Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Structural Evolution of Nanostructured Palladium during Potential Cycling: A Liquid-Cell TEM Study

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Methods

Chemical Reagents: All chemicals were obtained in the highest available purity and used without further purification. Palladium (II) chloride powder (≥ 99.9%) and Hydrochloric acid (ACS reagent, 37%) were purchased from Sigma-Aldrich, Saint Louis, MO, USA. All solutions were made using milli Q water and bubbled with nitrogen for 20 minutes to remove dissolved oxygen before in-situ experiments.

Liquid-cell TEM setup: The *in situ* liquid cell TEM system (Poseidon 500, Protochips Inc., Raleigh, NC, USA) used in this study included a special designed TEM holder containing a liquid electrochemical cell at the tip. This holder is also integrated with electrical and fluidic circuitry for interfacing the electrochemical cell with a potentiostat (Gamry Reference 600, Gamry Instruments Inc., Warminster, PA, USA) for electrochemical control and a syringe pump (Harvard 11 Elite standard infuse only syringe pump, Harvard Apparatus Inc., Holliston, MA, USA) for fluidic control. The liquid cell is composed of two micro-fabricated silicon chips which seal the electrolyte in between. Both chips contained electron transparent silicon nitride windows (back-etched on a silicon substrate) for *in situ* observation, and spacers for controlling the liquid thickness. The top chip included patterned silicon nitride structures for guiding the liquid flow, and the bottom chip contained three micro-electrodes for creating a miniaturized electrochemical cell. The commercially available bottom chips (ECT24-CO, Protochips Inc., Raleigh, NC, USA) used in this work integrated carbon working electrodes, Pt reference electrodes, and Pt counter electrodes on silicon/silicon nitride chips and contained 500 nm spacers. The top chips with 150 nm (EPB-55DF, Protochips Inc., Raleigh, NC, USA) were used in this study.

Potential Cycling: *In situ* cyclic voltammetry on carbon electrode was performed using a solution of 5 mM H_2PdCl_4 with and without 15 mM HCl at a flow rate of 5 µL/min and a scan rate of 100 mV/s. In order to compare the Pt micro-reference electrode versus standard reference electrode, the potential difference between the Pt electrode from the E-chip and Ag/AgCl reference electrode was measured by using the Pt microelectrode as working electrode and a Ag/AgCl reference electrode in 5 mM H_2PdCl_4 in 15 mM HCl solution and a constant reading of about 0.475V was obtained for about 3 min (See Fig. S2)

During the *in situ* CV scans, the applied potential started from open circuit potential, firstly went towards negative values and then towards positive values and finally back to the open circuit potential, which was considered as one single cycle in this study. The real time imaging was performed using bright-field scanning TEM (BF-STEM) with beam dose of 21 electrons/frame.nm2. The imaging and electron energy loss spectroscopy (EELS) were performed using a JEOL 2010F TEM operated at 200 kV, the microscope is equipped with a GIF for the acquisition of the electron energy loss spectra. Bright-filed scanning transmission electron microscope (BF-STEM) imaging was performed using a DigiScan II (Gatan, model 788) unit with a BF detector with time resolution of 0.555 s/frame. The whole *in situ* process was recorded frame by frame and in-situ images were then extracted from the *in situ* videos.

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***Post situ* SEM-EDS:** *Post situ* SEM-EDS was performed using the JEOL JSM-7000F field emission SEM, integrated with Oxford Instruments X-Maxn 50 mm^2 EDS detector to obtain the morphology of the deposits and elemental analysis.

***In situ* electron energy loss spectroscopy (EELS):** *In situ* EELS was performed on the liquid cell with palladium salt solution, and the spectrum is shown in Fig. S1. The ratio of zero-loss electrons to the total transmitted intensity gives a relative measure of the specimen thickness in units of the local inelastic mean free path λ[1]. By obtaining the thickness over mean free path λ from the spectrum, the thickness of the liquid is estimated to be about 510 nm.

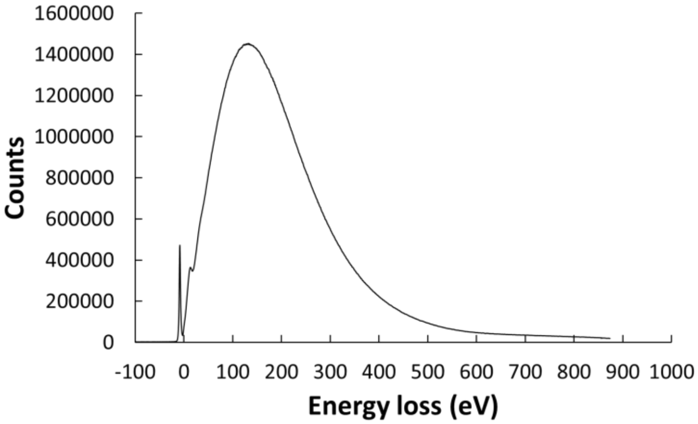


Fig. S1 *In situ* EELS spectrum acquired from the liquid cell with Pd salt solution (5 mM H_2PdCl_4 in 15 mM HCl).

Potential difference between Pt microelectrode on E-chip as reference electrode versus Ag/AgCl reference electrode in 5mM H_2PdCl_4 in 15 mM HCl.

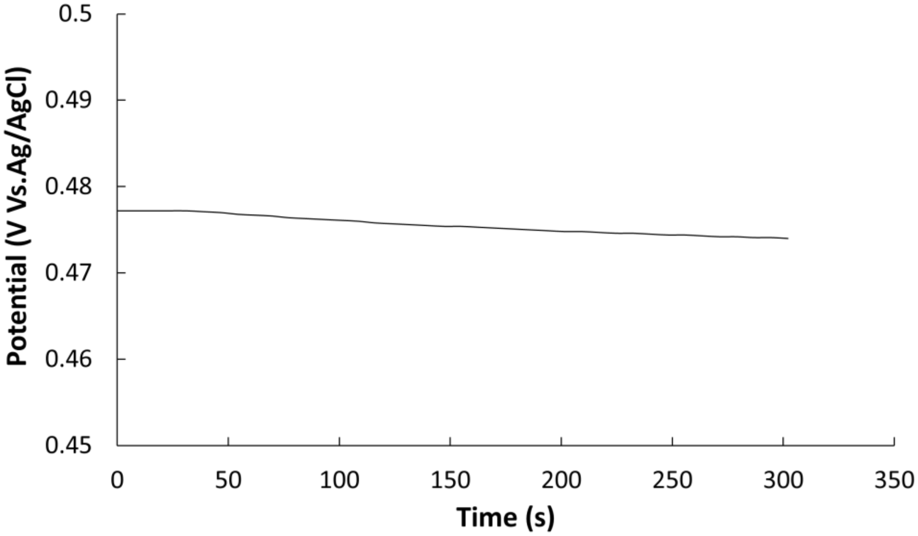
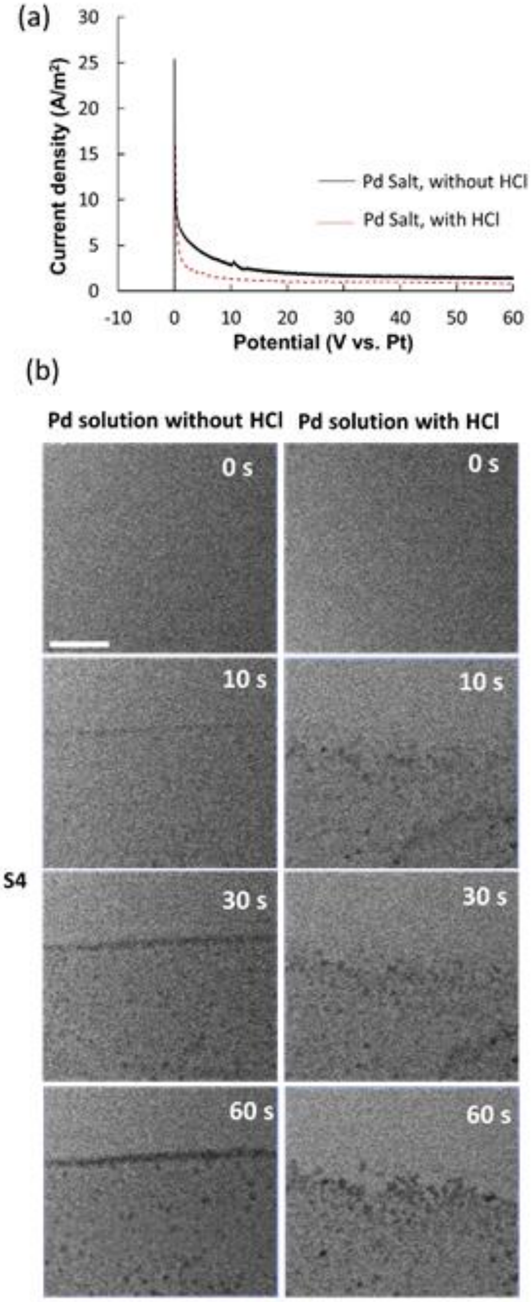


Fig. S2 Measurement of potential difference between Pt reference electrode versus Ag/AgCl electrode.

***In situ* electrodeposition of Pd on carbon electrode under fixed potential from Pd salt solution with and without HCl:** The current transients and time series of bright field STEM images are shown in Fig. S4 (a) and (b).



S4

Fig. S3 *In situ* deposition of Pd on carbon electrode under fixed potential of -0.6V vs. Pt reference electrode from 5 mM H_2PdCl_4 without and with 15mM HCl. (a). Current transients obtained during the electrodeposition.(b). Bright field STEM images showing growth of Pd at different time points in both solutions. Scale bar: 1 µm.

***Post situ* Scanning electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS):** SEM images and EDS elemental mapping and spectrum on the areas under *in situ* observation are shown in Fig. S5.

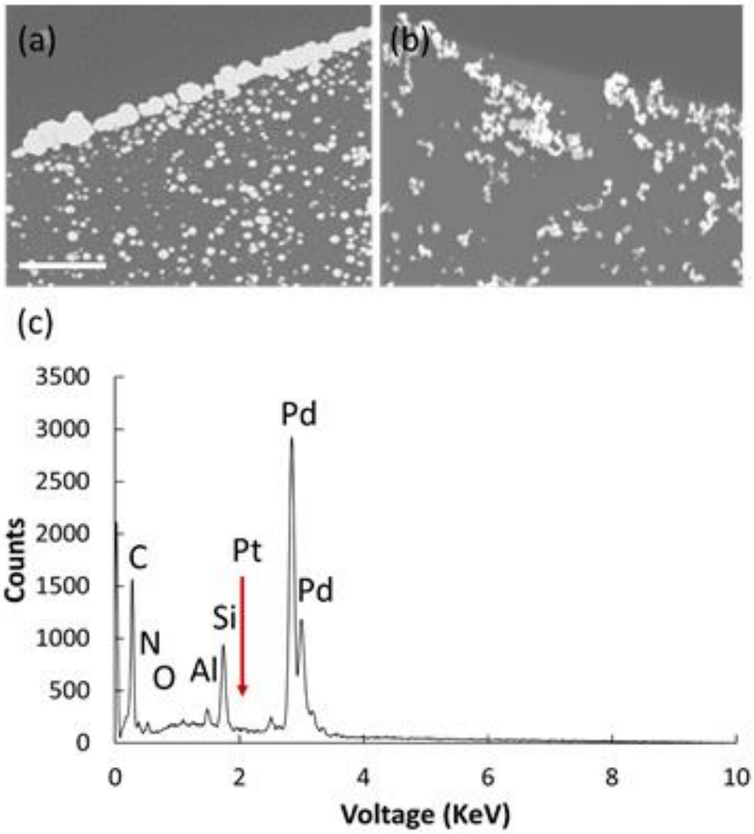


Fig. S4 *Post situ* SEM-EDS analysis on the areas under *in situ* observation shown in Figure 2 and Figure 3. SEM images showing Pd deposits from Pd salt solution (a). without HCl and (b). with HCl. (c). EDS spectrum showing the composition of the deposits on carbon electrode from Pd salt solution (5 mM H_2PdCl_4 in 15 mM HCl). Scale bar: 1 μm.

Quantitative analysis on deposited palladium structures: The measurements included several tens of structures in the images displayed in Fig. 4. The estimated average sizes from these images is about: 130 nm for particles formed without HCl supporting electrolyte, 380 nm for aggregates formed with HCl supporting electrolyte.

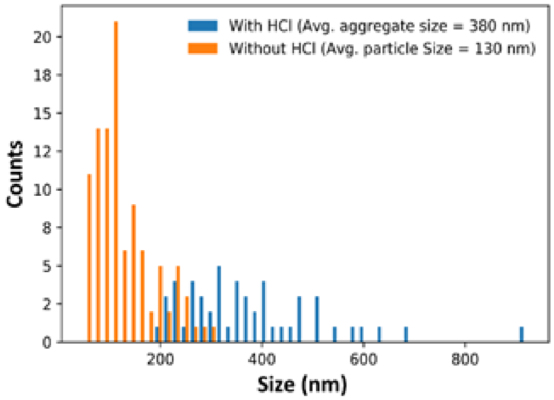


Fig. S5 ize-distribution and the estimated average sizes for (i) particles and (ii) aggregates formed by electrodeposition with/without HCl shown in Figure 4.

References

1. Malis, T.; Cheng, S. C.; Egerton, R. F., *J. Electron Microsc. Tech.* 1998, ***8***, 193–200.