Supporting Information for

Controlling the Deposition of Pd on Au Nanocages: Outer Surface Only *versus* Both Outer and Inner Surfaces

Miaoxin Yang,[†,⊥] Wenxia Wang,[‡,§,⊥] Kyle D. Gilroy,[‡] and Younan Xia[*,†,‡]

[†]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]The Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, Georgia 30332, United States

[§]School of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, Guangdong, P. R. China

[*]Corresponding author: younan.xia@bme.gatech.edu

EXPERIMENTAL SECTION

Chemicals and Materials. *L*-ascorbic acid (AA, >99.0%), sodium hydroxide (NaOH, >98%), poly(vinyl pyrrolidone) (PVP, $M_W \approx 29{,}000$), hydrogen peroxide (H_2O_2, 30% in H_2O), potassium bromide (KBr, >99.0%), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, >99.9%), potassium tetrachloropalladate (K_2PdCl_4, >99.99%), and potassium tetrabromopalladate (K_2PdBr_4) were all obtained from Sigma-Aldrich (St. Louis, MO). All chemicals were used as received. Deionized (DI) water with a resistivity of 18.2 MΩ·cm at room temperature was used throughout the experiments.

Synthesis of Au Nanocages to Be Used as the Seeds. The Au nanocages with an average edge length of 37 nm were prepared by following a previously reported method.[1] In a typical synthesis, 2 mL of aqueous PVP (1 mM) was placed in a 20-mL vial, followed by the introduction of 0.5 mL of aqueous NaOH (200 mM), 0.5 mL of aqueous AA (100 mM), and 40 μL of Ag nanocube suspension. To the reaction mixture, 0.4 mL of aqueous $HAuCl_4$ (0.1 mM) was injected using a syringe pump at a rate of 0.02 mL/min. After completing the addition of Au precursor, the reaction mixture was maintained under magnetic stirring for additional 5 min. The solid products were collected by centrifugation at 8000 rpm for 10 min. After removing the supernatant, the pellet was re-dispersed in an aqueous solution containing PVP (0.7 mM) and AA (30 mM), and this suspension was incubated at room temperature (22 ^{o}C) for 20 min. After that, the particles were collected by centrifugation and re-dispersed in 0.1 mL DI water. To finalize the synthesis, 1 mL of aqueous H_2O_2 (3%) was added to selectively etch away the Ag component. The final products were collected by centrifugation and dispersed in water at a particle concentration of 0.3 nM for future use.

Seed-mediated Growth of Pd on Au Nanocages. In a standard protocol, 0.75 mL of aqueous $PdCl_4^{2-}$ (0.1 mM) or $PdBr_4^{2-}$ (0.1 mM) was titrated into 2 mL of an aqueous suspension containing 43.5 mg of PVP, 8.8 mg of AA, and 0.1 mL of the Au nanocages at an injection rate of 0.02 mL/min using a syringe pump. The reaction mixture was hosted in a 20-mL glass vial and held at room temperature for a certain period of time to ensure complete reaction. For the cases of $PdCl_4^{2-}$ and $PdBr_4^{2-}$, the reaction was maintained for 2 h and 6 h, respectively. After reaction, the product was collected by centrifugation at 10,000 rpm for 10 min and washed three

times with water.

Measurement of the Thicknesses of Pd Overlayers Deposited on the Outer and Inner Surfaces of a Au Nanocage. To obtain the thicknesses of Pd overlayers, we carefully measured and averaged the dimensions of 100 individual nanocages on different TEM images. The detailed calculation method is illustrated in Figure S1 and described below.

The thickness of Pd overlayer deposited on the outer surface of a Au nanocage is calculated as:

$$d_{Pd\text{-}outer} = 1/2(d_{Au\text{-}Pd\ NC} - d_{AuNC})$$

where $d_{Au\text{-}Pd\ NC}$ is the overall edge length of Au-Pd nanocages after Pd deposition and d_{AuNC} is the overall edge length of the original Au nanocages. The thickness of Pd overlayer deposited on the inner surface of a Au nanocage is calculated:

$$d_{Pd\text{-}inner} = 1/2(d_{AuNC\text{-}hollow} - d_{Au\text{-}Pd\text{-}hollow})$$

where $d_{AuNC\text{-}hollow}$ is the edge length of the cubic hollow space inside the Au nanocage before Pd deposition and $d_{Au\text{-}Pd\text{-}hollow}$ is the edge length of the cubic hollow space inside a Au-Pd nanocage after Pd deposition.

Instrumentation. Transmission electron microscopy (TEM) images were taken using a Hitachi HT7700 microscope operated at 120 kV. The samples for TEM analysis were prepared by drop-casting an aqueous suspension containing the nanoparticles on carbon-coated Cu grids and drying under ambient conditions. High resolution electron microscopy was carried out with an aberration-corrected Hitachi HD-2700 scanning transmission electron microscope (STEM) operated at 200 kV.

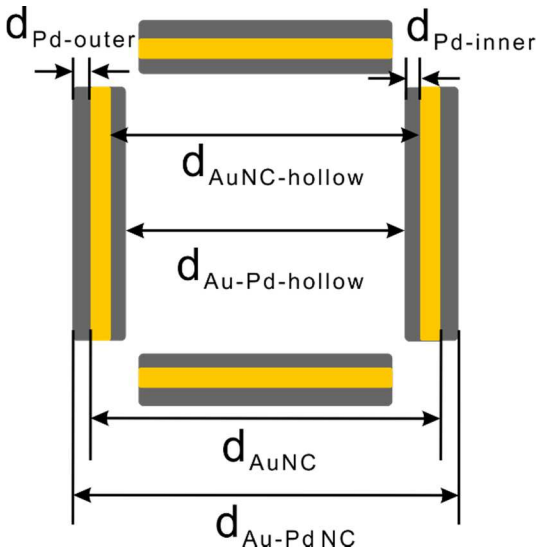

Figure S1. Schematic illustration showing that the thicknesses of Pd overlayers on the outer surface ($d_{Pd\text{-}outer}$) and inner surface ($d_{Pd\text{-}inner}$) of a Au nanocage can be calculated from the overall edge lengths of the Au-Pd nanocage ($d_{Au\text{-}Pd\ NC}$) and pristine Au nanocage (d_{AuNC}), as well as the dimensions of the hollow spaces before and after Pd deposition ($d_{Au\text{-}Pd\text{-}hollow}$ and $d_{AuNC\text{-}hollow}$).

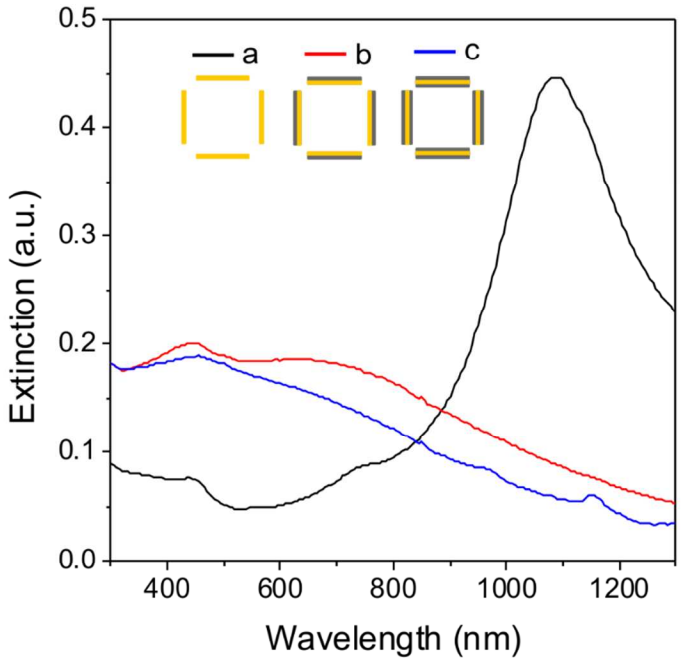

Figure S2. UV-Vis spectra recorded from aqueous suspensions of (a) the pristine Au nanocages, (b) the Au@Pd double-shelled nanocages prepared using 1.5 mL of $PdCl_4^{2-}$ (Figure 2c), and (c) Pd@Au@Pd triple-shelled nanocages prepared using 1.5 mL of $PdBr_4^{2-}$ (Figure 3b).

REFERENCE

(1) Sun, X.; Kim, J.; Gilroy, K. D.; Liu, J.; König, T. A. F.; Qin, D. *ACS Nano* **2016**, *10*, 8019–8025.