Supporting Information for

Quantitative investigation of the formation and growth of palladium fractal nanocrystals by liquid-cell transmission electron microscopy

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Materials and Methods.

Materials: Sodium tetrachloropalladate (Na_2PdCl_4) was used as received and used without further purification. Solvent is ultrapure water (18.2 MΩ·cm). The 1.0 mM and 5.0 mM precursor solutions arre prepared by dissolving sodium tetra-chloropalladate in water, which is furtherly treated with 250 nm thick filter membrane prior to use. The whole liquid-cell system comes from Hummingbird scientific Inc. USA. The liquid cell consisted of spacer chip and blank chip, has two 50 nm thick electron-translucent membrane window with 50 μm × 200 μm amorphous silicon nitride (Si_3N_4) membrane. Herein, a 100 nm thick spacer chip is used to set the nominal thickness of the precursor solution in liquid cell. The Si_3N_4 membranes are plasma cleaned to render the membrane surfaces hydrophilic.

Methods: About 0.3 μL precursor solution is placed onto the central region of spacer chip and then sealed by another window chip. Leak checking is performed before imaging. Then, the liquid specimen holder is inserted into the TEM. In situ experiments were carried out using a FEI Tecnai G2 F20 microscopy operated at 200 kV. Two different imaging modes (STEM and TEM imaging) are used for in situ LC-TEM experiments. The STEM image time series are recorded using an image size of 512 × 512 pixels and have been aligned before analysis. All in situ movies can be found in the Supporting Information. Image analysis is done with Image-J to determine the projected area, fractal dimension of nanocrystal. Ex situ data is got using a FEI Tecnai G2 F20 operated at 200 kV.

Supplementary Movies.

Movie S1: Representative in situ HADDF STEM movie showing Pd nanodendrites formation process in 5.0 mM Na_2PdCl_4 in the liquid cell. The areal electron dose rate is 9.46 × 10^3 e/nm^2·s. Graphical data shown in Fig. 1, main text.

Movie S2-S5: In situ HADDF STEM movie of Pd fractal nanocrystal growth at the different electron dose rate of 0.61 × 10^3 e/nm^2·s, 1.12 × 10^3 e/nm^2·s, 4.47 × 10^3 e/nm^2·s, 1.77 × 10^4 e/nm^2·s, respectively. Graphical data shown in Fig. 2a-d, main text.

Movie S6-S7: In situ HADDF STEM movie of Pd fractal nanocrystal growth at different precursor concentration of 1.0 mM and 5.0 mM Na_2PdCl_4, respectively. The areal electron dose rate is 4.47 × 10^3 e/nm^2·s. Graphical data shown in Fig. 3a-b, main text.

Estimating the production rate of Pd atoms.

The number of electrons per second is simply: n_e=6.24×10^{18}I (e/s), where *I* is the irradiation current (0.48 nA), resulting in the total electrons numbers of ~3.0×10^9 e/s.[1] According to previous work, reducing one Au^{3+} ion to Au atom thus requires ~ 4920 primary electrons with an energy of 200 kV.[2] Assuming the reduction potential of Pd is similar to Au, reducing one Pd^{2+} ion to Pd thus requires ~ 3280 primary electrons. Therefore, it will produce total 9.1×10^5 Pd atoms/s ($N_{Pd}^0{}_{tot}$) so that the numbers of Pd (N_{Pd}^0) can be described by equation:

$$N_{Pd}^0 = N_{Pd}^0{}_{tot}/S\ (\text{counts}\cdot\text{s}^{-1}\cdot\text{nm}^{-2}) \quad (1)$$

And the solution layer in the liquid cell is 100 nm thick, hence we can estimate roughly the production rate per unit volume of Pd atoms as shown in Table S1. Obviously, the local supersaturation is higher for higher electron dose rate according to production rate of Pd atoms. Note that these values were calculated under the condition of ignoring the diffusion effect.

Table S1. The estimation of the production rate of Pd atoms at the different electron dose rates.

Mag	**80K**	**115K**	**160K**	**225K**	**320K**
Area (S)/nm^2	2684355	1268777	671089	317194	169328
d_{eff}/(10^3 e^-·s^{-1}·nm^{-2})	1.12	2.36	4.47	9.46	17.7
N_{Pd}^0/(counts·s^{-1}·nm^{-2})	0.34	0.72	1.36	2.88	5.40
N_{Pd}^0/(counts·s^{-1}·nm^{-3})	34	72	136	288	540

Supplementary figures.

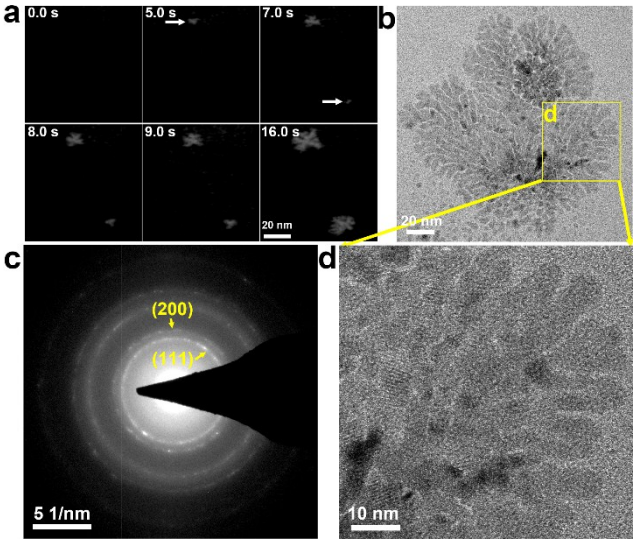

Figure S1. (a) Formation process of Pd nanodendrites using an electron dose rate of 2.37 × 10^3 e/nm^2·s; (b-d) Ex situ TEM image and selected area electron diffraction and high resolution TEM images of Pd nanodendrites synthesized in a liquid cell.

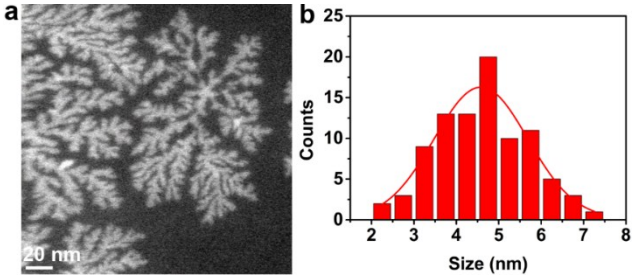

Figure S2. Branch width of nanodendrites. (a-b) HAADF STEM image of nanodendrites and a corresponding histogram of dendritic branches width distribution.

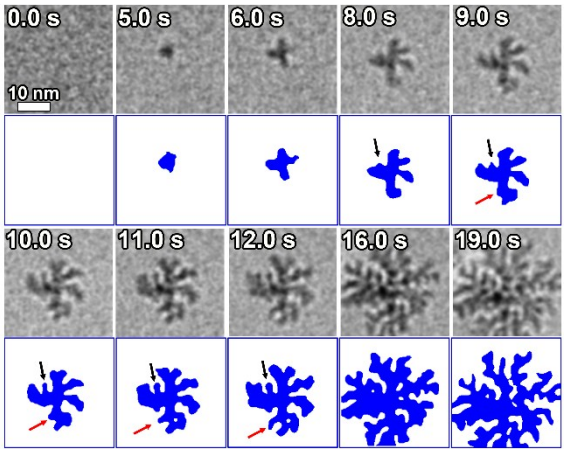

Figure S3. TEM image series show that a nanocluster (~ 5 nm) first form and then grow into nanodendrite.

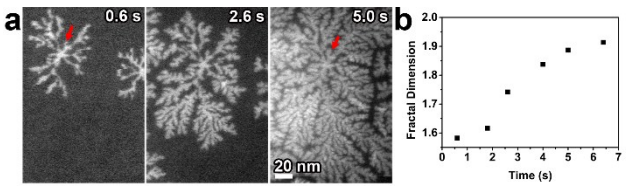

Figure S4. Electron dose rate effects on the Pd nanodendrite growth process. (a) The growth process of Pd nanodendrite using an electron dose rate of 6.71×10^4 e/nm^2·s; (b) Fractal dimension of Pd nanodendrite as a function of time.

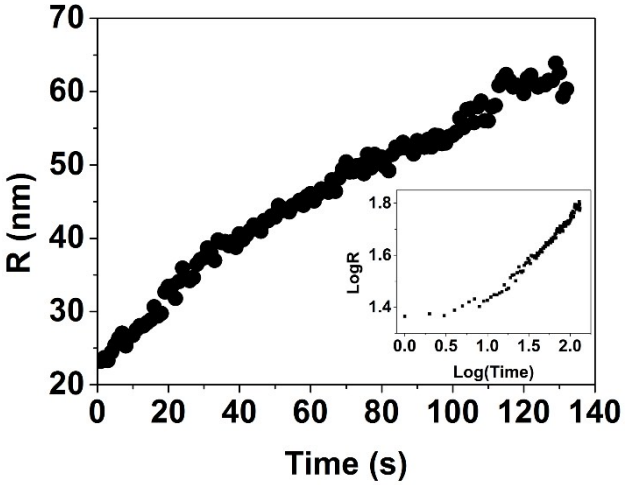

Figure S5. Radius of the fractal-like island nanocrystals (Figure 3a in main text) as a function of growth time at 1 mM precursor concentration using an electron dose rate of 4.47×10^3 e/nm^2·s.

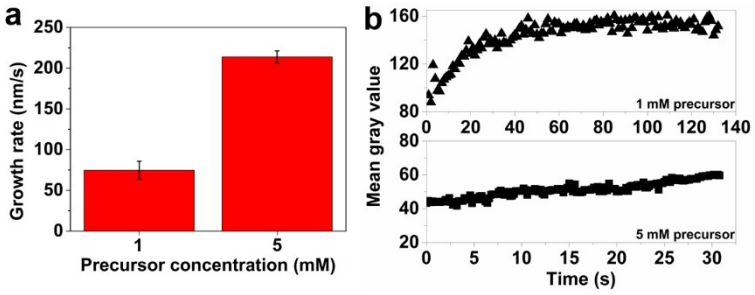

Figure S6. Differences of growth rate and contrast of Pd nanocrystals during growth process: (a) Different growth rates are showed at 1.0 mM and 5.0 mM precursor concentration using an electron dose rate of 4.47×10^3 and 1.12×10^3 e/nm^2·s, respectively; (b) Difference of contrast evolution of Pd nanocrystals at 1.0 mM and 5.0 mM precursor concentration using an electron dose rate of 4.47×10^3 e/nm^2·s.

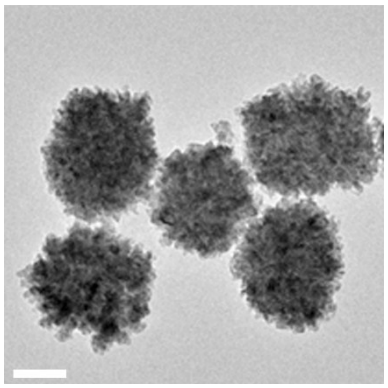

Figure S7. TEM image of Pd island-like nanocrystals synthesized in flask. Scale bar: 50 nm.

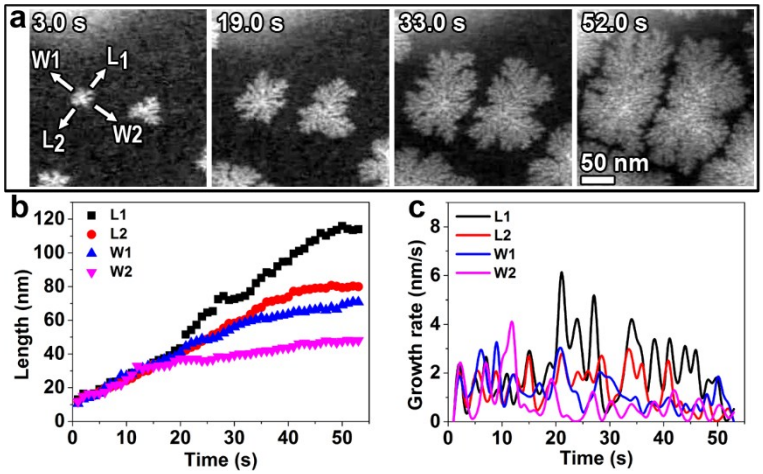

Figure S8. Influence of adjacent nanodendrites on the of growth process of Pd nanodendrites. (a) A time lapse series of HAADF-STEM images at an electron dose rate of 2.37×10^3 e/nm^2·s; (b) Nanodendrites length and (c) growth rates along different directions.

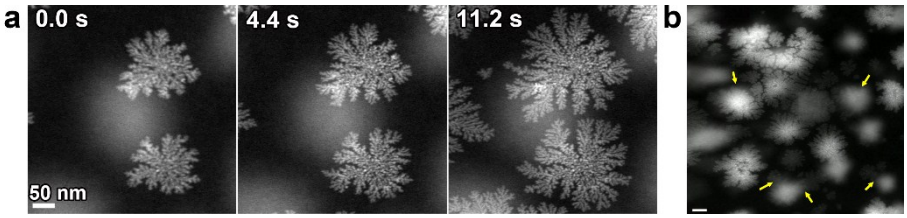

Figure S9. (a) Pd nanodendrites formation process closing to the two Si_3N_4 membranes using an electron dose rate of 9.46×10^3 e/nm^2·s. (b) Overlapped nanodendrites in liquid cell. Scale bar: 100 nm.

References

1. J. H. Park, N. M. Schneider, J. M. Grogan, M. C. Reuter, H. H. Bau, S. Kodambaka and F. M. Ross, *Nano Lett.*, 2015, **15**, 5314-5320.

2. N. Ahmad, Y. Le Bouar, C. Ricolleau and D. Alloyeau, *Advanced Structural and Chemical Imaging*, 2016, **2**.