**Supporting Information**

**Experimental Methods**

1. Multilayer assembly and nanoparticle electrodeposition

Prior to multilayer assembly, carbon felt electrodes (National Electric Carbon Products, a division of Morgan Specialty Graphite; Greenville, South Carolina, United States of America; http://www.morganamt.com/felt_cloth.php) were cut into 20 mm x 10 mm x 3 mm pieces, thoroughly washed with 1:1 isopropanol : Milli-Q water and finally rinsed with Milli-Q water. PEMs were formed by alternate immersion in continuously stirred PAH (pH 8) and PAA (pH 4) solutions for 30 minutes, starting from PAH. Between adsorption steps, carbon felt electrodes were washed twice in Milli-Q water with mechanical stirring for 15 min. The capping layer in multilayers films was always PAH in order to facilitate $\text{PdCl}_4^{2-}$ adsorption. The samples were then soaked in 1 mM $\text{PdCl}_4^{2-}$ solution for 24 hs, thoroughly rinsed with water and potentiostatically reduced at -500 mV (vs Ag/AgCl) for 180 s. The exchange/reduction step was then repeated the desired number of times.

2. Preparation of Microcrystalline Pd-C electrodes by reduction of aqueous Pd solutions

Carbon Felt electrodes were modified under potentiostatic control at 300 mV vs Ag/AgCl for 180 s in aqueous solutions of $1\times10^{-3}$ M in $\text{PdCl}_2$ and 0.1 M in HCl under nitrogen atmosphere.

3. Determination of Palladium content in carbon felt electrodes

For each electrode type, carbon felt electrodes were ground in a mortar and three portions of approximately 100 mg each one were individually treated with 5 ml of a 1:1 nitric acid (Merck Ultra Pure) - MilliQ water solution for 7 days in order to dissolve palladium. The insoluble carbon support was removed by filtration and thoroughly
washed with Milli-Q. The filtered solution and the washing waters were combined and MilliQ water was added up to a final volume of 50.0 ml. The content of Pd was determined in these samples by ICP-OES.

4. Electrochemical Experiments

Electrochemical measurements were carried out at room temperature (20±2ºC) with an Autolab PGSTAT 30 potentiostat (Autolab, Ecochemie, Holland) A glass standard three-electrode electrochemical cell was employed. A Ag/AgCl; 3 M KCl was employed as the reference electrode and the potentials were then transformed to the NHE scale by adding 210 mV. A platinum gauze auxiliary electrode of large area was employed. All solutions were purged with nitrogen for a minimum of 20 min before each experiment, and the measurements were carried out under that atmosphere. Electrochemically active areas were estimated from the reduction peak of palladium oxide, using a relationship of 420 μC.cm⁻²

5. Electrocatalytic Hydrogenation Procedure

Electrocatalytic reduction of acetophenone was carried out under potentiostatic control (-480 mV vs Ag/AgCl) in a two compartment cell. The cathodic compartment containing the working and reference electrodes was continuously bubbled with nitrogen and mechanically stirred during the experiment. It was separated from the anodic chamber containing the auxiliary electrode by a glass frit. The cathodic compartment initially contained 14.5 ml of a 0.06 M acetophenone solution in acid hydroalcoholic medium (0.1 M H₂SO₄ in 1 : 1 ethanol-water). The hydroalcoholic solution without acetophenone was used in the anodic chamber. The reduction process was monitored by UV-vis spectroscopy. At the end of the experiment the content of the cathodic chamber was analyzed by HPLC Shimatzu Prominence equipped with a SPD-20A UV-Vis detector and a LiChrospher 100 RP-8 (5μm) column.
6. X-ray Photoelectron Spectroscopy

XPS measurements were performed using a commercial XPS system (Specs SAGE 150) equipped with a dual anode Mg/Al X-Ray source and an hemispherical electron energy analyzer. The reported binding energies (BEs) are based on the analyzer energy calibration using reference samples (Ag 3d$_{5/2}$ and Au 4f$_{7/2}$). No charge compensation was necessary and no differential charging features were observed (e.g. low BE tails) given that we have measured sufficiently thin films on grounded conducting substrates. Atomic ratios were calculated from the integrated intensities of core levels after instrumental and photoionization cross-section corrections$^2$.

7. Scanning Electron Microscopy

Images were acquired with a FEG-SEM (Zeiss DSM 982 GEMINI, Carl Zeiss, Oberkochen, Germany) operating at 10kV. An in-lens SE detector was used.

8. Ellipsometry

Film thickness was estimated from ellipsometric experiments performed on HOPG substrates. A Sentech SE400 equipped with a 632.8 nm laser as polarized light source was employed. All measurements were performed at an incidence angle of 70.00°. All adsorption steps were carried out avoiding any variations of the electrode position in order to keep the system alignment. Ellipsometric parameters variations lower than the data dispersion for a single measurement (0.01 in $\psi$ and 0.05 in $\Delta$) were guaranteed in this way. After each adsorption step, the sample was rinsed with Milli-Q water and dried with N$_2$. Then, the ellipsometric parameters, $\psi$ and $\Delta$, were collected manually. The experimental data was fitted as described elsewhere$^3$. 
Figure 1S: XPS Pd 3d spectra for A) PAH + 2 Pd, B) (PAH₂/PAA₄)PAH + 2 Pd and C) (PAH₄/PAA₄)PAH + 2 Pd nanoparticle modified electrodes. The fraction of reduced Pd in these samples was 0.79, 0.45 and 0.22, respectively.

Figure 2S: Plot of the ellipsometric angles for PAH/PAA multilayer films on HOPG bearing different number of layers. Films finished in PAH are shown with blue squares and those finished in PAA with red circles. The curve simulated using the best fit optical parameter shown in the plot is presented in solid black line. B. Ellipsometric thickness vs. layer number from the data in A.