Electronic Supplementary Information for

## Pd@Rh Core-Shell Nanocrystals with Well-Defined Facets and Their Enhanced Catalytic Performance towards CO Oxidation

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\*Corresponding authors: frank.tsung@bc.edu (C.K.T. for CO oxidation measurements); younan.xia@bme.gatech.edu (Y.X. for synthesis and characterization) **Table S1.** The average number (n) of Rh atomic layers calculated from the ICP–MS data for the Pd and Rh contents in the Pd@Rh core-shell nanocrystals, the weight percentage (wt%) of Rh obtained from the ICP–MS data, and the wt% of Rh derived from the average number of Rh atomic layers and the size of the Pd seeds such as octahedra and cubes.

Samples	Average number of Rh atomic layers (n)	wt% of Rh obtained from the ICP–MS data	wt% of Rh calculated from the value of n
Pd@Rh octahedra	2.1	42.2	39.8 (n=2)
Pd@Rh cubes	2.9	36.6	37.8 (n=3)



**Fig. S1** TEM images of (A) Pd octahedra and (B) Pd cubes with average edge lengths of 6.4 and 7.2 nm, respectively, which served as seeds for the overgrowth of Rh.



**Fig. S2** TEM image of Pd@Rh core-shell octahedra at a relatively low magnification to show uniformity in both size and shape.



Fig. S3 TEM image of a product containing both Pd@Rh core-shell octahedra and small Rh nanocrystals when a larger volume (81  $\mu$ L) of Rh(OAc)<sub>3</sub> solution was used while all other conditions were kept the same as the standard protocol.



**Fig. S4** TEM images of Pd@Rh core-shell octahedra prepared using different Rh precursors, including (A) RhCl<sub>3</sub>, (B) Rh(NO<sub>3</sub>)<sub>3</sub>, and (C, D) Rh(acac)<sub>3</sub>, respectively, using a protocol similar to what was used for the Pd@Rh octahedra shown in Fig. 1.



**—** 10 nm

**Fig. S5** TEM images of (A) Pd cubes and (B) Pd cuboctahedra. TEM images of Pd@Rh octahedra grown from the (C) cubic and (D) cuboctahedral, respectively, seeds of Pd, with a protocol similar to what was used for the Pd@Rh octahedra shown in Fig. 1.



**Fig. S6** Arrhenius plots for determining the ignition temperatures (ITs) of CO oxidation for (A) octahedral Pd@Rh/SBA15, (B) cubic Pd@Rh/SBA15 (C) cubic Rh/SBA15, and (D) Rh/C. The trend line analysis displays percentage conversion as a function of the reciprocal of temperature in Kelvin. (E) IT of CO oxidation for Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, which was supposed to be at 160 °C.



**Fig. S7** TEM and high-resolution TEM images of (A, B) Pd@Rh/SBA15 octahedra and (C, D) Pd@Rh/SBA15 cubes after going through the catalytic CO oxidation reaction.