

# Conjugated Polymer Papers for Metal Ion Detection

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## ABSTRACT

It is of great importance to detect heavy metal ion in solution. Here, we describe the electrochemical detection of metal ions using polypyrrole/cellulose (PPCL) composite papers in both static and flow systems. A home-made electrochemical sensing device with a counter electrode and a reference electrode was fabricated to measure real-time sensor responses in flow systems. Simply, the conjugated polymer membranes had different chemical/physical properties by applying different potentials to them, which resulted in differentiable response patterns and adsorption efficiencies for individual metal ions. The sorption of metal ions by PPCL papers was examined in the flow system. The ability of the PPCL papers to recognize metal ions was examined in static and flow cells, in which real-time current change was monitored at five different applied potentials. Under different applied potentials, the conjugated polymer membrane gave rapid, selective, and quantitative responses to metal ions through principal component analysis. Particularly, the PPCL papers yielded unique signatures for three metal ions. Importantly, principal components analysis technique was employed to screen the unique response profile of the membranes to Hg(II), Ag(I), and Cr(III) ions from many response signals, even in a real sample, groundwater.

**Keywords:** metal ion detection, conducting polymer, polypyrrole, cellulose, composite paper

## 1 EXPERIMENTAL

### 1.1 Fabrication of PPCL composite papers

Cellulose paper was impregnated with 2 M ferric chloride aqueous solution and allowed to dry in a vacuum oven at 25 °C for 24 h. The cellulose paper was placed in a 60 mL-reactor chamber with two inlets and liquid monomer pyrrole (0.25 mL) was introduced at 70 °C. The polymerization proceeded in the sealed reactor for 2 h at the controlled temperature (70 °C). The resulting product was washed with distilled water and vacuum-dried for 24 h. The above synthesis condition was determined *via* an optimization process. Namely, the coating of polypyrrole was controlled by adjusting the reactor temperature and pyrrole input amount, and the resulting products were

characterized by the four-probe conductivity measurement and cyclic voltammetry analysis.

### 1.2 Detection and sorption of metal ions

PPCL paper was exposed to metal ions in a closed cell and a flow cell. Current changes were monitored in the cells with a Pt counter electrode and a Ag/AgCl reference electrode. In a closed cell, the PPCL paper was stuck onto a nickel plate electrode with the aid of carbon paste. A home-made flow cell whose counter and reference electrodes were equipped on blocks of Teflon cells was fabricated. Metal ion solutions were passed through the flow cell, in which the flow rate was regulated at 100 mL min<sup>-1</sup> using a peristaltic pump. PCA was conducted using the MATLAB software to examine the ability of the PPCL paper to discriminate between metal ions. The raw dataset contained two response magnitudes (maximum and saturated ones) measured with five different applied potentials for seven metal ions at six different concentrations. The dataset was thus used to construct a 42 × 10 matrix with the metal ions in rows and the response magnitude in columns. Sorption tests of metal ions were performed at three representative potentials, +1, 0, and -1 V (*vs.* Ag/AgCl), and inductively coupled plasma (ICP) analysis was conducted using an OPTIMA 4300 DV to calculate the adsorption efficiency of metal ions.

## 2 RESULTS AND DISCUSSION

Cellulose has a regular ring-structured linear chain with side hydroxyl groups, which allows the bundling of the polymer chains into a microfibrillar structure via strong intra- and inter-chain interactions. Cellulose architectures therefore feature high surface-to-volume ratios with robust structural property. These advantages make cellulose suitable for application in membranes and composites, as well as paper and textiles. In this work, the large-scale, uniform coating of conducting polymer polypyrrole on cellulose paper was successfully achieved using vapor deposition polymerization. Ferric ions as the oxidizing agent interact with the hydroxyl groups of cellulose *via* ion-dipole attraction. Vaporized pyrrole monomers can efficiently penetrate into the microstructure of the cellulose membrane, which allows the coating of a thin polypyrrole layer by chemical oxidation polymerization on the cellulose. Fig. 1a presents a photograph showing a flexible and free-

standing PPCL paper with a diameter of 5 cm. Black polypyrrole was easily coated on the large-area cellulose paper in a uniform manner. Fig. 1b displays scanning electron microscopy (SEM) images of the PPCL paper at different magnifications.

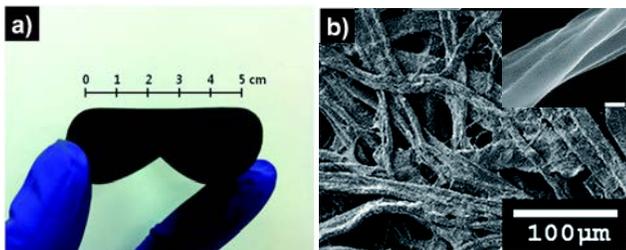


Figure 1: Formatting dimensions for manuscripts. (a) Photograph showing the flexibility of a large-area, free-standing PPCL paper. (b) SEM images of a PPCL paper (inset: high magnification image, the scale bar is 200 nm).

The ability of the PPCL paper to recognize metal ions was further examined in a flow system. A flow sensing cell was designed, as shown in fig. 2. The flow cell consisted of two Teflon blocks with an inlet/outlet and electrode holders, where the PPCL paper was inserted between the Teflon blocks. Tiny holes in the center of the Teflon blocks enabled a solution to flow through the PPCL paper. The real-time response was recorded under the same concentration and potential conditions as in the case of the closed cell. The real-time response curves and the sensitivity are given in Fig. 3 and 4, respectively. The response profiles changed overall. While the maximum response magnitude slightly decreased, the steady-state response considerably decreased. In particular, the response profiles of the PPCL paper to Hg(II) and Ag(I) in the flow cell were completely changed compared to those in the closed cell. Physical desorption of ions by external perturbation including mechanical vibration in the flow system might lead to the different response profiles. Upon cyclic exposure to metal ions, PPCL papers rendered reproducible responses more than five times without significant deviation (relative standard deviation: 2.8 to 6.5%).

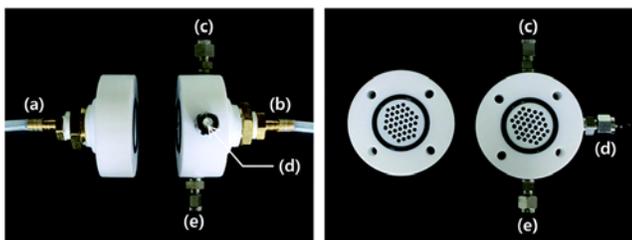


Figure 2: Formatting dimensions for manuscripts. (a) Photograph showing the flexibility of a large-area, free-standing PPCL paper. (b) SEM images of a PPCL paper (inset: high magnification image, the scale bar is 200 nm).

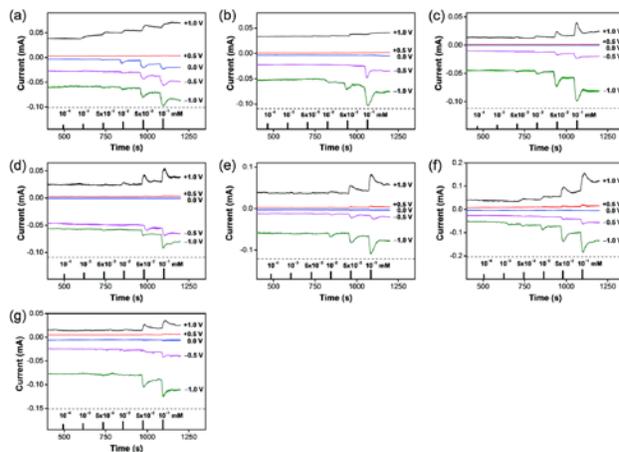


Figure 3: Real-time responses of PPCL papers in the flow cell measured at different applied potentials: (a) Hg(II), (b) Ag(I), (c) Pb(II), (d) Ni(II), (e) Cd(II), (f) Cr(III), and (g) Zn(II).

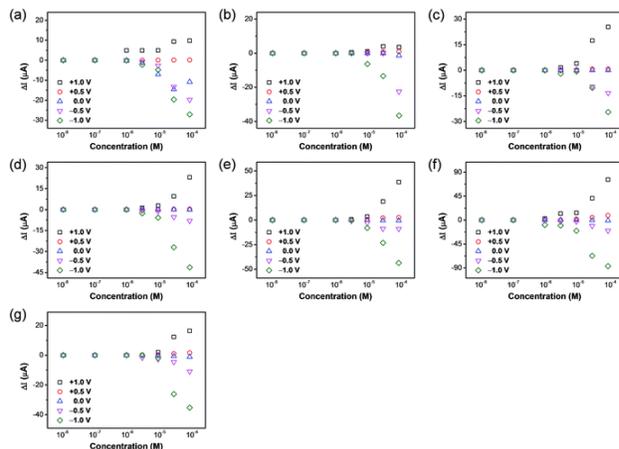


Figure 4: Changes in the sensitivity of PPCL papers as a function of metal ion concentration for the flow cell: (a) Hg(II), (b) Ag(I), (c) Pb(II), (d) Ni(II), (e) Cd(II), (f) Cr(III), and (g) Zn(II).

PCA was performed to the dataset obtained in the flow system and the results are presented in Fig. 4. The first three PCs accounted for 94.0% of the data variance. The PCA generated differentiable fingerprints for the metal ions in a manner analogous to that previously found for the closed cell. The separately plotted scores depending on the type and concentration of metal ions support the potential of this system for application in the detection of metal ions in the flow system. The categories Hg(II), Ag(I), and Cr(III) again particularly revealed unique signatures in the PCA plots, which further support the suitability of the PPCL paper for recognizing and quantifying the three metal ions.

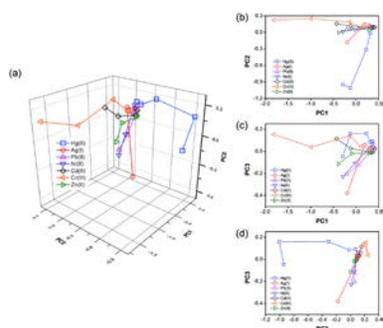


Figure 5: Changes in the sensitivity of PPCL papers as a function of metal ion concentration for the flow cell: (a) Hg(II), (b) Ag(I), (c) Pb(II), (d) Ni(II), (e) Cd(II), (f) Cr(III), and (g) Zn(II).

Polypyrrole has an unsaturated nitrogen atom in its repeating unit, which makes it a promising candidate for the adsorption or removal of metal ions from an aqueous solution. The nitrogen atom with unpaired electrons has the ability to form a chelate complex with metal ions that are Lewis acids.<sup>38</sup> Importantly, the electronic properties of the nitrogen atom change when an electrical potential is applied. Thus, the interaction between the PPCL paper and the metal ions depends on the applied potentials, which results in differentiable responses. For a greater understanding, the adsorption efficiency of the PPCL paper for metal ions was calculated by ICP analysis in the flow system. Fig. 6 shows the adsorption rates of metal ions on the PPCL paper measured at the applied potentials of +1, 0, and -1 V. The percentage adsorption of metal ions by the PPCL paper increased over time to a maximum and then finally reached an equilibrium state. The adsorption efficiencies depended on the kinds of metal ions. Particularly, the metal ions Hg(II), Ag(I), and Cr(III) showed good adsorption efficiencies at all applied potentials compared to the others. Depending on the applied potential, the adsorption of 74–83% Hg(II), 39–44% Ag(I), and 1–4% Cr(III) occurred within 5 min, while only 0–2% Pb(II), 0–4% Ni(II), 0–1% Cd(II), and 0% Zn(II) were adsorbed during the same period.

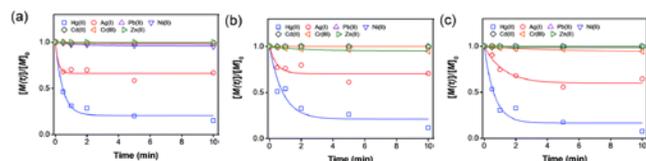
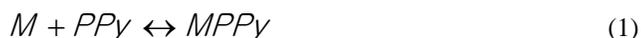


Figure 6: ICP adsorption curves of PPCL papers recorded at the applied potentials of (a) +1 V, (b) 0 V, and (c) -1 V.



where M, PPy, and MPPy represent metal ion, polypyrrole, and metal ion-bound polypyrrole, respectively. The rate equation for the above reaction is:

$$-\frac{d[M]}{dt} = k_f[M][PPy] - k_r[MPPy] \quad (2)$$

where  $k_f$  and  $k_r$  are forward and reverse rate constants, respectively. Integrating eqn (2) gives

$$[M(t)] = \frac{M_T + \{[1 + K_{eq}[PPy]] [M]_0 - M_T\} e^{-(k_f[PPy] + k_r/K_{eq})t}}{1 + K_{eq}[PPy]} \quad (3)$$

Here,  $K_{eq}$  is the equilibrium binding constant for metal ion and polypyrrole and  $M_T$  is the total metal ion concentration.

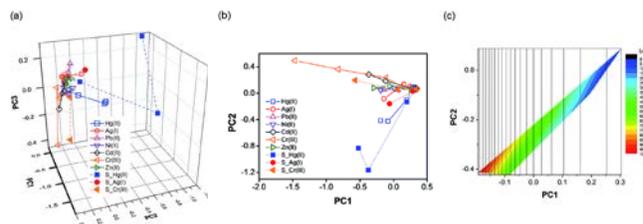


Figure 7: PCA plots of the responses of PPCL papers calculated with data from the real sample, in which the score points from the same metal ions were connected by a solid line (the existing dataset) or dotted line (the real sample) in the order of concentration: (a) 3D plot and (b) PC1–PC2 plane. (c) Calibration plot obtained from the PC1–PC2 plane to calculate Hg(II) concentrations in groundwater.

The ability of PPCL papers to detect metal ions was finally examined with a real sample, groundwater. The biocompatibility of PPCL composites has been demonstrated by Ferraz *et al.* Thus, it is believed that PPCL papers produce no toxic substances. The real-time responses toward the three metal ions, Hg(II), Ag(I), and Cr(III) were representatively measured using the flow cell. The selectivity of PPCL papers toward the three metal ions was found to be reasonably maintained even for the real sample (Fig. 7a and 7b). Particularly, an easy discrimination of Hg(II) from the metal ions was possible. Thus, a calibration plot was extracted from the PC1–PC2 plane to determine Hg(II) concentration (Fig. 7c) and well fitted to the following two-dimensional exponential function.

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