proceedings

MDPI

Proceedings

A Gravure Printed Flexible Electrochemical Sensor for the Detection of Heavy Metal Compounds †

Dinesh Maddipatla *, Binu Narakathu, Vikram Turkani, Bradley Bazuin and Massood Atashbar

Department of Electrical and Computer Engineering, Western Michigan University, Kalamazoo, MI 49008, USA; binubaby.narakathu@wmich.edu (B.N.); vikramshreeshail.turkani@wmich.edu (V.T.); brad.bazuin@wmich.edu (B.B.); massood.atashbar@wmich.edu (M.A.)

* Correspondence: dinesh.maddipatla@wmich.edu; Tel.: +1-269-873-4436

† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 3 December 2018

Abstract: An electrochemical sensor was fabricated on a flexible polyethylene terephthalate (PET) substrate for the detection of cadmium sulfide (CdS), a heavy metal compound. The sensor consists of a working and reference electrode that were gravure printed using silver (Ag) ink on the PET substrate. The performance of the sensor was investigated by measuring electrical impedance spectroscopy (EIS) for varying concentrations of the CdS. From the EIS based response, an impedance change of 11 ± 1%, 23 ± 1%, 34 ± 2% and 50 ± 3% was observed for the 1 pM, 1 nM, 1 μM and 1 mM concentrations of CdS, respectively when compared to de-ionized (DI) water, thus demonstrating the potential of employing gravure printed electrochemical sensors for heavy metal detection applications.

Keywords: additive gravure printing process; cadmium sulfide; electrical impedance spectroscopy (EIS); Electrochemical sensor; flexible; heavy metals; PET substrate; silver ink

1. Introduction

In recent years, the development of flexible electrochemical sensors for detecting various biochemicals has been a major research focus for applications in diverse fields including environmental, food and biomedical industries [1–3]. Electrochemical sensors are typically fabricated using conventional silicon (Si) based processes which require sophisticated lithography techniques and utilizes special equipment operating at high temperatures and in vacuum [4–6]. In addition, the Si-based processes are labor intensive and time consuming, thus resulting in a relatively high fabrication cost. Moreover, in this process, the sensors are often fabricated on rigid and/or brittle substrates and lacks flexibility, thereby limiting its application [6–8].

To alleviate the drawbacks associated with Si-based fabrications techniques, additive print manufacturing processes such as screen, gravure, and inkjet can be employed for the fabrication of electrochemical sensors on flexible platforms [9–11]. These processes offer numerous benefits including roll-to-roll high volume production with rapid prototyping capabilities, reduced fabrication steps and relatively lower costs when compared to conventional lithography techniques. There are several reports available on the fabrication of electrochemical sensors using screen and inkjet printing processes [12–16]. However, there are very few reports on the development of electrochemical sensors using gravure printing process that offers relatively fine feature sizes at high print speeds [17].

In this paper, an electrochemical sensor with a working and reference electrode was fabricated on a flexible polyethylene terephthalate (PET) substrate using gravure printing process. The capability of the flexible electrochemical sensor was quantitatively investigated by analyzing the

electrical impedance spectroscopy (EIS) measurements towards the detection of a heavy metal compound, cadmium sulfide (CdS).

2. Materials and Methods

2.1. Materials

PET (MELINEX® ST730) from DuPont Teijin Films was employed as a substrate. Silver (Ag) ink (AG-800) from Applied Ink Solutions was used for the fabrication of the electrodes, as the metallization layer. CdS was purchased in powder form from Sigma–Aldrich (Missouri, USA). Varying concentrations of CdS (1 pM, 1 nM, 1 µM and 1 mM) were prepared by suspending CdS in deionized (DI) water. Isopropyl alcohol from Sigma–Aldrich was used as the cleaning agent.

2.2. Sensor Fabrication

The schematic of the two-electrode configuration electrochemical sensor is shown in Figure 1a. The overall dimension of the sensor is 2 cm × 1 cm with a working electrode of 1700 µm radius and a reference electrode with outer radius and inner radius of 3900 µm and 2900 µm, respectively. A contact angle of 40.9 ± 3.1° was measured for the Ag ink with respect to the PET substrate with a First Ten Angstroms FTA-200 goniometer, using equilibrium contact angle method, thus showing good wetting properties [18]. K-Printing Proofer, a laboratory scale gravure press along with a gravure plate engraved electromechanically with 45 cell angle and 300-line screen was used for gravure printing the Ag ink on the flexible PET substrate. The printed Ag was then thermally cured at 130 °C for 5 min in a VWR 1320 temperature-controlled oven. Figure 1b shows the photograph of the printed electrochemical sensor on flexible PET substrate. An average thickness and roughness of 0.66 ± 0.02 µm and 0.14 ± 0.01 µm was measured for the printed Ag layer using a Bruker Contour GT-K vertical scanning interferometer respectively (Figure 2a).

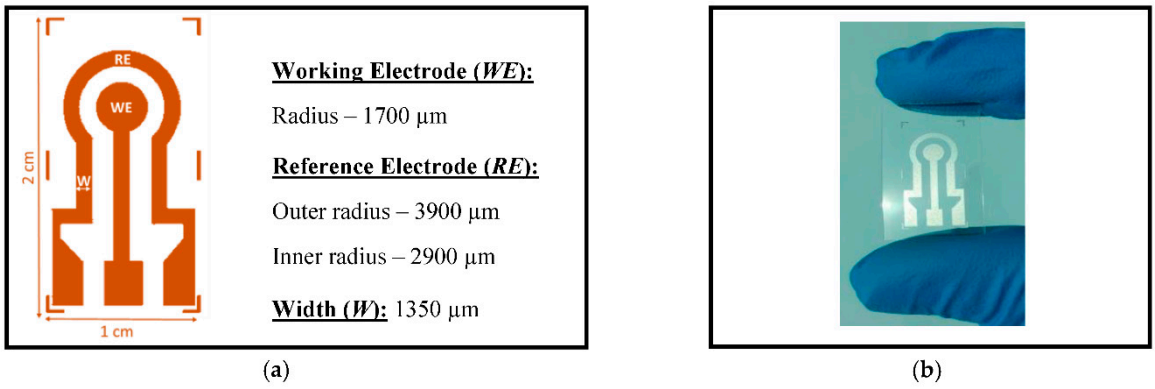

Figure 1. (**a**) Schematic of the electrochemical sensor; (**b**) Gravure printed flexible electrochemical sensor.

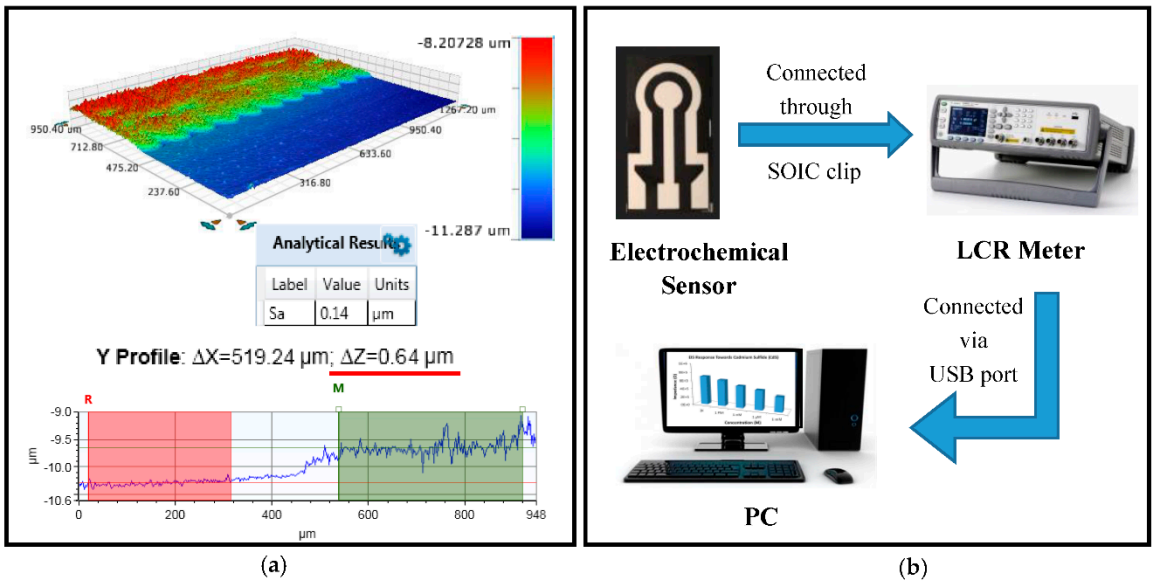

Figure 2. (**a**) 3D Profilometry scan of the printed gravure printed Ag layer on PET illustrating a total thickness (ΔZ) of 0.64 µm and roughness (Sa) of 0.14 µm; (**b**) Experiment setup.

2.3. Experiment Setup

Figure 2b shows the experiment setup for obtaining EIS response of the printed electrochemical sensor. The printed sensor was connected to an Agilent 4980A precision LCR meter using small outline integrated chip (SOIC) test clips for measuring impedance. A PC with a custom built LabView program was connected to the LCR meter for recording the EIS responses. A 120 µL of DI water was then drop casted on the sensor to establish a reference signal at an operating frequency of 20 Hz and applied potential of 100 mV. Following this, 120 µL of 1 pM, 1 nM, 1 µM and 1 mM ionic concentrations of CdS were drop casted for obtaining EIS measurements, at room temperature.

3. Results and Discussion

The EIS response of the printed sensor was tested towards varying ionic concentrations of CdS solution at an applied potential of 100 mV and 20 Hz operating frequency. From the EIS response, it was observed that the impedance of the printed sensor decreased from 690 ± 20 kΩ to 616 ± 23 kΩ to 532 ± 20 kΩ to 459 ± 27 kΩ to 346 ± 29 kΩ as the concentration of the CdS solution increased from DI to 1 pM to 1 nM to 1 µM to 1 mM, respectively as shown in Figure 3a. This resulted in an impedance change of 11 ± 1%, 23 ± 1%, 34 ± 2% and 50 ± 3% for the 1 pM, 1 nM, 1 µM and 1 mM concentrations of CdS, respectively when compared to DI water (Figure 3b) and this change can be attributed to the change in the ionic concentrations at sensor/analyte interface. The results demonstrated picomolar concentration detection capability of the electrochemical sensor as well as the potential of employing additive gravure printing process for the fabrication of light weight and cost effective electrochemical sensors for the detection of heavy metal compounds. It is worth noting that the picomolar level detection capability of the printed sensor is several orders of magnitude lower than the specified toxicity limit of CdS by the USFDA which is 3 µM [19].

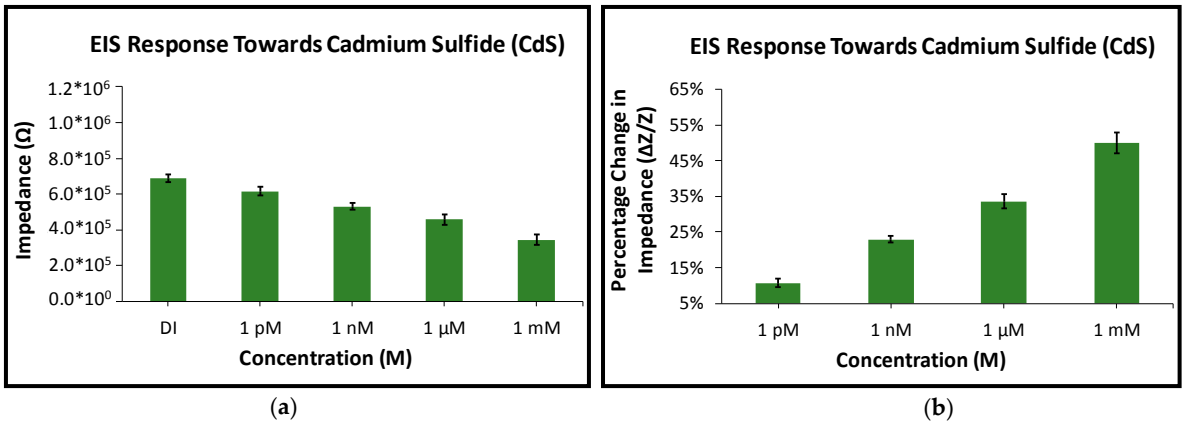

Figure 3. (**a**) EIS response of the printed sensor towards varying concentrations of CdS; (**b**) Percentage change in impedance of the printed sensor for varying concentrations of CdS.

4. Conclusions

In this work, a gravure printed electrochemical sensor was successfully fabricated on a flexible PET substrate for the detection of CdS. The capability of the printed electrochemical sensor was investigated by measuring the EIS response for varying concentrations of the CdS. An impedance change of 11 ± 1%, 23 ± 1%, 34 ± 2% and 50 ± 3% was observed for the 1 pM, 1 nM, 1 µM and 1 mM concentrations of CdS, respectively when compared to DI water, thus demonstrating the potential of employing gravure printed electrochemical sensors for heavy metal detection applications. Future work includes testing the capability of the sensor to detect other heavy metal compounds such as mercury sulfide (HgS) and lead sulfide (PbS) as well as enhancing the selective detection capability of the sensor using ion selective sensing layers. Integration of the sensor within miniature portable Lab-on-a-Chip (LOC) sensing systems is also part of our future research.

Acknowledgments: This work has been partially funded by the Western Michigan University (WMU) Graduate Student Research Grant (GSRG).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tang, L.; Zeng, G.M.; Shen, G.L.; Li, Y.P.; Zhang, Y.; Huang, D.L. Rapid detection of picloram in agricultural field samples using a disposable immunomembrane-based electrochemical sensor. *Environ. Sci. Technol.* **2018**, *42*, 1207–1212, doi:10.1021/es7024593.
2. Vashist, S.K.; Luppa, P.B.; Yeo, L.Y.; Ozcan, A.; Luong, J.H. Emerging technologies for next-generation point-of-care testing. *Trends Biotechnol.* **2015**, *33*, 692–705, doi:10.1016/j.tibtech.2015.09.001.
3. Avuthu, S.G.; Wabeke, J.T.; Narakathu, B.B.; Maddipatla, D.; Arachchilage, J.S.; Obare, S.O.; Atashbar, M.Z. A screen printed phenanthroline based flexible electrochemical sensor for selective detection of toxic heavy metal ions. *IEEE Sens. J.* **2016**, *16*, 8678–8684, doi:10.1109/JSEN.2016.2572184.
4. Warsinke, A. Point of care testing of proteins. *Anal. Bioanal. Chem.* **2009**, *393*, 1393–1405, doi:10.1007/s00216-008-2572-0.
5. Dong, X.C.; Wang, X.; Wang, L.; Song, H.; Zhang, H.; Huang, W.; Chen, P. 3D graphene foam as a monolithic and macroporous carbon electrode for electrochemical sensing. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3129–3133, doi:10.1021/am300459m.
6. Rios, A.; Zougagh, M.; Avila, M. Miniaturization through lab-on-a-chip: Utopia or reality for routine laboratories? A review. *Anal. Chim. Acta* **2012**, *740*, 1–11, doi:10.1016/j.aca.2012.06.024.
7. Narakathu, B.B.; Guo, W.; Obare, S.O.; Atashbar, M.Z. Novel approach for detection of toxic organophosphorus compounds. *Sens. Actuators B Chem.* **2011**, *158*, 69–74, doi:10.1016/j.snb.2011.05.040.
8. Whitesides, G.M. The origins and the future of microfluidics. *Nature* **2006**, *442*, 368–373, doi:10.1038/nature05058.

9. Khan, S., Lorenzelli, L.; Dahiya, R. Technologies for printing sensors and electronics over large flexible substrates: A review. *IEEE Sens. J.* **2014**, *15*, 3164–3185, doi:10.1109/JSEN.2014.2375203.
10. Turkani, V.S.; Maddipatla, D.; Narakathu, B.B.; Bazuin, B.J.; Atashbar, M.Z. A carbon nanotube based NTC thermistor using additive print manufacturing processes. *Sens. Actuators A Phys.* **2018**, *279*, 1–9, doi:10.1016/j.sna.2018.05.042.
11. Maddipatla, D.; Narakathu, B.B.; Ali, M.M.; Chlaihawi, A.A.; Atashbar, M.Z. Development of a novel carbon nanotube based printed and flexible pressure sensor. In Proceedings of the IEEE Sensors Applications Symposium (SAS), Glassboro, NJ, USA, 13–15 March 2017; pp. 1–4, doi:10.1109/SAS.2017.7894034.
12. Avuthu, S.G.R.; Wabeke, J.T.; Narakathu, B.B.; Maddipatla, D.; Eshkeiti, A.; Emamian, S.; Chlaihawi, A.A.; Joyce, M.; Obare, S.O.; Atashbar, M.Z. Development of screen printed electrochemical sensors for selective detection of heavy metals. In Proceedings of the 2015 IEEE SENSORS, Busan, Korea, 1–4 November 2015; pp. 490–493, doi:10.1109/ICSENS.2015.7370297.
13. Medina-Sanchez, M.; Cadevall, M.; Ros, J.; Merkoci, A. Eco-friendly electrochemical lab-on-paper for heavy metal detection. *Anal. Bioanal. Chem.* **2015**, *407*, 8445–8449, doi:10.1007/s00216-015-9022-6.
14. Reddy, A.S.G.; Narakathu, B.B.; Atashbar, M.Z.; Rebros, M.; Hrehorova, E.; Joyce, M. Printed electrochemical based biosensors on flexible substrates. In Proceedings of the 2010 IEEE SENSORS, Kona, HI, USA, 1–4 November 2010; pp. 1596–1600, doi:10.1109/ICSENS.2010.5690281.
15. Narakathu, B.B.; Devadas, M.S.; Reddy, A.S.; Eshkeiti, A.; Moorthi, A.; Fernando, I.R.; Miller, B.P.; Ramakrishna, G.; Sinn, E.; Joyce, M.; et al. Novel fully screen printed flexible electrochemical sensor for the investigation of electron transfer between thiol functionalized viologen and gold clusters. *Sens. Actuators B Chem.* **2013**, *176*, 768–774, doi:10.1016/j.snb.2012.10.069.
16. Maddipatla, D.; Narakathu, B.B.; Bazuin, B.J.; Atashbar, M.Z. Development of a printed impedance based electrochemical sensor on paper substrate. In Proceedings of the 2016 IEEE SENSORS, Orlando, FL, USA, 30 October–3 November 2016; pp. 1138–1140.
17. Grau, G.; Cen, J.; Kang, H.; Kitsomboonloha, R.; Scheideler, W.J.; Subramanian, V. Gravure-printed electronics: Recent progress in tooling development, understanding of printing physics, and realization of printed devices. *Flex. Print. Electron.* **2016**, *1*, 023002, doi:10.1088/2058-8585/1/2/023002.
18. Good, R.J. Contact angle, wetting, and adhesion: A critical review. *J. Adhes. Sci. Technol.* **1992**, *6*, 1269–302, doi:10.1163/156856192x00629.
19. Sheets, R.W. Extraction of lead, cadmium and zinc from overglaze decorations on ceramic dinnerware by acidic and basic food substances. *Sci. Total Environ.* **1997**, *197*, 167–175, doi:10.1016/S0048-9697(97)05431-4.