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Title	Facile electrochemical synthesis of Pd nanoparticles with enhanced electrocatalytic properties from surfactant-free electrolyte
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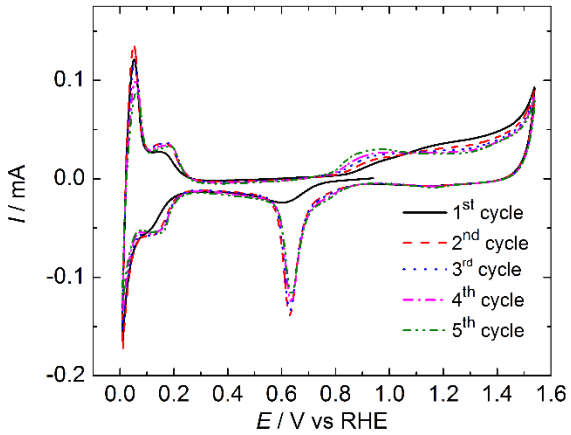


Figure S1. Typical cyclic voltammetry of the Pd deposited on Au (111) electrode at 0.54 V for 1 s and CVs were recorded in deaerated 0.1 M H_2SO_4 electrolyte with a scan rate of 20 mV s^{-1} (initial/conditioning: 0.9 V_{REH}, 10 s).

Figure S2a shows a linear sweep voltammetry (LSV) of the Au(111) substrate measured in the same electrolyte used for the CV analysis. The marked circles on the LSV curve are three potentials selected for the Pd deposition in the small (0.54 V_{RHE}), medium (0.16 V_{RHE}) and large (-0.002 V_{RHE}) potential regions. Figure S2b shows typical time dependencies of the electrode potential-current density curves during the potentiostatic electrodeposition of Pd at the selected potentials. When a small overpotential (0.54 V_{RHE}) was applied, the cathodic current dropped initially but increased gradually to reach a maximum of ca. -0.53 mA cm^{-2} at 2 s. After that the current decreased again and became constant at ca. -0.28 mA cm^{-2} for longer deposition times to 600 s. The behaviour indicated that deposition proceeded in a well-established nucleation and growth mode.[1, 2] At all other electrode potentials, the cathodic current started to flow with a high value and dropped sharply to a constant maximum current of ca. -0.39 mA cm^{-2} for 0.16 V_{RHE}, and -0.67 mA cm^{-2} for -0.002 V_{RHE} for 600 s deposition time.

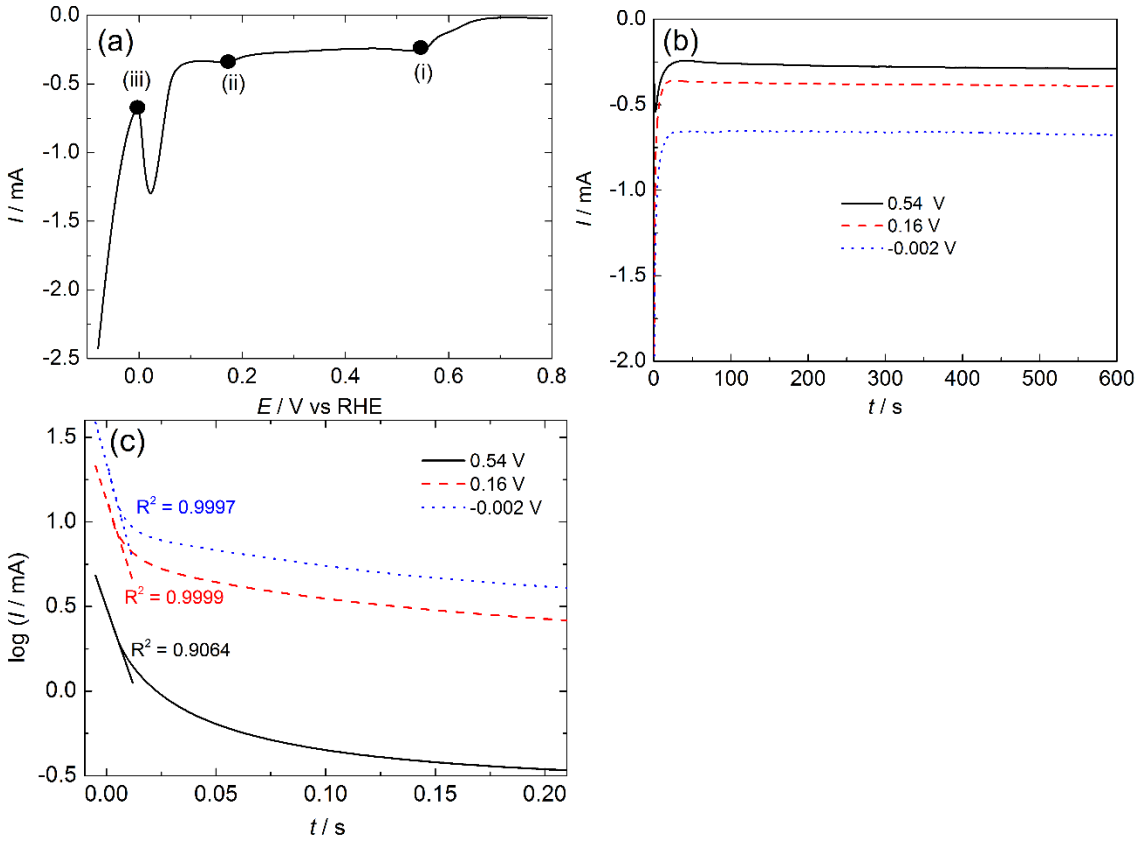


Figure S2. Pd electrodeposition on a Au(111) substrate in deaerated 0.1 mol/L HCl solution containing 0.001 mol/L $PdCl_2$ (a) by liner sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1} (initial/conditioning: 0.79 V_{RHE}, 10 s) and (b) by constant potential (potentiostatic) at three deferent potentials as marked by closed circles on LSV curve at (i) 0.54 V_{RHE} (small), (ii) 0.16 V_{RHE} (medium) and (iii) -0.002 V_{RHE} (large) (initial/conditioning: 0.79 V_{RHE}, 10 s), (c) plot of log (j) vs. time showing the linear dependency for the initial part of the current-time transient. The legend shows the corresponding Pd deposition overpotential at 0.54 V_{RHE} (solid line), 0.16 V_{RHE} (dash line) and -0.002 V_{RHE} (dot line).

The adsorption of ions is usual process in electrodeposition and therefore, the adsorption current for ions on the surface can be estimated from Langmuir type adsorption-desorption process as expressed by the following equation [2].

$$j_{ads} = k_1 \exp(-k_2 t) \qquad (1)$$

where $k_1 = k_2 q_{ads}$ and q_{ads} is the total adsorbed charge per unit area, in which all the constants of equation (1) are measured from the linear relationship between logarithm of current and time of the recorded transient. As seen from the Figure S2c that initial part of the plot is fitted to equation (1) and after subtraction of the adsorption current and charge, the electrochemical deposition corresponds to the Faradaic process.[2] The measured constant values of equation (1) are shown in Table S1. The charge due to ions adsorption is as high as 201.44 µC cm^{-2} in the higher overpotential region, and as low as 36.45 µC cm^{-2} at lower overpotential.

Table S1. The constants of equation (2) measured from linear fitting curve of the Figure S2c.

V_{RHE} for Pd NPs deposition	$k_1 \times 10^{-3}$ (A cm^{-2})	k_2 (s^{-1})	q_{ads} (µC cm^{-2})
0.54	3.13	85.86	36.45
0.16	13.54	91.92	147.30
-0.002	22.28	110.60	201.44

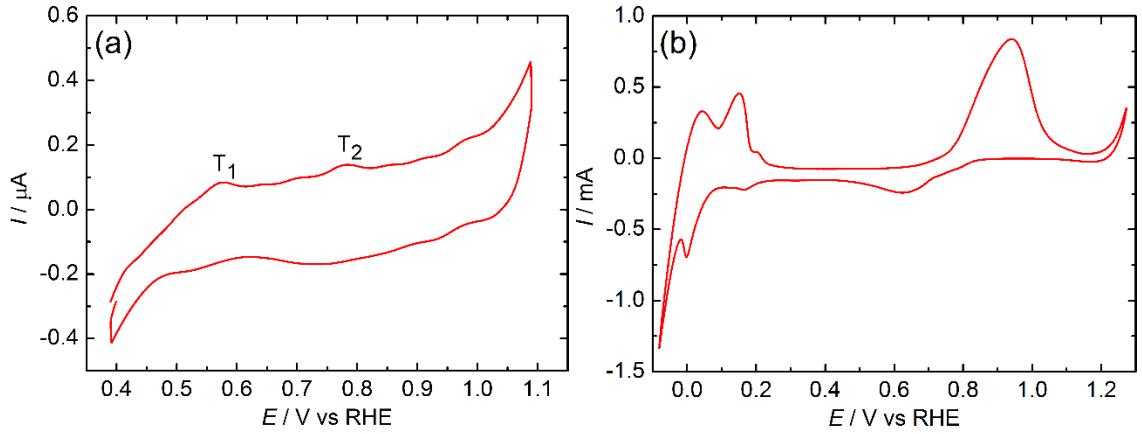


Figure S3. (a) CV of the Au(111) textured substrate in deaerated perchlorate in 0.1 mol L^{-1} $HClO_4$ electrolyte containing 0.005 mol L^{-1}chloride (Cl^-) ions as NaCl. (b) CV of Pd electrodeposition on a Au(111) substrate in deaerated 0.1 mol L^{-1} HCl solution containing 0.001 mol L^{-1} $PdCl_2$ by cyclic voltammetry with a scan rate of 1 mV s^{-1} (initial/conditioning: 0.79 V_{RHE}, 10 s).

The behaviour of CV (Figure S3a) is similar to the Au(111) surface as reported elsewhere, in which the peak T_1 (0.57 V_{RHE}) in the anodic scan corresponds to the structural transition of the Au(111) textured surface.[3] The peak (T_2) at more positive potential was attributed to the structural transition within the adlayers and the corresponding peaks in the cathodic scan were not visible.[3]

In the absence of convection, the current in the current-time transient is given by the Cottrell equation:

$$I(t) = n.F.A.C.\left(\sqrt{\frac{D}{\pi t}}\right) \qquad (2)$$

In which, n is the number of electrons transferred per molecule, F is the Faraday constant (96484.6 C/mol), A is the electrode area (cm^2), D is the diffusion coefficient ($cm^2\ s^{-1}$), and C is the concentration of the species in the solution (mol cm^{-3}). The plot of the measured current versus $t^{-1/2}$ gives a straight line if the current is not influenced by the charge transfer kinetics but by the rate of mass transport to the electrode.

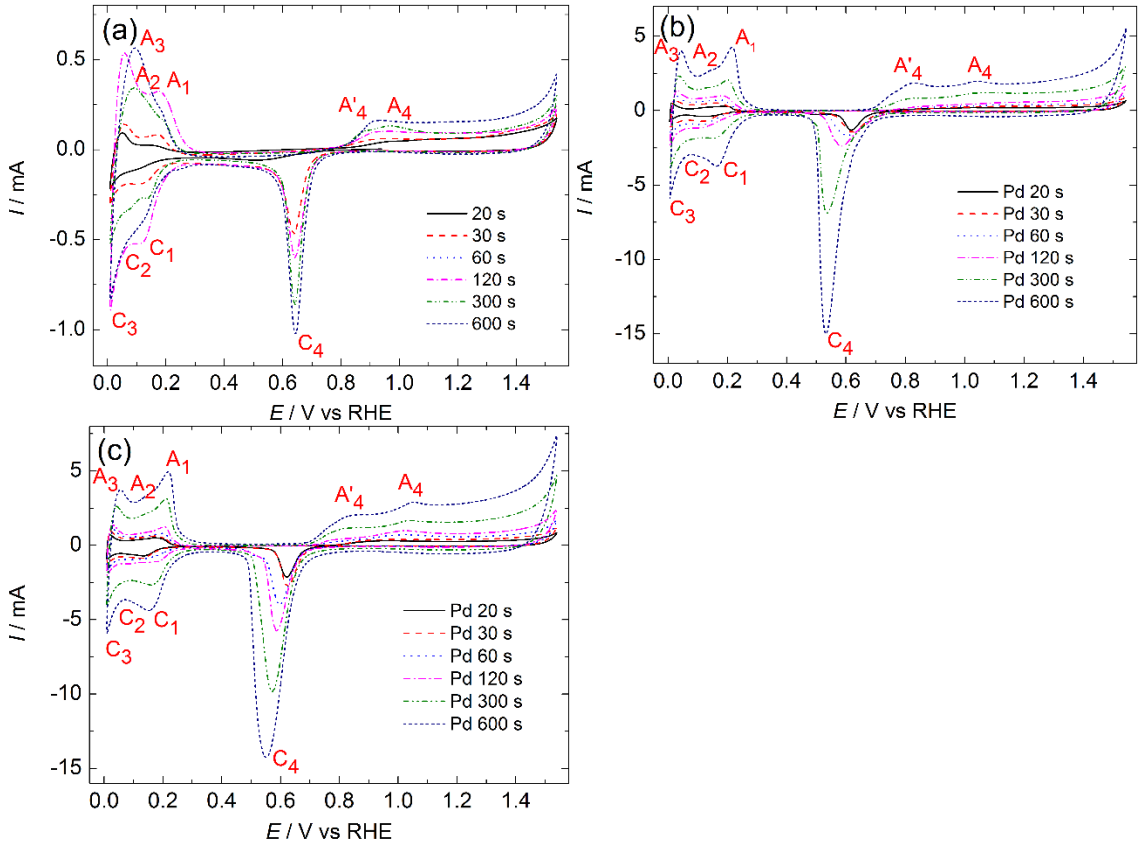


Figure S4. Cyclic voltammetry of the Pd deposited on Au (111) electrodes at (a) 0.54 V_{RHE}, (b) 0.16 V_{RHE}, (c) 0.06 V_{RHE} and (d) -0.002 V_{RHE} shows H_{UPD} as well as oxide formation and reduction in deaerated 0.1 M H_2SO_4 solution with a scan rate of 20 mV s^{-1} (initial/conditioning: 0.9 V_{RHE}, 10 s). CVs were recorded in static conditions and the legend indicates the corresponding deposition time.

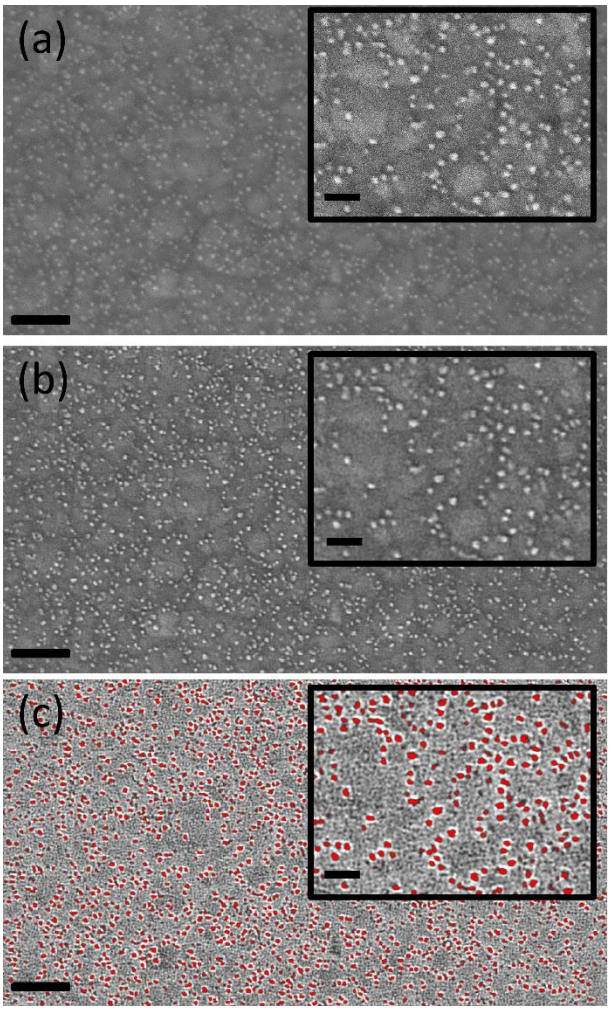


Figure S5. Size determination of nanoparticles. A) Original FEG-SEM image of the sample. B) Convoluted Image. C) Detected particles by Particle Analysis function available in ImageJ software. The size analysis assumes the particles are circular and calculates the diameter based on the detected area of the particles. Scale bars in the big panel and in the inset are 100 nm and 20 nm, respectively.

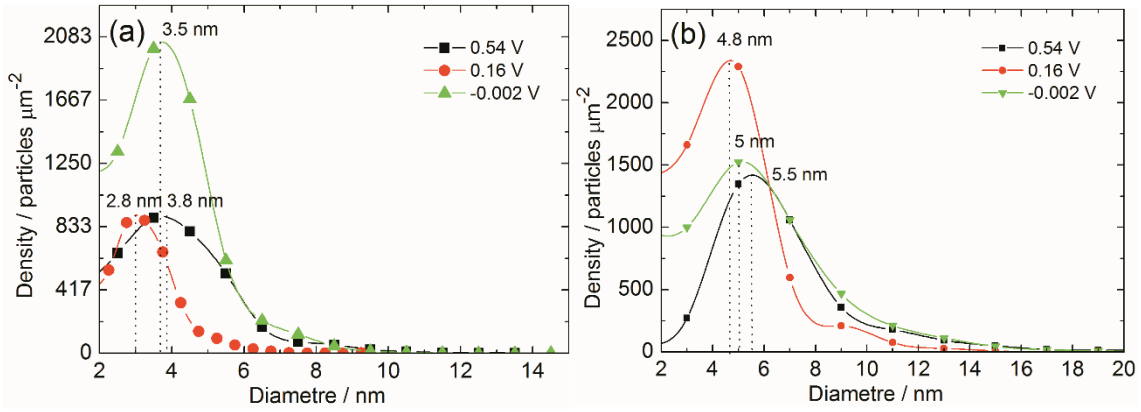


Figure S6. The density of the particle size for (a) 433 µC cm^{-2} and (b) 3183 µC cm^{-2} deposition charge electrodeposited potentiostatically at 0.54 V_{RHE}, 0.16 V_{RHE} and -0.002 V_{RHE}.

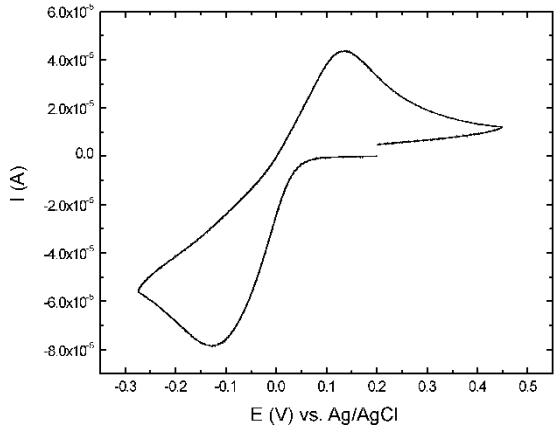


Figure S7: CV of 0.011 M L^{-1} $K_3[FeCN]_6$ + 0.1 M L^{-1} KCl on a glassy carbon electrode. (Conditioning/initial potential: 0.2 V, 30 s; scan rate: 0.0 50 V/s).[4]

A redox couple in which both species rapidly exchange electrons with the working electrode is termed as an electrochemically reversible system. The separation of peak potentials (∆Ep), for a reversible process is related to the number of electrons transferred (n) in the electrode reaction by ∆Ep = 0.058/n at 250C.[1] Thus, for reversibility this one electron process should exhibit a peak separation value close to 0.058 V. But in our case on the glassy carbon electrode, the value is approximately 0.250 V, which indicates that the system is quasi-reversible.

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