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Electrochemical Sensors for Point-of-Care Measurements of Metals

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In this work, we report on development of a point-of-care sensor for electrochemical measurements of heavy metals. Our sensor features a new, low-cost electrode material—copper (Cu)—which offers simple fabrication and competitive performance in electrochemical detection. These features make our sensor suitable for disposable, point-of-care applications.

The Cu-based sensor is microfabricated with new material but traditional three-electrode layout. [1] A basic sensor consists of Cu working electrode (WE) and auxiliary electrode (AE), with a new $Cu/CuCl_2$ reference electrodes (RE). An interface for potentiostat connection through a mini USB cable is developed (Fig1.a). To perform electrochemical experiments, the sensor is simply inserted into connector. The Cu WE of the sensor provides potential window (Fig1.c) for detection of most metals, including lead (Pb) and zinc (Zn), using anodic stripping voltammetry (ASV) (Fig1.d) with low limit of detection (LOD).

For more electronegative metals, such as manganese (Mn), hydrolysis affects anodic stripping [2] and thus cathodic stripping voltammetry (CSV) is often a better choice. [3] Since Cu is oxidized at potentials more positive than -0.1V, it alone does not have the potential range for CSV. To address this, we electroplate palladium (Pd) on the WE to extend the potential window into the positive range (Fig1.c/e). The AE is also electroplated with Pd for longer pre-deposition time.

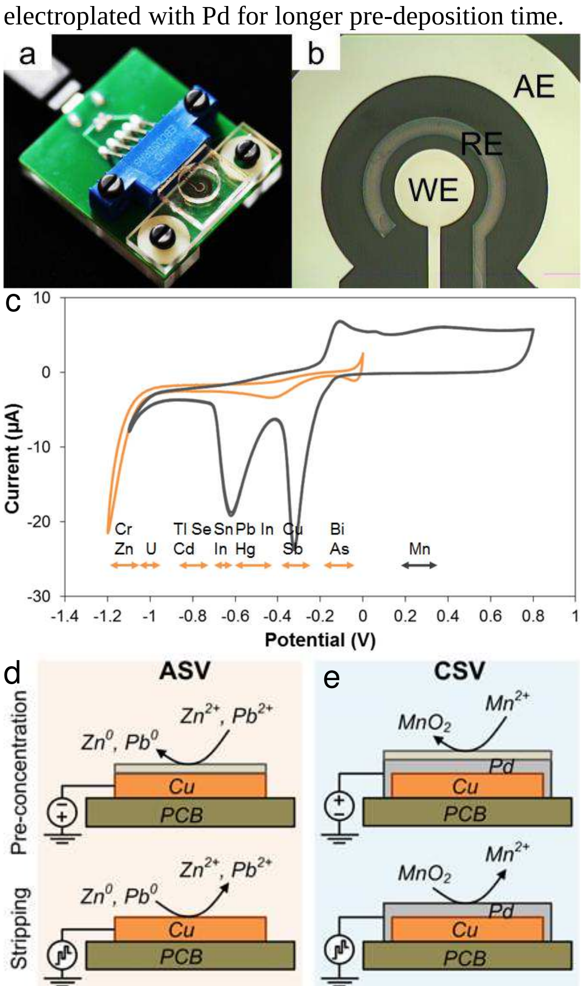

Fig1. a .Image of the sensor and interface. b.Image of the three electrodes of Pd-based sensor. c. Cyclic voltammetry (CV) of Cu-based sensor in acetate buffer and Pd-based sensor in borate buffer. Illustration of the two steps of d). ASV of Cu-based sensor and e) CSV of Pd-based sensor.

Both sensors offer great performance for metal detection in buffer and have been used for environmental [4,5] and biological [1] applications. The Cu-based sensor exhibits low LOD for Pb, measured at 21 nM (4.4 ppb) of ASV in acetate buffer, good sensitivity of 3.4 µA/µM, and good linearity (R^2=0.999) below 10 µM. ASV of Pb can provide stable response in environmental samples with no need of complex pretreatment and demonstrate there is no Pb contamination in river water sample (Fig2.a). For Mn, the Pd-based sensor exhibits LOD of 330nM (18.6ppb) in borate buffer, and sensitivity of 0.1µA/µM with linearity (R^2=0.986) below 10 µM. We use the Pd-based sensor to detect unknown Mn concentration in river water sample with standard addition approach (Fig2.b). The Mn concentration in Ohio River was calculated as 1.74µM (95.5ppb).

In addition to these environmental applications, we also have used the Cu-based sensors for detection of metals in biological samples, e.g., Zn in serum. [1] The sensor exhibits LOD of 91 nM (6.0 ppb) in acetate buffer, and is able to determine the concentration of Zn in serum 14.8 µM, which is within the physiological range.

In conclusion, we developed a new electrochemical sensor for heavy metal detections. We demonstrated the sensors for measuring Pb, Zn, and Mn in environmental and biological samples. The disposable sensors are low-cost and easy to fabricate, which are highly desirable for point-of-care applications.

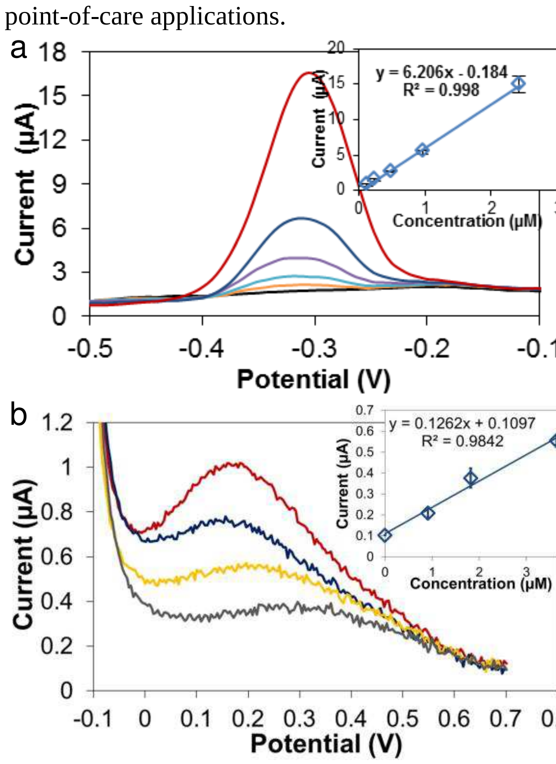

Fig2.a) ASV of Pb in Ohio River water. b) CSV of Mn in Ohio River water.

References

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