SUPPORTING INFORMATION


M. A. Villalba, M. L. Bossi, E. J. Calvo

Figure 1 SI. A) Ellipsometric angles and B) thickness at 632.9 nm versus number of self-assembled layers for (PAH)$_n$(PAA)$_m$ from solutions of pH 7.5 and 3.5, respectively. PAH (red squares) and PAA (blue circles).

Figure 2 SI. A) Individual adsorption step of self-assembled film of PAH (red squares) and PAA (blue circles) on Au-MPS modified electrode. B) Mass evolution of the film with each polyelectrolyte adsorption.
Figure 3 SI. PMIRAS spectra of Au-MPS substrate modified with: PAH$_3$-PAA$_2$ (black line), PAH$_3$-PAA$_2$ + PdCl$_4^{2-}$ (red line), PAH$_3$-PAA$_2$ + Pd$^0$ (blue line) and PAH$_3$-PAA$_2$ + Pd$^0$ treated at 350 °C (green line).

Figure 4 SI. Spectrum deconvolution in $\nu_{as}$ (COO$^-$) and $\nu_{as}$ (COOH) gaussian contributions of A) PAH$_3$-PAA$_2$ + PdCl$_4^{2-}$ and B) PAH$_3$-PAA$_2$ + Pd$^0$ films.

Polymer bands correspond to CH$_2$ bendings modes in PAH and PAA monomers at 1453 cm$^{-1}$, a shoulder at 1637 cm$^{-1}$ that probably arises from asymmetric bending mode of NH$_3^+$ in PAH and three bands at 1405, 1574 and 1724 cm$^{-1}$ for symmetric and asymmetric stretching band for carboxilate groups $\nu_s$(COO$^-$), $\nu_{as}$(COO$^-$), and C=O stretching bond in protonated carboxylic acids respectively. Assuming the same extinction coefficients for both bands, the degree of ionization of PAA at a given pH was calculated from

$$\text{Ionization Degree} = \frac{A_{\nu(COO^-)}}{A_{\nu(COOH + COO^-)}} \times 100$$
Charge is calculated taking into account theoretical values for polycation at pH 7.5 (80 % protonated) and the polyanion at pH 3.5 (just 5 % deprotonated), as we show in the next table:

<table>
<thead>
<tr>
<th></th>
<th>1 PAH</th>
<th>1 PAA</th>
<th>2 PAH</th>
<th>2 PAA</th>
<th>3 PAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (ng.cm(^{-2}))</td>
<td>198</td>
<td>319</td>
<td>253</td>
<td>480</td>
<td>331</td>
</tr>
<tr>
<td>Mol (nmol.cm(^{-2}))</td>
<td>2.12</td>
<td>4.43</td>
<td>2.72</td>
<td>6.67</td>
<td>3.56</td>
</tr>
<tr>
<td>Charge (nmol.cm(^{-2}))</td>
<td>1.7</td>
<td>0.2</td>
<td>2.2</td>
<td>0.3</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Figure 5 SI. Chromatograms and calibration curves of A) acetophenone, B) 1-phenylethanol and C) ethylbenzene using a mobile phase proportions 65:35 methanol:water. \( f_d \) represents the dilution factor and it is equal to 20/1020.
Figure 6 SI. Chromatograms and calibration curves of A) benzophenone, B) diphenylmethanol and C) diphenilmethane using a mobile phase proportions 75:25 methanol:water. $f_d$ represents the dilution factor and it is equal to 10/1010.

Figure 7 SI. Cyclic voltammetry of type II with $n = 2$ (black), 4 (orange), 6 (green) y 8 (blue) in 0,1 M sulfuric acid and 0.05 V.s$^{-1}$ scan rate in A) PdO and B) active potential region. Inset: evolution of palladium electrochemical active areas as function cycle $n$. 
Figure 8 SI. A) Cyclic voltammetry of Type I-C electrodes with PAH (red line), PAH$_2$-PAA (blue line) and PAH$_3$-PAA$_2$ (green line) in 0.1 M H$_2$SO$_4$ at 0.05 V.s$^{-1}$. B) Peak potential and full width at half maximum of PdO reduction as function of the number of PAH adsorbed layers.

Figure 9 SI. Cyclic voltammetry of type II (A and C) and type II-C (B and D) with $n = 2$ (black), 4 (orange), 6 (green) y 8 (blue) in 0.1 M sulfuric acid and 0.05 V.s$^{-1}$ scan rate. Inset: evolution of palladium electrochemical active areas as function cycle $n$. 