## Electronic Supplementary Material (ESI) for

## On the Role of Wall Thickness in Determining the Plasmonic Properties of Silver-Gold Nanocages

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## **Experimental Section**

**Chemicals and Materials.** Ethylene glycol (EG) was obtained from J. T. Baker. Silver Nitrate (AgNO<sub>3</sub>,  $\geq$ 99.0%), gold (III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O,  $\geq$ 99.9%), poly(vinylpyrrolidone) (PVP55, Mw  $\approx$  55,000), sodium hydrosulfide hydrate (NaHS·xH<sub>2</sub>O), L-ascorbic acid (AA,  $\geq$ 99%), sodium chloride (NaCl,  $\geq$ 99.5%), sodium borohydride (NaBH<sub>4</sub>,  $\geq$ 98%), cetyltrimethylammonium bromide (CTAB,  $\geq$ 99%), and cetyltrimethylammonium chloride (CTAC,  $\geq$ 98%) were all obtained from Sigma-Aldrich and used as received. All aqueous solution were prepared using deionized (DI) water with a resistivity of 18.2 MΩ·cm.

**Instrumentations.** The transmission electron microscope (TEM) images were taken using a JEOL JEM-1011 microscope operated at 100 kV. The scanning electron microscope (SEM) images were taken using a Zeiss Ultra 55 field emission gun scanning electron microscope operated at 10 kV. Scanning TEM (STEM) images and energy dispersive X-ray (EDX) mapping images were acquired using a FEI 200 kV Titan Themis scanning transmission electron microscope. The concentrations of Ag and Au elements in nanoparticles were determined using an inductively coupled plasma mass spectrometry (ICP-MS, a JY2000 Ultrace ICP atomic emission spectrometer), in which the nanoparticles were dissolved to metal ions with aqua regia. UV-vis

spectra were recorded using an Agilent Cary 60 UV-vis spectrophotometer. Photographs of the samples in vials were taken using a Canon EOS 80D digital camera.

Synthesis of Ag Nanocubes. Ag nanocubes were synthesized according to a published protocol with minor modifications.<sup>1,2</sup> In a standard synthesis, 6.0 mL of ethylene glycol (EG) was added to a 20 mL glass vial and preheated at 150 °C in an oil bath under magnetic stirring for 1 h. Then, 80  $\mu$ L of 3 mM NaHS solution (in EG) was injected into the glass vial using a pipet. After ~8 min, 1.5 mL of 20 mg/mL PVP55 solution (in EG) and 0.5 mL of 282 mM AgNO<sub>3</sub> solution (in EG) were sequentially injected into the vial using a pipet. To monitor and control the size of Ag cubes, a small volume (a few drops) of the reaction solution was taken out from the flask using a glass pipette every 10 minutes, which was immediately diluted with DI water in a cuvette and subjected to UV/vis measurement by a spectrophotometer. The 42.9 nm, 50.3 nm, 55.2 nm, 60.0 nm, and 64.4 nm Ag cubes (samples in Figure S2) were obtained when the major localized surface plasmon resonance (LSPR) peaks of the reaction solution had reached to ~430 nm, ~440 nm, ~450 nm, ~460 nm, and ~470 nm, respectively. All the samples were collected by washing with acetone once and DI water twice via centrifugation. Final products were dispersed in 8.0 mL of DI water for future use.

Synthesis of singly-walled Ag-Au nanocages ([Ag-Au]<sub>1</sub> cages). The singly-walled Ag-Au nanocages, termed "[Ag-Au]<sub>1</sub> cages", were synthesized through conventional galvanic replacement reaction between the Ag nanocubes as sacrificial templates and Au<sup>3+</sup> ions, according to a previously published protocol with minor modifications.<sup>1</sup> Using the synthesis of ~47.5 nm [Ag-Au]<sub>1</sub> cages (sample in Figure 1b) as an example, a typical synthetic procedure is described in the following: 1.0 mL of the 42.9 nm Ag cubes and 10 mL of 0.5% (w/v) PVP55 aqueous solution were first mixed in a 25 mL round-bottom flask and were preheated at 95 °C in an oil bath under magnetic stirring for 10 min. Then, 5 mL of 0.02% (w/v) HAuCl4 aqueous solution was injected into the flask at a rate of 100 µL/min using a syringe pump. After complete injection of the HAuCl4 solution, the reaction mixture was kept stirring at 95 °C for additional 10 min to allow the reaction to complete. The products were collected by centrifugation, washed once with saturated NaCl solution and 10 times with DI water, and finally redispersed in 1.0 mL of DI water for future use.

Unless otherwise stated, all other [Ag-Au]1 cages of different sizes (e.g., sample in Figure 2b)

were synthesized using the same procedure mentioned above, except for the use of Ag cubes of different sizes as the sacrificial templates.

Synthesis of [Ag-Au]o-n Cages (O: wall thickness change toward outer surfaces; n: number of consecutive Ag-Au layers, n = 2, 3, 4, and 5). The [Ag-Au]o-n cages (samples in Figure 1c-f) were synthesized using the strategy based on sequential processes of template regeneration and galvanic replacement, according to our recently reported protocol with minor modifications.<sup>3</sup> Specifically, the [Ag-Au]<sub>0-2</sub> cages (sample in Figure 1c) were prepared through the following two steps: i) Ag template regeneration: 1.0 mL of above-mentioned 47.5 nm [Ag-Au]<sub>1</sub> cages and 5 mL of DI water were mixed in a 20 mL of glass vial at room temperature under magnetic stirring. Then, 5.0 mM of AgNO<sub>3</sub> aqueous solution and 2.5 mM of AA aqueous solution were injected simultaneously at a rate of 5 µL/min using a two-channel syringe pump. The reaction was terminated when the major LSPR peak of the solution stopped shifting to the shorter wavelengths. The Ag@Ag-Au core@shell nanocubes as products were collected via centrifugation and redispersed in 1.0 mL of DI water; ii) galvanic replacement: as-synthesized Ag@Ag-Au nanocubes were then used as new templates for galvanic replacement reaction with Au<sup>3+</sup> ions, according to the procedure used for synthesis of [Ag-Au]1 cages. The final products (i.e., [Ag-Au]<sub>0-2</sub> cages) were collected through centrifugation and re-dispersed in DI water. The [Ag-Au]<sub>0-</sub> 3, [Ag-Au]<sub>0-4</sub>, and [Ag-Au]<sub>0-5</sub> cages (samples in Figure 1d-f) were prepared by repeating such template regeneration plus galvanic replacement processes for 1, 2, and 3 times, respectively.

Synthesis of  $[Ag-Au]_{I-n}$  Cages (I: wall thickness change toward inner surfaces; *n*: number of consecutive Ag-Au layers, n = 2, 3, 4, and 5). First,  $[Ag-Au]_1$  cages of four different sizes were prepared using 60.0, 55.2, 50.3, and 42.9 nm Ag cubes, respectively, as the sacrificial templates. The  $[Ag-Au]_{I-n}$  cages (n = 2, 3, 4, and 5, samples in Figure 2c-f) were prepared by applying the aforementioned template regeneration plus galvanic replacement processes to these four  $[Ag-Au]_1$  cages (with the order of decreasing sizes) for 1, 2, 3, and 4 times, respectively.

**Numerical Modeling.** Discrete Dipole Approximation (DDA) method was applied to calculate the extinction spectra of [Ag-Au]<sub>0-n</sub> and [Ag-Au]<sub>I-n</sub> cages.<sup>4</sup> Specifically, an Ag-Au cage was divided into N polarizable dipoles with a length of one nanometer in all calculations. The dielectric

constants of Ag and Au were taken from Baber et al.<sup>5</sup> and McPeak et al.'s,<sup>6</sup> respectively. Size correction of the dielectric constants was performed using method described in Coronado et al.'s work.<sup>7</sup> The environment was modeled as water, which is consistent with the experimental conditions. The molar ratio of Au and Ag was set to be 1:1 based on ICP-MS analysis. Both Au and Ag elements in the cages were assumed to be homogeneously mixed in the form of alloy. The physical parameters used in simulations are listed in Figure S9.



Figure S1. Schematics showing the method for manipulating nanocage wall thickness through the processes of sequential template regeneration and galvanic replacement. Wall thickness (t), outer size (L), and size of void (L') of the final nanocage are labeled.



**Figure S2.** (a-e) TEM images of Ag nanocubes that have average edge lengths of (a) 42.9 nm, (b) 50.3 nm, (c) 55.2 nm, (d) 60.0 nm, and (e) 64.4 nm. The 50 nm scale bar applies to all the images. (f) Normalized UV-vis spectra recorded from aqueous suspensions of the Ag cubes shown in (a-e).



**Figure S3.** SEM images of [Ag-Au]<sub>0-n</sub> cages (samples in Figure 1b-f). The 100 nm scale bar applies to all the SEM images.



**Figure S4.** SEM images of [Ag-Au]<sub>I-n</sub> cages (samples in Figure 2b-f). The 100 nm scale bar applies to all the SEM images.



**Figure S5.** EDS mapping images recorded from: (a) an individual [Ag-Au]<sub>0-5</sub> cage (sample in Figure 1f) and (b) an individual [Ag-Au]<sub>I-1</sub> cage (sample in Figure 2a).



**Figure S6.** Plots of the major LSPR peaks  $\lambda_{max}$  (LSPR  $\lambda_{max}$ ) of [Ag-Au]<sub>O-n</sub> cages (a) and [Ag-Au]<sub>I-n</sub> cages (b) against the reciprocal of wall thickness (1/*t*).



**Figure S7.** Extinction of aqueous suspensions of  $[Ag-Au]_{O-n}$  cages at the same particle concentration (~6.6 × 10<sup>-12</sup> M). (a) A photograph taken from the aqueous suspensions of  $[Ag-Au]_{O-n}$  cages. (b) Corresponding LSPR extinction spectra recorded from the samples in (a). (c) Calculated extinction spectra of the  $[Ag-Au]_{O-n}$  cages after size correction. (d) Calculated extinction spectra of the  $[Ag-Au]_{O-n}$  cages before size correction.



**Figure S8.** Extinction of aqueous suspensions of  $[Ag-Au]_{I-n}$  cages at the same particle concentration (~6.6 × 10<sup>-12</sup> M). (a) A photograph taken from the aqueous suspensions of  $[Ag-Au]_{I-n}$  cages. (b) Corresponding LSPR extinction spectra recorded from the samples in (a). (c) Calculated extinction spectra of the  $[Ag-Au]_{I-n}$  cages after size correction. (d) Calculated extinction spectra of the  $[Ag-Au]_{I-n}$  cages before size correction.



**Cross section** 



	Nanocages	<i>L</i> (nm)	<i>L'</i> (nm)	<i>t</i> (nm)	<i>d</i> (nm)
	[Ag-Au] <sub>0-1</sub> cage, sample in Fig. 1b	48	38	5	10
Cages with	[Ag-Au] <sub>0-2</sub> cage, sample in Fig. 1c	54	38	8	8
Fixed Void	[Ag-Au] <sub>0-3</sub> cage, sample in Fig. 1d	62	38	12	0
Size	[Ag-Au] <sub>0-4</sub> cage, sample in Fig. 1e	66	38	14	0
	[Ag-Au] <sub>0-5</sub> cage, sample in Fig. 1f	72	38	17	0
	[Ag-Au] <sub>I-1</sub> cage, sample in Fig. 2b	72	62	5	16
Cages with	[Ag-Au] <sub>I-2</sub> cage, sample in Fig. 2c	72	58	7	10
<b>Fixed Outer</b>	[Ag-Au] <sub>I-3</sub> cage, sample in Fig. 2d	72	48	12	0
Size	[Ag-Au] <sub>I-4</sub> cage, sample in Fig. 2e	72	42	15	0
	[Ag-Au] <sub>I-5</sub> cage, sample in Fig. 2f	72	38	17	0

**Figure S9.** Schematics along with a table showing the physical parameters of different Ag-Au cages that are used for the purpose of DDA simulations.

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