Flexible liquid crystal polymer-based electrochemical sensor for in-situ detection of zinc(II) in seawater

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

| Citation          | Wang, Nan. "Flexible liquid crystal polymer-based electrochemical sensor for in-situ detection of zinc(II) in seawater." Microchimica Acta 184, 8 (May 2017): 3007–3015 © 2017 Springer-Verlag |
|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| As Published      | http://dx.doi.org/10.1007/s00604-017-2280-6                                                                                                                                                        |
| Publisher         | Springer Science and Business Media LLC                                                                                                                                                           |
| Version           | Author’s final manuscript                                                                                                                                                                          |
| Citable link      | https://hdl.handle.net/1721.1/128657                                                                                                                                                              |
| Terms of Use      | Creative Commons Attribution-Noncommercial-Share Alike                                                                                                                                              |
| Detailed Terms    | http://creativecommons.org/licenses/by-nc-sa/4.0/                                                                                                                                                  |
Flexible liquid crystal polymer-based electrochemical sensor for in-situ detection of zinc(II) in the seawater

Nan Wang¹,²,*, Elgar Kanhere¹, Ajay Giri Prakash Kottapalli², Jianmin Miao¹,*, Michael S. Triantafyllou²,³

¹School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
²Center for Environmental Sensing and Modeling (CENSAM) IRG, Singapore-MIT Alliance for Research and Technology (SMART) Centre, 1 CREATE Way, 138602, Singapore
³Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
*Corresponding author (Email): Nan Wang – WANG0845@e.ntu.edu.sg
Jianmin Miao – jmiao@pmail.ntu.edu.sg

Keywords: Bismuth film electrode ∙ Microelectromechanical systems ∙ Chemical sensor array ∙ Cyclic voltammetry ∙ Anodic stripping voltammetry ∙ Autonomous kayak

Acknowledgements
The authors would like to express special appreciation to Ms. Meghali Bora, Mr. Vignesh Subramaniam, Mr. Gonzalo Carrasco, Mr. Tawfiq Taher, Mr. Snehal Jain, Mr. Hongchuan Jiang and Mr. Tony Varghese for their help during the sea trial testing. This research is supported by the National Research Foundation (NRF), Prime Minister’s Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme. The Center for Environmental Sensing and Modeling (CENSAM) is an interdisciplinary research group (IRG) of the Singapore MIT Alliance for Research and Technology (SMART) centre.
Abstract
The authors describe a liquid crystal polymer (LCP) based bismuth (Bi) film electrode that can be directly deployed for in-situ determination of zinc(II) ions. The use of an LCP warrants improved operational reliability, high durability and flexibility of the sensor, allowing it to be mounted on any flat or shaped surface. Square wave anodic stripping voltammetry shows the sensor to be able to detect Zn(II) (-1.64 V vs. thin-film Ag/AgCl reference electrode) in concentrations as low as 1.22 nM at a deposition time of 180 s. Other figures of merit include (a) an analytical sensitivity of 1.55 nA·nM⁻¹·mm², (b) a linear detection range extending from 4.59 to 1071 nM, (c) a repeatability with a relative standard deviation of 3.35% (for n = 10), (d) a reproducibility with a relative standard deviation of 1.64% (for n = 6). Real-time applicability of the sensor for in-situ detection was demonstrated by determination of Zn(II) in seawater. In an extension of the method, a flexible sensor array consisting of four LCP-based sensors was attached to the hull of an autonomous kayak, which was remotely operated. The response of the sensor array indicated a clear trace of Zn(II) concentrations in seawater. This was confirmed by ICP-MS analysis. The results suggest the potential usage of the flexible LCP electrochemical sensor for in-situ monitoring.

1. Introduction
Water quality degradation, particularly heavy metal contamination, has become a global concern due to the ecotoxicological adverse effects that heavy metals pose to both human and ecosystem health. Zinc (Zn(II)), one of the common water pollutants, is widely used in several industries, especially galvanization, petroleum, lubrication, pigmentation, alloy manufacturing and battery production. Zn(II) metal ions can easily get into the groundwater through discharge of untreated industrial wastewater as well as excessive fertilization in some farmlands. The recommended value of Zn(II) ions in drinking water, as provided by the World Health Organization (WHO), is 3 mg·L⁻¹ [1]. Over-intake may induce nausea, vomiting, epigastric pain, lethargy, fatigue, etc. [2]. Conventional water quality monitoring requires water samples to be manually collected and analyzed in the centralized laboratory. Analytical methods, such as atomic absorption spectrometry (AAS) [3, 4], inductively coupled plasma atomic emission spectrometry (ICP-AES) [5, 6], and inductively coupled plasma mass spectrometry (ICP-MS) [7, 8], are usually adopted to determine the
concentration of target metal ions. Although these approaches are capable of quantifying the water quality, their complicated operation, high instrumentation cost, and bulky size limit the application for on-site/in-situ measurement. Real-time data regarding the levels of metal ions in concerned sites cannot be obtained by using the aforementioned techniques. Therefore, research pertaining to the development of simple-to-use, inexpensive, miniaturized, and compact sensors/devices that can be directly used for point-of-care/in-situ detection is of great interest to both academics and industries.

To circumvent the complexity of conventional testing techniques, researchers have started to use electroanalytical methods, especially anodic stripping voltammetry (ASV). ASV exhibits several advantages, including simplicity of experimental arrangement, low cost, and favorable sensitivity. The material of the working electrode is an essential sensing element of ASV to ensure successful stripping analysis. Over the last decade, bismuth (Bi) film electrodes (BFEs) have gained wide acceptance because of their non-toxic property, making them potential alternatives to replace mercury electrodes. BFEs also offer a number of attractive merits, such as reproducible voltammetric response, easily distinguishable stripping peak, more negative potential window and high signal-to-background ratio [9]. BFEs can be prepared by simultaneously accumulating Bi ions together with target heavy metal ions onto the surface of supporting electrodes, e.g. glassy carbon electrode [10-12], pencil-lead [13], iridium microwire [14], gold micropillar electrode array [15], etc. In addition, BFEs can be modified with different materials, such as graphene oxide [16], chitosan [17], and carbon nano-fragments [18]. Usually, a silver/silver chloride (Ag/AgCl) reference electrode with aqueous inner electrolyte and a platinum (Pt) wire counter electrode are needed to successfully perform the ASV measurement. However, the overall size and cumbersome preparation procedures make them unsuitable for in-situ heavy metal determination, though such commercial electrodes have more reliable performance.

On the other hand, chemical sensors having ex-situ prepared BFEs with thin-film/screen-printed reference and counter electrodes provide a promising candidature for in-situ quantification of heavy metal ions. This is mainly attributed to the possibility to integrate all necessary sensing and accessory components onto a single device. Applications of this type of sensors towards Zn(II) [19], cadmium (Cd(II)) [20, 21], and lead (Pb(II)) [20-22] detection have been reported. To achieve long-term in-situ measurement, the material of the sensor substrate also plays a critical role in maintaining operational reliability of the sensor as unremitting subjection to rigorous surroundings is inevitable. Therefore, the most desired properties of such material should include strong mechanical stability, low moisture
absorption, superior hermetic sealing and excellent chemical inertness. Liquid-crystal polymer (LCP) is chosen as the sensor substrate due to its compliance with the aforementioned features. LCP, made up of aligned molecule chains with crystal-like spatial regularity, is a class of aromatic thermoplastic polymers. It demonstrates a highly ordered structural configuration in the solid state [23]. LCP improves the operational reliability of the sensors since it has higher fracture strength as compared to other materials such as plastic, cloth, paper, silicon, and glass. This will enable the chemical sensors with LCP substrate to be deployed for harsh environmental applications. LCP also demonstrates high weatherability in seawater due to its extremely low moisture absorption (~0.02%, [23]) even after extended periods of exposure to the seawater. LCP is exceptionally inert and does not suffer attacks from various corrosive chemicals that can easily damage materials like plastic, paper, silicon, etc. LCP also maintains stable dimensional properties in the fluid environment due to its low permeability to water [24].

In addition, the flexibility of LCP allows the sensors to be surface-mounted on the streamlined bodies of underwater vehicles. Arrays of chemical sensors can be batch fabricated on LCP and the entire array can be surface-mounted as it is on the vehicle. This feature is impractical when it comes to silicon or glass substrate. The process of device fabrication, dicing and packaging with LCP is highly compatible with established microelectromechanical systems (MEMS) techniques [25-27]. Particularly, LCP complies with photoresist patterning through lithography, deep reactive ion etching, thin film sputtering and metallization. These merits allow it to be easily incorporated into the design of disposable and compact chemical sensors for point-of-care applications. In this work, a flexible electrochemical sensor with Bi film sensing electrode (200 nm thickness) fabricated on LCP substrate is developed. The sensing principle of the sensor relies on the fact that target metal ions dissolved in the testing solution are able to form alloys with Bi in the deposition process. The metal alloys will subsequently strip off from the working electrode at a certain potential, during which the stripping current is recorded. The magnitude of the stripping current is correlated with the concentration of the target ions. Laboratory characterization reveals an excellent analytical performance of the sensor towards Zn(II) measurement. The application of the sensor for in-situ Zn(II) detection in seawater is successfully demonstrated by performing a sea trial testing. A flexible sensor array consisting of four LCP electrochemical sensors is attached to the hull of an autonomous kayak that is remotely operated to perform various missions.
2. Experimental

2.1 Chemicals and reagents

The chemicals and reagents used in this study were of analytical grade and purchased from Sigma-Aldrich, Singapore (www.sigmaaldrich.com/singapore.html) unless stated otherwise. Deionized (DI) water (18.2 MΩ·cm) collected from a Milli-Q system (Millipore, Singapore, www.merckmillipore.com/SG/en) was used for the preparation of all solutions. A sheet of LCP 3908 (100 µm thickness) with two-sided copper (Cu, 18 µm thickness) protective layer was purchased from Rogers Corporation, USA (www.rogerscorp.com/index.aspx). Polydimethylsiloxane (PDMS) was obtained from Dow Corning, Singapore (www.dowcorning.com). Sodium chloride (NaCl) with a concentration of 0.6 M was used for all laboratory-based experiments. This concentration was determined in accordance with the salinity of seawater, which is about 3.5%. Zn(II) standard stock solution (1000 mg·L\(^{-1}\)) was obtained from Merck, Singapore (www.merck.com.sg/en/index.html). Solutions for interference study, including ammonium chloride (NH\(_4\)Cl), potassium chloride (KCl), magnesium chloride (MgCl\(_2\)), and calcium chloride (CaCl\(_2\)), were prepared by dissolving an appropriate amount of powder into the DI water. Whereas, solutions of copper nitrate (Cu(NO\(_3\))\(_2\)), lead nitrate (Pb(NO\(_3\))\(_2\)), and cadmium nitrate (Cd(NO\(_3\))\(_2\)) used for interference study were prepared from the atomic absorption standard solution (1000 mg·L\(^{-1}\)).

2.2 Fabrication of the LCP electrochemical sensor

The fabrication of the LCP electrochemical sensor is accomplished by means of standard MEMS techniques. A schematic describing the steps involved in the sensor fabrication is shown in Fig. 1. The first step during the fabrication was to dip the LCP thin film into Cu etchant to etch away the protective layer. After thoroughly cleaning with DI water followed by drying with nitrogen gas, the LCP film was attached to a silicon wafer (4-inch diameter and 300 µm thickness) using AZ9260 positive photoresist (10 µm). Then the wafer was baked on a hotplate at 80 °C for 40 minutes to bond the LCP film to the silicon wafer (step 1). A layer of the photoresist (5 µm) was spin-coated on the LCP film and exposed to 365 nm i-line ultraviolet (UV) light. The pattern of three electrodes was formed after removing the exposed areas of the photoresist in AZ 400K developer (step 2). Subsequently, a layer of chromium/gold (Cr/Au, 50/200 nm) was sputtered by using magnetron sputtering system, in which the Cr layer was used to promote adhesion (step 3). Thereafter, the entire wafer was
immersed in acetone for 12 hours to remove the unexposed photoresist along with the metal layer left on top of these areas (step 4).

Another layer of photoresist (5 µm) was spin-coated on the LCP film and patterned with UV light to expose only the reference electrode area. Subsequently, a layer of Ag/AgCl (150/250 nm) was deposited (step 5). The wafer was then immersed in acetone for 12 hours to remove the remaining photoresist (step 6). After that, another layer of photoresist (5 µm) was spin-coated on the LCP film and patterned to open the area of the working electrode. A layer of Bi (200 nm) was sputtered using the magnetron sputtering system (step 7). By immersing the wafer into acetone for another 12 hours, all remaining photoresist was removed and the fabrication of the sensor was completed (step 8). The counter electrode was defined by the previously-sputtered Au layer without any further modification. Photograph of an individual sensor after fabrication is depicted in Fig. 2a. The LCP electrochemical sensor can be easily flexed without damaging the thin-film electrode layers. Such high flexibility of a sensor bent using a tweezer is shown in Fig. 2b. Prior to experiments, the fabricated sensor was packaged by wiring contact pads of the three electrodes with conductive epoxy and baked at 80 °C for 3 hours. Following this step, a few drops of non-conductive epoxy were applied to cover the contact pads and the sensor was baked at 80 °C for 1.5 hours to ensure proper insulation.

2.3 Experimental apparatus
All electrochemical experiments were performed by using a portable EmStat 3 potentiostat (PalmSens BV, Netherlands, www.palmsens.com). PSTrace 4.7 software was used to control the potentiostat. During the sea trial testing, a channel multiplexer (PalmSens BV, Netherlands) and a connection terminal equipped with shielded cables (PalmSens BV, Netherlands) were used to connect the sensor array with the potentiostat. All experimental apparatus, including glass vial (Alpha Analytical, Singapore, www.alphalab.com), Teflon cap (Alpha Analytical, Singapore), and magnetic stirrer bar (Sigma-Aldrich, Singapore) were thoroughly cleaned with DI water before the experiments. Eppendorf pipettors (Sigma-Aldrich, Singapore) were used to deliver aliquots of the standard solutions into the testing vial.

2.4 Measurement procedures
Experiments of cyclic voltammetry (CV) were carried out under quiescent condition by fully immersing the LCP electrochemical sensor in the solution of 0.6 M NaCl. Experimental
parameters were chosen as an initial potential of -2.0 V, a final potential of -0.5 V, and a scan rate of 50 mV/s. Electrochemical investigation of the LCP electrochemical sensor for Zn(II) detection was initiated by accumulating target ions to the working electrode under a deposition potential of -1.6 V (after optimization) for 180 s (after optimization). After a 5 s equilibration time, voltammograms were recorded from -1.8 to -1.2 V by square wave anodic stripping voltammetry (SWASV) with a frequency of 10 Hz, amplitude of 20 mV, and a step potential of 5 mV. A conditioning potential of -1.0 V was applied to the working electrode for 120 s for the purpose of refreshing the electrode surface. During deposition and conditioning steps, the solution was stirred with the aid of the magnetic stirrer bar. All solutions (around 25 °C) in the laboratory-based experiments were used without prior deaeration. For sea trial testing, seawater (around 28 °C) was constantly replenished into PDMS channel during the deposition and conditioning steps by controlling the kayak to slowly move in a straight line. The potentials controlled and measured during all the electrochemical experiments were with respect to the fabricated thin-film Ag/AgCl reference electrode.

3. Results and discussion

3.1 Preliminary investigation and optimization of the sensor

For an electrochemical sensor with a quasi-reference electrode, the potential window is an important parameter to study since it defines the range of heavy metal ions that can be determined by the sensor. The potential window of the LCP electrochemical sensor was evaluated by conducting CV experiments with three sensors in the solution of 0.6 M NaCl. The cyclic voltammograms recorded are shown in Fig. S1a. The potential window of the sensor was estimated between -1.7 and -0.8 V with respect to the fabricated thin-film Ag/AgCl reference electrode. A preliminary SWASV experiment was conducted in the solution of 0.6 M NaCl with 0.15 µM Zn(II). The anodic stripping voltammogram, as illustrated in Fig. S1b, shows a well-defined Zn(II) stripping peak near the potential of -1.64 V. This suggests that the LCP electrochemical sensor is suitable for Zn(II) detection. It is well known that accumulation of metal ions to the working electrode is significantly affected by deposition potential as well as deposition time. Therefore, a series of SWASV experiments were conducted in order to optimize these two parameters. The detailed results
are presented in Fig. S2a and S2b. Finally, a deposition potential of -1.6 V and a deposition time of 180 s were selected as optimal values for further experiments.

3.2 Repeatability, reproducibility and interference

The analytical performance of the LCP electrochemical sensor in terms of repeatability over multiple measurements was investigated by performing ten consecutive runs of SWASV in the solution of 0.6 M NaCl with 0.15 µM Zn(II). The response in stripping peak current of one sensor is depicted in Fig. 3a. The sensor displayed consistent stripping currents among the first six runs, after which the current gradually dropped to a lower value. The repeatability of the LCP electrochemical sensor over ten times of measurements, calculated from the relative standard deviation (RSD), is 3.35%. To evaluate the reproducibility over multiple sensors, SWASV experiments were further conducted using six LCP electrochemical sensors in the same solution. The responses in stripping peak current of the six sensors during three consecutive runs of SWASV are illustrated in Fig. 3b. It can be observed that all sensors exhibited comparable stripping currents. According to the calculation from RSD, the reproducibility among six LCP electrochemical sensors is 1.64%. These experimental outcomes suggest that repeatable responses for Zn(II) detection can be expected with a strategically placed array of the LCP electrochemical sensors.

The influence of possible interfering ions on the analytical performance of the LCP electrochemical sensor was also investigated and the results are presented in Fig. S3. Few common ions, including NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$, were selected owing to their wide availability in natural waters. During the experiments, the concentration of interfering ions was adjusted to be 100 times higher than that of the Zn(II) ions. It is observed that there was no significant interference effect for NH$_4$, K, Mg, and Ca cations on the Zn(II) stripping signal of the sensor. However, Cu(II), Pb(II), and Cd(II) ions did have interference effect on the Zn(II) stripping current. This was possibly due to the strong competition between these metal ions to form intermetallic compounds deposited on the working electrode. The tolerance limits of the sensor for Cu(II), Pb(II), and Cd(II) ions were around 5, 20, and 20 times higher than the concentration of Zn(II) ions, respectively. This interference phenomenon was also reported by Meng et al. [28] using Bi-film-modified montmorillonite doped carbon paste electrode and Krolicka et al. [29] using Bi film screen-printed electrode.
3.3 Analytical performance of the sensor
Investigation pertaining to the analytical performance of the LCP electrochemical sensor was conducted by monitoring responses of several SWASV experiments in the solutions of 0.6 M NaCl with elevated concentration of Zn(II) ions. Figure 4a shows a series of anodic stripping voltammograms recorded. Undistorted and legible stripping peaks were easily distinguished near the potential of -1.64 V. The magnitude of these peaks became higher when the concentration of Zn(II) ions was changed from 4.59 to 1071 nM. The calibration plot is shown in Fig. 4b, from which a linear correlation (R²=0.997) between the magnitude of peak currents and Zn(II) concentrations was obtained. These experimental data reveal that the LCP electrochemical sensor exhibited linear responses toward Zn(II) metal ions over the concentration range of 4.59 to 1071 nM. The sensor also displayed a relatively high analytical sensitivity of 1.55 nA·nM⁻¹·mm⁻². The limit of detection (LOD) of the sensor, calculated based on the signal-to-noise ratio of 3, was as low as 1.22 nM. A comparison regarding analytical performance between the LCP electrochemical sensor and other Bi-based electrochemical sensors reported in the literature is listed in Table 1. In view of the data from the table, it is not an overstatement to claim that the LCP electrochemical sensor has great potential to be used for trace Zn(II) detection.

3.4 In-situ application of the sensor
With the purpose of exploring the potential application of the LCP electrochemical sensor for in-situ Zn(II) detection, a flexible sensor array was designed and assembled. As shown in Fig. 5, four sensors, denoted as ‘S1’, ‘S2’, ‘S3’, and ‘S4’ respectively, were placed on a flexible PDMS slab with a thickness of 10 mm. Each sensor was covered by a PDMS channel with a volume of 0.18 cm³. The function of the channel is to filter coarse particles in seawater while maintaining continuous flow to stay in contact with the sensor during measurement. As depicted in the inset of Fig. 5, the PDMS channel was designed to have a rectangular inlet (4 mm width × 3 mm height) and a circular outlet (2.5 mm diameter). An enclosed chamber was inlaid near the main channel to protect the soldering points. Three long narrow slots were used to cover the connection wires. Fabrication of the PDMS channel was accomplished by casting degassed solution onto a 3D-printed mold, followed by a heat treatment in an oven at 75 °C for 3 hours.

The sensor array was attached to the hull of an autonomous kayak, as shown in Fig. 6a. Edges of each PDMS channel were completely glued by Sil-Poxy silicone rubber adhesive to prevent possible peel-off during measurement, as shown in Fig. 6b. Wires of the
sensor array were separately connected to different channels of the portable EmStat 3 potentiostat, which was mounted inside the kayak. A USB cable was used to connect the potentiostat to one of the onboard computers of the kayak, with which the measurement was remotely controlled. The kayak was equipped with another onboard computer, which was used to navigate the movement of the kayak. After deployment of the kayak into the sea, the kayak was commanded to move in a straight line, during which the deposition step was executed. Then the kayak was set to be in the stationary mode to collect the voltammogram of each sensor. Thereafter, the kayak was directed to next location, in between a conditioning step was provided in order to clean the working electrode. The responses of the sensor array were independently recorded at three locations, denoted as ‘L1’, ‘L2’, and ‘L3’. The map of these locations, calculated from the GPS coordinates, is shown in Fig. 6c. In consideration of avoiding possibly-biased testing results due to potential contamination of the electrode surface, the sensor array was tested one time at each location. Besides, the seawater samples at three locations were also collected. By doing so, the concentration of different metal ions at each location can be verified through commercially-established method for comparison.

The responses of the sensor array during the sea trial testing are presented in Fig. S4, S5, S6, and S7. For all the sensors, distinct stripping peaks were observed near the potential of -1.64 V, demonstrating a clear trace of Zn(II) ions at the testing locations. The seawater samples collected during the sea trial testing were analyzed by means of ICP-MS and the results are listed in Table S1. Results of the ICP-MS analysis confirmed the presence of Zn(II) metal ions at all testing locations. The quantified Zn(II) concentrations were converted to current values using the calibration equation (refer to Fig. 4b). Table 2 lists the comparison between the converted current (designated as ‘reference value’) and the stripping peak current detected by each sensor at three locations. It is unambiguous that the sensor array displayed comparable current values with respect to the reference ones. This indicates high feasibility to directly deploy the LCP electrochemical sensor for in-situ Zn(II) detection.

4. Conclusions

In this paper, a flexible electrochemical sensor with Bi film sensing electrode constructed on LCP substrate was developed. The sensor fabrication was carried out via standard MEMS techniques. Analytical performance of the sensor pertaining to Zn(II) detection was investigated by conducting a series of laboratory-based experiments. The sensor exhibited
favorable sensing capabilities in the aspects of sensitivity, detection limit, as well as detection range. Application of the sensor for in-situ Zn(II) measurement was successfully demonstrated by performing sea trial testing with a sensor array attached to the hull of an autonomous kayak. The responses of the sensor array were confirmed by the ICP-MS analysis of the collected seawater samples. The laboratory and field investigations suggest promising application of the LCP electrochemical sensor for in-situ Zn(II) determination. However, there are still some limitations for the sensor to achieve long-term, multi-location heavy metal monitoring. For instance, if the seawater is highly turbid or heavily polluted, the sensor with current design may not function well in consideration of rapid contamination imposed to the working electrode. Such kind of barrier can be possibly surpassed by integrating a miniaturized filter into the sensor in such a way that the seawater sample is pretreated before passing through the working electrode.

Conflict of Interest:
The authors declare that they have no conflict of interest.

References
[1] World Health Organization (2011) Guidelines for drinking-water quality (4th ed.). World Health Organization, Switzerland.
[2] Fosmire GJ (1990) Zinc toxicity. Am J Clin Nutr 51: 225-227.
[3] Adolfo FR, do Nascimento PC, Bohrer D, de Carvalho LM, Viana C, Guarda A, Colim AN, Mattiazzi P (2016) Simultaneous determination of cobalt and nickel in vitamin B12 samples using high-resolution continuum source atomic absorption spectrometry. Talanta 147: 241-245.
[4] Dias Peronico VC, Raposo Jr. JL (2016) Ultrasound-assisted extraction for the determination of Cu, Mn, Ca, and Mg in alternative oilseed crops using flame atomic absorption spectrometry. Food Chem 196: 1287-1292.
[5] Zhao J, Yan X, Zhou T, Wang J, Li H, Zhang P, Ding H, Ding L (2015) Multi-throughput dynamic microwave-assisted leaching coupled with inductively coupled plasma atomic emission spectrometry for heavy metal analysis in soil. J Anal At Spectrom 30: 1920-1926.
[6] Rosende M, Magalhaes LM, Segundo MA, Miro M (2014) Assessing oral bioaccessibility of trace elements in soils under worst-case scenarios by automated in-line dynamic extraction as a front end to inductively coupled plasma atomic emission spectrometry. Anal Chim Acta 842: 1-10.
[7] Lamsal RP, Beauchemin D (2015) Estimation of the bio-accessible fraction of Cr, As, Cd and Pb in locally available bread using on-line continuous leaching method coupled to inductively coupled plasma mass spectrometry. Anal Chim Acta 867: 9-17.

[8] Tai CY, Jiang SJ, Sahayam AC (2016) Determination of As, Hg and Pb in herbs using slurry sampling flow injection chemical vapor generation inductively coupled plasma mass spectrometry. Food Chem 192: 274-279.

[9] Wang J (2005) Stripping analysis at bismuth electrodes: a review. Electroanalysis 17: 1341-1346.

[10] Hocevar SB, Wang J, Deo RP, Ogorevc B (2002) Potentiometric stripping analysis at bismuth-film electrode. Electroanalysis 14: 112-115.

[11] Xu H, Zeng L, Huang D, Xian Y, Jin L (2008) A Nafion-coated bismuth film electrode for the determination of heavy metals in vegetable using differential pulse anodic stripping voltammetry: an alternative to mercury-based electrodes. Food Chem 109: 834-839.

[12] Lee S, Park SK, Choi E, Piao Y (2016) Voltammetric determination of trace heavy metals using an electrochemically deposited graphene/bismuth nanocomposite film-modified glassy carbon electrode. J Electroanal Chem 766: 120-127.

[13] Demetriades D, Economou A, Voulgaropoulos A (2004) A study of pencil-lead bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry. Anal Chim Acta 519: 167-172.

[14] Kyrisoglou C, Economou A, Efstathiou CE (2012) Bismuth-coated iridium microwire electrode for the determination of trace metals by anodic stripping voltammetry. Electroanalysis 24: 1825-1832.

[15] Wang N, Kanhere E, Miao J, Triantafyllou MS (2016) Miniaturized chemical sensor with bio-inspired micropillar working electrode array for lead detection. Sens. Actuators B 233: 249-256.

[16] Hu X, Pan D, Lin M, Han H, Li F (2016) Graphene oxide-assisted synthesis of bismuth nanosheets for catalytic stripping voltammetric determination of iron in coastal waters. Microchim Acta 183: 855-861.

[17] Hao C, Shen Y, Shen J, Xu K, Wang X, Zhao Y, Ge C (2016) A glassy carbon electrode modified with bismuth oxide nanoparticles and chitosan as a sensor for Pb(II) and Cd(II). Microchim Acta 183: 1823-1830.

[18] Liu L, Ma Z, Zhu X, Alshahrani LA, Tie S, Nan J (2016) A glassy carbon electrode modified with carbon nano-fragments and bismuth oxide for electrochemical analysis of trace catechol in the presence of high concentrations of hydroquinone. Microchim Acta 183: 3293-3301.

[19] Pei X, Kang W, Yue W, Bange A, Heineman WR, Papautsky I (2014) Improving reproducibility of lab-on-a-chip sensor with bismuth working electrode for determining Zn in serum by anodic stripping voltammetry. J Electrochem Soc 161: B3160-B3166.

[20] Niu P, Fernandez-Sanchez C, Gich M, Navarro-Hernandez C, Fanjul-Bolado P, Roig A (2016) Screen-printed electrodes made of a bismuth nanoparticle porous carbon nanocomposite applied to the determination of heavy metal ions. Microchim Acta 183: 617-623.
[21] Maria-Hormigos R, Gismera MJ, Procopio JR, Sevilla MT (2016) Disposable screen-printed electrode modified with bismuth–PSS composites as high sensitive sensor for cadmium and lead determination. J Electroanal Chem 767: 114-122.

[22] Quintana JC, Arduini F, Amine A, Punzo F, Destri GL, Bianchini C, Zane D, Curulli A, Palleschi G, Moscone D (2011) Part I: a comparative study of bismuth-modified screen-printed electrodes for lead detection. Anal Chim Acta 707: 171-177.

[23] Wang X, Engel J, Liu C (2003) Liquid crystal polymer (LCP) for MEMS: processes and applications. J Micromech Microeng 13: 628-633.

[24] Kottapalli AGP, Asadnia M, Miao J, Triantafyllou M (2014) Touch at a distance sensing: lateral-line inspired MEMS flow sensors. Bioinspir Biomim 9: 046011.

[25] Kottapalli AGP, Bora M, Asadnia M, Miao J, Venkatraman SS, Triantafyllou M (2016) Nanofibril scaffold assisted MEMS artificial hydrogel neuromasts for enhanced sensitivity flow sensing. Sci Rep 6: 19336.

[26] Asadnia M, Kottapalli AGP, Miao J, Warkiani ME, Triantafyllou MS (2015) Artificial fish skin of self-powered micro-electromechanical systems hair cells for sensing hydrodynamic flow phenomena. J R Soc Interface 12: 20150322.

[27] Kanhere E, Wang N, Kottapalli AGP, Asadnia M, Subramaniam V, Miao J, Triantafyllou M (2016) Crocodile-inspired dome-shaped pressure receptors for passive hydrodynamic sensing. Bioinspir Biomim 11: 056007.

[28] Meng J, Li F, Luo L, Wang X, Xiao M (2014) Determination of zinc in acacia honey by square wave stripping voltammetry with a bismuth-film-modified montmorillonite doped carbon paste electrode. Monatsh Chem 145: 161-166.

[29] Krolicka A, Bobrowski A (2016) Employing a magnetic field to amplify zinc signal obtained at bismuth film screen-printed electrodes generated using dual bismuth precursor. Electrochim Acta 187: 224-233.

[30] Pan D, Zhang L, Zhuang J, Yin T, Qin W (2012) A novel tin-bismuth alloy electrode for anodic stripping voltammetric determination of zinc. Microchim Acta 177: 59-66.

[31] Khairy M, Kadara RO, Kampouris DK, Banks CE (2010) Disposable bismuth oxide screen printed electrodes for the sensing of zinc in seawater. Electroanalysis 22: 1455-1459.
**Fig. 1** Schematic drawing to show fabrication procedures of the LCP electrochemical sensor, where metal layer left on top of the unexposed photoresist is not shown in order to improve clarity

**Fig. 2 a** Photograph of the LCP electrochemical sensor after fabrication, where ‘WE’, working electrode; ‘CE’, counter electrode; ‘RE’, reference electrode. **b** Photograph of a LCP electrochemical sensor bent using a tweezer to show high flexibility
Fig. 3 Stripping peak current measured during a ten consecutive runs of SWASV for one LCP electrochemical sensor and b three consecutive runs of SWASV for six LCP electrochemical sensors in the solution of 0.6 M NaCl with 0.15 µM Zn(II). Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.
Fig. 4  

a A series of anodic stripping voltammograms recorded for the LCP electrochemical sensor with increased concentration of Zn(II) ions from 4.59 to 1071 nM. 

b Corresponding calibration plot of the stripping peak current with respect to Zn(II) concentration. Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.
Table 1 Comparison of different electrochemical sensors for determination of Zn(II)

| Sensing electrode                              | Sensitivity (nA∙nM⁻¹∙mm⁻²) | LOD (nM)       | Linear range (nM)     | Reference |
|------------------------------------------------|-----------------------------|----------------|-----------------------|-----------|
| Ex-situ sputtered bismuth film                 | 1.55                        | 1.22           | 4.59 – 1.07 × 10³    | This work |
| In-situ electroplated bismuth film             | NA#                         | 4.59           | 61.18 – 0.55 × 10³   | [11]      |
| In-situ electroplated bismuth film             | NA#                         | 6.12           | 30.59 – 0.37 × 10³   | [13]      |
| In-situ electroplated bismuth film             | 0.70                        | 130            | 2,500 – 30 × 10³     | [19]      |
| Ex-situ evaporated bismuth film                | 0.51                        | 60             | 1,000 – 30 × 10³     | [19]      |
| Tin-bismuth alloy                              | 0.46                        | 50             | 500 – 25 × 10³       | [30]      |
| Ex-situ screen-printed bismuth oxide           | 0.02                        | 504.74         | 1,147.14 – 9.18 × 10³| [31]      |

#NA stands for ‘not available’.

Fig. 5 Photograph of the sensor array prepared for sea trial testing, where four LCP electrochemical sensors are denoted as ‘S1’, ‘S2’, ‘S3’, and ‘S4’. The inset shows an enlarged view of one PDMS channel.
Fig. 6  
(a) Photograph of the autonomous kayak used during the sea trial testing, where the yellow arrow shows the direction of the kayak movement and the yellow box shows the location of the sensor array.  
(b) A close-up of the sensor array attached to the hull of the kayak.  
(c) Schematic drawing of the map of three testing locations, which are denoted as ‘L1’, ‘L2’, and ‘L3’

Table 2 Comparison between the converted current and the current detected by the sensor array during the sea trial testing

| Testing location | Reference value (µA) | S1 (µA) | S2 (µA) | S3 (µA) | S4 (µA) |
|------------------|----------------------|--------|--------|--------|--------|
| L1               | 5.729 ± 0.002        | 5.868  | 5.873  | 5.880  | 5.918  |
| L2               | 5.758 ± 0.003        | 5.944  | 5.970  | 5.998  | 6.032  |
| L3               | 5.718 ± 0.001        | 5.778  | 5.782  | 5.838  | 5.844  |
Flexible liquid crystal polymer-based electrochemical sensor for in-situ detection of zinc(II) in the seawater

( Supplementary Material )

Nan Wang1,2,*, Elgar Kanhere1, Ajay Giri Prakash Kottapalli2, Jianmin Miao1,*, Michael S. Triantafyllou2,3

1School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
2Center for Environmental Sensing and Modeling (CENSAM) IRG, Singapore-MIT Alliance for Research and Technology (SMART) Centre, 1 CREATE Way, 138602, Singapore
3Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
*Corresponding author (Email): Nan Wang – WANG0845@e.ntu.edu.sg
Jianmin Miao – jmiao@pmail.ntu.edu.sg

1. Preliminary investigation of the sensor

Figure S1a shows the cyclic voltammograms recorded using three LCP electrochemical sensors in the solution of 0.6 M NaCl. The negative limit of the potential window for the sensor was about -1.7 V with respect to the fabricated thin-film Ag/AgCl reference electrode. When the potential became lower than -1.7 V, the magnitude of the negative current started to dramatically increase. This mainly resulted from the fast evolution of the hydrogen bubbles.

The positive limit of the potential window for the sensor was around 0.8 V with respect to the fabricated thin-film Ag/AgCl reference electrode. A clear positive current was observed when the potential became higher than -0.8 V. This was possibly caused by the oxidation of the Bi working electrode. Figure S1b shows the anodic stripping voltammogram recorded using the LCP electrochemical sensor in the solution of 0.6 M NaCl with 0.15 µM Zn(II).
Investigation of the potential window using three LCP electrochemical sensors in the solution of 0.6 M NaCl. Initial potential: -2.0 V; final potential: -0.5 V; scan rate: 50 mV·s⁻¹. b Anodic stripping voltammogram recorded in the solution of 0.6 M NaCl with 0.15 µM Zn(II). Deposition potential: -1.4 V; deposition time: 120 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.

2. Optimization of the sensor

The influence of deposition potential on stripping peak current of the LCP electrochemical sensor was evaluated in the solution of 0.6 M NaCl with 0.15 µM Zn(II). The potential was varied in the range between -1.2 and -1.9 V with fixed deposition time of 120 s. As shown in Fig. S2a, a rapid increase in the current was observed when the deposition potential was changed from -1.2 to -1.6 V. Increase of peak current was probably contributed by the elevated energy provided to the metal ions to participate in the process of accumulation. When the deposition potential became more negative than -1.6 V, the stripping current started to decrease. This was likely due to the generation of hydrogen bubbles that impeded metal ions from being deposited on the electrode surface. Hence, an optimum deposition potential of -1.6 V was selected for further experiments. By maintaining the deposition potential, the influence of deposition time on stripping peak current in the same solution was further studied between 60 and 360 s. As shown in Fig. S2b, the stripping current increased almost in
a linear manner. This behavior was possibly on account of the reason that Zn(II) ions were constantly supplied to the vicinity of the working electrode as the testing solution was stirred during the deposition step. In view of possible saturation of the working electrode with prolonged deposition time, a deposition time of 180 s was selected for further experiments.

![Graph showing effects of deposition potential and time on stripping peak current.](image)

**Fig. S2** Effects of **a** deposition potential and **b** deposition time on stripping peak current for the LCP electrochemical sensor in the solution of 0.6 M NaCl with 0.15 µM Zn(II). Deposition time: 120 s for (a); deposition potential: -1.6 V for (b). Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode. Data are presented as the mean of three replicates.

### 3. Interference test of the sensor

Figure S3 depicts the results of interference test for the LCP electrochemical sensor. The concentration of NH₄⁺, K, Mg, and Ca ions was 100 times higher than that of Zn(II) ions. While the concentration of Cu(II), Pb(II), and Cd(II) ions was 5, 20, and 20 times higher than that of Zn(II) ions, respectively.
Fig. S3 Effects of possible interfering ions on stripping peak current for the LCP electrochemical sensor in the solution of 0.6 M NaCl with 0.15 µM Zn(II). Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode. Data are presented as the mean of three replicates.
4. Responses of the sensor array during the sea trial testing

Figures S4, S5, S6, and S7 display the responses of the sensor array (including sensor ‘S1’, ‘S2’, ‘S3’, and ‘S4’) during the sea trial testing at three locations.

![Graph a: Sensor S1 at Location L1](image)

![Graph b: Sensor S1 at Location L2](image)
Fig. S4 Anodic stripping voltammograms recorded during the sea trial testing for the sensor ‘S1’ at location a ‘L1’, b ‘L2’, and c ‘L3’. Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.
Fig. S5 Anodic stripping voltammograms recorded during the sea trial testing for the sensor ‘S2’ at location a ‘L1’, b ‘L2’, and c ‘L3’. Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.
Fig. S6 Anodic stripping voltammograms recorded during the sea trial testing for the sensor ‘S3’ at location a ‘L1’, b ‘L2’, and c ‘L3’. Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.
Fig. S7 Anodic stripping voltammograms recorded during the sea trial testing for the sensor ‘S4’ at location a ‘L1’, b ‘L2’, and c ‘L3’. Deposition potential: -1.6 V; deposition time: 180 s. Potentials were measured with respect to the fabricated thin-film Ag/AgCl reference electrode.
5. ICP-MS analysis of the seawater samples

Table S1 shows the ICP-MS results of the seawater samples collected during the sea trial testing. It can be noticed that the concentration of Cu(II) ions is about 2 to 3 times higher than that of Zn(II) ions. The concentration of Pb(II) ions is slightly higher than that of Zn(II) ions. On the other hand, the concentration of Cd(II) ions is much lower than that of Zn(II) ions. These ICP-MS data imply that there was no significant interference effect on the Zn(II) stripping current for the sensor array during the sea trial testing.

| Testing location | Zn(II) (µg·L⁻¹) | Cu(II) (µg·L⁻¹) | Pb(II) (µg·L⁻¹) | Cd(II) (µg·L⁻¹) |
|------------------|-----------------|-----------------|-----------------|-----------------|
| L1               | 0.574 ± 0.017   | 1.120 ± 0.047   | 0.717 ± 0.001   | 0.012 ± 0.003   |
| L2               | 0.883 ± 0.029   | 1.379 ± 0.028   | 0.715 ± 0.0002  | 0.017 ± 0.001   |
| L3               | 0.453 ± 0.006   | 1.508 ± 0.033   | 0.715 ± 0.0001  | 0.017 ± 0.003   |