Electrocatalytic Determination of Cd$^{2+}$ and Pb$^{2+}$ using L-Cysteine Tungestophosphate Self-Assembled Monolayer on Polycrystalline Gold Electrode

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Supporting information

Characterization of the (Cys)PW

The results [%] of elemental analysis for (Cys)PW.9H$_2$O were theoretically calculated as: C, 3.33; S, 2.97; H, 0.65; N, 1.29; P, 0.95; W, 68.02 and they were experimentally found as: C, 3.31; S, 2.83; H, 0.68; N, 1.26; P, 0.96; W, 68.21. These values correspond to molar ratios of W:P = 11.9:1.0. It can be seen that during the functionalization of POM with Cys, the ratio of W:P is still 12:1, which indicated that the HPW did not change during the reaction.

In order to demonstrate whether Cys was functionalized on the POM, FT-IR measurements were recorded on the powder samples of parent POM, Cys-POM, and Cys as shown in Fig. 1S-A. The FT-IR spectra of HPW and (Cys)PW have four characteristic peaks related to: P-O$_a$, W-O$_{b,c}$-W, and W-O$_d$. Asymmetric stretching vibration peaks suggest that the POM moiety of the complexes still retains the basic Keggin structure form (Table 1S).

In comparison with the parent POM, bonds arising from the (Cys)PW were changed in position. This demonstrated an interaction between the nitrogen atom of the amino acid and the oxygen atom of the heteropoly acid $^1$. Furthermore, the obtained results are in good accordance with

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previous reports. In addition, the presence of Cys was confirmed through distinguishing peaks in the FT-IR spectrum around 1731, 1510, 1251, and 1137 cm\(^{-1}\) which are the characteristic peaks of COO\(^-\) stretching, C-O stretching, and C–N stretching vibrations, respectively. This information is given in Table 1S.

The UV-Vis absorption spectrum of HPW (Fig. 1S-B) displays two strong absorptions at 205 and 256 nm. The higher energy band was assigned to O\(_d\)→W charge transfer absorption band, whereas the lower energy band was attributed to O\(_b\)/O\(_c\)→W charge transfer transitions, which is characteristic of a Keggin type polyoxoanion. These absorption bands appeared at 210 and 260 nm for (Cys)PW. However, both absorption bands are red-shifted to the near-UV region. From the viewpoint of structural chemistry, the red-shift or blue-shift phenomenon of the O\(_d\)→W or O\(_b\)/O\(_c\)→W charge transfer absorption bands may be related to interactions between the polyoxoanions and organic cations (mainly including a static electronic interaction, covalent bonding interaction, and \(\pi-\pi\) stacking interactions).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\tilde{\nu})(COO(^-))</th>
<th>(\tilde{\nu})(CH(_2))</th>
<th>(\tilde{\nu})(C-O)</th>
<th>(\tilde{\nu})(C-N)</th>
<th>(\tilde{\nu})(P-O(_a))</th>
<th>(\tilde{\nu})(W-O(_d))</th>
<th>(\tilde{\nu})(W-O(_b)-W)</th>
<th>(\tilde{\nu})(W-O(_c)-W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPW</td>
<td>-</td>
<td>-</td>
<td>1079</td>
<td>972</td>
<td>887</td>
<td>753</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cys</td>
<td>1740, 1512</td>
<td>1432, 1400</td>
<td>1218</td>
<td>1138</td>
<td>-</td>
<td>-</td>
<td>887</td>
<td>753</td>
</tr>
<tr>
<td>(Cys)PW</td>
<td>1731, 1510</td>
<td>1470</td>
<td>1251</td>
<td>1137</td>
<td>1073</td>
<td>967</td>
<td>883</td>
<td>750</td>
</tr>
</tbody>
</table>

\(\tilde{\nu}\): Central oxygen
\(\tilde{\nu}\): Bridging oxygen
\(\tilde{\nu}\): Terminal oxygen
Fig. 1S (A) FT-IR spectra of HPW (a), Cys (b) and (Cys)PW (c) and (B) UV-Vis spectra of 35.7 mM HPW (a) and 35.7 mM (Cys)PW (b) in purified water.?
Surface morphologies and Energy dispersive analysis of X-ray spectroscopy (EDS) measurement of the modified electrode

Morphologies of the bare poly Au and poly Au-(Cys)PW SAM electrodes were characterized by FESEM and are shown in Fig. 2S-A and B(a–c), respectively. From the FESEM images (Fig. 2S-A), it can be seen that the surface of the bare poly Au electrode is smooth and homogeneous. This smooth surface was totally changed to a rough and heterogeneous surface after immobilization of (Cys)PW on the poly Au electrode (Fig. 2S-B, image (a)). From the FESEM images (Fig. 2S-B, images (b) and (c)), it can be observed that (Cys)PW is made up of nanoparticles in the form of a granular aggregate with particle sizes in the range of 65–76 nm.

The EDS of the bare poly Au and poly Au-(Cys)PW SAM (asterisk site in Fig. 2S-B, image (a)) electrodes are presented in Fig. 2S-A and B(d), respectively. The EDS analysis confirms the elemental composition, which reveals the existence of C, N, O, P, S and W elements on the gold surface. Moreover, the elemental mapping images also confirmed the immobilization of (Cys)PW on the poly Au electrode (Fig. 2S-B, images (e–k)).
Fig. 2S (A) FESEM images (a–c) and, EDS pattern (d) of a bare poly Au electrode and (B) FESEM images (a–c), EDS pattern of asterisk site (d), and EDS element mapping for different elements (e–k) of the poly Au-(Cys)PW SAM-modified electrode. 

**Table for EDS Analysis**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>6.31</td>
<td>21.29</td>
</tr>
<tr>
<td>N</td>
<td>0.76</td>
<td>2.11</td>
</tr>
<tr>
<td>O</td>
<td>27.71</td>
<td>98.86</td>
</tr>
<tr>
<td>P</td>
<td>1.06</td>
<td>3.38</td>
</tr>
<tr>
<td>S</td>
<td>0.94</td>
<td>0.31</td>
</tr>
<tr>
<td>W</td>
<td>87.81</td>
<td>14.90</td>
</tr>
</tbody>
</table>

Totals 100 100
Electrochemical characterization of the modified electrode

Because POMs have good redox activity and are extensively used as electrocatalysts, various electrochemical methods were chosen to verify the formation of the poly Au-SAMs in this work. The number of total active sites was estimated by using the oxidation-reduction behavior of poly Au in H$_2$SO$_4$ (0.5 M). Voltammetric formation–reduction of gold oxide on bare poly Au, poly Au-Cys SAM, poly Au-HPW SAM, and poly Au-(Cys)PW SAM electrodes in H$_2$SO$_4$ (0.5 M) are displayed in Fig. 3S-A. According to Fig. 3S-A, as expected, the gold oxide reduction peak current, in comparison with the bare poly Au electrode, was suppressed at the poly Au-Cys SAM-modified electrode (Fig. 3S-A, curves a and b), which is due to coverage of active sites on the poly Au surface with a Cys monolayer for charge transfer process, whereas the gold oxide reduction current at the poly Au-HPW SAM or poly Au-(Cys)PW SAM-modified electrodes increased in comparison with the bare poly Au electrode (Fig. 3S-A, curves c and d). This accessibility effect can include the presence of the POM with chemical, structural, and electronic properties which improve the surface charge transfer process. However, in a poly Au-(Cys)PW SAM-modified electrode, the accessibility effect is higher due to the presence of the POM accompanying the poly Au–S bond.

Also, [Fe(CN)$_6$]$_{3/-4}$ (0.5 mM) was selected as a redox probe to study the interfacial electron transfer properties of poly Au SAM-modified electrodes. The cyclic voltammetric responses of the poly Au electrode before and after modification were obviously different (Fig. 3S-B). The electron transfer kinetics of a redox couple in solution on the poly Au SAM-modified electrodes depends on the compactness and thickness of the monolayer. As can be seen, [Fe(CN)$_6$]$_{3/-4}$ shows a couple of well-defined redox waves at the bare poly Au electrode with a peak-to-peak separation ($\Delta E_p$) of about 63 mV at pH 3. Formation of Cys SAM or HPW SAM on the poly Au
electrode decreased the faradaic peak currents ($i_p$) and increased $\Delta E_p$ (Fig. 3S-B, curves a, b, and c). Decrease of the $i_p$ and an increase of the $\Delta E_p$ on the poly Au-Cys SAM or poly Au-HPW SAM-modified electrodes was attributed to the slow electron transfer rate as a result of the presence of Cys or HPW monolayers on the poly Au’s surface, which served as a barrier layer and imparted resistance to electron transfer. However, a more reversible behavior was observed for the negatively or positively charged redox probe reaction in SAMs with opposite charges. Therefore, after the self-assembly of (Cys)PW, an obvious increase in $i_p$ accompanied by a decrease in $\Delta E_p$ was observed (Fig. 3S-B, curve d). This enhanced electrochemical activity of the poly Au-(Cys)PW SAM modified electrode can be ascribed to a synergistic effect between HPW and Cys in the structure of the (Cys)PW and also electrostatic attraction between positively charged amine groups on the top-side of Cys in poly Au-(Cys)PW SAM and the [Fe(CN)$_6$]$^{3-/4-}$ redox probe in solution (Scheme 1S). Initial quantitative information obtained from CV on bare and modified poly Au electrodes in the presence of 0.5 mM [Fe(CN)$_6$]$^{3-/4-}$ in PBS (0.11 M, pH 3) is presented in Table 2S.
Fig. 3S Cyclic voltammograms obtained on bare poly Au electrode (a), and poly Au-Cys SAM (b), poly Au-HPW SAM (c) and poly Au-(Cys)PW SAM (d) modified electrodes in: (A) aqueous 0.5 M H$_2$SO$_4$ and scan rate of 100 mVs$^{-1}$ and (B) 0.5 mM [Fe(CN)$_6$]$^{3-/4-}$ in PBS (0.11 M, pH 3). Scan rate: 50 mVs$^{-1}$.
Scheme 1S Schematic representation of the formation of (A) poly Au-HPW SAM and (B) poly Au-(Cys)PW SAM modified electrode.

Table 2S Electrochemical parameters extracted from CVs (Fig. 2B) on bare poly Au and poly Au SAM-modified electrodes in the presence of $[\text{Fe(CN)}_6]^{3-/-4-}$ (0.5 mM) in PBS (0.11 M, pH 3).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$i_{p,a}$ (μA)</th>
<th>$\Delta E_{p}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare poly Au</td>
<td>6.42±0.11</td>
<td>63±5</td>
</tr>
<tr>
<td>poly Au- Cys SAM</td>
<td>5.79±0.06</td>
<td>88±10</td>
</tr>
<tr>
<td>poly Au- HPW SAM</td>
<td>2.31±0.18</td>
<td>127±8</td>
</tr>
<tr>
<td>poly Au- (Cys)PW SAM</td>
<td>8.24±0.24</td>
<td>61±4</td>
</tr>
</tbody>
</table>

Electrochemical studies of the poly Au-HPW SAM and poly Au-(Cys)PW SAM electrodes were carried out in acidic aqueous solution because POM compounds are unstable in neutral and basic aqueous solutions. As shown in Fig. 4S, curve a, cyclic voltammograms of the poly Au-(Cys)PW SAM in the potential range of 0.40 to -0.43 V (vs. Ag/AgCl), exhibit two-step redox peaks with half wave potentials ($E_{1/2} = (E_{p,a} + E_{p,c})/2$), of 0.037 (I, I') and -0.241 (II, II') V vs. Ag/AgCl, which correspond to the two consecutive one-electron processes of W atoms. The half wave potentials $E_{1/2}$ of PW in a poly Au-(Cys)PW SAM are shifted towards more cathodic potentials compared to the parent HPW (Fig. 4S, curve b), when their values are -0.010 (I, I') and -0.300
(II,II') V vs. Ag/AgCl. This means that in the presence of the Cys, HPW is more easily reduced. Moreover, there is a huge increase of peak currents in the poly Au-(Cys)PW SAM electrode (Fig. 4S curve a) with respect to the case of the poly Au-HPW SAM electrode (Fig. 4S, curve b). This is direct proof that Cys is able to mediate electron transfer between the gold electrode and POM in a more efficient way. In contrast, no peak was observed in the potential range from 0.40 to -0.43 V at the bare gold electrode or at the poly Au-Cys SAM-modified electrode under identical experimental conditions (Fig. 4S, curves c and d).

**Fig. 4S** Cyclic voltammograms of poly Au-(Cys)PW SAM (a), poly Au-HPW SAM (b), and poly Au-Cys SAM (c) modified electrodes and bare poly Au electrode (d) in 0.1 M HClO₄ at a scan rate of 100 mV s⁻¹.⁶
In order to calculate the poly Au SAM-modified electrode surface coverage, a linear sweep voltammogram (LSV) of the poly Au-(Cys)PW SAM electrode was recorded in NaOH (0.5 M) solution at a potential range from -0.2 to -1.4 V and a scan rate of 50 mV s\(^{-1}\) (Fig. 5S). As a negative control, the LSVs of poly Au-Cys and poly Au-HPW were also recorded under similar conditions. Prior to the reductive desorption scan, the solution was deaerated with argon gas for at least 15 minutes.

Fig. 5S shows the LSVs for the reductive desorption of Cys (curve a) and (Cys)PW (curve c) monolayers formed on the poly Au. Voltammograms (a) and (c) depict the appearance of multiple reduction peaks, the origin of which is attributed to the existence of different crystal faces of Au on the poly Au surface \(^9,10\). These different crystal faces of the poly Au electrode exhibit different binding strengths to the chemisorbed Cys molecules. The first reduction peaks of voltammograms (a) and (c) at a relatively low-cathodic potential (-710 and -730 mV, respectively) are ascribed to the reductive desorption of Cys molecules loosely bounded to the Au(111) domain (the so-called smooth domain) of the poly Au surface atoms, while the second peak (-1030 mV) of voltammogram (a) and also the other two peaks (-1047 and -1108 mV) of voltammogram (c) are attributable to the reductive desorption of Cys molecules that strongly bounded to the Au(100) and Au(110) domains of the poly Au surface (the so-called rough domains).

The voltammogram of HPW (curve b), shows two broad cathodic peaks at -215 (I\(_b\)) and -859 (II\(_b\)) mV that are attributed to the two-step reduction of W atoms (W\(^{VI}\)→ W\(^V\) and W\(^V\)→ W\(^{IV}\)) in the adsorbed HPW molecules. For the determination of \(\Gamma_{\text{SAM}}\) based on desorption charge calculations from alkaline media, it must be considered that the electrochemical reaction for
monolayer reductive desorption on poly Au accomplished the following one electron stoichiometric relationship:\textsuperscript{10}:

\begin{equation}
\text{Au-SAM} + e^- \rightarrow \text{Au} + \text{SAM}^-
\end{equation}

(1)

Desorption charges ($Q_d$) were extracted from the LSV data after correction for the related backgrounds obtained from the average of base currents on the sides of the related peaks. The values of the electric charges were used to calculate the surface coverage as well as the number of molecules in a monolayer (Table 3S).

The values for surface coverage ($\Gamma$), given in mol cm$^{-2}$, were obtained from the integrated desorption charges ($Q_d$) of the cathodic desorption peaks in 0.5 M NaOH aqueous solution by Eq. (2)\textsuperscript{11}:

\begin{equation}
\Gamma = \frac{Q_d}{n_e F A}
\end{equation}

(2)

Where $F$ is Faraday’s constant (C mol$^{-1}$), $n_e$ the number of electrons transferred per redox event, and $A$ is the area of the working electrode (cm$^2$). Calculations considered a single-electron process for Cys or (Cys)PW desorption.

With respect to the results presented in Table 3S, the calculated value of $\Gamma_{\text{Cys}}$ (1.9 ± 0.22 nmol cm$^{-2}$) is in accordance with the reported value (1.5 ± 0.2 nmol cm$^{-2}$) in pervious literature\textsuperscript{12}. However, in the presence of POM, $\Gamma_{(\text{Cys})\text{PW}}$ is slightly increased (about of 2.1 ± 0.2 nmol cm$^{-2}$).
**Fig. 5S** linear sweep voltammograms of reductive desorption of Cys (a), HPW (b), and (Cys)PW (c) from the poly Au-SAM modified electrode in 0.5 M NaOH solution. Scan rate: 50 mV s$^{-1}$. A = 0.071 cm$^2$.$^6$

**Table 3S** Monolayer coverage calculated for Cys and (Cys)PW adsorbed at poly Au electrode from 0.5 M NaOH medium (Fig. 5S).$^6$

<table>
<thead>
<tr>
<th>Monolayers</th>
<th>$n_e$</th>
<th>$Q_d$ (µC cm$^{-2}$)</th>
<th>$\Gamma$ (nmol cm$^{-2}$)</th>
<th>$\Gamma_{\text{total}}$ (nmol cm$^{-2}$)</th>
<th>Coverage_{total}×10^{-15} (molecules cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cys</td>
<td>1</td>
<td>12.37</td>
<td>173.3</td>
<td>0.1309</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>(Cys)PW</td>
<td>1</td>
<td>123.7</td>
<td>71.01</td>
<td>1.476</td>
<td>2.1 ± 0.2</td>
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References