

Electrochemical Nucleation of Stable N₂ Nanobubbles at Pt Nanoelectrodes

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1. Characterization of Pt nanodisk electrodes

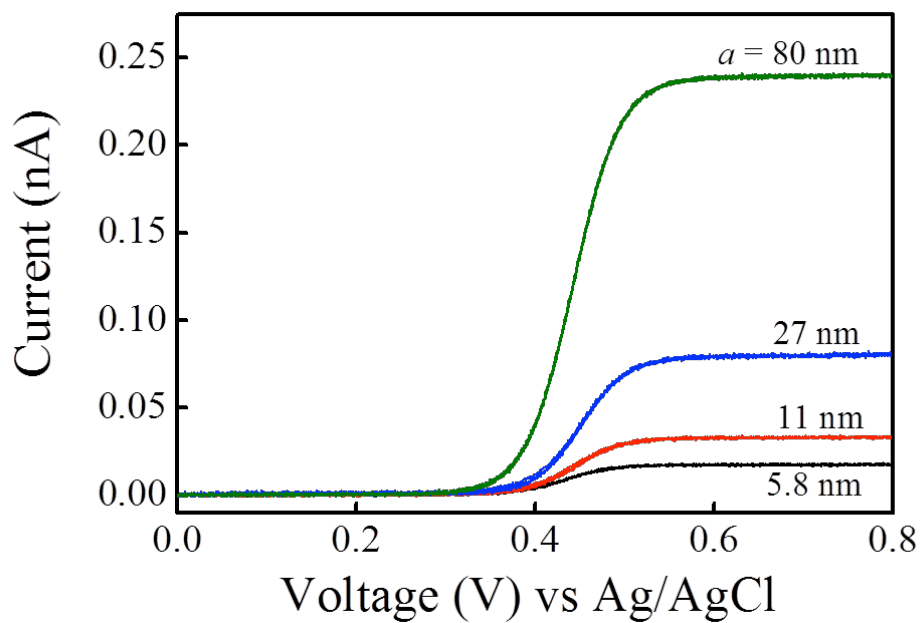


Figure S1. Voltammetric response of Pt nanodisk electrodes immersed in $\text{CH}_3\text{CN}/0.1$ M TBAPF_6 containing 5.0 mM ferrocene (Fc) at 20 mV/s. The electrode radii, a , were calculated from the diffusion limiting current, i_d , using the expression $i_d = 4nFD_{\text{Fc}}C_{\text{Fc}}^*a$, where D_{Fc} and C_{Fc}^* are the diffusivity and bulk concentration of Fc, respectively, F = Faraday's constant, and $n = 1$. The curves show both the forward and reverse scans.

2. Dependence of the voltammetric responses on immersion time

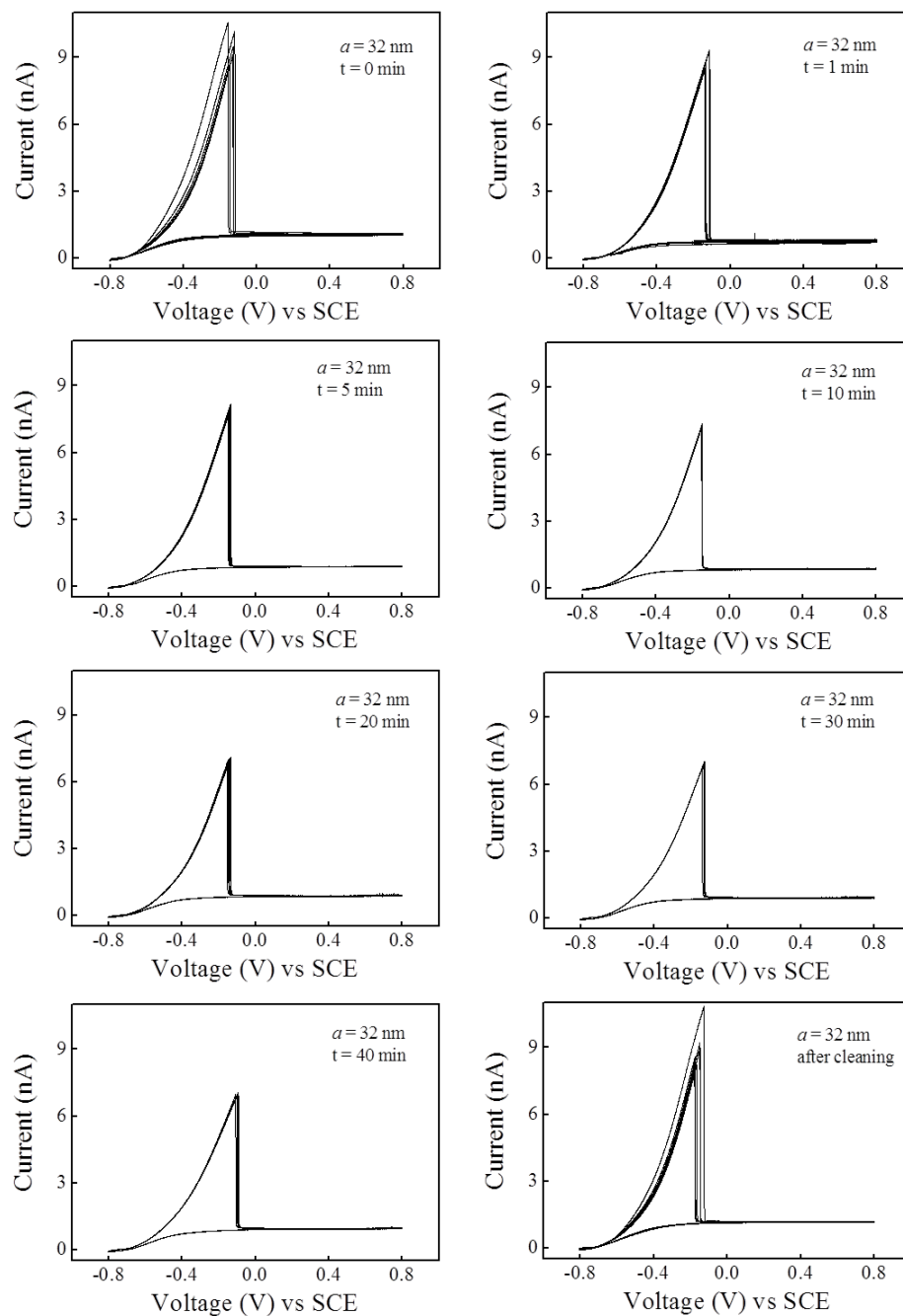


Figure S2. Cyclic voltammograms at 200 mV/s for a 32-nm radius disk electrode in 1.0 M N_2H_4 solution after various immersion times: fresh electrode ($t = 0$ min), $t = 1, 5, 10, 20, 30$ and 40 min, and after the electrode was carefully cleaned (bottom right) by rinsing with copious amounts of CH_3CN and water to remove adsorbed species. The electrode potential was continuously scanned during the time intervals between two consecutive voltammetric measurements.

3. Voltammetric response of a 98 nm-radius Pt electrode

On the initial scan, a sudden current drop occurs at potential ~ 0 V, but immediately recovers to a constant current level that is the characteristic of the diffusion limited oxidation of N_2H_4 . The response indicates that a N_2 nanobubble nucleates, but fails to cover the entire electrode surface. In the subsequent scans, we observed sigmoidal-like voltammetric response with significant hysteresis. A significant drop of the current plateau between two consecutive cycles is also observed (the direction of increasing scans is indicated by the arrow labeled *c*), which is most likely due to the Pt deactivation by adsorption of N_2H_4 and the intermediates.

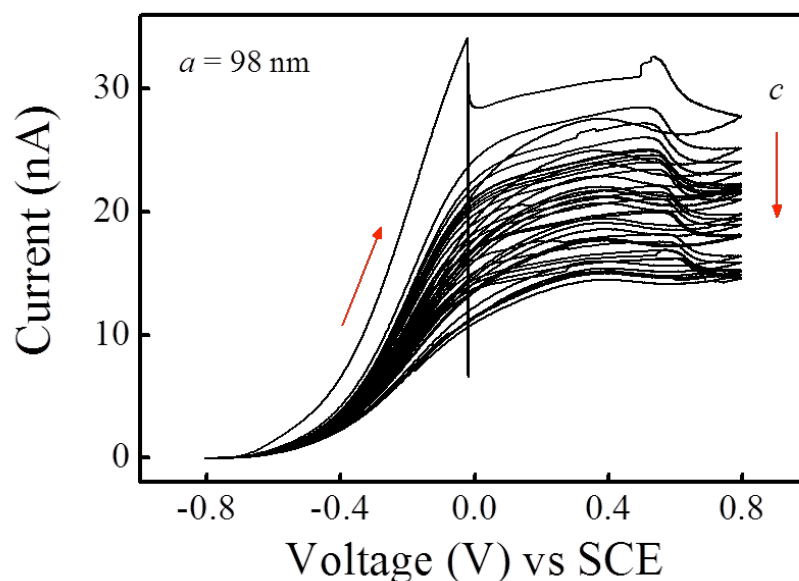


Figure S3 Cyclic voltammograms at 200 mV/s for a 98-nm radius disk electrode in 1.0 M N_2H_4 solution at different scan cycles (within 5 min of immersion). In the initial scan cycle, a peak shaped voltammetric response appeared at ~ 0 V.