Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Selective electrocatalytic hydrogenation using Layer-by-Layer palladium nanoparticles electro-chemical formed in multilayer films.

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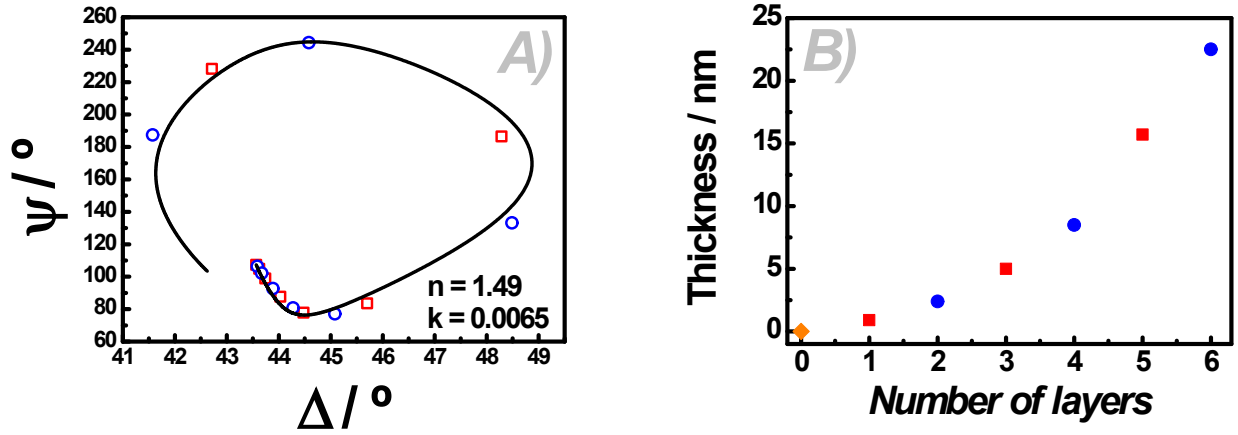

Figure 1 SI. A) Ellipsometric angles and B) thickness at 632.9 nm versus number of self-assembled layers for $(PAH)_n(PAA)_m$ from solutions of pH 7.5 and 3.5, respectively. PAH (red squares) and PAA (blue circles).

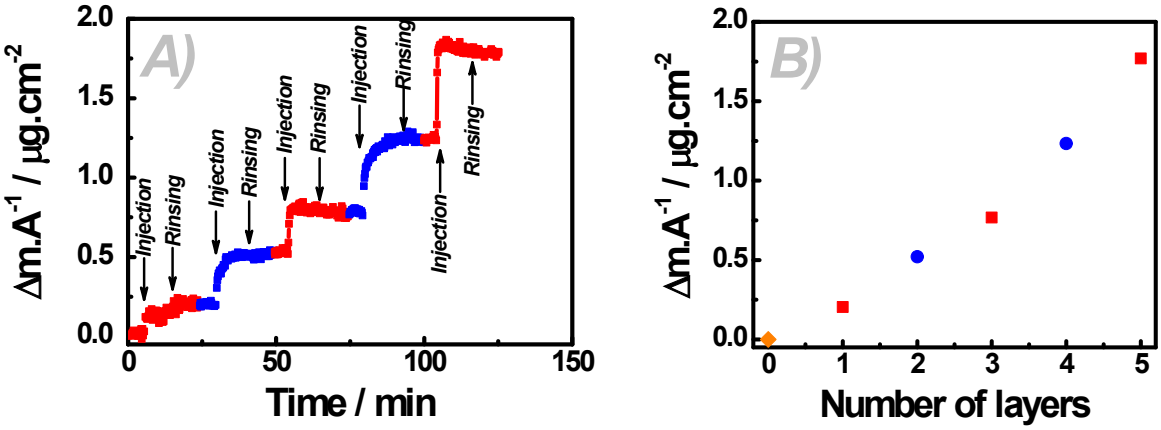

Figure 2 SI. A) Individual adsorption step of self-assembled film of PAH (red squares) and PAA (blue circles) on Au-MPS modified electrode. B) Mass evolution of the film with each polyelectrolyte adsorption.

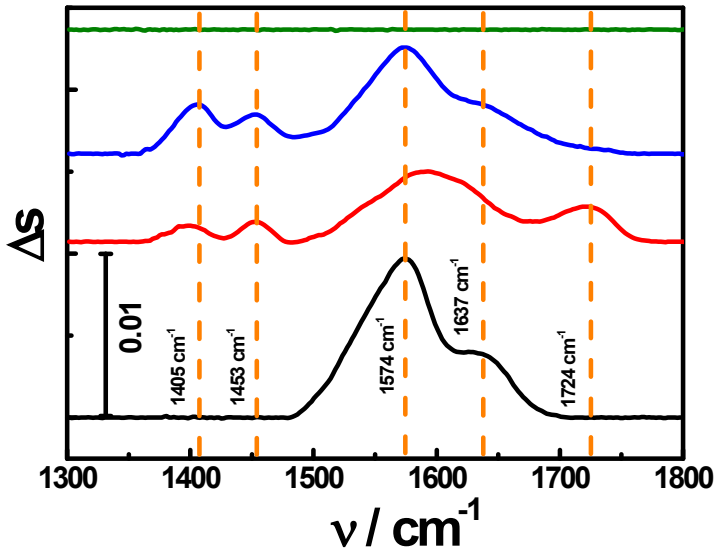

Figure 3 SI. PMIRRAS spectrua of Au-MPS substrate modified with: PAH_3-PAA_2 (black line), PAH_3-PAA_2 + $PdCl_4^{2-}$(red line), PAH_3-PAA_2 + Pd^0 (blue line) and PAH_3-PAA_2 + Pd^0 treated at 350 ^{0}C (green line).

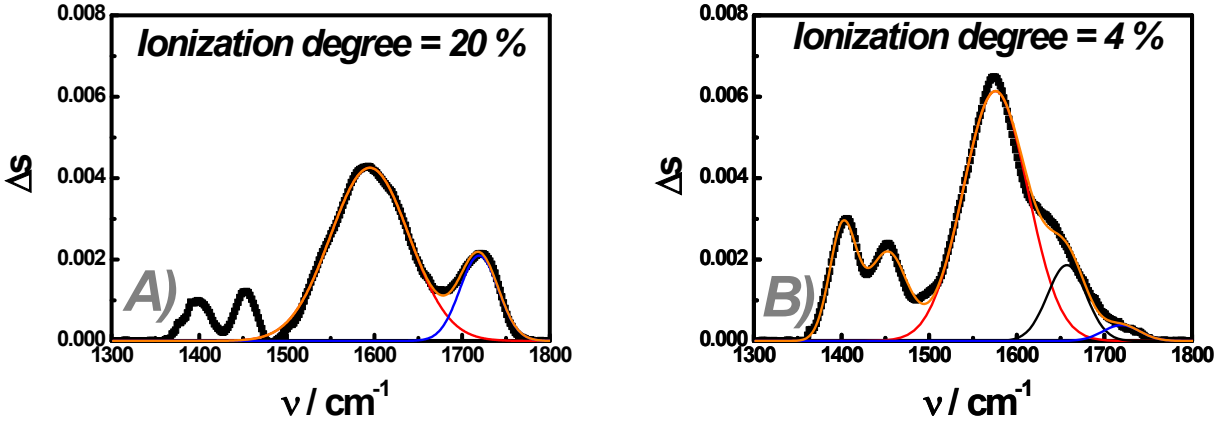

Figure 4 SI. Spectrum deconvolution in $\nu_{as}(COO^-)$ and $\nu_{as}(COOH)$ gaussian contributions of A) PAH_3-PAA_2 + $PdCl_4^{2-}$ and B) PAH_3-PAA_2 + Pd^0 films.

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

$$Ionization\ Degree = \frac{A_{\nu(COO^-)}}{A_{\nu(COOH+COO^-)}} * 100$$

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:

	1 PAH	1 PAA	2 PAH	2 PAA	3 PAH
Mass (ng.cm^{-2})	**198**	**319**	**253**	**480**	**331**
Mol (nmol.cm^{-2})	**2.12**	**4.43**	**2.72**	**6.67**	**3.56**
Charge (nmol.cm^{-2})	**1.7**	**0.2**	**2.2**	**0.3**	**2.8**

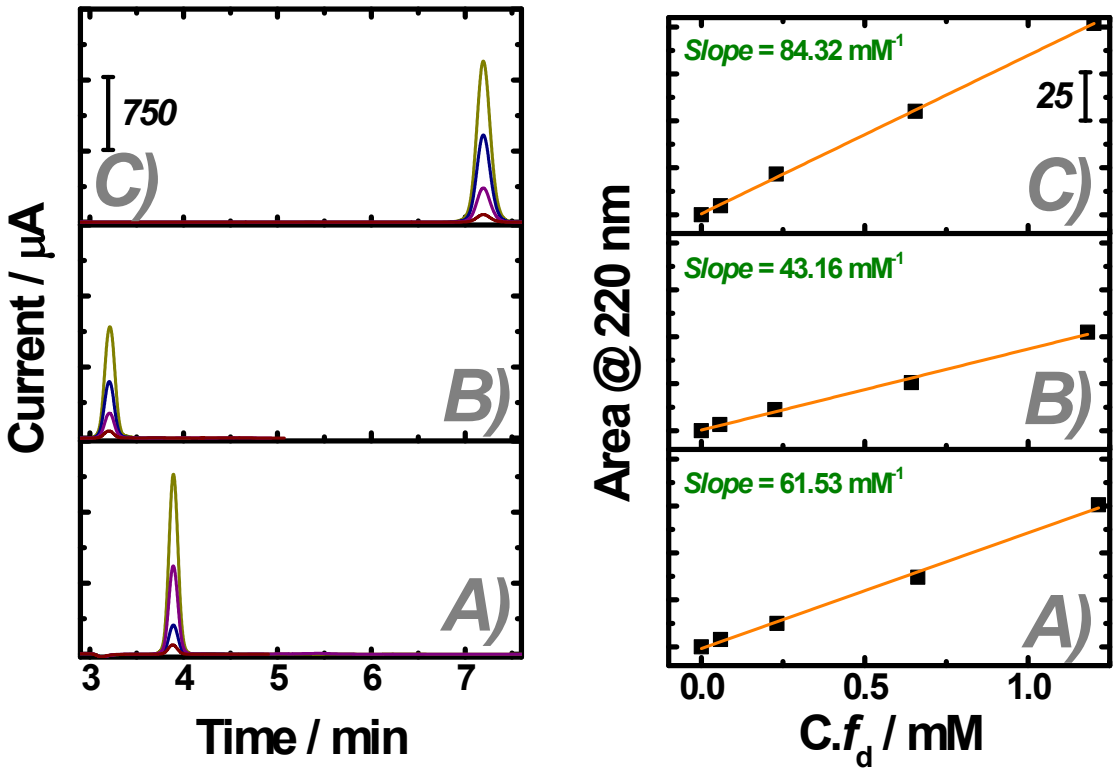

Figure 5 SI. Chromatograms and calibration curves of A) acetophenone, B) 1-phenylethanol and C) ethylbenzene using a mobile phase proportions 65:35 methanol:water. f_d represents the dilution factor and it is equal to 20/1020.

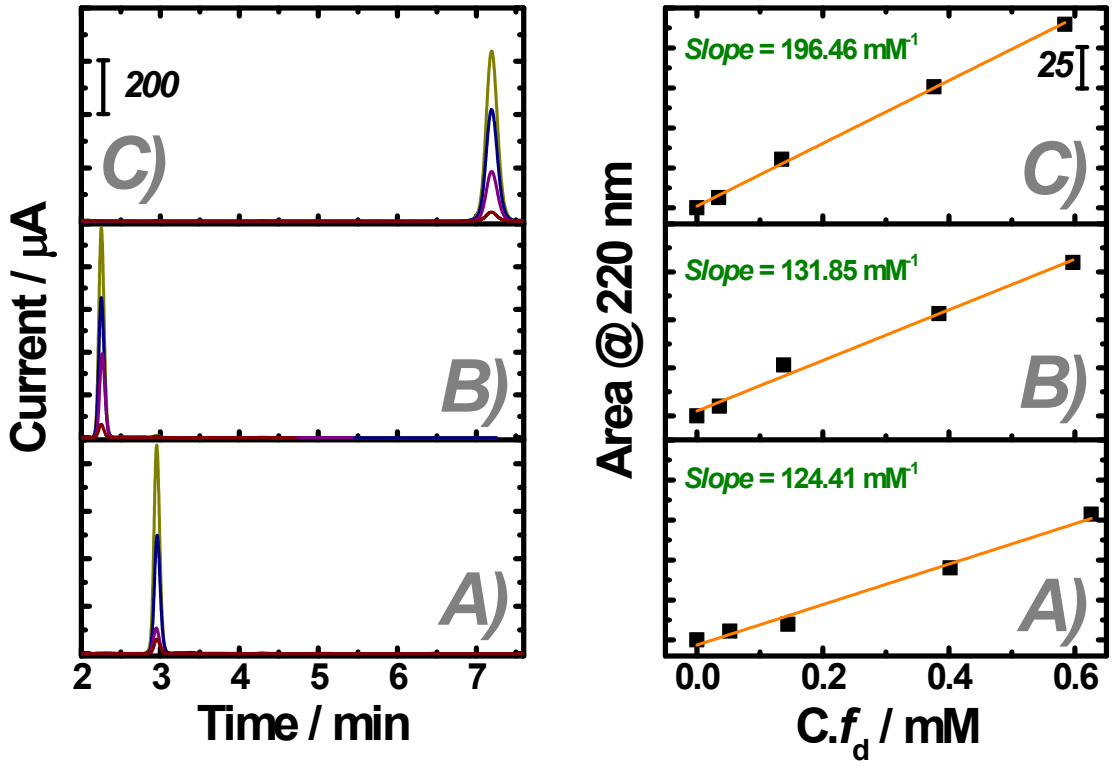

Figure 6 SI. Chromatograms and calibration curves of A) benzophenone, B) diphenylmethanol and C) diphenilmethane using a mobile phase proportions 75:25 methanol:water. f_d represents the dilution factor and it is equal to 10/1010.

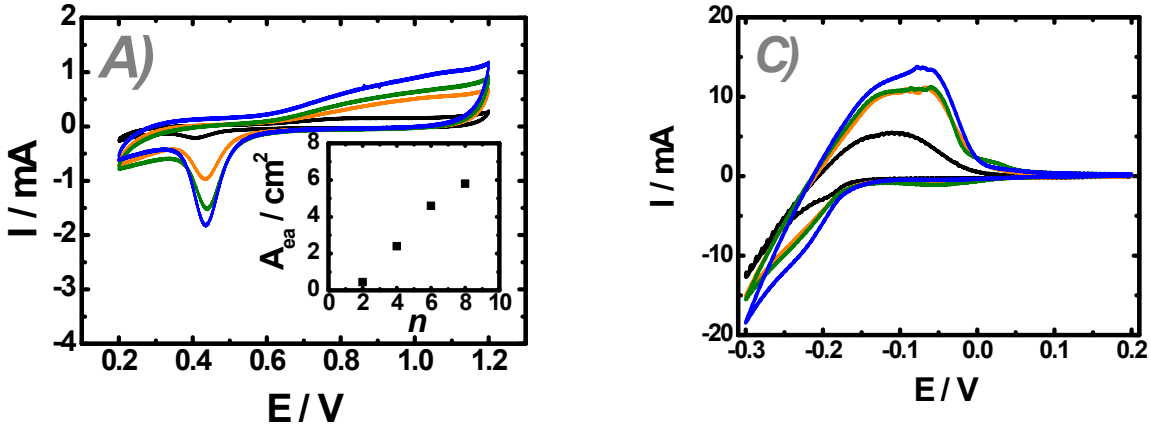

Figure 7 SI. Cyclic voltammetry of type II with n = 2 (black), 4 (orange), 6 (green) y 8 (blue) in 0,1 M sulfuric acid and 0.05 $V.s^{-1}$ scan rate in A) PdO and B) active potential region. Inset: evolution of palladium electrochemical active areas as function cycle n.

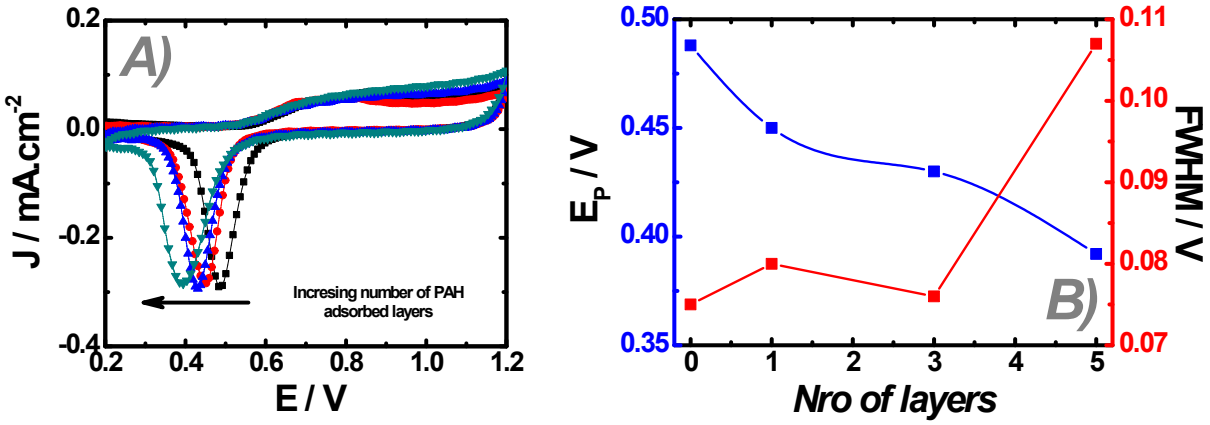

Figure 8 SI. A) Cyclic voltammetry of Type I-C electrodes with PAH (red line), PAH_2-PAA (blue line) and PAH_3-PAA_2 (green line) in 0,1 M H2SO4 at 0,05 V.s^{-1}. B) Peak potential and full width at half maximum of PdO reduction as function of the number of PAH adsorbed layers.

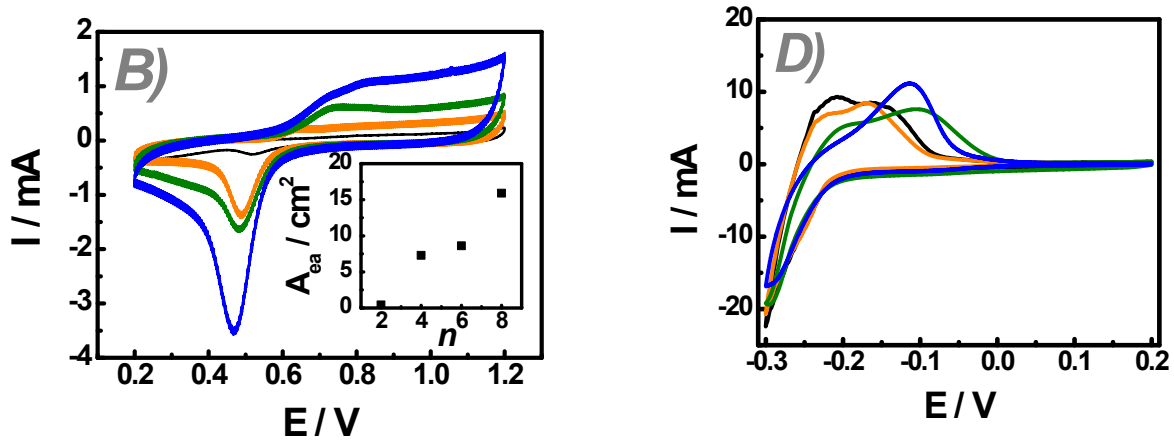

Figure 9 SI. Cyclic voltammetry of type II (A and C) and type II-C (B and D) with *n* = 2 (black), 4 (orange), 6 (green) y 8 (blue) in 0,1 M sulfuric acid and 0.05 V.s^{-1} scan rate. Inset: evolution of palladium electrochemical active areas as function cycle *n*.