Supporting Information

In situ Preconcentration and Quantification of Cu$^{2+}$ via Chelating Polymer-Wrapped Multiwalled Carbon Nanotubes

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1. Methods regarding fabrication of the sensor and Surface Characterization of the sensor during the fabrication steps

1.1 Design and Fabrication of the electrodes for the sensor

The sensor devices were fabricated using several different material deposition techniques. Initially, the CAD-designed device configuration was laser cut into 127-µm-thick molybdenum (Mo) sheet using an Oxford Instruments Nd: YAG (1032 nm) laser to fabricate a stencil mask. Polyethylene terephthalate (PET) at 180-µm sheets were cut into 100-mm wafer disks and cleaned in isopropanol (IPA)-filled glass dish that was placed in a water sonication bath for 2 min. The PET wafers were then treated in a UV ozone chamber at a substrate temperature of 50°C for 5 min. The Mo stencil was then placed on the cleaned PET substrate which was then loaded into a Semicore sputter deposition system. Gold (Au) was then sputter-deposited up to a final film thickness of 100 nm through the stencil mask to fabricate the base metal electrodes into the desired device configuration. A silver/silver chloride (DuPont 5874) screen printable ink was then deposited onto the designated reference electrode of the 3 sputter-deposited Au electrodes. The Ag/AgCl layer was screen printed onto the end of the reference electrode next to the working electrode using a (ATMA OE 67) screen printer with a corresponding screen (stainless steel mesh 230 calendared with 0.0011” wire diameter) aligned to the Au electrodes, and thermally cured at 130°C (HIX Corporation NP-2410). An encapsulant (DuPont 5018) screen printable ink was then deposited to mask off the working counter and reference electrodes. The encapsulant layer was screen printed using a (ATMA OE 67) screen printer with a corresponding screen (stainless steel mesh 230 calendared with 0.0011” wire diameter) that aligned to the Au electrodes and cured under UV irradiation (Heraeus DRS 10/12 UV belt oven).

1.3. Raman spectroscopy and Atomic force microscopy (AFM)

Raman spectra were collected on a Raman Imaging Microscope with a 532nm laser at 1.0mW with a 1 second exposure time. AFM images were captured with e Bruker Dimension Icon AFM in ScanAsyst® mode using a tip with a 2 nm nominal tip radius. The AFM data were plotted and analyzed with Gwyddion software. Raw MWCNTs were dispersed in 1% SDS and sonicated with a probe-tip sonicator for 30 seconds. SDS-dispersed MWCNTs were deposited on a gold substrate coated with poly-L-lysine as described by Vater et al.[1] P4VP-coated MWCNTs were deposited directly onto the poly-l-lysine coated gold and dried.

1.4. Scanning electron microscopy and Energy Dispersive X-Ray Spectroscopy (EDX)

For these surface studies, raw MWCNTs were deposited on carbon tape and blown with compressed air to remove loose material. For the polymer wrapped MWCNT dispersions; a drop of the suspension in methanol deposited onto the carbon tape and dried under nitrogen. The surface was imaged with a Phenom ProX scanning electron microscope (SEM) using a backscatter electron detector with accelerating voltage 15kV and spot size of 3.0. Samples were mounted on carbon in a charge reduction sample holder and dried before imaging. EDX was captured with a silicon drift detector (SDD) with a detector at 15 kV. SEM imaging of carbon nanotubes was carried out with a FEI Nova NanoSEM 630 Field Emission scanning electron microscope using both a backscatter electron (BSE) and a secondary electron (SE) detector with accelerating voltages between 5 kV and 10 kV and spot sizes between 3.0 and 5.0. In order to minimize surface charging, samples were coated with a thin layer of gold (< 5 nm).
1.5. General electrochemical methods used with the copper sensor and calibration curves

Multiple experiments were conducted with the use of cyclic voltammetry (CV) and square wave voltammetry (SW). For CV the scanning range from -0.6 V to 0.6 V was used (Figure 6 shows a representation of the sensor setup). This range enabled us to monitor the events related to copper oxidation and reduction. The scan rate of 50 mV/sec was used to obtain a better quality reading and voltammograms. As for square wave voltammetry 5 second equilibration time was used. The scanning range was set to -0.6 V to +0.6 V, with a 0.001 V step increment, 0.025 V amplitude and frequency of 25.0 Hz. For these studies 0.1 M NaNO₃ supporting electrolyte was used. The sensor does work without a supporting electrolyte but the voltammograms are not as well defined compared to when the supporting electrolyte was used. To perform the calibration regarding the copper sensitivity, copper was sequentially added with a 10-minute interval to accommodate stable equilibrium. With each addition of copper, CV was recorded and peak currents were used at specific voltages to obtain a calibration curve for different oxidation and reduction events present from copper.

**Figure S1.** (A) Change in contact angle with time with the exposure to UV/Ozone treatment of PET sensors, (B) Oxidation initiated by the UV/Ozone treatment

**Figure S2.** Contact angle measurement on the gold surface before, after treating with UV/Ozone and after treating with APTES and APTmbr solution for 48 hours.
Synthetic step of sensor fabrication | Contact angle value
---|---
PET films without gold before any modification | 80-83
PET films with gold before any modification | 58-65
PET films with gold after 120 mins in UV/Ozone | 20-30
PET films with gold after APTES treatment | 9-15
PET films with gold after MWCNT-COOH spray coating (No copper) | 44-48
PET films with gold after MWCNT-COOH spray coating (With copper) | 41-45

**Table S1.** Comparison of Contact angle measurement for each synthetic step

![PET surface: After UV/Ozone treatment for 120 mins](image1)

![PET surface: After APTES treatment](image2)

**Figure S3.** Contact angle measurement on the PET surface before and after treating with APTES and APTmbr solution for 48 hours

![FT-IR absorbance spectra before and after APTES/APTM Br treatment](image3)

**Figure S4.** FT-IR absorbance spectra before and after APTES/APTM Br treatment
- ICP-MS studies for Cu$^{2+}$ ion binding towards to PVP polymer

- Method for ICP-MS studies:

The sample set was analyzed for the full suite of TAL metals by Inductively Coupled Plasma Atomic Emission Spectroscopy and Mass Spectrometry following modifications of USEPA methods 6010 and 6020, respectively. The aqueous samples were diluted with ultrapure nitric acid in deionized water prior to an analysis. An 800 µL aliquot of sample was pipetted into 7.2 mL of 2% Optima Grade nitric acid in 15-mL test tubes (1:10 dilution). The samples were inverted until thoroughly mixed and then analyzed on a Perkin Elmer Optima 8300 Inductively-Coupled Optical Emission Spectrometer for Ca, Al, Na, K and Mg, with Sc and Y added on-line as internal standards to correct for instrumental drift. All other metals were analyzed on a Perkin Elmer NexION 350D Inductively-Coupled Mass Spectrometer using Ge, Y, Rh, In, Ho, and Bi as internal standards. The instruments were calibrated with NIST-traceable commercially available standards with calibration correlation coefficients greater than 0.999. Independent secondary source standards were used to verify the calibration accuracy, with recoveries within 10% of the nominal value. Continuing calibration verification standards were analyzed periodically throughout the analytical sequence, and yielded recoveries within 10% of the nominal concentration. Sample duplicates and matrix spikes were not able to be performed due to limited sample volume. However, method blanks all yielded either non-detects or J-values. All analytes in the Laboratory Control Samples were recovered within the acceptable range of ± 20%.

Figure S5. Binding curve for P4VP and Cu$^{2+}$ (For this work 1 g of the polymer was used with starting concentration of Cu$^{2+}$ being 50 ppm)
Figure S6. After adsorption of copper on to the sensor surface

| Element Number | Element Symbol | Element Name | Atomic Conc. | Weight Conc. |
|----------------|----------------|--------------|--------------|--------------|
| 6              | C              | Carbon       | 59.45        | 48.28        |
| 8              | O              | Oxygen       | 22.02        | 23.82        |
| 7              | N              | Nitrogen     | 14.30        | 13.54        |
| 29             | Cu             | Copper       | 2.41         | 10.34        |
| 16             | S              | Sulfur       | 1.36         | 2.95         |
| 14             | Si             | Silicon      | 0.44         | 0.83         |

Figure S7. (A) MWCNT-COOH in methanol without polymer wrapping after a few minutes, (B) MWCNT-COOH with P4VP polymer wrapped in methanol with 3 drops of Triton X-100 after 5 months
Figure S8. (From L to R) Before and after wrapping with PVP

Figure S9. SEM imaging and elemental analysis after UV/Ozone and APTES treatment
Figure S10. SEM imaging and elemental analysis after spray coating with P4VP wrapped CNT solution

| Element Number | Element Symbol | Element Name | Atomic Conc. | Weight Conc. |
|----------------|----------------|--------------|---------------|--------------|
| 6              | C              | Carbon       | 68.91         | 63.39        |
| 8              | O              | Oxygen       | 20.65         | 25.30        |
| 7              | N              | Nitrogen     | 10.33         | 11.08        |
| 14             | Si             | Silicon      | 0.11          | 0.23         |
• Details of the spray coating process, related calculations and MWCNT dispersions

![Image of spray coating process]

**Figure S11.** Crucial components of the Sono-Tek Exactacoat spray printer

2.1. Spray coating of the CNT based dispersion via automated spraying instrument

The printing of copper sensors was completed using the Sono-Tek Exactacoat spray printer. The Exactacoat is a benchtop system that can be programmed to spray consistent coats) and is paired with the Sono-Tek Impact ultra-sonicating nozzle. The nozzle produces a flat, fan-like spray that was controlled by the flow rate of the solution. The MWCNT dispersion is supplied via a syringe pump with a flow rate of 0.5 mL/min. The Impact nozzle atomizes the MWCNT dispersion that is then forced to the substrate by scrubbed house air at a rate of 0.6 L/min for consistent patterns of 1 cm width to ensure maximum coverage of each coating. Each sensor was coated in 30 layers of CNT dispersion. The nozzle was located 45 mm above the machined stencil that covered the PET substrate. The substrate rested on the existing hot plate and was set to a temperature of 60 °C for the annealing of the CNT dispersion to the substrate while evaporating the excess methanol from the surface.
The calibration curve of P4VP-MWCNT in methanol in Figure S10 was used to calculate the concentration of the P4VP-MWCNT dispersion after centrifugation. A 10x dilution of the centrifuged dispersion had an absorbance of 0.282. Factoring for the dilution and using the slope equation presented in Figure S13, the concentration of the centrifuged dispersion was calculated to be 2.52μg/mL. From this concentration we could calculate the areal density of the spray coating using the equation below.
The spray printer (Sonotek, Exactocoat,) was loaded with a CNT dispersion and sprayed through a nozzle (Sono-Tek, Impact) at a lowered 30 mm from the calibrated z direction at a rate of 0.5 mL/min (.0083 mL/s). A single pass of the print head covers a total surface area of 130.53 cm² in 24 s, giving an areal density that is dependent on the concentration of CNTs in the dispersion for each pass. 30 passes were used in the printing of these sensors. The areal density was determined to be 0.116 ug/cm².

2. Supplementary Electrochemical Studies

**Figure S14.** Complete CV w.r.t the calibration curve shown in Figure 5b

**Figure S15:** Calibration curves from cyclic voltammetry (CV) before EDTA (Blue) and after EDTA wash step (Orange)
Figure S16. The un-referenced CV was carried out using 0.1 M sodium sulfate as the supporting electrolyte, with a sweep rate of 0.1 V/s, using the modified PET printed electrodes. The cyclic voltammetric curves, 20 ppm each for Fe(II) (A), Ca(II) (B), and Pb(III) (C) (all blue) mixed in with 20 ppm Cu(II) ions. The cyclic voltammetric curve (D) is 10 mM Copper sulfate in 0.2 M Sodium sulfate from the literature is for comparison drawn as cartoon representation[2].

Figure S17: Calibration curve at lower concentrations of copper, 0 to 13.8 ppm monitored at -0.051 V
### Table S2. Spike study with different matrices

| Water Samples                     | Initial Concentration (ppm) found by ICP-MS | Added / spiked (ppm) | Found (ppm) via Sensor | Found (ppm) via ICP-MS | Recovery (%) |
|-----------------------------------|---------------------------------------------|-----------------------|------------------------|------------------------|--------------|
| Tap water (Vicksburg, MS)         | 0.025                                       | 1.06                  | 1.12                   | 1.30                   | 103.2        |
| Synthetic Ocean water             | 0.025                                       | 1.06                  | 1.02                   | 0.76                   | 94.0         |
| Durden Creek (Vicksburg, MS)      | 0.20                                        | 1.06                  | 1.30                   | 1.10                   | 103.2        |
| Tap water (Vicksburg, MS)         | 0.025                                       | 4.23                  | 4.21                   | 3.50                   | 98.9         |
| Synthetic Ocean water             | 0.025                                       | 4.23                  | 4.26                   | 3.70                   | 100.1        |
| Durden Creek (Vicksburg, MS)      | 0.20                                        | 4.23                  | 4.40                   | 3.80                   | 99.3         |

\[
\text{Recovery (\%)} = \frac{[\text{Found (ppm) via sensor}]}{[(\text{Initial concentration via ICP – MS}) + (\text{Added ppm})]} \times 100
\]

### References

[S1] W. Vater et al., “Scanning force microscopy of microtubules and polymorphic tubulin assemblies in air and in liquid,” J. Cell Sci., no. 108, pp. 1063–1069, 1995.

[S2] A. Jaikumar, S. G. K., K. S. V. Santhanam, I. B. P. Raya, and Raghupathi, “Electrochemical Deposition of Copper on Graphene with A High Heat Transfer Coefficient,” ECS Trans., vol. 66, no. 30, pp. 55–64, 2015.