Electronic Supplementary Information

Experimental details:

Liquid cell TEM experiment procedure: The chemical sodium tetrachloropalladate (99%, Aldrich) was used as received, and then dissolved with mill-Q water. The liquid-cell TEM experiments were conducted with a fluid holder (Hummingbird Scientific, USA). Two silicon micro-chips with electron transparent window (50 nm thick) were used to seal the liquid. Prior to loading, the Si microchips were cleaned with oxygen plasma cleaned for 5 minutes in order to remove organic contamination and render the surfaces hydrophilic. 1 μL of aqueous sodium tetrachloropalladate was dropped onto a chip with spacers (200 nm thick) with a pipette, and followed by covering another blank chip on it. The whole setup was schemed in Figure S1.

All the in-situ experiments were carried out using a Tecnai G^2 F20 microscope (FEI, USA) equipped with a HAADF detector from Fischione and a model 832 CCD from Gatan. The typical dwell time of each pixel during STEM imaging was set to 3.16μs. Serial images were recorded in the form of movies by capturing screens done with CamStudio, and then analyzed frame-by-frame for further information with ImageJ developed in National Institute of Health.

Synthesis of Pd nanocubes of 18 nm in size. The Pd nanocubes were synthesized by reducing Na_2PdCl_4 with ascorbic acid (AA) in the presence of KBr, according to our previous report.[1] In a typical synthesis, 8.0 mL of an aqueous solution containing 50 mg of PVP, 60 mg of AA, and 600 mg of KBr was hosted in a vial, and pre-heated to 80 ℃ in an oil bath under magnetic stirring for 10 min. Subsequently, 3.0 mL of an aqueous solution containing 57 mg of Na_2PdCl_4 was added with a pipette. After the vial had been capped, the reaction was allowed to continue at 80 ℃ for 3 h. The product was collected by centrifugation, washed three times with water to remove excess PVP, and re-dispersed in 11 mL water. Shown in Figure S2 is a typical TEM image of the as-formed Pd nanocubes.

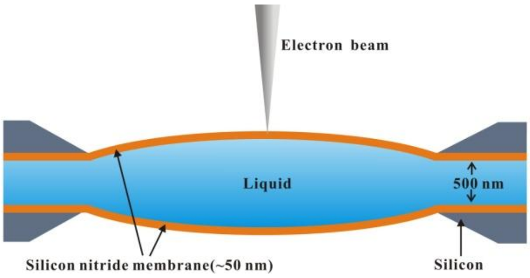

Fig. S1 Cross-sectional Scheme of the liquid cell used in this experiment. Liquid layer was sandwiched by two Si micro-chips with an electron-transparent window made of SiN membra

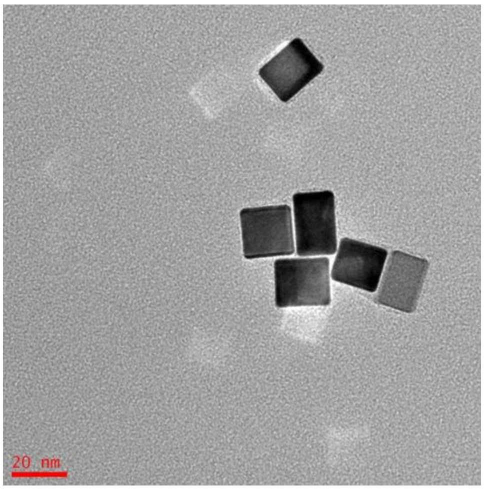

Fig. S2 A typical TEM image of Pd nanocubes used in this experiment.

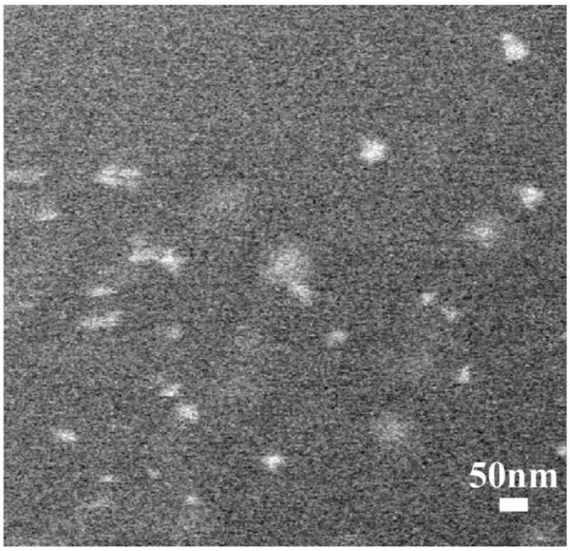

Fig. S3 A typical STEM image of Pd nanoparticles located in thick layer of liquid (without formation of any large bubbles). The settings of imaging condition of the microscope is the same as that used as shown in Figure 4.

Movie Captions

Movie S1: A movie showing the evolution a bubble under e-beam radiation (as shown in Figure 1). The movie plays three times faster.

Movie S2: A movie showing the migration and assembly of Pd nanoparticles in a ultrathin layer of liquid (as shown in Figure 4). The movie plays three times faster.

Movie S3: A movie showing the rotation of a single palladium nanocube in the ultrathin liquid layer (as shown in Figure 5).

Thickness Estimate[2,3,4]

We followed the method proposed by a few other groups to estimate the thickness of liquid layer within the liquid cell. For a sample composed of n layers of different materials, the mass thickness contrast can be quantified from the log-ratio formula:

$$\frac{I_{out}}{I_0} = 1 - e^{[-(\frac{t_1}{\lambda_1}+\frac{t_2}{\lambda_2}+\cdots+\frac{t_n}{\lambda_n})]}$$

Where t is the thickness, I_{out} and I_0 are the currents of the output and incident electron beam. λ is the inelastic mean free path (IMFP). Where t_1,t_2…t_n are the thickness and λ_1, λ_2…λ_n are IMFPs for multiple materials. The total thickness of the silicon nitride is 100nm and the inelastic mean free path for silicon nitride is 135.94nm, λ_{water} =105.4nm. We adopt different probe conditions to calculate the average thickness of the water layer.

Table S1. The calculated thickness of the ultrathin liquid layer (Note that there would be two ultrathin water layers within the cell, so the average thickness of the single ultrathin layer is around 40nm) under different imaging condition. (current of electron beam)

NO.	I_O(Na)	I_{OUT}	t_{water}
(1)	518	393	72.3
(2)	289	229	88.2
(3)	163	127	81.6
(4)	295	215	60.1

[1] M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu, Y. Xia, Nano Res. 2011, 4, 83-91.

[2] N. de Jonge, D. B. Peckys, G. J. Kremers and D. W. Piston, *P. Natl. Acad. Sci.*, 2009, **106**, 2159-2164.

[3] N. de Jonge, N. P. Demers, H. Demers, D. B. Peckys and D. Drouin, *Ultramicroscopy*, 2010, **110**, 1114-1119.

[4] T.-W. Huang, S.-Y. Liu, Y.-J. Chuang, H.-Y. Hsieh, C.-Y. Tsai, Y.-T. Huang, U. Mirsaidov, P. Matsudaira, F.-G. Tseng, C.-S. Chang and F.-R. Chen, *Lap Chip*, 2012, **12**, 340-347.