Sensor Fabrication for Determination of Cadmium Using Nafion/Ionic Liquid/Graphene Composite with Thick Film Technology

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Abstract. The cadmium (Cd (II)) detection sensor consists of working electrode, counter electrode and reference electrode made with thick film technology on sensitive material-based carbon electrodes (G / N / IL / SPCE) and coated with Bismuth film. Carbon (C) paste, Ag | AgCl is used as working electrode, counter electrode and reference electrode material on alumina substrate by screen printing. The working electrode was doped with Graphene (G), Nafion (N) and Ionic liquid (IL). Furthermore, Bismuth-Film (BiF) is coated with electrodeposition on the surface of the working electrode. Electrode characterization with SEM is conducted to see the morphology of sensitive materials. It showed that the particles were distributed evenly on the surface of the electrode with spherical particles. Analysis using EDS shows the element's atomic composition is C 91.57%, N 3.48%, O 3.23%, Bi 0.01%. The performance of the cadmium sensor was tested with a potentiostat in a standard Cd solution with a concentration of 0.05 mgL⁻¹ – 1 mgL⁻¹ indicating an average output voltage range of 10.36 volts - 10.37 volts. This can be explained that the sensor can detect Cd (II) content properly according to performance.

1. Introduction
Cadmium (Cd) is one of toxic elements that can be found in the environment. Therefore, detection of cadmium levels in the environment, food and biological samples is of concern to researchers. Methods and analysis in determining the content of Cd continue to be efficiently developed such as Atomic Absorption Spectrophotometry [3] [4] [5], differential pulsed anodic stripping voltammetry (DPAS) [6], square wave anodic stripping voltammetry [7].

Electrochemical methods, especially electro polymerization have been widely recognized as electrode coatings for heavy metal detection sensors because of their low cost, easy operation, excellent stability, high sensitivity, and low detection limits [8] [9] [10] [11]. The use of mercury film-based electrodes (MFE) [12] [13] has been used in electrode coating techniques because of advantages such as surface purity, reproducibility, high sensitivity, high hydrogen potential [14]. However, the disadvantage is that mercury is a toxic material. The alternative developed in the study was using
bismuth film. The characteristics of electrode coating are almost the same as coating with mercury electrodes. The formation of bismuth films was carried out by electrodeposition such as at the Glass Carbon Electrode (GCE) [15] [16], Carbon Paste Electrode (CPE) [17], Boron Doped Diamond Electrode (BDDE) [18] and Screen Printed Carbon Electrode (SPCE) [19] [20] [21]. In this study the SPCE method based on thick film was chosen in the manufacture of electrodes because the process is easy and fast with low production costs.

Graphene (G) has been used in many studies because of its properties like extremely high thermal conductivity, high mobility of charge carriers, good mechanical strength, large specific surface area and outstanding electrical properties [22]. Ionic Liquid (IL) is a high ionic conductivity material, widely used as an electrochemical solvent and electrode modifier for the manufacture of sensors [23] [24]. The use of Nafion (N) [25] which has excellent anti-pollution capacity properties, chemical inertia, and high permeability to relevant cations to increase detection sensitivity to heavy metals.

In this study, the SPCE electrode was modified by G, IL and N composite coating on a working electrode by electropolymerization technique. Integration of IL and N composites can cause synergistic effects in electrochemical applications. Furthermore, the addition of Bismuth-film to the working electrode makes the electrode strong and good for the determination of heavy metals. Finally, this simple, inexpensive and sensitive sensor is applied to determine Cd (II) content by using potentiostat analysis and morphological analysis using Scanning Electron Microscope (SEM).

2. Experiment

2.1. Tools and Materials

The printing process of Carbon paste and Ag | AgCl uses the Accu-coat 3230 (Aremco Products Inc.) screen printer machine. After the printing process is dried using a National laboratory oven at 150°C for 10 minutes. Then proceed with the combustion process on a conveyor furnace machine (RTC Radiant Technology Corp.) at a temperature of 800°C for 30 minutes. Measurement and determination of the sensor response to Cd concentration is carried out using a home made potentiostat (SOLITON EM 10/20), APPA 505 digital multimeter connected to a computer.

The electrode material uses carbon paste (Dupont, BQ242) and Ag AgCl material (Dupont 5874). Graphene was obtained from ACS Material, LLC (Medford, USA). As an anion Amoniumhydrogen phosphate (MERCK) is used. Ionic Liquid uses types 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate and Nafion D-521 5% (Alfa Aesar), N-dimethylformamide (DMF) from Sigma-Aldrich (Buchs, Switzerland). Buffer solution is obtained from Merck (Darmstadt, Germany). Cd standard solutions in 1000 mg L⁻¹ concentration were obtained from Certipur (Germany). Aquadesk 17MΩ is purified by Ultrapure Water Purification Systems (USA) Ultrapure Water Purification Systems (USA) water purification systems (Thermo Scientific™ E-Pure™).

2.2. Fabrication of Electrodes

Thick film technology screen printing method is used to make cadmium detection sensor electrodes. This technology was first used in the mid 1960s and became popular in 1970. This process was chosen to obtain a microelectronics circuit with the advantage of the size of the sensor can be diminutur and conductor lines in small sizes (mm). Layer thickness in thick film technology ranges from 100 micrometers. Printing carbon paste material (Dupont, BQ242) is applied to make working electrodes and counters. Whereas silver | Silver chloride (Ag | AgCL) paste is applied to make reference electrodes. The stages of thick film processing include screen film making, printing of paste materials, drying, combustion, assembly, packaging and other additional processes. Figure 1 shows the flow of the electrode fabrication process.
2.3. Preparation of the N/IL/G composite
First, 2.0 mg of graphene was dispersed in 2.0 mL of DMF by stirring for about 2 hours. Next, 0.5% (m:v) of ionic liquid and 0.1% (v:v) of Nafion solution were added to the graphene dispersion and stirred for further 30 minutes.

2.4. Nafion / Ionic Liquid / Graphene Coating
The N/IL/G composite is applied to the surface of the working electrode which has been evenly polymerized and left to dry. Then reference voltage measurement is conducted in the KCL 3M solution to see the voltage stability of the sensor electrode.

2.5. Bismuth-film Electropolymerization
The bimuth film coating on the surface of the working electrode is done by electropolymerization. The electropolymerization solution used consists of 200.0 ng mL⁻¹ Bi (III), 0.1 M acetate buffer solution with pH 4.5. The solution is mixed and stirred and at the same time given a voltage of -1.4 V for 2 minutes. The sensitive membrane doping process is shown in Figure 2. After that amperometrik measurement is conducted on the sensor electrode to evaluate and characterize the sensor according to different Cd standard solutions.

3. RESULT AND DISCUSSION

3.1. Electrode Characterization Using SEM

Morphological characteristics were tested using Scan electron microscopy (SEM SU3500), 10kV with an enlargement of 20k secondary electron. Tests were carried out on carbon electrode samples (SPCE) before and after conductive material coating. The morphological characteristics of SPCE before coated
with conductive material are shown in Figure 3A. The carbon layer dominates on the surface of the SPCE. Whereas in Figure 3B) is the G / N / IL / Bi / SPCE SEM morphology shows the particles are distributed evenly (uniformly) at all surfaces of the working electrode. So it shows that G / N / IL / Bi / SPCE conductive performance has increased due to carbon and other composite contributions.

Furthermore, testing is done to see the composition of each element in the electrode layer which consists of carbon (C), Nitrogen (N), Oxygen (O) and Bismuth (Bi). Based on the results of testing with Energy Dispersive Spectroscopy (EDS) the atomic composition of elements is C 91.57%, N 3.48%, O 3.23%, and Bi 0.01% as in Table 1 according to the material specified. Carbon elements are more dominant than other elements because they use thick films with a thickness of 100 micrometers. The composition of each element shows a good relationship to the specifications of the electrode.

### Table 1. Energy dispersive spectroscopy testing (EDS)

| Element | Weight % | Atomic % | Error % | Net Int. | K Ratio | Z | A | F |
|---------|----------|----------|---------|----------|---------|---|---|---|
| C       | 89.16    | 91.57    | 2.75    | 3140.86  | 0.7873  | 1.0064 | 0.8774 | 1 |
| N       | 3.95     | 3.48     | 31.35   | 91.16    | 0.003   | 0.9792 | 0.0774 | 1 |
| O       | 4.19     | 3.23     | 20.4    | 51.86    | 0.0044  | 0.9559 | 0.1092 | 1 |
| F       | 2.65     | 1.72     | 15.43   | 63.65    | 0.0035  | 0.886  | 0.149  | 1 |
| Bi      | 0.05     | 0.01     | 73.23   | 14.32    | 0.0022  | 0.5294 | 8.0027 | 0.9969 |

#### 3.2. Electrochemical Characterization of Electrodes

#### 3.2.1. Stability of reference electrodes

![Average voltage](image)

**Figure 4.** Output response of Ag|AgCl electrode vs Ag|AgCl comercial electrode

Reference electrode Ag | AgCl is used to maintain the voltage stability produced by working electrodes and counter electrodes. The reference voltage test results are shown in Figure 5. Testing is conducted in KCL electrolyte solution with a concentration of 3 M. In quadrant I there is a decrease in voltage affected by the spread of KCL solution which is not evenly distributed on the electrode surface. Whereas in quadrant II it is relatively stable. This result shows that the output voltage is quite good (stable) with a range of 8.5 - 9 mV and can be used as a detection sensor device for Cd (II) content.
3.2.2. • Cadmium (Cd) Electrochemical Detection

The performance of the sensor electrode was tested with a potentiostat to control electrodes (WE, RE, and CE) and measure the experiment electroanalytically. The source voltage used was 700mV with 10KΩ resistance. Figure 5 shows the output voltage of the Cd content test using a standard Cd solution. The prepared test concentration consisted of 0.001 mgL⁻¹, 0.005 mgL⁻¹, 0.3 mgL⁻¹, 0.5 mgL⁻¹, and 1 mgL⁻¹. The average output voltage for each sample test solution is 0.001 mgL⁻¹ of 10.360 volts, 0.005 mgL⁻¹ of 10.362 volts, 0.3 mgL⁻¹ of 10.37 volts and 0.5 mgL⁻¹ of 10.366 volts, and 1 mgL⁻¹ of 10.37 volts. The biggest voltage difference occurs between 0.001 mgL⁻¹ test solution and 1 mgL⁻¹ test solution with a difference of 1.02 volts. When viewed from the sensor liner of 64.5%, the results indicate that the sensor can detect Cd (II) content properly.

4. Conclusion

Based on this research, G / N / IL was successfully deposited on carbon electrodes plus Bismuth films. The morphology of the surface of the working electrode using SEM shows that the particles are distributed evenly (uniformly) on all surfaces. So this shows that G / N / IL / Bi / SPCE conductive performance has increased due to carbon and other composite contributions. The voltage stability of the reference electrode shows good results with a voltage range of 8.5 - 9 mV. The sensitivity of the sensor electrode increases by depositing bismuth film by electrodeposition for 2 minutes. The electrode was applied to galvanostatic potential with the measurement results showing that the electrode had a linear response (R = 64.5%). Measured detection limits are 0.01 mgL⁻¹ - 1mgL⁻¹ concentrations indicating an average output voltage of 10.36 volts - 10.37 volts. This can be explained that the sensor can detect Cd (II) content well according to performance. The electrode has been used as a working electrode for Cadmium sensor.

References
[1] Kwon J. Y., Jang Y. J., Lee Y. J., and Kim K. M., 2005 J. Am. Chem. Soc 127 10107–10111.
[2] Ma R., Van Mol W., and Adams F., 1994 Anal. Chim. 285 33–43.
[3] Tu Y., Ju S., and Wang P., 2016 Spectrosc. Lett. 49 249–256.
[4] Flores É. M. M. et al., 2009 Int. J. Environ. Anal. Chem. 89 129–140.
[5] Silva E. L. and Dos P., Roldan S., 2009 J. Hazard. Mater. 161 142–147.
[6] Li N. B., Duan J. P., and Chen G. N. 2004 Chinese J. Chem. 20377007 553–557.
[7] Anastasiadou Z. D., Sipaki I., Jannakoudakis P. D., and Girousi S. T. 2011 Anal. Lett. 44 37–41.
[8] Guell R., Aragay G., Fontas C., Antico E., and Merkoc A. 2008 ScienceDirect 7 219–224.
[9] Rojas C., Segura R., and Nagles E. 2012 Talanta 99 119–124.
[10] Liu X., Venkatraman K., and Akolkar R. 2018 J. Electrochem. Soc. 165 B9–B11.
[11] Dai Y. and Liu C. C. 2017 Sensors 17 950.
[12] Palchetti I., Majid S., Kicela A., Marrazza G., and Mascini M. 2003 Int. J. Environ. Anal. Chem. 83 701–711.
[13] Lara J., Torres J. F., Beltrán O. G., Nagles E., and Hurtado J. 2017 Int. J. Electrochem. Soc. 12 6920–6929.
[14] De Oliveira M. F., Saczk A. A., Okumura L. L., Fernandes A. P., De Moraes M., and Stradiotto N. R. 2004 Anal. Bioanal. Chem. 380 135–140.
[15] Guzsvány V., Papp Z., Zbiljic J., Vajdle O., and Rodic M. 2011 Molecules 16 4451–4466.
[16] Wang Z. M., Guo H. W., Liu E., Yang G. C., and Khun N. W. 2010 Electroanalysis 22 209–215.
[17] Ashrafi A. M. and Vytřas K. 2013 Int. J. Electrochem. Sci. 8 2095–2103.
[18] Toghill K. E., Wildgoose G. G., Moshar A., Mulcahy C., and Compton R. G. 2008 Electroanalysis 20 1731–1737.
[19] Chaiyo S., Mehmeti E., Žagar K., Siangproh W., Chailapakul O., and Kalcher K. 2016 Anal. Chim. Acta.
[20] Paukpol A. and Jakmunee J. 2016 Chiang Mai Univ. J. Nat. Sci. 15 77–88.
[21] Lu Z., Zhang J., Dai W., Lin X., and Ye J. 2017 Microchim. Acta 184 4731–4740, 2017.
[22] Guo S.J. and Dong S.J. 2011 Journal of Materials Chemistry 21 18503-18516.
[23] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, and B. Scrosati, “Ionic-liquid materials for the electrochemical challenges of the future,” Nat. Mater., vol. 8, no. 8, pp. 621–629, 2009.
[24] Niu X., Zhao H., and Lan M. 2011 Electrochim. Acta 56 9921–9925.
[25] Segura R. A., Pizarro J. A., Oyarzun M. P., Castillo A. D., Díaz K. J., and Placencio A. B. 2016 Int. J. Electrochem. Sci. 11 1707–1719.