Electronic Supplementary Information

One pot synthesis of nanoscale phase-segregated PdPt nanoarchitectures via unusual Pt-doping induced structural reorganization of Pd nanosheet into PdPt nanotent

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Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology and a JEOL ARM200F Cs STEM.

Experimental Section

Preparation of Pd nanosheet.

A slurry of $Pd(acac)_2$ (0.005 mmol, Aldrich, 99 %) and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 ^{o}C and then evacuated for 10 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 100 ^{o}C, and kept at that temperature for 90 min under 1 atm CO. Finally, grey precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/25 mL).

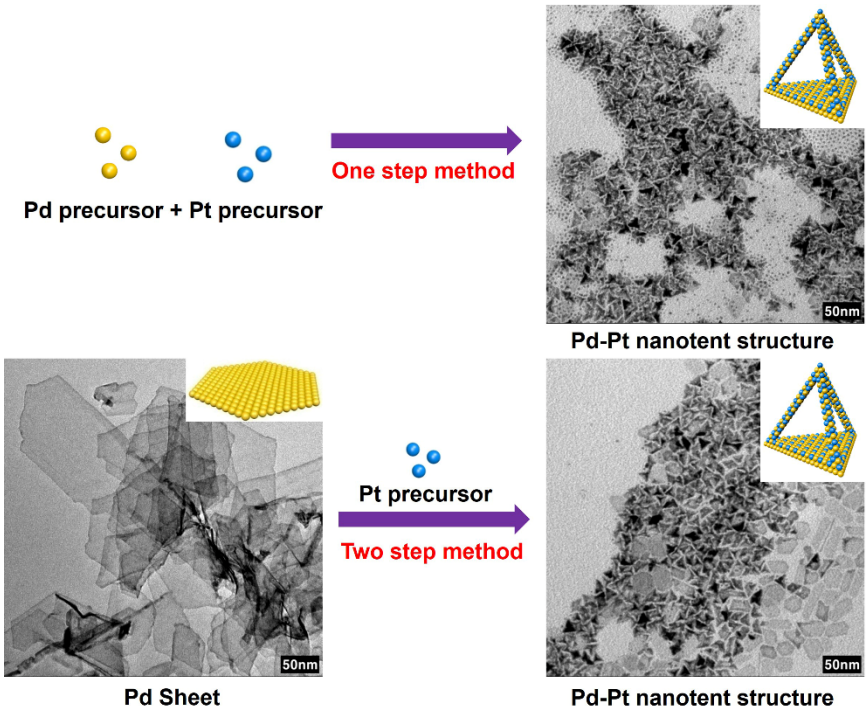
One step preparation of PdPt nanotent structure.

A slurry of $Pd(acac)_2$ (0.005 mmol, Aldrich, 99 %), $Pt(acac)_2$ (0.08 mmol, Aldrich, 97%), and octadecylamine (15 mmol, Aldrich, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring. The tube, placed in the oil bath, was heated

to 78 °C and evacuated for 10 min with a magnetic stirring, and finally purged with CO gas. Resulting reaction mixture was heated up to 100 °C, and kept at that temperature for 90 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/25 mL).

Preparation of PdPt nanotent structure from reaction of Pd nanosheet and $Pt(acac)_2$.

Pd nanosheets (1.5 mg) were dispersed in a mixture of $Pt(acac)_2$ (0.08 mmol, Aldrich, 97%) and octadecylamine (15 mmol, Aldrich, 90%) in a Schlenk tube (100 mL) with a magnetic stirring. The tube, placed in the oil bath, was heated to 78 °C and evacuated for 10 min with a magnetic stirring, and finally purged with CO gas. Resulting solution was heated up to 100 °C, and kept at that temperature for 90 min under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/25 mL).



Preparation of Pt popped out PdPt nanostructure.

Stearic acid (0.01 mmol, Aldrich, 95%) was added to the reaction mixture. And then, the tube, placed in the oil bath, was heated to 78 °C and evacuated for 10 min with a magnetic stirring, and finally purged with CO gas. Resulting solution was heated up to 160 °C, and kept at that temperature for 6 h with a magnetic stirring. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/25 mL).

Preparation of Pt overgrown PdPt nanostructure.

Stearic acid (0.01 mmol, Aldrich, 95%) was added to the reaction mixture. And then, the tube, placed in the oil bath, was heated to 78 ^{o}C and evacuated for 10 min with a magnetic stirring, and finally purged with Ar gas. Resulting solution was heated up to 160 ^{o}C, and kept at that temperature for 12 h with a magnetic stirring. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/25 mL).

Fig. S1 TEM images of a) {111}Pd nanosheets and b) {100}Pt nanocubes formed respectively from $Pd(acac)_2$ only and $Pt(acac)_2$ only reaction conditions.

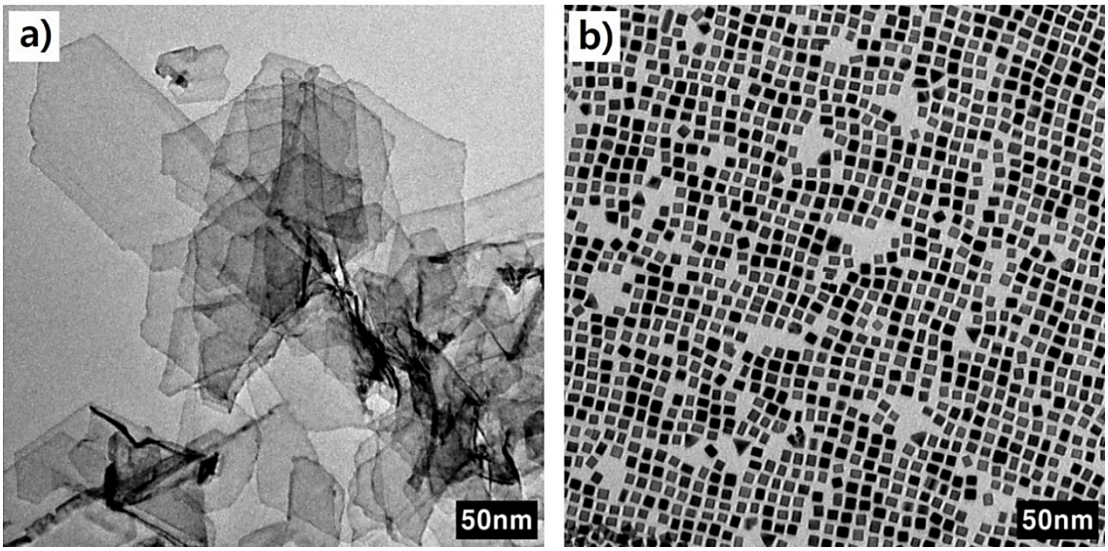


Fig. S2 a-c) STEM images of PdPt nanotent structures recorded at different tilting angles. d) HRTEM image of PdPt nanotent structure. The yellow arrows indicate the existence of basal nanosheet. Also, the HRTEM image clearly demonstrates the unexcavated nature of basal nanoplate. Instead of being excavated, the basal nanoplate seems to be edge-ruptured in certain cases.

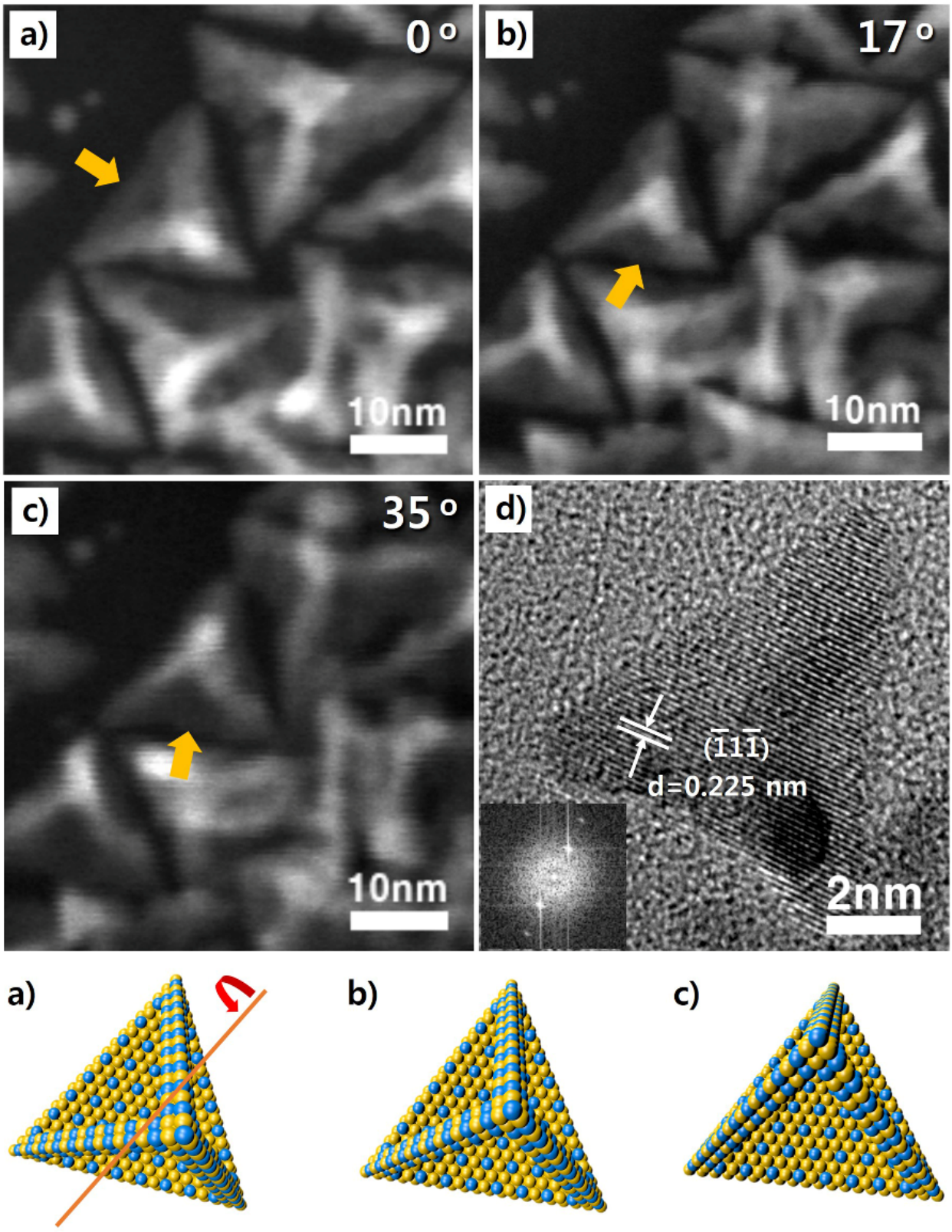


Fig. S3 HAADF STEM images and element profiles along with the red line of PdPt nanotent, partially Pt filled PdPt nanotent, and Pt overcoated PdPt nanotent. The alloy composition of the PdPt mainframe is seen in all three structures.

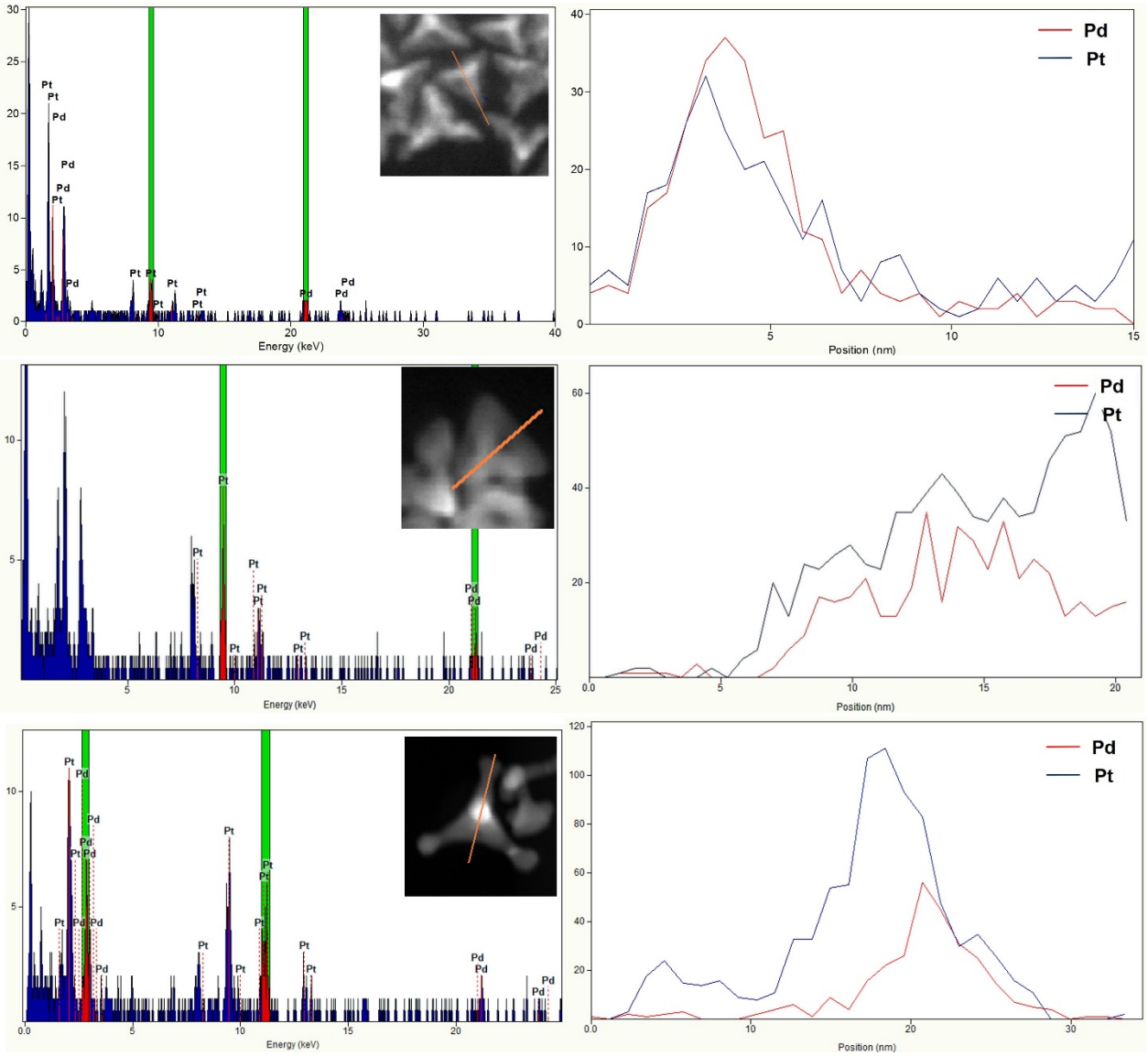


Fig. S4 Energy dispersive X-ray spectrum of a PdPt alloy nanotent structure, Pt popped out PdPt nanostructure, and Pt overgrown PdPt nanostructure.

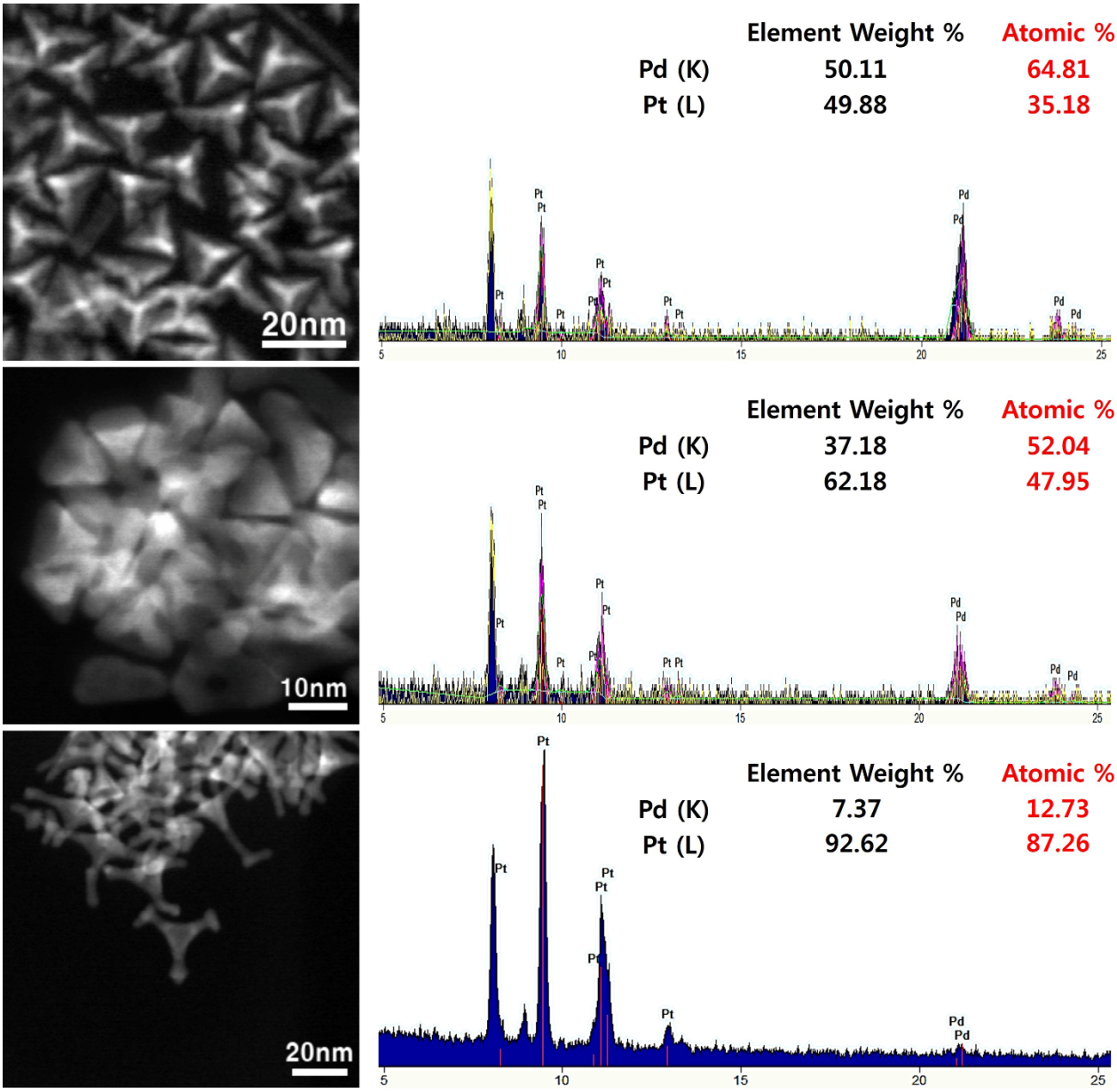


Fig. S5 a) TEM image and b) STEM image of small PdPt alloy nanosheets. Bright spots indicate the genesis of small 3D structures on 2D structures. c) HAADF-STEM image and corresponding elemental mapping data. The scale bars are 40 nm.

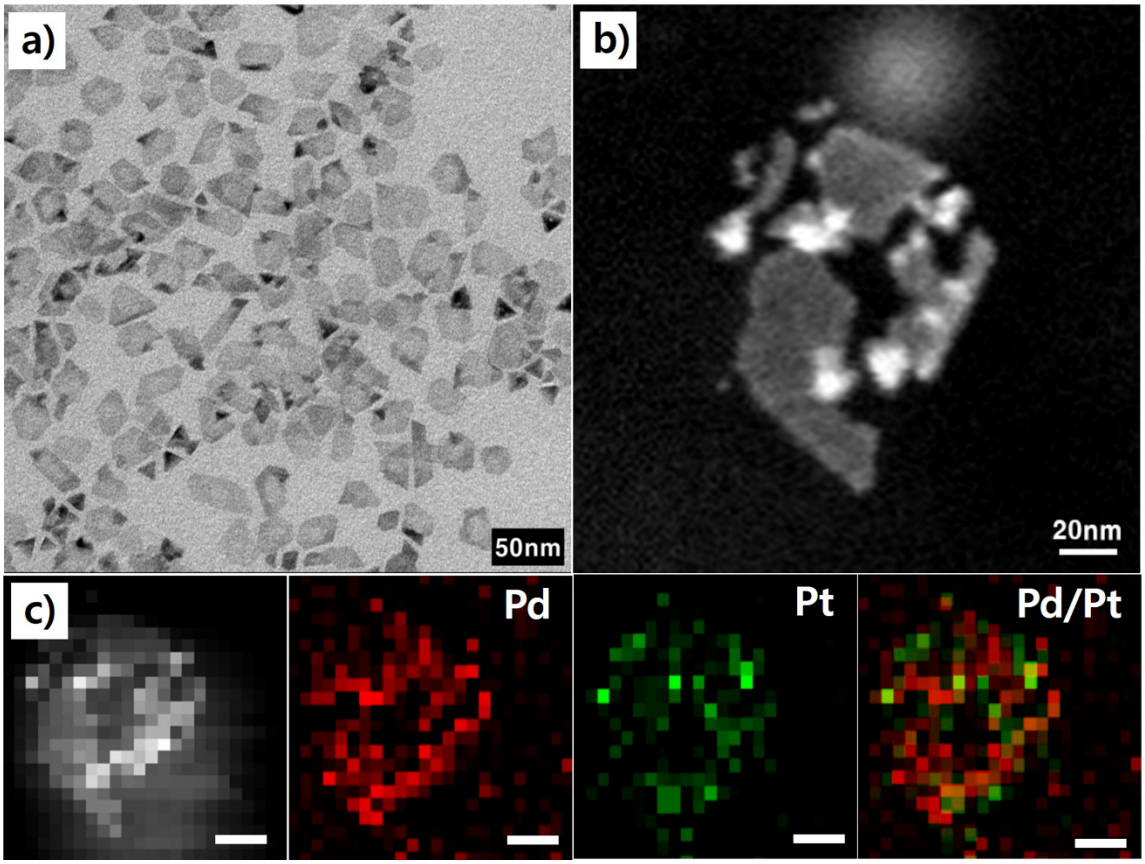


Fig. S6 TEM image of products from thermal decomposition of $Pt(acac)_2$ and $Pd(acac)_2$ at high temperature of 200 ^oC under CO. Separate formation of Pd nanosheet and Pt nanocube is obvious.

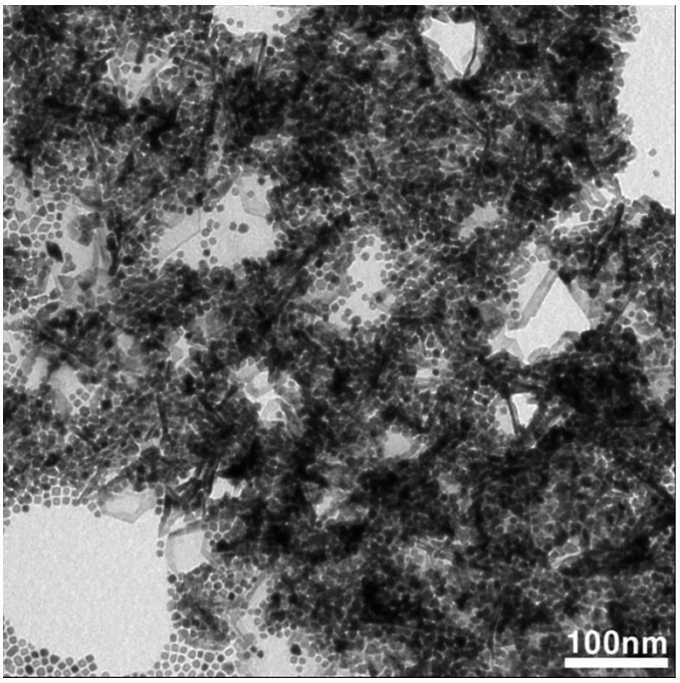
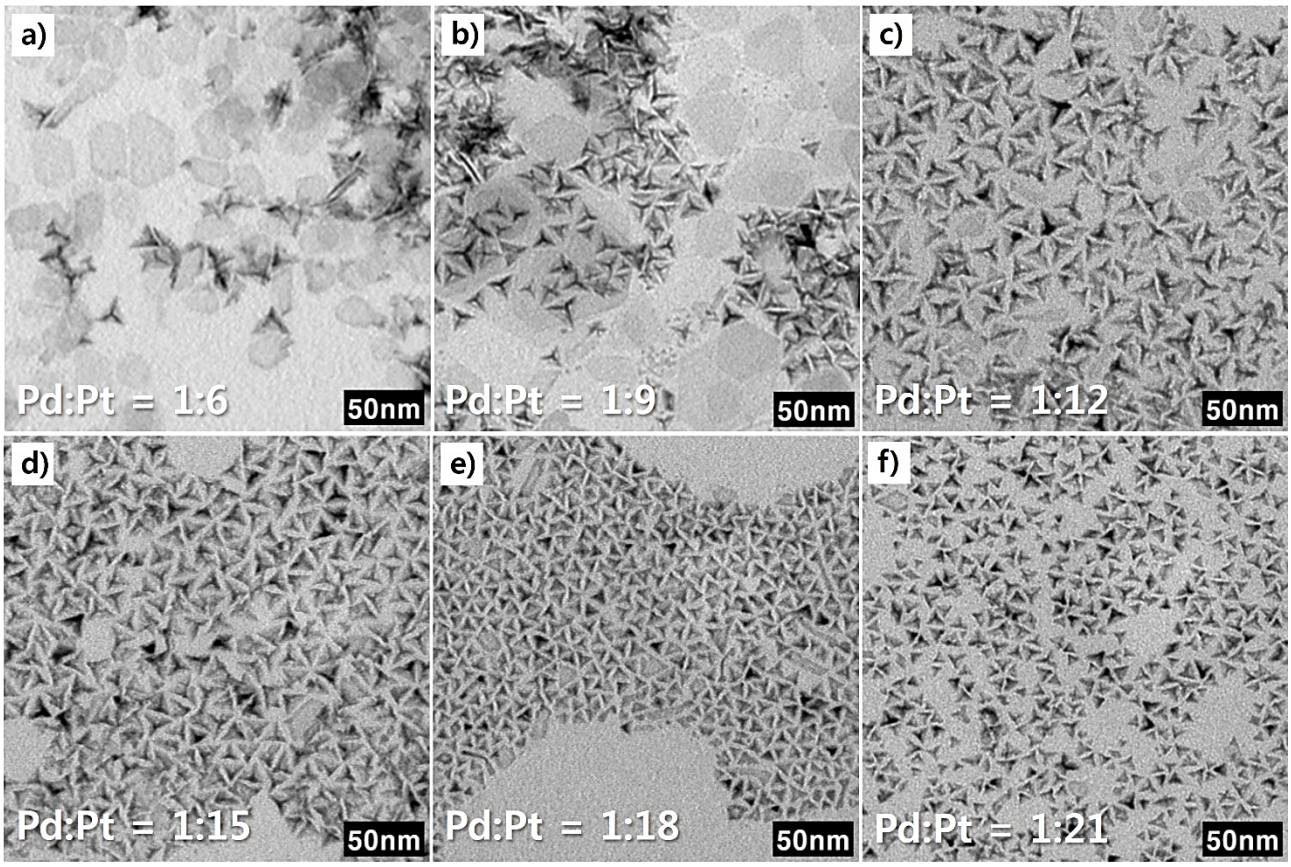


Fig. S7 TEM images of Pt/Pd ratio dependent structural evolution of PdPt nanostructures. The amount of formed PdPt nanosheet decreases as Pt/Pd ratio increases.



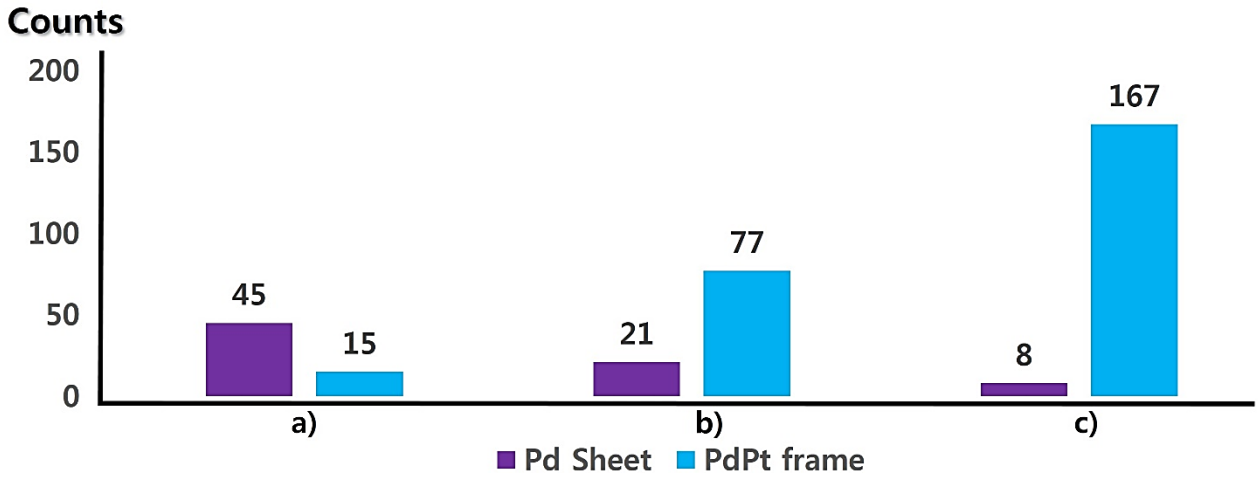


Fig. S8 a) TEM image and b) HRTEM image of the intermediate PdPt nanotent structure with partial Pt filling. c) HAADF-STEM image and elemental mapping data. The scale bars are 5 nm.

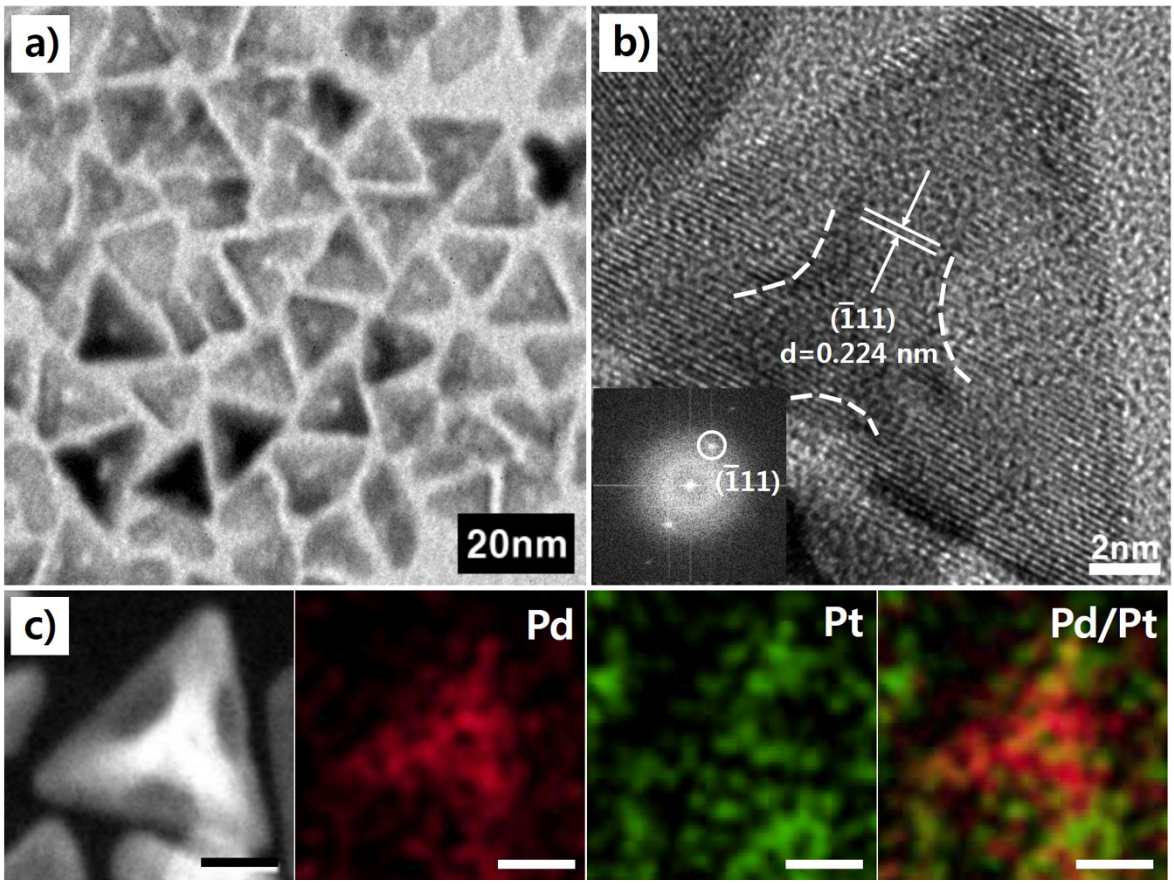


Fig. S9 HRTEM images of a PdPt nanotent structure completely filled with Pt, which is found as a minor product from a reaction described in Fig. 3a.

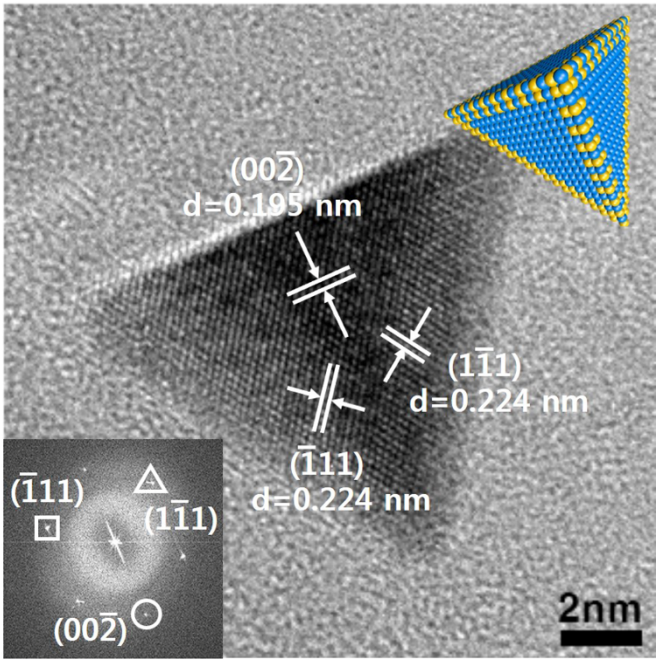


Fig. S10 Temporal TEM images of Pt popped out PdPt nanotent structure (a,b,c) and Pt overgrown PdPt nanotent structure (d,e,f). Formation of Pt overgrown PdPt nanotent structures is slow because the reduction is not assisted by CO.