Int. J. Electrochem. Sci., 13 **(2018)** 1931 – 1944, doi: 10.20964/2018.02.20

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Development of Poly(3,4-ethylenedioxythiophene(PEDOT)/carbon Nanotube Electrodes for Electrochemical Detection of Mancozeb in Water

Roy Zamora[1,*], *Federico Masís-Meléndez*[2], *Hayden Phillips*[3], *Luis A. Alvarado-Marchena*[4], *Ricardo Starbird*[1]

[1] School of Chemistry, Costa Rica Institute of Technology, Cartago, Costa Rica
[2] Research Center and Chemical and Microbiological Services CEQIATEC, Costa Rica Institute of Technology, Cartago, Costa Rica
[3] School of Electronic Engineering, Costa Rica Institute of Technology, Cartago, Costa Rica
[4] Electron Microscopy Laboratory, Costa Rica Institute of Technology, Cartago, Costa Rica
[*]E-mail: rzamorasequeira@ina.ac.cr

Received: 25 August 2017 / *Accepted:* 28 September 2017 / *Published:* 28 December 2017

Assessments of the risk of water contamination caused by pesticides in agricultural areas are typically conducted using laborious methods and expensive instruments. Severe chronic diseases have been connected to the presence of Mancozeb (MCZ) in several bodies of water. Consequently, it is necessary to have new tools to access MCZ residues in drinking water. The purpose of this work is to develop a novel and economical electrode to detect and quantify MCZ in water using electrochemical techniques. Electrodes coated with poly(3,4-ethylenedioxythiophene) (PEDOT) and MWCNTs were characterized using transmission electron microscopy (TEM), profilometry and Raman techniques. Cyclic voltammetry was used to characterize and quantify MCZ in solution. The electrochemical behavior of the modified electrodes was studied to obtain specific signals due to MZC and MWCNT interaction. The results confirmed that this approach is a sensitive and selective electroanalytical method for determining MCZ with a working linear range of 25–150 µM and a limit of detection set at 10 µM. The advantages of this PEDOT/MWCNT electrode coat include quick and feasible detection of pesticides in drinking water as well as a new approach for sensing analysis in monitoring programs and research studies.

Keywords: Mancozeb, Nanotubes, Electrode, Cyclic voltammetry, Conductive polymers

1. INTRODUCTION

Fungicides and insecticides are widely used to control pests in crops [1]. Mancozeb [[(manganese ethylene-bis (dithiocarbamate) complex with zinc salt)]] is a subclass of carbamate pesticides known as dithiocarbamates (DTC) [2]. It is used as a fungicide in fruits, vegetables, rice and ornamental plants. Reported health effects due to Mancozeb (MCZ) exposure include metal overload in human colon cells [1], thyroid hormone disruption in rats [2], toxic effects on mammalian granulosa cells [3], and more importantly, tumor-initiating activity in mouse skin [4]. Specifically, in Costa Rica during 2007, residues for MCZ were detected in the urine samples of children living close to agricultural plantations [5, 6].

Quantification of MCZ in water has been conducted after conversion to carbon disulfide (CS_2) [7] through hydrolysis and has been determined by CG (gas chromatography) [8] or optical analysis [9]. On the other hand, cyclic voltammetry is a potential technique for quantifying MZC due its broad spectrum effects and versatility [10]. Quantification of MZC by electrochemical techniques has been reported [11–17] using cyclic voltammetry and linear scanning voltammetry, which demonstrates low interference and high sensitivity [17]. The sensing capabilities rely on the electrode properties and carbon nanotubes anchored to a conductive polymer that could serve as a novel material for the electro-quantification of MCZ in water.

Some remarkable properties of CNT include a high aspect ratio, high electrical conductivity and high mechanical strength and elasticity [18]. Despite many advantages of CNT, they tend to form aggregates and parallel beams during processing, which makes this material immiscible in most common solvents [19]. The dispersion and arrangement of nanoparticles plays a key role in the properties of the resulting composites [10]. The critical micellar concentration (CMC) is the concentration of surfactants in which the micelles form spontaneously [19]. Control of the CMC is an important aspect for achieving homogenous dispersions. Using a surfactant, such as sodium dodecyl sulfate (SDS), allows the nanotubes to disperse their aggregates to optimize their properties [20].

Poly(3,4-ethylenedioxythiophene (PEDOT) is a conductive polymer that has several advantages, such as low impedance, high charge injection density, and electrical stability along with an increase in the electroactive surface area [21, 22]. The electrochemical properties of PEDOT can be improved by adding carbon nanotubes (CNT) to the electrodes. Therefore, we report the synthesis, fabrication and characterization of an electroactive PEDOT/MWCNT electrode. Characterization of the electroactive coat was accomplished through a transmission electron microscope (TEM), Raman spectroscopy, profilometry and cyclic voltammetry. The novel PEDOT/MWCNT electrode coat may enhance the performance of electronic monitoring systems and quantitative assessment of risk to bodies of water from land contamination. This strategy may reduce the response time of health authorities, especially in remote areas where facilities are not currently available.

2. EXPERIMENTAL

2.1. Materials

The 80% (w/w) Mancozeb was purchased from RIMAC MANCOZEB 80 WP (Cartago, Costa Rica). Sodium dodecyl sulfate (SDS) ACS reagent, 3,4-ethylenedioxythiophene (EDOT) (97%), (Ethylenedinitrilo)tetraacetic acid disodium (ETDA), potassium chloride (KCl), boric acid (H_3BO_3), phosphoric acid (H_3PO_4), Spurr® low viscosity resin, 99% purity sodium dodecyl sulfate and acetic acid (CH_3COOH) (analytical reagent grade) were obtained from Sigma-Aldrich (San José, Costa Rica). Multi-Walled Carbon Nanotubes (MWCNT) with outer diameters of 20-30 nm, 30-50 nm, and 50-80 nm were acquired from Cheap tubes (Grafton, USA). The positive photoresist system S1805™ Series Photoresist was purchased from Hauque Enterprises (Texas, USA). The Tetramethylammonium hydroxide (4%) UN1835 Developer was acquired from Microposit (PA, USA). Polyimide DuPont™ Kapton® (12.7 µm) was obtained from DuPont (Texas, USA).

2.2.1 MWCNT solutions

Pristine MWCNTs with a purity >99 wt% and outside diameters of 30–50 nm (Cheap Tubes Inc., USA) were dispersed in a mixture of water and SDS (i.e., the anionic surfactant of the sodium dodecyl sulfate (SDS) (9 mM) added to ultrapure water) and then stirred for 60 minutes to obtain 0.00, 0.15, 0.25, 0.35 and 0.50 mg/ml MWCNTs dispersions, and then, the dispersions were ultrasonicated (Qsonica, model Q500, Newtown, Connecticut, USA). Finally, only the dispersed supernatant was extracted after using a centrifuge at 4000 rpm for 30 min (Thermo, model IEC HN-SII, Needham Heights, MA-USA).

2.2.2 Standard solutions

Robinson-Britton buffer (BR) was prepared using boric acid, glacial acetic acid, and phosphoric acid to maintain a pH of 7.0 and adjusted to 0.1 M ionic strength with potassium chloride. Stock solutions of MCZ (1000 µmol/L) were prepared daily by dissolving an accurately weighed amount of the compound in an EDTA solution (3% wt.), Robinson-Britton buffer and ultrapure water. These solutions were stored in the dark at 4 °C until they were used. MCZ solutions were denoted as MCZX, where X=0 to 250 µmol/L depending on the concentration.

2.3. Microfabrication and polymerization

Gold electrodes were electrodeposited on polyimide film and were subsequently passivated and etched using photolithography methods. Later, an exposed active area of the electrodes was polymerized. The polymer (PEDOT) was deposited in its monomer form, dispersed with a 0.35% mass concentration of MWCNT in a micellar media of SDS and the EDOT monomer in an aqueous phase. The solution EDOT/SDS/MWCNT was electropolymerized under galvanostatic conditions with an Autolab Potentiostat supplied by Metrohm (AUTOLAB, model: PGSTAT-302, Utrecht, Netherlands) using a fixed charge density of 240 mC/cm^2 according to the methods of a previous study [23]. MWCNT Samples with an outer diameter of 20-30 nm, 30-50 nm and 50-80 nm were polymerized from EDOT/SDS dispersions that were characterized by cyclic voltammetry, and the correlation between current and MWCNT diameter was determined.

2.4. Characterization

The stabilities of the MWCNT/SDS/monomer dispersions were studied through quantification of ξ-Potential using a Malvern Zeta Potential model: Zetasizer Nano Range, 90° angle and PCS8501 sample cells (Grovewood Road, UK). From this dispersion, electrodes were polymerized with PEDOT and CNTs (20-30, 30-50 and 50-80 nm diameters). The electrode surface was studied with profilometry (Bruker, model: Dektak TX Advance, AZ, USA). Raman spectroscopy was conducted using a Thermo-Raman Microscope (Model: DXR, MA- USA) with a 632.8 nm laser. The morphology of the CNTs was studied through transmission electron microscopy (TEM), (Jeol, Model: JEM 2011, Tokyo, Japan) before and after polymerization. CNTs dispersed in SDS were dropped on metal grids and dried before observation. PEDOT/CNT coats were passed through a transition solvent process and embedded into a Spurr® low viscosity resin. After embedding the samples, the resin block was thin sectioned (50 - 70 nm) and collected on metal grids for TEM observation.

2.5. Voltammetry analysis

Concentrations of MCZ at 250 μM and 500 μM were measured in triplicate to compare the performance of the polymerized electrodes at different density charges. The equipment was set to measure cyclic voltammetry from 0.0 to 1.0 V at a 100 mV/s scan rate. All electrochemical measurements were achieved using an electrochemical workstation (AUTOLAB, model: PGSTAT-302, Utrecht, Netherlands) with a conventional three-electrode cell configuration: Ag/AgCl (3 M KCl) as a reference electrode, platinum foil as a counter electrode and the PEDOT/MWCNT (50-80 nm diameters) electrode (diameter of 0.12 cm) as the working electrode. Electrochemical experiments were carried out in a 20-mL voltammetric cell with a scan rate of 100 mV/s. The equipment was set to measure cyclic voltammetry from 0.0 to 1.0 V.

2.6. Recovery study

To validate the feasibility of our sensing electrode strategy for analysis of MCZ in environmental samples, we used our electrochemical system to determine the concentration of MCZ from a leaching experiment setup (W_{le}) and in a tap water sample (W_t).

First, the leachate (W_{le}) was produced by leaching an input volume of 150 mL of 1000 ppm MCZ into a vertical repacked sand column at a steady flow rate. The average particle size, D_{50}, of the sand particles is 259 μm with a uniformity coefficient (Cu) of 2.1, which is less than 3.0 and therefore considered to be relatively uniform or poorly graded. The length of the column was 11.4 cm, and it has a cross-section area (A) of 253 cm^2. The column was saturated to a water content of 0.41 L with ultrapure water MCZ (C_o), which was applied right after the first water drops in the effluent were observed. After 30 minutes, five consecutive fractions (160 mL) from the effluent were collected and merged into a single composite sample for consecutive electrochemical analysis of MCZ. The water from the effluent exiting the bottom of the sand column was monitored using pH measurements. The tap water sample (W_t) was obtained by spiking the sample with a known concentration of MCZ (50 μmol/L) in an EDTA solution (3% wt.), RB buffer (pH 7.0) and ultrapure water, respectively. These solutions were stored in the dark at 4 °C until they were used. The samples were electrochemically evaluated to determine the interference from the matrix.

2.7. Statistical analysis

All results were expressed as the mean ± standard deviation. One-Way ANOVA, the Ryan-Joiner normality test (correlation coefficient) and the Standard Deviation Test were performed. Statistical significance set at $p<0.05$ was used to evaluate the effect of MCZ concentration (Minitab® 17.1.0., Pennsylvania, USA).

3. RESULTS AND DISCUSSION

3.1 Emulsification

Despite the remarkable electrical properties of MWCNT, its dispersion in water is difficult to achieve without a surfactant (i.e., SDS). The surfactant has an important role in stabilizing the MWCNT dispersion along with the ultrasonication process.

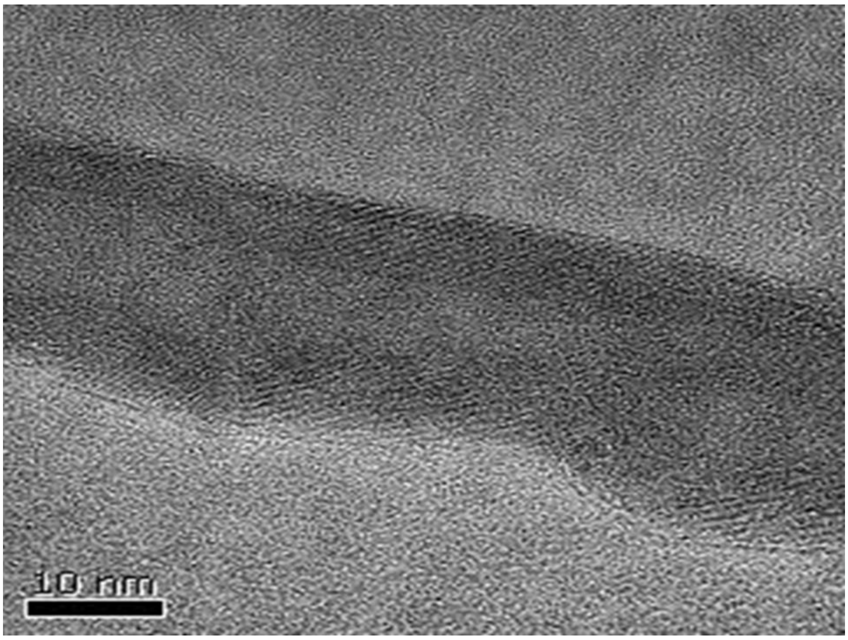


Figure 1. Transmission electron microscopy image of MWCNTs along with sodium dodecyl sulfate (SDS) as surfactant.

The stability of the dispersion was evaluated by Zeta Potential (ζP) to optimize the amount of MWCNT to be added to the dispersion. Different dispersions of 0.15, 0.25, 0.35 and 0.50 mg/mL showed high stability since the minimum value for all the samples was -45.4 mV. The ζP value increased gradually with MWCNT concentration, and the highest ζP value was observed when the MWCNT concentration was 0.35 mg/mL. This result is attributed to the absorption of anionic charges on the carbon nanotube surface [24]. Meanwhile, the SDS-EDOT dispersion presented a potential of -77.1 mV.

The dispersed MWCNTs were characterized by TEM (Fig. 1) to determine the diameter and to confirm the multiple-walled nature of the CNT. The multiwall structure and a diameter of 30 nm agree with the values reported in the datasheet for this material.

3.2 Polymerization and characterization

The solution PEDOT/SDS/MWCNT was electropolymerized under galvanostatic conditions with a charge density of 240 mC/cm^2 according to a method from a preliminary study [22].

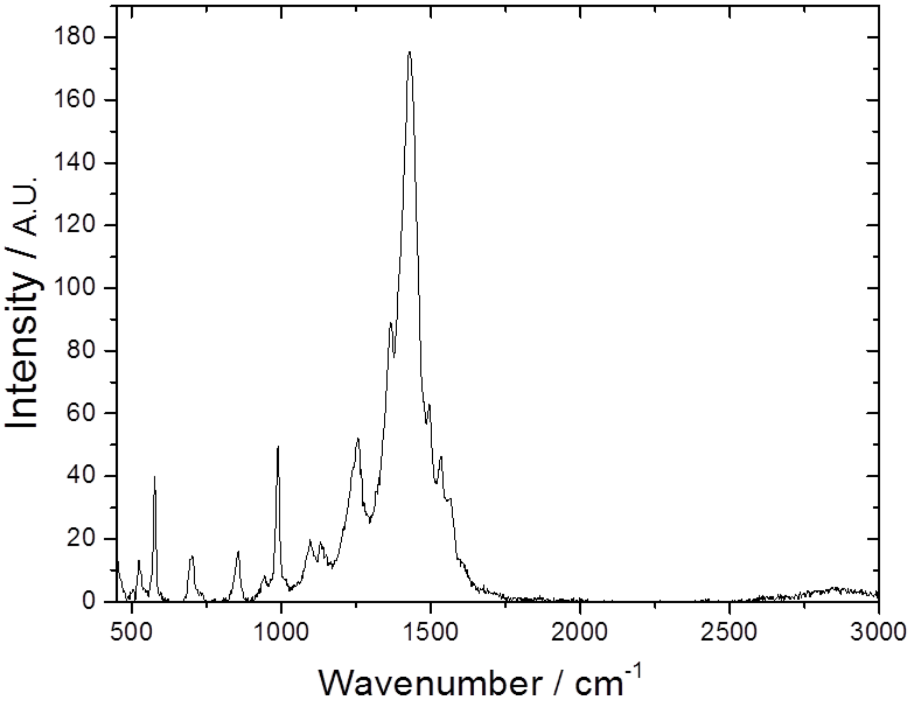


Figure 2. Raman spectra of MWCNTs electropolymerized in the PEDOT matrix.

Raman spectroscopy is a suitable tool for the study of PEDOT structure, particularly due to the doping state of the chain showing differences between quinoid and benzoic absorption. Some vibrations for the PEDOT samples are summarized in Table 1, which shows the importance of this technique for the study of polymerization and doping state. A strong band at 1426 cm^{-1} and one weak peak at 1532 cm^{-1} were observed due to the $C_\alpha=C_\beta$ symmetric stretching vibration and $C_\alpha=C_\beta$ asymmetric stretching, respectively. One band at 1365 cm^{-1} is assigned to C_β-C_β thiophene ring stretching [25-27]. The deformation of the oxyethylene ring band is observed at 990 cm^{-1}, and the broad band approximately 697 cm^{-1} occurs due to C–S–C ring deformation. Finally, a weak peak approximately 1266 cm^{-1} is related to inter-ring C_{α}-C'_{α} stretching.

Table 1. A summary of the principle infrared bands and their assignments [25-27]

Wavenumber (cm^{-1})	Intensity	Functional group
	PEDOT	
439	m	C-O-C deformation
576	m	Oxyethylene deformation
697	m	Symmetric C-S-C deformation
990	m	oxyethylene ring band
1090	w	C_{α}-C_{α} (inter ring) deformation
1262	w, multiplet	Multiplet C–C inter-ring stretching
1365	m	C_{α}-C_{β} stretching
1426	S, multiplet	Symmetric C_{α}=C_{β} stretching C-C stretching (symmetric)
1500	s	Asymmetric C_{α}=C_{β} stretching
	MWCNT	
2683	w	Overtone of the D band (G′ band)
1580	m	In-plane vibration of the C–C bond (G band)
1342	m	Defective graphite 1 (D band)

The PEDOT/CNT sample shows typical signals for benzoic structure (Fig. 2), but no signals from MWCTN have been observed. This result probably occurred because of the overlap with PEDOT signals. Moreover, the presence of the MWCNT in the polymer matrix was confirmed by transmission electron microscopy (TEM) [28, 29]. The nature and distribution of MWCNT are important for an electrode coat, since the properties (diameter, length and interconnection) affect the detection of a specific compound.

The electrodeposition of PEDOT with MWCNTs on the electrode led to an improvement of surface roughness (Fig. 3a). However, the electrochemical response has been attributed to the MWCNT presence and its availability during the analysis because of its unique structure, topology, and dimensions. Some authors addressed this electroactivity at the open ends in the MWCNTs [30] and its electron transfer capabilities [31]. Furthermore, the electrical conduction mechanisms have been related to the influence of the type of carbon nanotube, content (wt%) and the dispersion in the matrix [32]. In Figure 3b, it seems that the MWCNT formed some aggregates inside the conductive polymer, which may improve the electron transfer. Meanwhile, some MWCNTs are in contact with the solution and the polymer matrix (Fig. 3c), and those MWCNTs may enhance the electrochemical response through direct oxidation of the analyte on the electrode surface.

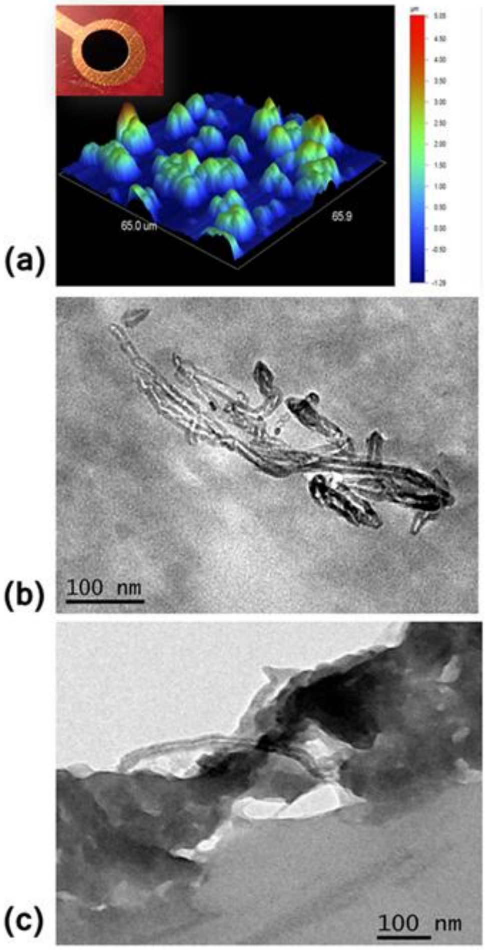


Figure 3. Coated electrode images: a) electrode surface roughness (inset: PEDOT/MWCNT-coated electrode), b) MWCNT aggregates inside the PEDOT layer and c) MWCNT anchored to the PEDOT layer.

3.3 Electrochemical response

The electrochemical behavior of MCZ was evaluated using cyclic voltammetry in a range from 0.0 to 0.8 V with various electrodes showing an oxidation signal approximately 625 mV (Fig. 4). Silva attributed this signal to oxidation of the amide functional groups in the MCZ molecule [16]. However, this signal may be associated with irreversible oxidation of the RSS group in the molecule [33], which might allow researchers to evaluate the MCZ and its main degradation metabolites [34]. The peak increased along with the mancozeb concentration up to 250 μM, and at that concentration, the electrode is saturated.

Additionally, we found that the current value increases as the MWCNT diameter increases (MWCNTs 20-30 nm and MWCNTs 30-50 nm diameters) (see Supplementary Figure S1), which is consistent with previous studies [35]. The limited electrical performance in the MWCNTs 30-50 nm coat may be related to common defects, including flakes, which were previously reported in the higher diameter MWCNT-growing process [36]. These flakes could affect the conductivity mechanism by increasing the electrical resistance of the structure of the MWCNT. No oxidation process has been observed using only PEDOT as a coating material. The evaluation of MZC was optimized using MWCNT in a range of 50-80 nm.

3.4 Method validation

The oxidation of MCZ was evaluated at pH 7 using RB buffer as an electrolyte in cyclic voltammetry conditions. MCZ generates a signal at 625 mV that is associated with its oxidation process (Fig. 4). In our study, this signal was used for quantification as a function of the concentration. Linearity with a value of R> 0.99 was obtained in a range of 25 to 150 µmol/L (Fig. 5). However, above 200 µmol/L (Fig. 6), the response of the electrode is no longer linear, as shown by the higher standard deviations. All samples were analyzed using 6 replicates and a blank for each electrode. The standard stock solution of MCZ was prepared daily. With the optimized cyclic voltammetry conditions, the limit of detection (LOD) was 10 µmol/L (Table 2), which is close to other studies that reported similar LOD values (7 µmol/L) [11]. An advantage of this PEDOT/MWCNT electrode over conventional methods is the reduced time for sample preparation and quantification under laboratory conditions or in the field. In addition, this approach is more environmentally friendly because it reduces the use of solvents and other chemicals.

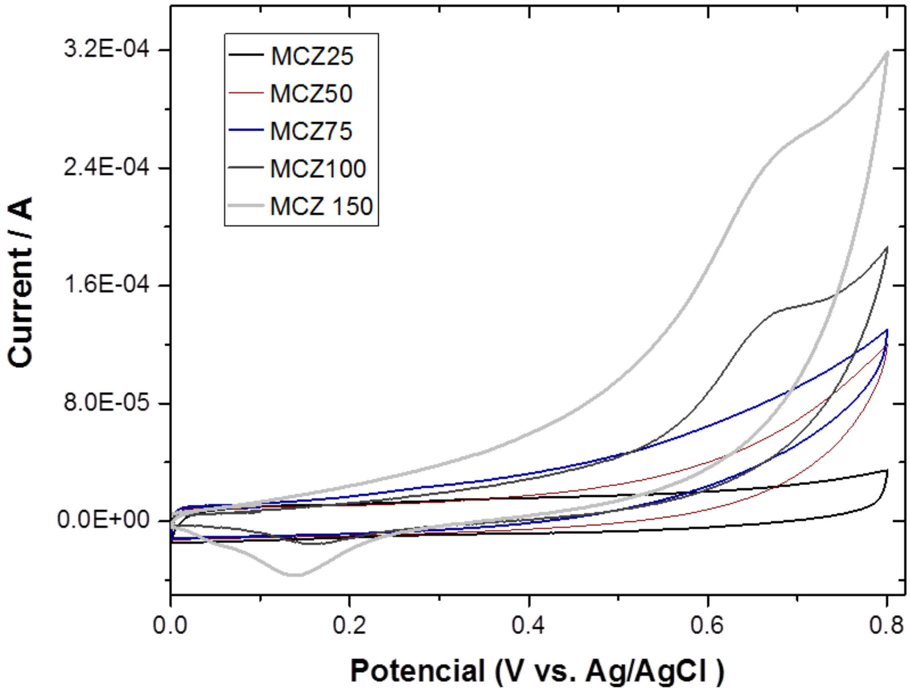
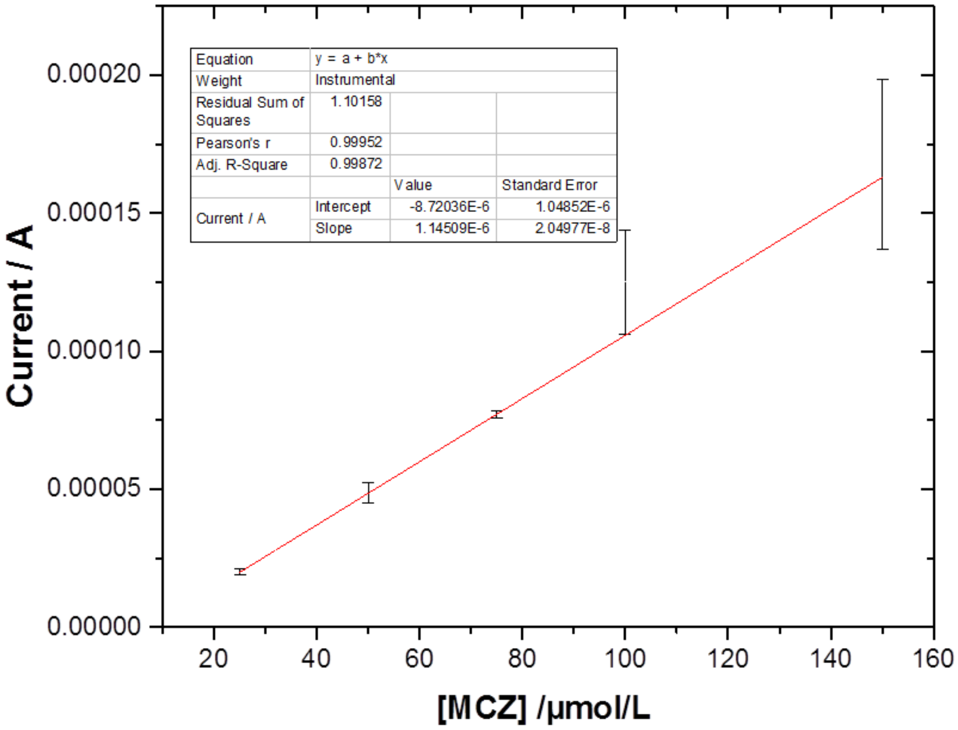


Figure 4. Voltammograms obtained for different MCZ concentrations of 0, 25, 50, 75, 100, 150, 200 and 250 µmol/L in BRBS at pH 7 using the PEDOT/MWCNT electrode.



Equation	y = a + b*x		
Weight	Instrumental		
Residual Sum of Squares	1.10158		
Pearson's r	0.99952		
Adj. R-Square	0.99872		
		Value	Standard Error
Current / A	Intercept	-8.72036E-6	1.04852E-6
	Slope	1.14509E-6	2.04977E-8

Figure 5. Calibration curve MCZ (25, 50, 75, 100 and 150 µmol/L) in BRBS at pH 7 using a PEDOT/MWCNT electrode.

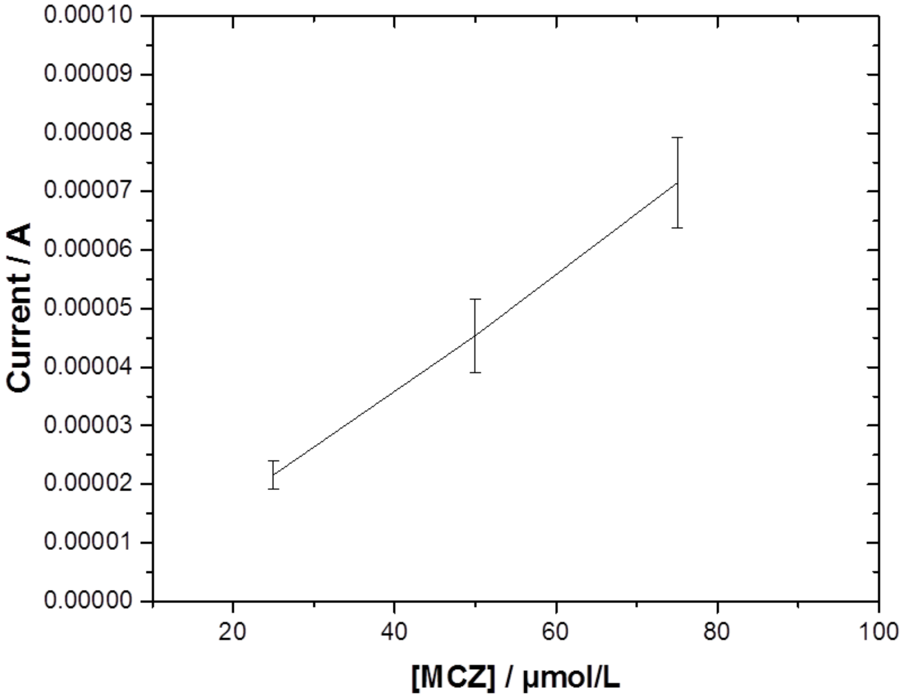


Figure 6. Calibration curve MCZ (25, 50 and 75 µmol/L) in BR buffer at pH 7 using a PEDOT/MWCNT electrode.

Table 2. Figure of merit for the developed PEDOT/MWCNT electrode for the analysis of MCZ and a comparison with other electrochemical methods for the analysis of MCZ.

Figure of merit	**MCZ**	**López-Fernández, O. *et al.* [11]**
Linear range (µmolL-1)	25-150	10.0–90.0
N	5	9
Correlation coefficient (r)	0.99	0.99
Slope (m) (A/ µmol/L	1.14E-6	0.0186
Intercept (A)	8.72E-6	0.091
Limit of detection (LOD) (µmol/L)	10	7

The statistical analysis shows no unusual data points in all the samples. One-Way ANOVA for high concentration samples (MCZ100, MCZ150, MCZ200 and MCZ250) could not prove that there was a significant difference (p-value: 0.117) among the means at the 0.05 level. Those data do not provide sufficient evidence to conclude that there are differences among the means. Meanwhile, the samples MCZ25, MCZ50 MCZ75 and MCZ150 demonstrated differences (p-value: 0.001) among the means at the 0.05 level of significance. Finally, variability in samples MCZ25, MCZ50, MCZ75 and MCZ150 occurred that was independent and maintained a high correlation with concentration with values of R greater than 0.99. The Ryan-Joiner normality test shows that the obtained values are near 1 for the correlation coefficient, which shows normal behavior in this range. Linearity is observed in the range of 25 to 150 µmol/L using a proposed cyclic voltammetry method. In this investigation, the PEDOT/MWCNT electrode provides a robust electrochemical response in the linear range in addition to a faster procedure that can be performed with fewer solvents and is more environmentally friendly compared to other techniques used for measuring MCZ.

3.4 Analytical application

To evaluate the analytical ability of the sensor, it was used for simultaneous determination of MCZ in leachate (W_{le}) and tap water (W_t) samples. The W_t sample was fortified with a known concentration of MCZ (50 µmol/L). The W_{le} sample was obtained as described in the section 2.6, Recovery Study. Both samples were analyzed using the developed sensor and a calibration curve for MCZ (see Table 3). The value obtained for the tap water was 51.2 µmol/L with a relative standard deviation (RSD) of 0.74, and a recovery value of 102% was generated in a shorter time and with better recovery occurred compared to other studies [11, 37]. The results indicated that the proposed method is highly accurate, precise and reproducible. It can be used for direct analysis in aqueous samples that potentially have MCZ in a shorter time and for a lower cost.

Table 3. Results obtained in an analysis of MCZ in real samples

Sample	**Added** (µmol/L)	**Found** (µmol/L)	**Recovery (%)**	**RSD (%)**
W_t	50	51.2	102	0.74
W_{le}	unknown	87.93	-	0.02

4. CONCLUSIONS

A novel electrode of PEDOT mixed with MWCNTs was developed to determine the presence of mancozeb (MCZ) in water. In cyclic voltammetry, the modified electrode exhibited electrocatalytic activity towards the oxidation of MCZ with a working linear range of 25–150 µmol/L and a limit of detection of 10 µmol/L. The developed electrochemical sensor provides economic and environmental advantages, and the results aimed to utilize a new electrochemical method for *in situ* and real-time detection of pollutants. Therefore, the novel electrode could be implemented in monitoring programs and research endeavors for assessing the contamination risk for bodies of water. In further studies, the effects of functionalized CNTs will be determined to improve electrochemical specificity.

ACKNOWLEDGEMENTS
This work was financially supported by Costa Rica Institute of Technology (ITCR) and FEES funding (CONARE). Roy Zamora-Sequeira thanks the Technology Bureaus of Costa Rica (MICITT and CONICIT) and National Learning Institute (INA) for the scholarship during this project. We are grateful Esteban Avendaño, Ph.D. from the Materials Science and Engineering Research Center (CICIMA), University of Costa Rica, Costa Rica for his support with the electrode fabrication and to Oscar Rojas-Carrillo, Ph.D., from the School of Chemistry, National University (UNA), Costa Rica, for his help with the zeta potential analysis. Finally, we would like to thank Diana Robles from the Research Center and Chemical and Microbiological Services (CEQIATEC)".

SUPPLEMENTARY INFORMATION:

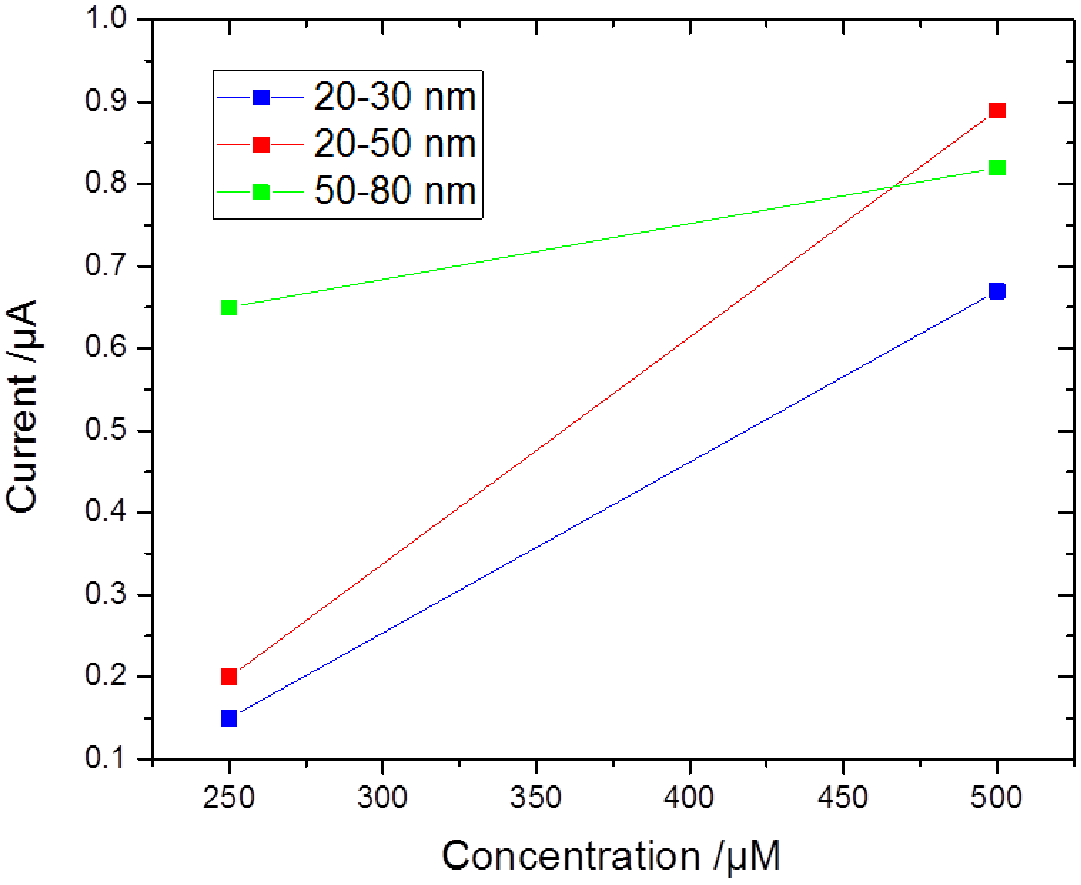


Figure S1. Current peaks vs concentration for polymerized electrodes with CNTs at 20-30 nm, 30-50 nm and 50-80 nm diameters in PEDOT.

References

1. L. Hoffman, L. Trombetta, D. Hardej, *Environ. Toxicol. Pharmacol.* 41 (2016) 78
2. M. Axelstad, J. Boberg, C. Nellemann, M. Kiersgaard, P.R. Jacobsen, S. Christiansen, K.S. Hougaard, U. Hass, *Toxicol. Sci.* 120 (211) 439
3. R. Paro, G.M. Tiboni, R. Buccione, G. Rossi, V. Cellini, R. Canipari, S. Cecconi, *Toxicol. Appl. Pharmacol.* 260 (2012) 155
4. N.K. Mehrotra, S. Kumar, Y. Shukla, *Cancer Lett.* 36 (1987) 283
5. B. Van Wendel De Joode, B. Barbeau, M.F. Bouchard, A.M. Mora, Å Skytt, L. Córdoba, R. Quesada, T. Lundh, C.H. Lindh, D. Mergler, *Environ. Pollut.* 215 (2016) 247
6. Health, E. & Isa, S. Research, *Environ. Health Perspect.* 122 (2014) 1321
7. D. Sreenivasulu, T.B. Patrudu, T. Nadu, O. Chemicals 2 (2013) 41
8. S. Mujawar, S.C. Utture, E. Fonseca, J. Matarrita, K. Banerjee, *Food Chem.* 150 (2014) 175
9. J.V. Rohit, J.N. Solanki, S.K. Kailasa, *Sens. Actuators B Chem.* 200 (2014) 219
10. W. Lian, S. Liu, J. Yu, X. Xing, J. Li, M. Cui, J. Huang, *Biosens. Bioelectron.* 38 (2012) 163
11. O. López-Fernández, M.F. Barroso, D.M. Fernandes, R. Rial-Otero, J. Simal-Gándara, S. Morais, H.P.A. Nouws, C. Freire, C. Delerue-Matos, *J. Electroanal. Chem.* 758 (2015) 54

12. N. Oturan, M.A. Oturan, *Agron. Sustain. Dev.* 25 (2005) 267
13. D.M. Stanković, D.M., *Electroanalysis* 29 (2017) 352
14. D. Du, X. Ye, J. Cai, J. Liu, A. Zhang, *Biosens. Bioelectron.* 25 (2010) 2503
15. C. Swarupa, M. Siva Prasad, M. Dhananjayulu, N.Y. Sreedhar, *Int. J. Sci. Eng. Res.* 4 (2013) 1234
16. R.A.G. Silva, L.A.J. Silva, R.A.A. Munoz, E.M. Richter, A.C. Oliveira, *J. Electroanal. Chem.* 733 (2014) 85
17. S. Kumar, P. Karfa, S. Patra, R. Madhuri, P.K. Sharma, *RSC Adv.* 6 (2016) 36751, doi: 10.1039/C6RA03204D
18. H.A. Zeinabad, A. Zarrabian, A.A. Saboury, A.M. Alizadeh, M. Falahati, *Sci. Rep.* 6 (2016) 26508
19. J.Y. Shin, T. Premkumar, K.E. Geckeler *Chemistry* 14 (2008) 6044
20. V.C. Moore, M.S. Strano, E.H. Haroz, R.H. Hauge, R.E. Smalley, J. Schmidt, Y. Talmon, *Nano Lett.* 3 (2003) 1379
21. T.F. Otero, J.G. Martinez, K. Hosaka, H. Okuzaki, *J. Electroanal. Chem.* 657 (2011) 23
22. R. Starbird, W. Bauhofer, M. Meza-Cuevas, W. H. Krautschneider, Effect of experimental factors on the properties of PEDOT-NaPSS galvanostatically deposited from an aqueous micellar media for invasive electrodes, Biomedical Engineering International Conference (BMEiCON), Ubon Ratchathani, Thailand, 2012.
23. R. Starbird, W. Bauhofer, M. Meza-Cuevas, W.H. Krautschneider, *Eng. Int. Conf. BMeiCon.* (2012) doi: 10.1109/BMEiCon.2012.6465500
24. E.F. de la Cruz, Y. Zheng, E. Torres, W. Li, W. Song, K. Burugapalli, *Int. J. Electrochem. Sci.* 7 (2012) 3577
25. F. Tran-Van, S. Garreau, G. Louarn, G. Froyer, C. Chevrot, *J. Mater. Chem.* 11 (2001) 1378
26. W.W. Chiu, J. Travaš-Sejdić, R.P. Cooney, G.A. Bowmaker, *J. Raman Spectrosc.* 37 (2006) 1354
27. X. Cui, D.C. Martin, *Sens. Actuators B Chem.* 89 (2003) 92
28. E.A. Bengio, D.E. Tsentalovich, N. Behabtu, O. Kleinerman, E. Kesselman, J. Schmidt, Y. Talmon, M. Pasquali, *ACS Appl. Mater. Interfaces* 6 (2014) 6139
29. C. Branca, F. Frusteri, V. Magazù, A. Mangione, *J. Phys. Chem. B* 108 (2004) 3469
30. A. Merkoçi, M. Pumera, X. Llopis, B. Pérez, M. del Valle, S. Alegret, *TrAC Trends in Analytical Chemistry* 24 (2005) 826
31. L. Agüí, P. Yáñez-Sedeño, J. M.Pingarrón, *Anal. Chim. Acta* 622 (2008) 11
32. F.H. Gojny, M.H.G. Wichmann, B. Fiedler, I.A. Kinloch, W. Bauhofer, A.H. Windle, K. Schulte, *Polymer* 47 (2006) 2036
33. C.H. Chen, J.S. Wang, Y.T. Lin, M.S. Lin, *Sens. Actuators B Chem.* 173 (2012) 197
34. S.M.F. Calumpang, M.J.B. Medina, N.P. Roxas, E.D. Magallona, *Int. J. Pest Manag.* 39 (1993) 161
35. J. Liang, L. Zhang, N. Azemard-Crestani, P. Nouet, A. Todri-Sanial, Physical description and analysis of doped carbon nanotube interconnects, 26th International Workshop on Power and Timing Modeling, Optimization and Simulation (PATMOS), Bremen, Germany, 2016, 250
36. B.Q. Ta, H.Q. Nguyen, N. Hoivik, E. Halvorsen, K.E. Aasmundtveit, Observations on defects and contact modes for locally grown CNTs, Proceedings of the IEEE Conference Nanotechnology, Birmingham, UK, 2012, doi: 10.1109/NANO.2012.6322008
37. G. Crnogorac, W. Schwack, *TrAC Trends Anal. Chem.* 28 (2009) 40