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Coordination Effect Assisted Synthesis of Ultrathin Pt Layers on Second Metal Nanocrystals as Efficient Oxygen Reduction Electrocatalysts

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Experimental

Materials. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Sigma-Aldrich), oleylamine ($C_{18}H_{37}N$, OAm, Sigma-Aldrich, 80% - 90%), glucose ($C_6H_{12}O_6$, Sigma-Aldrich), and L-ascorbic acid ($C_6H_8O_6$, AA, Sigma-Aldrich), sorbitol ($C_6H_{14}O_6$, Alfa Aesar), all chemicals were used as received.

Synthesis of the 20-nm Au octahedral seeds.[1] For a typical synthesis of Au nano-octahedra, 10 ml of an aqueous solution containing $HAuCl_4$ (0.25 mM) and CTAB (75 mM) was prepared in a flask. To this mixture, 0.6 ml of ice-cold $NaBH_4$ (10 mM) was rapidly injected with stirring vigorously, generating a brown solution. The whole solution was kept stirring slowly for three hours at room temperature to promote the decomposition of the remaining $NaBH_4$ in solution. Then, 1 ml of prepared hydrosol was diluted to 100 ml with water, using as a seed solution. A colorless mixture with 0.1 ml of $HAuCl_4$ (10 mM), 2 ml of CTAB (0.2 M), and 1.5 ml of ascorbic acid (AA, 0.1 M) was diluted to 25 ml, and then 0.3 ml of seed hydrosol was added to the mixture immediately. The reaction mixture was shaken, and then left undisturbed at room temperature for 8 hours. Finally, a typical light purple colloid was obtained, indicating the formation of Au nano-octahedra. Au nano-octahedra were then collected by centrifugation, washed three times with hot water, and re-dispersed in water.

Preparation of the 18-nm Pd cubic seeds.[2] The Pd cubic seeds with an average edge length of 18 nm were synthesized according to a previously reported protocol. In a typical synthesis, 105 mg of PVP (MW $\approx$ 55,000, Aldrich), 60 mg of AA (Aldrich), 600 mg of KBr (Aldrich), and 8.0 mL of deionized (DI) water were mixed together in a 25 mL vial and pre-heated at 80 °C for 10 min in an oil bath under magnetic stirring. 57 mg of Na_2PdCl_4 were dissolved in 3 mL of DI water and then introduced into the pre-heated solution. The vial was capped and maintained at 80 °C for an additional 3 h and the final product was collected by centrifugation, washed three times with DI water, and re-dispersed in 11 mL of DI water.

Preparation of the 37-nm Pd octahedral seeds.[3] In a standard procedure, 3 mL of aqueous Na_2PdCl_4 (29 mg) solution was introduced into 8 mL of an aqueous solution containing 105 mg PVP, 100 mL formaldehyde (HCHO), and

0.3 mL of an aqueous suspension (1.8 mg/mL in concentration) of Pd cubic seeds 18 nm in edge length, which had been heated at 60 °C for 5 min under magnetic stirring in a capped vial. The reaction was allowed to proceed at 60 °C for 3 h. After collection by centrifugation and washing three times with water, the final product was redispersed in water.

Synthesis of Pd@Pt and Au@Pt nanocrystals. For the synthesis of Pd@Pt and Au@Pt core-shell nanocrystals, 1 mL of a suspension of the as-prepared seed nanocrystals (e.g., 18-nm Pd nanocubes, 37-nm Pd octahedrons, or 20-nm Au octahedrons) (2 mg/mL) was washed with ethanol three times and redispersed in 1 mL of OAm. Then, 1 mL of the suspension of seed nanocrystals and 4 mL of OAm solution containing glucose (20 mg) and $H_2PtCl_6·6H_2O$ (5 mg) were added into a 20 mL vial, which connected with air through a syringe needle on the cap. The mixture was heated at 200 ºC in an oil bath under magnetic stirring for 3 h, and then cooled down to room temperature. The final products were washed with ethanol twice and finally dispersed in hexane. The morphology of Pd@Pt nanocrystals was controlled by manipulating the concentration of glucose. For example, with the concentration of glucose increased from 0.2 mg/mL to 20 mg/mL, the shape of the obtained Pd@Pt nanocrystals transferred from concave to core-shell nanocubes gradually.

Preparation of the working electrodes. First, the Pd@Pt and Au@Pt core-shell samples were loaded on a carbon support (Ketjen Black EC-300J) with a metal loading content of 20% based on the total mass of Pd and Pt (determined by ICP-MS). The carbon-supported Pd@Pt catalyst was then dispersed in 10 mL of acetic acid and heated at 60 °C for 24 h to clean the surface of the particles, and then washed twice with ethanol. After drying, 5.0 mg of the carbon-supported Pd@Pt catalysts were re-dispersed in a mixture of 0.5 mL of deionized water, 0.5 mL of isopropanol, and 20 µL of 5% Nafion under ultrasonication for 20 min. 5 µL of the suspension were deposited on a precleaned glassy carbon RDE with a geometric area of 0.19635 cm^2 and dried in an oven that was pre-set to 50 °C. For the Pt/C catalyst (20 wt%, Alfa Aesar), the working electrode was prepared using the same procedure except a heating treatment in acetic acid. Therefore, the loading amount of metal for Pd@Pt and Pt/C catalysts was 5 µg or 25.5 $\mu g/cm^2$ based on the geometric electrode area.

Electrochemical measurements. Electrochemical experiments were conducted on an Autolab electrochemistry station, which was equipped with a rotating disk electrode system (No. 1154-R65WHPL) in a thermostatic glass cell. A leak-free Ag/AgCl (3M) electrode was used as the reference. All potentials were converted to values with reference to a reversible hydrogen electrode (RHE). The counter electrode was a Pt sheet (1 × 1 cm^2). The electrolyte was 0.1 M $HClO_4$ prepared by diluting a commercial solution (70%, ACS Reagent grade, T. J. Baker) using Millipore ultrapure water. The cyclic voltammetry curves were recorded at room temperature in an N_2-purged (ultrahigh purity, Airgas) 0.1 M aqueous $HClO_4$ solution at a sweep rate of 50 mV/s. The ORR measurements were performed at a sweep rate of 10 mV/s from 0.03 to 1.17 V at 1,600 rpm under continuous O_2 flow. The Kouteck-Levich equation was applied to calculate the kinetic current density, which can be described as:

$$1/j = 1/j_k + 1/j_d$$

where j is the experimentally measured current, j_d is the diffusion-limiting current, and j_k is the kinetic current. For each catalyst, the kinetic current was normalized to the loading of metals (both Pt and Pd for the Pd-Pt bimetallic nanocrystals or only Pt for Pt/C) in order to obtain mass activity.

Characterizations. Transmission electron microscopy (TEM) images were performed at a Hitachi HT-7700 microscope equipped with a tungsten filament, operating at 100 kV. High-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission microscopy (HAADF-STEM) images and EDX elemental mapping were performed at a JEM-2100F (JEOL) equipped with a built-in EDS. The percentages of Pd and Pt in the samples were determined using inductively-coupled plasma mass spectrometry (ICP-MS) (Agilent 7500ce ICP-MS).

Reference

1 F. R. Fan, D. Y. Liu, Y. F. Wu, S. Duan, Z. X. Xie, Z. Y. Jiang & Z. Q. Tian. *J. Am. Chem. Soc*. 2008, **130**, 6949-6951.

2 M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu & Y. Xia. *Nano Res*. 2011, **4**, 83-91.

3 M. Jin, H. Zhang, Z. Xie & Y. Xia. *Energy Environ. Sci*. 2012, **5**, 6352-6357

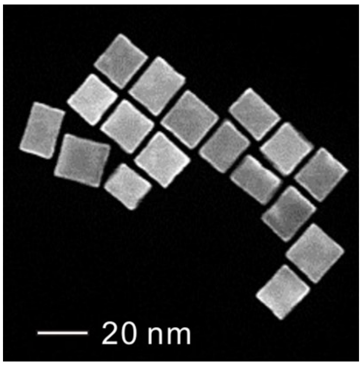

Fig. S1. HAADF-STEM image of the Pd@Pt core-shell nanocubes prepared with 20.0 mg/mL glucose.

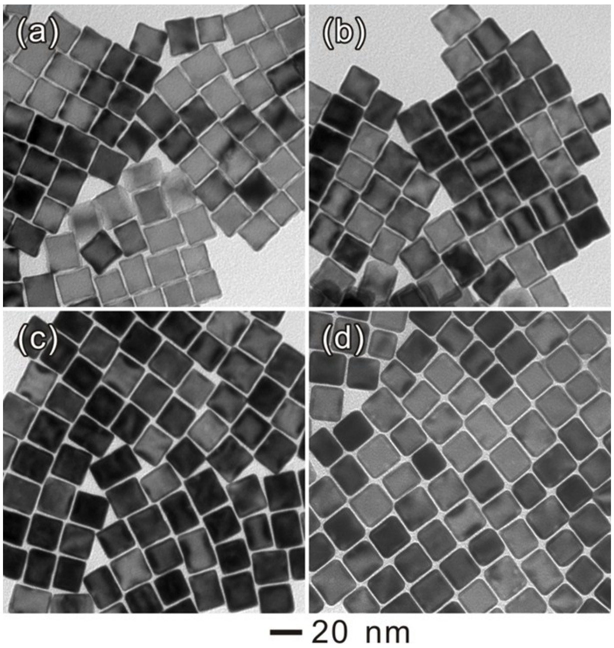

Fig. S2. TEM images of Pd@Pt core-shell nanocubes obtained at different reaction times: (a) 20, (b) 40, (c) 60, and (d) 180 min.

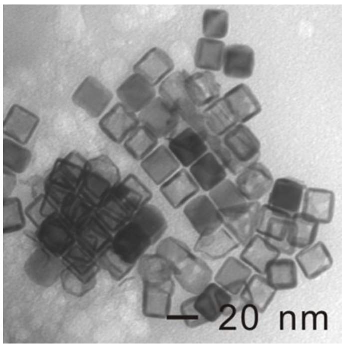

Fig. S3. TEM image of Pt nanocages prepared from Pd@Pt core-shell nanocubes by etching away the Pd cores.

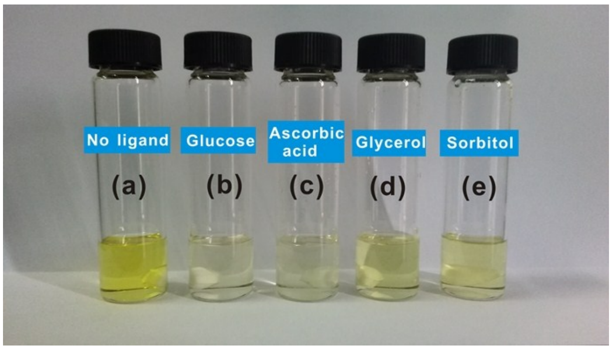

Fig. S4. Photographs of the reaction solutions contain Pt4+ ions and different types of the coordination ligands: (a) without any coordination ligand, (b) glucose, (c) L-ascorbic acid, (d) glycerol and (e) sorbitol.

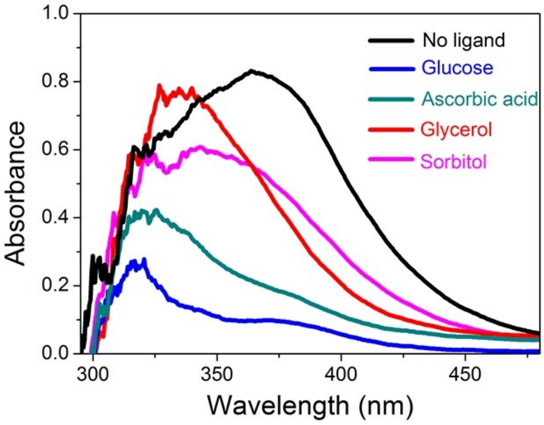

Fig. S5. UV-vis spectra of the reaction solutions contain Pt4+ ions and different types of the coordination ligands: (a) without any coordination ligand, (b) glucose, (c) L-ascorbic acid, (d) glycerol and (e) sorbitol.

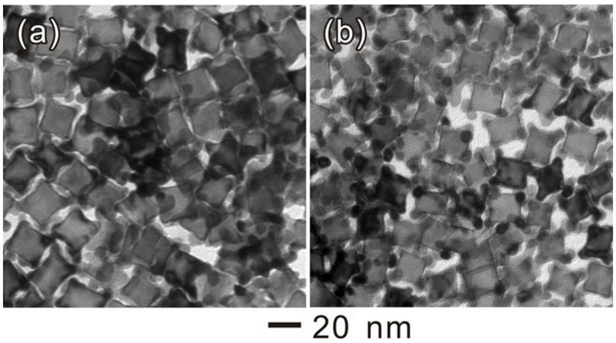

Fig. S6. TEM images of the obtained bimetallic nanocrystals prepared under the standard reaction condition except different types of the coordination ligands: (a) EG and (b) decanal.

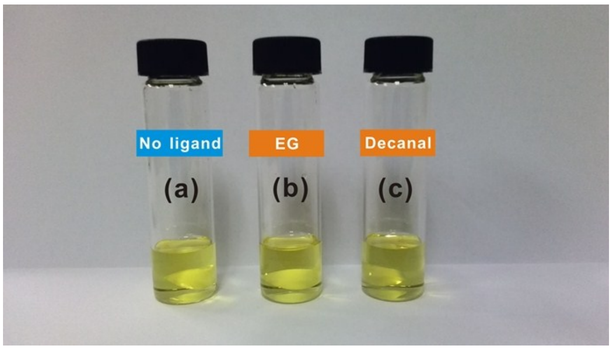

Fig. S7. Photographs of the solutions contain Pt4+ ions and different types of the coordination ligands: (a) without any coordination ligand, (b) ethylene glycol, (c) decanal.

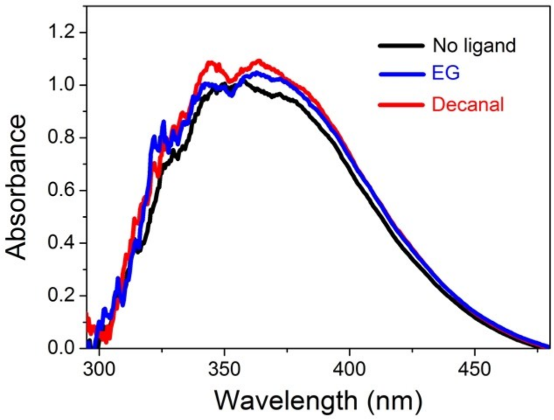

Fig. S8. UV-vis spectra of the solutions contain Pt4+ ions and different types of the coordination ligands: (a) without any coordination ligand, (b) ethylene glycol, (c) decanal.

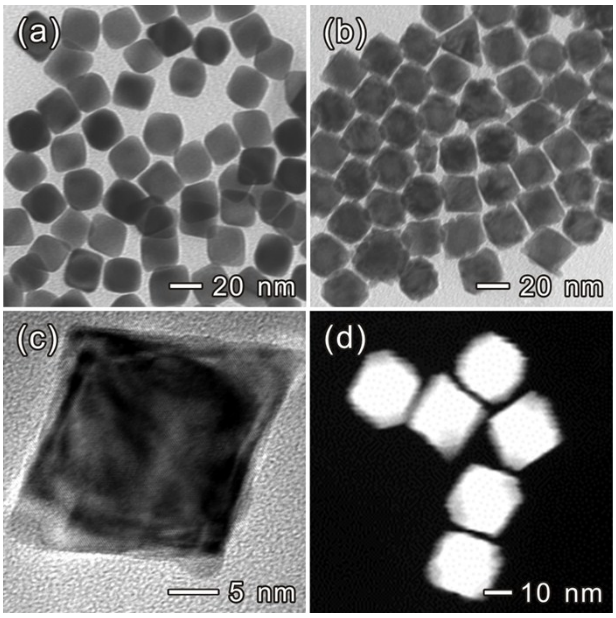

Fig. S9. (a) TEM image of Au octahedrons that served as the seeds for the deposition of ultrathin Pt shells. (b-d) TEM, HRTEM, and HAADF-STEM images of the corresponding Au@Pt core-shell octahedrons.

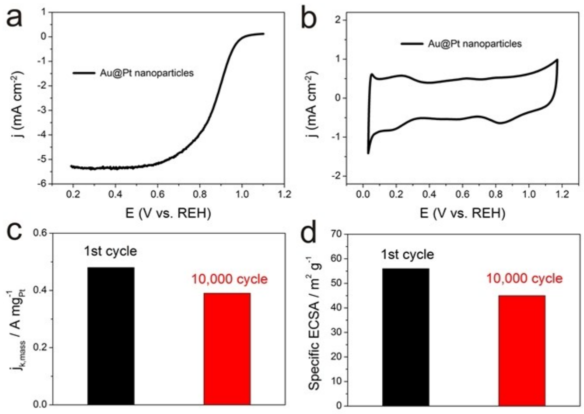

Fig. S10. (a) ORR polarization curve for the Au@Pt catalysts at room temperature in O_2-saturated 0.1 M aqueous $HClO_4$ solutions. (b) CVs of the catalysts recorded at room temperature in N_2-purged 0.1 M aqueous $HClO_4$ solutions with a sweeping rate of 50 mV/s. (c) Mass and (d) specific activities given as kinetic current densities (j_k).

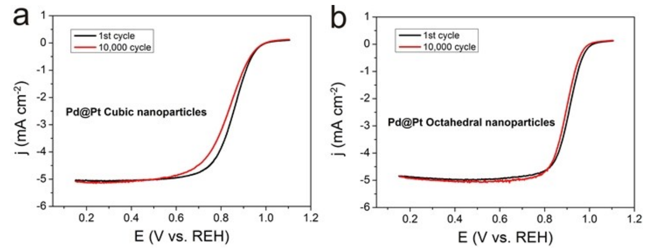

Fig. S11. Polarization curves of (a) Pd@Pt cubic nanocatalysts and (b) Pd@Pt octahedral nanocatalysts before and after accelerated durability tests.

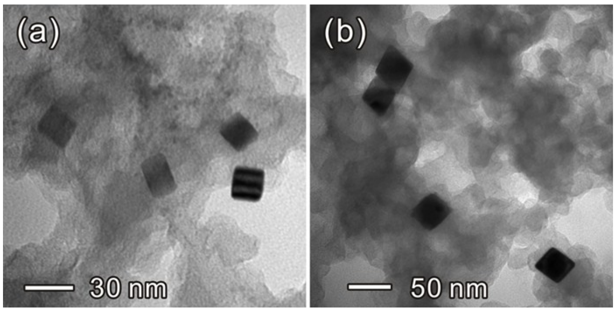

Fig. S12. TEM images of (a) Pd@Pt cubic nanocatalysts and (b) Pd@Pt octahedral nanocatalysts after accelerated durability tests.