

Supplementary Information

Atomic Layer Deposition of Platinum Catalysts on Nanowire Surfaces for Photoelectrochemical Water Reduction

Neil P. Dasgupta^{1‡}, Chong Liu^{1,2‡}, Sean Andrews^{1,2}, Fritz B. Prinz³ and Peidong Yang^{*1,2,4}

¹Department of Chemistry, and ²Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, United States

³Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, United States

⁴Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

[‡]These authors contributed equally to this work

*Correspondence should be addressed to: p_yang@berkeley.edu

Experimental details:

Atomic Layer Deposition (ALD): Growth of TiO₂ thin films and Pt nanoparticles was performed in two separate customized flow-type ALD reactors based on a previously reported design¹. The precursors used for TiO₂ growth were tetrakis(dimethylamido)titanium(IV) (Aldrich) and water. The titanium precursor source was maintained at 60 °C. The substrate temperature for TiO₂ growth was 180 °C. The precursors used for Pt growth were trimethyl(methylcyclopentadienyl)platinum(IV) (Aldrich) and air². The Pt precursor was sublimated at 65 °C. The substrate temperature for Pt growth was 250 °C. The Pt precursor was exposed to the substrate for 1 second using a stop-valve to isolate the chamber from the vacuum pump. Argon was used in both processes as a carrier gas at a flow rate of 20 sccm.

Scanning Transmission Electron Microscopy (STEM): Images were acquired in an FEI Titan 80-300 equipped with two hexapole-type spherical aberration correctors operated at 80 KV. Surface diffusion of species was observed when operated at 300 KV. A High Angle Annular Dark Field (HAADF) detector provided Z-contrast between the TiO₂ shell and Pt particles. Sizes of Pt particles were measured by first setting a local contrast threshold; then circles were circumscribed around the pixels above the threshold.

X-ray Photoelectron Spectroscopy (XPS): XPS measurements were performed with a PHI VersaProbe Scanning XPS Microprobe with a monochromated Al(k α) source. An angle of 70 degrees with respect to the surface normal was used to improve surface sensitivity of the measurement.

Total Reflectance X-ray Fluorescence (TXRF): TXRF measurements were performed with a TREX 610-T TXRF instrument at Evans Analytical Group (Sunnyvale, CA, USA). The source was a Mo($k\alpha$) tube with a beam energy of 40 kV and a beam current of 40 mA. The incident angle was 0.04° , and the integration time was 1000 sec. Measurements were made on a polished Si(100) wafer, coated with 12 nm of TiO₂ and 1 cycle of Pt to replicate the ALD conditions for the PEC experiments. Measurements were taken at 3 locations: at the center of the wafer (0,0) and at (17,-17) and (-17,17) where the positions are given in Cartesian coordinates in units of mm relative to the origin at the center of the wafer.

Nanowire Array Synthesis: Silicon (Si) nanowire arrays with different surface-aspect ratios were used in this study. Well-defined periodic Si nanowire arrays (noted as gas-phase etched nanowires in Figure 2) were fabricated using reactive-ion etching of patterned single-crystalline Si wafers. P-type boron-doped 4" Si wafers (<100> oriented, $0.1\text{--}0.2 \Omega\cdot\text{cm}$) were first patterned with a photoresist dot array using a standard photolithography stepper. Next, the wafer underwent inductive-coupled plasma deep reactive-ion etching (Surface Technology Systems, Inc.) to produce nanowire arrays with uniform diameter of ~ 850 nm and length of ~ 30 μm . After removing the residual photoresist by an O₂ plasma, 50 nm of dry thermal oxide was grown on the nanowires at 1050 °C for 40 min. After a 5:1 buffered HF etch and critical point drying (Tousimis, Inc.), Si nanowire arrays with wires whose diameters were ~ 800 nm were obtained, corresponding to a roughness factor of ~ 21 . For Si nanowire arrays with larger surface area, electroless etching was applied to a wafer of the same characteristics, using a method reported previously³. Si wafers cleaned by Piranha treatment were treated first with a 1:10 buffered HF etch to remove the native oxide, and then were immersed in the electroless etching solution, which comprises of 720ml DI water, 160ml concentrated HF, and 2.96g AgNO₃. By controlling the time of electroless etching, the length of nanowires was ~ 8 μm . The diameter of the wires from this technique ranges from $\sim 20\text{--}100$ nm. Due to this variation, an exact roughness factor for these wires can not be determined, but is several times larger than the vapor-phase etched wires.

Photoelectrochemistry (PEC) measurements: Electrochemical and photoelectrochemical measurements of electrodes were performed using a Gamry reference 600 potentiostat. All measurements were performed under purged Ar gas environment and in a 0.5 M sulfuric acid electrolyte (pH = 0.52). Ag/AgCl in 3 M NaCl (ALS, Corp.) was used as the reference electrode when needed, and all voltages reported were calculated *versus* the reversible hydrogen electrode (RHE) using the following equation:

$$V \text{ vs RHE (volt)} = V \text{ vs Ag/AgCl (volt)} + 0.234 \text{ (volt)}$$

The light source used for simulated sunlight in this report was a 300-Watt xenon lamp equipped with an air mass 1.5G filter (Newport). Before each measurement, a calibrated silicon photodiode determined the light intensity at the position of the electrode being measured. All photo-response data were measured right after the co-catalyst loading procedures described above.

The j - V photocurrent data for individual photoelectrodes were measured using a standard three-electrode setup under simulated one-sun illumination, with a scan rate of 10 mV/sec. The dark currents were orders of magnitude lower than photocurrent in all cases within the voltage ranges measured.

ALD cycles	XPS intensity (a.u.)	Pt loading amount ^a (ng/cm ²)	j_0 ^c (μ A/cm ²)	j_{sc} ^d (mA/cm ²)
1	4.4±0.9	13±3	27±4	7.1
2	9.7±1.9	24±5 ^b	59±9	8.3
3	11±2	34±7 ^b	85±10	12.5
10	26±7	105±21 ^b	130±20	20.7

Table 1 Electrochemical characteristics of ALD Pt for proton reduction. ^a The absolute Pt loading amount is calculated based on the TXRF and XPS measurements on planar Si substrates. ^b Linear extrapolation of TXRF data are based on one cycle ALD Pt sample, using the relative XPS intensity for higher cycle numbers. ^c j_0 exchange current density calculated from the Tafel plots in Figure 2b. ^d j_{sc} is the current density of Si nanowire array photocathode synthesized via gas-phase etching, at 0V vs. RHE, from Figure 2.

References:

- (1) Dasgupta, N. P.; Mack, J. F.; Langston, M. C.; Bousetta, A.; Prinz, F. B. *Review of Scientific Instruments* 2010, **81**, 044102.
- (2) Chao, C.-C.; Motoyama, M.; Prinz, F. B. *Advanced Energy Materials* 2012, **2**, 651.
- (3) Hochbaum, A. I.; Chen, R.; Delgado, R. D.; Liang, W.; Garnett, E. C.; Najarian, M.; Majumdar, A.; Yang, P. *Nature* 2008, **451**, 163.

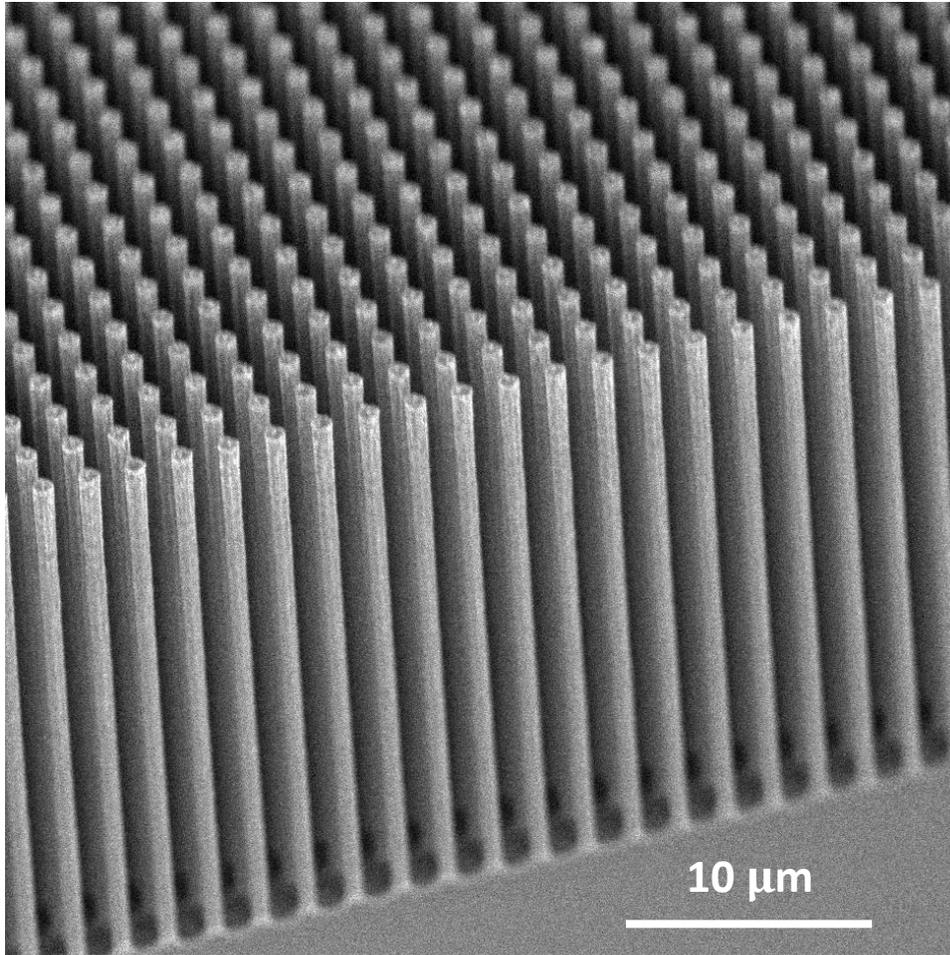


Figure 1: Scanning electron microscope (SEM) image (45 degree tilt) of well-defined Si nanowire arrays synthesized via gas phase etching.

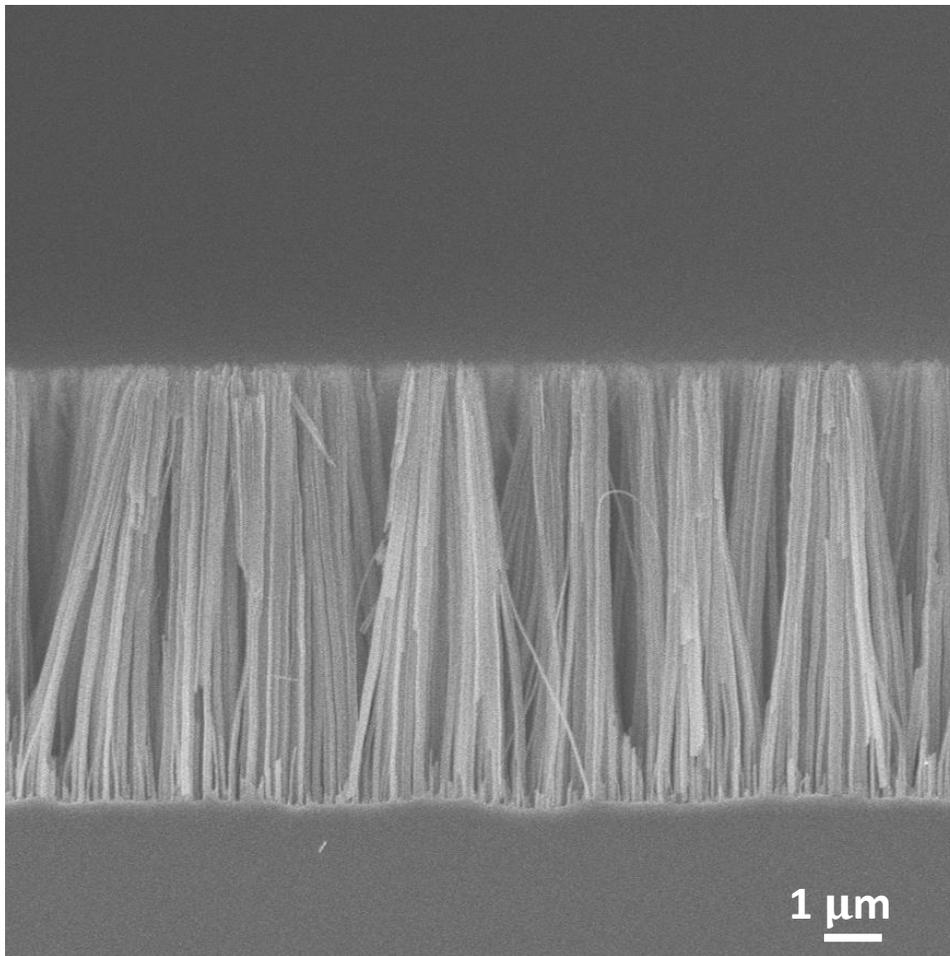


Figure 2: SEM image of a high surface area Si nanowire array synthesized via the electroless etching technique.

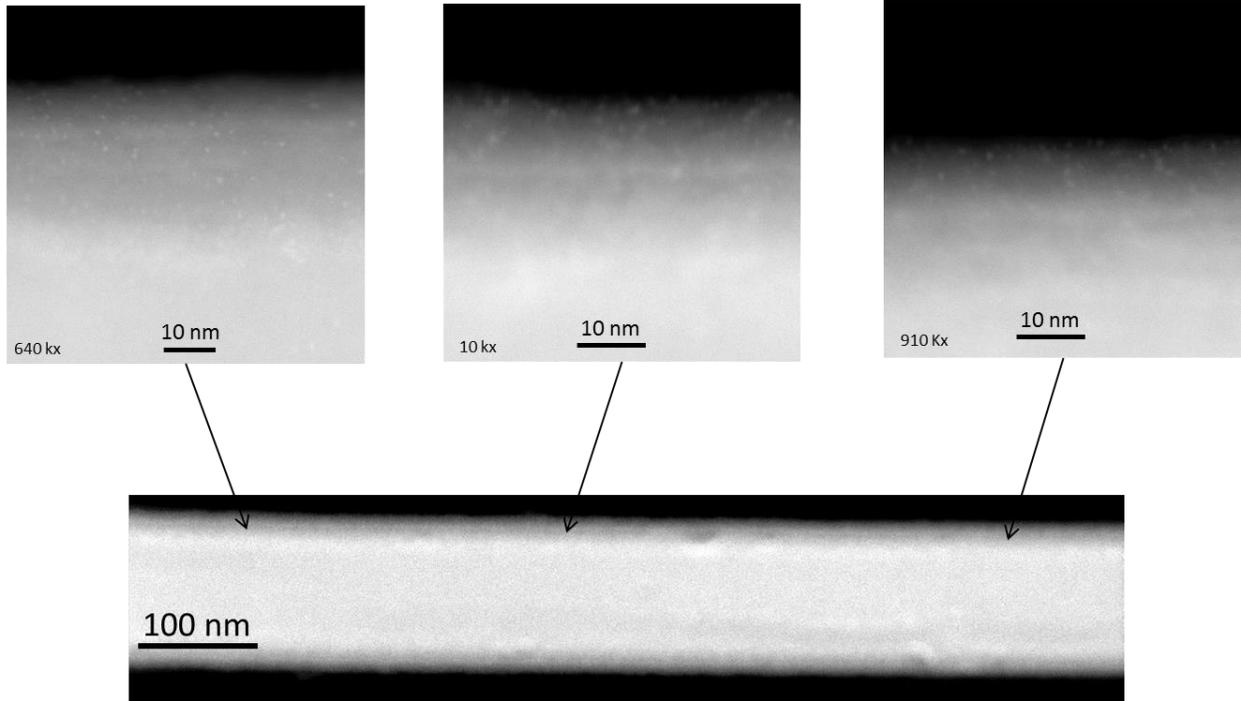


Figure 3. High magnification STEM images of a NW coated with ALD TiO₂ and 1 cycle of Pt at different regions of a single NW, demonstrating uniform distribution in size and density of the isolated Pt nanoparticles at different points along the NW length. The low magnification image on the bottom shows the location of the higher magnification images on the top.

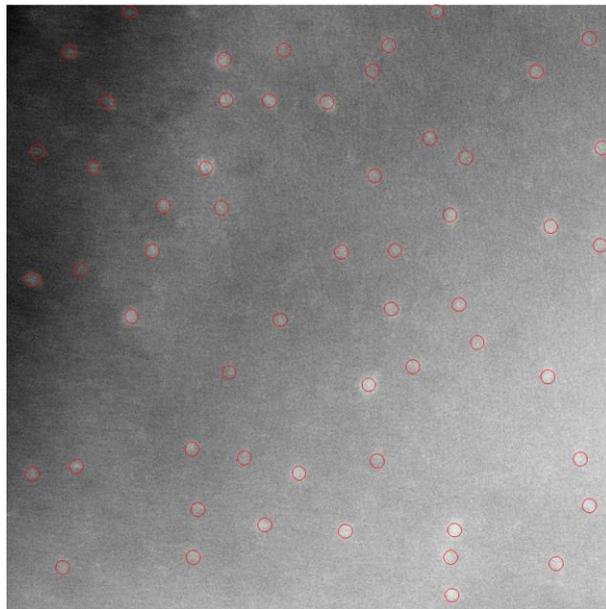


Figure 4. Surface coverage estimation of the Pt nanoparticles on the NW surface from the high-magnification STEM analysis. 56 particles were measured, with an average diameter of 0.837 nm,

corresponding to a surface coverage of ~2.3% of the field of view in the STEM image, which is consistent with the TXRF analysis.

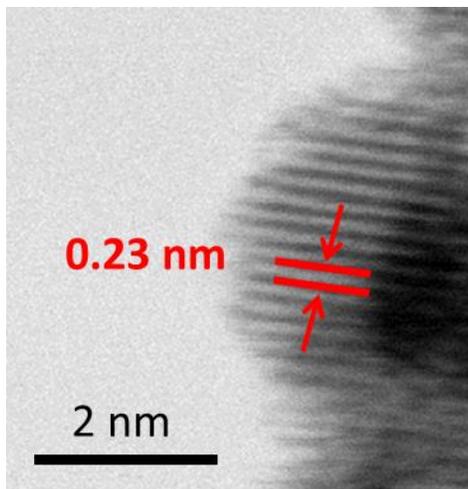


Figure 5. High-resolution STEM image of a Pt nanoparticle fabricated by ALD.

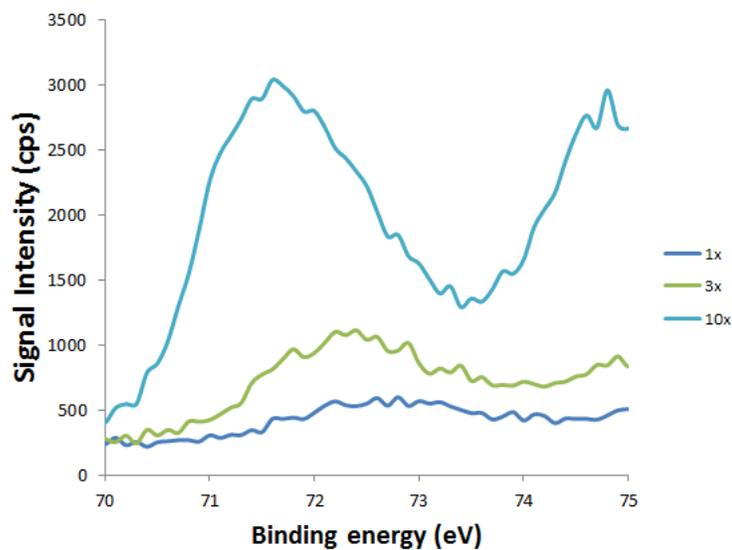


Figure 6. Pt 4f binding energy measured by XPS for various cycle numbers of ALD Pt deposited on TiO₂-coated planar Si substrates. An increase in the peak intensity was observed with increasing cycle number, which was used to quantify the surface Pt loading.

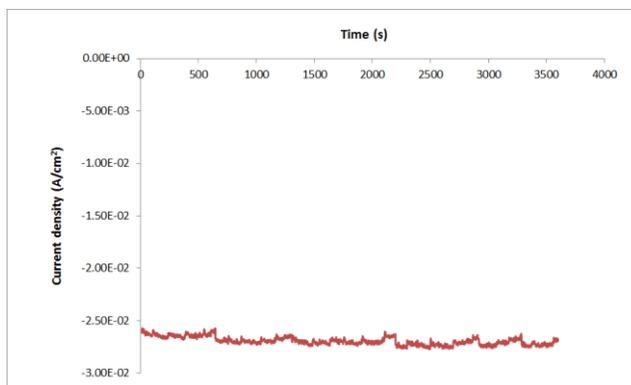


Figure 7. Chronoamperometry measurement of an ALD coated STS NW array sample with 3 cycles of Pt held at a constant potential of -1.67V vs. RHE. A stable photocurrent density was observed, with no degradation after one hour of measurement.