

Supplementary Information

Cyclic Voltammogram (CV) of the Pd/PyPP1/Au(111) Samples

The first three cycles of the CV of a Pd²⁺/PyPP1/Au(111) electrode in 0.1 M H₂SO₄ are shown in the full scan range. Prior to the CV, the sample was immersed into a 5 μM PdSO₄ + 0.1 M H₂SO₄ solution for coordination of Pd²⁺ with pyridine-nitrogens of the thiols. As mentioned in the main article, upon reduction of the coordinated Pd²⁺ ions a cathodic peak at -0.02 V was viewed on the voltammogram (peak A). Microscopical and spectroscopical studies evidenced that reduction resulted in top-residing spherical metallic Pd NPs. Hence, this peak cannot be assigned to defect-mediated over-potential deposition (OPD) of Pd on the Au substrate. As already stated in the discussion section of the main article, the idea of passivation of Pd NPs through hydrogen adsorption indirectly implies a certain electrochemical activity of the metallic Pd formed by reduction of complexed Pd²⁺ ions. Taking this argument into account, the observed hydrogen evolution currents after peak formation must originate from the Pd top layer (see currents

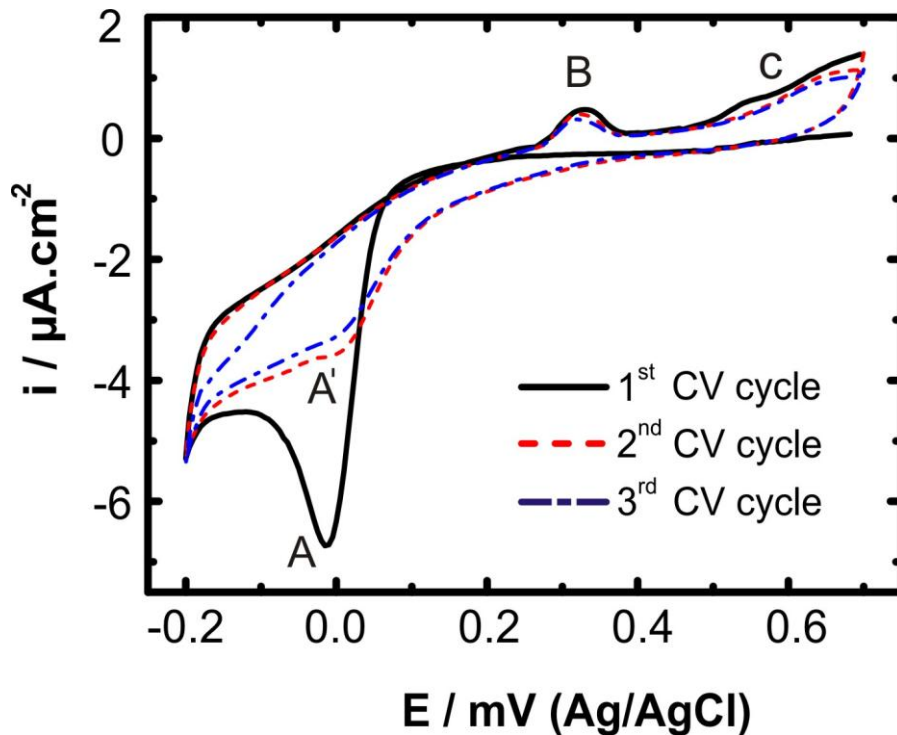


Figure 1. First three CV cycles of a Pd²⁺/PyPP1 sample in 0.1 M H₂SO₄. Prior complexation time 15 min. Complexation solution: 5 μM PdSO₄ + 0.1 M H₂SO₄. Scan rate: 5 mV/s.

at -0.2 V). Note that on a Pd-NP free PyPP1/Au(111) sample, hydrogen evolution currents at the same potential region is negligible compared to the currents observed for Pd/PyPP1/Au(111) samples (See Fig. 1 in the main article). Naturally, if hydrogen evolution occurs on Pd NPs, a corresponding hydrogen UPD peak as well as an oxidation peak in the reverse scan should be observable. In this context, after formation of the Pd NPs, in the reverse potential scan the anodic peak observed at 0.33 V (peak B) may be assigned to oxidation of the adsorbed hydrogen on the Pd NPs. This peak appears a few hundred millivolts more anodic potentials compared to hydrogen oxidation expected on a Pd adlayer, with direct contact to Au(111)¹ and still below the equilibrium potential between Pd and Pd²⁺.² The strong anodic shift can be related to slow charge transfer due to the present thiol monolayer on the surface. Scanning the potential further in anodic direction yields further anodic currents (peak C), which may indicate either Pd oxidation or splitting of the hydrogen oxidation peak due to different adsorption sites or NP types. Note that splitting of the hydrogen oxidation into several peaks has been observed on ultrathin Pd adlayers (a few monolayers) on Au(111) as well¹. On the other hand, these potentials are close to the range at which oxide monolayer forms on Pd adlayers on Au. In order to find out whether a transition from Pd⁰ to Pd²⁺ is possible within the investigated potential scan range a set of XPS measurements were carried out after polarizing samples to different potentials.

Fig. 2a represents the XP spectra obtained from Pd²⁺/PyPP1/Au(111) samples after withdrawing the sample from 0.1 M H₂SO₄ solution at different potential values during CV scans. Four different samples were prepared with 15 min prior complexation time in 5 μM PdSO₄ + 0.1 M H₂SO₄. During the subsequent CV, which started from 0.7 V, these samples were withdrawn at 0.2 V in the forward scan and 0.2 V, 0.45V and 0.7 V in the reverse scan as marked on the CV presented in Fig. 2b from I to IV, respectively. Sample I yielded a peak at 343.5 eV and another one at 338.2 eV, which are assigned to Pd²⁺ 3d_{3/2} and Pd²⁺ 3d_{5/2} core levels, respectively³. This result clearly indicates that Pd²⁺-pyridine nitrogen complexes stay intact until this potential. For sample II, the peak observed at 340.9 eV for Pd 3d_{3/2} core level demonstrates transition from ionic to metallic state for the Pd top layer. Sample III and IV have similar spectra like sample II, showing

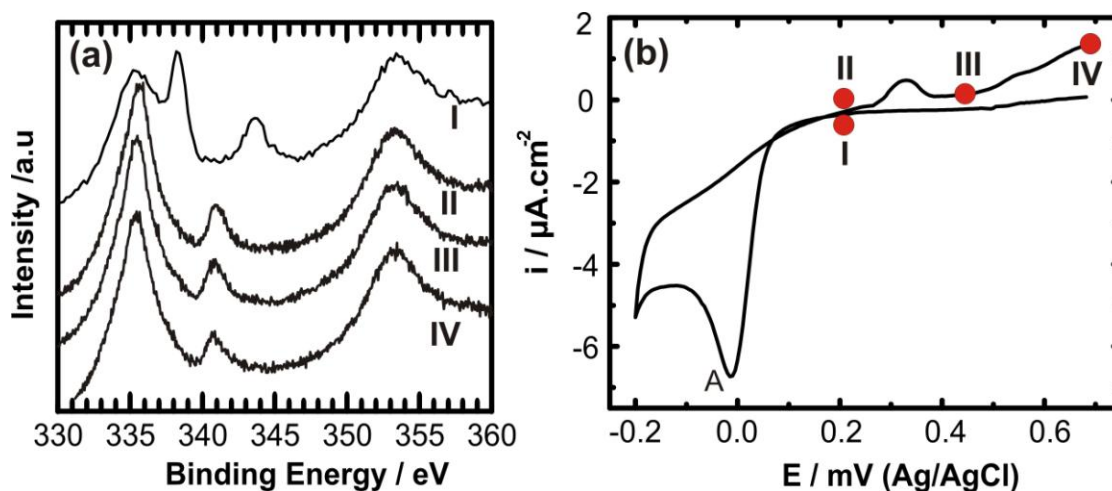


Figure 2. (a) XPS spectra for $\text{Pd}^{2+}/\text{PyPP1}$ samples with 15 min complexation times after voltammetric scan (I) from 0.7V to 0.2 V (II) from 0.7 V to 0.2 V in the reverse scan, (III) from 0.7 V to 0.45 V in the reverse scan and (IV) from 0.7 V to 0.7 V in the reverse scan. (b) CV of a typical 15 min $\text{Pd}^{2+}/\text{PyPP1}$ sample in 0.1 M H_2SO_4 with marks indicating the withdrawal potentials for the four related samples. CV scan rate: 5 mV/s. in 0.1 M H_2SO_4 . Complexation solution: 5 μM PdSO_4 + 0.1 M H_2SO_4 .

that the Pd NPs are still mainly in the metallic form even when potential values beyond the anodic peaks have been reached. Consequently, assignment of the anodic peak B to hydrogen oxidation is further confirmed. On the other hand the peak charge at C corresponds to about 1% of an active Pd adlayer, which is at the limit of the detection range of XPS. Therefore the XPS results cannot be used to assign this peak neither to hydrogen oxidation nor to oxide formation.

Turning back to the voltammetric response of Pd/PyPP1 samples which is shown in the second and third CV cycles in Fig. 1, the cathodic peak at 0.0 V (peak A') cannot be due to a Pd reduction process, since this peak corresponds to a larger charge than peak C, which is the only possible peak that may result from oxide formation as confirmed by the XPS results. Hence peak A' most likely may be assigned to hydrogen deposition on Pd NPs. The proportional gradual decrease in the intensities of A' and B and similar corresponding charges hint for related processes at these potentials. It is assumed that here hydrogen deposition and oxidation reactions occur at active sites, such as step edges, on the top residing Pd NPs.

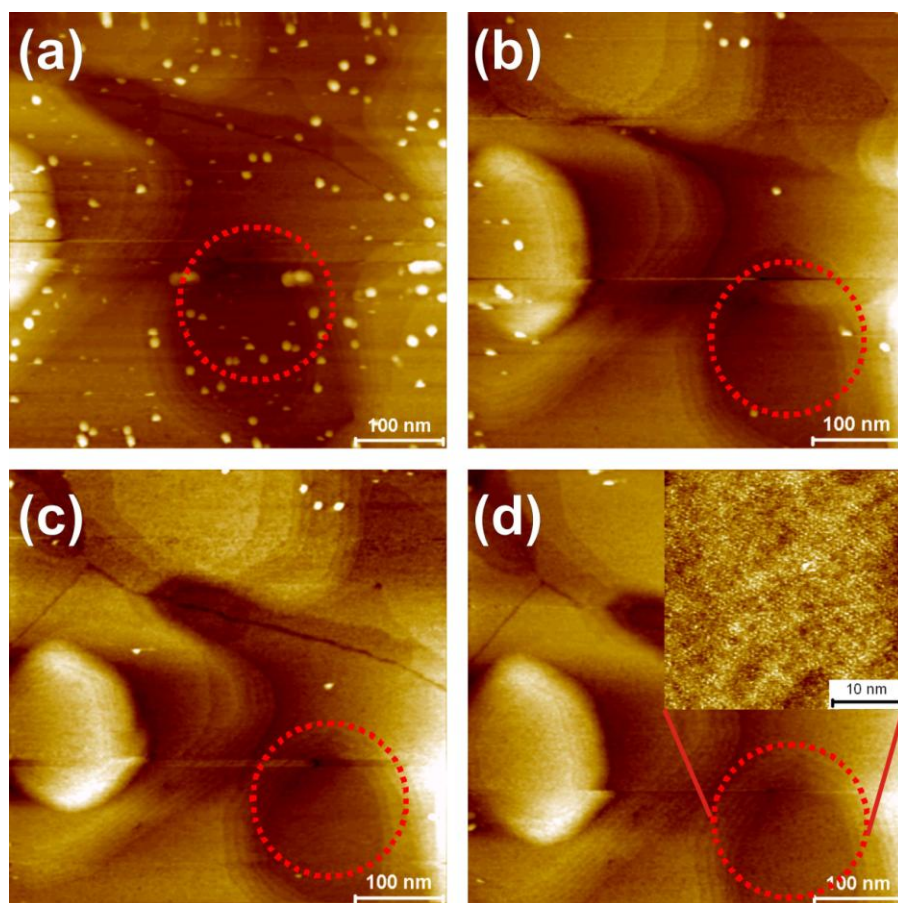


Figure 3. (a-d) Subsequently taken STM images from the same surface region of a Pd/PyPP1/Au sample after continuous scanning until all Pd NPs are removed. Scan dimensions: 500 nm x 500 nm. $I_t \sim 80$ pA, $E_{\text{Tip}} \sim 1.2$ V. The inset in (d) shows the molecular resolution obtained from a zoomed area after removal of the Pd NPs. Scan dimensions: 30 nm x 30 nm. $I_t \sim 150$ pA, $E_{\text{Tip}} \sim 0.3$ V.

The gradual decrease indicates less electrochemical activity for the Pd layer after subsequent cycles. This may hint a slow decrease of active sites (e.g. by slight further growth of the average particle size).

Mobility of the Pd clusters on SAM

STM investigations on the electrochemically formed Pd clusters on PyPP1 have revealed extra information about the interaction between the NPs and the SAM surface. Fig. 3 shows a set of STM images taken from a randomly chosen area on Pd deposited PyPP1/Au(111) sample. Repetitive STM scans cause removal of the Pd NPs from the surface due to poor adhesion of the NPs on the SAM surface. The inset in Fig. 3d shows

the high resolution image taken from the PyPP1 monolayer after removing all Pd NPs from the surface. In this image, individual thiol molecules are seen, which are still in a certain degree of order. No accumulation of Pd clusters around the scanned region was observed. Presumably the NPS are not swept to the sides but attracted by the STM tip.

References

- 1 M. Baldauf and D. M. Kolb, *Electrochimica Acta*, 1993, **38**, 2145-2153.
- 2 J. Tang, M. Petri, L. A. Kibler and D. M. Kolb, *Electrochimica Acta*, 2005, **51**, 125-132.
- 3 H. Kind, A. M. Bittner, O. Cavalleri, K. Kern and T. Greber, *Journal of Physical Chemistry B*, 1998, **102**, 7582-7589.