

Electronic Supplementary Information

One-Pot Synthesis of Pd@Pt₃Ni Core-Shell Nanobranches with Ultrathin Pt₃Ni{111} Skins for Efficient Ethanol Electrooxidation

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Experimental Details

Chemicals. Pd(acac)₂ (≥99.0%) and Pt(acac)₂ (≥99.0%) were purchased from Kunming Institute of Precious Metals; NiCl₂·6H₂O, ethanol (AR) and N,N-Dimethylformamide (DMF) were purchased from Xilong Chemical Co. Ltd. (China); poly(vinylpyrrolidone) (PVP, Mw~55000, AR) was purchased from Sigma-Aldrich; Hexadecyl trimethyl ammonium Chloride (CTAC) was purchased from J&K Scientific; tungsten hexacarbonyl (W(CO)₆, 97%) was purchased from Alfa Aesar. All chemicals were used without further purification.

Synthesis of Pd@Pt₃Ni Core-Shell Nanobranches. In a typical synthesis, 100 mg of CTAC, 100 mg of PVP, 8 mg of Pd(acac)₂, 10 mg of Pt(acac)₂, 8 mg of NiCl₂, 50 mg W(CO)₆, 8.0 mL of DMF and 4.0 mL of ethanol were added together into a 25 mL Teflon-lined stainless steel autoclave, capped and then stirred at 600 rpm for 30 min. The mixture was heated from 30 °C to 180 °C in around 30 min and kept at 180 °C for 30 min before it was cooled to room temperature. The products were collected by centrifugation (10000 rpm, 10 min) and washed with ethanol and acetone several times.

Characterization. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were performed on a JEOL JEM 2100 operating at 200 kV. High-angle annular dark-field scanning

TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mappings were performed on a FEI Talos F200s operating at 200 kV. EDS was performed on a Hitachi S4800 equipped with an energy dispersive X-ray spectroscopy. Powder X-ray diffraction pattern (PXRD) was performed on a Rigaku Smart Lab with a Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) at 30 mA and 40 kV. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Thermo Fisher Scientific ESCALAB 250 with a monochromatic Al K α X-ray (500 μm , 150 W, 20 eV). The metal concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7800).

Electrochemical Study. Electrochemical experiments were carried out on a CHI 660E (Shanghai Chenhua Co., Ltd., China) with a three-electrode cell. A Pt mesh was used as the counter electrode, a saturated calomel electrode (SCE) or Hg/HgO was used as the reference electrode. The Pd@Pt₃Ni/C was dispersed in a mixture consisting of isopropyl alcohol, DI water and 5% Nafion (v/v/v = 0.5/0.5/0.005) to form a 0.1 mg_{Pt}/mL dispersion. Next, the catalysts ink was dropped onto a glassy carbon electrode (GCE) (diameter 5 mm, area 0.196 cm²) and dried in air. The cyclic voltammograms (CVs) measurements were carried out in a N₂ ($\geq 99.999\%$)-saturated, 0.5 M H₂SO₄ solution between -0.2 and 1.0 V (vs. SCE) at 50 mV s⁻¹. The ethanol oxidation reaction (EOR) measurements were conducted in a N₂ ($\geq 99.999\%$)-saturated, 1 M KOH and 1 M ethanol solution between -0.7 and 0.4 V (vs. Hg/HgO) with a scan rate of 50 mV s⁻¹. For the long-term stability test, we used the chronoamperometric (i~t) measurement with a potential at -0.19 V (vs. Hg/HgO).

Table S1. The mole ratios of Pd/Pt/Ni measured by EDS, ICP-MS and XPS, respectively.

Element	EDS (%)	ICP-MS (%)	XPS (%)
Pd	86.4	86.6	77.5
Pt	10.2	10	18.6
Ni	3.4	3.4	3.9

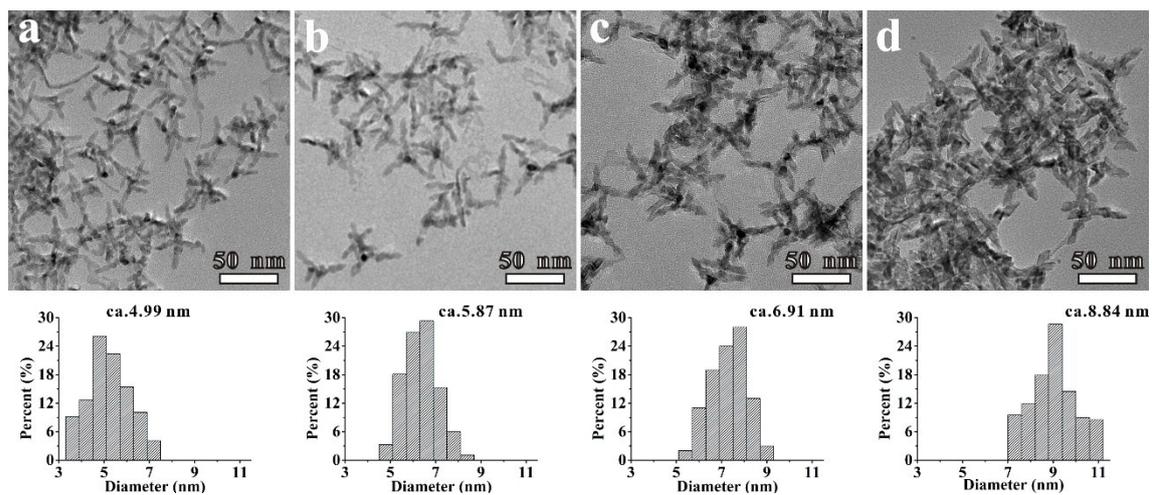


Figure S1. TEM images and the corresponding histograms of diameters distribution of products obtained at different reaction points: (a) 150 °C, 0 min; (b) 180 °C, 0 min; (c) 180 °C, 30 min; (d) 180 °C, 45 min.

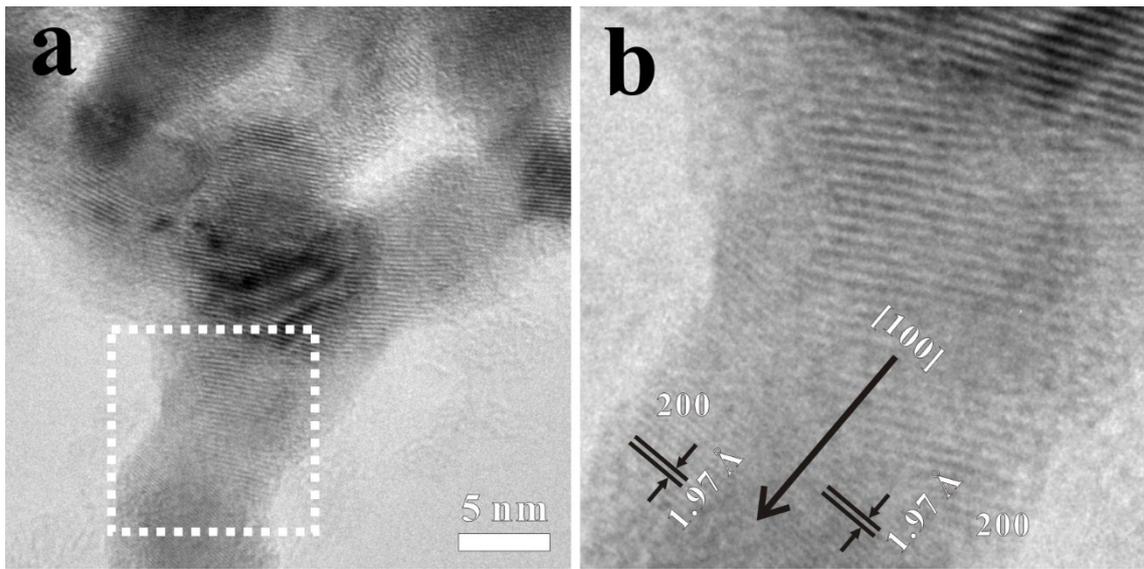


Figure S2. HRTEM images on a branch of the Pd@Pt₃Ni products showing the [100] direction along the radial of the branch.

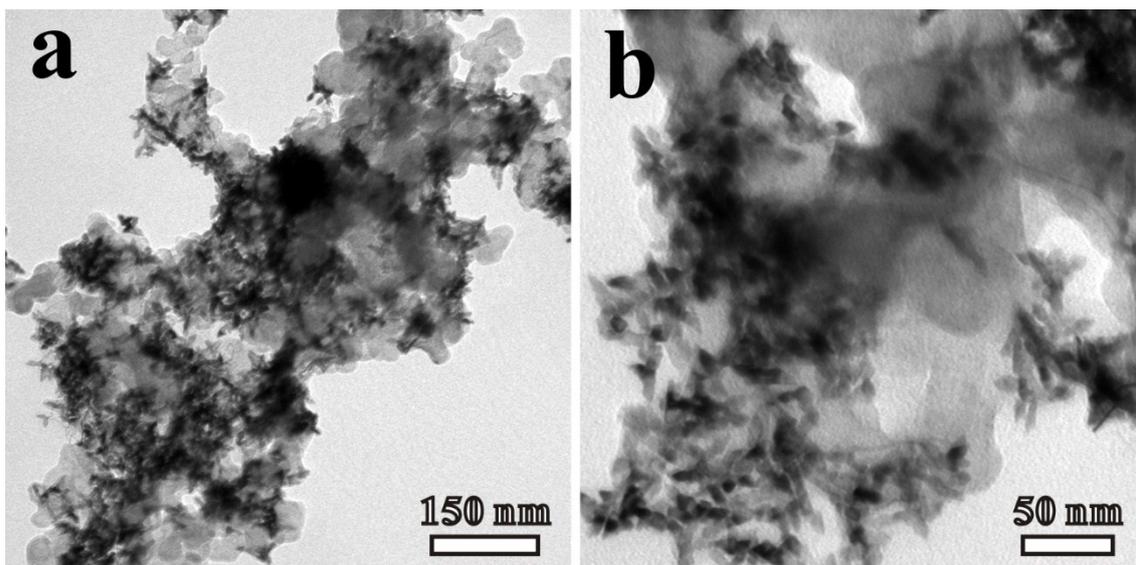


Figure S4. TEM images of the carbon-loaded Pd@Pt₃Ni/C catalysts.

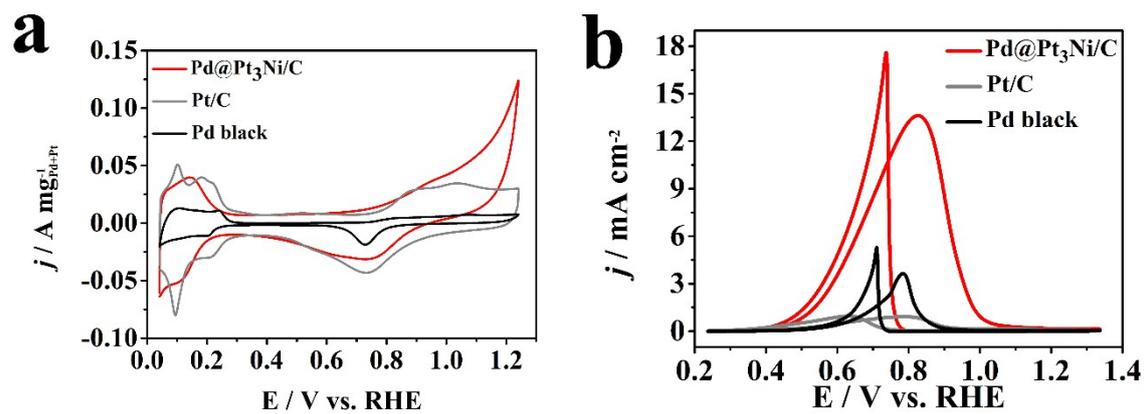


Figure S5. (a) CV curves of the Pd@Pt₃Ni/C, commercial Pt/C and Pd black in a 0.5 M H₂SO₄ solution at 50 mV/s. (b) Special activities of the catalysts for EOR normalized by the ESCAs.

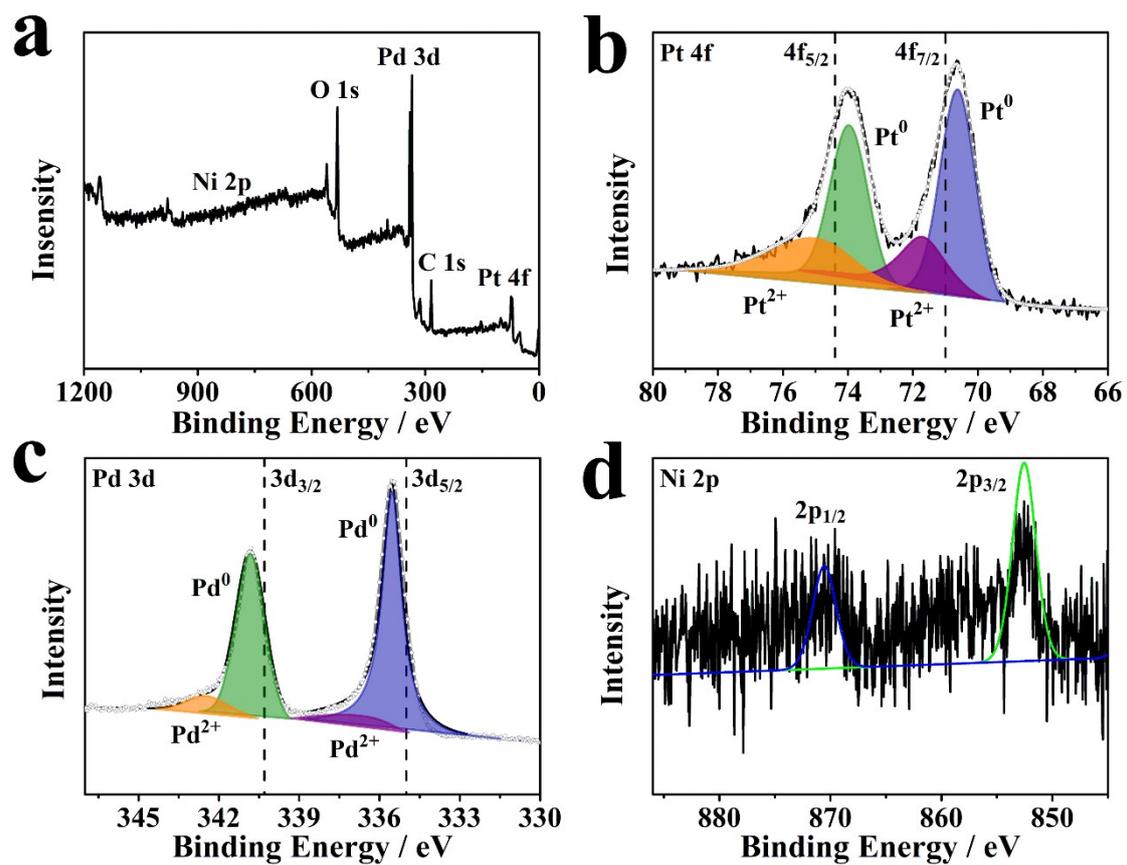


Figure S6. (a) Complete XPS survey spectra, (b) Pt 4f, (c) Pd 3d and (d) Ni 2p high-resolution XPS spectra record from the as-prepared Pd@Pt₃Ni core-shell nanobranched structures. The mole ratio of Pd/Pt/Ni obtained by XPS was around 77.5:18.6:3.9.