Dual Detection of Nitrate and Mercury in Water using Disposable Electrochemical Sensors

Minh-Phuong N. Bui, John Brockgreitens, Snober Ahmed and Abdenmour Abbas*

*Department of Bioproducts and Biosystems Engineering, University of Minnesota Twin Cities, Saint Paul,
Minnesota 55108, United States*

*Corresponding author:

Dr. Abdenmour Abbas

Email: aabbas@umn.edu

Tel: 612-624-4292

Abstract

Here we report a disposable, cost effective electrochemical paper-based sensor for the detection of both nitrate and mercury ions in lake water and contaminated agricultural runoff. Disposable carbon paper electrodes were functionalized with selenium particles (SePs) and gold nanoparticles (AuNPs). The AuNPs served as a catalyst for the reduction of nitrate ions using differential pulse voltammetry techniques. The AuNPs also served as a nucleation sites for mercury ions. The SePs further reinforced this mercury ion nucleation due to their high binding affinity to mercury. Differential pulse stripping voltammetry techniques were used to further enhance mercury ion accumulation on the modified electrode. The fabricated electrode was characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and electrochemistry techniques. The obtained results show that the PEG-SH/SePs/AuNPs modified carbon paper electrode has a dual functionality in that it can detect both nitrate and mercury ions without any interference. The modified carbon paper electrode has improved the analytical sensitivity of nitrate and mercury ions with limits of detection of 8.6 μM and 1.0 ppb, respectively. Finally, the modified electrode was used to measure nitrate and mercury in lake water samples.

Keywords: mercury detection, nitrate detection, gold nanoparticles, selenium nanoparticles, disposable electrodes, electrochemical sensors.

1 Introduction

Contaminants in rivers, lakes, and drinking water are a serious environmental problem and have been a major concern for many researchers all over the world. It is extensively recognized that heavy metals are the cause of many disorders in plants, animals, and humans as these metals bio-accumulate in food chains and threaten both human and ecological health (Aragay et al., 2011; Yantasee et al., 2007). Mercury is considered one of the most hazardous heavy metal pollutants because of its toxicity and the mobility of its species throughout different environmental systems. Nitrate contamination also continues to be a problem for the world given the increased use of nitrate fertilizers in agricultural fields leading to runoff levels exceeding the maximum contaminant level defined by the US Environmental Protection Agency (EPA) (Kanter et al., 2015). This nitrate runoff leads to many water quality issues like eutrophication, and it can affect human health if it contaminates drinking water supplies. As a result, the development of simple, highly sensitive, low cost, disposable sensors for nitrate and mercury ions is of continuing interest. For heavy metal detection, methods including atomic absorption spectrometry and induced coupled plasma mass spectroscopy have been widely used, although they require a controlled laboratory setting, sophisticated instrumentation, and long analysis times that incur high costs (Saitoh et al., 2002; Shkinev et al., 1989; Soylak et al., 2005). In addition, functionalized gold nanoparticles (AuNPs) have been widely used in the colorimetric detection of nitrate and mercury (Hung et al., 2010; Mura et al., 2015; Wang et al., 2008). Although selective testing of nitrate and mercury can be accomplished via colorimetric methods, it requires complicated spectrophotometric instrumentation for readout and quantitative analysis (Daniel et al., 2009). Selenium-based materials have demonstrated an extremely high affinity for mercury ions and were used in removing mercury vapor for stockpile stabilization and long-term storage

(Jiang et al., 2012; Ke et al., 2014; Khanna et al., 2015). In the environment, selenium sequesters mercury into an insoluble form ultimately reducing its mobility, bioavailability and ecotoxicity (Johnson et al., 2008; Newland et al., 2006; Skerfving, 1978).

Electrochemical methods offer a useful approach over conventional methods, and through research, these techniques are continuously achieving higher sensitivities and greater selectivity for the inexpensive detection of heavy metals as well as nitrate ions in environmental and medical settings (Gross et al., 2015; Mikkelsen and Schröder, 2001; Shen et al., 2015). Nanomaterials have been widely used to improve electrochemical sensing platforms for heavy metal detection since they form unique three-dimensional structures that provide a large reactive surface area that improves both sensitivity and selectivity (Bui et al., 2012; Gong et al., 2010; Zhang et al., 2015). Electrochemical methods are often faster, cheaper, and safer analyses that can be conducted on-site without complicated equipment. Among the variety of techniques used in electrochemical sensing, differential pulse voltammetry (DPV) has been recognized as one of the most sensitive techniques due to its favorable portability, suitability for automation, short analysis time, and inexpensive instrumentation (Li et al., 2011; Zhang et al., 2011). Here, we demonstrate the fabrication of a simple, disposable electrochemical sensor on carbon print paper with the capability to analyze both nitrate and mercury ions in lake and drinking water. The electrode was fabricated on disposable paper with the combination of selenium and gold nanoparticles. Selenium particles (SePs) act as an absorbing agent for mercury while the AuNPs catalyze the reduction of nitrate and mercury ions. Our pre-synthesized selenium particles (200 nm to 1 μ m in diameter) were deposited on the layer of poly(ethylene glycol) methylether thiol (PEG-SH) coating carbon paper electrode. AuNPs (12 $\pm$ 2 nm in diameter) were then deposited on the electrode surface. This deposition was facilitated by the high binding affinity of AuNPs to

the thiol groups on PEG-SH (Smith et al., 2015). The approach takes advantage of the high adsorption of SePs to mercury ions to enhance the anodic stripping voltammetry of mercury, which occurs on the surface of AuNPs. Furthermore, the usage of AuNPs could serve a secondary function as a catalyst for the reduction of nitrate ions. DPV was used to detect nitrate ions while differential pulse stripping voltammetry (DPSV) was used to measure mercury ions (Scheme 1). We found that the disposable electrodes described here provided high sensitivity for the dual detection of both nitrate and mercury ions in a broad linear range.

Scheme 1. Schematic illustration of the fabrication process and reactions occurring on the modified PEG-SH/SePs/AuNPs paper electrode. A PEG-SH/SePs/AuNPs-functionalized electrode was employed for the detection of nitrate and mercury ions.

2 Materials and Methods

2.1 Reagents and instruments.

Mercury chloride, ammonium nitrate, gold (III) chloride trihydrate (99.99%), trisodium citrate, potassium chloride, hydroquinone, selenium acid (98%), sucrose (99.5%), hydroquinone (99%), poly(ethylene glycol) methylether thiol (PEG-SH, $M_n=5000$ Da) were purchased from Sigma-Aldrich (St Louis, MO, USA). The print carbon paper electrodes were purchased from CH Instrument. Inc, (Austin, TX, USA). Electrochemical measurements were carried out using an electrochemical workstation (CHI 660E, CH Instruments Inc., USA). The morphology of the AuNPs was characterized by transmission electron microscopy (TEM, Technai T12). Selenium nanoparticles were synthesized according to literature with a slight modification (Zhang et al., 2004). The electrode morphology was characterized by a field emission scanning electron microscope (FE-SEM, JEOL 6500) equipped with an energy dispersive spectrophotometer.

2.2 Synthesis of AuNPs and SePs.

Gold nanoparticles were synthesized based on a modification of Turkevich's method using citrate as a stabilizing agent (Demirci et al., 1978; Enustun and Turkevich, 1963; Turkevich et al., 1951). Briefly, a 100 mL solution of 1 mM HAuCl_4 was boiled under stirring and uniform temperature until the formation of bubbles was observed. The solution was then heated for another 25 min. Then, 10 mL of preheated trisodium citrate (38.8 mM) was quickly added to the boiling HAuCl_4 solution. During this process, the solution turns colorless for a moment followed by a transition from violet to dark ruby/red. The solution was heated for another 5 min before cooling to room temperature. The final red solution of AuNPs was stored at room temperature and covered with aluminum foil. The AuNPs were found to be 12 ± 2 nm in diameter.

Selenium particles were synthesized in solution by adopting the procedure described by Kumar et al. (Kumar et al., 2014). Briefly, 100 mL of selenous acid (1.4 M) and 50 mL of hydroquinone (2.2 M) were prepared in nanopure water. Then 10 mL of 25% sucrose was added to the solution of selenous acid. The selenous acid/sucrose solution was then quickly added to the hydroquinone solution, which was previously heated to 65°C with stirring for 10 min. The mixture was stirred at 65°C for another 20 more minutes to ensure the complete reduction of selenous acid to selenium nanoparticles.

2.3 Fabrication of the carbon PEG-SH/SePs/AuNPs paper electrodes.

The PEG-SH/SePs/AuNPs modified paper electrodes were fabricated on disposable paper print carbon electrodes using a drop-casting method. Briefly, the print carbon paper electrode was cleaned several times with nanopure water and was dried under nitrogen before modification. Then, 0.125 M PEG-SH solution was deposited on print carbon electrodes for 30 min at room temperature. After quickly washing with nanopure water, the pre-synthesized SePs solution (centrifuged 3 times and re-dispersed in nanopure water) was dropped cast (20 µL) on the surface of the PEG-SH electrodes. The solution was dried at room temperature then 20 µL of AuNPs solution (12 ± 2 nm in diameter) was deposited on the electrode. The film was set to air dry and washed two times with nanopure water. All electrodes were stored at room temperature in a covered petri dish and cleaned with nanopure water before each measurement.

2.4 Electrochemical characterization and measurement.

Cyclic voltammetry (CV) was utilized to ascertain the deposition of the nanomaterials on the print carbon electrode using 5 mM $K_3[Fe(CN)_6]$ as a redox model in 0.1 M KCl solution. Differential pulse voltammetry (DPV) and differential pulse anodic stripping voltammetry (DPSV) were used for the detection of nitrate and mercury (Hg^{2+}) ions under optimum

conditions, respectively. For anodic stripping voltammetry, the electrode was treated with Hg^{2+} solution at a potential of 0 V for 10 min in a 0.1 M KCl electrolyte solution. The reduced form of mercury (Hg^0) was then stripped from the modified electrode by applying a positive-way potential scan from 0.0 V to 0.8 V. Using DPV, a negative-way potential scan was applied to the PEG-SH/SePs/AuNPs modified paper electrodes from 0.2 V to -0.8 V (pulse amplitude: 50 mV; pulse width: 0.05 s; pulse period: 0.5 s, sample period: 0.017 s). The potential in all experiments was reported in comparison to the Ag/AgCl reference electrode. Peak currents corresponding to different analyte concentrations were analyzed using Origin Pro v9.0 software (OriginLab Corp., USA). Oxygen was removed from all solutions with pre-purified nitrogen gas for 30 min before measurement.

2.5 Real samples collection and preparation.

Water samples collected from two different lakes in near St. Paul, MN, USA were used for environmental sample testing. The sample was filtered through 0.2 μm size filter paper and mixed with 0.1 M KCl electrolyte solution at a ratio of 1:1. The water samples were spiked with Hg^{2+} and NO_3^- . DPV and DPSV electrochemical techniques were used to electrochemically detect nitrate and mercury ions, respectively, at optimum conditions. The water samples were also analyzed using common commercial methods for comparison including atomic adsorption spectrometry (AAS) for mercury detection and flow injection analysis (FIA, Lachat Quikchem 8500, Hatch Company, USA) for total nitrate detection (Henriksen and Selmer-Olsen, 1970).

3 Results and discussion

3.1 Characterization of the PEG-SH/SePs/AuNPs modified paper carbon electrode.

We carried out the modification method to provide **densely packed**, strongly adsorbed nanoparticles on the surface of the carbon paper electrodes. As shown in Figure S1-A, the SEM images of the printed carbon layer **show that this base layer of the** paper electrode is porous in nature. As such, the carbon paper electrodes have to be modified with chemicals and/or nanoparticles to improve their surface properties and functionality (de Araujo and Paixao, 2014; Ge et al., 2014; Moorcroft et al., 2001). The water soluble, poly(ethylene glycol) methylether thiol provides more uniform adsorption surface on the carbon electrode and generates many thiol functional groups **that** interact with AuNPs (Figure 1-A). Although AuNPs have proven to be good catalytic nanoparticles and **have been** used in variety of applications (Jia et al., 2007; Lin et al., 2015; Xu and Han, 2004), stable modification of AuNPs on the electrode surface is still challenging. As shown in Figure 1-B, AuNPs are densely packed, homogenously distributed, and strongly adsorbed to the surface of the PEG-SH modified carbon electrode, thus providing a large reactive surface area **compared** to the non-modified carbon electrode as shown in Supplementary materials (Figure S1-B and S1-C). The modification of SePs on carbon printed electrode could increase their surface area. However, the heterogeneous size of our synthetic SePs might affect the electrochemical property toward mercury detection (Figure 1-C). It is worth noting that the size of AuNPs deposited here is around 12 ± 2 nm and the combination of AuNPs and SePs on the carbon paper electrode again yields a densely packed surface consisting of AuNPs on the carbon electrode and AuNPs on the SePs surface which served as dual functions for specific detection of nitrate and mercury ions, respectively (Figure 1-D). The atomic

composition of gold and selenium nanoparticles on the modified carbon paper electrode was further confirmed using energy-dispersive X-ray spectroscopy (EDS) (Figure S2).

Figure 1. SEM images of the modified carbon paper electrode surface with different materials: (A) PEG-SH, (B) PEG-SH/AuNPs, (C) PEG-SH/SePs, and (D) PEG-SH/SePs/AuNPs layers. The nanoparticle showed high density and strongly adsorption on the electrode surface. Insets are the higher magnification of the modified carbon electrode.

3.2 Electrochemical characterization of PEG-SH/SePs/AuNPs electrode.

The electrochemical performance of the fabricated PEG-SH/SePs/AuNPs electrode was evaluated by cyclic voltammetry (CV) measurements using the redox couple

$\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ as a model probe. Figure S3-A shows the cyclic voltammograms of the modified PEG-SH/SePs/AuNPs electrode in 10 mM KCl solution containing 2.5 mM of $\text{K}_3(\text{FeCN})_6$ at different scanning rates from 10 mVs^{-1} to 400 mVs^{-1} . A pair of well-defined, symmetric oxidation and reduction peaks was observed for the PEG-SH/SePs/AuNPs electrode at 0.187 V and 0.085 V, respectively. The electrical potential separation of about 102 mV on the PEG-SH/SePs/AuNPs electrode was lower than that of the PEG-SH/AuNPs modified electrode (112 mV) (Figure S4), both of which exhibit quasi-reversible electron transfer reactions. In addition, the anodic and cathodic peak current responses were linearly proportional to the square root of the scan rate ranging from 10 to 400 mVs^{-1} following the Randles-Sevcik equation. These responses also showed a diffusive controlled process on the PEG-SH/SePs/AuNPs electrode surface (Figure S3-B) (Bard and Faulkner, 2001).

Figure 2 showed the cyclic voltammograms of different modified electrodes in the absence (Figure 2-A) and presence of 5 mM NH_4NO_3 (Figure 2-B) and 5 ppm of HgCl_2 (Figure 2-C) in 0.1 M KCl solution. In figure 2-A, as expected, no redox peak was observed on the PEG-SH (curve a) and PEG-SH/SePs (curve b) modified carbon paper electrode both in the absence and presence of nitrate ions. The electrochemical response on PEG-SH/AuNPs and PEG-SH/SePs/AuNPs modified electrodes are more capacitive with larger current response (curve c and d, respectively). In the presence of NO_3^- ions (Figure 2-B), a clear redox peak was observed at 0.16 V and -0.47 V for the PEG-SH/AuNPs modified carbon paper electrode (curve c). The redox peak was further shifted to a more positive potential at 0.27 V and -0.38 V for the PEG-SH/SePs/AuNPs modified electrode (curve d). It should be noted that the reducing peak of nitrate ions took place at very low overpotential (-0.38 V) compared to the reduction peaks of Hg^{2+} ions (0.0 V and -0.18 V) as shown in Figure 3-C (curve b and d). The large differences in

the reduction peaks of NO_3^- and Hg^{2+} ions on PEG-SH/SePs/AuNPs modified electrodes are advantageous for the dual measurement of nitrate and mercury ions in its mixture solution.

Figure 2. Cyclic voltammograms of different modified electrodes in the absence and presence of nitrate and mercury solution: (A) in KCl 0.1 M; (B) NH_4NO_3 5mM in KCl 0.1 M; (C) HgCl_2 5ppm in KCl 0.1 M. (D) Different pulse stripping voltammetric responses of different modified electrodes in HgCl_2 4 ppm solution. (a) PEG-SH, (b) PEG-SH/SePs, (c) PEG-SH/AuNPs and (d) PEG-SH/SePs/AuNPs modified carbon paper electrodes, respectively.

In the case of mercury ions (Figure 2-C), a small oxidation peak was observed at 0.1 V corresponding to the oxidation of the Hg^{2+} ion after absorption on the surface of SePs. By

modifying the carbon paper electrodes with AuNPs, a higher electrocatalytic activity can be observed. A large oxidation peak at 0.52 V can be observed for the oxidation of Hg^{2+} ions on the surface of the AuNPs. Two reduction peaks can be clearly observed for the PEG-SH/SePs/AuNPs modified electrode (curve d). Although the oxidation peaks of Hg^{2+} on the PEG-SH/AuNPs and PEG-SH/SePs/AuNPs modified electrode are almost similar, we have found that the DPSV response of these electrodes were significantly different after allowing 600s for Hg^{2+} ion accumulation on the electrode surface (Figure 2-D, curve c and d). The peak current response at 0.52 V was further enhanced with the use of SePs on PEG-SH/SePs/AuNPs modified electrodes. A possible explanation comes from the high binding affinity of SePs to Hg^{2+} ions which is in good agreement with literature reports (Civin-Aralar and Furness, 1991; Dang and Wang, 2011; Shanker et al., 1996). The DPSV responses of Hg^{2+} ions on PEG-SH/SePs/AuNPs modified carbon paper electrode were slightly shifted towards a higher, positive potential at higher concentrations of Hg^{2+} .

3.3 Detection of nitrate ions.

Differential pulse voltammetry was used for the determination of nitrate ions in 0.1 M KCl solution. The PEG-SH/SePs/AuNPs electrodes were used for analysis at optimum DPV parameters. As shown in Figure 3-A, the electrode response of NH_4NO_3 at PEG-SH/SePs/AuNPs electrode showed an irreversible reduction peak at -0.31 V. The electrochemical reduction of nitrate to nitrite ions on the surface of the PEG-SH/SePs/AuNPs electrodes exhibited a two-electron transfer process, as shown in equation (1):

The reduction peak was slightly shifted a to negative potential at lower concentrations and increased linearly with nitrate concentration in the range of 16 μM up to 5 mM ($R^2 = 0.98$, $S/N =$

3, $n = 3$) (Figure 3-B). The limit of detection was calculated to be $8.6 \mu\text{M}$ for NO_3^- ions, which is far below the maximum nitrate level allowed in drinking water by the United States Environmental Protection Agency (EPA) (**).

Figure 3. (A) Differential pulse voltammograms obtained at the PEG-SH/SePs/AuNPs modified carbon paper electrode at different concentrations of NH_4NO_3 in KCl 0.1 M. (B) Calibration plot between the reduction peak current (i_{pc}) and the concentration (c). (C) Differential pulse stripping voltammetric responses of the PEG-SH/SePs/AuNPs modified carbon paper electrode at different concentrations of HgCl_2 in KCl 0.1 M solution. (D) The calibration plot shows the linear relationship between oxidation peak current (i_{pa}) and the concentration (c).

3.4 Detection of mercury ions.

Anodic stripping voltammetry is a common electrochemical technique usually used for detection of heavy metal ions. The pulse stripping technique is also known to provide higher sensitivity and greatly reduce signal background noise (Aragay and Merkoçi, 2012; Zhu et al., 2004). The process usually involves two major steps: (i) accumulation of heavy metal ions on the electrode surface at optimized potential and (ii) anodic stripping of the accumulated metal. The stripping signal current corresponds to the concentration of metal ions in solution. AuNPs are broadly used as catalysts for detection of different heavy metal ions in solution, however, the sensitivity of these systems greatly depends on the morphology, structure and density of AuNPs on the electrode surface (Aragay et al., 2011). Here, we take advantage of the high binding efficiency of SePs to Hg^{2+} ions to concentrate Hg^{2+} ions on the surface of the AuNPs modified carbon electrodes. AuNPs were chemically attached to the carbon surface via interaction with the thiol functional groups of polyethylene glycol. As expected, the DPSV responses of Hg^{2+} ions at the PEG-SH/SePs/AuNPs electrode in 0.1 M KCl showed approximately Gaussian stripping peaks and revealed favorable electro-analytical performance with well-defined and reproducible stripping signals. Optimum stripping voltammetry behavior of the PEG-SH/SePs/AuNPs electrode was investigated. Figure S5 shows the influence of deposition time and accumulation potential on the stripping peak current in response to Hg^{2+} ions. The optimized stripping potential was observed at 0.0 V at the PEG-SH/SePs/AuNPs electrode. A slight decrease of stripping peak current was found at lower negative potentials. However, a quick drop in the stripping peak current was found when the deposition potential was above 0.0 V indicating the incomplete reduction of Hg^{2+} ions on the electrode surface which weakens the stripping peak current (Figure

S5-A). Thus, an applied potential at 0.0 V was used as optimized. It is worth noting that the accumulation potential used here at 0.0 V will eliminate the reduction ability of NO_3^- ions in case of a sample mixture containing both NO_3^- and Hg^{2+} ions. The stripping peak current was also gradually increased after lengthening the Hg^{2+} accumulation time from 30 s to 700 s. A slight saturation was observed at 700 s (Figure S5-B). Considering the appropriate time required for analytical measurements in the field and the stability of our carbon paper electrode as well as the increasing of signal deviation after lengthening the deposition time, the parameters of 0.0 V deposition potential and 600 s accumulation time were used for all the stripping process of subsequent experiments.

The DPSV current responses for the detection of different Hg^{2+} ions concentration at PEG-SH/SePs/AuNPs electrode in 0.1 M KCl solution are shown in Figure 3-C. A well-defined stripping peak at 0.52 V with high current response was observed. The peak was slightly shifted towards a positive potential at higher concentration of Hg^{2+} indicating the enrichment of Hg^{2+} ions on the electrode surface by the SePs and its interaction with AuNPs. A good linear relationship in the range of 14 – 3500 ppb of Hg^{2+} ions was obtained. The limit of detection was calculated to be 1.0 ppb ($R^2 = 0.981$, $S/N = 3$, $n = 3$), which is well below the maximum contamination level of mercury in drinking water by United States EPA (*) and by the World Health Organization (***) (Figure 3-D).

3.5 Real sample analysis.

Lake waters from the St. Paul, MN (USA) area were used as a real sample matrix for the dual detection of nitrate and mercury. Water samples were spiked with NO_3^- and Hg^{2+} ions and analyzed using the fabricated sensor. The detection results presented in Table 1 showed high accuracy with favorable recovery percentages. Furthermore, the water samples were spiked with

different concentrations of NH_4NO_3 and HgCl_2 and analyzed using FIA and AAS techniques for nitrate and mercury, respectively. The results were calculated and presented in Table 2. The fabricated PEG-SH/SePs/AuNPs electrode **are comparable** with conventional methods without influence in the detection of either NO_3^- or Hg^{2+} ions in the sample mixture (Figure S6). **Although our fabricated sensor is disposable, we have found that the electrode is rather stable as measurements were still 75 ± 2 % accurate even after 20 successive measurements.**

Table 1. Determination of nitrate and mercury ions on the PEG-SH/SePs/AuNPs electrodes in lake water samples. DPV and DPSV techniques were used for detection of NO_3^- and Hg^{2+} ions, respectively.

Samples	Amount added		Test results		Recovery
	NO_3^- (mM)	Hg^{2+} (ppm)	NO_3^- (mM)	Hg^{2+} (ppm)	$\text{NO}_3^- : \text{Hg}^{2+}$ (%)
Lake water 1	3.0	1.0	3.2 ± 0.2	0.8 ± 0.2	$107 \pm 7 : 80 \pm 20$
Lake water 2	3.0	0.7	3.3 ± 0.7	0.6 ± 0.1	$110 \pm 23 : 86 \pm 14$
Lake water 3	3.0	0.5	3.4 ± 0.6	0.4 ± 0.1	$113 \pm 20 : 80 \pm 20$

Table 2. Comparison of electrochemical **methods** on the PEG-SH/SePs/AuNPs electrodes using conventional methods. Lake water samples were spiked with different NO_3^- and Hg^{2+} ions concentrations. DPV and AAS were used for the detection of NO_3^- ions. DPSV and FIA were used for detection of Hg^{2+} ions, respectively.

Samples	Amount added		Conventional methods		Electrochemical sensor	
	NO_3^- (μM)	Hg^{2+} (ppm)	FIA (μM)	AAS (ppm)	DPV (μM)	DPSV (ppm)
Lake water 1	25	10	25.2	8.1	N/A	12.7 ± 0.5
Lake water 2	125	0.3	124.8	0.3	138.5 ± 1.8	0.4 ± 0.1
Lake water 3	250	0.5	233.7	0.7	291.6 ± 1.4	0.7 ± 0.1

4 Conclusions

We report the development of an electrochemical sensor with that can detect both NO_3^- and Hg^{2+} ions in water. SePs and AuNPs were synthesized and deposited on the surface of disposable carbon paper electrodes with PEG-SH as a linker. The modified electrode was characterized with SEM, XRD and electrochemical techniques. The electrode exhibited favorable electron transfer, high sensitivity and the ability to detect both Hg^{2+} and NO_3^- ions in water limits of detection of 8.6 μM and 1.0 ppb respectively. Finally, this electrode was successfully applied in real lake water samples. We believe our PEG-SH/SePs/AuNPs electrochemical sensor holds great potential for the simultaneous detection of nitrate and/or mercury ions in drinking and environmental water samples.

Acknowledgments

This work was supported by the University of Minnesota MnDRIVE Robotics, Sensors and Manufacturing, the MnDRIVE Global Food Venture, and the USDA National Institute of Food and Agriculture, Hatch project 1006789.

Supplementary material. SEM images of AuNPs modified printed-carbon electrode with and without PEG-SH functionalization. EDS mapping atomic composition of different nanomaterials on the fabricated electrode. CV characterization of different modified electrodes in $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution. Optimization parameters of DSPV technique. DPV and DSPV techniques performed on real water samples containing a mixture of different nitrate and mercury concentration

References

- * <http://water.epa.gov/drink/contaminants/index.cfm>
 - ** <http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants>
 - *** http://www.who.int/water_sanitation_health/dwq/GDW8rev1and2.pdf
- Aragay, G., Merkoçi, A., 2012. Electrochim. Acta 84, 49-61.

- 1 Aragay, G., Pons, J., Merkoci, A., 2011. *Chem. Rev.* 111, 3433-3458.
- 2 Bard, A.J., Faulkner, L.R., 2001. *Electrochemical Methods: Fundamentals and Applications*, 2nd
3 Edition. John Wiley & Sons, Hoboken, New York.
- 4 Bui, M.-P.N., Li, C.A., Han, K.N., Pham, X.-H., Seong, G.H., 2012. *Anal. Sci.* 28, 699-704.
- 5 Cuvín-Aralar, M.L.A., Furness, R.W., 1991. *Ecotoxicol. Environ. Saf.* 21, 348-364.
- 6 Dang, F., Wang, W.-X., 2011. *Environ. Sci. Technol.* 45, 3116-3122.
- 7 Daniel, W.L., Han, M.S., Lee, J.-S., Mirkin, C.A., 2009. *J. Am. Chem. Soc.* 131, 6362-6363.
- 8 de Araujo, W.R., Paixao, T.R.L.C., 2014. *Analyst* 139, 2742-2747.
- 9 Demirci, S., Enustun, B.V., Turkevich, J., 1978. *J. Phys. Chem.* 82, 2710-2711.
- 10 Enustun, B.V., Turkevich, J., 1963. *J. Am. Chem. Soc.* 85, 3317-3328.
- 11 Ge, L., Yu, J., Ge, S., Yan, M., 2014. *Anal. Bioanal. Chem.* 406, 5613-5630.
- 12 Gong, J., Zhou, T., Song, D., Zhang, L., Hu, X., 2010. *Anal. Chem.* 82, 567-573.
- 13 Gross, A.J., Holmes, S., Dale, S.E.C., Smallwood, M.J., Green, S.J., Peter Winlove, C.,
14 Benjamin, N., Winyard, P.G., Marken, F., 2015. *Talanta* 131, 228-235.
- 15 Henriksen, A., Selmer-Olsen, A.R., 1970. *Analyst* 95, 514-518.
- 16 Hung, Y.-L., Hsiung, T.-M., Chen, Y.-Y., Huang, Y.-F., Huang, C.-C., 2010. *J. Phys. Chem. C*
17 114, 16329-16334.
- 18 Jia, F., Yu, C., Ai, Z., Zhang, L., 2007. *Chem. Mater.* 19, 3648-3653.
- 19 Jiang, S., Ho, C.T., Lee, J.-H., Duong, H.V., Han, S., Hur, H.-G., 2012. *Chemosphere* 87, 621-
20 624.
- 21 Johnson, N.C., Manchester, S., Sarin, L., Gao, Y., Kulaots, I., Hurt, R.H., 2008. *Environ. Sci.*
22 *Technol.* 42, 5772-5778.
- 23 Kanter, D.R., Zhang, X., Mauzerall, D.L., 2015. *J. Environ. Qual.* 44.
- 24 Ke, J., Li, X., Zhao, Q., Hou, Y., Chen, J., 2014. *Scientific Reports* 4, 5624.
- 25 Khanna, P.K., Bhanoth, S., Dhanwe, V., Kshirsagar, A., More, P., 2015. *RSC Advances* 5,
26 92818-92828.
- 27 Kumar, A., Sevonkaev, I., Goia, D.V., 2014. *J. Colloid Interface Sci.* 416, 119-123.
- 28 Li, H., Li, J., Yang, Z., Xu, Q., Hou, C., Peng, J., Hu, X., 2011. *J. Hazard. Mater.* 191, 26-31.
- 29 Lin, Y., Peng, Y., Di, J., 2015. *Sens. Actuators, B* 220, 1086-1090.
- 30 Mikkelsen, Ø., Schrøder, K.H., 2001. *Electroanalysis* 13, 687-692.
- 31 Moorcroft, M.J., Davis, J., Compton, R.G., 2001. *Talanta* 54, 785-803.

1 Mura, S., Greppi, G., Roggero, P.P., Musu, E., Pittalis, D., Carletti, A., Ghiglieri, G., Irudayaraj,
2 J., 2015. *Int. J. Environ. Sci. Technol.* 12, 1021-1028.

3 Newland, M.C., Reed, M.N., LeBlanc, A., Donlin, W.D., 2006. *NeuroToxicology* 27, 710-720.

4 Saitoh, K., Sera, K., Gotoh, T., Nakamura, M., 2002. *Nucl. Instrum. Meth. B* 189, 86-93.

5 Shanker, K., Mishra, S., Srivastava, S., Srivastava, R., Dass, S., Prakash, S., Srivastava, M.M.,
6 1996. *Food Chem. Toxicol.* 34, 883-886.

7 Shen, J., Birdja, Y.Y., Koper, M.T.M., 2015. *Langmuir* 31, 8495-8501.

8 Shkinev, V.M., Gomolitskii, V.N., Spivakov, B.Y., Geckeler, K.E., Bayer, E., 1989. *Talanta* 36,
9 861-863.

10 Skerfving, S., 1978. *Environ. Health Perspect.* 25, 57-65.

11 Smith, A.M., Marbella, L.E., Johnston, K.A., Hartmann, M.J., Crawford, S.E., Kozycz, L.M.,
12 Seferos, D.S., Millstone, J.E., 2015. *Anal. Chem.* 87, 2771-2778.

13 Soylak, M., Saracoglu, S., Divrikli, U., Elci, L., 2005. *Talanta* 66, 1098-1102.

14 Turkevich, J., Stevenson, P.C., Hillier, J., 1951. *Discuss. Faraday Soc.* 11, 55-75.

15 Wang, H., Wang, Y., Jin, J., Yang, R., 2008. *Anal. Chem.* 80, 9021-9028.

16 Xu, S., Han, X., 2004. *Biosens. Bioelectron.* 19, 1117-1120.

17 Yantasee, W., Lin, Y., Hongsirikarn, K., Fryxell, G.E., Addleman, R., Timchalk, C., 2007.
18 *Environmental Health Perspectives* 115.

19 Zhang, S.-Y., Zhang, J., Wang, H.-Y., Chen, H.-Y., 2004. *Materials Letters* 58, 2590-2594.

20 Zhang, Y., Liu, Y., Ji, X., Banks, C.E., Zhang, W., 2011. *Chem. Commun.* 47, 4126-4128.

21 Zhang, Y., Zeng, G.M., Tang, L., Chen, J., Zhu, Y., He, X.X., He, Y., 2015. *Anal. Chem.* 87,
22 989-996.

23 Zhu, N., Zhang, A., Wang, Q., He, P., Fang, Y., 2004. *Electroanalysis* 16, 577-582.

24