Supporting information for

A Rational Design of Carbon-Supported Dispersive Pt-Based Octahedra as Efficient Oxygen Reduction Reaction Catalysts

Xiaoqing Huang,^{†#} Zipeng Zhao,^{†#} Yu Chen,[†] Enbo Zhu,[†] Mufan Li,[‡] Xiangfeng Duan,^{‡§} and Yu Huang^{*†§}

 [†]Department of Materials Science and Engineering, [‡]Department of Chemistry and Biochemistry, and [§]California NanoSystems Institute, University of California, Los Angeles, California 90095, United States
^{*}To whom correspondence should be addressed. Email: yhuang@seas.ucla.edu
^{*}These authors contributed equally.

Experimental Details

Chemicals: platinum(II) acetylacetonate(Pt(acac)₂, 97%), nickle(II) acetylacetonate (Ni(acac)₂, 95%), cobalt (II) acetylacetonate (Co(acac)₂, 95%), Benzoic acid (C₆H₅COOH, ≥99.5%), aniline (C₆H₅NH₂, ≥99.5%), Benzaldehyde (C₆H₅CHO, ≥99%) and N, N-dimethylformamide (DMF, ≥99.9%) were all purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra pure purification system (Aqua Solutions).

Synthesis of octahedral PtNi/C, octahedral PtNi/CNT and octahedral PtNi/rGO catalysts: In a typical synthesis of octahedral PtNi/C catalyst, platinum(II) acetylacetonate (Pt(acac)₂, 10 mg), nickle(II) acetylacetonate (Ni(acac)₂, 5.0 mg), benzoic acid (C_6H_5COOH , 61 mg) and 10 mL commercial carbon black dispersed in DMF (2 mg/mL, Vulcan XC72R carbon) were added into a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for around 5 minutes. The resulting homogeneous mixture was then heated at 160 ° C for 12 h in an oil bath, before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with an ethanol/acetone mixture. The synthesis of octahedral PtNi/CNT and octahedral PtNi/rGO catalysts was similar to that of PtNi/C catalysts except that carbon black was replaced by CNT and GO, respectively.

Synthesis of octahedral PtNiCo/C catalysts: In a typical synthesis of octahedral PtNiCo/C catalyst, platinum(II) acetylacetonate ($Pt(acac)_2$, 10 mg), nickle(II) acetylacetonate ($Ni(acac)_2$, 5.0 mg), coalt(II) acetylacetonate ($Co(acac)_2$, 5.0 mg), benzoic acid (C_6H_5COOH , 61 mg) and 10 mL commercial carbon black dispersed in DMF (2 mg/mL, Vulcan XC72R carbon) were added into a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for around 5 minutes. The resulting homogeneous mixture was then heated at 160 ° C for 12 h in an oil bath, before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with an ethanol/acetone mixture.

Characterization: TEM images were carried out on a FEI CM120 transmission electron microscope operated at 120 kV. High resolution TEM images and the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM)-energy-dispersive X-ray

spectroscopy (EDS) was were taken on a FEI TITAN transmission electron microscope operated at 300 kV. The samples were prepared by dropping ethanol dispersion of samples onto carbon-coated copper TEM grids (Ted Pella, Redding, CA) using pipettes and dried under ambient condition. X-ray powder diffraction patterns were collected on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-Kα radiation. The concentration of catalysts was determined by the inductively coupled plasma atomic emission spectroscopy (TJA RADIAL IRIS 1000 ICP-AES).

Electrochemical Measurements:

A three-electrode cell was used to do the electrochemical measurements. The working electrode was a glassy-carbon Rotating Disk Electrode (RDE) (diameter: 5 mm, area: 0.196 cm²) from Pine Instruments. Ag/AgCI (3 M Cl⁻) was used as reference electrode. Pt wire was used as counter electrode. The Pt loading of octahedral PtNi/C and octahedral PtNiCo/C catalysts were 6.38 μ g/cm² and 7.65 μ g/cm², respectively. The electrochemical active surface area (EASA) measurements were determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) at room temperature in nitrogen saturated 0.1 M HClO₄ solution. The potential scan rate was 100 mV/s for the CV measurement. Oxygen reduction reaction (ORR) measurements were conducted in a 0.1 M HCIO₄ solution which was purged with oxygen during, the measurement. The scan rate for ORR measurement was 10 mV/s. The ORR polarization curves were collected at 1600 rpm. The accelerated durability tests (ADTs) were performed at room temperature in O₂-saturated 0.1 M HClO₄ solutions by applying cyclic potential sweeps between 0.6 and 1.1 V versus RHE at a sweep rate of 50 mV/s for 6000 cycles. For comparison, Commercial Pt/C catalyst (Alfa Aesar, 20 wt% Pt) was used as the baseline catalysts, and the same procedure as described above was used to conduct the electrochemical measurement, and the Pt loadings was 7.65 µg_{Pt}/cm² for Pt/C catalyst.



20 40 60 80 0 3 6 9 12 20 /degree Energy /KeV Figure S1. Additional (A) low-magnification TEM, (B) low-magnification HAADF-STEM, (C) PXRD pattern and (D) TEM-EDX spectra of the prepared octahedral PtNi/C catalyst.



Figure S2. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of octahedral PtNi/C catalyst but in the absence of benzoic acid (A, B) on carbon back, (C, D) on carbon nanotube, and (E, F) on reduced graphene oxide.



Figure S3. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of octahedral PtNi/C catalyst but changing benzoic acid into (A, B) phenol and (C, D) benzaldyhyde.



Figure S4. Representative TEM image of Pt/C catalyst collected from the reaction with the same condition used in the synthesis of octahedral PtNi/C catalyst but adding only $Pt(acac)_2$.



Figure S5. Representative TEM image of the products collected from the reaction with the same condition used in the synthesis of octahedral PtNi/C catalyst but without adding any carbon black.



Figure S6. Representative TEM images of octahedral PtNi/C catalysts prepared with different input molar ratio of Pt/Ni (A, B) 3/1 and (C, D) 3/3. (E) is the corresponding PXRD patterns.

Figure S7. Electrocatalytic properties of octahedral PtNi/C, octahedral PtNi/CNT and octahedral PtNi/rGO. (A) Cyclic voltammograms recorded at room temperature in N₂-purged 0.1 M HClO₄ solution with a sweep rate of 100 mV/s. (B) ORR polarization curves recorded at room temperature in an O₂-saturated 0.1 M HClO₄ aqueous solution with a sweep rate of 10 mV/s and a rotation rate of 1600 rpm. (C) EIS of octahedral PtNi/C, PtNi/CNT and PtNi/rGo in 0.1 M HClO₄ solution. We can see that, while the internal resistances of PtNi/CNT and PtNi/C are almost the same, the octahedral PtNi/rGO has higher internal resistance. The higher internal resistance can partially explain why the PtNi/rGO has lower activities compared with that of PtNi/CNT and PtNi/C. In (A) and (B), current densities were normalized in reference to the geometric area of the RDE (0.196 cm²). We can see that, although all the catalysts are active towards the ORR, their performances are different. While the octahedral PtNi/CNT catalyst had an ORR activity of 2.45 mA/cm² and 1.24 A/mg_{Pt}, the octahedral PtNi/rGO catalyst had an ORR activity of 1.86 mA/cm² and 0.93 A/mg_{Pt}, which are all worse than those of octahedral PtNi/C catalyst (2.53 mA/cm² and 1.62 A/mg_{Pt}). When CNT is used as support, it is hard to get uniform film during the working electrode preparation. Due to the nature of the 2D material, rGO sheets tend to stack together through π - π interaction when they are dired, even when they are loaded with NCs. The stacking blocks a substantial amount of catalytic sites on NCs, which also retards the catalytic reaction (Huang etc., *J. Am. Chem. Soc.* 2012, 134, 12326).

Figure S8. (A) Additional low-magnification TEM and (B) PXRD pattern of the prepared octahedral PtNiCo/C catalyst.

Energy /KeV Energy /KeV Figure S9. Representative TEM images of (A, B) commercial Pt/C, (C, D) octahedral PtNiCo/C catalysts, and (E, F) TEM-EDS spectra of octahedral PtNiCo/C catalysts before (left panels) and after (right panels) 6,000 potential sweep cycles between 0.6 and 1.1 V in an O_2 -saturated 0.1 M HClO₄ solution at 50 mV s⁻¹. The insets show their corresponding diameter distributions.

Figure S10. A comparison of cyclic voltammetry (CV) of the octahedral PtNi/C catalyst before and after anchoring with PVP. The EASA of octahedral PtNi/C catalyst is reduced after anchoring with PVP.

Figure S11. Electrocatalytic properties of octahedral Pt/C catalyst and octahedral PtNi/C. (A) Cyclic voltammograms recorded at room temperature in N₂-purged 0.1 M HCIO₄ solution with a sweep rate of 100 mV/s. (B) ORR polarization curves recorded at room temperature in an O₂-saturated 0.1 M HCIO₄ aqueous solution with a sweep rate of 10 mV/s and a rotation rate of 1600 rpm. In (A) and (B), current densities were normalized in reference to the geometric area of the RDE (0.196 cm²). The octahedral Pt/C catalyst has an ORR activity of 1.01 mA/cm² and 0.79 A/mg_{Pt}, which are lower than those of octahedral PtNi/C catalysts (2.53 mA/cm² and 1.62 A/mg_{Pt}).

Figure S12. A comparison of ORR measurements of the octaheral PtNi/C catalyst in O_2 -saturated 0.1 M HClO₄ before and after adding methanol. The ORR performance of octahedral PtNi/C catalyst is seriously withheld in the presence of 0.1 M methanol.