Supplementary Materials for

Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction

Mufan Li, Zipeng Zhao, Tao Cheng, Alessandro Fortunelli, Chih-Yen Chen, Rong Yu, Qinghua Zhang, Lin Gu, Boris Merinov, Zhaoyang Lin, Enbo Zhu, Ted Yu, Qingying Jia, Jinghua Guo, Liang Zhang, William A. Goddard III,* Yu Huang,* Xiangfeng Duan *

*Corresponding author. E-mail: wag@wag.caltech.edu (W.A.G.); yhuang@seas.ucla.edu (Y.H.); xduan@chem.ucla.edu (X.D.)

Published 17 November 2016 on Science First Release
DOI: 10.1126/science.aaf9050

This PDF file includes:
Materials and Methods
Figs. S1 to S13
Tables S1 and S2
References
Materials and Methods

Chemicals
Platinum(II) acetylacetonate (Pt(acac)_2, 97%), nickel(II) acetylacetonate (Ni(acac)_2, 95%), cobalt (II) acetylacetonate (Co(acac)_2, 97%), glucose, tungsten(0) hexacarbonyl (W(CO)_6, 97%), polyvinylpyrrolidone (PVP mw. 40,000), Oleylamine (> 70%), 1-octadecene (ODE, > 90%), Ethanol (200 proof), perchloric acid (HClO_4, 70%, PPT Grade) were all purchased from Sigma-Aldrich. All aqueous solutions were prepared using deionized (DI) water (18.2 MΩ/cm) obtained from an ultra-pure purification system (Aqua Solutions).

Preparation of jagged Pt nanowire (J-PtNW) catalysts
In a typical synthesis, 0.025 mmol Pt(acac)_2, 0.10 mmol Ni(acac)_2 and 0.75 mmol glucose were pre-dissolved in mixture of 2 mL 1-octadecene (ODE) and 3 mL oleylamine (OAm). After sonicated for 10 min, 0.0015 mmol PVP (mw. 40,000) and 0.0050 mmol W(CO)_6 were added into the pre-dispersed solution and sealed with argon. The mixture was further heated up to 140 °C for 6 hours to obtain Pt/NiO core/shell nanowires, which were then washed and cleaned using acetone/cyclohexane/ethanol mixture, and collected by centrifuging at 7000 rpm.

The as-prepared Pt/NiO NWs were suspended in 15 mL cyclohexane/ethanol mixture. To load the sample on to carbon black, 36 mg of carbon black was added for each 4 mg Pt/NiO NWs and sonicated for 2 hours. The resulting Pt/NiO-NWs/C catalysts were collected by centrifugation and cleaned with cyclohexane/ethanol mixture, the R-PtNWs were collected by centrifuging at 12,000 rpm, and resuspended in 15 mL cyclohexane/ethanol mixture and loaded onto carbon black using the same approach described above, flowed by a moderate annealing at 250 °C.

Preparation of regular Pt nanowire (R-PtNW) catalysts
In a typical synthesis, 0.025 mmol platinum Pt(acac)_2, 0.10 mmol Co(acac)_2 and 0.75 mmol glucose were pre-dissolved in mixture of 2 mL 1-octadecene (ODE) and 3 mL oleylamine (OAm). After sonicated for 10 min, 0.0015 mmol PVP (mw. 40,000) and 0.0050 mmol W(CO)_6 were added into the pre-dispersed solution and sealed with argon. The mixture was further heated up to 120 °C for 3 hours to get regular nanowires. After cleaned the product by acetone/cyclohexane/ethanol mixture, the R-PtNWs were collected by centrifuging at 7000 rpm, and re-suspended in 15 mL cyclohexane/ethanol mixture and loaded onto carbon black using the same approach described above, flowed by a moderate annealing at 250 °C.

Preparation of Pt-Ni nanoparticles
In a typical synthesis, 0.025 mmol platinum Pt(acac)_2, 0.075 mmol Ni(acac)_2 and 0.75 mmol glucose were pre-dissolved in mixture of 2 mL 1-octadecene (ODE) and 3 mL oleylamine (OAm). After sonication for 10 min, 0.0015 mmol PVP (mw. 40,000) and 0.050 mmol W(CO)_6 were added into the pre-dispersed solution and sealed with argon. The mixture was further heated up to 170 °C for 6 hours with stirring to obtain PtNi nanoparticles (NPs). After cleaning with a mixture of acetone/cyclohexane/ethanol, the PtNi NPs were collected by centrifuging at 12,000 rpm, and re-suspended in 15 mL
cyclohexane/ethanol mixture and loaded onto carbon black using the same approach described above, flowed by a thermal annealing at 450 °C.

**Preparation of Pt-Co nanowires**

In a typical synthesis, 0.025 mmol platinum Pt(acac)$_2$, 0.100 mmol Ni(acac)$_2$, and 0.75 mmol glucose were pre-dissolved in mixture of 2 mL 1-octadecene (ODE) and 3 mL oleylamine (OAm). After sonication for 10 min, 0.0015 mmol PVP (mw. 40,000) and 0.0050 mmol W(CO)$_6$ were added into the pre-dispersed solution and sealed with argon. The mixture was further heated up to 170 °C for 6 hours with stirring to obtain Pt/Co core/shell nanowires (NWs). After cleaning with a mixture of acetone/cyclohexane/ethanol, the PtNi NPs were collected by centrifuging at 12,000 rpm, and re-suspended in 15 mL cyclohexane/ethanol mixture and loaded onto carbon black using the same approach described above, flowed by a thermal annealing at 450 °C.

**Structure and composition characterization**

Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were collected on ZEISS Supra 40VP SEM. The EDS analysis of the as-prepared Pt/NiO core/shell NWs show a Pt/Ni ratio of 15/85 (Fig. S3A, B).

Powder X-ray diffraction (XRD) patterns were collected on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-Kα radiation.

X-ray photoelectron spectroscopy (XPS) tests were done with Kratos AXIS Ultra DLD spectrometer. Transmission electron microscopy (TEM) images were carried out on an FEI T12 transmission electron microscope operated at 120 kV. High resolution TEM images (HRTEM), energy-dispersive X-ray spectroscopy (EDS) line-scan file were taken on FEI TITAN transmission electron microscope operated at 300 kV. The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) were performed on aberration corrected TEM. The samples were prepared by dropping ethanol dispersion of catalysts onto carbon-coated molybdenum TEM grids.

The concentration of catalysts was determined by the inductively coupled plasma (ICP) atomic emission spectroscopy. The ICP sample we used for jagged Pt nanowires was annealed material before electro chemical activation. The Pt loading for J-PtNWs was 2.2 µg/cm$^2$ on glassy carbon electrode. ICP test of the concentrated electrolyte from 10 activation processes indicates 1.2% Pt is leached off from the PtNi NWs during the dealloying process, suggesting >98.8% of Pt was retained during the electrochemical activation process.

**Electrochemical experiment**

All the electrochemical experiments were conducted using a three-electrode cell system. The working electrode was a glassy carbon rotating disk electrode (RDE) from Pine Instruments, the glassy carbon geometry area is 0.196 cm$^2$. Pt wire and Ag/AgCl (1 M Cl$^-$) were used as the counter and reference electrodes respectively. Pt loadings were 2.2 µg/cm$^2$, 2.55 µg/cm$^2$, and 7.65 µg/cm$^2$ for J-Pt NWs, R-Pt NWs, and Pt/C respectively (All the loading mass were normalized over the geometric electrode area of 0.196 cm$^2$).
Cyclic voltammetry (CV) activations were performed in N₂-saturated 0.1 M HClO₄ electrolyte with potential scan rate of 100 mVs⁻¹. All the electrochemical active surface area (ECSA) was determined by integrating hydrogen adsorption charge on CV curve by assuming a value of 210 µC/cm² for the adsorption of a hydrogen monolayer. Double-layer correction was applied. The ECSA for J-PtNWs, R-PtNWs, and Pt/C were calculated via same method.

Oxygen reduction reaction (ORR) tests were conducted in N₂-saturated 0.1 M HClO₄ electrolyte with potential scan rate of 20 mVs⁻¹. The current density of ORR polarize curve were iR corrected during the measurements.

The stability test was performed at room temperature in O₂-saturated 0.1 M HClO₄ solution with a potential scan rate of 100 mVs⁻¹.

For CV test in alkaline solution, the J-PtNWs and partially activated (150 cycles) Pt-Ni alloy nanowires were firstly activated in N₂-saturated 0.1 M HClO₄ electrolyte with potential scan rate of 100 mVs⁻¹. After rinsed the electrode by DI water, the CV was performed in N₂-saturated 0.1 M KOH electrolyte at a scan rate of 50 mVs⁻¹.

**Computational studies**

To generate realistic structural models of PtNi alloy nanowires, we extended the computational protocol developed previously to simulate Ni de-alloying of Pt₃Ni₇ nanoparticles (0D systems) (16).

Thus:

1. We started from an infinite nanowire (1D system), based on the fcc Pt crystal structure. The z axis of the nanowire is along the (111) crystal direction, while in the xy plane we have 13 Pt atoms along the x axis and 9 Pt atoms are along the y axis. This choice was made to expose some (100) facets along the NW axis.
2. We built a periodic model by replicating 220 individual unit cells along the axis of the wire.
3. The overall ratio of Ni to Pt is 85:15 consistent with experiment, which was achieved by randomly replacing 85% of the Pt atoms with Ni atoms, while ensuring that the Ni composition is roughly constant along the nanowire axis.
4. We erase all the Ni atoms and perform a fixed-cell conjugate-gradient local relaxation using the ReaxFF force field. Here at each conjugate-gradient step limits the maximum change in Cartesian coordinates to 0.1 Å to ensure a smooth local minimization that avoids disruption of the original random fcc framework. The convergence threshold criteria are 4×10⁻⁶ eV on the energy and 4×10⁻⁸ eV/Å on the gradient.
5. We perform a second local relaxation allowing the cell dimension in the z-direction to equilibrate at a pressure of 1 atm.
6. We perform a final NPT Molecular Dynamics (MD) simulation at 343 K for 520 ps (20 ps equilibration followed by a 500 ps run)
7. We delete the least coordinated atoms which would be further leached away during ORR cycling and perform an additional NPT Molecular Dynamics (MD) simulation at 343 K for 520 ps (20 ps equilibration followed by a 500 ps run).
8. We locally relax the final structure using a SMA force field.

This protocol, in which we simultaneously remove Ni throughout the initial fcc nanostructure and locally relax and equilibrate the resulting configuration, is intended as a simplified mimic of the complex kinetics-driven de-alloying process induced by during electrochemical activation, where Ni surface atoms are progressively leached out of the system. The ReaxFF reactive force could be used in a more realistic gradual depletion of the Ni atoms under realistic conditions, but the size of the system and the long time scales of ORR-induced de-alloying makes this more realistic simulation impractical. However, we consider that the smooth local minimization of the initial randomly sparse fcc framework of Pt atoms provides a reasonable approximation to the relaxation processes through metastable configurations that retain memory of the original pattern. Our assumption that all Ni atoms are removed in step (4), corresponds in our previous nanoparticle study to propagating the topmost 4/6 surface layers devoid of Ni into the bulk (16). We consider that the experimental evidence showing that all Ni atoms are leached out in these small diameter nanowires fully justifies this approach. It can be noted that the ReaxFF reactive force field (28) has been derived from extensive quantum mechanics calculations validated by comparing to experiment and is used in the process generating structure and overall morphology of dealloyed NWs in which directionality terms in the potential are important. However, this force field tends to overestimate surface distances so that the SMA potential (29) was finally used to compare with experimental data from extended x-ray absorption fine structure (EXAFS) analysis.

We compare the nanowire structural characteristics with those of the Pt₃Ni₇ nanoporous particle obtained by de-alloying a 10-nm-diameter fcc Pt₃Ni₇ nanoparticle as a representative nanoparticles exhibiting peak ORR performance.

Thus we use:
1. Radial distribution functions (RDF);
2. A coordination vector threshold to distinguish surface and bulk atoms;
3. Number of first neighbors (coordination number);
4. Atomic stress and 5-fold index;
5. Analysis of surface arrangement in terms of rhombic structures.

The coordination vector is defined as the sum of all the vectors pointing from first-neighbors to the given atom, and a given Pt atom is defined as a bulk atom if the norm of the coordination vector is smaller than a given threshold (0.6 Å), and as a surface atom otherwise, in analogy with the approach taken in Ref. (16). The Cauchy atomic stress tensors on atom $i$ ($\sigma^i$) used in Fig.3 is defined as (37):

$$\sigma^i = \frac{1}{a_i} \cdot \left\{ \frac{1}{2} \sum_j F_{ij} \otimes r_{ij} \right\}$$
Where \( \Omega_i \) is the atomic volume of atom \( i \), and the sum is taken over all \( j \)-neighbors of \( i \), at a distance \( r_{ij} \) each and exerting a force \( F_{ij} \) upon \( i \). Given that atomic volumes are not well defined for a deformed solid, we follow common practice of reporting in Fig.3 the products \( \sigma' \cdot \Omega_i \) in units of atm \( \cdot \) nm\(^3\). Another useful quantity reported in the main text is the surface energy \( (E_{\text{surface}}) \), defined as:

\[
E_{\text{surface}} = \frac{1}{A} \cdot \{ E_{\text{system}} - N E_{\text{bulk}} \}
\]

Where \( A \) is the surface area, which is the excess energy of the system \( (E_{\text{system}}) \) with respect to the bulk \( (E_{\text{bulk}}) \). The 5-fold index is finally defined as the ratio of icosahedral fingerprint \([5,5,5]\) triplets to the total number of triplets in Common Neighbor Analysis \((31-34)\).

As shown in Figs. 3, S11 and Table S2, the jagged Pt nanowire exhibits structural features that are qualitatively and quantitatively similar to de-alloyed Pt\(_{3}\)Ni\(_{7}\) nanoparticles \((16)\), but with an increase in ORR-favorable patterns, thus explaining our experimentally observed superior ORR catalytic activity for these NW. A configuration from the protocol using Reactive Molecular Dynamics (steps 1-7 above) together with the structure locally relaxed using SMA potential are provided as a further Supplementary Material.

XAS data collection and analysis
The J-PtNWs/C powders were collected via sonication from RDE after CV activation and ORR test. The sample for XAS study was washed and dispersed in ethanol. The Pt loading is 3.6% based on ICP result. X-ray absorption spectroscopy (XAS) experiments were performed at Advanced Light Source (beamline 10.3.2) in Lawrence Berkeley National Laboratory. Full range Pt L\(_3\) spectra were collected in the fluorescence mode at room temperature with a Pt reference foil positioned between I\(_2\) and I\(_3\) as a reference. The data were processed and fitted using the Ifeffit-based Athena and Artemis programs \((38)\). Scans were calibrated, aligned and normalized with background removed using the IFEFFIT suite \((38)\). The \( \chi(R) \) were modeled using single scattering paths calculated by FEFF6 \((39)\). The extended x-ray absorption fine structure (EXAFS) spectrum was fitted using a fcc platinum model. The Pt L\(_3\)-edge XANES region is shown in Fig. S10.
Fig. S1. (A and B) TEM images for Pt/NiO core/shell nanowires and regular nanowires. (C and D) STEM images for Pt/NiO nanowires/C before and after annealing at 450 °C in Ar/H₂ (97/3) atmosphere for 12 hours.

Fig. S2. TEM images of PtNi NPs (A) before and (B) after annealing at 450 °C in Ar/H₂ (97/3) atmosphere for 12 hours.
Fig. S3. EDS spectrum of (A) as-prepared Pt/NiO core/shell NWs. (B) Pt-Ni alloy NWs obtained after 450 °C annealing.

Fig. S4. XRD spectra comparison of fresh and 450 °C annealed Pt/NiO core/shell nanowires/C. The standard XRD pattern for fcc NiO, Pt, Ni are displayed as grey, yellow, and green bars. The crystallinity of fresh sample (black line) showed existence of non-fcc phase, and since the size of Pt core NWs is ultrafine (sub 2 nm), the result XRD peak for fresh sample is broadened. The overlapped (111) and (200) peak region could be caused by the existence of NiO. For 450 °C annealed sample (red line), the narrowed symmetric XRD peak suggested the formation of larger alloyed crystal. The result (111) peak (2θ = 44.0°) was relatively closer to Ni (111) (2θ = 44.6°) than that of Pt (111) (2θ = 39.7°), indicates the result alloy is Ni-rich which is constant with our EDS result (Fig. S3B).
Fig. S5. XPS spectra comparison before and after annealing of Pt/NiO core/shell nanowires/C. (A) Ni 2P, (B) Pt 4f.

Fig. S6. The cyclic voltammetry (CV) curves for partially activated Pt-Ni alloy NWs (150 cycles in 0.1 M HClO4 solution) and J-PtNWs in alkaline electrolyte with scan rate of 50 mVs⁻¹. The current densities were normalized to the geometric area of the RDE (0.196 cm²).
Fig. S7. The CV and CO-stripping curves of the (A) Pt/C, (B) R-PtNWs, and (C) J-PtNWs. All the CO-stripping curves were recorded at room temperature in CO-saturated 0.1 M HClO₄ solution at scan rate of 50 mVs⁻¹. The current densities were normalized to the geometric area of the RDE (0.196 cm²). The ECSA₅₇₅₉: ECSA₂₅ ratio is 1:1.03, 1:1.06, 1:1.05 for Pt/C, R-PtNWs, J-PtNWs respectively.

Fig. S8. Schematic illustration of the difference in Ostwald ripening in 0D NPs vs. 1D NWs. Ostwald ripening in which Pt atoms are dissolved from one nanostructure and reattach to another one, can often lead to aggregation of ultrafine nanostructures. In such processes, the dissolved Pt atoms tend to reattach at new locations that are more energetically favorable, such as locations with smaller curvature or more coordinated neighbors. In this scenario the energetically more favorable sites for NPs are likely NPs with larger size because of smaller curvature (larger radius of curvature) (A), leading to Ostwald ripening and serious loss of ECSA. However, for 1D NWs, the energetically favorable sites are more likely located at the narrower constriction region with negative curvature (B), which would promote atom attachment to the narrow regions and prevent the breakup of 1D structure and thus lead to further stabilization of 1D NW structure.
Fig. S9. (A, C) TEM images, and (B, D) NW diameter distribution chart of J-PtNWs after CV activation and ADT test, respectively.

Fig. S10. Pt L₃-edge XANES of J-PtNWs after electrochemical test compared to Pt foil Standard.
Fig. S11. (A) Coordination number for surface atoms (red) and bulk atoms (blue) of the J-PtNWs, and atoms (black) of R-PtNWs evaluated by counting all neighbors within a distance cut-off of 3.0 Å. (B) Schematic depiction of a rhombus (inset) and the distribution of the dihedral angle between the two triangles of the rhombus as defined by the angle formed between the two lines connecting atom 1 and 2 to the middle point of atom 3,4 respectively (highlighted by the yellow arrows in the inset). Most of the angles are between 156° and 180°, which suggest that the surface of the J-PtNWs are highly comparable typical crystalline structure.

Fig. S12. (A) Annealed PtCo-NW/C samples (B) Dealloyed PtCo-NW/C. The dealloying process was conducted in N2- saturated 0.1M HClO₄ with a scan rate of 100 mV/s.

Fig. S13. (A) CV and (B) ORR polarization curves for the Pt/C, Co-dealloyed, and Ni-dealloyed J-PtNWs, respectively.
Table S1. EXAFS results obtained by fitting the Pt L\textsubscript{3} edge data for the J-PtNWs. $S_0^2$ is fixed at 0.83 for Pt as obtained by fitting the reference foils. The fit was done in $R$-space, $k^{1,2,3}$ weighting with 1.50 $< R < 3.11$ Å and $\Delta k = 3.06 - 13.39$ Å$^{-1}$ used. R-factor is a measure of the goodness of fit. The statistical errors of the least-squares fit were determined by ARTEMIS

<table>
<thead>
<tr>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>$E_0$ (eV)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Pt</td>
<td>2.71±0.01</td>
<td>9.1±1.0</td>
<td>6.8±0.6</td>
<td>0.007±0.003</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table S2. Geometric analysis of the final predicted structure of 46-nm-long de-alloyed Pt nanowire (snapshot from the RMD trajectory) compared with the typical predicted structure of a fully de-alloyed Pt$_3$Ni$_7$ NP (initially 10 nm in diameter, finally around 8 nm in diameter) taken from (16).

<table>
<thead>
<tr>
<th></th>
<th>vdW Surface Area (m$^2$/g$_{pt}$)</th>
<th>Surface Atoms N (%)</th>
<th>ORR-favorable Rhombi N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-alloyed NW</td>
<td>110</td>
<td>49%</td>
<td>76%</td>
</tr>
<tr>
<td>NP (70% Ni)</td>
<td>61</td>
<td>26%</td>
<td>57%</td>
</tr>
</tbody>
</table>
References


25. See supplementary materials on *Science* Online.


