% (w/w) which was evaluated by analyzing the total organic carbon with and without the use of a photooxidation pretreatment. This indicates that EDTA was mostly decomposed by the photooxidation reactor. After the pretreatment with the photooxidation reactor and the cation-exchange column, an ideal single peak was successfully observed that was comparable to an ASV peak without any interference (red line).

Figures 3(a) and 3(b) show calibration curves for Cd^{2+} and Pb^{2+} in both the presence and absence of EDTA with and without the pretreatment. By employing the photooxidation pretreatment, we successfully obtained calibration curves for Cd^{2+} and Pb^{2+} in the presence of 0.1 mM EDTA. We confirmed that the ASV peak completely disappears in the presence of 0.8 μM EDTA, as can be seen in Fig. 3(c), i.e., more than 99% of EDTA was decomposed by the pretreatment in Figs. 3(a) and 3(b). In addition, the products of EDTA decomposed by the photooxidation were confirmed to have no effect on the ASV measurement.

Figures 4(a) and 4(b) show the calibration curves for Cd^{2+} and Pb^{2+} using UBM (50:50) in the presence of Cu^{2+} both with and without a cation-exchange column treatment. With 100 μg L^{-1} Cu^{2+}, the signal current of Cd^{2+} was about 40% of that without Cu^{2+}, and the signal current of Pb^{2+} almost disappeared. However, the signal currents of the calibration curves for both targets recovered to about 90% as a result of the pretreatment. Thus, the detection limits of Cd^{2+} and Pb^{2+} became poor at about one order of magnitude (Cd: 0.25 → 1.0 μg L^{-1}, Pb: 1.0 → 10 μg L^{-1}). Some Cd^{2+} and Pb^{2+} would be trapped in the cation-exchange column. Although the detection limits deteriorated after the pretreatment, they still satisfied the WHO standards (Cd: 3.0 μg L^{-1}, Pb: 10 μg L^{-1}).

Conclusions

We employed UBM nanocarbon films to investigate the effect of the sp^{2}/sp^{3} ratio on the ASV performance for Cd^{2+} and Pb^{2+} measurements. The S/N improved as the sp^{3} content in the
UBM nanocarbon increased. Moreover, the repeatability also improved with increasing sp³. The lowest detection limits of 0.25 and 1.0 μg L⁻¹ for Cd²⁺ and Pb²⁺ were obtained with a UBM nanocarbon electrode containing 50% sp³. We also obtained detection limits that satisfied the WHO standard in the presence of interference by employing a pretreatment system that combined a photooxidation reactor and a cation exchange column.

Acknowledgements

We thank the staff of the Nano Processing Facility at AIST for their kind help with the AFM measurements.

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References

1. A. Azizullah, M. N. Khattak, P. Richter, and D. P. Hader, *Environ. Int.*, 2011, 37, 479.
2. K. W. Gardiner and L. B. Rogers, *Anal. Chem.*, 1953, 25, 1393.
3. R. D. DeMars and I. Shain, *Anal. Chem.*, 1957, 29, 1825.
4. J. Herdan, R. Feeney, S. P. Kounaves, A. F. Flannery, C. W. Storment, G. T. A. Kovacs, and R. B. Darling, *Environ. Sci. Technol.*, 1998, 32, 131.
5. M. A. Nolan and S. P. Kounaves, *Anal. Chem.*, 1999, 71, 3567.
6. R. W. Andrews and D. C. Johnson, *Anal. Chem.*, 1975, 47, 294.
7. J. Wang and B. Tian, *Anal. Chem.*, 1993, 65, 1529.
8. R. Feeney and S. P. Kounaves, *Anal. Chem.*, 2000, 72, 2222.
9. E. Kirowa-Eisner, M. Brand, and D. Tzur, *Anal. Chim. Acta*, 1999, 385, 325.
10. I. Švancara, C. Prior, S. B. Hočevar, and J. Wang, *Electroanalysis*, 2010, 22, 1405.
11. T. M. Florence, *J. Electroanal. Chem. Interfacial Electrochem.*, 1970, 27, 273.
12. B. Hoyer, T. M. Florence, and G. E. Batley, *Anal. Chem.*, 1987, 59, 1608.
13. J. F. van Staden and M. C. Matoetoe, *Anal. Chim. Acta*, 2000, 411, 201.
14. F. Fan, J. Dou, A. Ding, K. Zhang, and Y. Wang, *Anal. Sci.*, 2013, 29, 571.
15. D. Sun, X. Xie, Y. Cai, H. Zhang, and K. Wu, *Anal. Chim. Acta*, 2007, 581, 27.
16. T. M. Arantes, A. Sardinha, M. R. Baldan, F. H. Cristovan, and N. G. Ferreira, *Talanta*, 2014, 128, 132.
17. Y. Show, M. A. Witek, P. Sonthalia, and G. M. Swain, *Chem. Mater.*, 2003, 15, 879.
18. A. Manivannan, M. S. Seehra, D. A. Tryk, and A. Fujishima, *Anal. Lett.*, 2002, 35, 355.
19. Y.-C. Tsai, B. A. Coles, K. Holt, J. S. Foord, F. Marken, and R. G. Compton, *Electroanalysis*, 2001, 13, 831.
20. C. Babyak and R. B. Smart, *Electroanalysis*, 2004, 16, 175.
21. A. Sbartai, P. Natrella, M. E. T. Alguacil, J. M. Crumpton, and N. G. Ferreira, *Anal. Chim. Acta*, 2012, 84, 4805.
22. E. A. McGaw and G. M. Swain, *Anal. Chim. Acta*, 2006, 575, 180.
23. V. Bezerra dos Santos, E. L. F. Fava, O. D. Pessoa-Neto, S. R. Bianchi, R. C. Faria, and O. Fatibello-Filho, *Anal. Methods*, 2014, 6, 8526.
24. T. W. Stéphane Fierro, K. Akai, M. Yamanuki, and Y. Emaga, *J. Electrochem. Soc.*, 2011, 158.
25. A. A. Argun, A. M. Banks, G. Merlen, L. A. Tempelman, M. F. Becker, T. Schueltke, and B. M. Dweik, *Anal. Chim. Acta*, 2013, 773, 45.
26. L. Moreno-Baron, A. Merkoçi, and S. Alegret, *Electrochim. Acta*, 2003, 48, 2599.
27. F. Wantz, C. E. Banks, and R. G. Compton, *Electroanalysis*, 2005, 17, 655.
28. A. Zeng, E. Liu, S. N. Tan, S. Zhang, and J. Gao, *Electroanalysis*, 2002, 14, 1294.
29. B. Khadro, A. Sikora, A. S. Loir, A. Errachid, F. Garrelie, C. Donnet, and N. Jaffrezic-Renault, *Sens. Actuators, B*, 2003, 100, 243.
30. O. Niwa, J. Jia, Y. Sato, D. Kato, R. Kurita, K. Maruyama, K. Suzuki, and S. Hirono, *J. Am. Chem. Soc.*, 2006, 128, 7144.
31. J. Jia, D. Kato, R. Kurita, Y. Sato, K. Maruyama, K. Suzuki, S. Hirono, T. Ando, and O. Niwa, *Anal. Chem.*, 2007, 79, 98.
32. N. Sekioka, D. Kato, A. Ueda, T. Kamata, R. Kurita, S. Umemura, S. Hirono, and O. Niwa, *Carbon*, 2008, 46, 1918.
33. R. Kurita, K. Nakamoto, Y. Sato, T. Kamata, A. Ueda, D. Kato, S. Hirono, and O. Niwa, *Anal. Sci.*, 2012, 28, 13.
34. T. Kamata, D. Kato, H. Ida, and O. Niwa, *Diamond Relat. Mater.*, 2014, 49, 25.
35. H. Yanagisawa, R. Kurita, T. Kamata, D. Kato, and O. Niwa, *Electrochemistry*, 2014, 82, 949.
36. G. van Dijck and F. Verbeek, *Anal. Chim. Acta*, 1971, 54, 475.
37. Y. Bonfil, M. Brand, and E. Kirowa-Eisner, *Anal. Chim. Acta*, 2002, 464, 99.
38. W. Siriangkhawut, K. Grudpan, and J. Jakmunee, *Talanta*, 2011, 84, 1366.
39. O. El Tall, N. Jaffrezic-Renault, M. Sigaud, and O. Vittori, *Electroanalysis*, 2007, 19, 1152.
40. A. Sugitani, T. Watanabe, T. A. Ivandini, T. Iguchi, and Y. Einaga, *Phys. Chem. Chem. Phys.*, 2013, 15, 142.
41. C. Kokkinos, A. Economou, I. Raptis, and C. E. Efstathiou, *Electrochim. Acta*, 2008, 53, 5294.
42. D. Dragoe, N. Spătărău, R. Kawasaki, A. Manivannan, T. Spătărău, D. A. Tryk, and A. Fujishima, *Electrochim. Acta*, 2006, 51, 2437.
43. M. C. Granger, J. Xu, J. W. Strojek, and G. M. Swain, *Anal. Chim. Acta*, 1999, 397, 145.
44. T. Nakazato and H. Tao, *Anal. Chem.*, 2006, 78, 1665.
45. T. Satou, T. Nakazato, and H. Tao, *Anal. Sci.*, 2013, 29, 233.
46. C. E. Banks and R. G. Compton, *Analyst*, 2006, 131, 15.
47. X. Yang, L. Haubold, G. DeVivo, and G. M. Swain, *Anal. Chem.*, 2012, 84, 6240.
48. P. N. Bartlett, G. Denuault, and M. F. B. Sousa, *Analyst*, 2000, 125, 1135.
49. L. d. A. Pereira, I. G. de Amorim, and J. B. B. da Silva, *Talanta*, 2004, 64, 395.
50. P. Figura and B. McDuffie, *Anal. Chem.*, 1979, 51, 120.
51. P. Su-Cheng, *Anal. Chim. Acta*, 1988, 211, 271.