

Supporting Information

Sensing of H₂O₂ at Low Surface Density Assemblies of Pt Nanoparticles in Polyelectrolyte

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The supporting information contains:

1. Calibration plot at (PDDA/Pt NP)₁ up to 0.9 mM H₂O₂ (Figure S1)
2. Further discussion, and calibration plots at (PDDA/Pt NP)_n for $n = 1-10$ (Figure S2)
3. CVs at Pt NP film and polycryst-Pt disk electrodes in 0.1 M PBS (Figure S3)
4. Estimated fractional coverage θ corresponding to A_{real} vs. dipping time (Figure S4)
5. Calibration plot at PDDA/(Pt NP)_t up to 8 μM H₂O₂ (Figure S5)
6. Continuous amperometry and calibration plots at a Pt disk electrode (Figure S6)

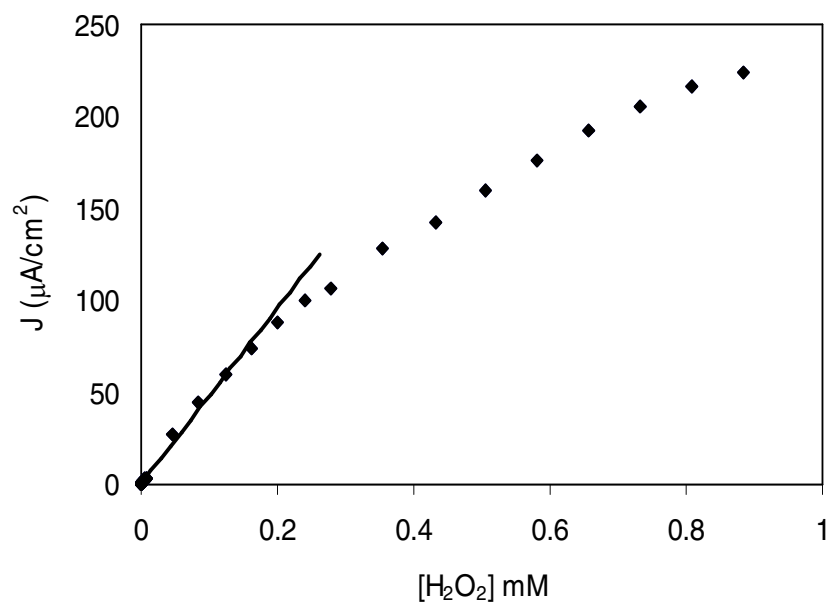


Figure S1. A calibration plot of steady-state current density vs. H₂O₂ concentration up to 0.9 mM at (PDDA/Pt NP)₁ biased at 0.6 V vs. Ag/AgCl, in stirred and air-saturated 0.1 M PBS pH 7.

Further Results and Discussion of Sensing at PDDA/Pt NP Multilayered Assembly.

H_{upd} measurements and TEM images showed that full monolayer coverage $\theta \geq 1$ is not reached at (PDDA/Pt NP)₁ but is approached at (PDDA/Pt NP)₄.³¹⁻³³ To investigate the possibility of extending the sensor linear range with increasing the number of catalytic sites, we studied H₂O₂ amperometric detection at 2-10 PDDA/Pt NP multilayers. The results showed that no advantage can be gained from increasing use of Pt mass in multilayers. Figure S2 shows that despite the increase in Pt loading with increasing the number of bilayers, the linear range narrowed with increasing n , and the sensitivity at 42 nM-8 μ M ($n= 1, 2, 4$) or 83 nM-8 μ M ($n=6, 8, 10$) where the electrodes response was linear still ranged between 0.4-0.5 $\text{AM}^{-1}\text{cm}^{-2}$. The similar sensitivities indicated that this reaction must be taking place at a similar *effective* surface at multilayers; meaning effectively the same number of catalytic sites and diffusion area. The mechanism of H₂O₂ oxidation at (PDDA/Pt NP) _{$n \geq 1$} is pictured to involve mass transport of H₂O₂ from solution and transport in the film, adsorption on Pt sites, charge transfer to H₂O₂, charge transport to the electrode via a mechanism of charge hopping, and transport of products (H⁺ and O₂) and possibly of other ions to maintain electroneutrality. Similar current output and narrower linear range with increasing n is attributed in this case to limitations in mass and/or charge transport rates with increased distance from the (substrate) electrode, and a possible buildup of products (O₂ and H⁺) inside the multilayers inhibiting the reaction.³⁹ A hypothesis that PDDA completely blocks mass transport or blocks Pt activity in underlying layers did not fully explain the response of the multilayers, since a PDDA-terminated Pt NP bilayer (PDDA/Pt NP/PDDA) retained ~40% of the response of PDDA/Pt NP.

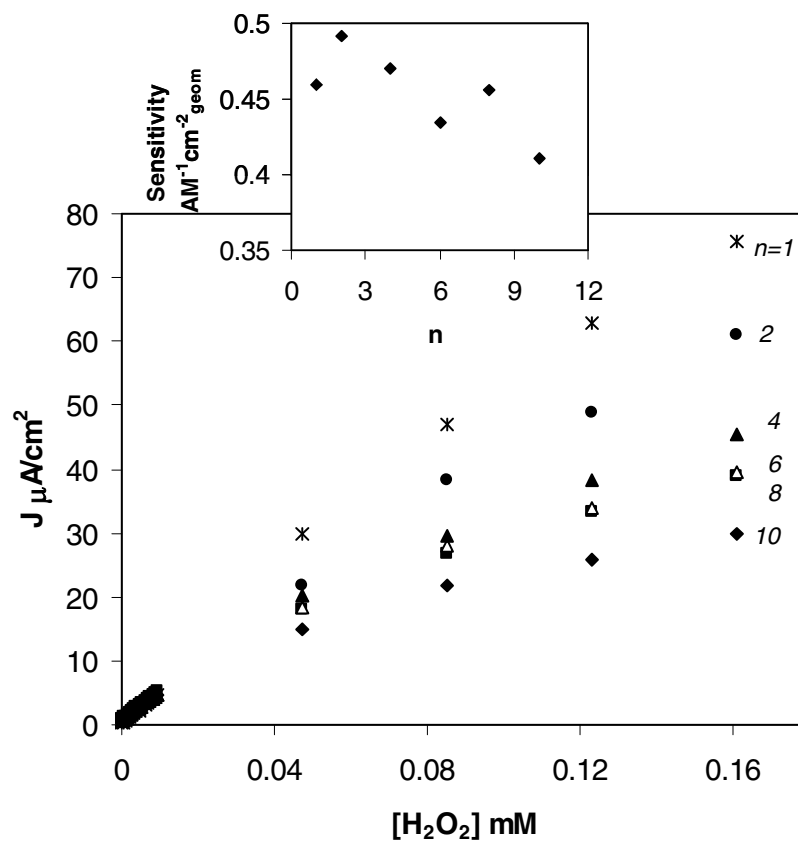


Figure S2. Steady-state current density vs. H_2O_2 concentration in air-saturated 0.1 M PBS pH 7 measured at $(\text{PDDA}/\text{Pt NP})_n$ on ITO, with $n = 1-10$ bilayers. The inset shows a plot of the apparent sensitivity over the linear range (from 42 nM to 8 μM at $n=1-4$, and from 83 nM to 8 μM at $n= 6-10$) as a function of the number of bilayers (n).

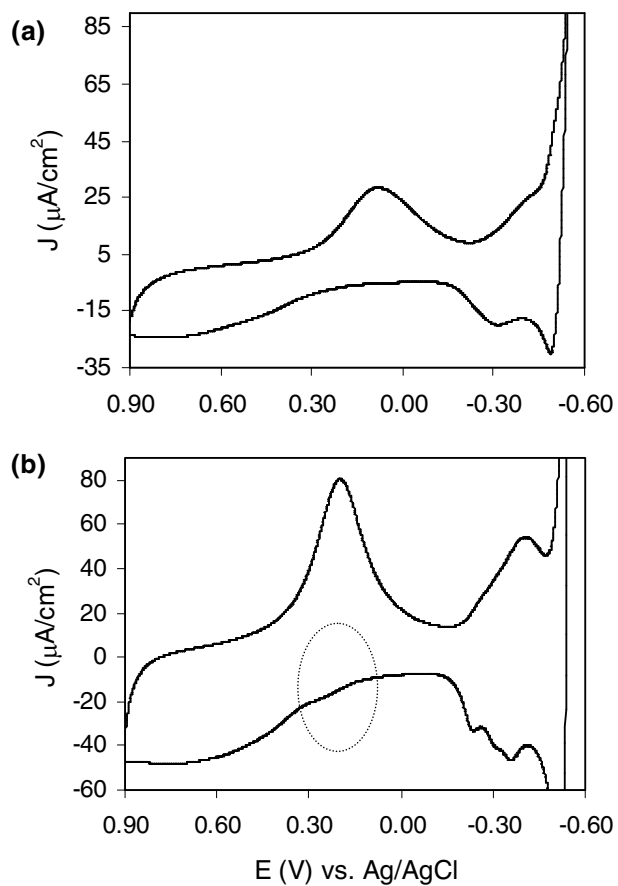


Figure S3. Cyclic voltammograms at (PDDA/Pt NP)₁ on ITO (a) and at a polycryst-Pt disk electrode (b) in deoxygenated 0.1 M PBS pH 7. Scan rate is 20 mV/s.

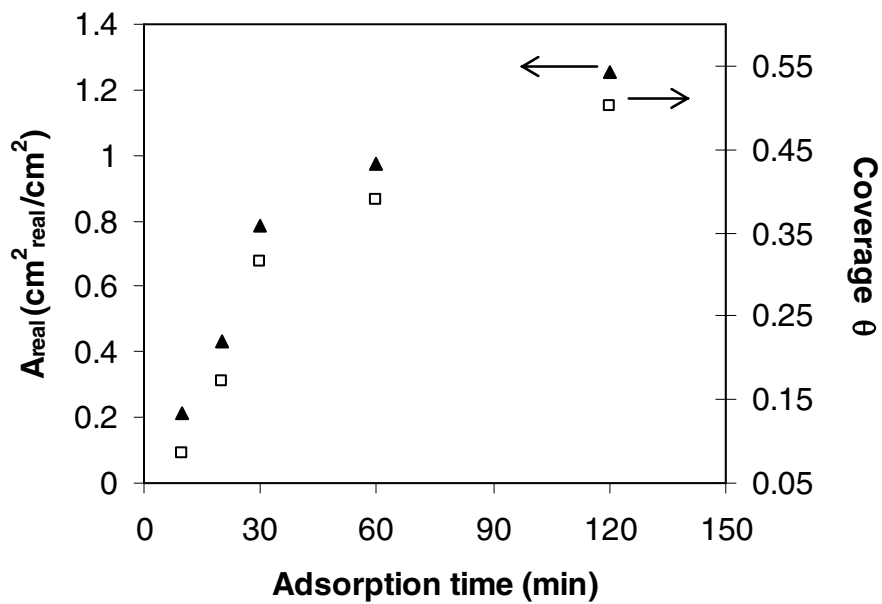


Figure S4. Real Pt NP surface area (A_{real} from the charge of H_{upd} per $\text{cm}^2_{(\text{geom})}$) of PDDA/(Pt NP)_{*t*} assemblies and the corresponding estimated fractional surface coverage (θ , secondary axis) as a function of the dipping time *t*.

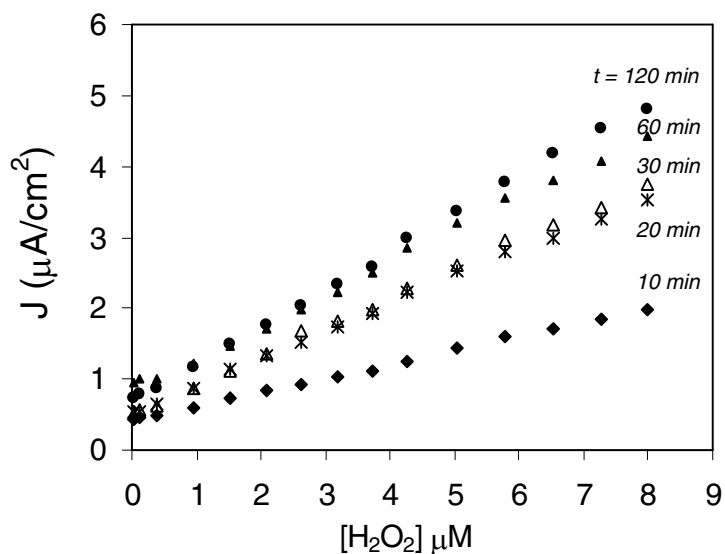


Figure S5. Current density at PDDA/(Pt NP)_t (*t* = 10, 20, 30, 60, and 120 min) as a function of H₂O₂ concentration in 0.1 M PBS pH 7 in the range of 42 nM to 8 μM H₂O₂.

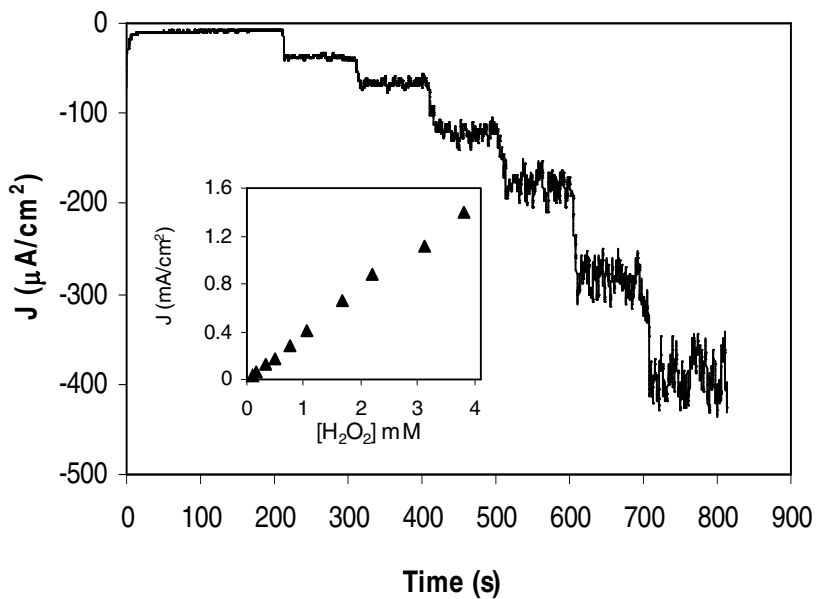


Figure S6. Continuous amperometry plot at Pt disk electrode (2 mm diam.) biased at 0.6 V vs. Ag/AgCl in response to H₂O₂ injections in stirred and air-saturated 0.1 M PBS pH 7, and a calibration plot of steady-state current density vs. H₂O₂ concentration from 0.08 mM (LOD at this electrode) to 3.8 mM (inset).