Real World Experience: Developing Novel Sensors - An Interdisciplinary Approach

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Abstract:

The Development of environmental sensors to detect harmful heavy metals and phenols in water have been an increased concern in the last few years. Our interdisciplinary approach to an inquiry -based lab experiences with the development of modified electrode sensors to detect heavy metals and phenols simultaneously without the need for prior separation has built a stronger tie to real world issues. The problem-based approach of how to develop an electrochemical sensor for heavy metal detection has gained momentum due to increased exposure to Lead (Pb) and Cadmium (Cd). Pb and Cd are neurotoxins in children with chronic exposure and there is a need for a reliable method to analyze heavy metals (Lead and Cadmium) in environmental and biological samples. Thus electrochemical techniques were integrated with the development of Carbon Nanotubes with selective polymers modified on to electrode surfaces with nanoparticles to enhance the detection of phenols and heavy metals will be discussed with real-world applications integrated with industry. The students have shown an enhancement in content knowledge gains with the problem-based real-world analysis of sensor development compared to the lecture based format of teaching. Also, students' collaboration among different universities/departments and industrial settings to learn novel instrumentation such as Scanning Electron Microscopy (SEM) have built upon their interdisciplinary approach as well.

Keywords: Inquiry-based learning, Real-world problem-solving, Problem-based learning, Environmental/medicinal sensors and Collaborative networking.

Introduction:

Our overriding goal for our undergraduate chemistry students are to engage into inquiry-based modules that have interest in the real-world. These real-world modules focus on development of environmental sensors to detect harmful heavy metals (Pb and Cd) and phenols in water to sensors on detection of our common neurotransmitters (biomedical sensors to detect catechol in presence of ascorbic acid). These problem-based labs have been extended to collaboration with other universities to ensure dissemination of the successful experiences gained in our undergraduate chemistry labs. Our students have gained insight into the various types of electrochemical techniques and higher technological instrumentation such as Scanning Electron Microscopy (SEM) used in the real-world settings with industrial collaboration with such industries as Bowser-Morner and AK Steel.

Our students have gained insight into the various types of electrochemical instrumentation such as Cyclic Voltammetry (CV), Square-Wave Anodic Stripping Voltammetry (SWASV), Differential Pulse Voltammetry (DPV) compared to various spectroscopic methods such as Inductively Coupled Plasma Mass Spectroscopy (ICPMS). The expensive maintenance and cost of ICPMS makes the inexpensive electrochemical voltammetric methods such as CV, SWASV, and DPV ideal for training students for the real-world analysis and simple instrumentation to solve detection of heavy metals to catecholamines without the need of prior separation. The voltammetric instrumentation offers on-site detection of contaminants in water with the need of prior separation and at a low cost for real-world analysis.

Lead (Pb) and Cadmium (Cd) pose great hazards to both human and environmental health and safety such as the most recent concern of Pb in the drinking water, Detroit Michigan.

The heavy metal contamination in waterways commonly is caused by industrial runoff and corrosion. Elevated concentrations and long term exposure to heavy metals can cause detrimental health effects such as renal damage, hypertension, and neurological disorders and developmental delays in children.

Carbon Nanotubes have attracted interest for over the last decade due to good electrode properties and petite size thus possible electrochemical sensor development for catecholamines to heavy metal detection. Carbon Nanotubes are light as a feather and 200 times stronger than steel thus utilized for such novel products as touch screens on cell phones. Due to these positive features carbon nanotubes (CNT) modified electrodes have expanded into uses as biosensors to detect medicinal and environmental compounds of interest with electrochemistry. CNTs have opened a new era in material science and these materials are used to enhance conductivity while using selective polymers as electrochemical sensors to detect common neurotransmitters (1,2-dihydroxybenzenes) to heavy metals such as lead and cadmium. These CNT modified electrodes: CNT-polyvinyl alcohol (PVA) electrode to detect 1,2-dihydroxybenzenes to phenol in the presence of ascorbic acid, poly-3-hexythiophene (P3HT) modified CNT electrode to detect heavy metal lead and polystyrene sulfonate (PSS)-Ag nanoparticle modified CNT electrode to detect lead and cadmium simultaneously with prior separation will be shown. Our understanding of CNT dispersed with certain polymers to selectively detect the chemical of interest and provided efficient hole or electron transport to successfully detect the compounds of interest. These inquiry-based educational research experiences have been beneficial in allowing expansion of content knowledge in the applications of CNTs while utilizing electrochemistry techniques such as cyclic voltammetry, differential pulse voltammetry and square wave anodic stripping voltammetry. The novel aspect of integrating CNT -PSS with nanoparticle incorporation to possibly further enhance the electrocatalytic activity of the electrode surface for heavy metal detection was carried out. In addition, our educational perspective from participating students content knowledge gains related to the CNT modified electrode labs from pre- and post-test assessments have shown enhanced content knowledge in electrochemical sensors.

Experimental:

A polished carbon electrode (1.6 mm) with the CNT-P3HT and the CNT-PVA was deposited onto the working electrode. Multiwalled carbon nanotubes (MWCNT) were purchased from Nano Lab, diameter 10-20 nm; length 5-20 μm with a purity of 95%. To make the dispersion of CNT-P3HT by mixing 20 mg MWCNT with 20 mg P3HT plus 20 mL tetrahydrofuran (THF) and ultrasonicated for 1 hr. To make a dispersion of MWCNT using PVA, 20 mg MWCNT was added to 20 mL of a 2.5% PVA aqueous solution and ultrasonicated for 1 hour. The suspension was drop casted on the bare carbon electrodes to make the MWCNT-PVA working electrode films. A three-electrode single compartment cell was utilized for the voltammetry studies with the platinum foil as the auxiliary and the reference was Ag/AgCl/3 M NaCl (MF-2074, BAS). Bioanalytical Systems Epsilon potentiostat-galvanostat instrument was utilized to carry out by cyclic voltammetry (CV), square wave anodic stripping voltammetry (SWASV), and DPV. PSS (poly(4-styrenesulfonic acid, sodium borohydride, 5% nafion solution, and silver nitrate from Sigma-Aldrich; 10 mg MWCNT's were dispersed in 10 mL of DI water with 0.3 mL of 18 wt. % PSS and 7.5 mg 5% Nation. 5.3 mg of silver nitrate was dissolved in the MWCNT dispersed followed by addition of 10 mg 10% sodium borohydride solution. Negative charged PSS layer on MWCNT attracted positive silver nanoparticles (10 nm).

Results and Discussion:

These inquiry-based lab experiences have assisted out students with solving detection of common neurotransmitters in the presence of common interferences to heavy metals without the need of prior separation will be shown below through Figures 1-5. Therefore, an urgent need to develop simple and affordable electrochemical sensors to detect common neurotransmitters in the presence of common interferences such as ascorbic acid (AA) will be displayed in Figure 1. As shown the success of the CNT-P3HT electrode by use of CPE to successfully detect the common neurotransmitter catechol in the presence of common interference AA. Figure 2 illustrates the DPV of a CNT-PVA electrode to detect a mixture of catechol and AA (5X concentration) in the mM concentration range without the need of prior separation. Figure 3 illustrates the SEM-EDX of the successfully modified CNT-P3HT carbon electrode. Figure 4 shows simultaneously the detection of Pb and Cd by SWASV with CNT-PSS-Ag modified electrode without the need of prior separation techniques, R^2 value about 0.95 with various deposition times. The SEM in Figure 5 of the CNT-PSS-Ag electrode morphology displays the distribution and character of the MWCNT's and the Ag nanoparticles throughout the PSS polymer coating.

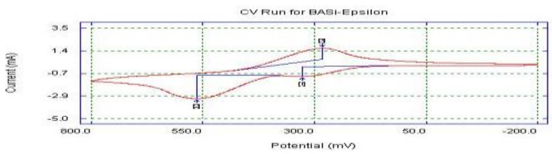

Figure 1. CV of CNT-P3HT by 1.4 V CPE of mixture 0.05 M catechol with 0.05 M AA in 0.1 M H_2SO_4, scan rate 100 mV/s.

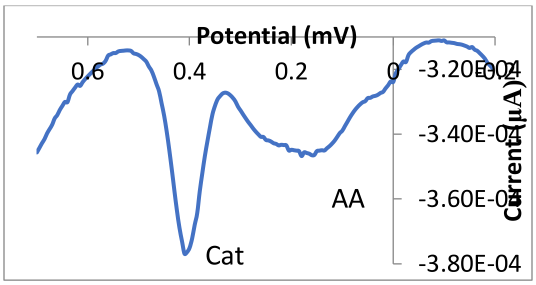

Figure 2. DPV for simultaneous detection of 0.1 mM catechol and 0.5 mM AA at CNT-PVA electrode.

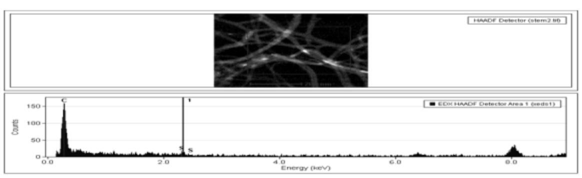

Figure 3. CNT-P3HT scanning electron microscope (SEM)-energy dispersive x-ray analysis (EDX) of CNT-P3HT electrode material.

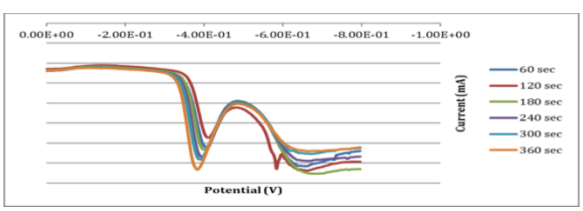

Figure 4. SWASV of CNT-PSS-Ag ; 10 ppm of Cd and 10 ppm of Pb-mixture with varying deposition times; Pb peak -500 mV and Cd peak -700 mV.

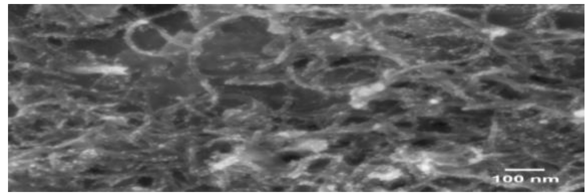

Figure 5. SEM image of Ag-PSS-CNT electrode surface.

Conclusion:

CNT-P3HT electrodes have been expanded into the detection of common neurotransmitters such as catechol in the presence of common interferences such as AA. These CNT-P3HT electrodes were coated by CPE at 1.4 V for 60 s, which illustrated effective detection of catechol without the need of prior separation by CV. The CNT-PVA electrode successfully detected catechol with AA five times more concentrated than catechol without prior separation utilizing the DPV technique.

The detection of heavy metals without the need of prior separation has been effectively achieved by the CNT-PSS-Ag electrode to detect Pb and Cd simultaneously by SWASV. SEM's have been provided to illustrate the successful growth of CNT materials and the EDX confirmed the conductive polymer P3HT was on the electrode surface by the presence of C and S. Our undergraduate students have found CNT modified electrodes to be excellent sensors to enhance the electrocatalytic activity of the electrode to detect specific compounds (1,2-dihydroxybenzenes to heavy metals) by various electroanalytical techniques. The use of SWASV has been found to be most suitable technique compared to DPV for heavy metal speciation in water. Therefore these lab experiences have been rewarding and achieved high gains in students content knowledge; above normalized gains of 0.7. These high gains greater than 0.7 are typical for pre-test and post-test analysis according to R.R. Hake in an inquiry-based setting for science experimentation. These real-world experiences have brought more interest to the students and have allowed our students to work with industry and collaborate with other universities to share their findings. Thus, our inquiry-based labs are building a stronger scientific network for our students to assist with the needed scientific skills for the 21st century industrial research positions.

References:

1.Stripping Voltammetry. 2008, 620, 44-49 http://ac.els-cdn.com/S000326700800932X/1-s2.0-S000326700800932X-main.pdf?_tid=03f86eec-f508-11e5-81a900000aacb360&acdnat=1459185228_011722abed0d22ff23e889a251e0b704 (accessed on Mar. 27, 2016).

2.Makelane, H.R.; Tovide. O.; Sunday, C.E.; Waryo, T.; and Iwuoha, E.I. Electrochemical Interrogation of G3-Poly(propylenethiophenomine) Dendritic Star Polymer in Phenanthrene Sensing. Sensors [Online] August 27, 2015, p 22343-22363.http://www.mdpi.com/1424-8220/15/9/22343/htm (accessed Mar. 27, 2016).

3.Spitalsky, Z.; Tasis, D.; Papagelis, K.; and Galiotis, C. Carbon Nanotube-Polymer Composites: Chemistry, Processing, Mechanical, and Electrical Properties. 2010, 35, 357-401 http://ac.els-cdn.com/S0079670009000859/1-s2.0-S0079670009000859-main.pdf?_tid=dae65e68-f509-11e5-b16900000aab0f02&acdnat=1459186018_cf59f0f619ff8c8f0a6818d735f0706f (accessed on Mar. 27, 2016).

4.Lin, Y.; Yantasee, W.; and Wang, J. Carbon Nanotubes (CNTs) for the Development of Electrochemical Biosensors. Frontiers Science [Online] 2005, 10, 492-505 https://www.researchgate.net/profile/Yuehe_Lin/publication/8154015_Carbon_nanotubes_(CNTs)_for_the_development_of_electrochemical_biosensors/links/0c9605167309cd7de8000000.pdf (accessed on Mar. 27, 2016).

5. Hake,R.R.,http://www.pkal.org/events/roundtable2002/papers.html. (June 2002).

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