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PALLADIUM-BASED SENSOR FOR ELECTROCHEMICAL DETECTION OF MANGANESE IN THE ENVIRONMENT

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ABSTRACT

Herein, we report a palladium-based electrochemical sensor for cathodic stripping voltammetry (CSV) detection of highly electronegative manganese (Mn). The unique aspect of the sensor is the integration of electroplated palladium (Pd) working and auxiliary electrodes on copper (Cu) substrate with a new Cu/$CuCl_2$ reference electrode, which reduces cost and simplifies fabrication. The sensor was fully characterized and was found to exhibit a linear response in borate buffer with limit of detection (LOD) of 330nM (18.6ppb). The sensor also demonstrated successful measurement of Mn in river water, and ultimately may be extended to other environmental sample matrices.

KEYWORDS

Manganese (Mn), cathodic stripping voltammetry (CSV), palladium (Pd) electrode

INTRODUCTION

Mn is an essential element, that is critical to metabolism due to its involvement in enzyme activation; yet in high concentrations it is harmful because of the correlation with Parkinson's disease [1-2]. Monitoring Mn in the environment is critically important, especially since Mn-based additive MMT has replaced Pb in gasoline as antiknock agent, and is commonly used in rechargeable cellphone batteries. Guidelines for Drinking-Water Quality issued by the World Health Organization set the highest acceptable level of Mn to be 100ppb (1.82μM) [3].

The conventional methods for measuring Mn are atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectroscopy (ICP-MS) which provide high accuracy and sensitivity but are expensive and suffer from severe time delays due to shipping to a centralized lab. The need for a more rapid analysis approach has been driving developments in point-of-care portable instrumentation. Electrochemical techniques such as anodic voltammetry offer a viable alternative. While anodic stripping voltammetry (ASV) has been considered as the most widespread electrochemical sensing technique, some previous work on Mn has reported that the highly negative reduction potential of Mn does not fit the working ranges of most solid electrodes. Therefore cathodic stripping voltammetry (CSV) becomes an advantageous alternative to circumvent the high electronegativity issues.

CSV is performed in the opposite direction to ASV by pre-depositing at positive potentials, oxidizing free ions into metal oxides; and stripping in the cathodic direction to reduce them back into ions as illustrated in Fig. 1. This approach favors platinum, glassy carbon or boron-doped diamond as the electrode materials [1-2], but miniaturization of such electrodes remains challenging.

This novel sensor was based on our previously designed bismuth microelectrode which demonstrated good performances for ASV measurements of zinc, lead and cadmium, but the results for Mn were far from perfect due to challenges in Mn deposition and excessive electrolysis at negative potentials [4-5]. Copper electrode has also been explored for zinc measurements; however it is not suitable for CSV because of easy oxidation of Cu at positive potentials [6]. To broaden the potential window, we electro-deposited palladium (Pd) on Cu to make the working electrode (WE) and auxiliary electrode (AE), and we used Cu/$CuCl_2$ reference electrode (RE) to facilitate microfabrication. This Pd-based sensor exhibits favorable response in 0.1M pH9 borate buffer with limit of detection (LOD) of 330nM (18.6 ppb). It demonstrated successful detections of Mn concentration in local river water calculated as about 1.74μM (95.5μg/L) and we are optimistic about its performances in other similar environmental samples.

METHODS

The Pd-based microsensor includes electrodeposited Pd AE and WE on Cu substrate, and an integrated Cu/$CuCl_2$ RE. We deposited approximately 200nm copper with 20nm titanium seed layer by e-beam evaporation onto glass slides cleaned thoroughly using piranha solution.

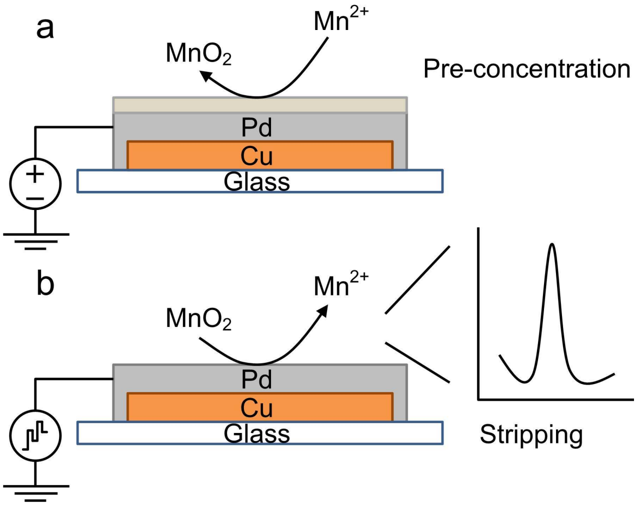

Figure 1: CSV of Mn on an electroplated Pd electrode: (a) pre-concentration step and (b) stripping step.

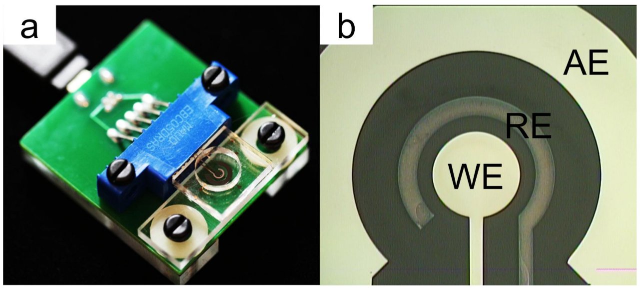

Figure 2: (a) Image of the interface between sensor and potentiostat. Sensor size: 15mm × 19mm. (b) Close-up of the three electrodes (WE = working electrode, RE = reference electrode, AE = auxiliary electrode).

Electrode patterns were created by photolithography followed by wet etching. We used standard soft lithography and plasma bonding technique to fabricate the PDMS sample layer. Then we electroplated about 100nm palladium onto copper electrodes by chronopotentiometry at 5mA/cm^2 current for 90 seconds to create WE and AE, and applied 3mA/cm^2 current for 30 seconds to chloridize Cu into Cu/CuCl$_2$ RE. The current density for Pd electroplating was specifically optimized to achieve high quality of Pd film and thus favorable stripping signals for Mn. To avoid thin Pd films being completely oxidized, all electroplating procedures were performed one day before experiments. Fig. 2 shows the edge-board connecter interface with a sensor inserted for easy connection with a potentiostat; and a microscopic view of three electrodes.

We characterized Pd electrode using cyclic voltammetry (CV) in 0.1M pH9 borate buffer and in buffer with Mn addition of 100ppm to obtain background and to estimate the position of Mn stripping peak. For cathodic stripping voltammetry, we did a series of optimization then selected 0.7V and 600s duration for pre-deposition parameters; default waveform parameters were used for the square wave: 25mV amplitude, 70ms period, and 4mV increment; and the stripping range was from 0.7V to -0.2V. Then we constructed the calibration plot ranging from about 10µM (600ppb or 600µg/L) to 460nM (25ppb); each data point included at least three independent measurements consuming one new device at a time, while the limit of detection (LOC) was calculated with seven repeats of the lowest measured concentration based on 3σ/slope.

To demonstrate the capability of the sensor to work in environmental matrices, we measured Mn in water samples collected from Ohio River shore (Newport, KY). Samples were diluted by factor of 2 with 0.2M pH9 borate buffer. Mn concentration was detected using standard addition approach by performing CSV of un-spiked diluted sample and samples spiked with 50ppb, 100ppb, 200ppb Mn at the same conditions as in buffer; we also repeated experiments for at least three times.

RESULTS AND DISCUSSIONS

Characterization of Pd Electrode

Performance of the Pd-based electrochemical sensor was first evaluated by cyclic voltammetry. Curve I in Fig. 3 exhibits the potential window of Pd electrodes from about -0.1V to over 0.7V in 0.1M pH9 borate buffer, which would properly fit cathodic stripping voltammetry. Curve II is the voltammogram of 0.1M pH9 borate buffer with presence of 100ppm Mn, illustrating Mn peak specifically. The double peaks overlapped in both curve I and II at about -650mV and -350mV are believed to be reduction peaks of Pd oxide formed at the positive end of the scan, while the peak occurred at about -100mV ~ 0V is considered as the reduction peak of Mn; these peaks have been further confirmed by the sequences in which they occured.

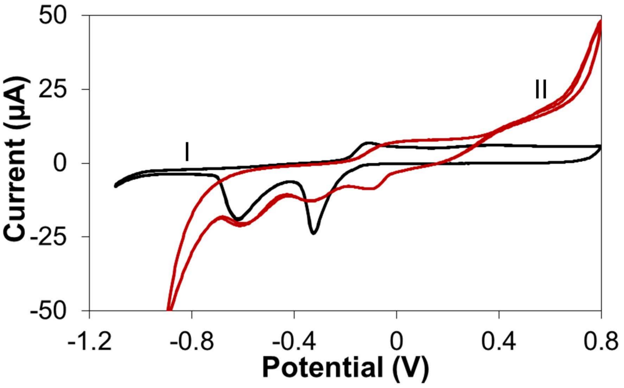

Figure 3: Cyclic voltammetry (CV) of electroplated Pd WE in I. 0.1M pH9 borate buffer; II. 0.1M pH9 borate buffer with additional100ppm Mn.

Optimization of CSV Parameters

We first determined the most suitable current density to deposit palladium film. Different currents from 700µA to 1mA were evaluated according to the film quality and morphology, and also peak heights of Mn stripping curves, as demonstrated in Fig. 4(a). The 1mA current could provide slightly thicker films than other currents, but the films looked burned to some extent and had curled edges which tended to peal under blowing nitrogen or running water, thus Mn stripping signals decreased a lot and had large variations. The 900µA current suffered from the same issue while 700µA current generated Mn stripping peaks with acceptable amplitude, but the error bar was not favorable. The 800µA current generated the largest signals while only had relatively small variations. The surface area of WE and AE altogether is 0.158cm^2, so the optimal current of 800µA is equivalent to 5mA/cm^2 in the format of current density.

We explored the influences of buffer pH on Mn stripping voltammograms from 8 to 9.75. Fig 4(b) shows we could hardly detect any Mn in pH8 buffer because the solution might be too acidic for Mn oxide to remain stable. pH8.5 buffer generated huge signal with enormous error bar. While pH9 remained the most suitable value in our case, compared to other more basic pHs.

We also examined and optimized the conditions to preconcentrate manganese. For predeposition potential, we examined 0.6V, 0.7V, 0.8V and 0.9V (Fig. 4(c)). It turned out that 0.6V was too negative to oxidize enough amount of Mn^{2+} into MnO$_2$; but Pd oxide formation became predominantly over 0.8V, and the peaks on the voltammograms shifted to 650mV instead of normal Mn peak potential which occurs around 250mV to 350mV. Thus we chose 0.7V which still fell in the range of

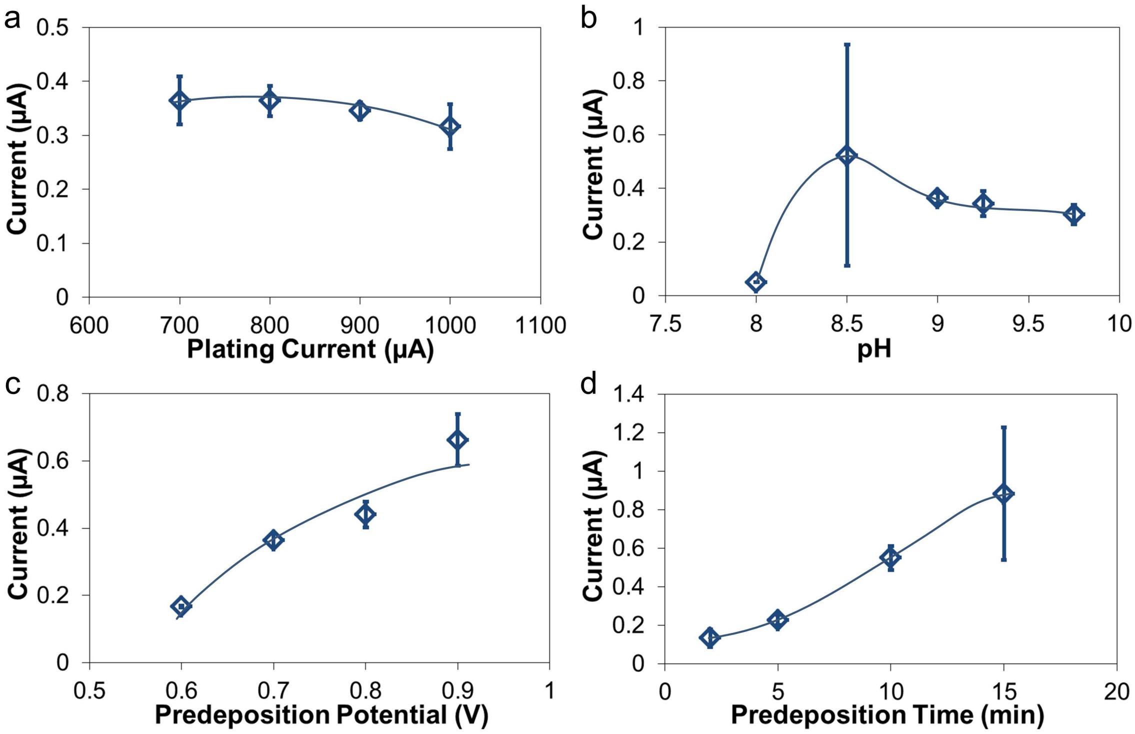

Figure 4: Optimization of parameters: (a) palladium electroplating current; (b) pH of borate buffer; (c) predeposition potential; (d) predeposition time.

generating Mn oxide not Pd oxide. In Fig. 4(d) we compared preconcentration time including 2min, 5min, 10min and 15min. We observed clear increase of Mn peak heights with longer deposition durations, but for 15min the thin Pd film could no longer protect Cu layer from being oxidized, the WE and AE became burned again. So apparently 10min was sufficient for this sensor.

For waveform parameters of the square wave, default settings of 25mV amplitude, 70ms period, and 4mV increment were used after attempts of optimization. If we adjusted the parameters, we might have increased the peak heights for some values, but all the alterations tended to distort the voltammograms, broaden the peaks or even create huge peaks in the background, making it challenging to subtract the valid Mn peak currents. Therefore we kept the default values for square wave.

Calibration of Pd WE in pH9 Borate Buffer

We calibrated the Pd electrode based on optimization results with parameters as followed: 800μA (5mA/cm^2) plating current, pH9 borate buffer, 0.7V predeposition potential with 10min duration. Waveform parameters for square wave were kept as 25mV amplitude, 70ms period, and 4mV increment. CSV in 0.1M pH9 borate buffer was performed in different concentrations of Mn: 600ppb, 300ppb, 200ppb, 150ppb, 100ppb, 75ppb, 50ppb and 25ppb to construct calibration curve. Fig. 5 exhibits favorable linear relationship between Mn stripping peak currents and Mn levels. Manganese peaks occurred at 250mV in higher Mn concentrations and shifted to 350mV in lower Mn levels. The shift might be due to reduction of tiny amount of Pd oxide formed on top of Pd electrode. Since a minor peak at 400mV in borate buffer background curve (black) could be observed, the peak itself was

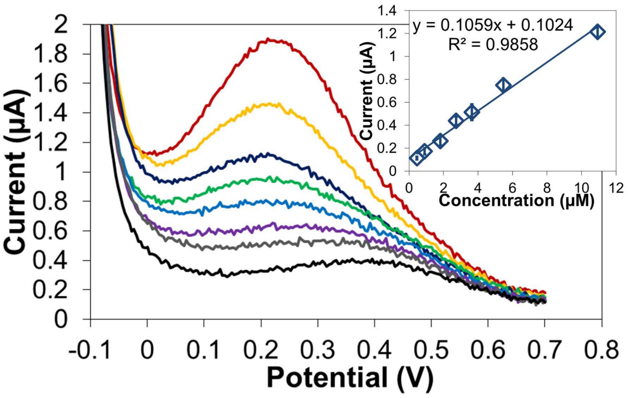

Figure 5: CSV of Mn in pH9/0.1M borate buffer, calibration curve is plotted after baseline subtraction, the limit of detection is calculated as 0.33μM (18.6ppb).

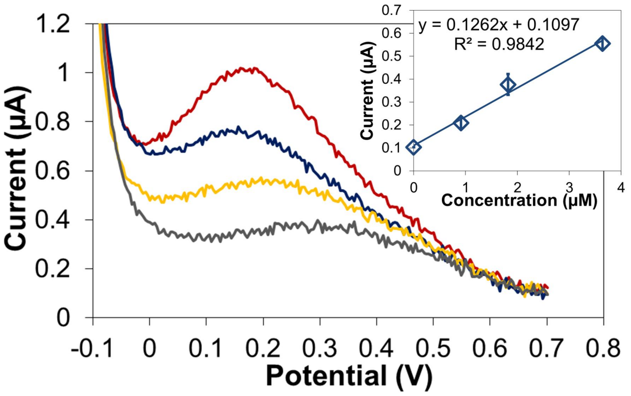

Figure 6: CSV of Ohio River water diluted with pH9/0.2M borate buffer by 1:1 and sample with Mn additions. Mn concentration is calculated as 1.74μM (95.5ppb).

attributed to Pd oxide only. As we added Mn, the stripping currents were based on both mechanisms; eventually when Mn levels were increased to a certain extent, the reduction of Mn oxide surpassed the reduction of Pd oxide, then Mn stripping became predominant and shifting the peaks to 250mV.

So we adopted a baseline subtraction method, which involved creating an average curve of all background curves from actual measurements, then subtracting it from every voltammogram. The resulted voltammograms were supposed to be related to reduction of Mn oxide only. After baseline subtraction, the LOD has been calculated as 330nM (18.6ppb) based on 3σ/slope, while the sensitivity is about 0.1µA/µM which may favor further improvement.

Manganese Detection in River Water

We used the Pd-based sensor to detect unknown Mn concentration in river water sample with standard addition approach. We collected water sample from the Ohio River shore (Newport, KY), then placed it still for 2 hours and collected the clear liquid to avoid impurities. Then we diluted the sample with 0.2M pH9 borate buffer by factor of 2 to match the ionic strength of 0.1M buffer. Some previous measurements failed because we used 0.1M buffer to dilute river water samples and found the working electrodes getting attacked from the edges, then Pd-films were complete stripped off. We speculated that the composition and conductivity of the diluted solution slightly differed from pure buffer; this difference might have caused bad connection issues around the edge areas and thus causing the destruction on WE.

CSV of un-spiked sample and samples spiked with 50ppb, 100ppb, 200ppb Mn were performed at the same conditions as in buffer. The voltammograms in Fig. 6 illustrates the Mn peaks are shifted 50mV negatively in average compared to Mn peaks in buffer; it might be because of the RE are potentially susceptible to the chlorides in natural waters. Other than that, the peak on the curve without Mn addition (grey) suggested baseline subtraction using the average curve acquired from buffer background as well, and the Mn concentration in Ohio River was calculated as about 1.74µM (95.5ppb).

CONCLUSIONS

We have demonstrated a Pd-based electrochemical sensor which consists of Pd WE and AE, and Cu/Cu_2 RE, for cathodic detection of Mn in river water. Compared with ASV, CSV has been reported as a promising alternative in detecting metals of high electronegativity. The microsensor is portable and disposable due to low cost materials and batch fabrication; it provides linear response and reproducible and robust performances in both borate buffer and buffer-diluted environmental sample, though there is still room for improving sensitivity and further reducing detection limits. This sensor would enable convenient on-site monitoring of Mn at low concentrations in many applications. Also the simple fabrication procedures of the sensor and the Cu substrate material would facilitate further integration with microfabrication techniques.

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