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Electronic Supplementary Information

Facile synthesis of Pd@Pt core-shell nanocubes with low Pt content via direct seed-mediated growth and their enhanced activity for formic acid oxidation

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Experimental Section

Synthesis of Pd@Pt core-shell nanocubes by continuous injection of reagents without a washing process

Polyvinylpyrrolidone (PVP, 36.93 mg, MW 55,000, Aldrich), L-ascorbic acid (AA, 50 mg, Aldrich), and potassium bromide (KBr, 300 mg, Aldrich) were dissolved in 8 mL of deionized water and heated to 80 °C for 20 min under magnetic stirring at 800 rpm. Then, 3 mL of an aqueous solution containing 57 mg of disodium tetrachloropalladate (Na_2PdCl_4, Aldrich) was then slowly added to the reaction solution. After 3 h of heating at 80 °C, 0.1 mL of an aqueous citric acid (CA) solution (800 mg/mL, Aldrich) was added to the reaction solution using a pipette. Then, 1 mL of a potassium tetrachloroplatinate (K_2PtCl_4, Aldrich) solution at different concentrations (0.19 mg/mL, 0.35 mg/mL, 0.88 mg/mL, 2.63 mg/mL, 4.39 mg/mL, 6.16 mg/mL, and 17.56 mg/mL) was rapidly injected. The resulting solution was heated to the same temperature for 5 h, and the products were collected by centrifugation and washed three times with a deionized (DI) water and acetone mixture.

Synthesis of Pd@Pt core-shell nanocubes with a washing process

Pd nanocubes were synthesized by reacting Na_2PdCl_4 with L-ascorbic acid in the presence of PVP and KBr, as reported previously.[1] The synthesized Pd nanocubes were separated using centrifugation, washed three times with acetone and water, and re-dispersed in 1 mL of water. To synthesize Pd@Pt core-shell nanocubes, 1 mL of the aqueous dispersion of washed Pd nanocubes was mixed with 11 mL of an aqueous solution containing 36.93 mg of PVP, 80 mg of CA, 50 mg of AA and 300 mg of KBr. The mixture solution was heated at 80 °C, and 1 mL of K_2PtCl_4 solution (6.16 mg/mL) was added using a pipette. The resulting solution was heated to the same temperature for 5 h, and products were collected by centrifugation and washed three times with a deionized (DI) water and acetone mixture. To better understand the role of each reagent during the reaction, four comparable experiments were carried out. K_2PtCl_4 solution was injected individually into Pd + KBr + CA + AA + PVP，Pd + CA + AA +

PVP，Pd + CA + PVP and Pd + PVP solutions.

Preparation of the carbon support catalysts

For carbon catalyst, 5 ml carbon black (Vulcan XC-72) solution (1 mg/mL) was dispersed in a solution of 20 mL of iso-propyl alcohol (IPA, Aldrich) and 5 mL of deionized water. After sonication for 10 min, Pd nanocubes and Pd@Pt core-shell nanocubes were added into the solution at a mass ratio of 20% (the concentrations of nanoparticles were measured by ICP). The resulting solution was sonicated for 10 min and stirred at room temperature for 24 h. The precipitate was retrieved by centrifugation to yield a black powder and was re-dispersed in water (0.15 mg/mL).

Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured using a JEM-2100F microscope operated at 200 kV. High-angle annular dark field scanning TEM (HAADF-STEM), scanning transmission electron microscope (STEM), and energy-dispersive X-ray spectroscopy (EDS) images were obtained using an FEI Talos F200X (Super-X EDS) electron microscope at 200 kV. The X-ray diffraction (XRD) patterns were measured using a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA. The elemental composition in the nanoparticle suspension was determined by direct reading using an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Evaluation of catalytic activity

All reagents including the Pt/C (20 wt% Pt on carbon support, Alfa Aesar, HiSPEC fuel-cell grade), Nafion solution (Sigma), perchloric acid ($HClO_4$, Merck), and sulfuric acid (H_2SO_4, Merck) were used without purification. Electrochemical measurements were performed using a CHI 600E (CH Instrument) potentiostat. A Pt wire and Ag/AgCl electrodes (3 M NaCl) were used as the counter and reference electrodes, respectively. A glassy carbon (GC) electrode (CH Instruments, 3 mm in diameter) was mechanically polished and used as the working electrode. An aqueous dispersion of each catalyst was sonicated for 15 min, and a portion of the dispersion was then dropped onto the GC rod (A = 0.0707 cm^2). The amount of metals loaded on a GC rod was 15.3 $\mu g/cm^{-2}$. After drying under air for 2 h, the electrode was covered with 5 µL of a Nafion solution (0.05 wt%), followed by evaporation of water and vacuum treatment for 30 min prior to electrochemical measurement. The voltammetric curves of formic acid oxidation (FAO) were obtained in N_2-saturated 0.5 M FA + 0.5 H_2SO_4 solution. Before the voltammetric measurements, several potential cycling steps between −0.2 and 1.0 V in 0.1 M $HClO_4$ solution were performed to clean the electrode surface.

Reference:

1 B. Lim, M. J. Jiang, J. Tao, P. H. C. Camargo, Y. M. Zhu and Y. N. Xia, *Adv Funct Mater*, 2009, **19**, 189.

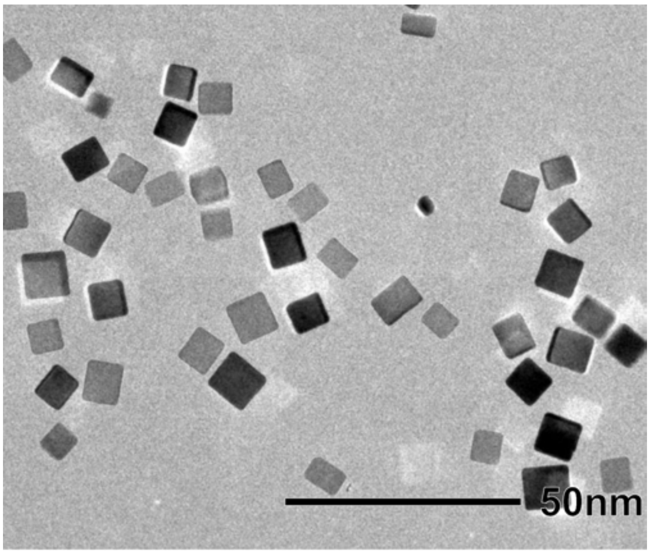

Fig. S1 TEM image of Pd@Pt 0.2 at%.

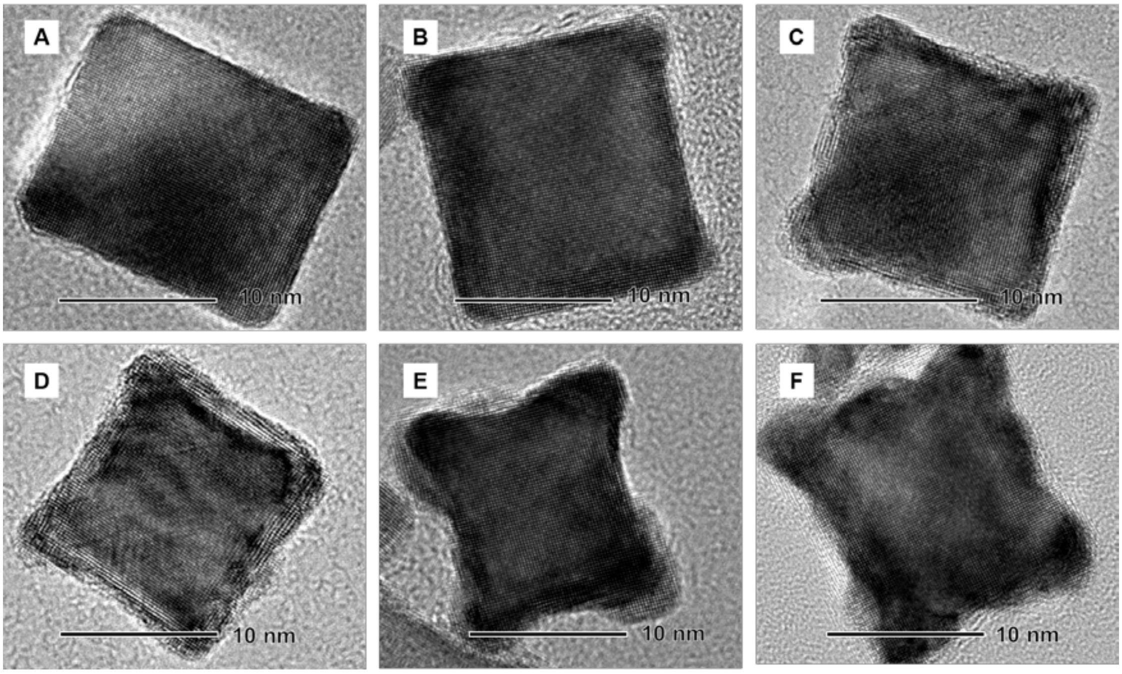

Fig. S2 HRTEM images of (A) Pd@Pt 0.4 at%, (B) Pd@Pt 1 at%, (C) Pd@Pt 3 at%, (D) Pd@Pt 5 at%, (E) Pd@Pt 7 at%, and (F) Pd@Pt 20 at%.

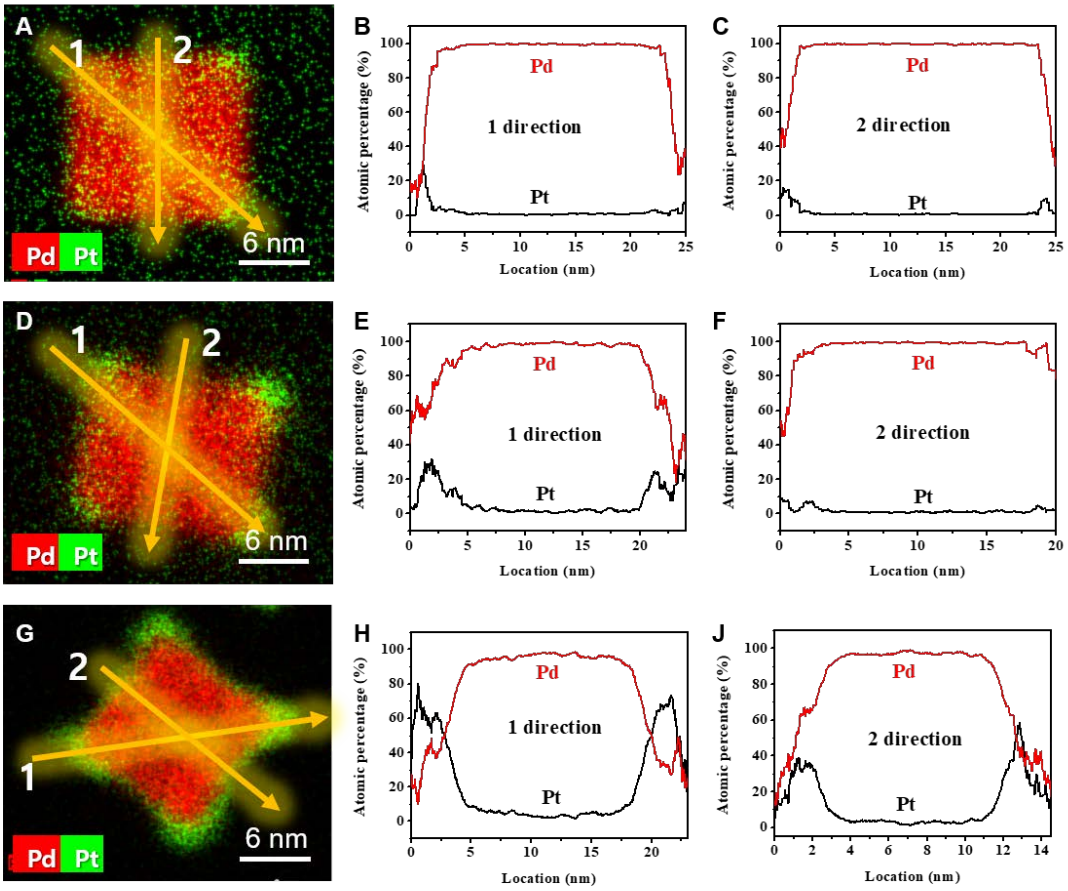

Fig. S3 EDX line profiles of Pd@Pt core-shell nanoparticles. The Pd/Pt atomic ratios were (A-C) 0.4 at%, (D-F) 5 at%, and (G-J) 20 at%, respectively.

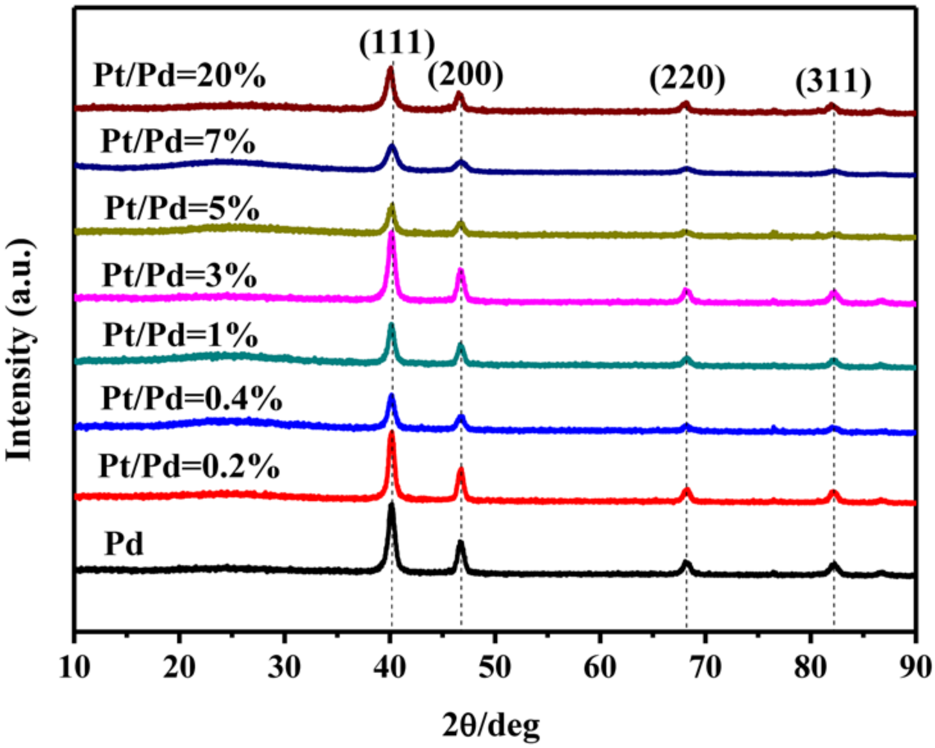

Fig. S4 XRD patterns of Pd and Pd@Pt core-shell nanocubes.

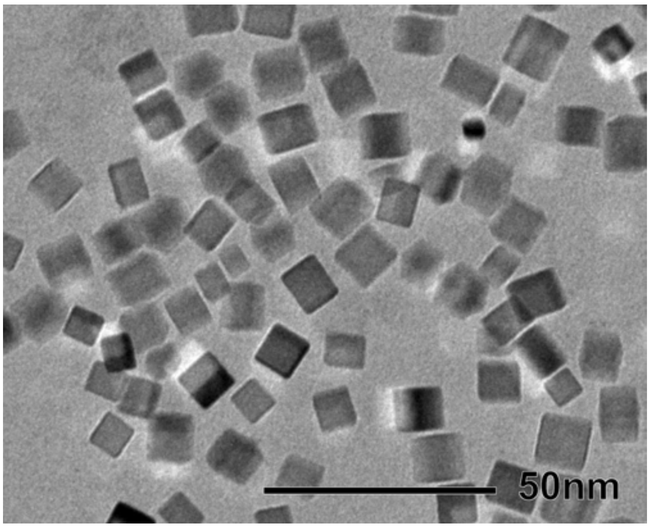

Fig. S5 TEM image of Pd nanocubes.

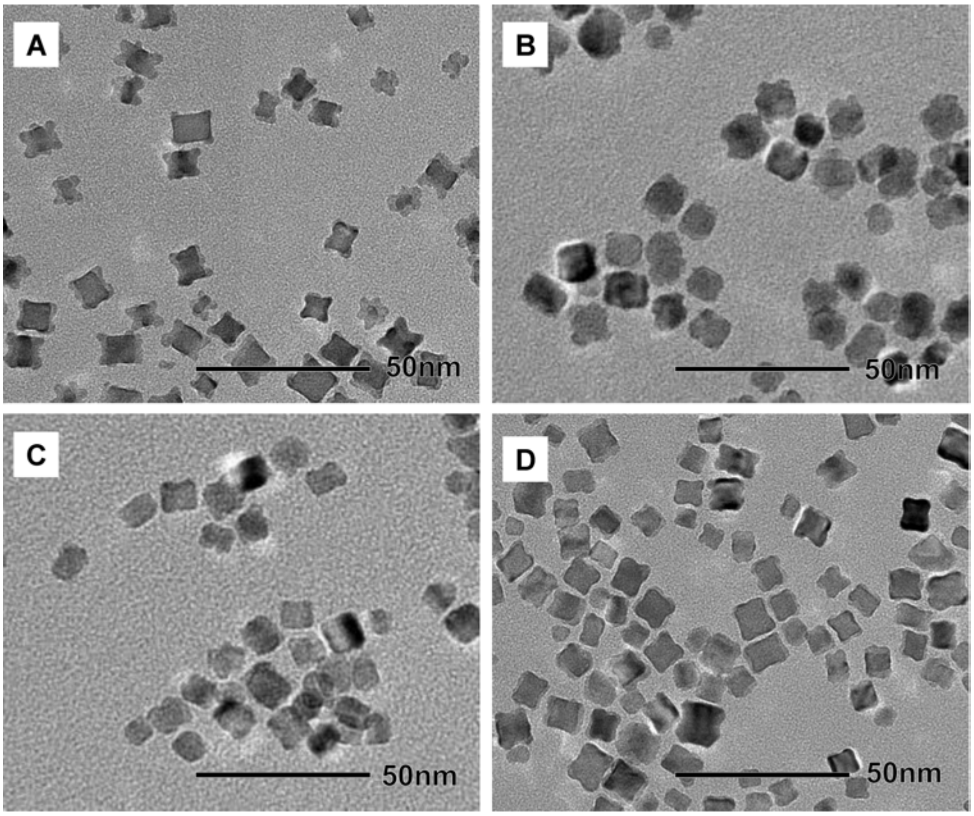

Fig. S6 TEM images of Pd@Pt core-shell nanocubes produced by addition of reagents to an aqueous solution containing washed Pd nanocubes. The amount of reagent was the same as that used for Pd/Pt 7 at% shown in Figure 1E. The injected reagents were (A) KBr + PVP + CA + AA + K_2PtCl_4, (B) PVP + CA + AA + K_2PtCl_4, (C) PVP + CA + K_2PtCl_4, and (D) PVP + K_2PtCl_4.

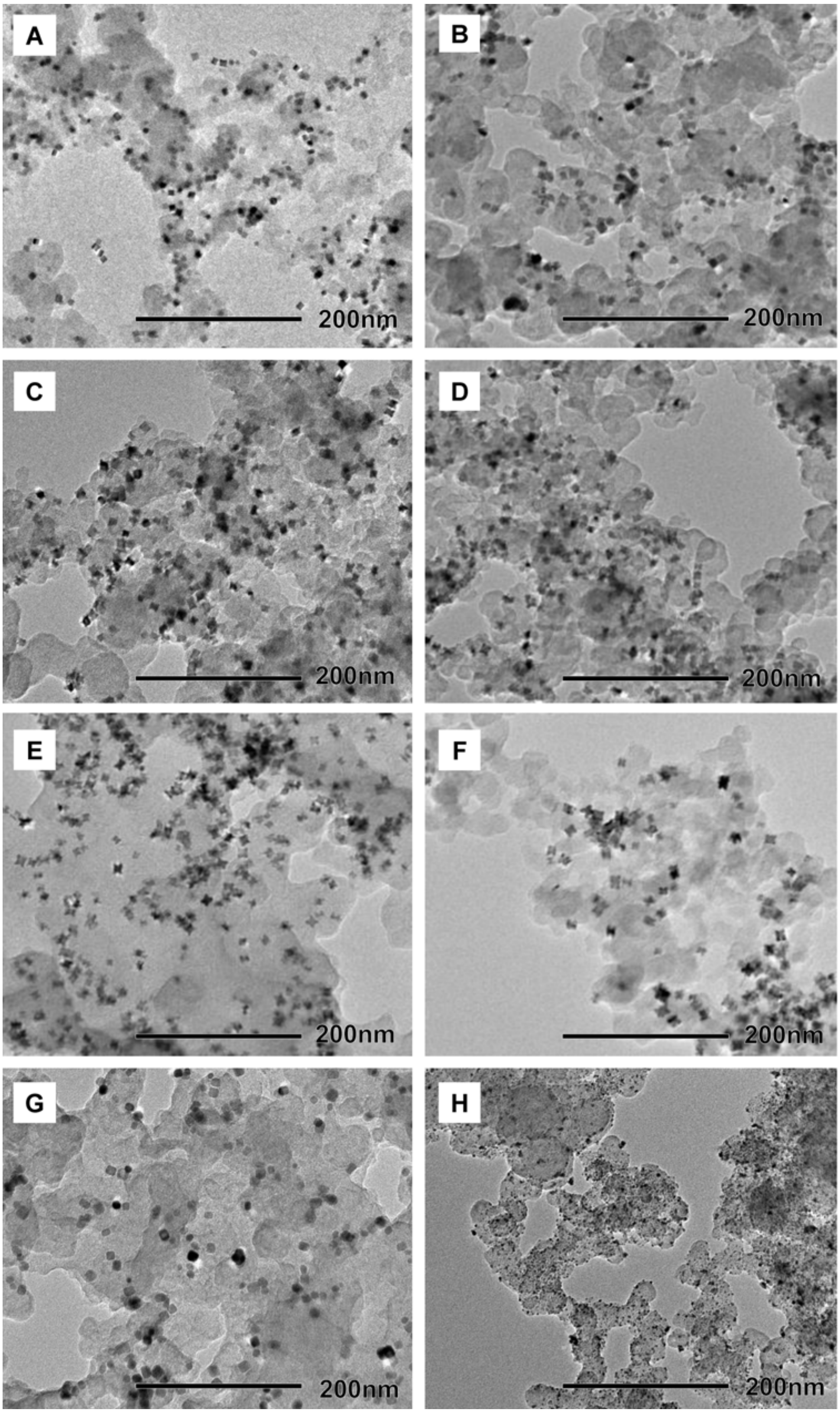

Fig. S7 TEM images of carbon-supported (A) Pd@Pt 0.4 at%, (B) Pd@Pt 1 at%, (C) Pd@Pt 3 at%, (D) Pd@Pt 5 at%, (E) Pd@Pt 7 at%, (F) Pd@Pt 20 at%, and (G) Pd nanocubes. (H) TEM image of commercial Pt/C.

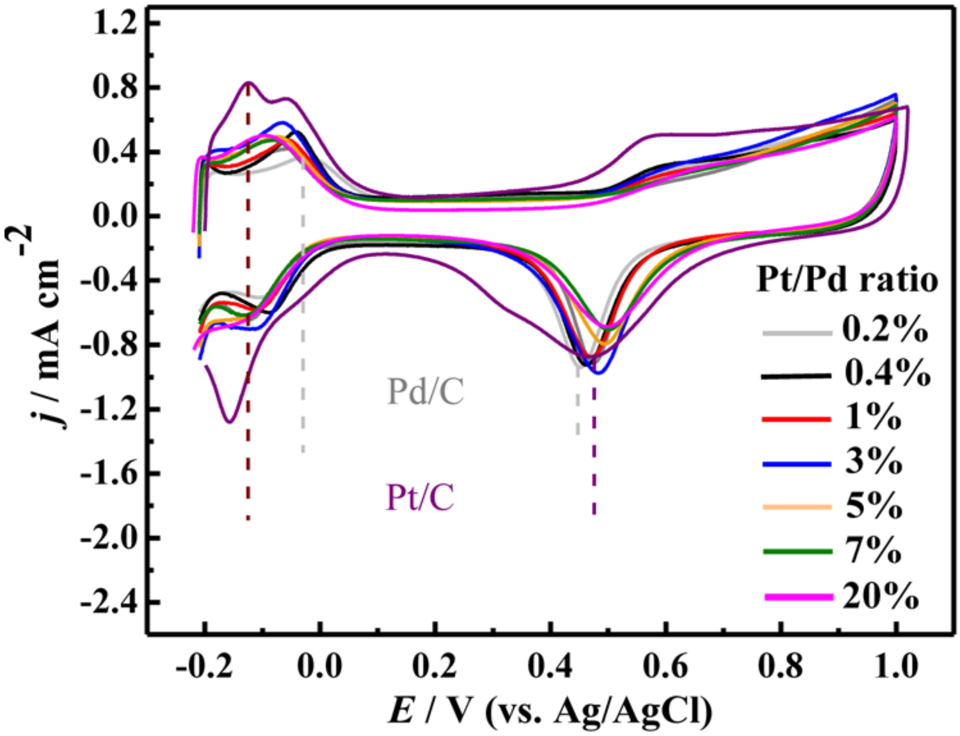

Fig. S8 Cyclic voltammograms of Pd/C, the Pd@Pt/C series, and commercial Pt/C obtained in 0.1 $HClO_4$ solution saturated with N_2 at a scan rate of 50 mV/s.

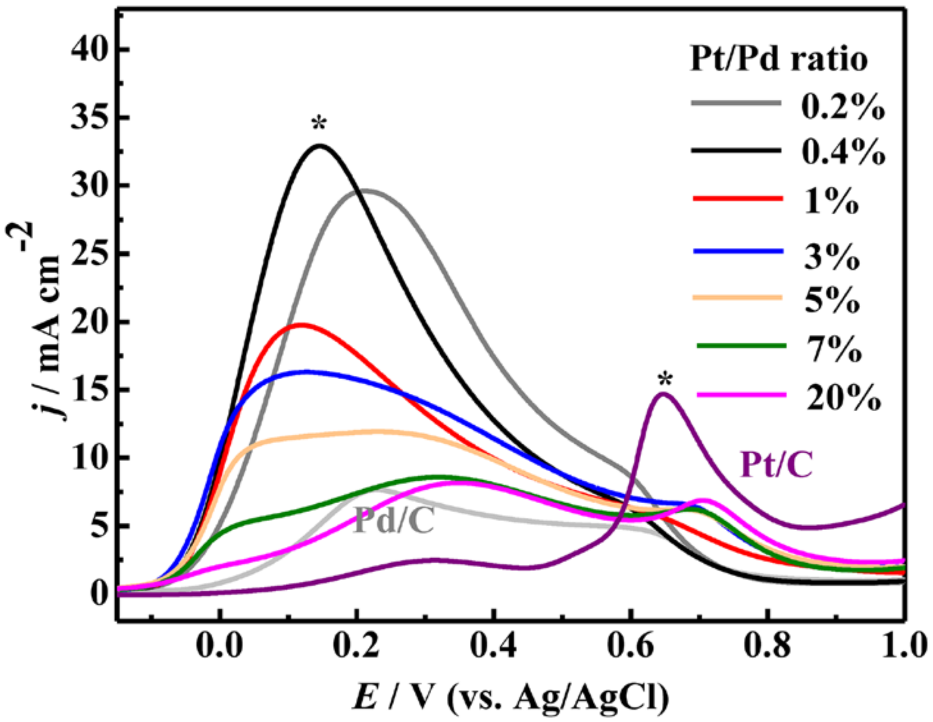

Fig. S9 Linear scan voltammograms of Pd/C, the Pd@Pt/C series, and commercial Pt/C obtained in 0.5 M FA + 0.5 M H_2SO_4 solution saturated with N_2 at a scan rate of 50 mV/s.

Table S1. ICP results of the Pd@Pt core-shell nanocubes.

Catalysts	**Molar fraction of metal (%)**			
	Pd	Pt	(Pd+Pt)	Pt/Pd ratio
Pd@Pt Pt/Pd=0.2%	14.4	0.056	14.456	0.21%
Pd@Pt Pt/Pd=0.4%	14.7	0.114	14.814	0.42%
Pd@Pt Pt/Pd=1%	5.14	0.129	5.269	1.37%
Pd@Pt Pt/Pd=3%	1.71	0.131	1.841	4.18%
Pd@Pt Pt/Pd=5%	1.70	0.193	1.893	6.19%
Pd@Pt Pt/Pd=7%	1.21	0.188	1.398	8.47%
Pd@Pt Pt/Pd=20%	1.06	0.419	1.479	21.56%