

Electronic Supplementary Information for

Pt–Ni octahedral nanocrystals as a class of highly active electrocatalysts toward hydrogen evolution reaction in an alkaline electrolyte

Reza Kaviani,^{a§} Sang-Il Choi,^{b§#} Jinho Park,^c Tianyuan Liu,^a Hsin-Chieh Peng,^b Ning Lu,^d Jinguo Wang,^d Moon J. Kim,^d Younan Xia,^{*bc} Seung Woo Lee^{*a}

^aThe George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States.

^bThe Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, Georgia 30332, United States.

^cSchool of Chemistry and Biochemistry, and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

^dDepartment of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States

Corresponding Authors

younan.xia@bme.gatech.edu (Y.X. for synthesis and characterization)

seung.lee@me.gatech.edu (S.W.L. for electrochemical measurements)

[§]These authors contributed equally to this work.

[#]Current affiliation: Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu 702-701, Republic of Korea

Materials and Methods

1. Chemicals and materials

Platinum(II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 99.99%), nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%), benzyl ether (98%), oleylamine (70%), oleic acid (90%), tungsten hexacarbonyl ($\text{W}(\text{CO})_6$, 99.99%), and acetic acid (HAc , $\geq 99.5\%$) were all purchased from Sigma–Aldrich and used as received.

2. Synthesis of Pt–Ni octahedra with an average edge length of 9 nm

$\text{Pt}(\text{acac})_2$ (0.051 mmol), $\text{Ni}(\text{acac})_2$ (0.039 mmol), oleylamine (2.0 mL) and oleic acid (1.0 mL) were added into benzyl ether (7.0 mL), and then dissolved under magnetic stirring and heated to 130 °C under argon protection. At 130 °C, argon purging was stopped and $\text{W}(\text{CO})_6$ (0.142 mmol) was concomitantly added. Next, the mixture was heated to 230 °C at a heating rate of 10 °C min^{-1} and maintained at 230 °C for 40 min. The mixture was allowed to cool down to room temperature and the nanocrystals were precipitated out by adding toluene (5 mL) and ethanol (15 mL). The supernatant was discarded after centrifugation at 6,000 rpm for 10 min. Then, the precipitated Pt–Ni octahedra were dispersed in toluene (10 mL).

3. Loading of Pt–Ni octahedra on carbon support

The toluene suspension of Pt–Ni octahedra (10 mL) was added into another 10 mL of toluene suspension containing 20 mg of porous carbon (Ketjenblack EC-300J, AkzoNobel, to achieve a Pt loading of ~25 wt%) under ultrasonic agitation for 10 min. The mixture was continued with ultrasonication for another 3 h. The resulting powders were collected by centrifugation at 12,000 rpm for 15 min, followed by drying in an oven at 70 °C for 30 min.

Characterization

1. Morphological, structural, and elemental characterization

Transmission electron microscopy (TEM) images were obtained using a JEM-1400 microscope (JEOL, Tokyo, Japan) operated at 120 kV. High-resolution TEM, high-angle annular dark-field scanning TEM (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS) spot analyses were performed using a JEOL ARM200F microscope (JEOL, Tokyo, Japan) with a STEM aberration corrector operated at 200 kV. The metal contents in the Pt–Ni octahedra loaded on

carbon were determined using inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer, NexION 300Q). X-ray diffraction (XRD) patterns were obtained with a PANalytical X'Pert PRO Alpha-1 diffractometer using a 1.8 kW Ceramic Copper tube source. X-ray photoelectron spectroscopy (XPS) was carried out using a spectrometer (Thermo Scientific, K-Alpha) with Al K α X-ray (1486.6 eV) as the light source.

2. Electrochemical measurements

The electrochemical measurements were carried out using a Biologic-VMP3 potentiostat. 0.5 mg of the Pt–Ni octahedra was dispersed in a mixture of DI-water (0.5 mL), isopropyl alcohol (0.5 mL), and Nafion (30 μ L, 0.025 wt% in aqueous solution, Ion Power, Inc.). 10 μ L of this suspension was then deposited on a pre-cleaned glassy carbon electrode (Pine Instruments) and allowed to dry. A Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All potentials reported in this work were calibrated and converted to the reversible hydrogen electrode (RHE). 0.1 M KOH (99.99%, Sigma-Aldrich) and 0.1 M HClO₄ (70% double distilled, GFS Chemicals) aqueous solutions were used as electrolytes. Cyclic voltammograms (CVs) were recorded after reaching steady state, between 0.08 and 1.0 V at a scan rate of 50 mV s⁻¹ in Ar-saturated electrolytes at room temperature. Hydrogen evolution reaction (HER) rates were measured using a rotating disc electrode (RDE) technique. Polarization curves were recorded between -0.4 and 0.2 V at a scan rate of 10 mV s⁻¹ and a rotation rate of 1,600 rpm in H₂-saturated electrolytes at room temperature for three cycles. All polarization curves were corrected for *iR*-contribution within the cell. The stability tests were performed by chronoamperometric and chronopotentiometric techniques in an H₂-saturated 0.1 M KOH solution at 1,600 rpm for 1h. Applied potential for chronoamperometry was -0.05 V vs. RHE and applied current for chronopotentiometry was -4 mA cm_{Pt}⁻².

Table S1. Comparison of the Ni/Pt atomic ratios and content of tungsten (W) measured by ICP-MS for Pt–Ni octahedra catalysts before and after treating with HAc and KOH solution, respectively.

Catalyst	Ni/Pt	Content of W^a (mol%)
Pt–Ni/C	0.61	4.8
Pt–Ni/C-HAc (30 min)	0.44	3.7
Pt–Ni/C-HAc (2 h)	0.40	-
Pt–Ni/C-HAc (10 h)	0.38	-
Pt–Ni/C-KOH	0.60	1.2
Pt–Ni/C-HAc (30 min)-KOH	0.43	0.43

^a Content of W was obtained as $n_W/(n_{Pt} + n_{Ni} + n_W) \times 100$, where n represents molarity of each element in the samples.

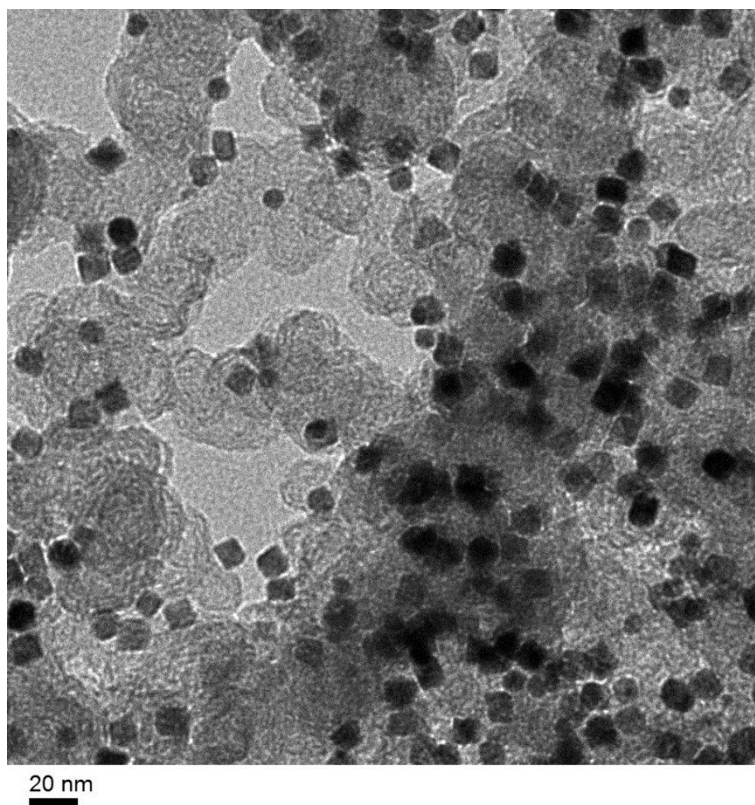


Figure S1. TEM image of the 9-nm Pt–Ni octahedra loaded on carbon (Pt–Ni/C).

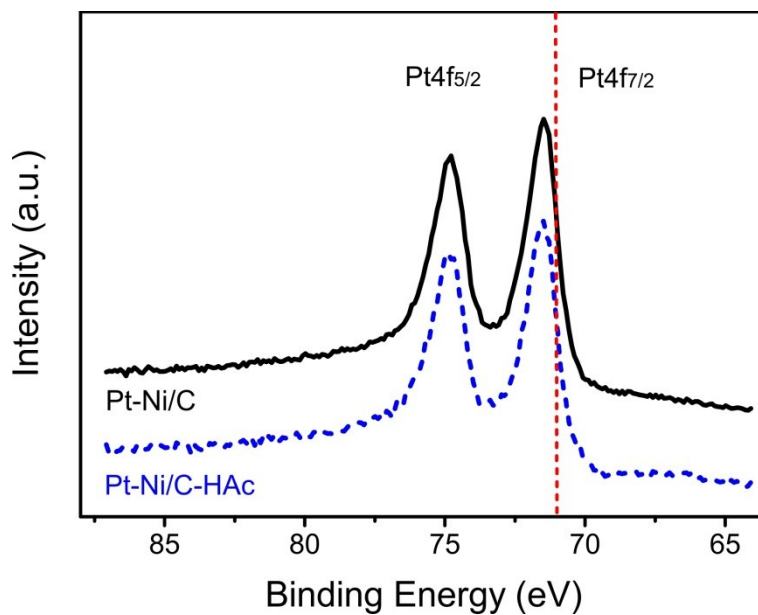


Figure S2. Pt 4f XPS peaks of the Pt–Ni/C and Pt–Ni/C-HAc. The Pt–Ni/C-HAc was obtained by treating the Pt–Ni/C in HAc at 60 °C for 30 min. The Pt 4f_{7/2} peaks in the both catalysts shifted to higher binding energies compared to that of pure Pt 4f_{7/2} marked by a red dashed line.

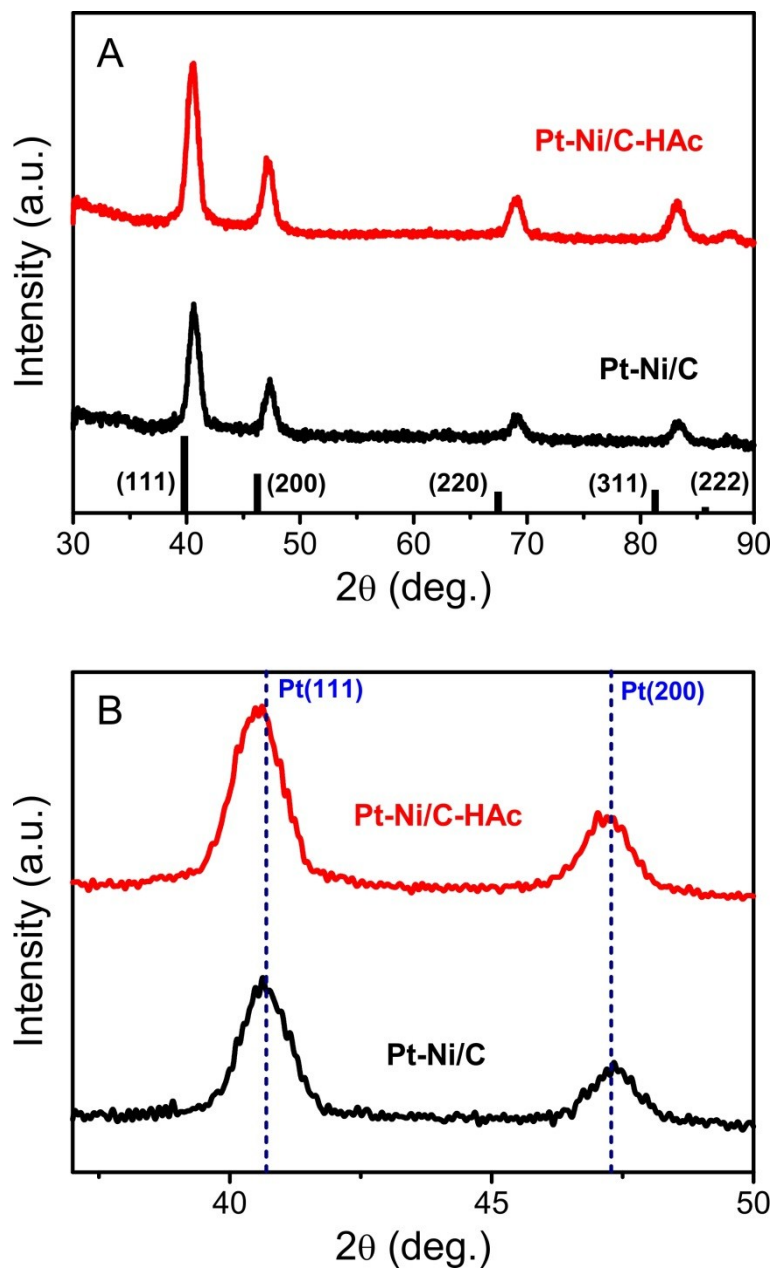


Figure S3. XRD patterns of the Pt–Ni/C and Pt–Ni/C-HAc. The Pt–Ni/C-HAc was obtained by treating the Pt–Ni/C in HAc at 60 °C for 30 min. The black bars in (A) correspond to the peaks for Pt in the JCPDS reference (#04-0802). The blue dashed lines in (B) correspond to the positions of diffraction peaks for Pt(111) and Pt(200).

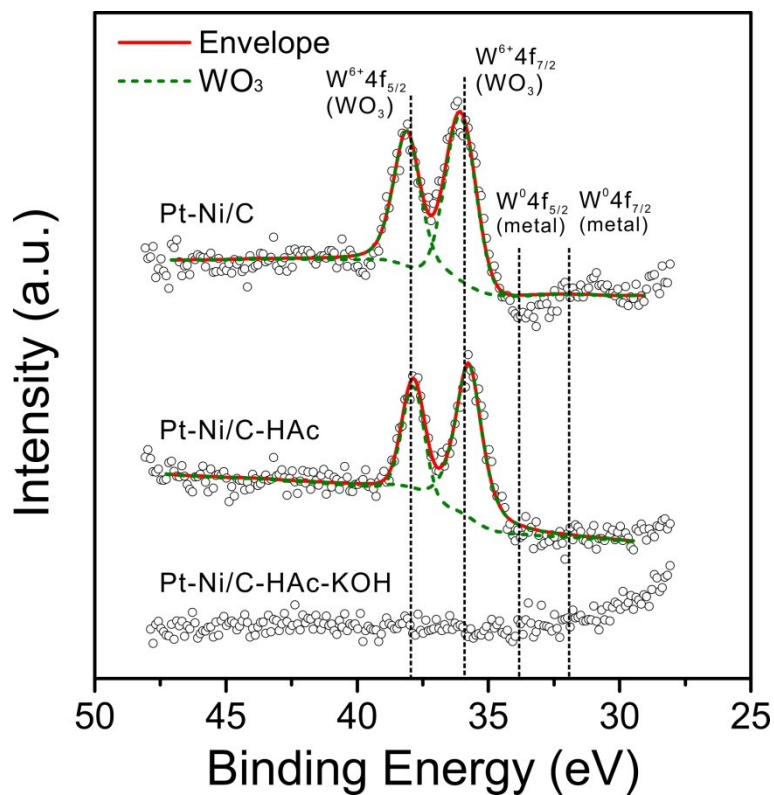


Figure S4. Comparison of the W 4f XPS spectra taken from the Pt–Ni/C catalysts before and after HAc and KOH treatments. The peaks could be fitted with references to WO₃. The binding energy of primary peaks of W(0) and WO₃ was marked with black dashed lines. The Pt–Ni/C-HAc was obtained by treating the Pt–Ni/C in HAc at 60 °C for 30 min and Pt–Ni/C-HAc-KOH was obtained by treating the Pt–Ni/C-HAc with 0.1 M KOH solution at room temperature for 1 h.

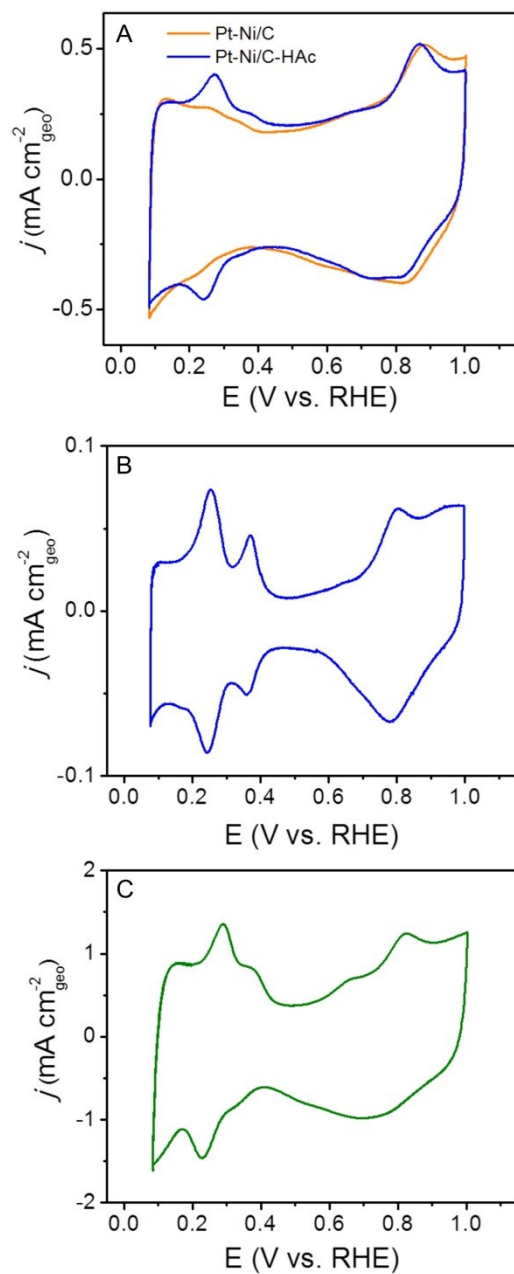


Figure S5. Steady-state cyclic voltammetry (CV) scans of (A) the Pt–Ni/C and the Pt–Ni/C-HAc (treated for 30 min), (B) the polycrystalline Pt electrode, and (C) the commercial Pt-TKK catalyst. The CV scans were recorded in Ar-saturated, 0.1 M KOH solution at a scan rate of 50 mV s^{-1} , in which the currents were normalized to the geometric area of the rotating disk electrode (0.196 cm^2).

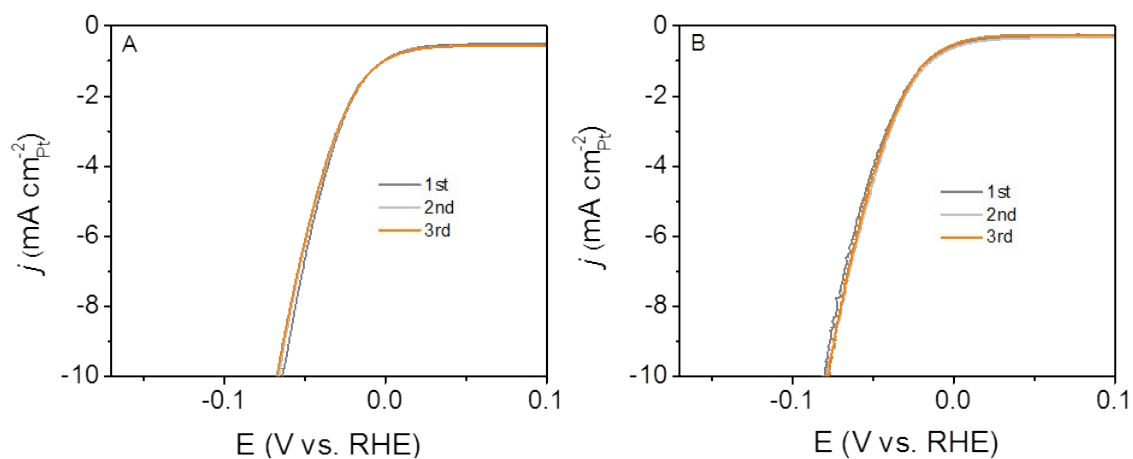


Figure S6. Steady-state HER polarization curves of (A) the Pt–Ni/C and (B) Pt–Ni/C-HAc. The Pt–Ni/C-HAc was obtained by treating the Pt–Ni/C in HAc at 60 °C for 30 min. The measurements were conducted in a H₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ and rotating speed of 1,600 rpm.