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Supporting Information

Activation of specific sites on cubic nanocrystals: a new pathway for controlled epitaxial growth towards catalytic applications

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Experimental Procedure:

Synthesis of Pd concave nanocubes (ref): We followed the method in literature (M. Jin, H. Zhang, Z. Xie and Y. Xia, *Angew. Chem. Int. Ed.*, 2011, **50**, 7850). In a standard procedure, 7.7 mL of an aqueous solution containing 105 mg PVP (M.W. ≈ 55.000), 60 mg L-ascorbic acid (AA) and 300 mg KBr, and 0.54 mg seeds of Pd nanocubes were mixed in a glass vial. The mixture was heated to 60 ºC in air under magnetic stirring. Meanwhile, 3.0 mL of an aqueous solution of K_2PdCl_4 (16 mg) was added to the mixture by pipette under magnetic stirring. The synthesis was allowed to proceed at 60 ºC for 3 h. Finally, the solution was centrifuged and washed three times with water to remove excess PVP before characterizations.

Synthesis of Cu nanocubes: We followed the method in literature (M. Jin, G. He, H. Zhang, J. Zeng, Z. Xie and Y. Xia, *Angew. Chem. Int. Ed.*, 2011, **50**, 10560). 21 mg $CuCl_2{\cdot}2H_2O$, 90 mg hexadecylamine (HDA), and 50 mg glucose were dissolved in 10 mL water in a 25-mL vial at room temperature. After the vial had been capped, the solution was magnetically stirred at room temperature overnight. The capped vial was then transferred into an oil bath and heated at 100 ºC for 6 h under magnetic stirring. The sample was washed with water at 60 ºC once to remove the excess HDA and glucose, and then dispersed into 10 mL water.

Synthesis of Cu-Pd nanocrystals: In a standard procedure, 6.0 mL of an aqueous solution containing 0.5 mL of oleylamine, 1.0 ml of HCl (2 M), 0.030 g of L-ascorbic acid, 3.5 mL of ethylene glycol and 1.0 mL of the Cu cube seeds were mixed in a glass vial. The mixture was heated to 80ºC in air under magnetic stirring for 5 min. Meanwhile, 1.0 mL of an aqueous solution of K_2PdCl_4 (3 mg) was added to the mixture by pipette under magnetic stirring. Heating of the reaction at 80 ºC was continued in air for 5 min. The samples were washed with acetone once and then with ethanol three times to remove most of the oleylamine and other molecules by centrifugation.

TEM characterizations: A drop of the aqueous suspension of particles was placed on a piece of carbon-coated copper grid and dried under ambient conditions. TEM images were taken on a JEOL JEM-2010 LaB6 high-resolution transmission electron microscope operated at 200 kV. HRTEM and STEM images and EDS mapping were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV.

Concentration measurements: Pd and Pd-Pt nanoparticles were dissolved with a mixture of HCl and HNO_3 (3:1, volume ratio) which was then diluted with 1% HNO_3. The concentrations of Pd and Pt were then measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS).

Zeta potential measurements: The zeta potentials of nanoparticles were measured using a Malvern Nano ZS dynamic light scattering (DLS) system.

Calculations for Atomic Numbers:

Calculations for the number of Pd atoms on the surface of a Pd concave nanocube: The atomic density of {730} planes is 3/7 of that of {100} planes. Considering a cube of 17 nm and 33 nm in edge length, the total surface areas of the cube are $(17\ nm)^2 \times 6 = 1.73 \times 10^3\ nm^2$ and $(33\ nm)^2 \times 6 = 6.53 \times 10^3\ nm^2$, respectively. The total numbers of Pd atoms on the {730} facets of a single concave nanocube are $(1.73 \times 10^3\ nm^2) / (0.151\ nm^2) \times 2 \times 3/7 = 9.81 \times 10^3$ and $(6.53 \times 10^3\ nm^2) / (0.151\ nm^2) \times 2 \times 3/7 = 3.71 \times 10^4$, respectively.

Calculations for the number of Pd atoms in a concave nanocube: The Pd concave nanocube can be considered as a cube with a truncated square pyramid excavated at the center of each side face. The volumes of a cube with an average size of 17 nm and 33 nm are $(17\ nm)^3 = 4.91 \times 10^3\ nm^3$ and $(33\ nm)^3 = 3.59 \times 10^4\ nm^3$, respectively. The volumes of a square pyramid are $1/3 \times (17\ nm)^2 \times (17/2 \times 3/7\ nm) = 3.51 \times 10^2\ nm^3$ and $1/3 \times (33\ nm)^2 \times (33/2 \times 3/7\ nm) = 2.57 \times 10^3\ nm^3$, respectively. As such, the volumes of a concave nanocube are $(4.91 \times 10^3\ nm^3) - [6 \times (3.51 \times 10^2\ nm^3)] = 2.80 \times 10^3\ nm^3$ and $(3.59 \times 10^4\ nm^3) - [6 \times (2.57 \times 10^3\ nm^3)] = 2.05 \times 10^4\ nm^3$, respectively. The numbers of Pd atoms contained in a single Pd concave nanocube are $(2.80 \times 10^3\ nm^3) / (0.0589\ nm^3) \times 4 = 1.90 \times 10^5$ and $(2.05 \times 10^4\ nm^3) / (0.0589\ nm^3) \times 4 = 1.39 \times 10^6$, respectively.

Calculations for the percentage of surface Pd atoms in a concave nanocube: The percentages of surface Pd atoms in a concave nanocube with an average size of 17 nm and 33 nm are $(9.81 \times 10^3) / (1.90 \times 10^5) = 5.16\%$ and $(3.71 \times 10^4) / (1.39 \times 10^6) = 2.66\%$, respectively.

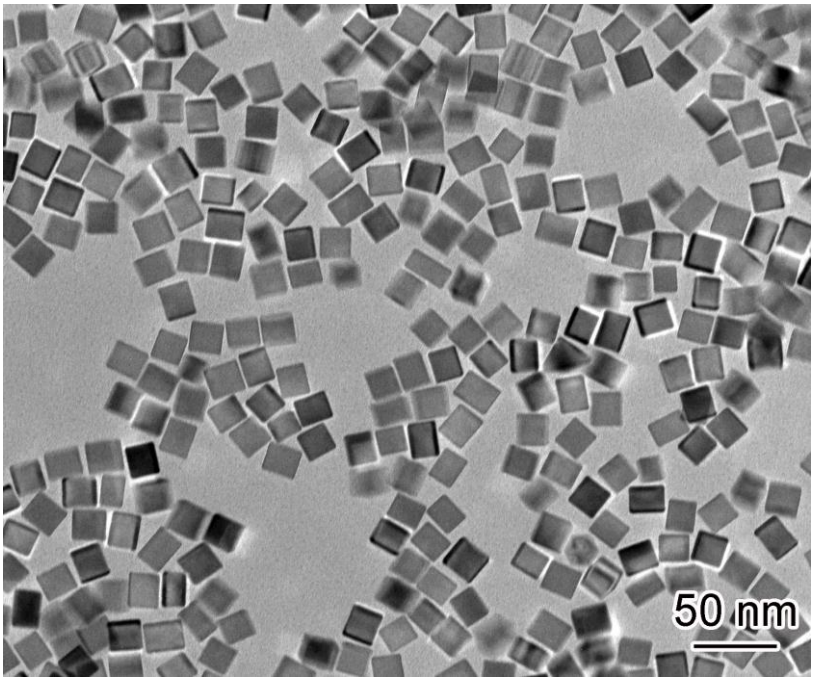

Fig. S1. TEM image of the sample in Fig. 1a.

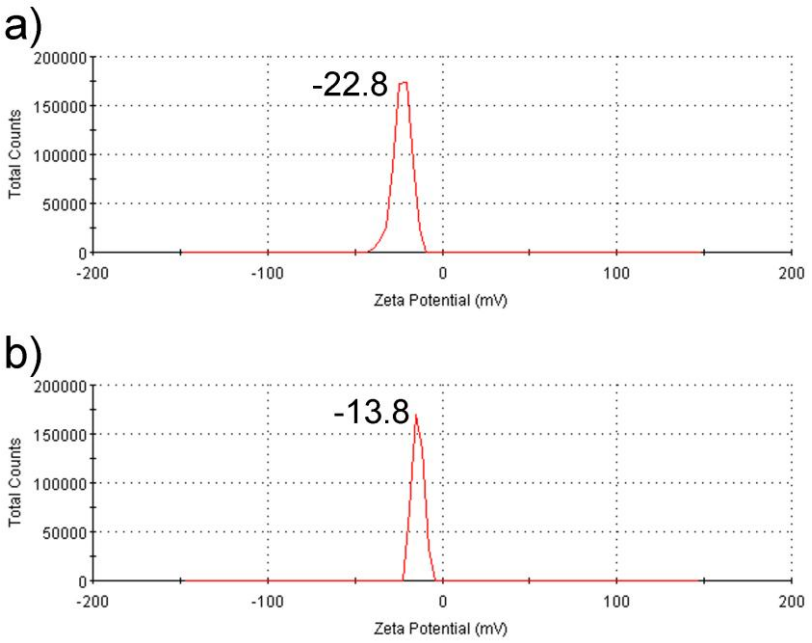

Fig. S2. Zeta potentials of the samples in a) Fig. 1a and b) Fig. 1c.

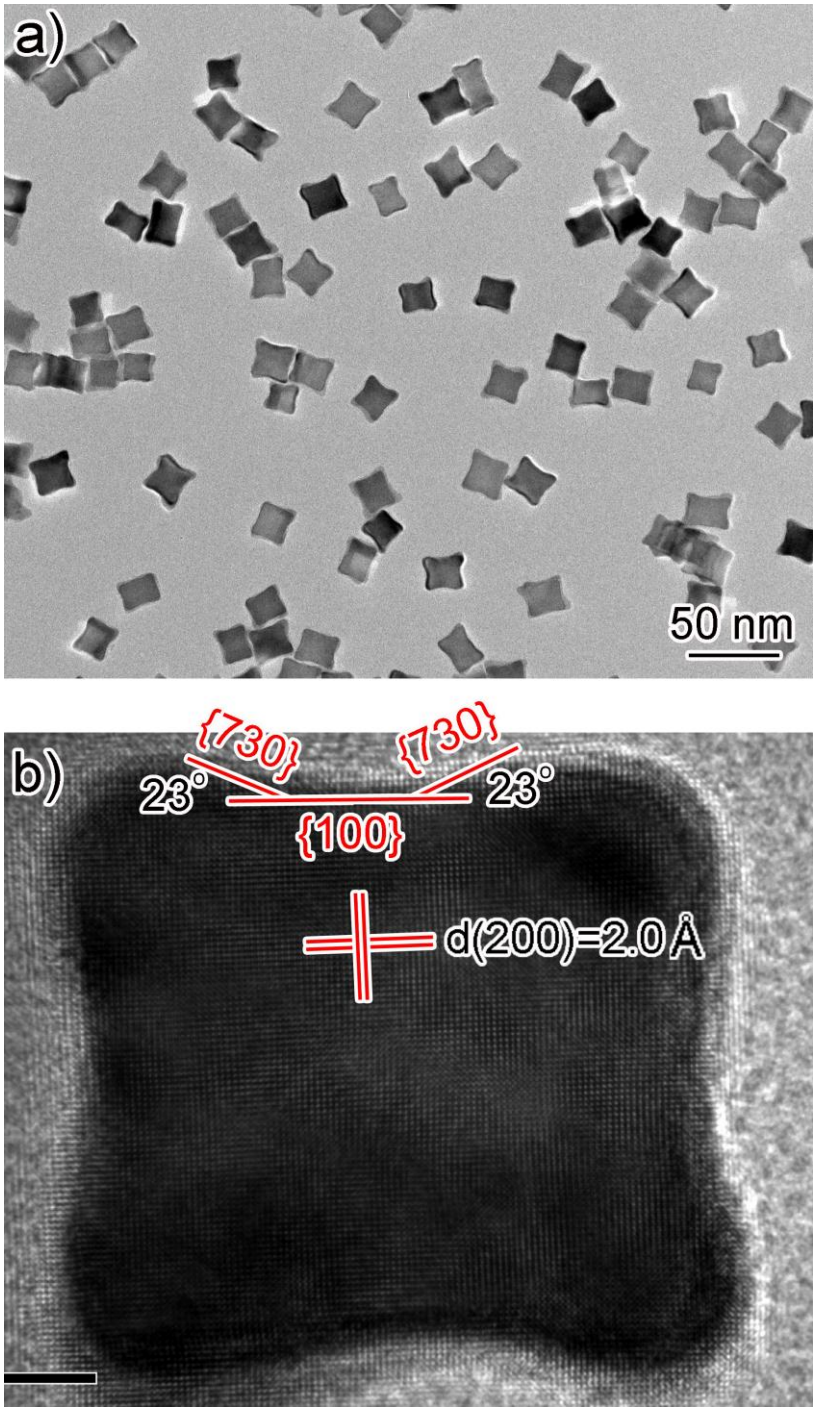

Fig. S3. a) TEM image and b) HRTEM image of the sample in Fig. 1e.

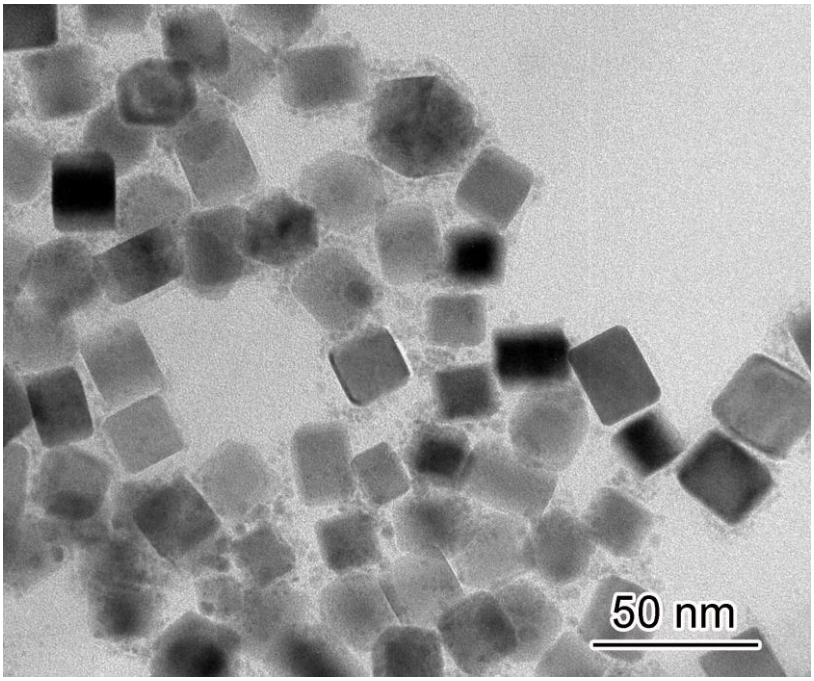

Fig. S4. TEM image of the sample prepared under the same condition as that in Fig. 1e, except the use of HNO_3 instead of HCl.

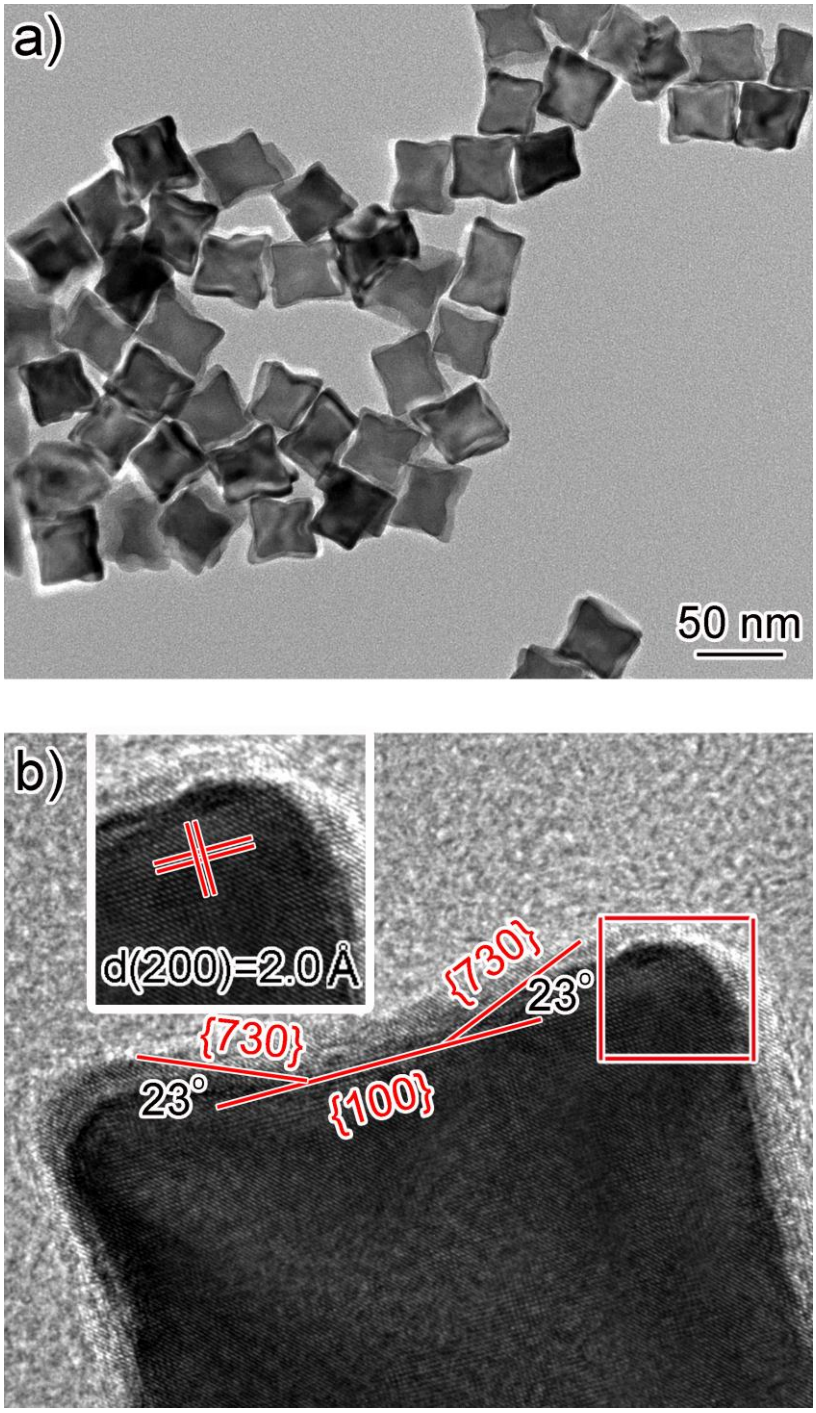

Fig. S5. a) TEM image and b) HRTEM image of the Pd concave nanocubes prepared by following the method in literature (M. Jin, H. Zhang, Z. Xie, Y. Xia, *Angew. Chem. Int. Ed.* **2011**, *50*, 7850).

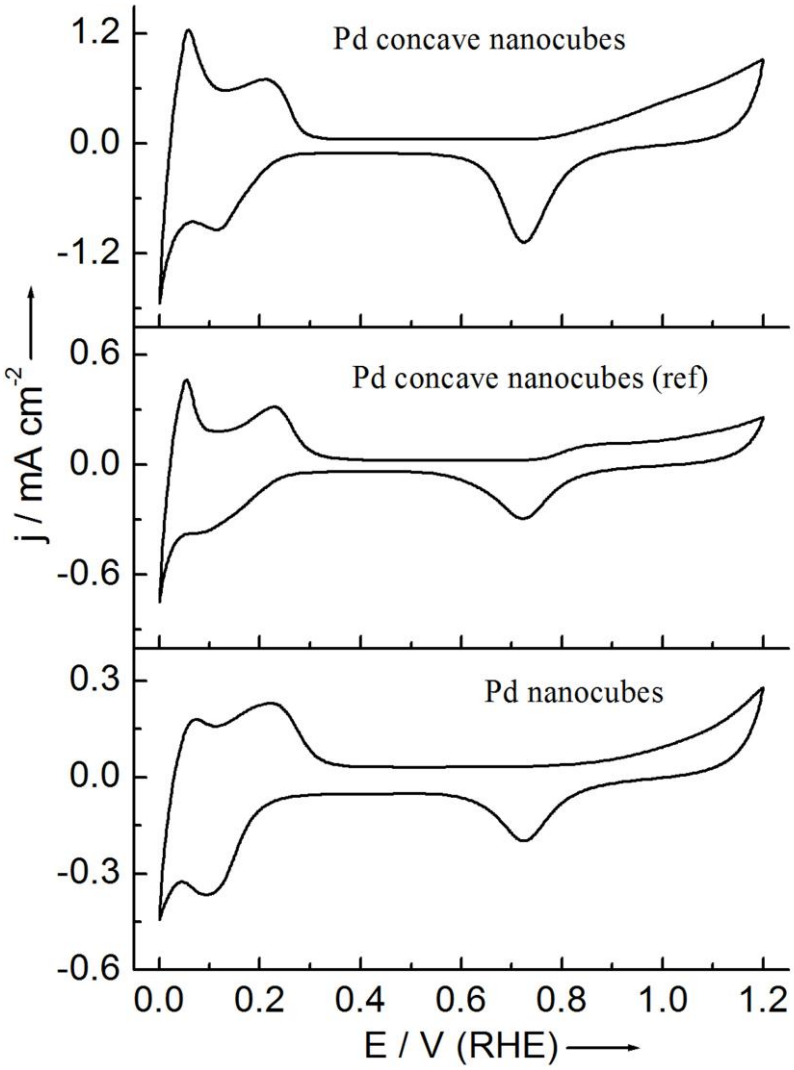

Fig. S6. Cyclic voltammograms of electrodes composed of Pd concave nanocubes that were prepared by our method and the method in literature (M. Jin, H. Zhang, Z. Xie, Y. Xia, *Angew. Chem. Int. Ed.* **2011**, *50*, 7850) and Pd nanocubes, respectively, in 0.5 M H_2SO_4 solution at a scan rate of 50 mV/s.

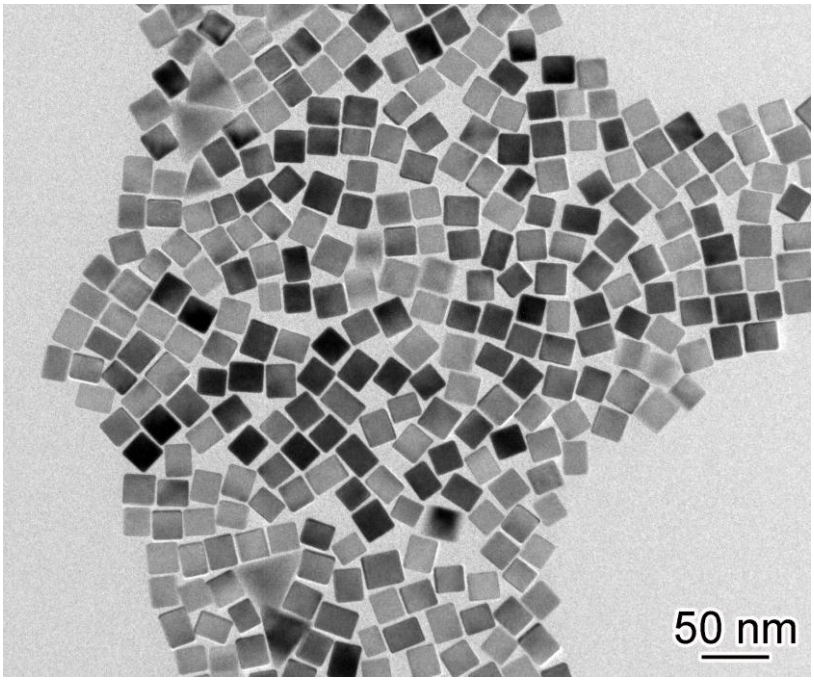

Fig. S7. TEM image of the Pd nanocube seeds used for Pt epitaxial growth.

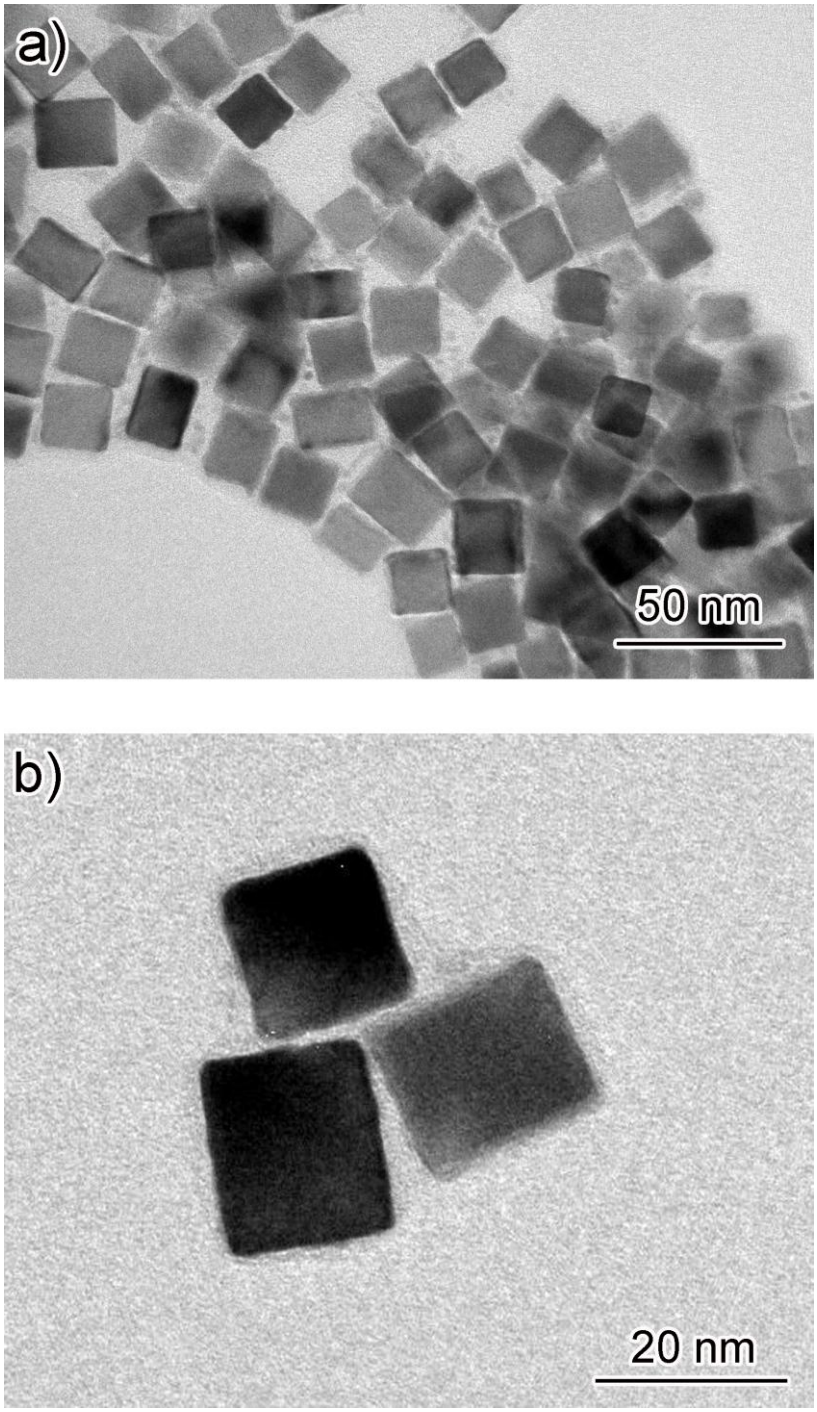

Fig. S8. TEM images of the Pd-Pt sample prepared by recycling the stock solution of K_2PtCl_6 from a completed synthesis.

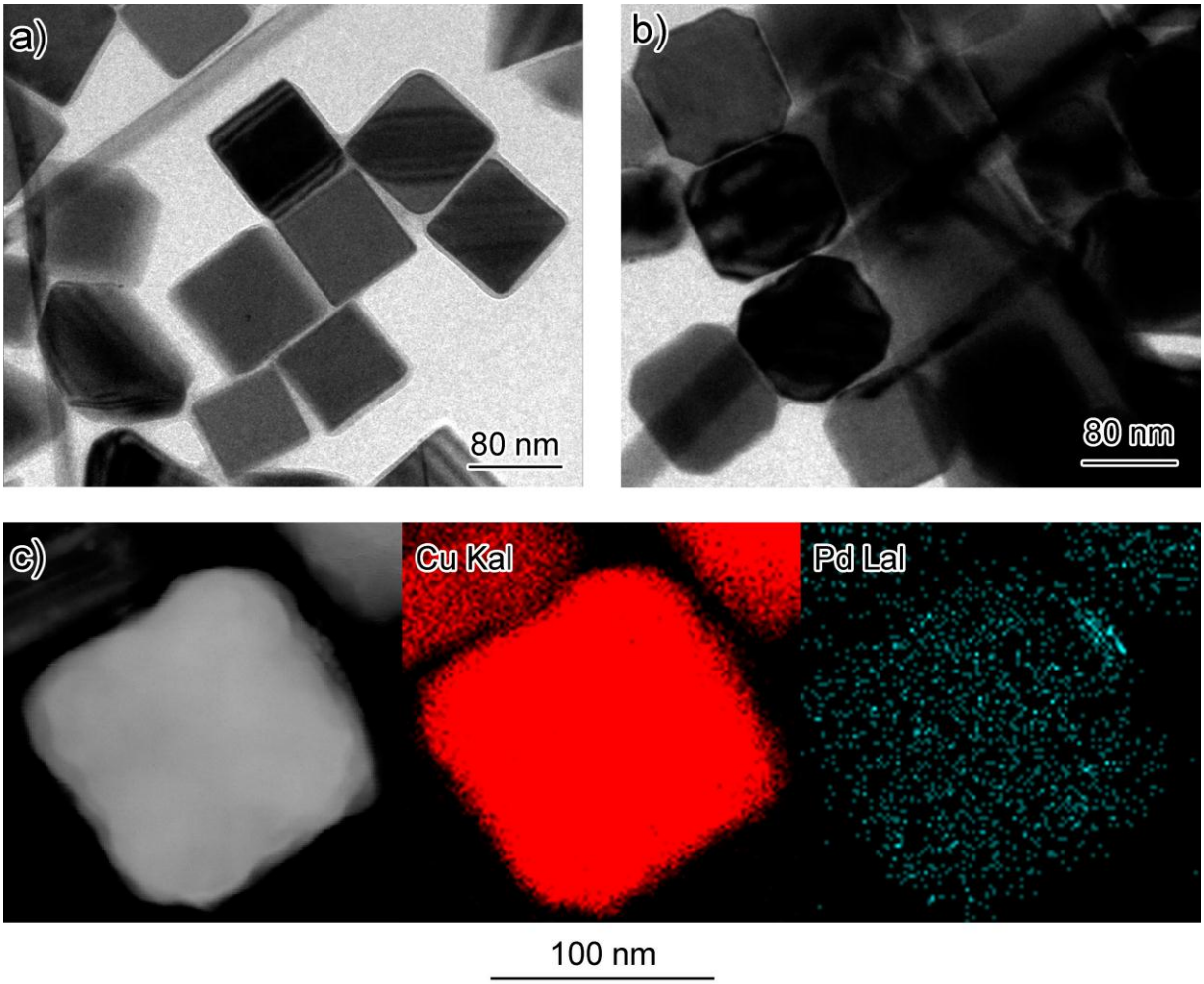

Fig. S9. TEM images of a) the seeds of Cu nanocubes; b) the Cu-Pd nanocrystals obtained by oleylamine capping and HCl activation. c) shows an EDS mapping profiles of Cu-Pd nanocrystals indicating the existence of Pd.