

Controllable Formation of Defect-rich Pd and Pd-Ag Bimetallic Nanocrystals through Coalescence Mechanism

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Materials and Methods

1. Synthesis of DRNCs

In a typical synthesis of DRNCs, poly (vinyl pyrrolidone) (PVP, 100mg, MW=58,000) and several amounts of iodobenzene (Alfa) were dissolved in 12.5 mL of Ethylene glycol hosted in a 50-mL, three-necked flask (equipped with a reflux condenser and a Teflon-coated magnetic stirring bar) and heated to 80, 100, 140 and 170 °C in air under magnetic stirring. Meanwhile, sodium tetrachloropalladate (II) (Na_2PdCl_4 , 8 mg, Alfa) was dissolved at room temperature in 2 mL of deionized water. The aqueous solution of Na_2PdCl_4 was then dropped into the flask. The reaction mixture was heated at 100 °C in air for 3 h, followed by suddenly addition with -30 °C ice-cooled acetone. (-20, -10 and 0°C for comparision) The mixture was then washed with acetone and ethanol for several times.

2. Synthesis of Palladium Nanobars and well-faceted NCs

In a typical synthesis of palladium Nanobars, 100 mg of PVP and 70 μL of iodobenzene were dissolved in 12.5 mL of EG hosted in a 50-mL, three-necked flask and heated to 100 °C in air under magnetic stirring. Meanwhile, 8 mg of Na_2PdCl_4 was dissolved at room temperature in 2 mL of deionized water. The aqueous solution of Na_2PdCl_4 was then dropped into the flask. The reaction mixture was heated at 100 °C in air for 3 h, and then cooled down to room temperature. The mixture was then washed with acetone and ethanol for several times. The well-faceted NCs were synthesized without the addition of iodobenzene at the same condition as Palladium nanobars.

3. Structural analysis

The shape and structure of the NCs was analyzed on a JEOL 2010 transmission electron microscope (TEM). The samples were prepared by placing a drop of NCs sol in ethanol onto a continuous carbon-coated copper TEM grid. Inductively coupled plasma (ICP) analysis of NCs and residual aqueous phase after extraction was performed on an Ultima 2 analyzer (Jobin Yvon). UV-vis spectra were obtained using a Lamda 35 UV-visible spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were analyzed on coated alumina using a Physical Electronics PHI- Quantum 2000 Scanning ESCA Microprobe. Infrared (IR) spectra were recorded on PerkinElmer Spectrum One as KBr pellets.

4. Electrochemical measurements

Ethanol dispersion of purified nanoparticles (0.01mL) and 0.01mL of 5 wt% nafion solution were deposited on a glassy carbon electrode to obtain the working electrodes after the solvent is dried by an IR lamp. Ag/AgCl electrode and a platinum foil were used as the reference and counter electrode, respectively. For the electrooxidation of formic acid, the cyclic voltammograms were recorded at a sweep rate of 50 mV/s in N_2 degassed 0.5 M H_2SO_4 + 0.25 M formic acid. Both positive and negative CV scans were performed on each sample. The arrows in the CV curves (Figure 3d) indicate the direction of the scan. The current is normalized by the weight of catalysts in the electrode. To compare the activity between Pd DRNCs and commercial Pd/C (Palladium 5% on Carbon), the washed Pd DRNCs were mixed with conductive carbon black in a mass ratio of 5:95 in absolute ethanol and spread onto a glassy carbon electrode. The mass of nanoparticles on working electrode was 2.5×10^{-3} mg.

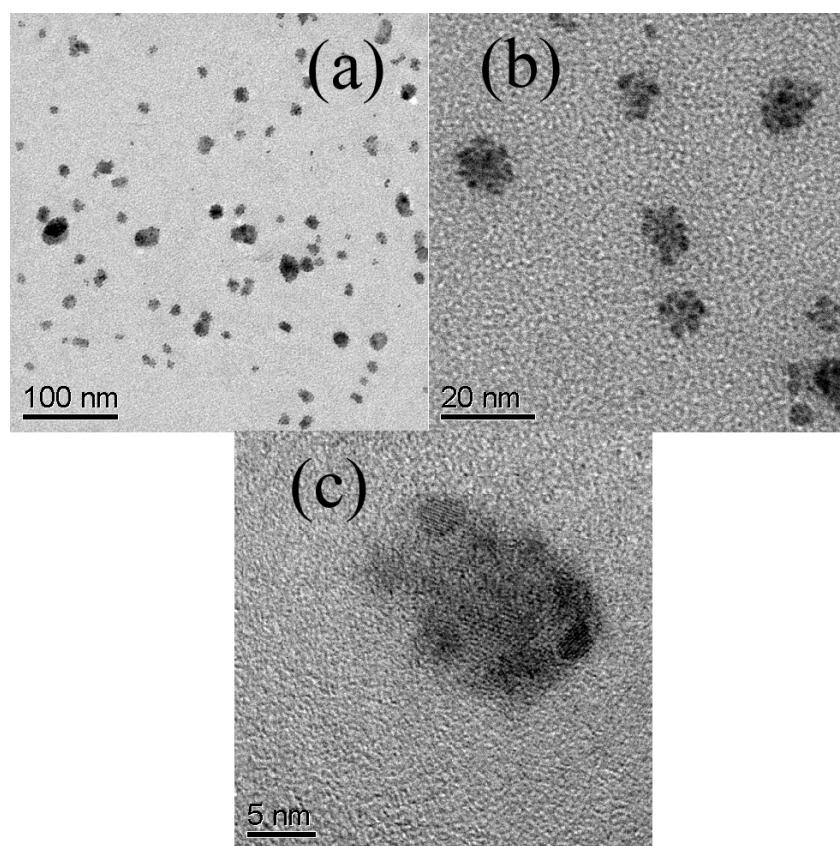


Figure S1. TEM and HRTEM images of Pd NCs when the DRNCs aged in air at RT for 15 days.

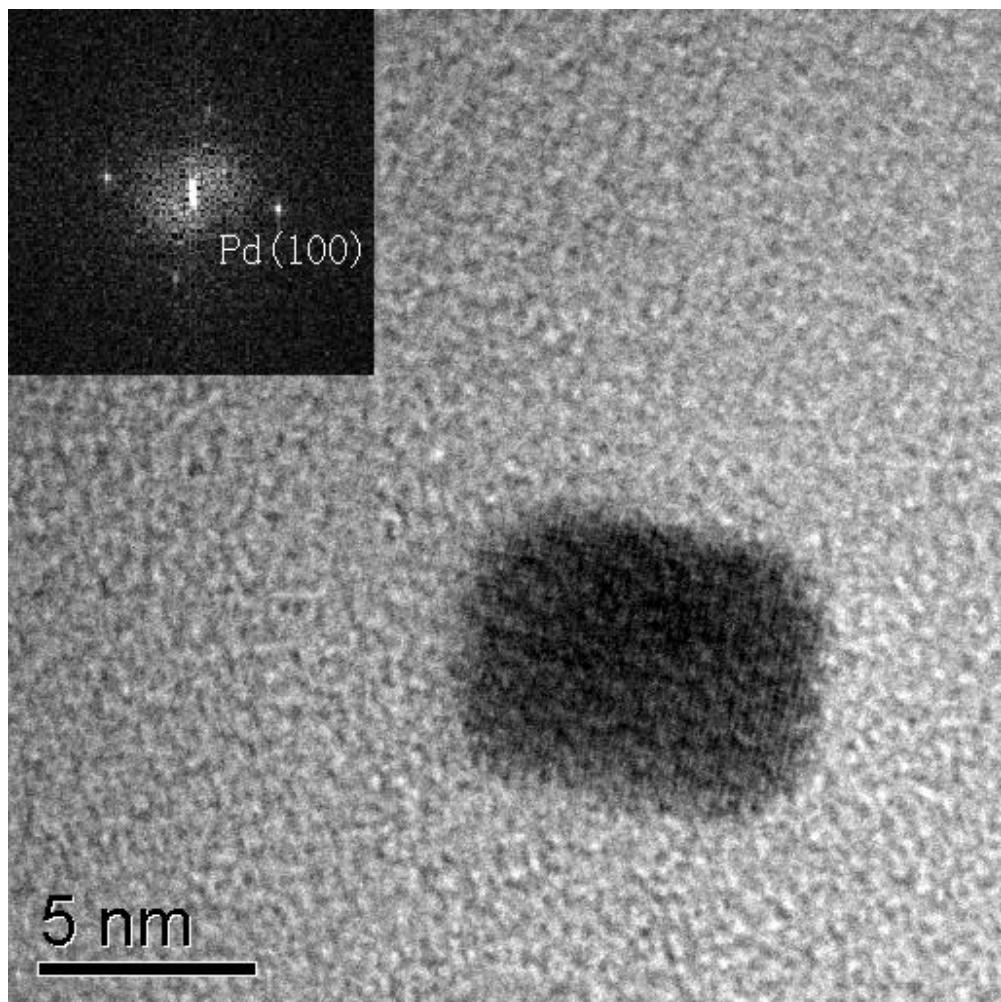


Figure S2. HRTEM and corresponding Fourier transform pattern of a Pd nanobar.

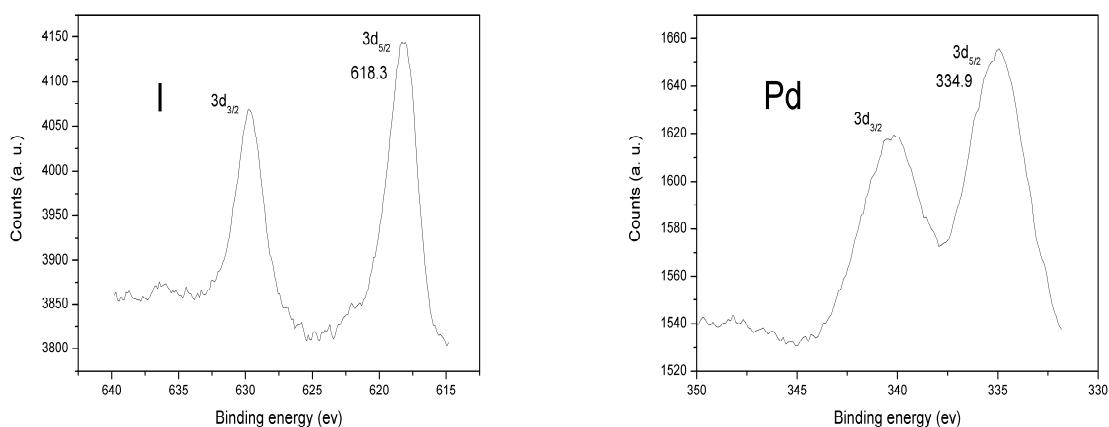


Figure S3. XPS spectra of Iodine and Pd in Pd DRNCs sample.

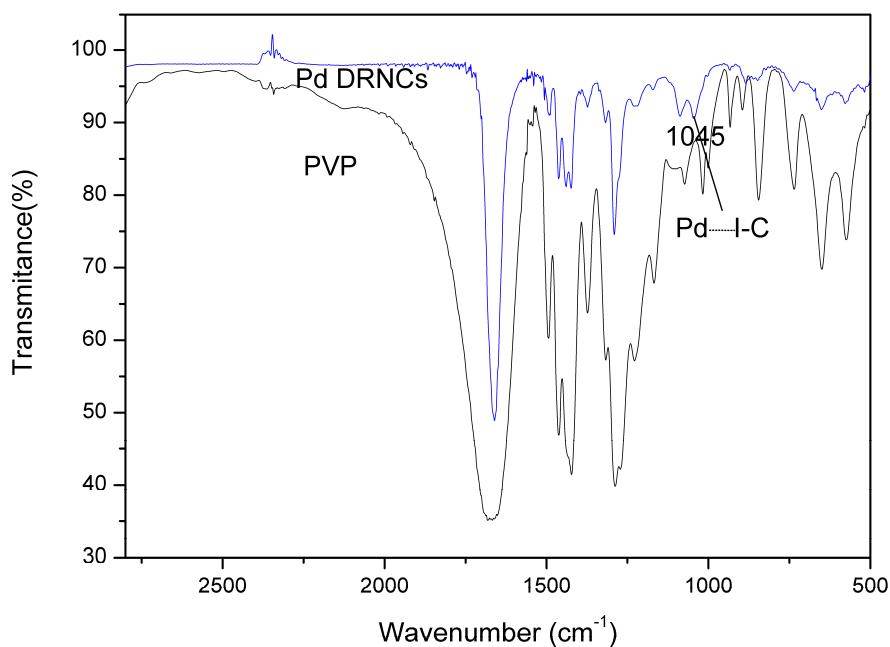


Figure S4. FT-IR spectra of Pd DRNCs and PVP.

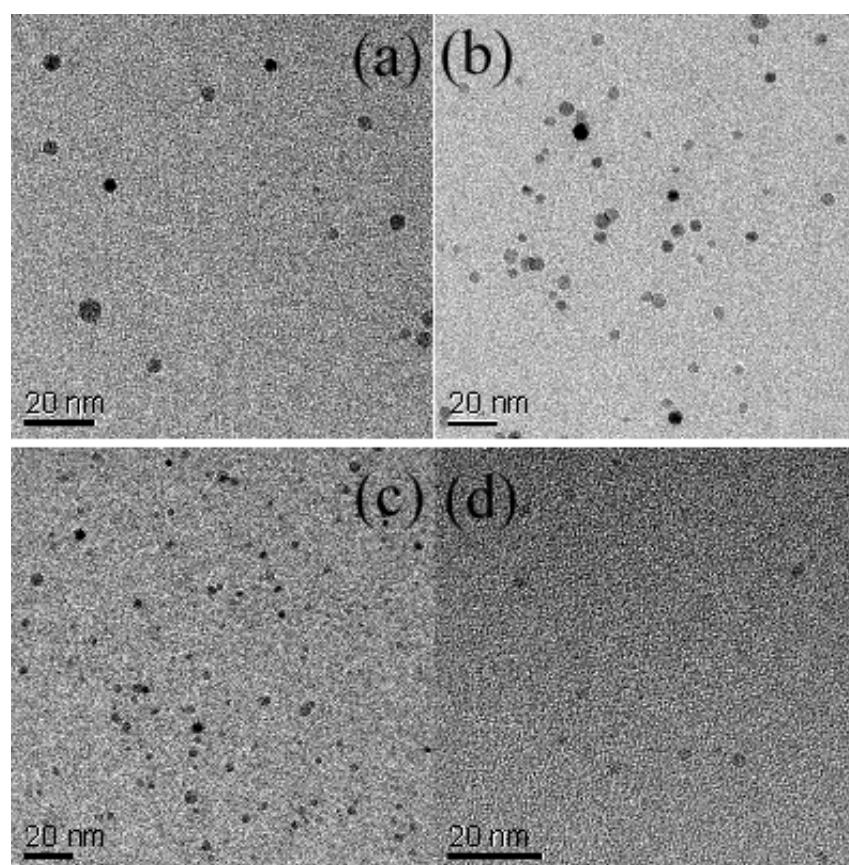


Figure S5. TEM images of Pd NCs produced when iodobenzene is (A) absent or replaced by (B)bromobenzene, (C)chlorobenzene and (D) potassium iodide in the same mole number. All of the syntheses were carried out under the same condition as in figure, except the capping agent.

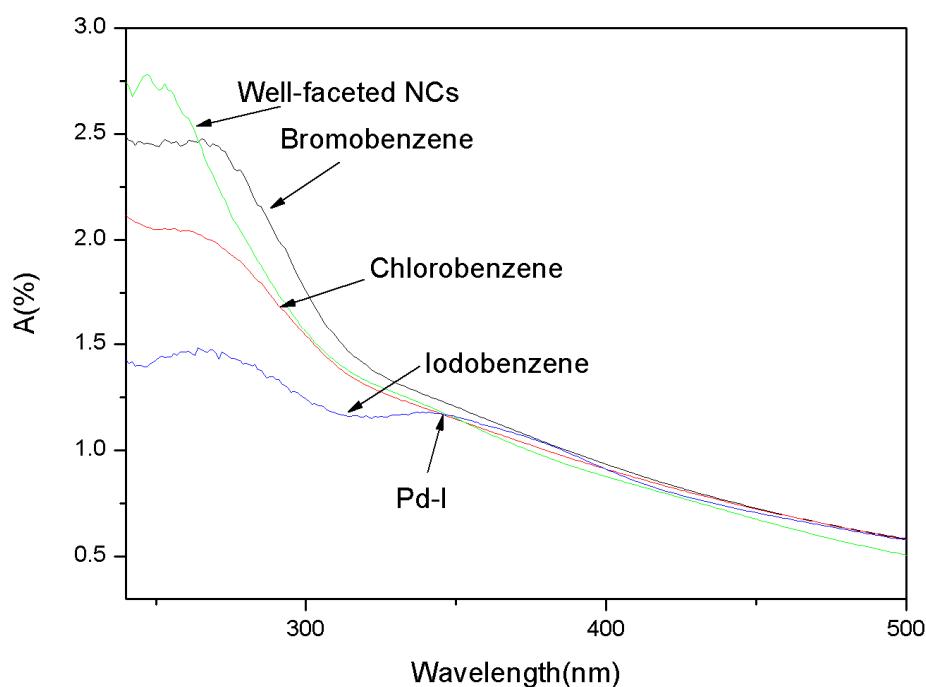


Figure S6. The UV-vis spectra of Palladium NCs synthesized after washing with acetone and ethanol, and redispersed in ethanol. The capping agents are iodobenzene, bromobenzene, chlorobenzene and absent.

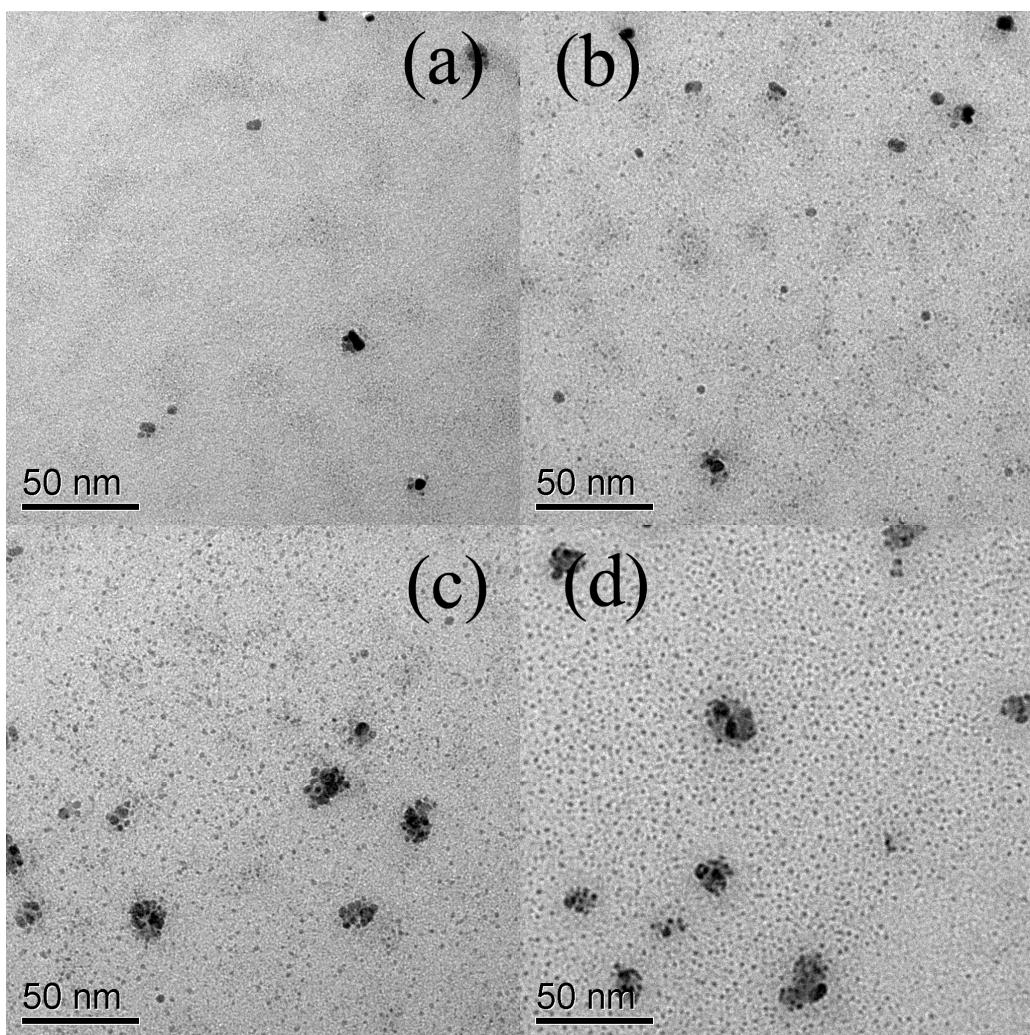


Figure S7. TEM images of nanostructures formed in the synthesis mixture at different stages of the reaction: (a) 30 min, (b) 1 h, (c) 2 h and (d) 3 h.

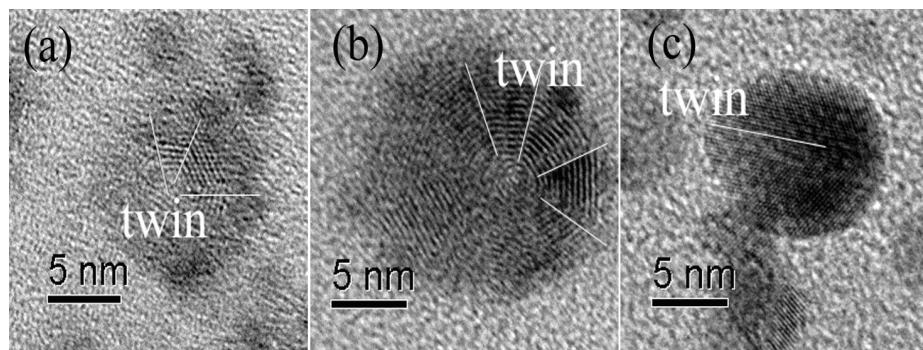


Figure S8. HRTEM images of Pd NPs synthesized after treatment with (a) -20 °C, (b)-10 °C and (c) 0°C ice-cooled acetone.

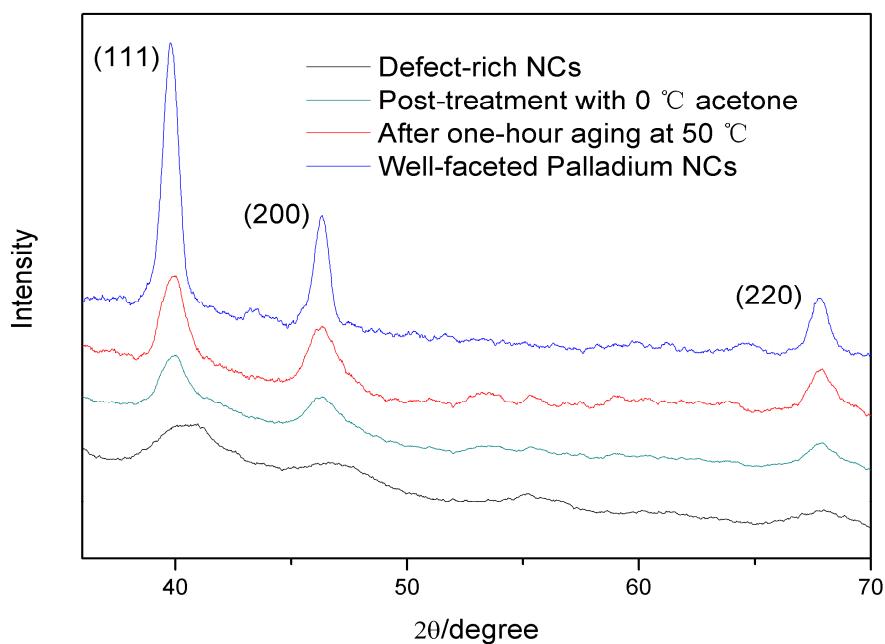


Figure S9. XRD patterns of four types of Palladium NCs.

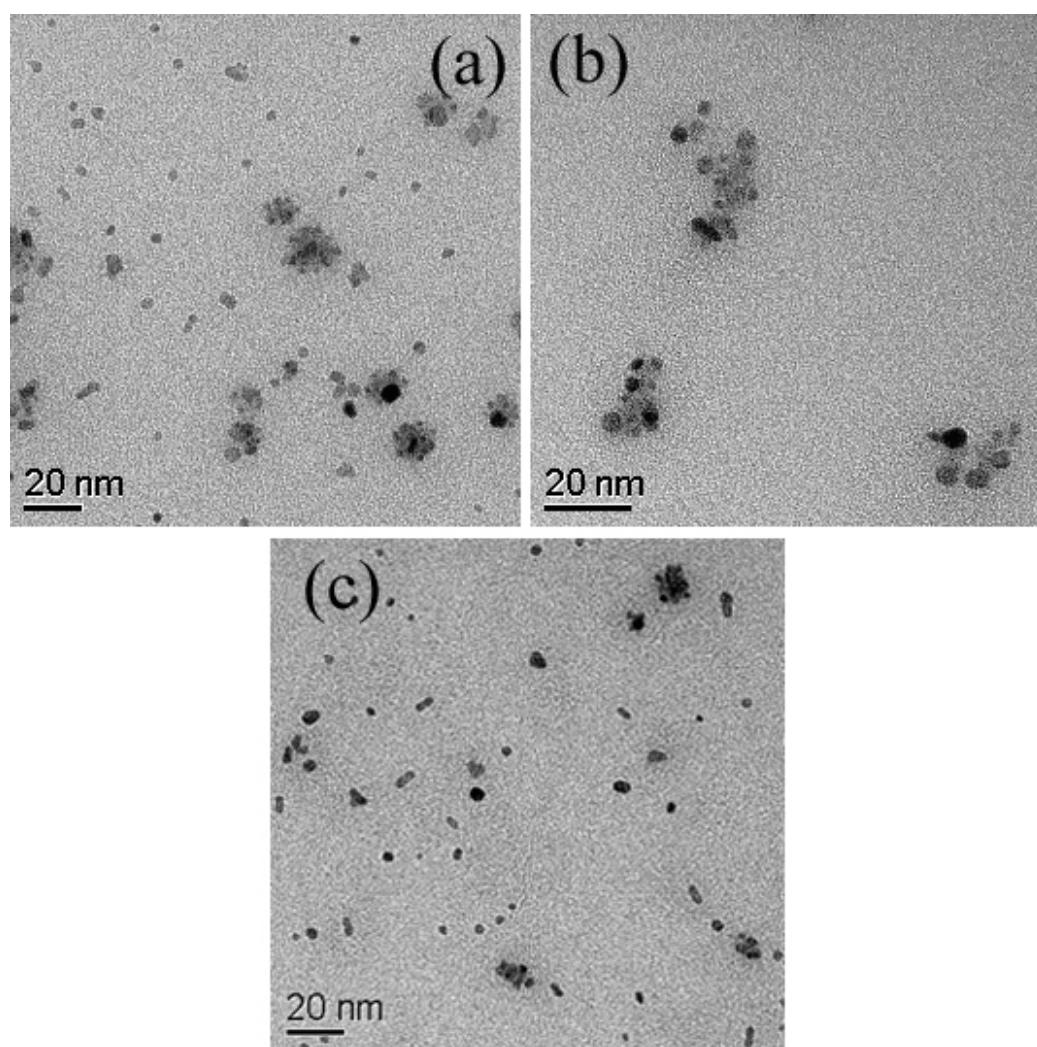


Figure S10. TEM images of Pd NCs produced in the presence of (a) 0.14mL, (b) 0.28mL and (c) 0.035mL iodobenzene. All of the syntheses were carried out under the same condition as in figure, except the capping agent.

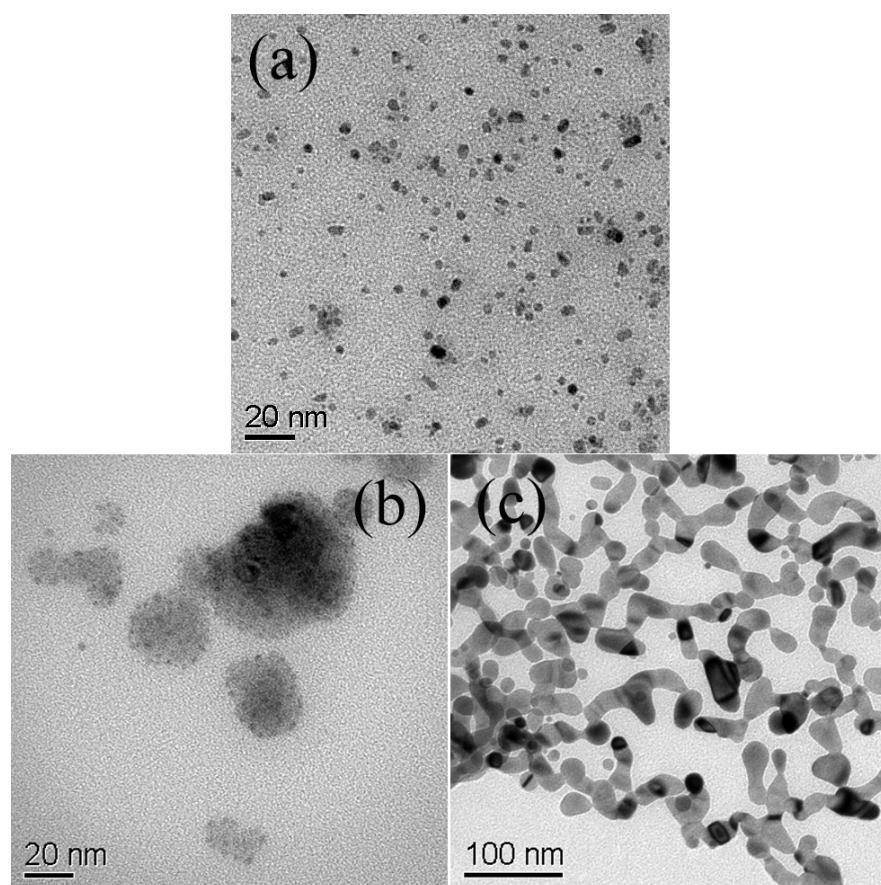


Figure S11. TEM images of Pd NCs produced at (a) 80 °C, (b) 140 °C and (c) 170 °C. All of the syntheses were carried out under the same condition as in figure, except the reaction temperature.

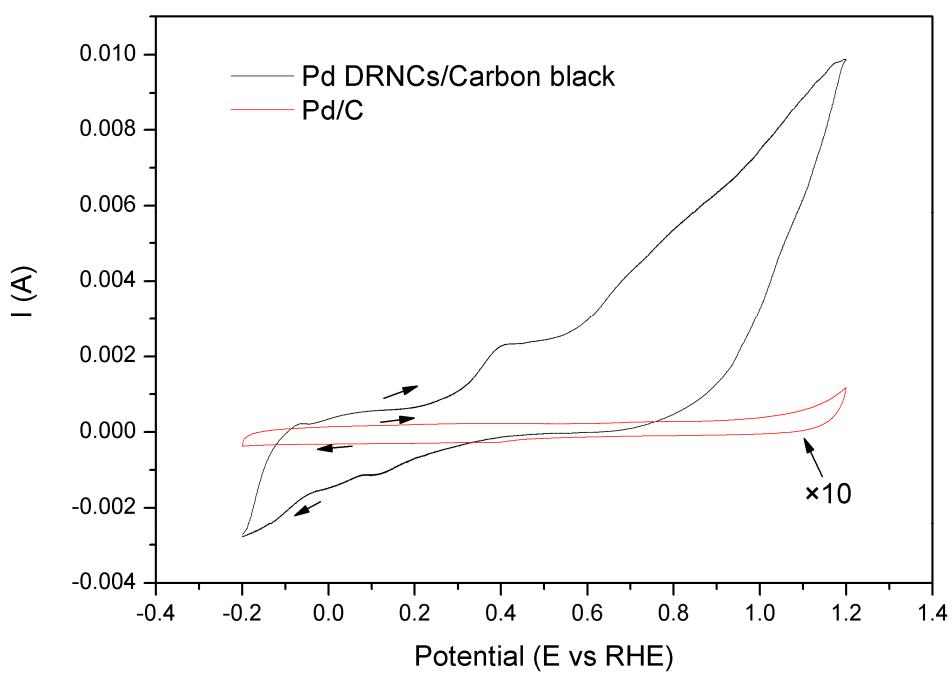


Figure S12. Electrocatalytic properties of Carbon black-loading Pd DRNCs and commercial Pd/C.