Supporting Online Material for

Synthesis and Characterization of 9-nm Pt-Ni Octahedra with a Record High Activity of 3.3 A/mg$_{Pt}$ for the Oxygen Reduction Reaction

Sang-Il Choi,[1] Shuifen Xie,[1] Minhua Shao,[2] Jonathan H. Odell,[2] Ning Lu,[3] Hsin-Chieh Peng,[4] Lesia Protsailo,[2] Sandra Guerrero,[2] Jinho Park,[4] Xiaohu Xia,[1] Jinguo Wang,[3] Moon J. Kim,[3,5] and Younan Xia*[1,4,6]*

*Corresponding authors: minhua@gmail.com (electrochemical measurements); younan.xia@bme.gatech.edu (synthesis and characterization)

[1]The Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, Georgia 30332, United States

[2]UTC Power, South Windsor, Connecticut 06074, United States

[3]Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States

[4]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[5]Department of Nanobio Materials and Electronics, World Class University, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea

[6]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

Materials and Methods

1. Chemicals and materials

Platinum(II) acetylacetonate ($Pt(acac)_2$, 99.99 %), nickel(II) acetylacetonate ($Ni(acac)_2$, 95 %), oleylamine (OAm, 70 %), oleic acid (OA, 90 %), benzyl ether (BE, 98 %), tungsten hexacarbonyl ($W(CO)_6$, 99.99 %), and acetic acid (HAc, ≥99.5 %) were all obtained from Sigma–Aldrich and used as received.

2. Synthesis of 9-nm Pt-Ni octahedra with BE a solvent

In a standard synthesis, $Pt(acac)_2$ (0.051 mmol), $Ni(acac)_2$ (0.039 mmol), OAm (2.0 mL) and OA (1.0 mL) were added into BE (7.0 mL), mixed, and heated to 130 °C under an argon atmosphere with magnetic stirring. $W(CO)_6$ (0.142 mmol) was then added quickly, and argon purging was stopped at the same time. The mixture was then heated to 230 °C for 10 min at a heating rate of 10 °C min^{-1} and kept at 230 °C for 40 min. The reaction mixture was allowed to cool down to room temperature naturally, and the Pt-Ni octahedra were precipitated out by sequentially adding toluene (5 mL) and ethanol (15 mL). The supernatant was removed by centrifugation at 6,000 rpm for 10 min. The resulting Pt-Ni octahedra could be easily dispersed in organic solvents such as toluene and hexane.

We also scaled up the synthesis from 0.03 g to 0.5 g, which corresponds to the total mass of the final Pt-Ni/C catalyst. In this case, we simply increased the amounts of $Pt(acac)_2$, $Ni(acac)_2$, OAm, and OA by 15 times relative to the standard synthesis and increased the volume of BE to 105.0 mL. The mixture was heated to 130 °C under magnetic stirring and argon protection. When $W(CO)_6$ (2.13 mmol) was added quickly, argon purging was stopped immediately. The following heating and work-up procedures were the same as those used for the standard synthesis.

3. Synthesis of Pt-Ni octahedra without using a solvent

In a typical synthesis, $Pt(acac)_2$ (0.051 mmol) and $Ni(acac)_2$ (0.117 mmol) were added into a mixture of OAm (6.0 mL) and OA (4.0 mL). The heating and work-up procedures were the same as those used for the synthesis with BE as a solvent.

4. Preparation of Pt-Ni/C catalysts

A suspension of the Pt-Ni octahedra in toluene was mixed with 20 mg of Ketjen Black (KB) carbon (to achieve a Pt loading of ~25 wt%) in toluene under ultrasonic wave agitation for 10 min. The mixture was continued with magnetic stirring and ultrasonication for 3 h. The resulting Pt-Ni/C catalyst was centrifuged at 12,000 rpm for 15 min, and then added into 20 mL of acetic acid and heated at 60 °C for 0.5 h, 2 h or 10 h to control the Pt/Ni ratio. The final catalyst was washed 3 times with ethanol and dried for 30 min in an oven at 70 °C before ORR measurements.

Characterization

1. Morphological, structural, and elemental characterization

Transmission electron microscopy (TEM) images were taken using a JEM-1400 microscope (JEOL, Tokyo, Japan) operated at 120 kV by drop casting the nanoparticle dispersions on carbon-coated copper grids and drying under ambient conditions. High-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray (EDX) mapping analyses were performed using a JEOL ARM200F microscope (JEOL, Tokyo, Japan) with STEM aberration corrector operated at 200 kV. The metal contents in the as-obtained catalysts were determined using inductively coupled plasma mass spectrometry (ICP-MS, Perkin–Elmer, NexION 300Q). XRD patterns were obtained with a PANalytical X'Pert PRO Alpha-1 diffractometer using 1.8 kW Ceramic Copper tube source. XPS measurements were carried out using a spectrometer (Thermo Scientific, K-Alpha) with Al Kα X-ray (1486.6 eV) as the light source.

2. Electrochemical measurements

Approximately 3 mg of the Pt-Ni/C catalysts was dispersed in a mixture of water (3.6 mL), isopropanol alcohol (3.6 mL), and 30 μL of 5 wt% Nafion (Aldrich). 10 μL of this suspension was deposited on a pre-cleaned glassy carbon electrode (Pine Instruments) and allowed to dry. An Ag/AgCl electrode (calibrated and converted to reversible hydrogen electrode, RHE) and Pt mesh were used as the reference and counter electrodes, respectively. The potentials are presented with reference to RHE. Each electrode was cycled in a N_2-saturated 0.1 M $HClO_4$ (GFS Chemicals) solution for 20 cycles between 0.05 and 1.0 V at

100 mV s^{-1}. For CO stripping experiments, CO was adsorbed on the pre-cleaned electrode by holding the potential at 0.05 V for 10 min in a CO-saturated 0.1 M $HClO_4$ solution. The CO stripping curve was recorded after the extra CO in the solution had been removed by purging N_2 for 30 min. The underpotential deposition (UPD) of Cu was conducted in a solution of 50 mM H_2SO_4 and 50 mM $CuSO_4$. The oxygen reduction polarization curves were measured in an O_2-saturated 0.1 M $HClO_4$ solution at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm. The kinetic current j_k at 0.9 V was derived from the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

where j is the measured current density, B is a constant, and ω is the rotation speed. The electrochemical measurements were performed using an EG&G 273 or CHI 730C potentiostat.

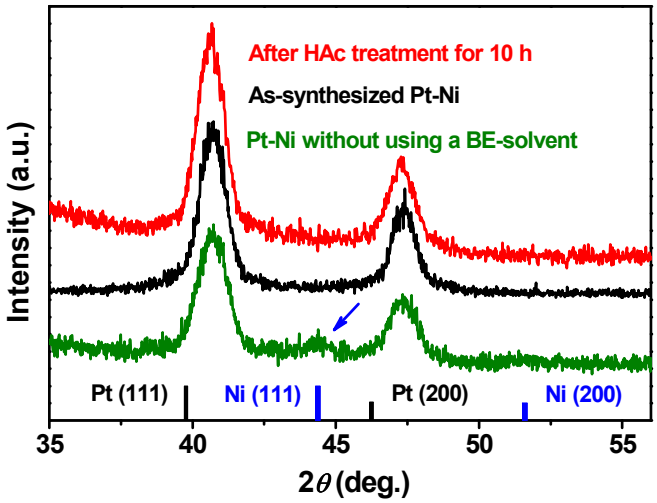

Figure S1. XRD patterns recorded from the 9-nm Pt-Ni octahedra before (black) and after (red) HAc treatment for 10 h, and the Pt-Ni octahedra prepared using the method reported in Ref. 14 that involved the use of no solvent (green). The 2θ maxima for Pt(111) shifted to a lower angle from 40.73 (black) to 40.62 (red) after HAc treatment due to the removal of Ni. Additional Ni(111) peak was observed (as indicated by an arrow) for the Pt-Ni octahedra prepared using the solvent-free protocol. Black bars: JCPDS #04-0802 (Pt); Blue bar: #01-1258 (Ni).

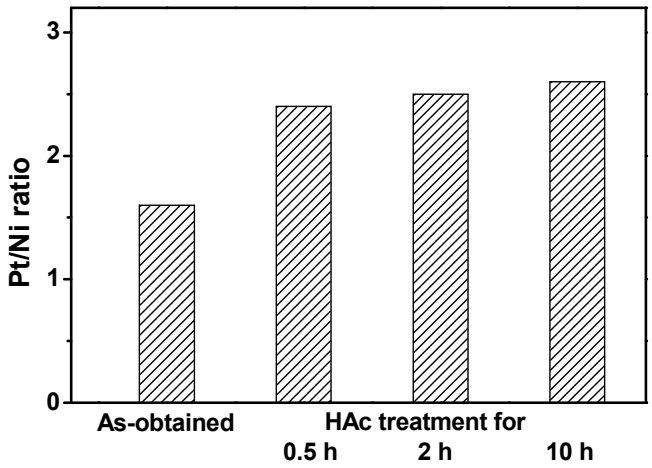

Figure S2. Comparison of the Pt/Ni ratios measured by ICP-MS for Pt-Ni/C catalysts based on octahedra without and with HAc treatment for different periods of time.

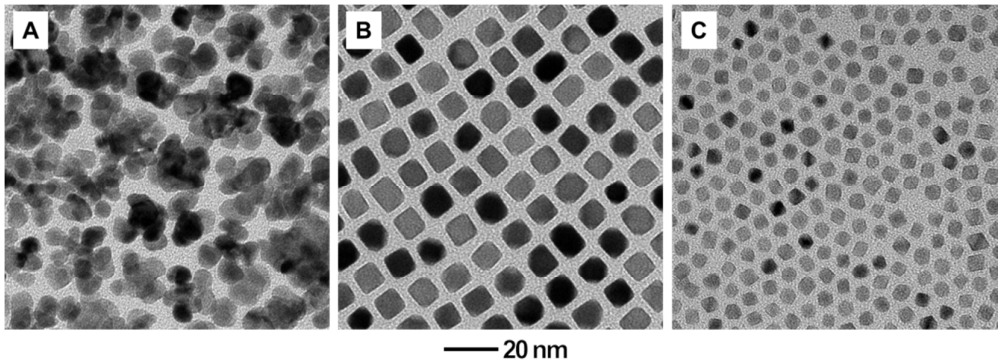

Figure S3. (A) TEM image of aggregated Pt-Ni nanocrystals prepared in the absence of $W(CO)_6$ while all other conditions were kept the same as the standard synthesis. (B) TEM image of Pt nanocubes obtained in the presence of $W(CO)_6$ but in the absence of $Ni(acac)_2$. In previous studies, adsorption of CO onto Pt{100} was found to be stronger than that on Pt{111} to result in the formation of Pt cubes in the presence of CO.[Ref. 17, 32] However, introducing a second metal such as Ni altered the adsorption preference of CO from Pt{100} to Pt{111} and thus the formation of octahedra. Similar to the Pt-Ni system, Pt-Cu nanocrystals with an octahedral shape was obtained by replacing $Ni(acac)_2$ with $Cu(acac)_2$, as shown in (C).

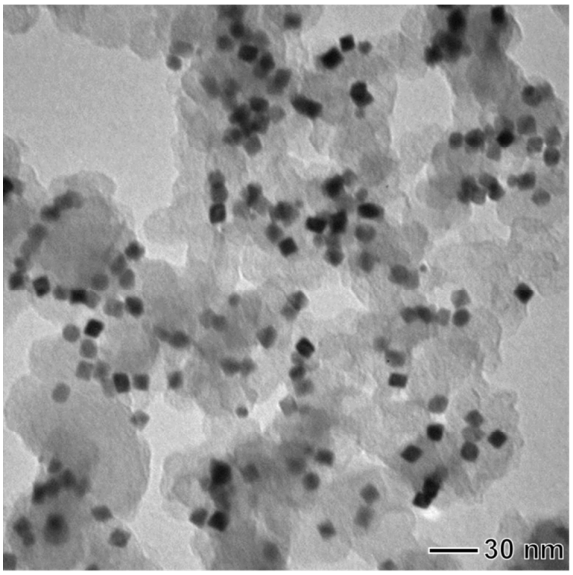

Figure S4. TEM image of the Pt-Ni/C catalyst based on the 0.5 g batch synthesis, where the Pt-Ni octahedra also went through HAc treatment for 2 h.

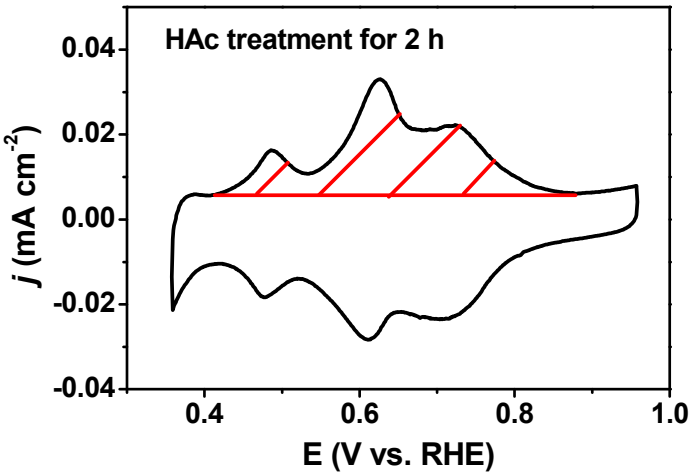

Figure S5. Cyclic voltammogram of Cu UPD for the octahedral $Pt_{2.5}Ni$/C catalyst (prepared with BE as a solvent, after treatment with HAc for 2 h) in a N_2-saturated solution containing 50 mM H_2SO_4 and 50 mM $CuSO_4$. The scanning rate was 5 mV s^{-1}.