

[Supporting Information]

**Controlled Synthesis of Pd-Pt Alloy Hollow Nanostructures with Enhanced
Catalytic Activities for Oxygen Reduction**

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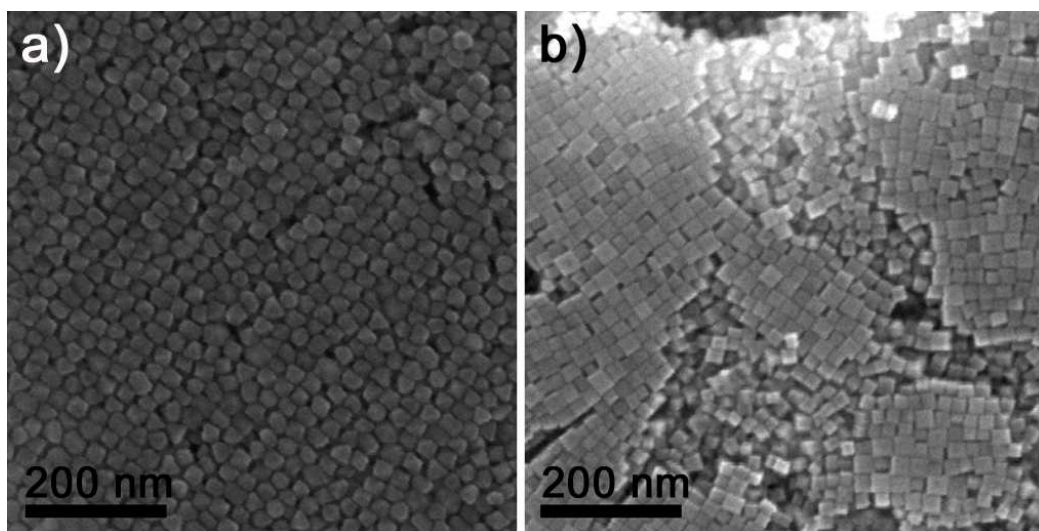


Figure S1. SEM images of Pd (a) octahedral and (b) cubic NC templates.

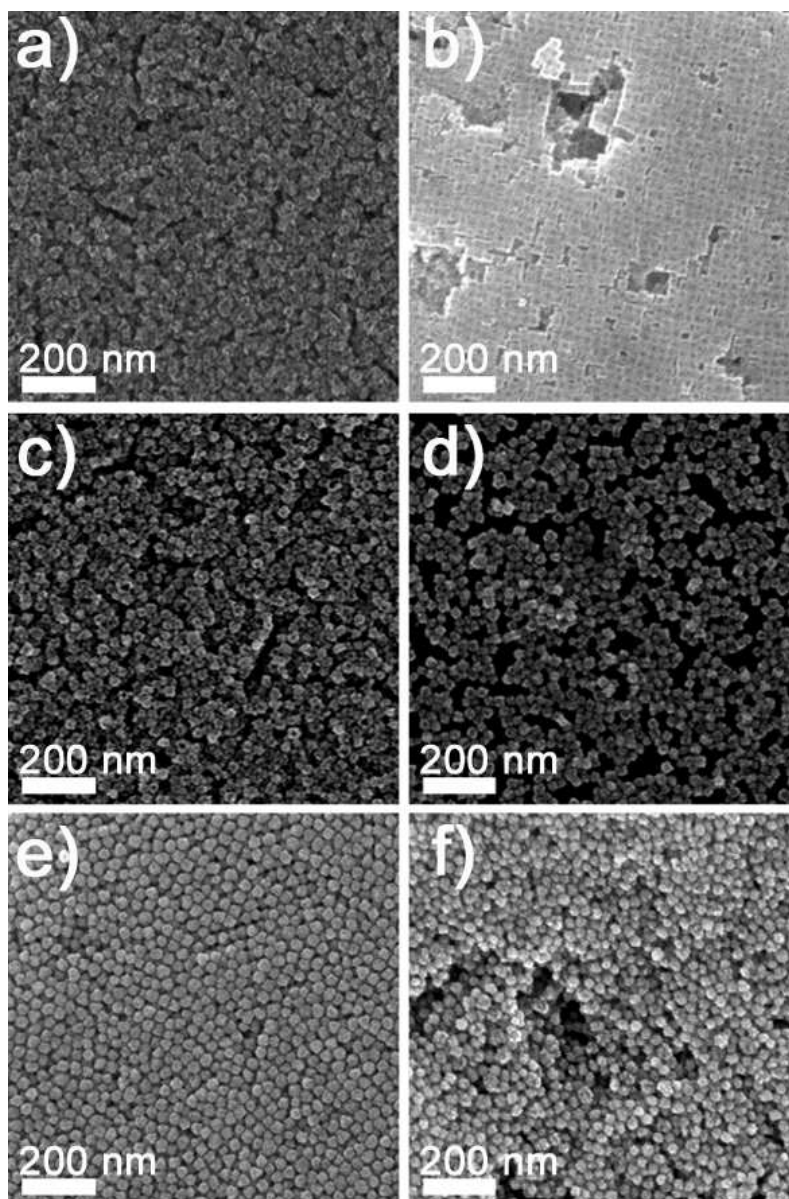


Figure S2. SEM images of (a) ONCs, (b) CNCs, (c) ODH NCs, (d) CDH NCs, (e) OD NCs, and (f) CD NCs.

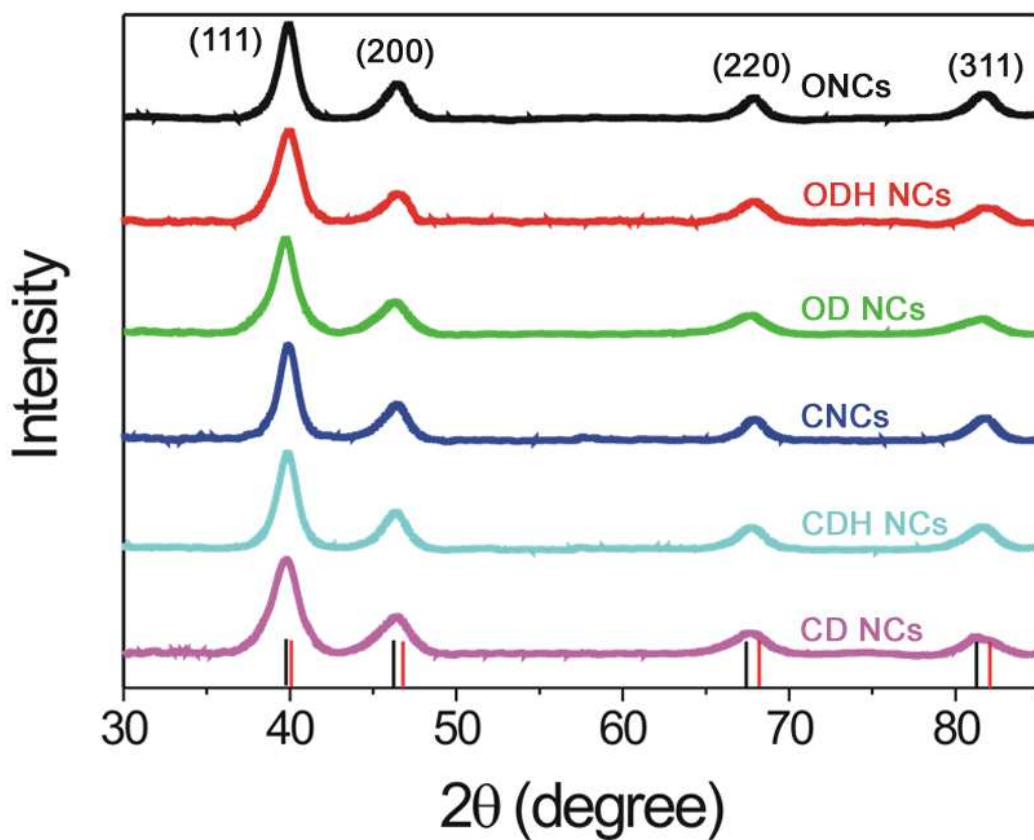


Figure S3. XRD patterns of the Pd-Pt NCs. The positions for pure Pt (black line at the bottom) and Pd (red line at the bottom) references were taken from the JCPDS database. Observed four peaks for each NC can be indexed to the (111), (200), (220), and (311) reflections of face-centered cubic (*fcc*) structure of metal, showing the pure crystalline nature of the prepared NCs.

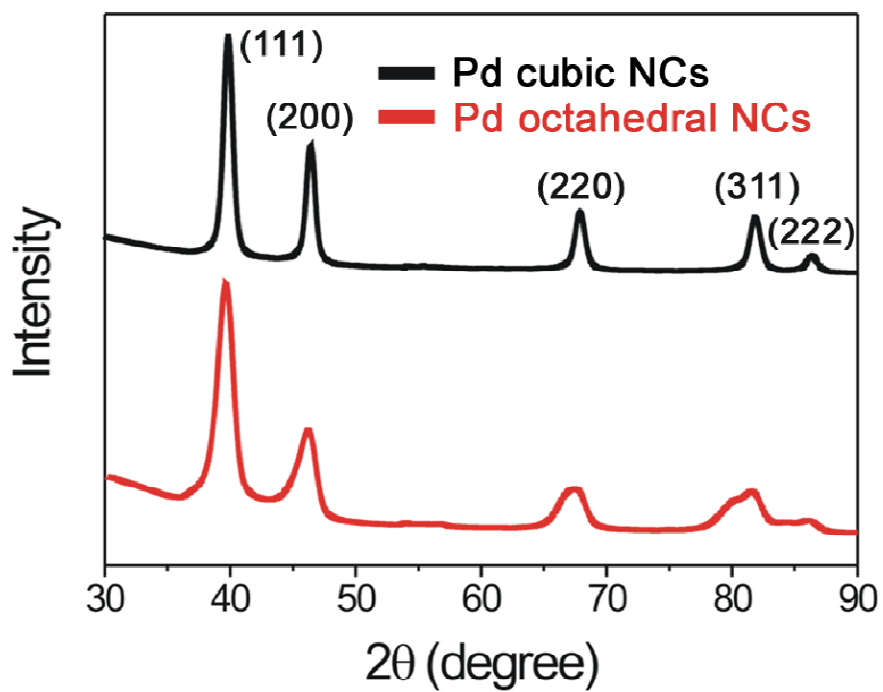


Figure S4. XRD patterns of the pristine Pd cubic and octahedral NCs. Observed diffraction peaks for each NC can be indexed to the (111), (200), (220), (311), and (222) reflections of face-centered cubic (*fcc*) structure of Pd, showing the pure crystalline nature of the prepared Pd NCs.

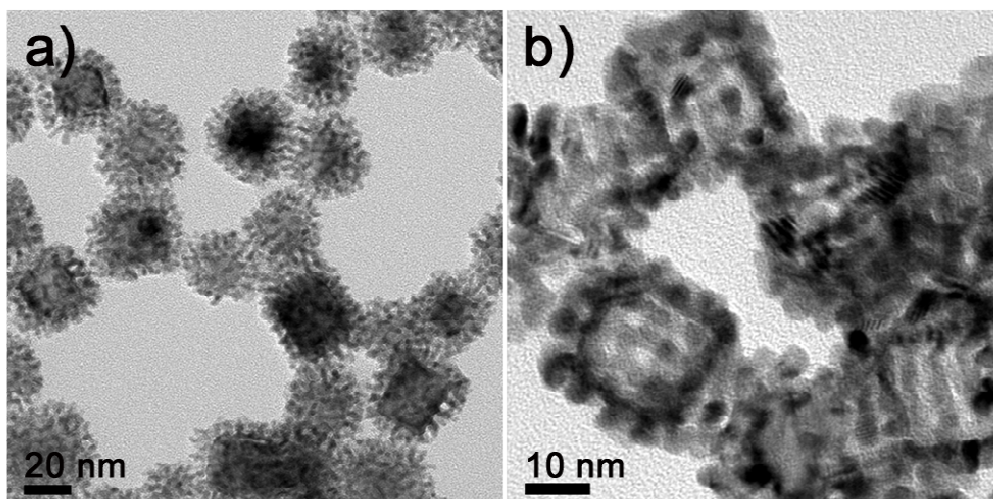


Figure S5. TEM images of (a) CD and (b) CDH NCs. CDH NCs were prepared by taking CD NCs shown in (a) and subjecting them to galvanic replacement in a second, decoupled step without ascorbic acid. In a typical experiment, pre-synthesized CD NCs were injected into a solution containing CTAC (20 mM, 7 mL) and K_2PtCl_4 (5 mM, 1 mL), and the resultant solution was then heated to 100 °C and maintained at this temperature for 13 h with vigorous stirring. As a result, CD NCs were successfully converted to CDH NCs through galvanic replacement reaction.

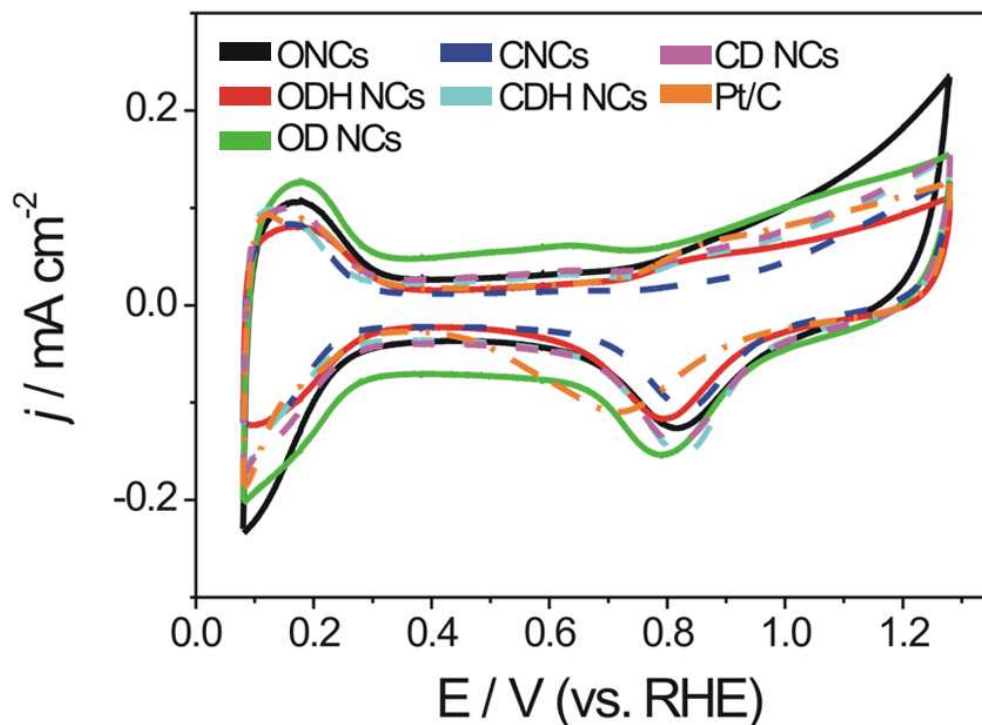


Figure S6. Cyclic voltammograms of the Pd-Pt bimetallic NCs and Pt/C in 0.1 M HClO_4 at a scan rate of 50 mV s^{-1} . Current values were normalized with respect to the electrochemically active surface areas (ECSA). ECSA were estimated by the following equation; $\text{ECSA} = Q_o/q_o$, where Q_o is the surface charge that can be obtained from the area under the CV trace of hydrogen desorption and q_o is the charge required for desorption of monolayer of hydrogen on the Pd-Pt or Pt surface ($211 \mu\text{C}/\text{cm}^2$ for ONCs, CNCs, ODH NCs, and CDH NCs, $210 \mu\text{C}/\text{cm}^2$ for OD NCs, CD NCs, and Pt/C. ref.: Woods, R. In *Electroanalytical Chemistry: A Series of Advances* (vol.9); Bard, A. J., Ed.; Marcel Dekker: New York, 1974; pp 1-162).

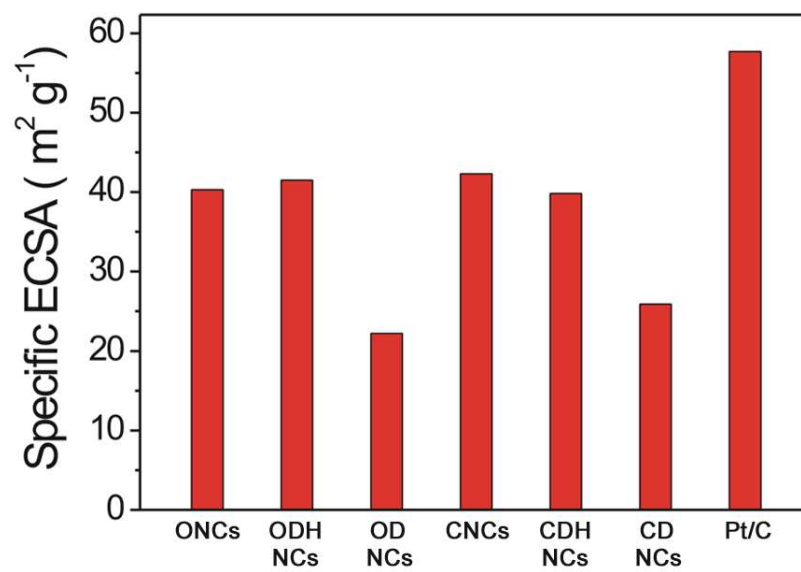


Figure S7. Specific ECSA for the Pd-Pt bimetallic NCs and Pt/C.

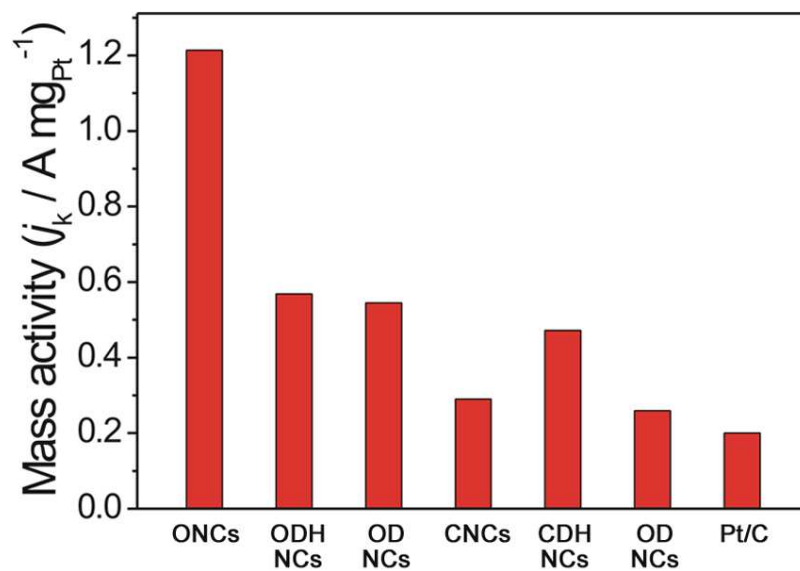


Figure S8. Pt mass activity at 0.85 V vs. RHE for the various catalysts..

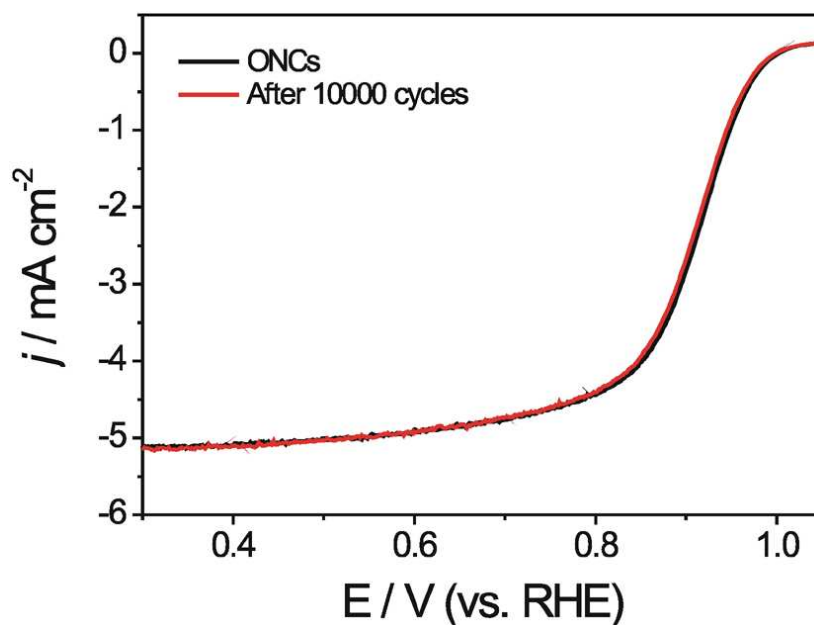


Figure S9. ORR polarization curves for the ONCs obtained using a rotating disc electrode (RDE) in O₂-saturated 0.1 M HClO₄ at scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm before and after 10,000 potential cycles between 0.6 and 1.0 V vs. RHE in 0.1 M HClO₄ at scan rate of 50 mV s⁻¹ (a protocol recommended by the U.S. automotive industry, ref.: G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* **2011**, 332, 433). The current densities were normalized to geometric surface area of working electrode (0.071 cm²). To prepare the working electrode, a 4 μ L of the catalysts dispersion (0.5 mg_{metal}/mL based on ICP-AES) was dropped onto a GC electrode (diameter: 3 mm). The electrode was then washed several times with ethanol and water to remove stabilizing agents, and a thin layer of Nafion was placed on the catalyst-loaded electrode by dropping 5 μ L of Nafion solution (0.05 %). The dried working electrode was cleaned again by sequentially washing with ethanol and water. The stability tests were carried out using a CH Instrument Model 600C potentiostat. The accelerated durability tests demonstrate that the ONCs have an excellent electrochemical stability: they showed almost constant ORR activity after 10,000 potential cycles.

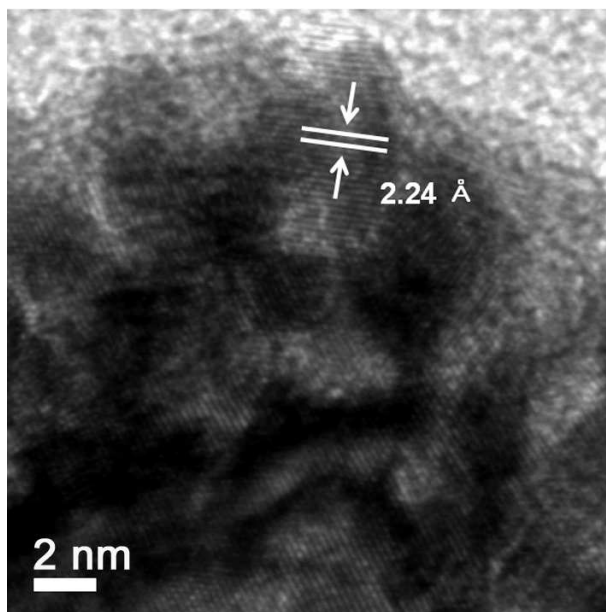


Figure S10. HRTEM image of the branch tip region of a CDH NC. The observed d -spacing of 2.24 Å for adjacent lattice fringes in some regions, which corresponds to that of the (111) planes of *fcc* Pd-Pt alloy, indicates that the {111} facets also developed to some extent in the branch tip regions of the CDH NCs due to a release of strain imposed by the {100} facets at the interface.