Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

The shape evolution from Pt_xCo_y@Co cubes to Pt_xCo_y multicubes for selective hydrogenation of α,β-unsaturated aldehyde

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Experimental

Materials

All chemicals were used as received from Aladdin unless specified. These include platinum acetylacetonate ($Pt(acac)_2$, 97%), cobalt acetylacetonate ($Co(acac)_2$, 97%), oleylamine (OAm, 80-90%), oleic acid (OA, 85%), cinnamaldehyde (CMA, 99%), dodecane (99%), chloroform (99%), ethanol (99%), platinum carbon catalyst (Pt/C, Pt wt.% = 5%), and carbon black (Vulcan XC-72).

Preparation of nanocrystals

Pt_xCo_y@Co cubes: In a typical process, under an argon atmosphere, 6.7 mg $Pt(acac)_2$ and 13.4 mg $Co(acac)_2$ were dissolved in 8 mL OAm and 2 mL OA in 130°C oil bath for 5 min, then directly dipped into oil bath which was preheated to 225°C and stirred at 225°C for 5 min, then a CO flow was applied into bottle with a flow (~190 mL/min) for 30 min. The dispersion was then cooled down to room temperature, washed and separated by dispersing the reaction mixture in 2 mL chroloform and 10 mL ethanol, followed by centrifugation at 5000 rpm for 5 min. This procedure was repeated three times to get rid of the excess reactants and capping agents. The final products were dispersed in chloroform or dried in vacuum at 60°C for further characterization and use.

Pt_xCo_y multicubes: In a typical process, under an argon atmosphere, 2.0 mg Pt_xCo_y@Co cubes and 6.7 mg $Pt(acac)_2$ and were dispersed in 9 mL OAm and 1 mL OA in 130°C oil bath for 5 min, then directly dipped into oil bath which was preheated to 210°C and simultaneously a CO flow was applied into bottle. The dispersion was stirred with a CO flow (~190 mL/min) at 210°C for 15 min, then cooled down to room temperature, washed and separated by dispersing the reaction mixture in 2 mL chroloform and 10 mL ethanol, followed by centrifugation at 5000 rpm for 5 min. This procedure was repeated three times to get rid of the excess reactants and capping agents. The final products were dispersed in chloroform or dried in vacuum at 60°C for further characterization and use.

Pt nanocubes: In a typical process, under an argon atmosphere, 20 mg $Pt(acac)_2$ were dispersed in 9 mL OAm and 1 mL OA in 130°C oil bath for 5 min, then directly dipped into oil bath which was preheated to 210°C and simultaneously a CO flow was applied into bottle. The dispersion was stirred with a CO flow (~190 mL/min) at 210°C for 30 min, then cooled down to room temperature, washed and separated by dispersing the reaction mixture in 2 mL chroloform and 10 mL ethanol, followed by centrifugation at 5000 rpm for 5 min. The final products were dispersed in chloroform or dried in vacuum at 60°C for further characterization and use

Carbon-Supported Catalysts

5 mg carbon black particles and 2 mg nanocrystals were dispersed in ethanol and sonicated for 30 min respectively, then the two dispersions were mixed and sonicated for 30 min. The resultant solids were precipitated out by centrifugation and dried under a stream of argon gas.

Cinnamaldehyde hydrogenation

The liquid-phase hydrogenation of cinnamaldehyde was carried out in a well-stirred pressure vessel (100 mL). 7 mg carbon-supported catalysts or 12 mg Pt/C (note: Pt content was similar in these catalysts) were dispersed in 35 mL ethanol by sonication, and then transferred into a pressure vessel. 100 μL CMA and 100 μL dodecane was added. H_2 flow was applied into the bottle to blow air away for several minutes in order to remove any trace of oxygen. The temperature was then raised to 60°C and the vessel was pressurized by 2 MPa H_2. Products were withdrawn at regular intervals, filtered and analyzed by a gas chromatography.

Characterization of catalysts

The transmission electron microscopy (TEM) including high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectrum (EDS) and selected-area electron diffractions (SAED) studies were performed on a FEI TECNAI G2 F20 STWIN transmission electron microscope at an operating voltage of 200 kV, equipped with a Gatan Orius CCD camera. Samples were prepared by dropping chloroform dispersion of samples onto 300-mesh carbon-coated copper grids and slowly evaporating the solvent. The X-ray photoelectron spectroscopies (XPS) of the samples were recorded on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. The catalytic products were analyzed by a gas chromatograph (Agilent Technologies: GC 7890A/MSD 5975C).

Supporting Figures

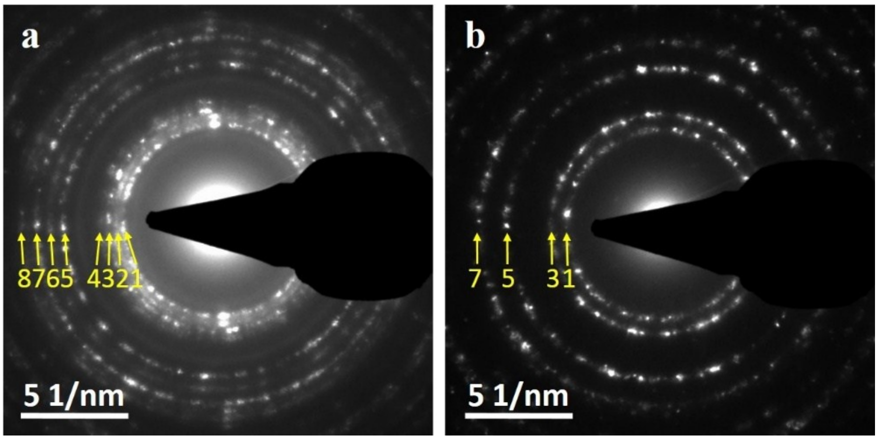

Figure S1. Selected-area electron diffractions (SAED) of (a) Pt_1Co_2@Co cubes and (b) Pt_2Co_1 multicubes. (1,3,5,7 correspond to electron diffraction pattern of *fcc* Pt-Co alloy {111} {200} {220} {311} planes; 2,4,6,8 correspond to electron diffraction pattern of *fcc* Co {111} {200} {220} {311} planes, respectively.)

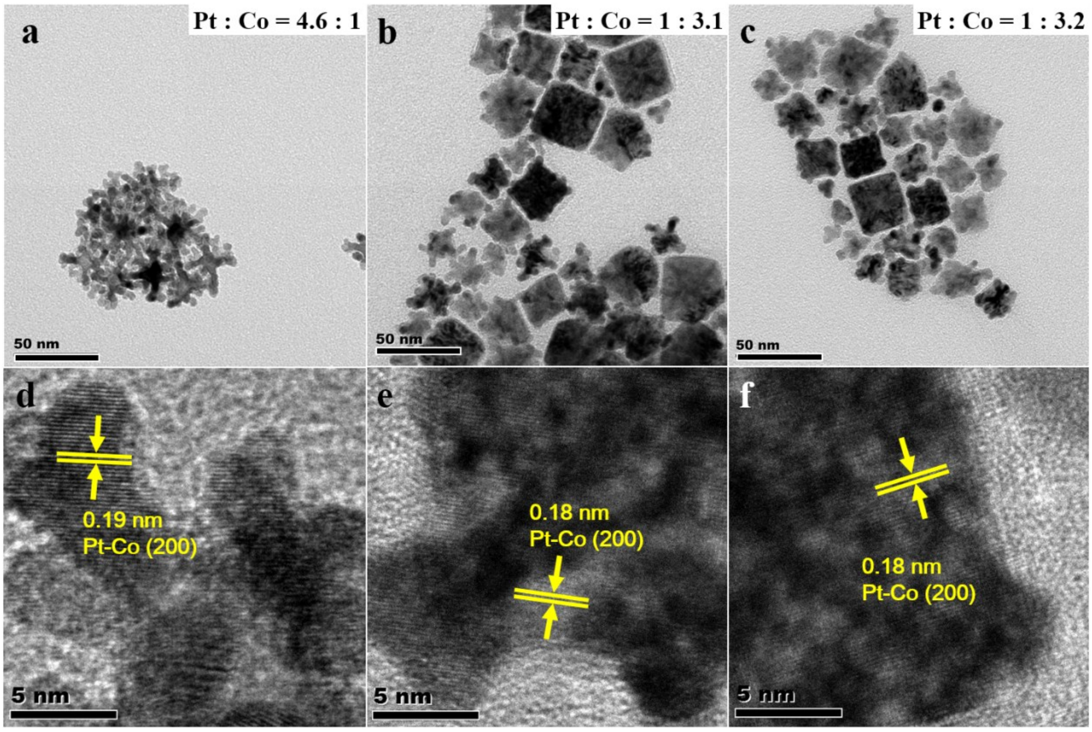

Figure S2. TEM and HRTEM images of Pt-Co nanocrystals as-synthesized without CO introduction under otherwise identical experimental condition of Pt_xCo_y@Co cubes. Reaction time was: (a, d) 5 min, (d, e) 30 min, and (c, f) 60 min.

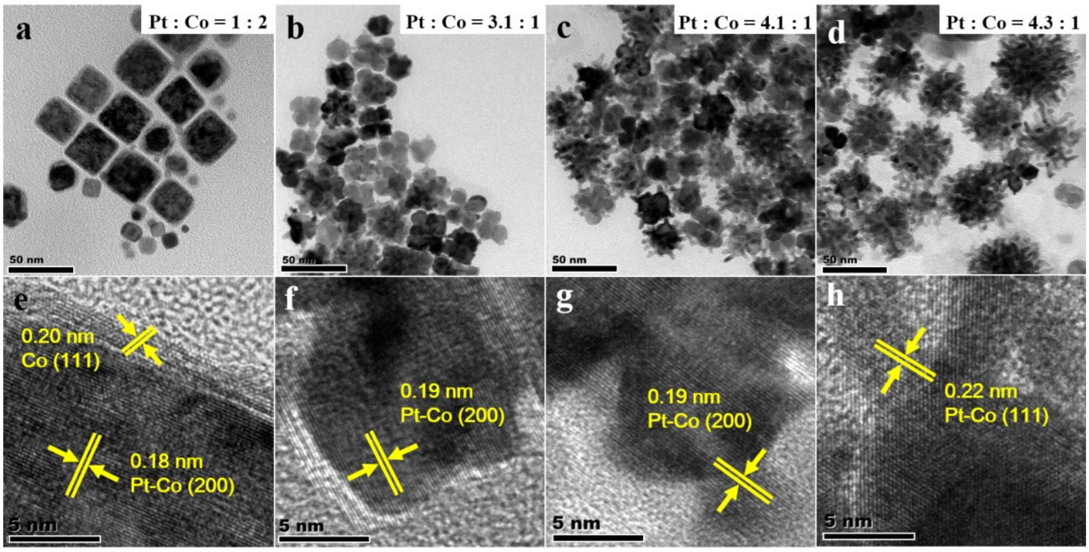

Figure S3. TEM and HRTEM images of Pt-Co nanocrystals as-synthesized without CO introduction under otherwise identical experimental condition of Pt_xCo_y multicubes. Reaction time was: (a, e) 0 min, (b, f) 5 min, (c, g) 15 min, and (d, h) 30 min.

If no CO was introduced into the synthetical system of core-shell structure, the mixture of Pt_xCo_y nanocubes and Pt_xCo_y multipods would be formed, as shown in Figure S2. In the absence of CO in the synthetical system of multicubes, Pt-Co nanodendrites rather than multicubes would be created in Figure S3. The observation reveals that CO has an impact on the synthesis of high-quality Pt-based nanocubes, due to the strong binding of CO on the surface of Pt to promote the formation of cubic morphology.[1,2] One question remains unanswered in this work, namely how CO controls the precisely defined structure of Pt_xCo_y nanocrystals under the reaction conditions. Further work in this area is required to gain deep insight into the role of CO in the formation of well-faceted Pt-based nanocrystals.

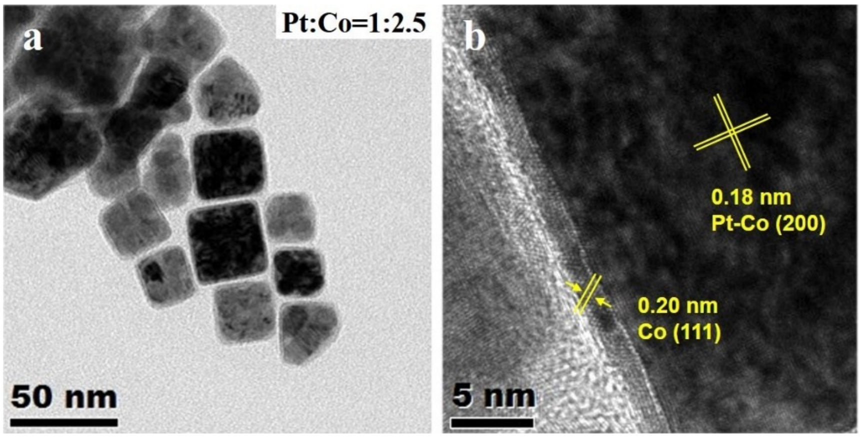

Figure S4. (a) TEM image of Pt_xCo_y@Co cubes obtained at 35 min, and inset is the atom ratio of Pt to Co. (b) the corresponding HRETM image.

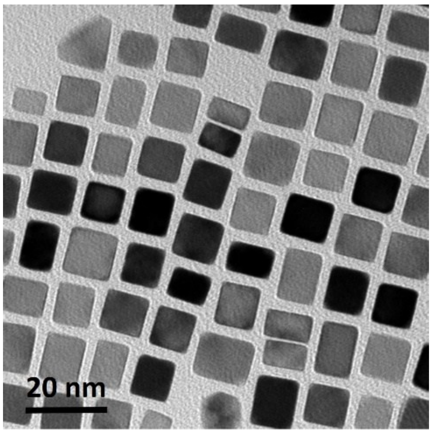

Figure S5. TEM image of pure Pt nanocubes.

Reference:

1. M. Chen, B. H. Wu, J. Yang, and N. F. Zheng, *Adv. Mater.* 2012, **24**, 862-879.
2. C. Wang, H. Daimon, Y. Lee, J. Kim, S. H. Sun, *J. Am. Chem. Soc.* 2007, **129**, 6974–6975.