Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Manipulating the Architecture of Pd@Pt Nanostructures through Metal-Selective Capping Agent Interactions

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Experimental Section:

Synthesis: Octopodal and dendritic Pd@Pt NPs were synthesized as follows: In a typical synthesis, 45.41mg of F127 was dissolved in 5 mL NaBr (25 mM) solution. 0.25 mL of H_2PtCl_6 (10 mM) and 0.25 mL of H_2PdCl_4 (10 mM) were added to the solution, followed by adding 5 mL of L-aa (150 mM). This reaction vial was capped and left undisturbed in a 40 °C oil bath for 5 h. Dendritic Pd@Pt NPs followed the same experimental procedure except using precursor solution without NaBr. To synthesize dendritic Pt NPs, 50 mg F127 was dissolved in 2.5 mL nanopure water. 5 mL of K_2PtCl_4 (20 mM) solution was added to the solution, followed by adding 2.5 mL of L-aa (200 mM). The reaction vial was allowed to sit undisturbed at room temperature for 24 h. In control experiments, NaBr was replaced by NaCl, NaCitrate and NaI with same concentration of 25 mM.

Chemicals and materials: Pluronic F127 ($(PEO)_{100}(PPO)_{65}(PEO)_{100}$, M_w =12600), L-ascorbic acid (L-aa, $C_6H_8O_6$, 99%), $PdCl_2$ (99.98%), NaCl (99%), NaBr (99%), K_2PtCl_4 (98%) and $H_2PtCl_6.6H_2O$ (99.98%), were used as purchased from Sigma Aldrich. Hydrochloric acid (HCl, 12.1 M) was purchased from Mallinckrodt. Nanopure water with resistivity of 18.2 MΩ.cm was used in all experiments. H_2PdCl_4 solution (10 mM) was prepared by stirring 17.7 mg of $PdCl_2$ in 10 mL of HCl (20 mM) for 2 h while heating and stirring at 40 °C.

Characterization: TEM images were taken by a JEOL JEM 1010 microscope operating at 80 kV. High resolution TEM images and energy dispersive X-ray spectra were obtained via a JEOL JEM 3500FS microscope (operating at 300 kV) interfaced with an Oxford INCA dispersive X-ray system. TEM samples were prepared by drop-casting a dispersed particle solution onto the carbon-coated copper grid. Powder X-ray diffraction (XRD) was performed with the Panalytical Empyrean diffractometer using Cu Kα as the radiation source.

Electrochemical experiments: All cyclic voltamogramms (CVs) were obtained by a WaveDriver 20 Bipotentiostat/Galvanostat (Pine Research Instrumentation Inc., USA) and a three-electrode cell including a platinum wire, an Ag/AgCl reference electrode and a glassy carbon electron coated with 8 µg of samples. Working electrodes were prepared by drop casting 8 µl of aliquot which is obtained by mixing 5mg of sample in 5 mL of aqueous solution containing 1 mL isopropanol and 20 µl Nafion solution (5 wt.%).

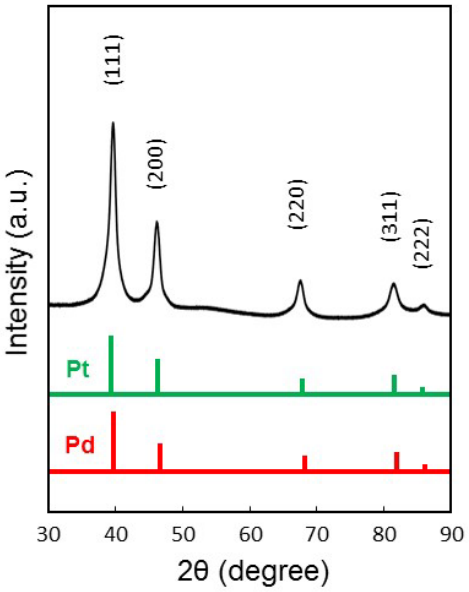

Figure S1. Wide-angle XRD profile of octopodal Pd@Pt nanoparticles. Green lines show the fcc Pt phase (JCPDS 04-0802) and red lines show the fcc Pd phase (JCPDS 05-0681).

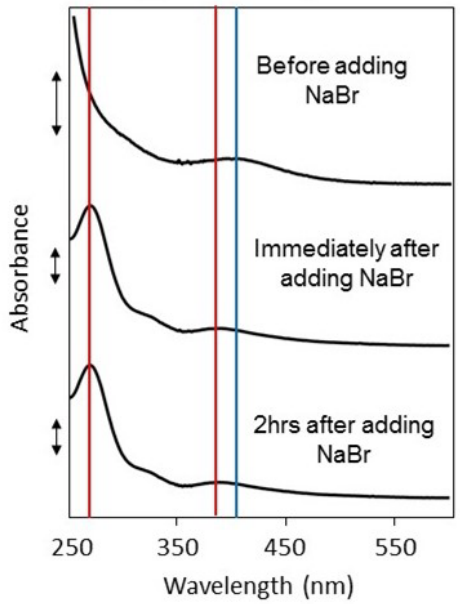

Figure S2. UV-Vis spectra of H_2PdCl_4 solution before and after adding NaBr. Blue line shows peak position before adding NaBr and red lines show peak positions appeared after adding NaBr. Black double arrows show 0.04 (A.U).

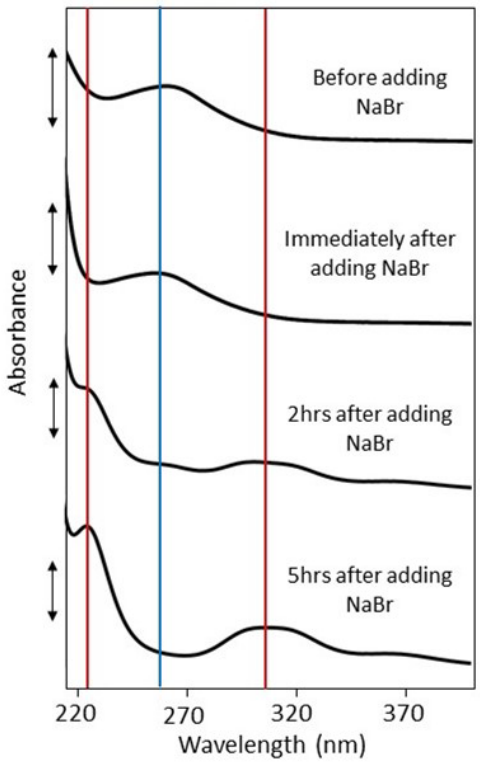

Figure S3. UV-Vis spectra of H_2PtCl_6 solution before and after adding NaBr. Blue line shows peak position before adding NaBr and red lines show peak positions appeared after adding NaBr. Black double arrows show 0.4 (A.U).

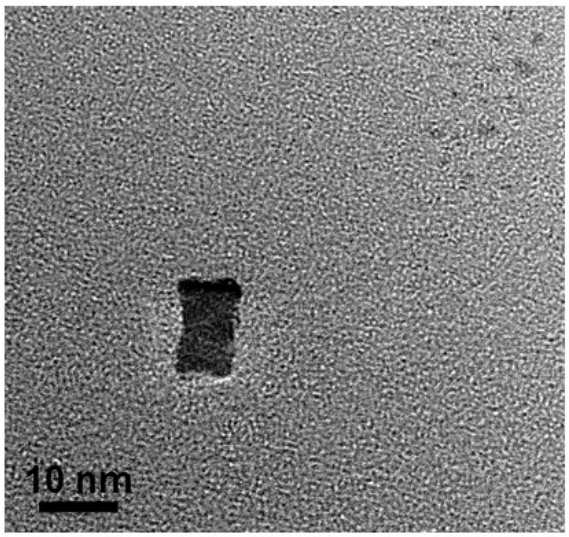

Figure S4. TEM image of Pd nanocubes and small Pt particles taken after 1 h of reaction.

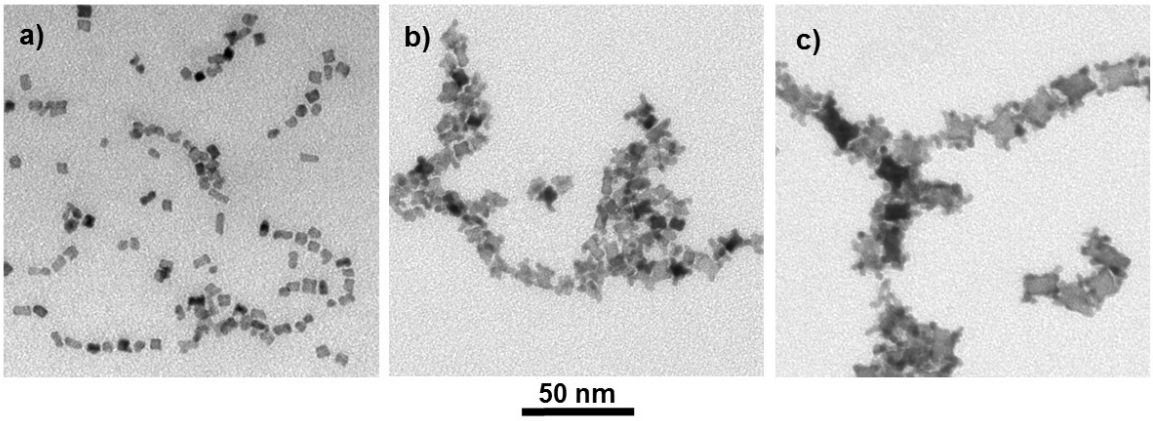

Figure S5. TEM images of Pd@Pt nanoparticles prepared using solutions with different NaBr concentrations. NaBr concentrations are a) 3.96, b) 7.93, and c) 23.78 mM.

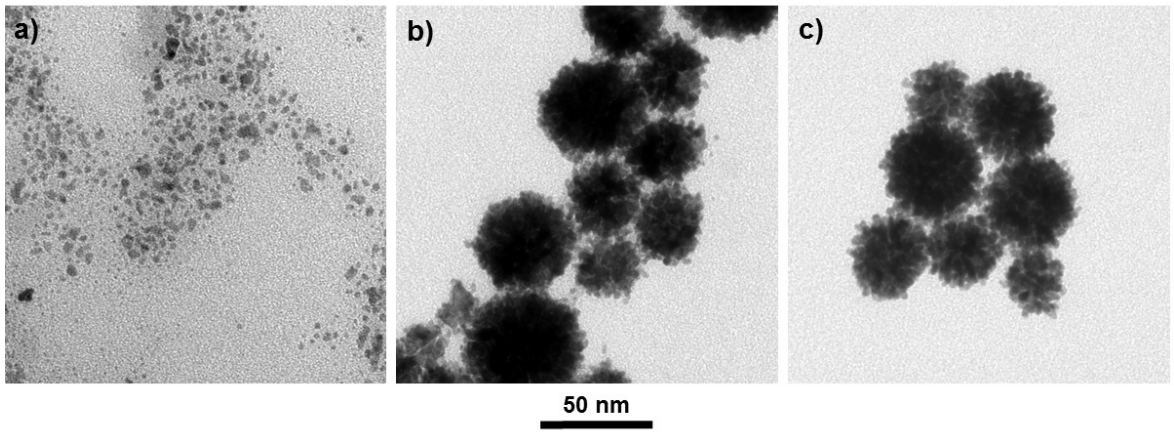

Figure S6. TEM images of Pd@Pt nanoparticles prepared using standard procedure, except for replacing NaBr by a) NaI b) NaCl, and c) NaCitrate.

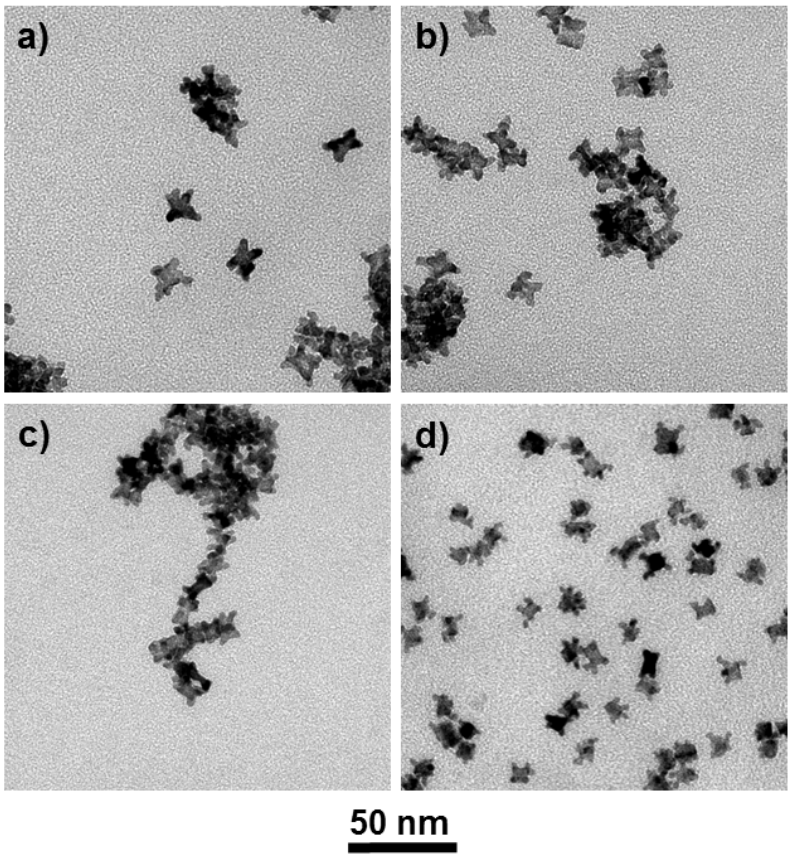

Figure S7. TEM images of Pd@Pt nanoparticles prepared using solutions with different amount of F127. Added F127 in reaction solutions are a) 0.35, b) 0.71, c) 11.35, and d) 90.82 mg.

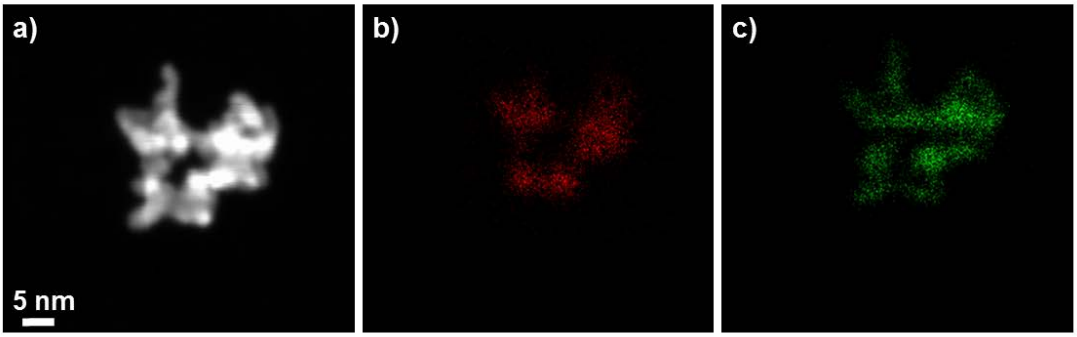

Figure S8. Dark-field STEM image (a), and Pt (b), and Pd (c) elemental mapping obtained from Pd@Pt sample prepared using solutions with 0.71 mg F127

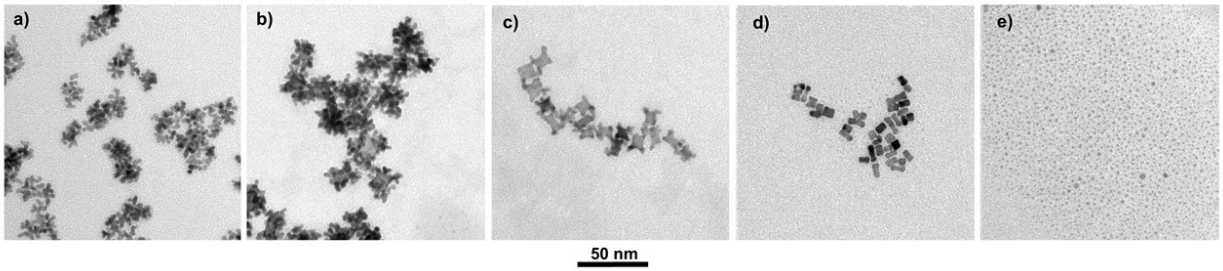

Figure S9. TEM images of Pd@Pt nanoparticles prepared using solutions with different Pt:Pd molar ratios. Pt:Pd molar ratios are a) 1:0, b) 3:1, c) 1:1, d) 1:3, and e) 0:1.

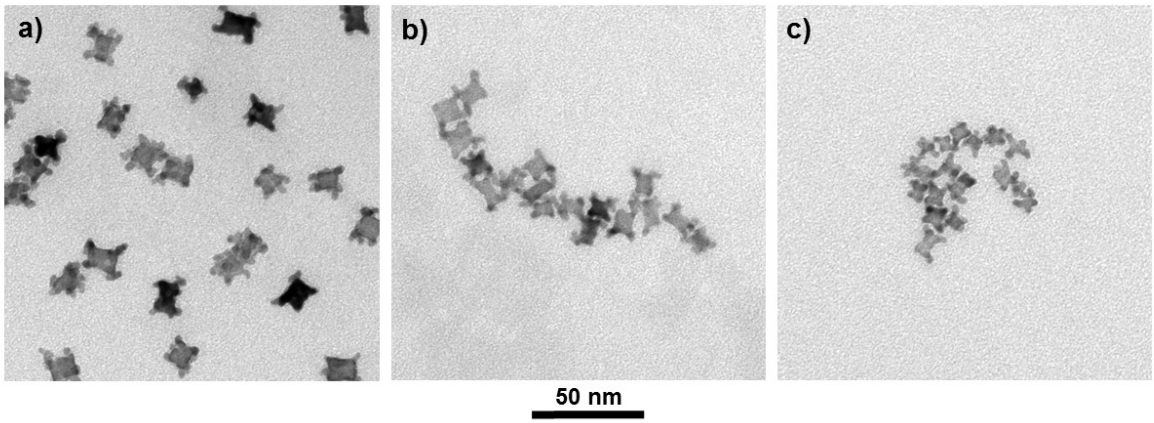

Figure S10. TEM images of Pd@Pt nanoparticles prepared using solutions with different total metal ion concentrations. Total metal ions concentrations ($[Pt^{4+}]+[Pd^{2+}]$) in reaction solutions are a) 0.24, b) 0.48, and c) 0.96 mM.

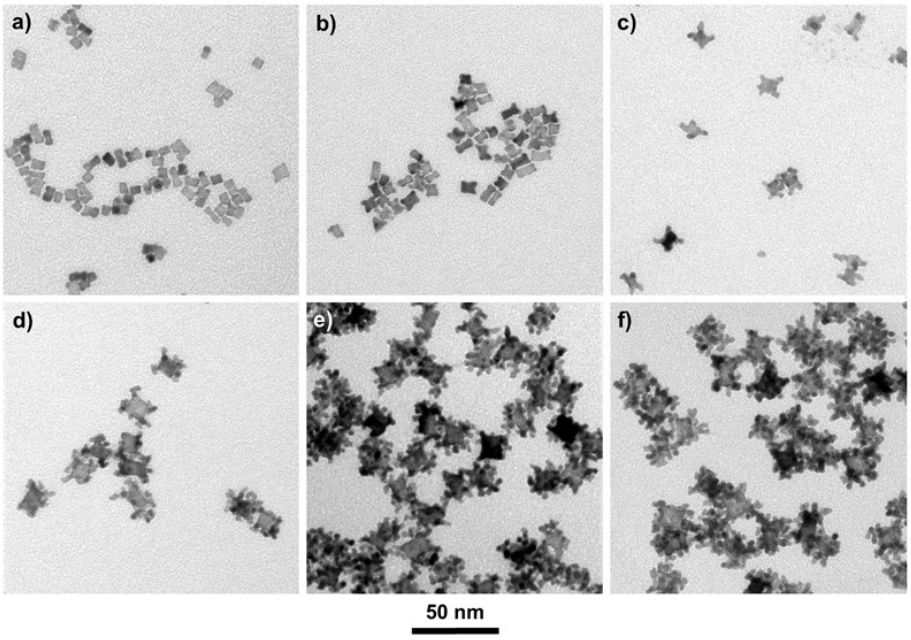

Figure S11. TEM images of Pd@Pt nanoparticles prepared using solutions with different Pt concentrations. Pt concentrations are a) 0.079, b) 0.159, c) 0.238, d) 0.317, e) 0.397, and f) 0.476 mM.

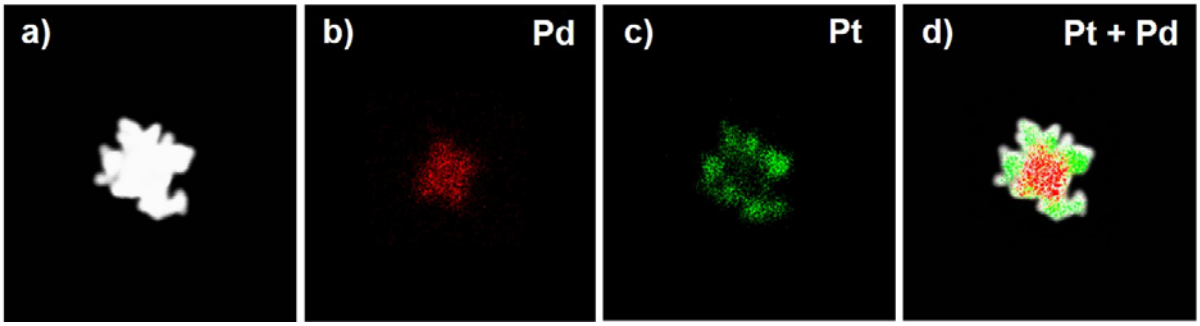

Figure S12. Dark-field STEM image (a), and Pt (b), Pd (c), and combined Pd and Pt (d) elemental mapping obtained from an individual octopodal Pd@Pt Nanoparticle prepared using solution with 0.476 mM Pt precursor concentration.

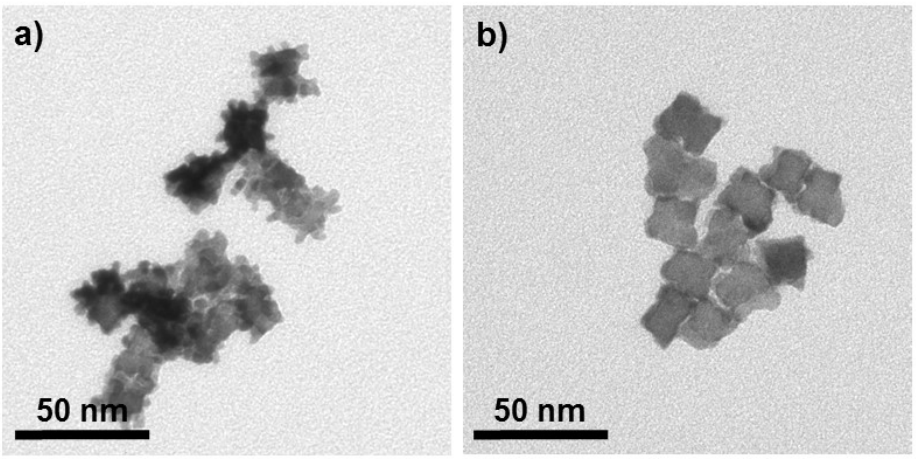

Figure S13. TEM images of Pd@Pt nanoparticles prepared using solutions with a) 0.25ml, and b) 1ml HCl (1N).

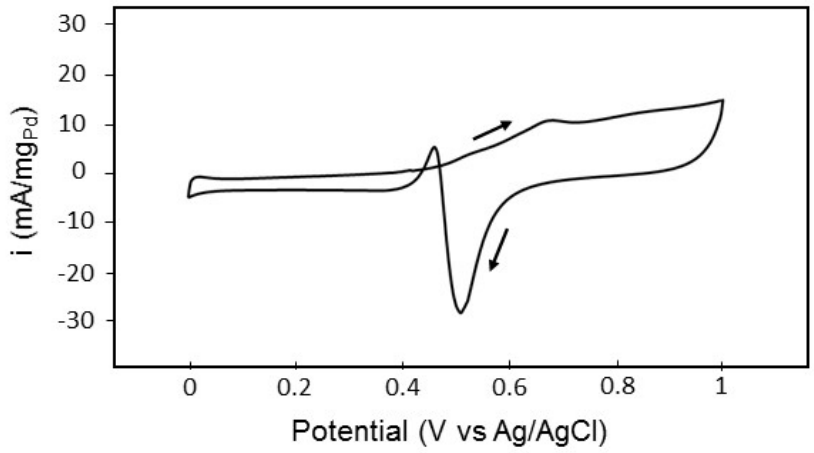

Figure S14. Cyclic voltammograms (CVs) of methanol oxidation using Pd cubes. The measured current is normalized to loaded Pt mass.