Supporting Information

Highly Branched Pt-Ni Nanocrystals Enclosed by Stepped Surface

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Experimental details:

Characterization: X-ray diffraction patterns were recorded with a Rigaku D/max 2500Pc X-ray powder diffractometer with monochromatized Cu Kα radiation (λ = 1.5406 Å). TEM and HRTEM images were recorded by a JEOL JEM-1200EX working at 100 kV and a FEI Titan 80–300 transmission electron microscope equipped with a spherical aberration (Cs) corrector for the objective lens working at 300 kV. Electrochemical measurements were conducted on CH Instrument 660D electrochemical analyzer.

Reagents: Reagents including hexachloroplatinic (IV) acid ($H_2PtCl_6 \cdot 6H_2O$, ≥ 37.0%), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, ≥ 98.5%), octadecylamine (ODA), methanol (≥ 99.7%), and perchloric acid (70.0% ~ 72.0%) were A. R. grade from Sinopharm Chemical Reagent Co., Ltd. Platinum (II) pentanedionate ([$Pt(acac)_2$], ≥ 48.0%), Pt black (12755), and Nafion solution (5% w/w) were purchased from Alfa Aecar. All the chemicals were used as received.

Synthesis of branched Pt seeds: 0.025 g $H_2PtCl_6 \cdot 6H_2O$ was mixed with 0.5 g ODA and heated at 120 ^oC to form a clear solution in a vial labeled as A. 7.5 g ODA was loaded in a 25 mL two-neck flask and heated to 230 ^oC. The solution in the vial A was then added into the flask with pipet. The reaction mixture was aged at 230 ^oC for 5 min after it turned black. The reaction mixture was cooled down to 70 ^oC, followed by addition of 20 mL ethanol. The resultant homogeneous solution was put aside for 30 min at 70 ^oC without magnetic stirring. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of branched Pt-Ni bimetallic NCs: 0.004 g $Ni(NO_3)_2 \cdot 6H_2O$ was mixed with 0.5 g ODA and heated at 120 ^oC to form a clear solution in a vial labeled as A. 7.5 g ODA was loaded in a 25 mL two-neck flask and heated to 80 ^oC. Pt seeds dispersed in hexane were added into the flask. After evaporating the hexane at 120 ^oC (about 10 min), the temperature of the flask was elevated to 230 ^oC. The solution in the vial A was subsequently added into the flask with pipette. The reaction mixture was aged at 230 ^oC for 5 min and then heated to 250 ^oC and maintained at this temperature for 20 min. The reaction mixture was cooled down to 70 ^oC, followed by addition of 20 mL ethanol. The resultant homogeneous solution was put aside for 30 min at 70 ^oC without

magnetic stirring. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of elongated Pt NPs: 0.032 g [$Pt(acac)_2$] dissolved in 0.5 mL toluene was added into 7.5 g ODA which was preheated to 150 ^oC. The reaction mixture was further heated to 230 ^oC and cooled down to 70 ^oC as soon as the solution turned black. 20 mL ethanol was then added into the reaction mixture at 70 ^oC. The resultant homogeneous solution was put aside for 30 min at 70 ^oC without magnetic stirring. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Working electrode preparation: The working electrode was prepared according the reported method in the literature.[9a] Carbaon black (Vulcan XC-72) was mixed with hexane and sonicated for 1 hour. A designed amount of Pt-based NCs (20 wt%) were added into this dispersion and further sonicated for 30 min. After overnight stirring, the solids was collected by centrifugation and stirred with n-butylamine at room temperature for 3 days. The solids was then precipitated by centrifugation and washed with methanol for several times. The final sample was dispersed in mixed solvent (H_2O : isopropanol : 5% Nafion = 4 :1 : 0.025) at a concentration of 1 mg/mL. For electrochemical measurement, 5 μL suspension of this Pt-based NCs/C catalyst was dropped on a glassy carbon electrode. The electrode was dried under ambient condition. Pt wire was used as counter electrode and Ag/AgCl as reference electrode. Methanol electro-oxidation was conducted in 1 M methanol and 0.1 M $HClO_4$ from 0 to 1.2 V (vs. RHE) at a scan rate of 50 mV s^{-1}.

CO stripping measurements: the working electrode was immersed in 0.1 M $HClO_4$ with CO bubbling. The electrode potential was held at 0.10 V to form a saturated CO adlayer. After the complete blockage of the surface by CO, the electrode was immersed in a fresh 0.1 M $HClO_4$ for CV tests from 0.05−1.0 V (vs. RHE) with a scan rate of 100 mV s^{-1}.

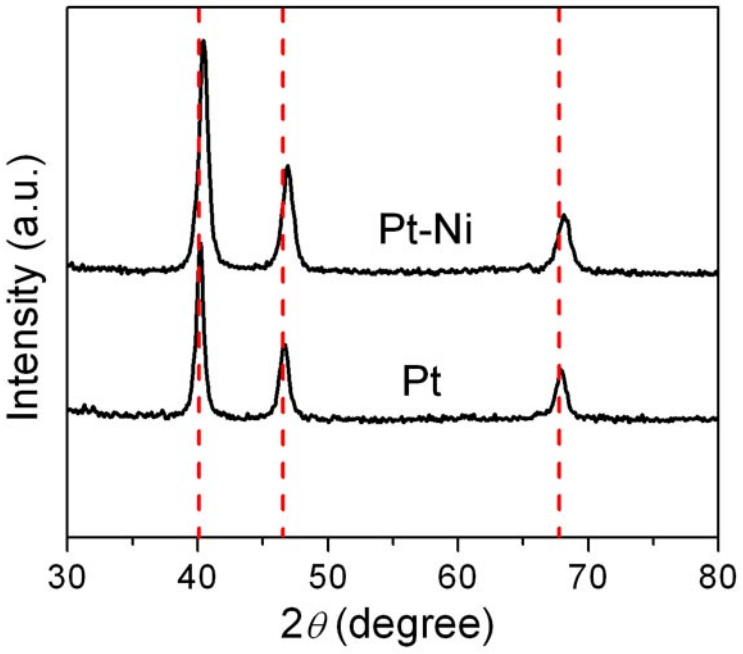

Figure S1. XRD patterns of Pt seeds and Pt-Ni NBs. Note that the peak positions of Pt-Ni NBs slightly shifted to higher 2θ values compared to those of pure Pt.

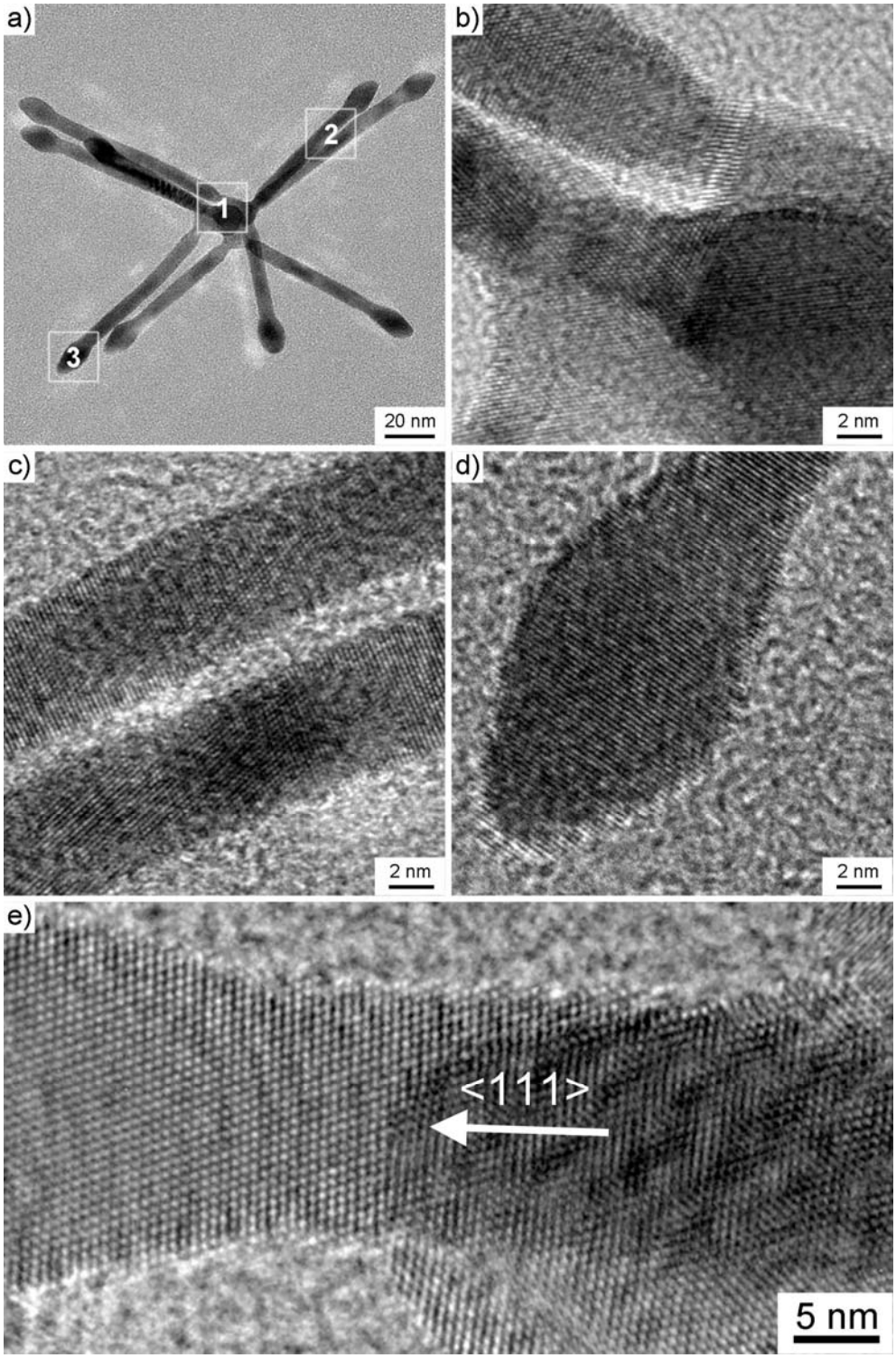

Figure S2. a) TEM image of one Pt-Ni NC chosen randomly; b–d) HRTEM images of the root, arm, and tip of the Pt-Ni NC as selected by the white square frames; e) HRTEM image with enlarged magnification of a single branch.

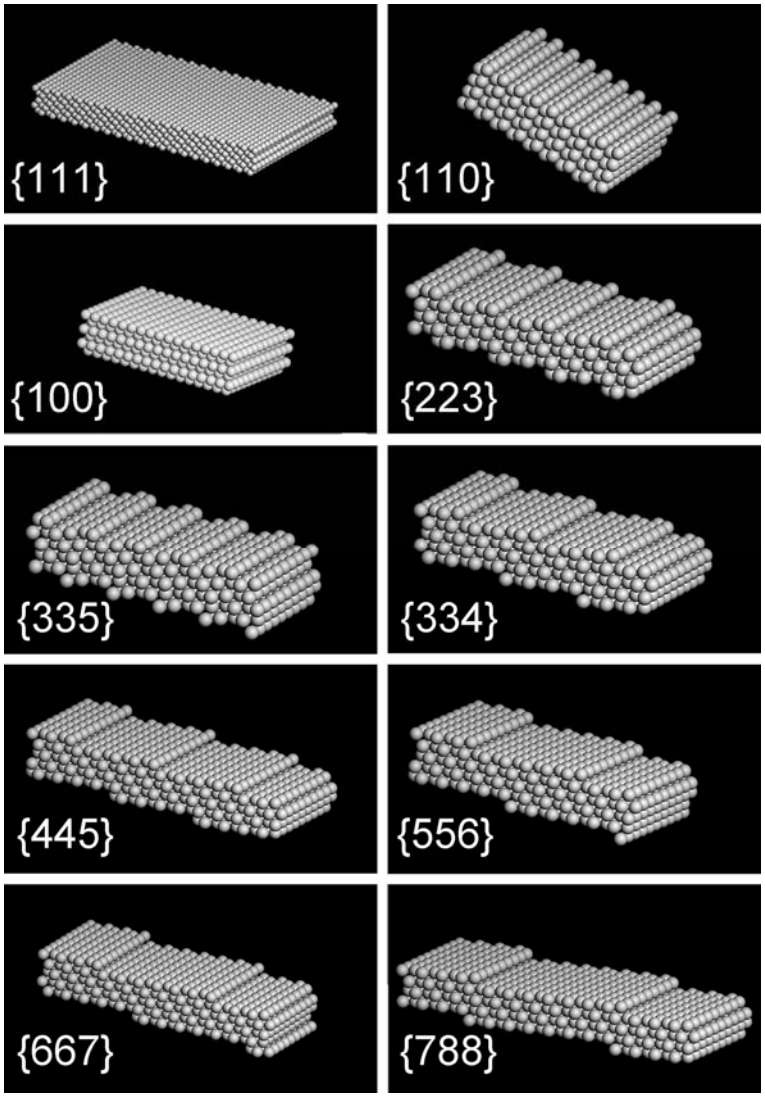

Figure S3. Models of crystal planes including {111}, {110}, {100}, {223}, {335}, {334}, {445}, {556}, {667}, {788}.

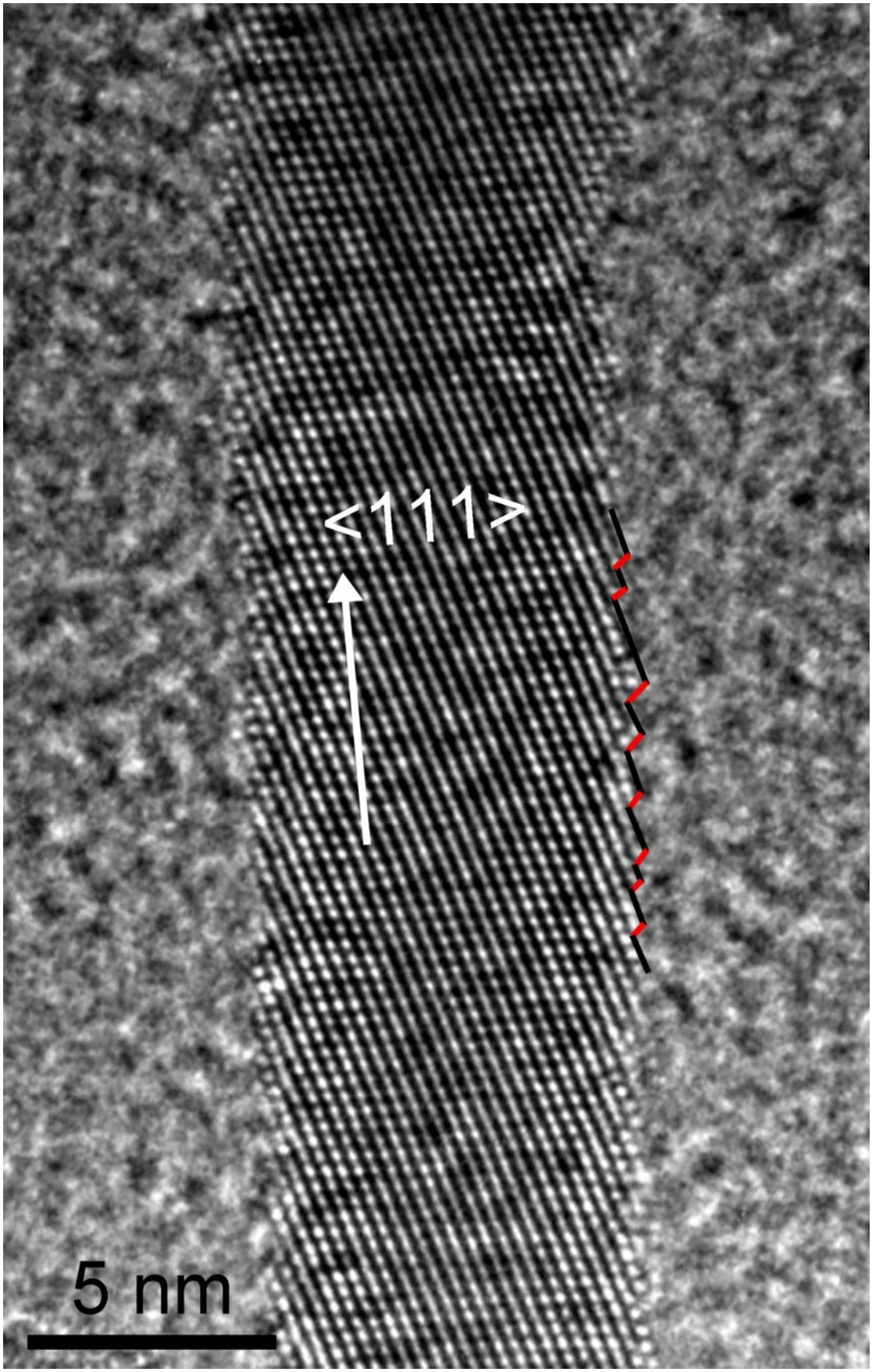

Figure S4. HRTEM image of branched Pt NCs. Note that the growth direction of the arm is <111> and the exposed surface contains rich steps and defects.

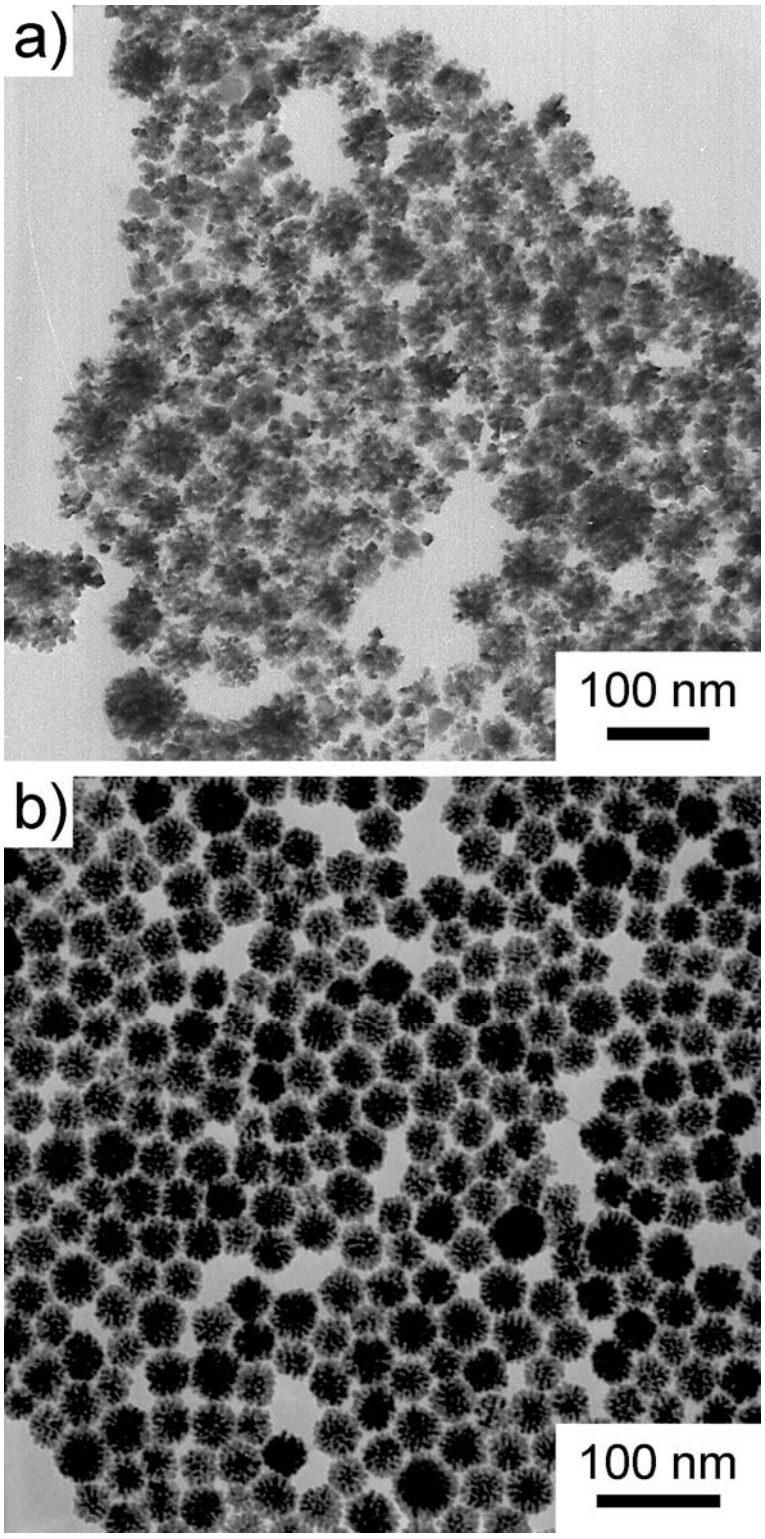

Figure S5. TEM image of Pt wool balls prepared at a) 210 ^{o}C, b) 250 ^{o}C.

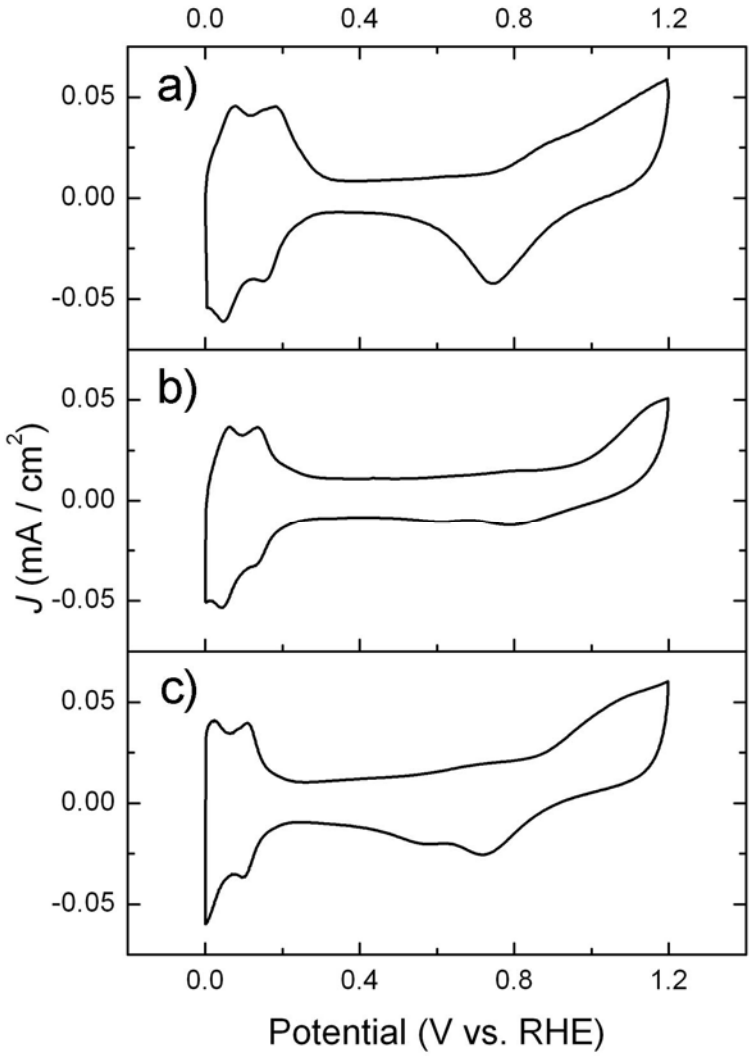

Figure S6. Cyclic voltammograms of a) elongated Pt NPs, b) Pt NBs, c) Pt-Ni NBs recorded in 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1}. The ECSAs estimated from the hydrogen adsorption peaks are 36 m^2 g^{-1} for elongated Pt NPs, 26 m^2 g^{-1} for Pt NBs, and 24 m^2 g^{-1} for Pt-Ni NBs, respectively.

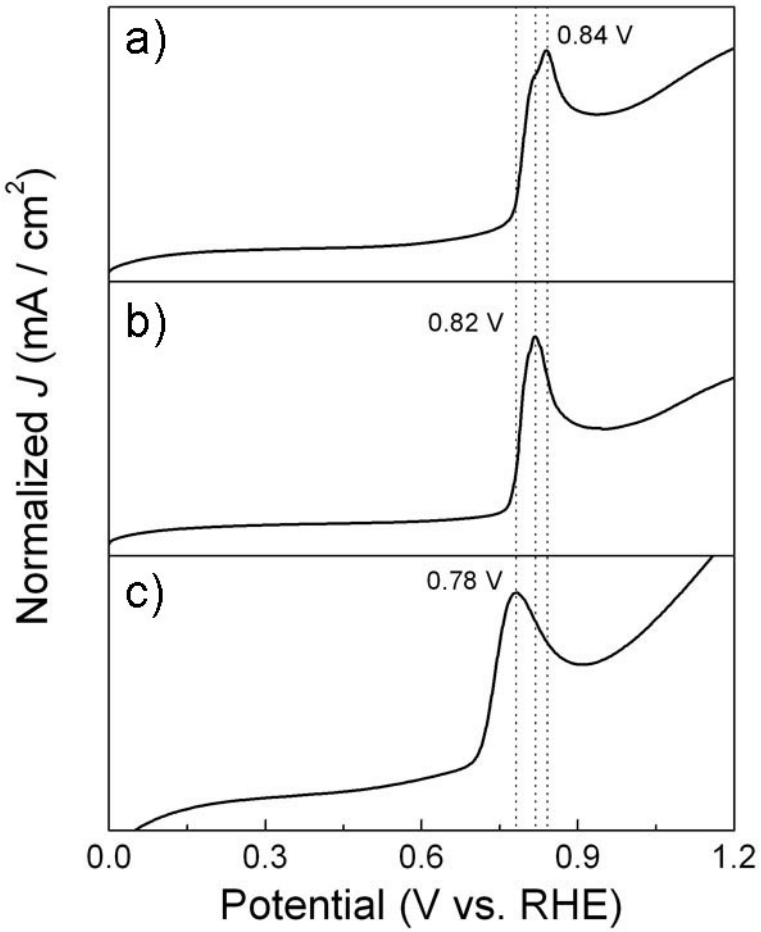

Figure S7. Cyclic voltammograms of CO stripping on a) elongated Pt NPs, b) Pt NBs, c) Pt-Ni NBs recorded in 0.1 M $HClO_4$ with a scan rate of 100 mV s^{-1}.

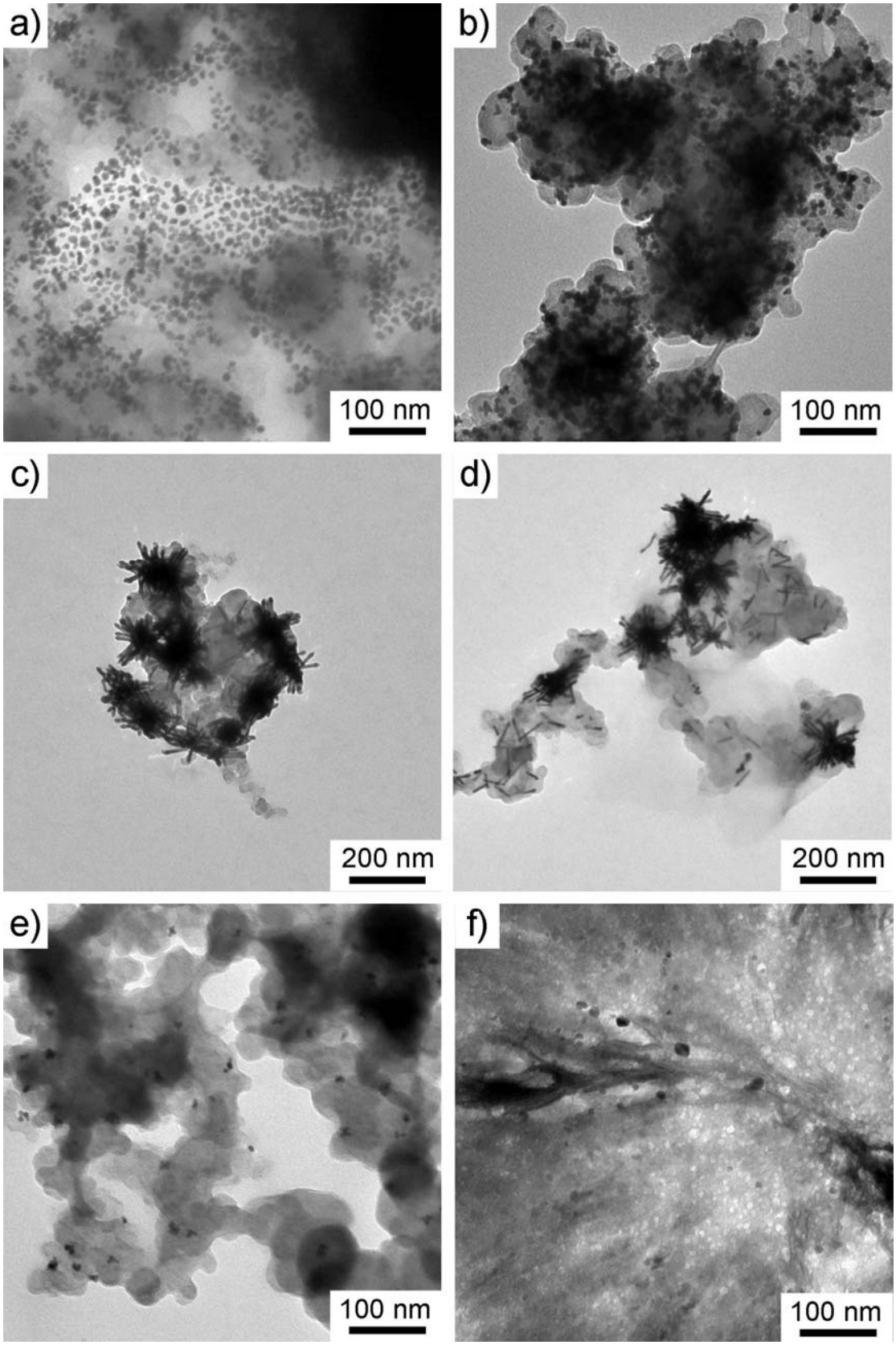

Figure S8. TEM images of supported Pt-based catalysts before and after durability test: a,b) elongated Pt NPs; c,d) Pt-Ni NBs; and e,f) commercial Pt black.

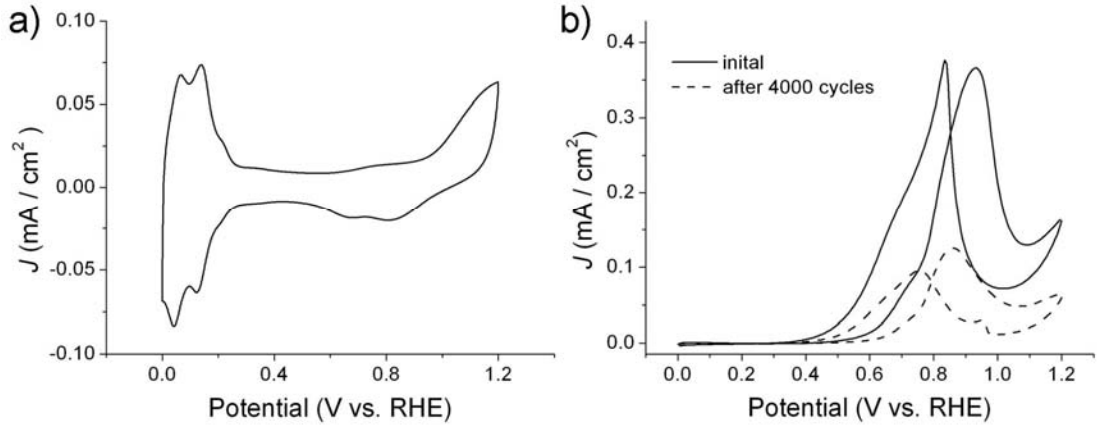

Figure S9. Cyclic voltammograms of commercial Pt black recorded in a) 0.1 M $HClO_4$ and b) 0.1 M $HClO_4$ + 1 M MeOH with a scan rate of 50 mV s^{-1}.