

## Electronic Supplementary Information

### Supersaturation-controlled surface structure evolution of Pd@Pt core-shell nanocrystals: enhance the ORR activity at sub-10 nm scale

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## Experimental details

### Material and reagents:

Palladium chloride ( $\text{PdCl}_2$ ,  $\geq 99.999\%$ ), chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\geq 37.50\%$ ), commercial Pd/C (10 wt. %) and Pt/C (10 wt. %) were obtained from Sigma-Aldrich. Hydrochloric acid (HCl, AR), L-ascorbic acid (AA, AR) were obtained from Beijing chemical works, China.  $\text{H}_2\text{PdCl}_4$  aqueous solution was prepared from hydrochloric acid (HCl) aqueous solution and palladium chloride ( $\text{PdCl}_2$ ). Cetyltrimethyl ammonium bromide (CTAB, AR), potassium hydroxide (KOH, AR), and ethanol (AR) were all purchased from Sinopharm chemical reagent, China. Nafion-ethanol solution was obtained from Adamas-beta Chemical Co., Switzerland. The water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) used in all experiments was prepared by passing through an ultrapure purification system.

### Synthesis of palladium nanocube seeds:

Cubic Pd seeds were synthesized according to a published procedure with appropriate modifications.<sup>1</sup> In a typical synthesis process, 300  $\mu\text{L}$  of 10 mM  $\text{H}_2\text{PdCl}_4$  was added to 10 mL of 100 mM CTAB at 90 °C. After gently mixing the solution, 100  $\mu\text{L}$  of 200 mM freshly prepared AA was added to the solution. The reaction was stopped after 90 °C oil bath for 1 hour and stored at 30 °C for future use.

### Synthesis of Pd-Pt binary nanocrystals:

In a typical synthesis, 20 mL of 0.1 M CTAB solution was injected into a 40 mL scintillation vial and kept in a 40 °C water bath. Then 500  $\mu\text{L}$  of 10 mM  $\text{H}_2\text{PtCl}_6$  solution was injected with magnetic stirring. 5 minutes later, corresponding amount of 1 M KOH solution was added into the solution. After completely mixed, 1.5 mL of Pd

nanocube seeds was added into the solution with gently mixing. The total volume of growth solution were quantified to 23 mL by adding additional water. Then, 700  $\mu$ L of freshly prepared 0.1 M ascorbic acid solution was injected and the solution was gently mixed. The resulting solution was placed in a water bath at 40  $^{\circ}$ C without disturbance. After 12 h, when the reaction completed, the products were collected by centrifugation (12000 rpm, 5 min). The supernatant was discarded and the precipitate was redispersed in 40  $^{\circ}$ C water. The centrifugation-redispersion procedures were repeated for another two times and the final product was redispersed in 1.5 mL of water.

#### **Characterization:**

Transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM), selected area electron diffraction (SAED), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-disperse X-ray (EDX) spectrum were acquired by using a FEI Tecnai G<sup>2</sup> F20 transmission electron microscope equipped with a high-angle annular dark-field detector (FEI Company, USA). Inductively coupled plasma mass spectrometry (ICP-MS) data were determined by an ELAN 9000/DRC ICP-MS system. TEM snapshot was achieved by quenching 800  $\mu$ L of the growth solution by high speed centrifugation (16000 rpm, 1 min) and washed two times with 40  $^{\circ}$ C deionized water. Finally, 5  $\mu$ L of the solution with suitable concentration was drop-cast onto a carbon supported film and dried at room temperature in an enclosed environment.

#### **Electrochemical measurements:**

Electrochemical measurements were performed using a glass carbon rotating disk electrode (RDE, Pine research instrumentation) connected to a CHI760D (Shanghai,

Chenhua Co., China). An ink for the electrochemical measurement was prepared by mixing 0.5 mL of the catalyst into 0.5 mL of Nafion-ethanol solution (5%), followed by sonication for 30 min. A working electrode was prepared by loading the ink (20  $\mu\text{L}$ ) on the glassy carbon electrode. Ag/AgCl electrode (4 M KCl) and a Pt mesh were used as the reference and counter electrodes, respectively. The potentials were converted to values with reference to the reversible hydrogen electrode. Before the data collection, all working electrodes were cleaned by a steady-state potential sweeping from 0.1 to 1.3 V at 50  $\text{mV s}^{-1}$  in  $\text{N}_2$ -saturated 0.1 M KOH solution. Once the curve was stable, the cyclic voltammograms (CV) at 50  $\text{mV s}^{-1}$  was recorded. From this CV, the electrochemically active surface area (ECSA) of the catalyst was determined by integrating the area surrounded by the hydrogen desorption curve and the CV baseline. The scan rate and rotation rate for ORR measurement were 10  $\text{mV s}^{-1}$  and 1600 rpm, respectively. The ORR electron transfer number ( $n$ ) per  $\text{O}_2$  molecule in ORR and kinetic current density ( $J_k$ ) were determined according to the Koutecky-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{0.62nFD^{2/3}\nu^{-1/6}C_{\text{O}_2}\omega^{1/2}}$$

where  $J$  is the measured current density,  $F$  is the Faraday constant (96485  $\text{C mol}^{-1}$ ),  $D$  is the diffusion coefficient of  $\text{O}_2$  in electrolyte ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $\nu$  is the kinetic viscosity of the solution ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ),  $C_{\text{O}_2}$  is the concentration of  $\text{O}_2$  in solution ( $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ), and  $\omega$  is the electrode rotation rate. The electrocatalytic results were obtained by averaging three independent measurements with an error margin <10%.

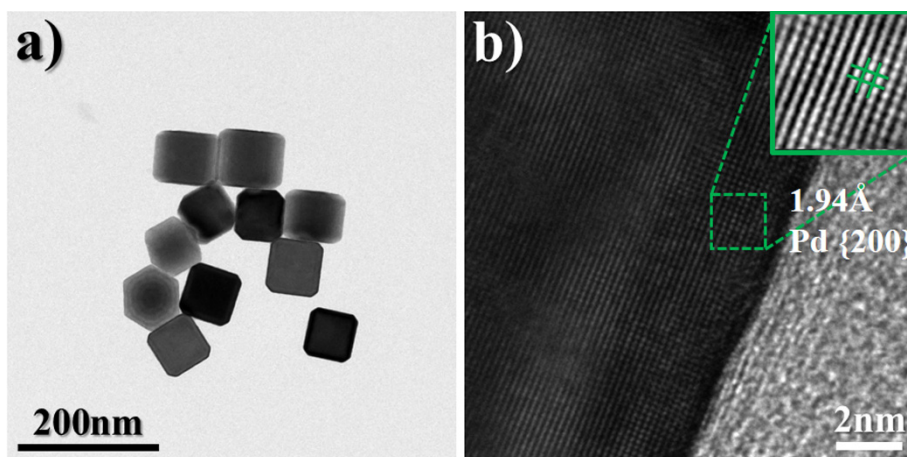


Figure S1. TEM and HRTEM images of Pd nanocube seeds.

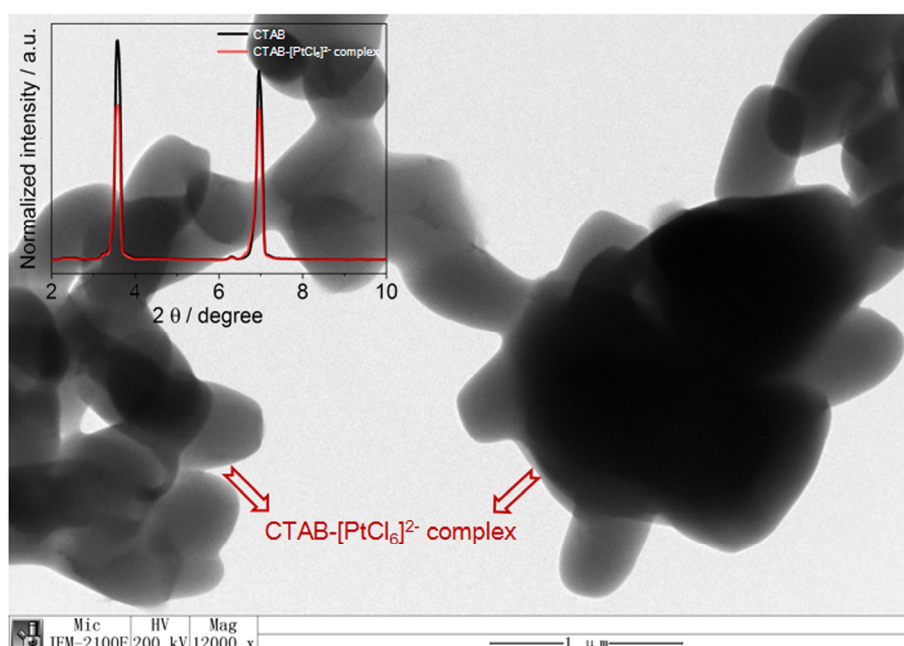


Figure S2. TEM image of CTAB- $[\text{PtCl}_6]^{2-}$  complex; inset shows the XRD pattern of CTAB powder and CTAB- $[\text{PtCl}_6]^{2-}$  complex.

*The TEM image of the complex shows a micelles structure that is different from the pure CTAB. The XRD pattern of CTAB show slightly peak intensity variation before and after the  $[\text{PtCl}_6]^{2-}$  complexing, however, the peak position is still same as that of CTAB.<sup>2</sup> No observable Pt XRD peak indicates that the micelles structure is not  $\text{Pt}^0$  nanostructure.*

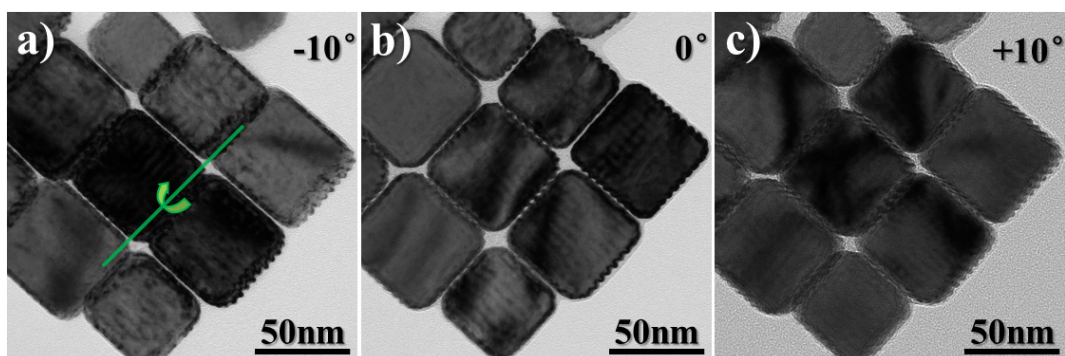


Figure S3. TEM images of Pd@Pt core-island shell nanocubes with different tilting angles.

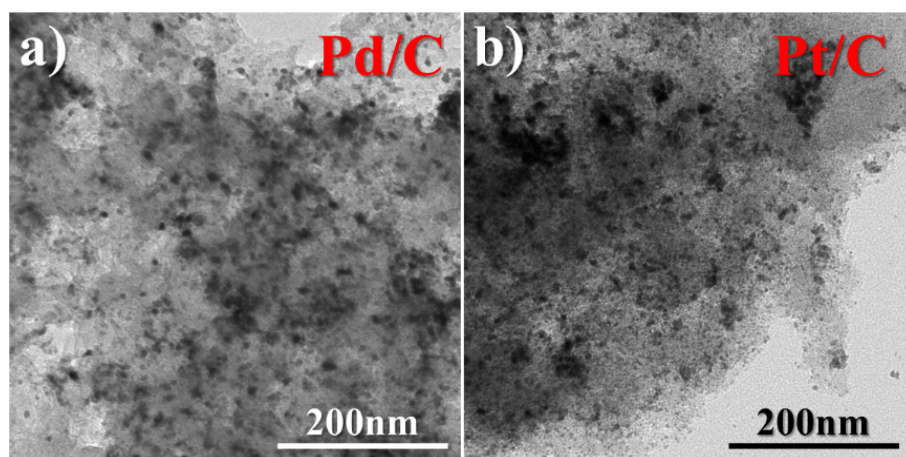


Figure S4. TEM images of (a) commercial Pd/C and (b) commercial Pt/C catalysts.

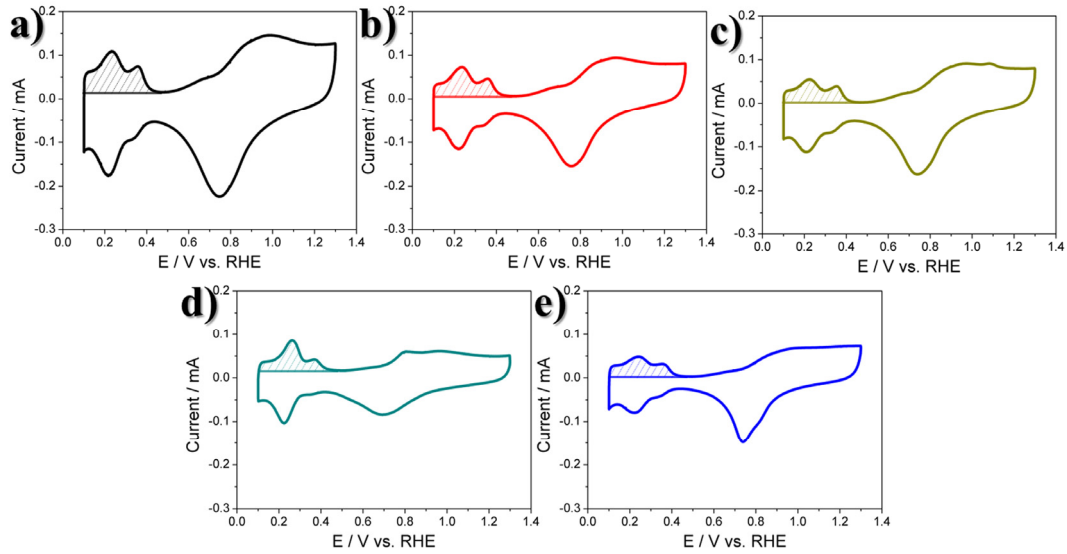


Figure S5. Blank cyclic voltammograms of (a) Pt/C, (b) Pd@Pt core-island shell NCs, (c) Pd@Pt core-conformal shell NCs, (d) Pd nanocubes, (e) Pd/C recorded at room temperature in a N<sub>2</sub> saturated 0.1 M KOH (aq) solution with a sweep rate of 50 mV s<sup>-1</sup>.

*Electrochemically active surface areas (ECSA) were estimated by the following equation:*

$$ECSA = Q_0 / q_0$$

*Where  $Q_0$  is the surface charge that can be obtained from the area under the CV trace of hydrogen desorption and  $q_0$  is the charge required for desorption of monolayer of hydrogen on the Pd or Pt surface (211  $\mu\text{C cm}^{-2}$ ).<sup>3</sup>*

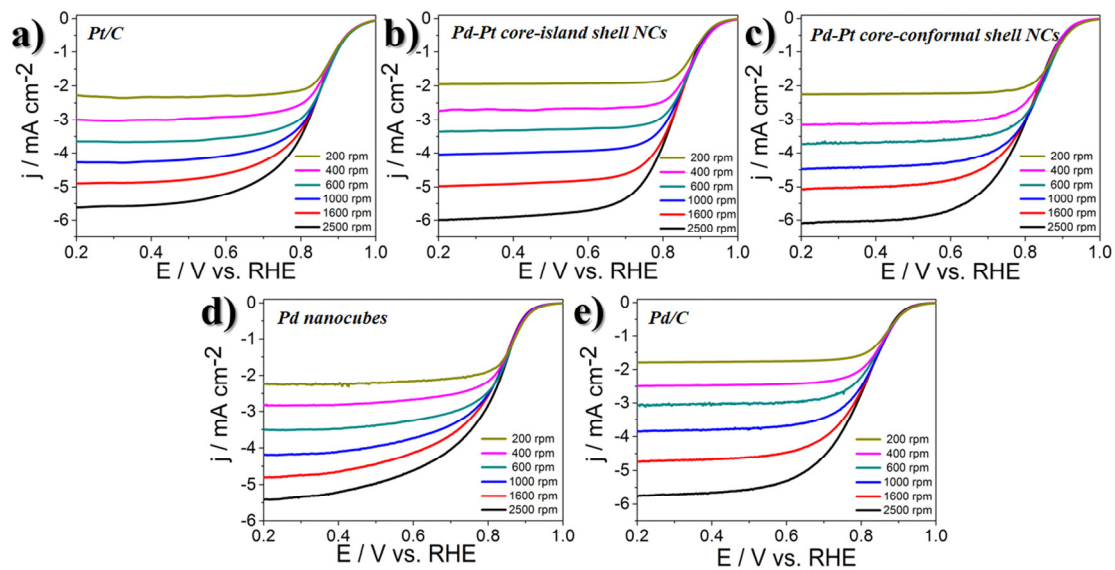


Figure S6. Linear sweep voltammograms for (a) Pt/C, (b) Pd@Pt core-island shell NCs, (c) Pd@Pt core-conformal shell NCs, (d) Pd nanocubes, (e) Pd/C; the measurements are performed at a sweep rate of  $10 \text{ mV s}^{-1}$  and different electrode rotation rates in  $\text{O}_2$ -saturated  $0.1 \text{ M KOH (aq)}$  solution.

Table S1. Specific surface free energy of fcc metals estimated by density of unsaturated bonds.<sup>4</sup>

Facets	$\sigma_{hkl}$	$\sigma_{hkl} (\varphi_1 / a^2)$
(111)	$\frac{1}{2}(3\varphi_1 + 3\varphi_2) / (\frac{\sqrt{3}}{4} a^2)$	3.81
(100)	$\frac{1}{2}(4\varphi_1 + 2\varphi_2) / (\frac{1}{2} a^2)$	4.20
(110)	$\frac{1}{2}(6\varphi_1 + 4\varphi_2) / (\frac{\sqrt{2}}{2} a^2)$	4.53



Table S2. ICP-MS data for the Pd@Pt core-island shell NCs, Pd@Pt core-conformal shell NCs and Pd NCs.

Catalyst	Measured mass of Pd [ $\mu\text{g}$ ]	Measured mass of Pt [ $\mu\text{g}$ ]
Pd@Pt core-island shell NCs	260.36	175.17
Pd@Pt core-conformal shell NCs	279.62	190.54
Pd NCs	245.71	–

**Reference:**

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3. J. W. Hong, S. W. Kang, B. S. Choi, D. Kim, S. B. Lee and S. W. Han, *ACS Nano*, 2012, 6, 2410-2419.
4. H.X. Lin, Z.C. Lei, Z.Y. Jiang, C.P. Hou, D.Y. Liu, M.M. Xu, Z.Q. Tian and Z.X. Xie, *J. Am. Chem. Soc.*, 2013, 135, 9311-9314.