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Supplementary Information

Assemblies of Polyvinylpyrrolidone-capped Tetrahedral and Spherical Pt Nanoparticles in Polyelectrolyte: Hydrogen Underpotential Deposition and Electrochemical Characterization

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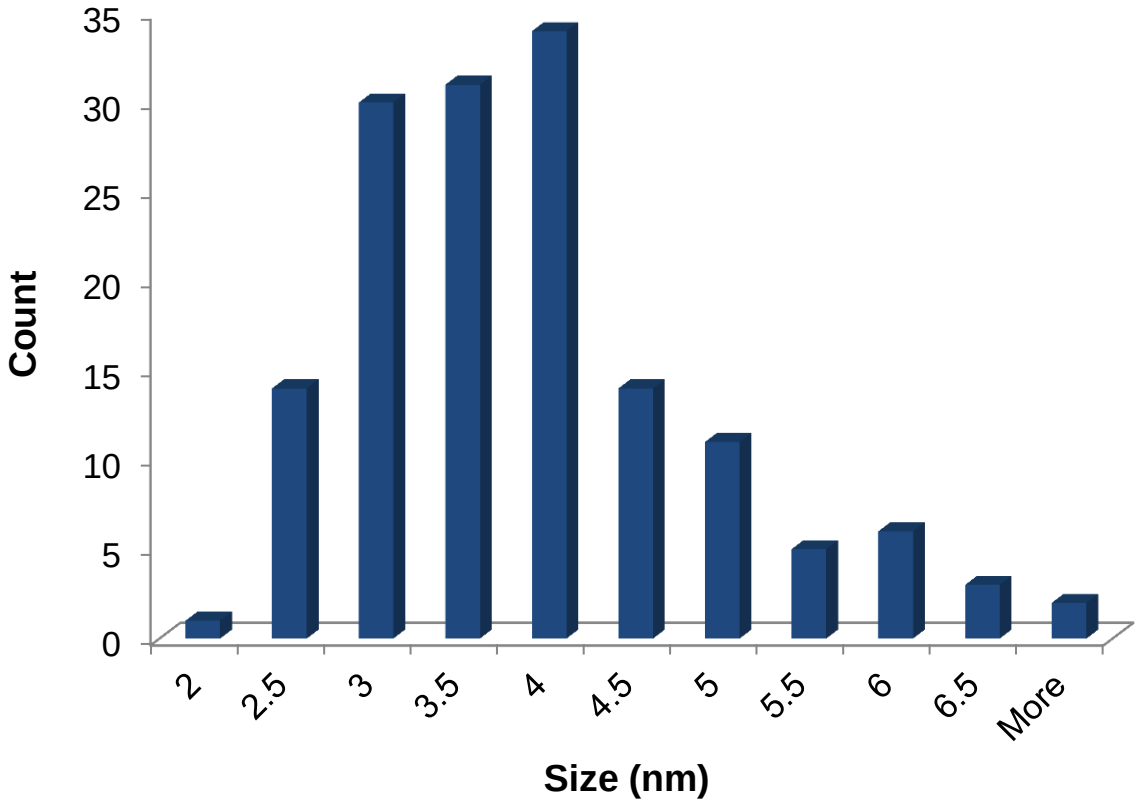

Figure SI.1 Histogram showing the size distribution of shapes (spherical/ellipsoidal, some rod-like or undefined) other than tetrahedral resulting from the preparation of PVP-TH-Pt NPs. The average size is 3.66 ±1.02 nm (N=151) by averaging the long and short axes.

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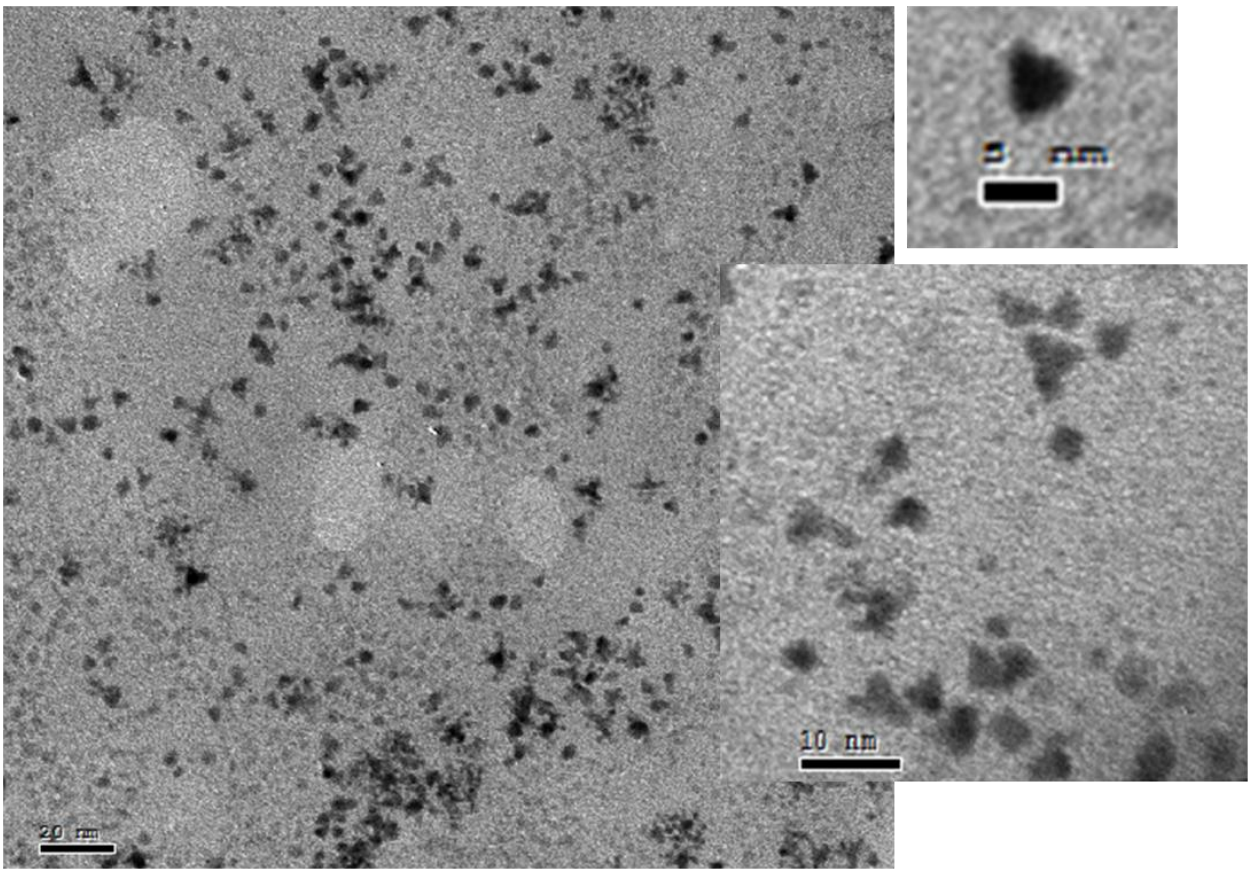
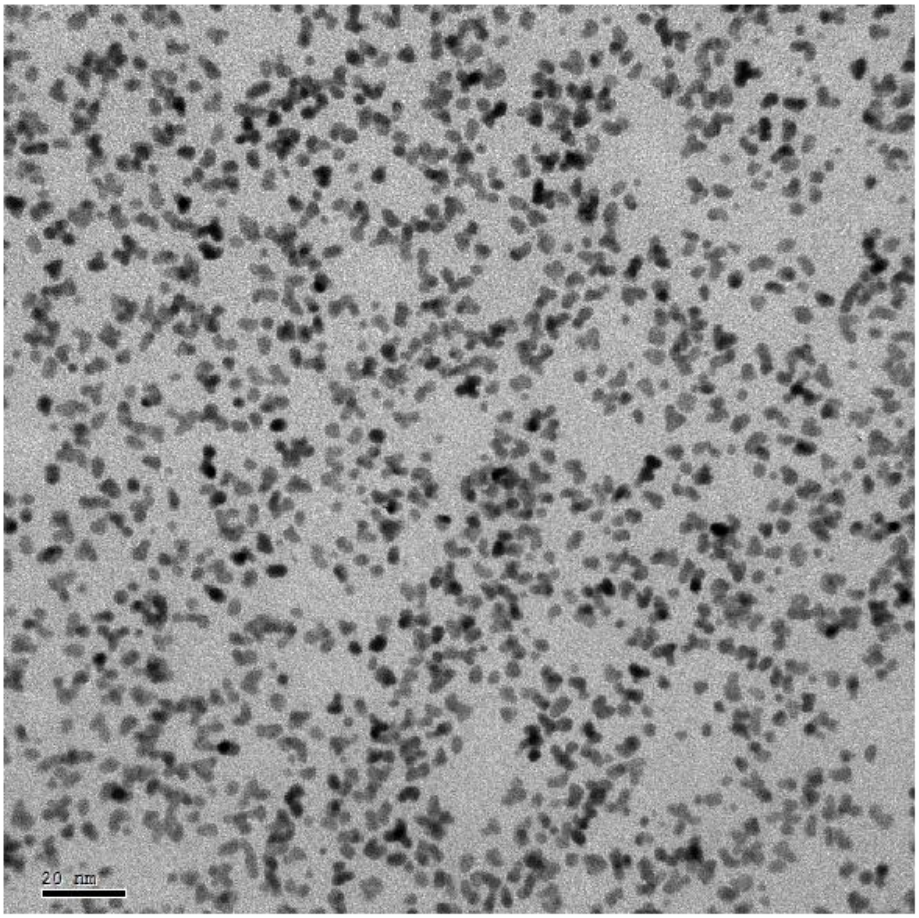


Figure SI.2 TEM images of PVP-TH-Pt NPs stored in solution for 4 months at 4 ^{o}C drop cast (of 8 μL of solution) on C/Cu grid.



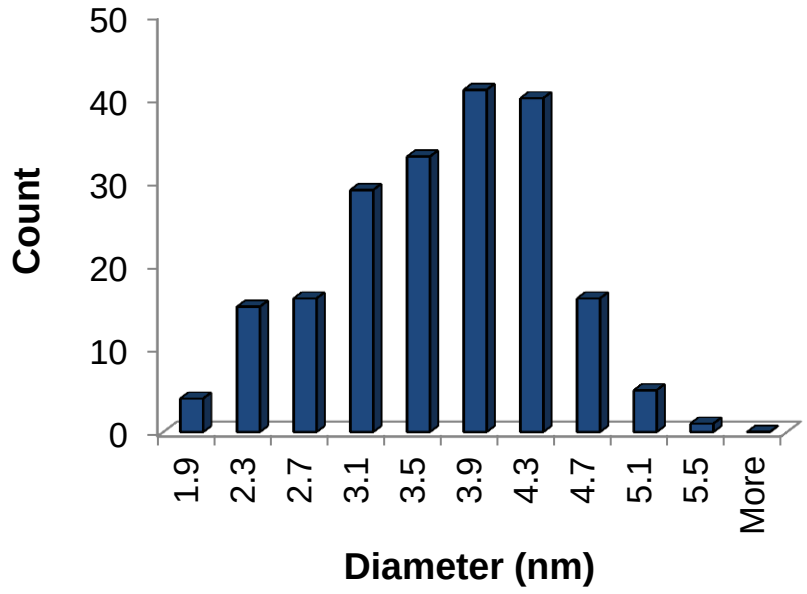


Figure SI.3 TEM image and size distribution (N=200) of PVP-S-Pt NPs prepared by reduction of Pt(II) (K_2PtCl_4) with ethanol. The film is $(PDDA/PVP\text{-}S\text{-}Pt)_1$ on SiO_x/Cu grid.

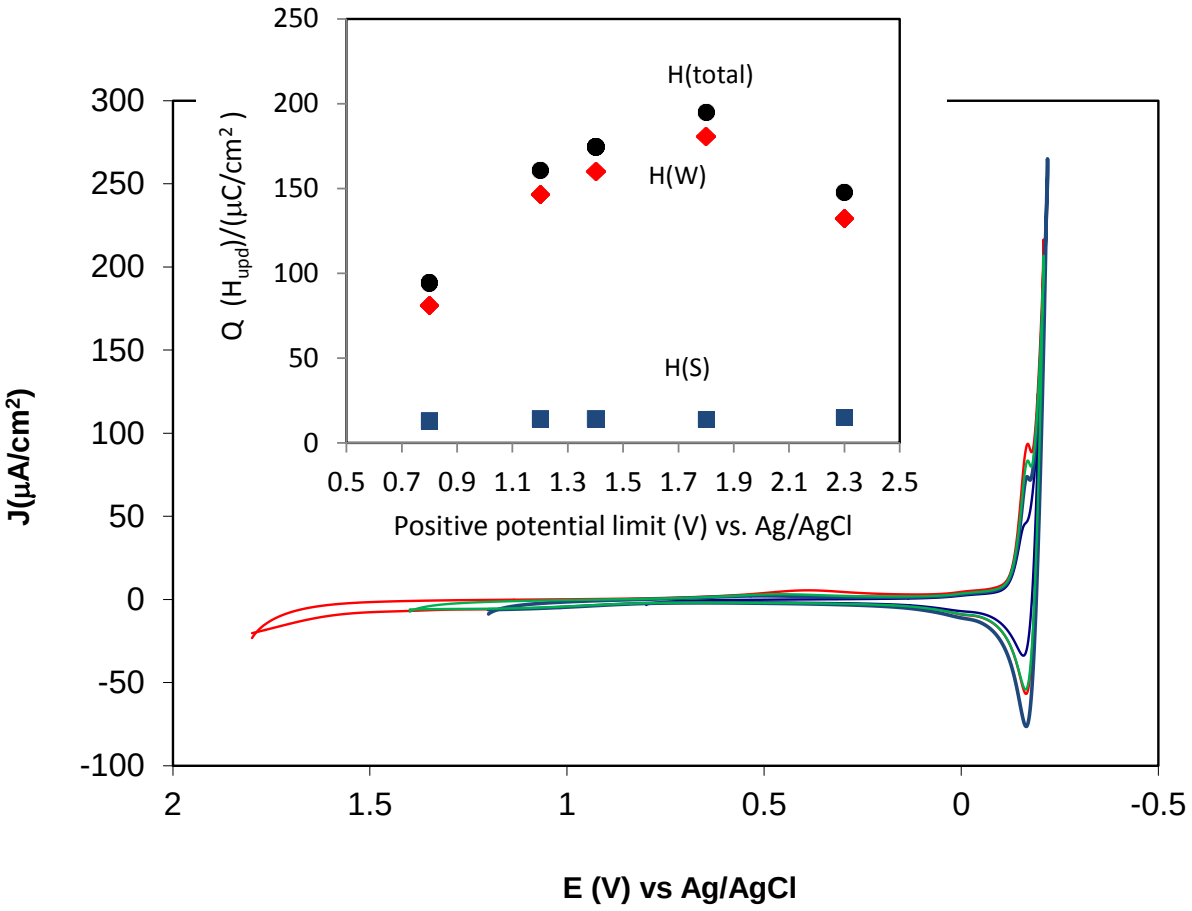


Figure SI.4 CVs in deaerated 1 M H_2SO_4 at $(PDDA/PVP\text{-}TH\text{-}Pt)_4$ with increasing the positive scan limit (first scan from 0.8 V, last scan from 1.8 V). The inset shows plots of the charge for H(S), H(W), and total charge for H_{upd} vs. the positive potential scan limit. Scan rate is 20 mV/s.

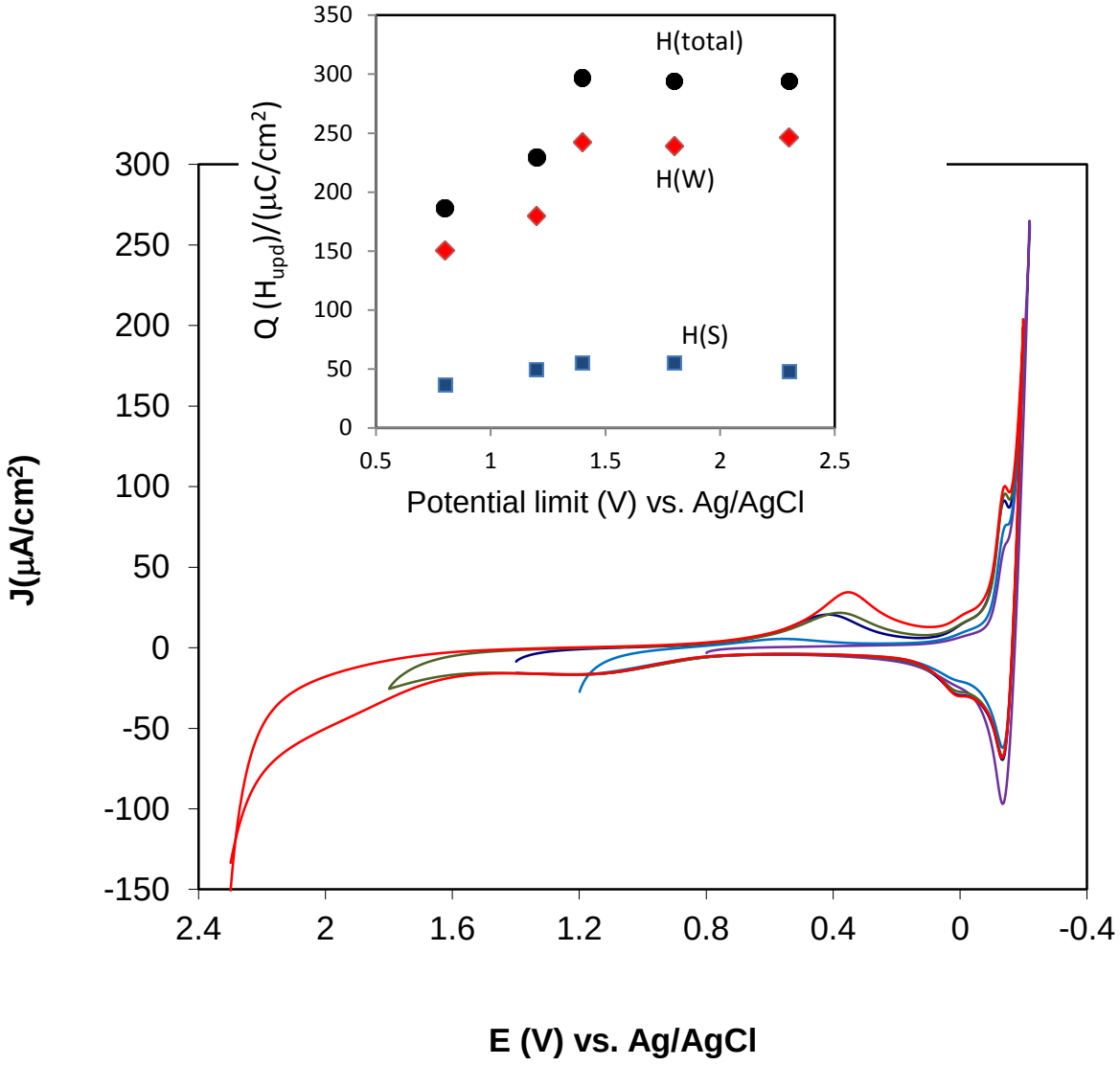


Figure SI.5 CVs in deaerated 1 M H_2SO_4 at $(PDDA/PVP\text{-}S\text{-}Pt)_4$ with increasing the positive scan limit (first scan from 0.8 V, last scan from 2.3 V). The inset shows plots of the charge for H(S), H(W), and total charge for H_{upd} vs the positive potential scan limit. Scan rate is 20 mV/s.

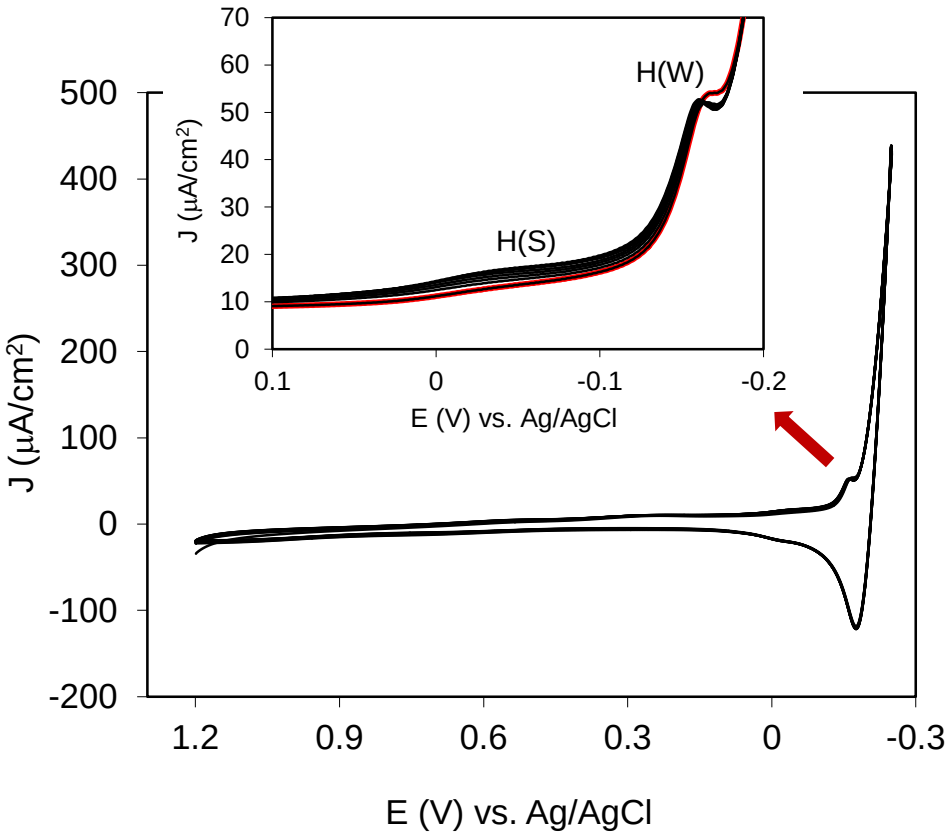


Figure SI.6 10 consecutive cyclic voltammograms at $(PDDA/PVP\text{-}TH\text{-}Pt\ NP)_4$ in 1 M H_2SO_4 at 20 mV/s. The line marked in red in the inset is the first scan, followed by nine scans in black. (Move to SI)

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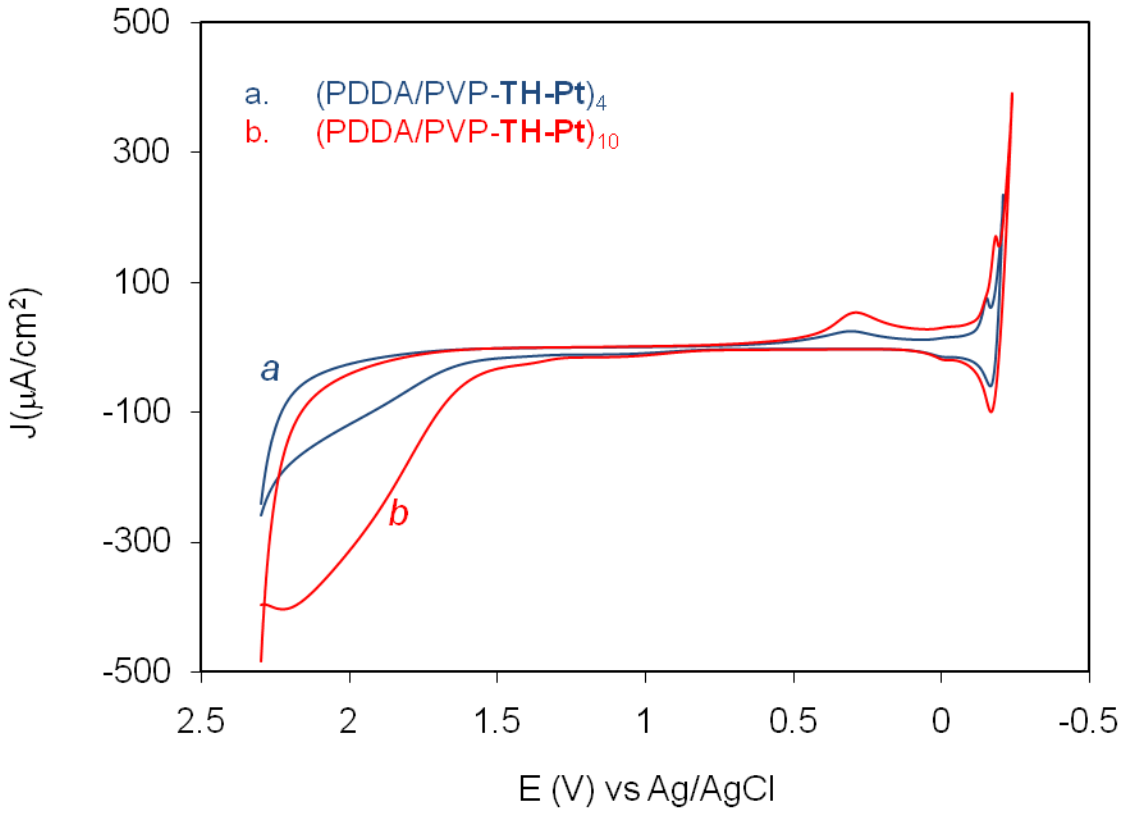

Figure SI.7 Cyclic voltammograms in deaerated 1 M H_2SO_4 at (a) $(PDDA/PVP\text{-}TH\text{-}Pt)_4$ and (b) $(PDDA/PVP\text{-}TH\text{-}Pt)_{10}$ scanned from 2.3 V. Scan rate is 20 mV/s.

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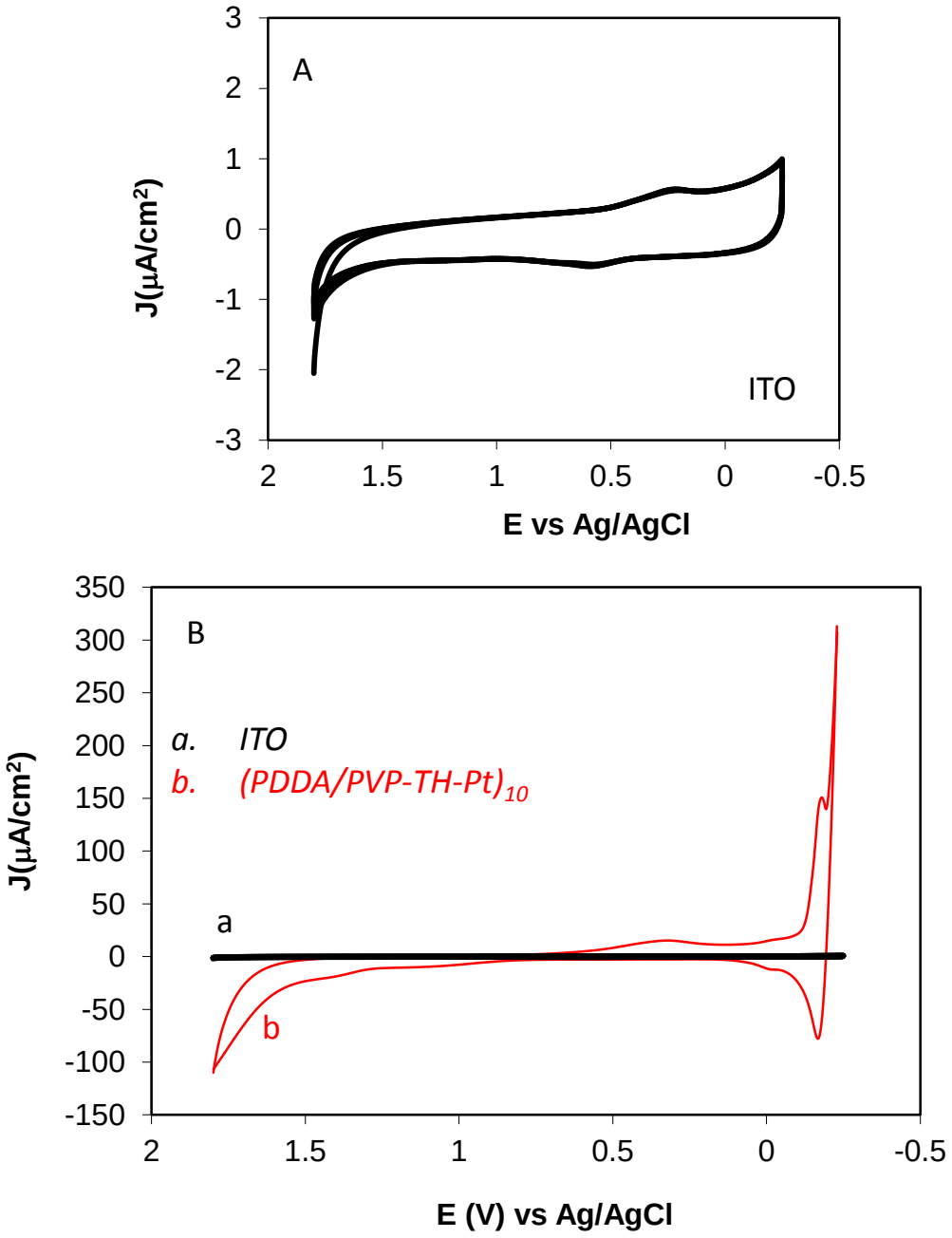

Figure SI.8 (A) 5 cyclic voltammograms acquired at an ITO electrode scanned consecutively between 1.8 V and -0.25 V in 1 M H_2SO_4 at 20 mV/s. (B) 5 CVs at ITO (a) and a CV at $(PDDA/PVP\text{-}TH\text{-}Pt)_{10}$ (b) acquired between 1.8 V and -0.25 V in 1 M H_2SO_4 at 20 mV/s. The scans started at the positive limit.

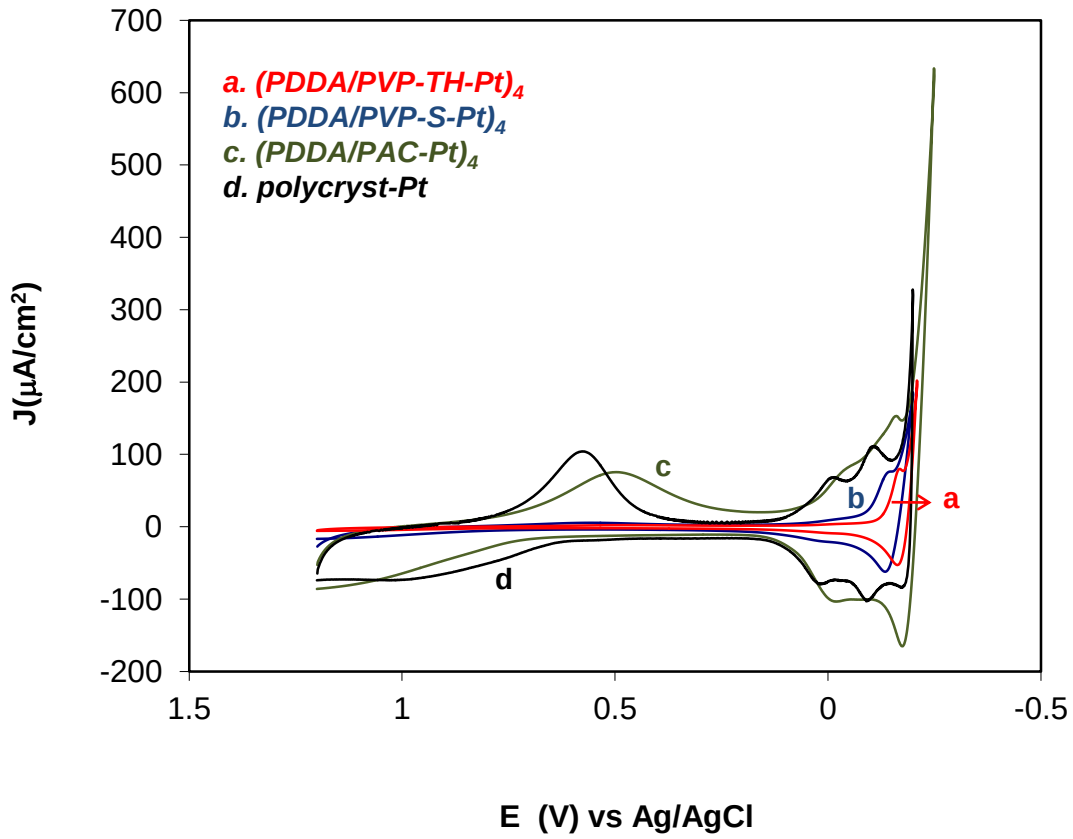

Figure SI.9 CVs in deaerated 1 M H_2SO_4 at $(PDDA/PVP\text{-}TH\text{-}Pt)_4$, $(PDDA/PVP\text{-}S\text{-}Pt)_4$, and $PDDA/PAC\text{-}Pt)_4$ and at a polycryst-Pt disk electrode. Scan rate is 20 mV/s.

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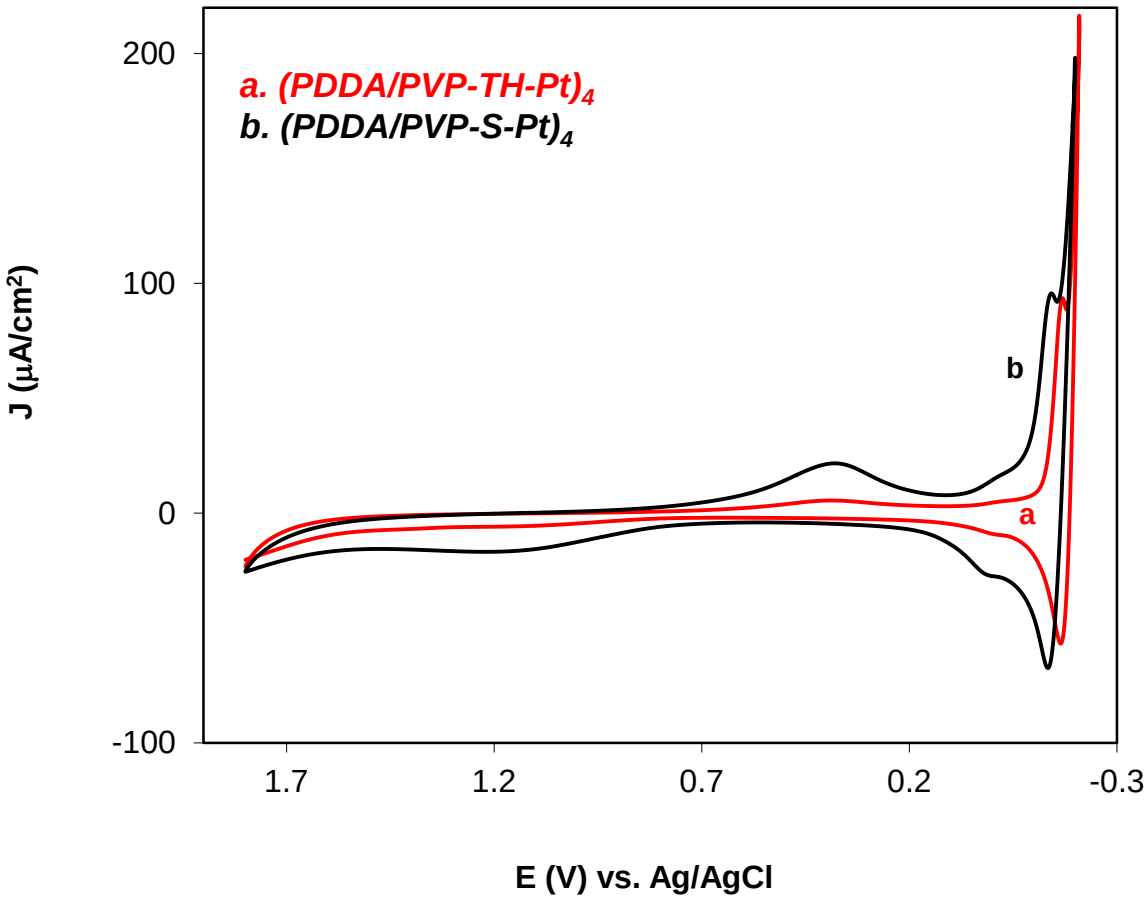

Figure SI.10 CVs in deaerated 1 M H_2SO_4 at $(PDDA/PVP\text{-}TH\text{-}Pt)_4$ (a, red), $(PDDA/PVP\text{-}S\text{-}Pt)_4$ (b, black). Scan rate is 20 mV/s.