Supporting Information

Electrogeneration of Single Nanobubbles at Sub-50 nm Radius Platinum Nanodisk Electrodes

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1. Characterization of Pt nanodisk electrodes

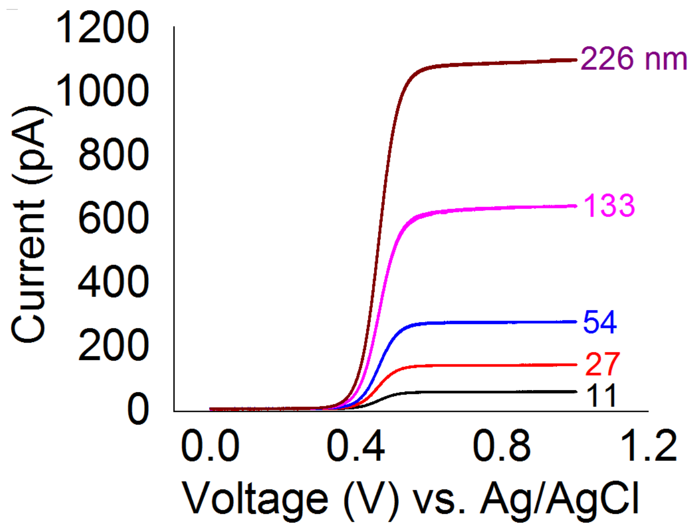

Figure SI1. The steady-state voltammetric response of Pt nanodisk electrodes with various radii immersed in a 5.0 mM ferrocene (Fc) in acetonitrile (supporting electrolyte 0.1 M $TBAPF_6$; scan rate = 10 mV/s). The electrode radii, *a*, were calculated from the limiting current, i_{lim}, using the expression $i_{lim} = 4nFDC^*a$, where *D* and *C** are the diffusivity and bulk concentration of Fc and *n* = 1. The curves show the forward and reverse scans. See main text for other details.

2. **Cyclic voltammetric response of an 11-nm-radius nanodisk electrode as a function of scan rate.**

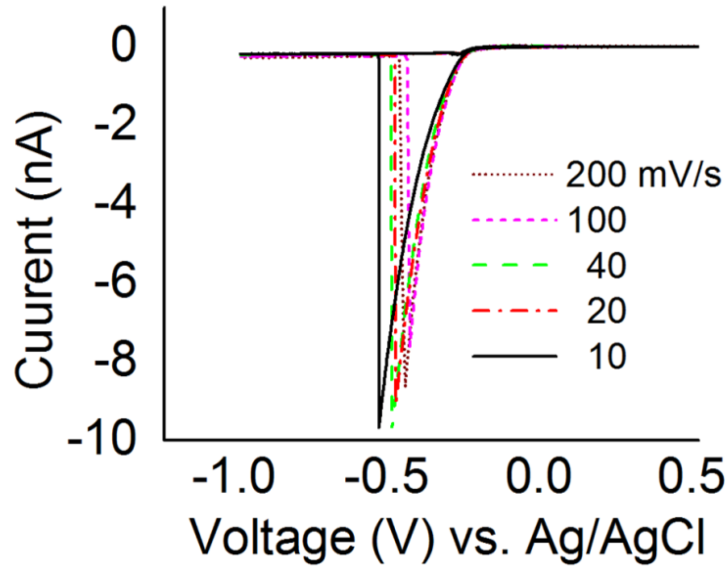

Figure SI2. Cyclic voltammetric response for an 11-nm-radius Pt nanodisk in a 0.5 M H_2SO_4 solution recorded at scan rates between 10 and 200 mV/s.

3. Cyclic voltammetric response of an 11-nm-radius nanodisk electrode as a function of H_2SO_4 concentration.

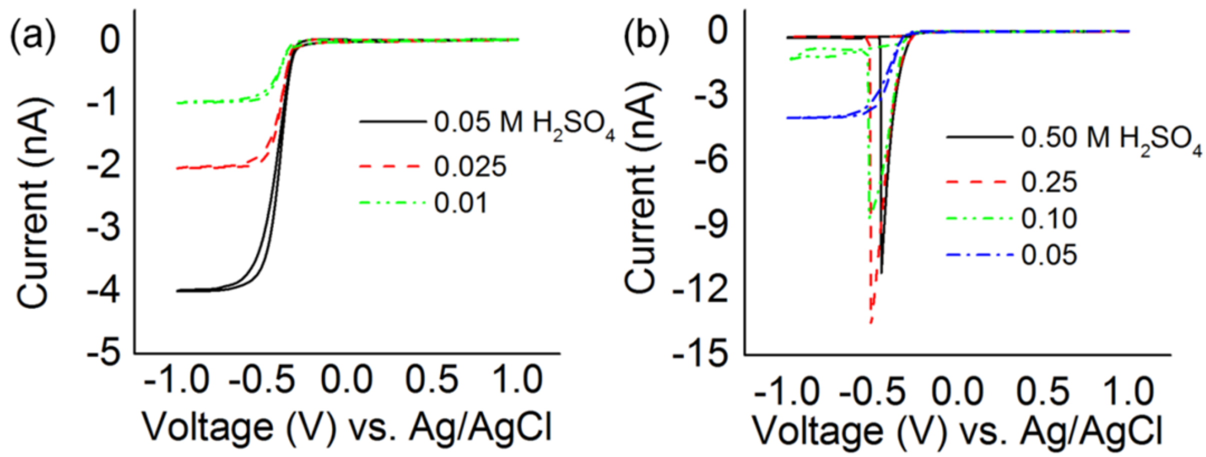

Figure SI3. Cyclic voltammetric response at an 11-nm-radius Pt nanodisk as a function of H_2SO_4 solution concentration: (a) 0.01 to 0.05 M and (b) 0.1 to 0.5 M. Scan rate = 100 mV/s.

4. Finite element simulation of H_2 profile at the critical current i_{nb}^{p}

We used Fick's first law combined with the relation between i_{nb}^{p} and the H_2 outflux J_{out,H_2} (SI 1) to obtain the H_2 concentration at the nanodisk surface (C^o) as well as the H_2 distribution. Since C^o is an unknown variable and $\mathbf{J}_{out,H_2}$ is a function of C^o, eq. SI1 can be written as $f(C^o)-i_{nb}^{p} = 0$ and solved to obtain C^o using the Newton-Raphson method. $f(C^o)$ is defined by *integrating coupling boundary variable* $\mathbf{J}_{out,H_2}$ (ntflux_c_chekf in COMSOL) over the nanodisk surface.

$$i_{nb}^{p} = 2F\int \mathbf{J}_{out,H_2} \bullet \mathbf{n}ds \qquad \text{(SI1)}$$

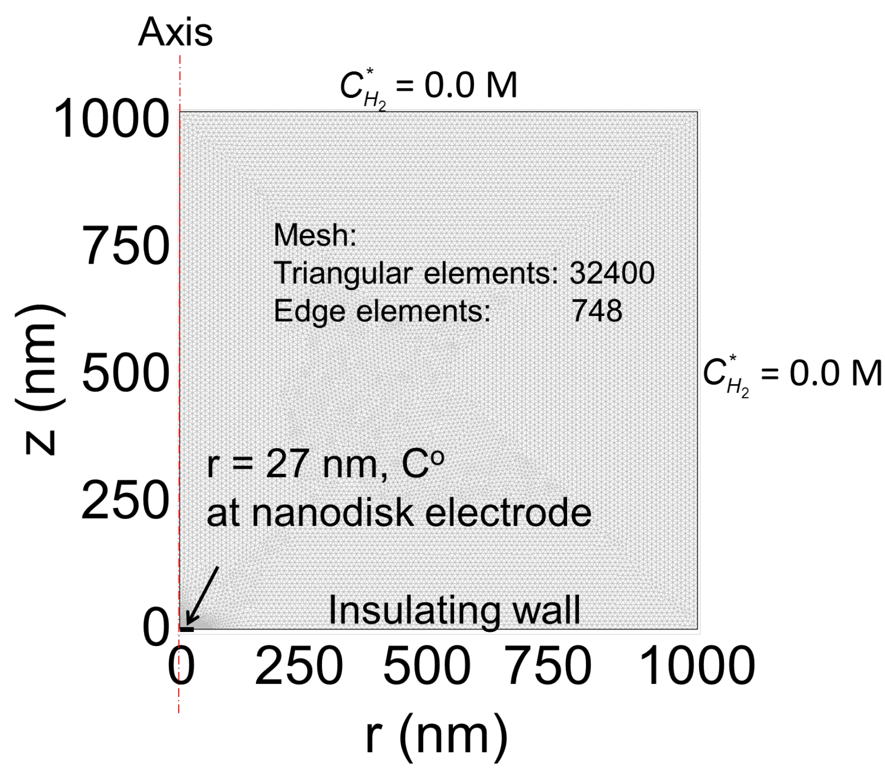

Figure SI4. The 2D axial-symmetric geometry of the nanodisk electrode embedded in glass and the mesh for the finite-element simulation (red dash line: the symmetry axis).

5. Simulated H_2 concentration profile for a 226-nm-radius nanodisk electrode at the critical current i_{nb}^{p}.

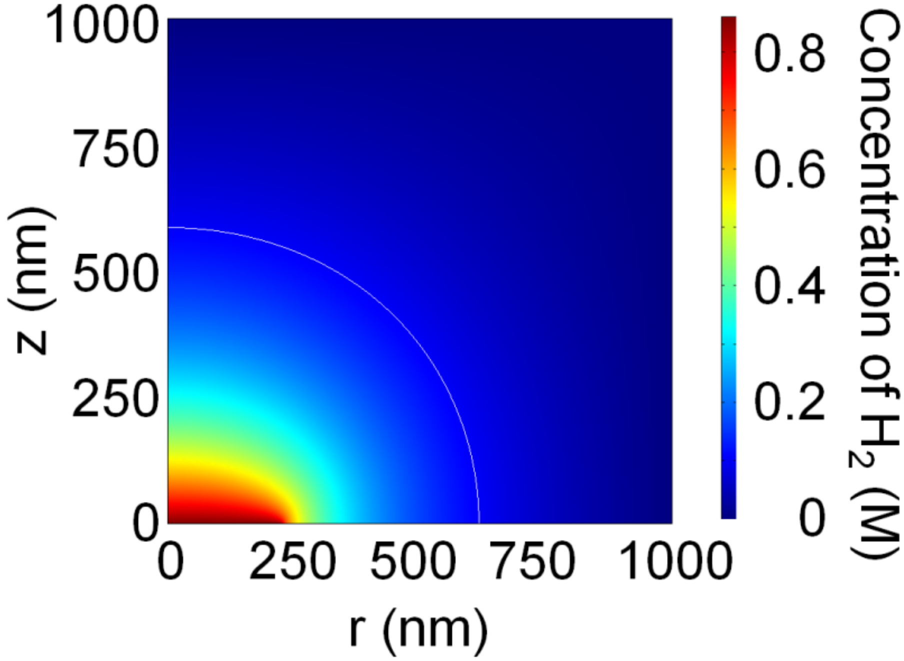

Figure SI5. Simulated H_2 distribution near a 226-nm-radius Pt nanodisk at the experimental critical current i_{nb}^{p} of 770 nA. The white line is the 0.1 M H_2 contour line, within which the concentration of H_2 is greater than the saturation concentration (0.102 M) to form a spherical nanobubble with a diameter of 20 nm. See main text for discussions of the H_2 saturation concentration and simulation.