

[Supporting Information]

Synthesis and Characterization of Pt₉Co Nanocubes with High Activity for Oxygen Reduction

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Materials:

Platinum (II) acetylacetonate (Pt(acac)₂), iron pentacarbonyl (Fe(CO)₅), 1,2-hexadecanediol, oleylamine (>70%), oleic acid (90%), and benzyl ether (99%) were purchased from Aldrich and used without further purification. Dicobalt octacarbonyl (Co₂(CO)₈) was purchased from Strem chemicals, Inc.

Experimental:

Synthesis of 8 nm Pt₉Co nanocubes and spherical Pt₉Co nanoparticles: To the mixture of Pt(acac)₂ (50 mg, 0.127 mol) and Co₂(CO)₈ (10.8 mg, 0.032 mol) were added 1,2-hexadecanediol (30 mg), benzyl ether (8mL), oleylamine (1 mL), and oleic acid (1mL) in a dry box. The slurry was heated at 120 °C and the temperature was raised to 200 °C (2-3 °C/min) and kept at 200 °C for 1.5 h under argon atmosphere to give a black-brown suspension. The resulting reaction mixture was diluted with toluene (10 mL), and Pt₉Co nanocubes were precipitated by adding ethanol (25 mL). The supernatant was removed by centrifugation at 3000 rpm for 10 min. The resulting nanocubes were easily dispersed in organic solvents such as toluene and hexane. 8 nm spherical Pt₉Co nanoparticles were prepared in the absence of oleic acid with a similar procedure to that described above.

Synthesis of 8 nm Pt nanocubes: Pt(acac)₂ (50 mg, 0.127 mol) was mixed with benzyl ether (8 mL), oleylamine (1 mL), and oleic acid (1 mL) in a dry box. The slurry was heated at 120 °C and one drop (0.01 ~0.03 mL) of Fe(CO)₅ was added to this slurry. The temperature was raised to 200 °C (2-3 °C/min) and kept for 1.5 h under argon atmosphere to give a black brown suspension. The work-up procedure was similar to that used for the preparation of Pt₉Co nanocubes.

Preparation of the catalysts: The solutions containing 26.3 mg (40 wt%) of cubic or spherical Pt₉Co

catalyst was added to the 38.4 mg of Ketjen Black carbon, dispersed in toluene under ultrasonic wave agitation for 10 min. The two mixtures were stirred and ultrasonicated for 5 h. The resulting Pt₉Co nanocubes/C catalyst was washed 5 times with diethyl ether to remove the surfactants. On the other hand, the resulting spherical Pt₉Co nanoparticles/C catalyst was heated in acetic acid at 100 °C for 10 h to eliminate the stabilizers, and then washed 5 times with diethyl ether to remove acetic acid. All the catalysts were dried under vacuum for 30 min before use.

Characterization:

TEM images were obtained with an Omega EM912 transmission electron microscope operating at 120 kV. HRTEM, SAED, and EDS characterizations were performed with a Philips F20 Tecnai transmission electron microscope operating at 200 kV. The compositions of Pt-Co bimetallic nanoparticles were determined by ICP-AES (SPECTRO CIROS VISION) and EDS. XRD patterns were obtained with a Rigaku D/MAX-RB diffractometer using Cu K α (0.1542 nm) radiation. XPS measurements were carried out using a Thermo MultiLab 2000 spectrometer, using Al K α X-ray (1486.6 eV) as the light source. Electrochemical studies were carried out in a three-electrode glass cell at room temperature using an Autolab potentiostat (Eco chemie, Netherlands). Pt wire and Ag/AgCl (in saturated NaCl) were used as the counter and reference electrodes, respectively. All the potentials are reported with respect to the NHE. To prepare catalyst-coated glassy carbon (GC) working electrode, 5 μ L of the catalysts dispersion which was prepared by mixing 5 mg of the carbon supported catalysts in a mixed solution of 100 μ L diluted Nafion alcohol solution (Fluka, 5.0 wt%) and 2 mL of de-ionized water (Modulab, US Filters, MA, >18 M Ω) was dropped onto a GC electrode and carefully dried in an oven at 70 °C for 10 min. For CV measurements, the electrode potential was cycled between -0.2 and 1.0 V with a scan rate of 20 mV s⁻¹ in 0.5 M H₂SO₄ aqueous solution purged with Ar prior to use for 30 min. RDE experiments were carried out using a rotator (ALS, RRDE-3A) and the potential was cycled between 0.0 and 1.0 V at a scan rate of 10 mV/s and a rotation rate of 1600 rpm in 0.5 M H₂SO₄ aqueous solution purged with O₂ prior to use for 30 min.

The electrochemically active surface area (ECSA) was estimated by the following equations:

$$Charge (C) = \frac{\int IdE}{v (V s)}$$

$$ECSA = \frac{C}{210 \mu C cm^2}$$

Where C is the surface charge that can be obtained from the area under the CV trace of hydrogen desorption current (Figure 3). The ECSA values were calculated to be $29.46 \text{ m}^2 \text{ g}^{-1}$ for 3 nm commercial spherical Pt, $8.89 \text{ m}^2 \text{ g}^{-1}$ for 8nm Pt-Co nanocubes, $9.08 \text{ m}^2 \text{ g}^{-1}$ for 8nm Pt nanocubes, and $7.14 \text{ m}^2 \text{ g}^{-1}$ for 8nm Pt-Co nanoparticles.

The specific kinetic current densities (J_k) were estimated by the following Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}}$$

where J_k is the kinetic current density, J_d is the diffusion-limited current density, ω is the angular frequency of rotation. The B parameter is defined by following equation:

$$B = 0.62 n F C_o D_o^{2/3} \nu^{-1/6}$$

where n is the overall number of electrons, F is the Faraday constant (96485 C mol^{-1}), C_o is the concentration of molecular oxygen in the electrolyte ($1.26 \times 10^{-6} \text{ mol cm}^{-3}$), D_o is the diffusion coefficient of the molecular O_2 in 0.5 M H_2SO_4 solution ($1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the viscosity of the electrolyte ($1.009 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) (Ref. C. Wang, H. Daimon, T. Onodera, T. Koda, S. Sun, *Angew. Chem. Int. Ed.* 2008, **47**, 3588).

Table S1. Molar Pt:Co ratio obtained by EDS and ICP-AES.

The shape of Pt-Co nanoparticles	Pt:Co molar ratio by EDS (atom %)	Pt:Co molar ratio by ICP-AES (atom %)
Cube	87.2:12.8	89.5:10.5
Sphere	87.4:12.6	92.3:7.7

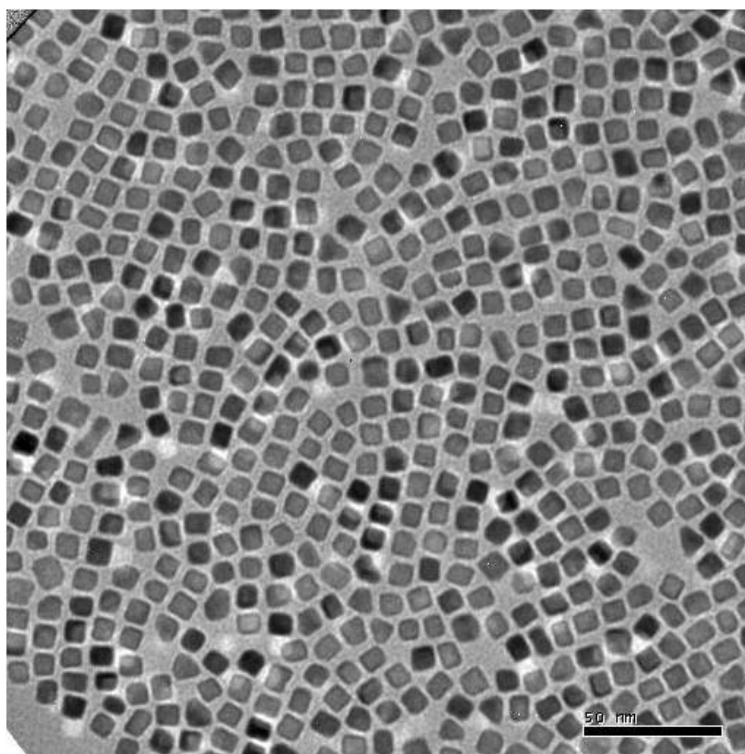


Figure S1. TEM image of as-synthesized Pt₉Co nanocubes.

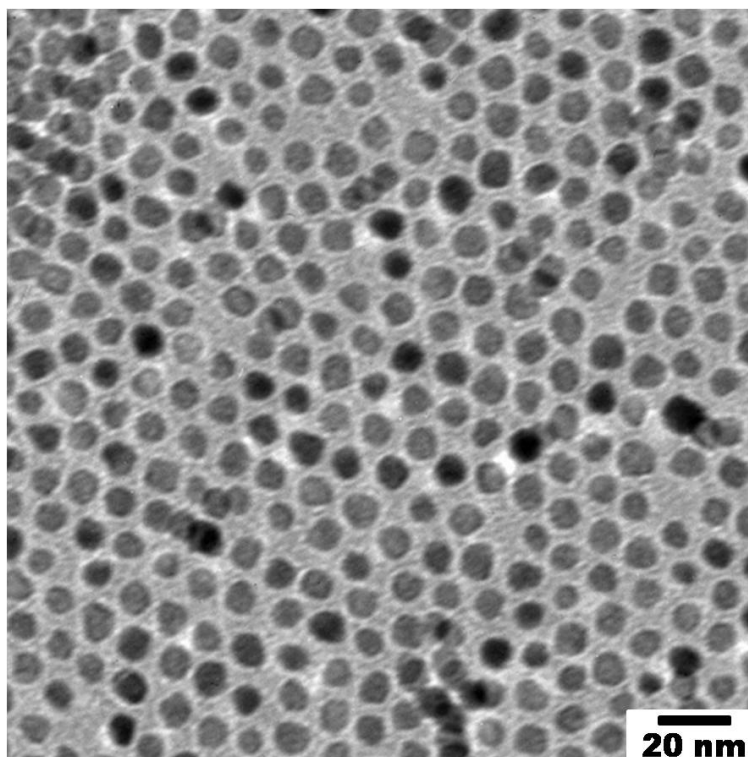


Figure S2. TEM image of spherical Pt₉Co nanoparticles prepared in the absence of oleic acid.

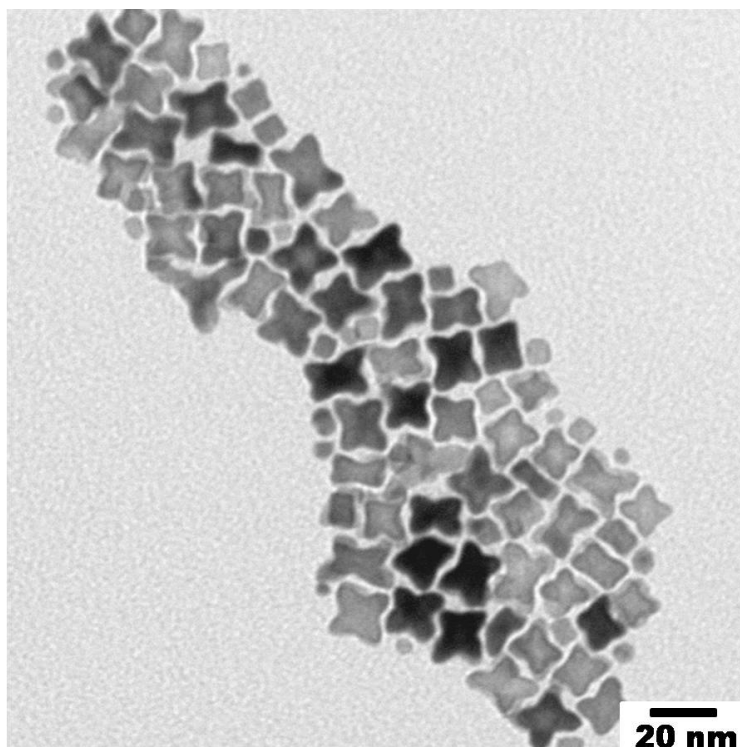


Figure S3. TEM image of Pt₉Co nanoparticles prepared in the presence of oleylamine (4 mL) and oleic acid (4 mL).

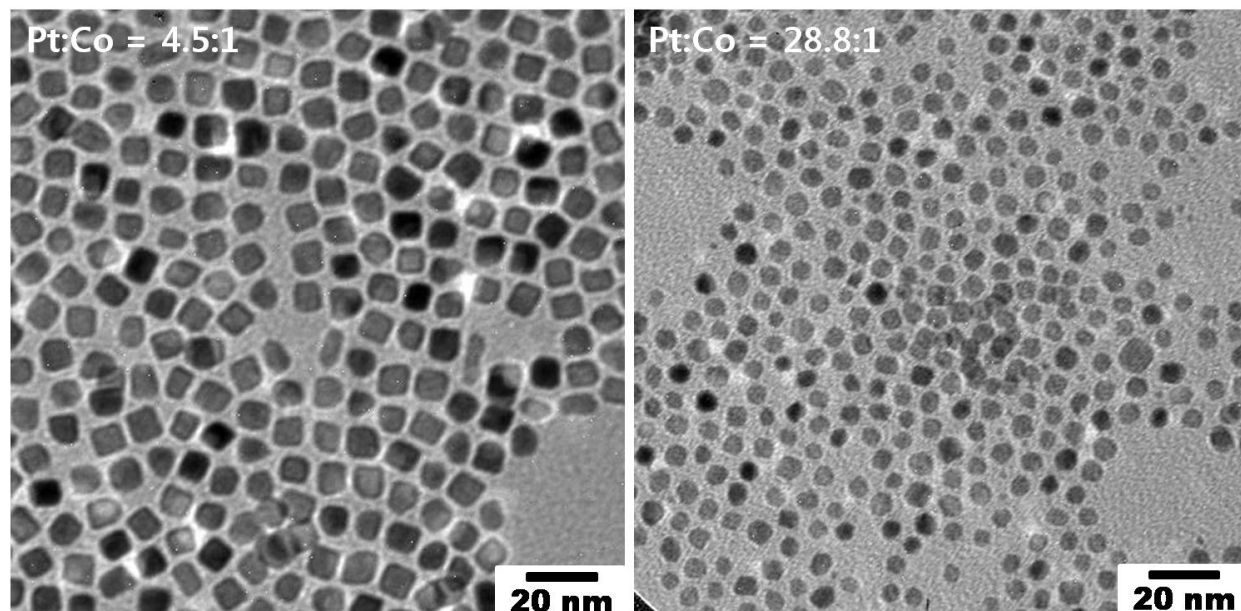


Figure S4. TEM images of Pt-Co nanoparticles prepared in the presence of (left) oleylamine (4 mL) and oleic acid (1 mL), and (right) oleylamine (1 mL) and oleic acid (4 mL).

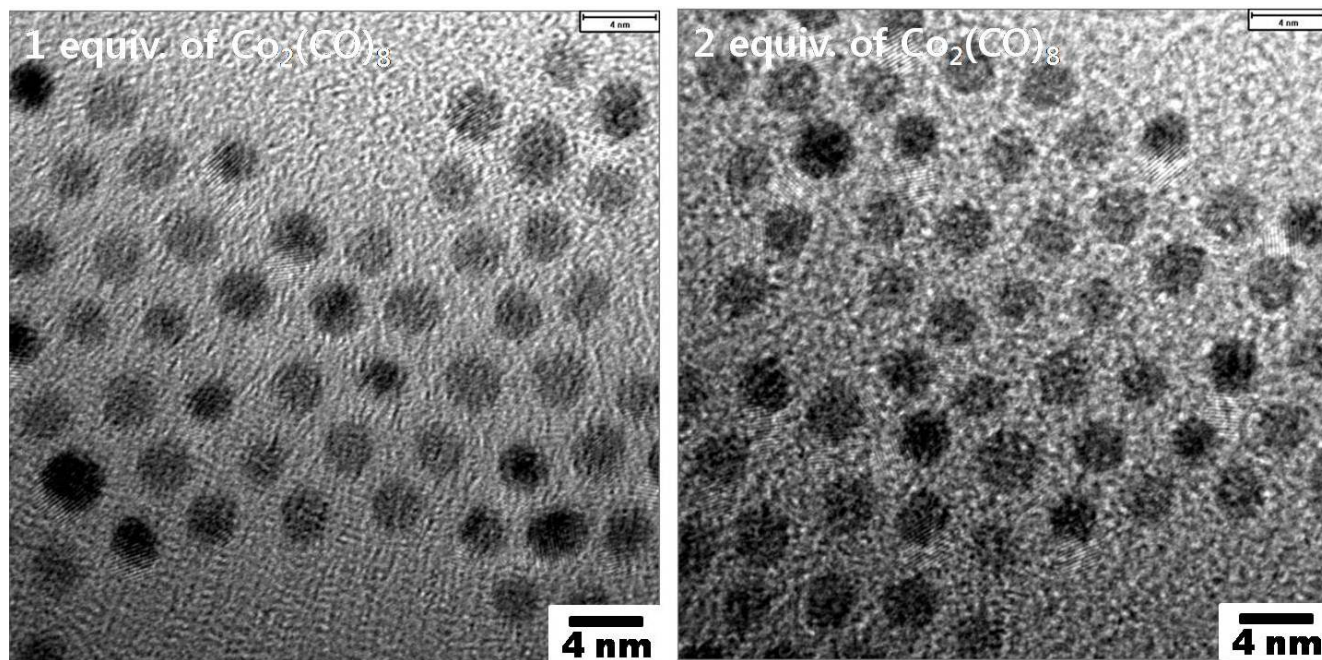


Figure S5. TEM images of Pt-Co nanoparticles synthesized with 1 or 2 equiv. of $\text{Co}_2(\text{CO})_8$ to $\text{Pt}(\text{acac})_2$. The particle size is 3-5 nm.

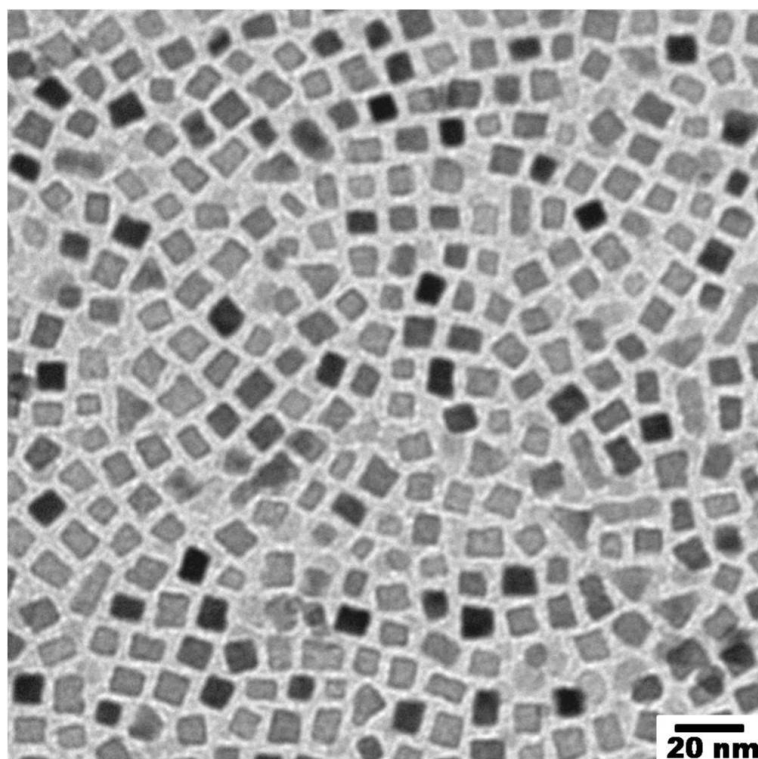


Figure S6. TEM image of as-synthesized Pt nanocubes with an average edge length of 8 nm.

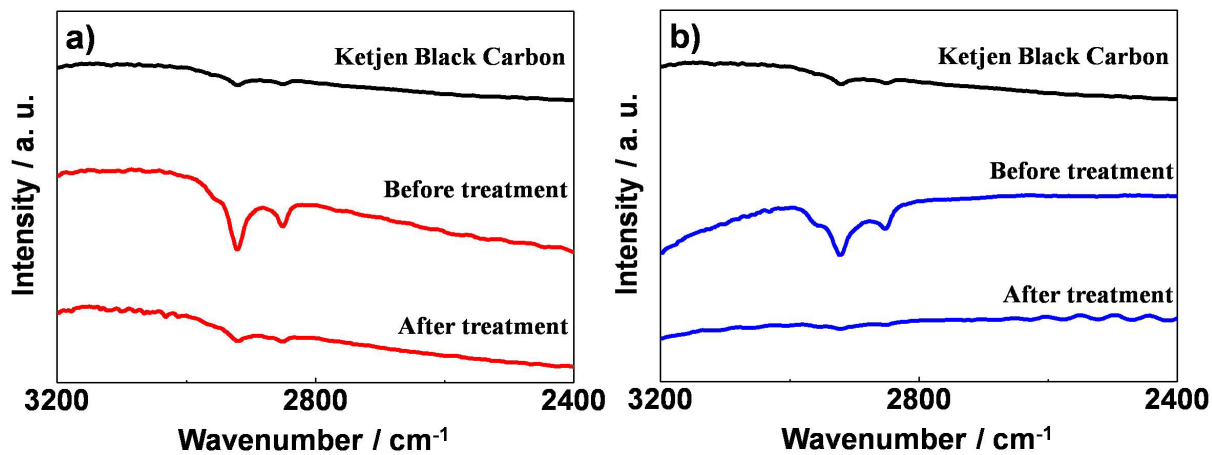


Figure S7. FTIR spectra of raw Ketjen Black carbon and a) the 8 nm cubic Pt₉Co/C before and after treatment with diethylether and b) the 8 nm spherical Pt₉Co/C before and after treatment with acetic acid.

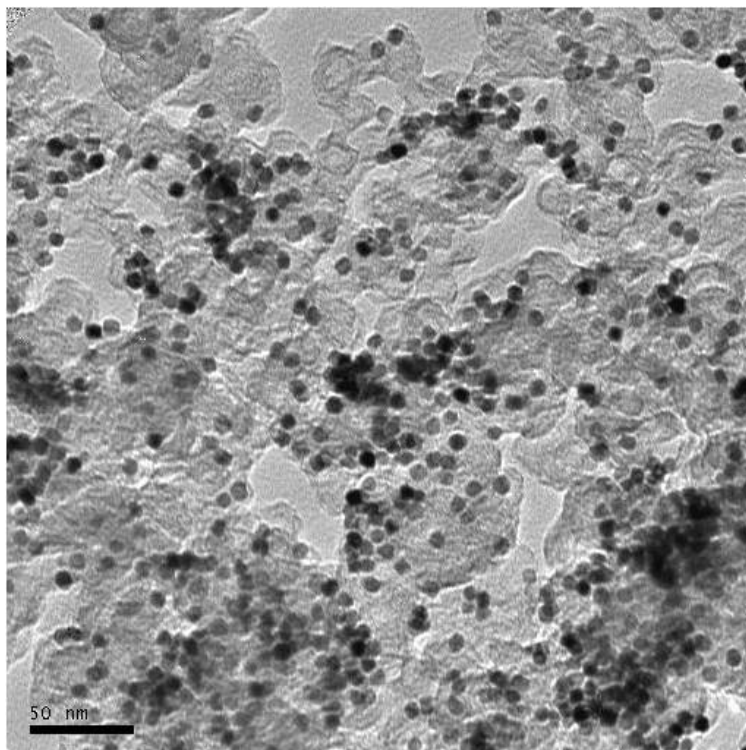


Figure S8. TEM image of the Pt-Co nanocubes deposited on Ketjen Black carbon with 40 wt% of metal loading.

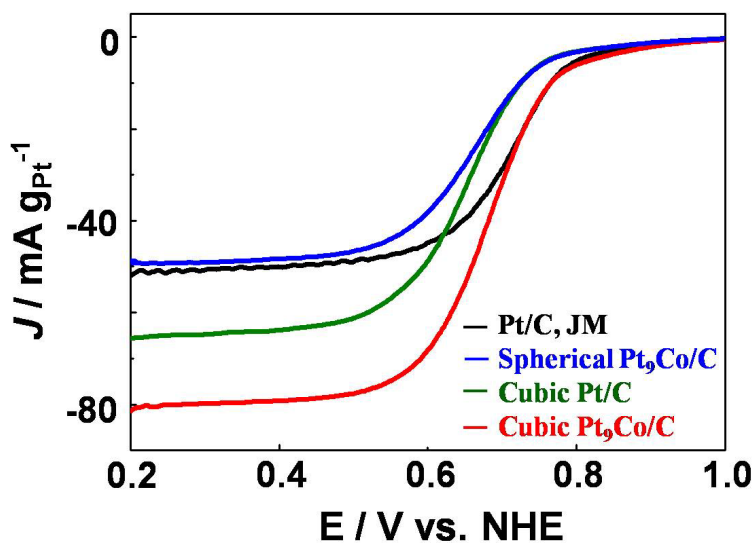


Figure S9. The specific mass current densities for the commercial Pt (black), spherical Pt₉Co (blue), cubic Pt (green), and cubic Pt₉Co (red) nanocatalysts.

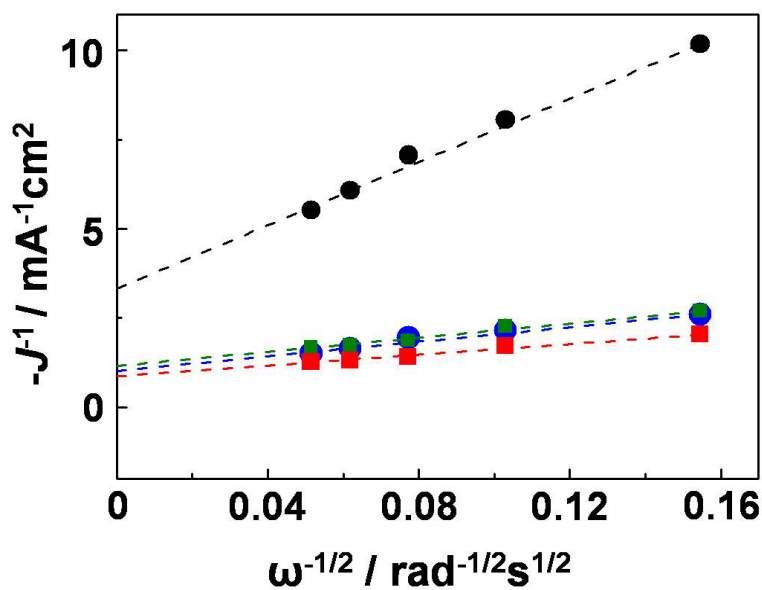


Figure S10. Koutecky-Levich plots for oxygen reduction with different catalysts at 0.6 V.

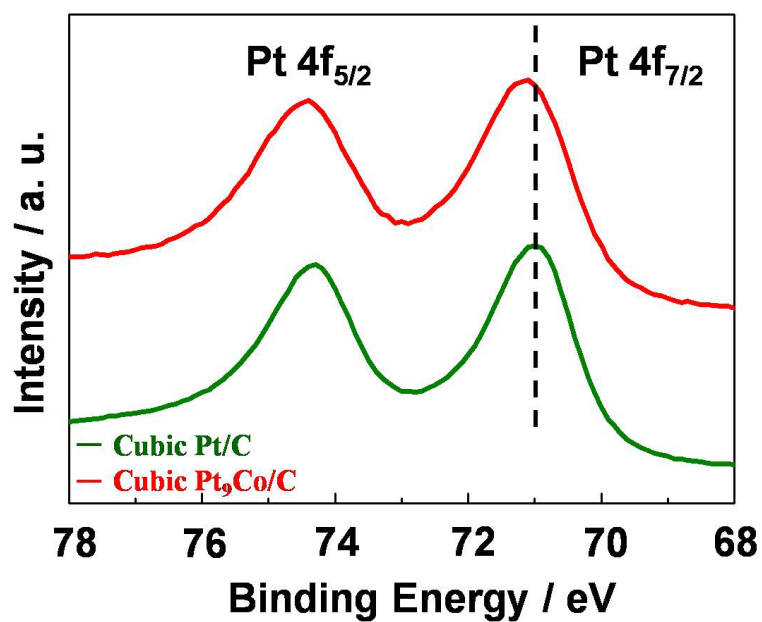


Figure S11. XPS spectra of Pt 4f for Pt and Pt₉Co nanocubes.