Supporting Information For

Electrochemical quartz crystal microbalance study of covalent tethering of carboxylated thiol to polyaniline for electrocatalyzed oxidation of ascorbic acid in neutral aqueous solution

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Table 1S The $M/n$ values of PANI–MSA composite films from data shown in Fig. 6 (B) and Fig. 7 (C) during potential cycling in 0.1 mol L$^{-1}$ PBS (pH 7.3)$^a$

<table>
<thead>
<tr>
<th>film</th>
<th>$Q_a$ ($\times 10^4$ C)</th>
<th>$\Delta f_{0,a}$ (Hz)</th>
<th>$(M/n)_a$ (g mol$^{-1}$)</th>
<th>$Q_c$ ($\times 10^4$ C)</th>
<th>$\Delta f_{0,c}$ (Hz)</th>
<th>$(M/n)_c$ (g mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI$<em>{post}$–MSA (P$</em>{a4}$/P$_{c4}$)</td>
<td>8.10</td>
<td>−90.0</td>
<td>18.5</td>
<td>11.4</td>
<td>−120</td>
<td>17.6</td>
</tr>
<tr>
<td>PANI$<em>{poly}$–MSA (P$</em>{a5}$/P$_{c5}$)</td>
<td>−7.20</td>
<td>70.0</td>
<td>16.3</td>
<td>−9.20</td>
<td>85.0</td>
<td>15.5</td>
</tr>
</tbody>
</table>

$^a$ $Q_a$, $\Delta f_{0,a}$ and $(M/n)_a$, as well as $Q_c$, $\Delta f_{0,c}$ and $(M/n)_c$, denote the oxidation peak charge, frequency shift and $M/n$ of PANI–MSA composite films during potential’s positive going as well as the reduction peak charge, frequency shift and $M/n$ of PANI–MSA composite films during potential’s negative going. See the text for definitions of other symbols.
Fig. 1S shows the EQCM responses during the cyclic voltammetric growth of PANI. The aniline monomer was electrooxidized at potentials positive of about 0.79 V vs SCE in the first positive sweep, and the simultaneous frequency decrease demonstrates the onset of polymer deposition on the electrode. Three pairs of redox current peaks, $P_a1/P_c1$, $P_a2/P_c2$ and $P_a3/P_c3$, increased cycle by cycle, while the frequency decreased simultaneously, demonstrating that the continuous growth of PANI was taking place. $P_a1/P_c1$ are attributed to the transition between leucoemeraldine and emeraldine, and $P_a2/P_c2$ result from the transition between emeraldine and pernigraniline.1, 2 $P_a3/P_c3$ are due to the side reactions of the polymer and oligomers of aniline.3
**Fig. 2S.** Frequency change versus charge curve during potential cycling of a PANI film ($\Delta f_{0,\text{PANI}} = -2$ kHz) in 0.1 mol L$^{-1}$ H$_2$SO$_4$ as shown in Fig. 1 (A).
Fig. 3S ESPR responses during aniline electropolymerization in 0.05 mol L\(^{-1}\) aniline + 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\). Scan rate: 50 mV s\(^{-1}\). Since the sensitivity of the ESPR response is higher than that of the EQCM frequency response, a PANI film thinner than that for EQCM studies had to be prepared here.
**Fig. 4S** Time-dependent frequency responses during the interaction of PANI with several thiols. See Table 1 in the main text for details.
**Fig. 5S** Cyclic voltammograms (30 mV s\(^{-1}\)) for the PANI\(_{\text{post}}\)–MSA composite films in 0.1 mol L\(^{-1}\) PBS (pH = 7.3). Panel A: after interaction of PANI (\(\Delta f_{0,d-PANI} = -2\) kHz) with 5 mmol L\(^{-1}\) MSA for different potential cycles (1, 3, 10, 20, 50, or 100 cycles at 30 mV s\(^{-1}\)) and thus with different \(r\); panel B: after interaction of –0.5, –1.0, –2.0, –4.0, –6.0, or –8.0 kHz PANI (\(\Delta f_{0,d-PANI}\)) with 5 mmol L\(^{-1}\) MSA for three potential cycles at 30 mV s\(^{-1}\); and panel C: after interaction of PANI (\(\Delta f_{0,d-PANI} = -2\) kHz) with 0.1, 1, 5, 20, 50, or 100 mmol L\(^{-1}\) MSA for three potential cycles at 30 mV s\(^{-1}\), respectively. Insets show the peak currents as functions of \(r\), the thickness of PANI films and the MSA concentrations, respectively.
Fig. 6S pH–dependent cyclic voltammograms for a PANIpost–MSA composite film ($r = 0.11$) in (a) 0.1 mol L$^{-1}$ H$_2$SO$_4$ (pH 0.8) and (b–g) pH 2.0, 3.0, 5.0, 7.0, 8.0 or 9.0 PBS. Scan rate: 30 mV s$^{-1}$. 
Fig. 7S Cyclic voltammograms for (A) –2.0 kHz PANI\textsubscript{post–thiol} (5 mmol L\textsuperscript{−1} thiol) composite films and (B) –1.6 kHz PANI\textsubscript{poly–thiol} composite films obtained from aniline electropolymerization in 0.1 mol L\textsuperscript{−1} aniline + 0.1 mol L\textsuperscript{−1} H\textsubscript{2}SO\textsubscript{4} + 0.1 mmol L\textsuperscript{−1} thiol in 0.1 M PBS (pH 7.3). Scan rate: 30 mV s\textsuperscript{−1}.

Fig. 8S Cyclic voltammograms (30 mV s\textsuperscript{−1}) for the PANI\textsubscript{poly–MSA} composite films in 0.1 mol L\textsuperscript{−1} PBS (pH = 7.3). Panel A: for 0.6, 0.8, 1.0, 1.6, 2.0, or 2.5 kHz PANI\textsubscript{poly–MSA} composite films (“wet” frequency), respectively. Panel B: for the PANI\textsubscript{poly–MSA} composite films obtained from aniline electropolymerization in 0.1 mol L\textsuperscript{−1} aniline + 0.1 mol L\textsuperscript{−1} H\textsubscript{2}SO\textsubscript{4} + 0.01, 0.1, 0.5, 1, 5, or 10 mmol L\textsuperscript{−1} MSA for 10 potential cycles. Insets show the peak currents as functions of the thickness of PANI\textsubscript{poly–MSA} films and the concentrations of MSA, respectively.
Fig. 9S Effects of the applied potential on the stable current response of the Au electrodes modified with PANI–MSA composite films in 0.1 mol L\(^{-1}\) PBS (pH7.3) containing 1 mmol L\(^{-1}\) AA.

Fig. 10S Anodic catalytic peak currents of PANI\(_{\text{post}}\)–thiol and PANI\(_{\text{poly}}\)–thiol measured in 0.1 mol L\(^{-1}\) PBS (pH7.3) in the presence of 1 mmol L\(^{-1}\) AA. Scan rate: 30 mV s\(^{-1}\).
Chronoamperometry was used to investigate the electrode process of AA at the PANI_{post}–MSA/Au electrode. **Fig. 11S** (A) shows the chronoamperometric measurements of AA at various concentrations at the PANI_{post}–MSA/Au electrode at 0.5 V. The Inset of **Fig. 11S** (A) shows the current responses of AA at different concentrations at fixed times of 4, 10 and 16 s, respectively. It can be seen from the plots that the slopes of the calibrations decrease with increasing time after the potential step application. However, there is a very similar intersection between currents measured at different time elapsed and AA concentrations. The typical $I$–$t$ curve in **Fig. 11S** (A) indicates that the currents observed must be controlled by AA diffusion in solution. Thus, the current corresponding to the electrochemical reaction obeys Cottrell’s law,\(^4\)

$$I = nFAD^{1/2}c_0/\pi^{1/2}t^{1/2}$$

(1)

where $D$ and $c_0$ are the diffusion coefficient (cm\(^2\) s\(^{-1}\)) and bulk concentration (mol cm\(^{-3}\)), respectively. Based on Eq. (1) the plot of $I$ versus $t^{1/2}$ is a straight line, and the slope of such lines can be used to estimate the diffusion coefficient of AA. The mean value of $D$ is found to be $8.3 \times 10^{-6}$ cm\(^2\) s\(^{-1}\), which is in good agreement with that obtained from the rotating disk electrode (RDE) voltammetry technique.\(^5\),\(^6\)

Chronoamperometry can also be employed to evaluate the catalytic rate constant for the reaction between AA and the redox sites of the surface confined PANI–thiol film according to the method of Galus\(^7\):

$$I_{cat}/I_l = \gamma^{1/2}(\pi^{1/2}\text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2})$$

(2)

where $I_{cat}$ is the catalytic current of AA at the PANI_{post}–MSA/Au electrode, $I_l$ is the limiting current in the absence of AA, and $\gamma = kc_0t$ ($c_0$ is the bulk concentration of AA). When $\gamma$
exceeds 2, the error function is almost equal to 1 and therefore the above equation can be reduced to

\[ \frac{I_{cat}}{I_l} = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (k c_0 t)^{1/2} \quad (3) \]

where \( t \) is the time elapsed (s). Based on the slope of the \( I_{cat}/I_l \) versus \( t^{1/2} \) plot, \( k \) can be obtained for a given AA concentration. One such plot is shown in Fig. 11S (B) constructed from the chronoamperogram of the PANI_{post}–MSA/Au electrode in the absence and presence of 2 mmol L\(^{-1} \) AA. The mean value of \( k \) in an AA concentration range of 0.5–5 mmol L\(^{-1} \) was obtained to be \( 7.2 \times 10^5 \) cm\(^3\) mol\(^{-1}\) s\(^{-1} \). This result is close to those obtained from RDE voltammetry.\(^5,6\) Under the same conditions, the \( k \) for PANI_{poly}–MSA/Au electrode was similarly obtained to be \( 2.7 \times 10^5 \) cm\(^3\) mol\(^{-1}\) s\(^{-1} \). The obtained \( k \) values agree well with the reported value from chronoamperometry for PANI doped with camphorsulfonic acid (5.6 \( \times \) \( 10^5 \) cm\(^3\) mol\(^{-1}\) s\(^{-1} \)) or \( \beta \)–naphthalenesulfonic acid (6.2 \( \times \) \( 10^5 \) cm\(^3\) mol\(^{-1}\) s\(^{-1} \)).\(^5,6\)

![Fig. 11S](image.png)

**Fig. 11S** (A) Chronoamperograms obtained in 0.1 mol L\(^{-1} \) PBS (pH 7.3) at the PANI_{post}–MSA/Au (\( r = 0.11 \)) electrode in the absence (a) and presence of 0.5 (b), 1 (c), 2 (d), 3 (e), 4 (f) or 5 (g) mmol L\(^{-1} \) AA. The first and second potential steps were 0.5 and –0.5 V, respectively. Inset shows the dependence of the fixed–time current (observed at 4, 10 and 16 s after the first potential step) versus AA concentration. (B) Dependence of \( I_{cat}/I_l \) on \( t^{1/2} \) derived from the data of chronoamperograms of (a) and (d) in Fig. 11S (A).
References


