Supporting information for

Synthesis of Morphology Controlled PtAu@Ag Nanorings through Concentric and Eccentric Growth Pathways

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Table of Contents:

Experimental details

Chemicals and materials

We purchased trisodium citrate dihydrate, sodium iodide (≥99.5%), hexadecyltrimethylammonium bromide (CTAB, ≥98%), L-ascorbic acid (99%), and 2-naphthalenethiol (99%) from Sigma-Aldrich. We purchased hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4 \cdot nH_2O$, 99%), hydrogen hexachloroplatinate(IV) hydrate ($H_2PtCl_6 \cdot nH_2O$, 99%), and silver nitrate ($AgNO_3$, 99.9%) from Kojima, Japan. We purchased sodium borohydride ($NaBH_4$, 98.0%) from Junsei, Japan. We purchased hydrochloric acid (HCl, 35%) and sodium hydroxide (NaOH, 98.0%) from Samchun, Korea. We purchased hexadecyltrimethylammonium chloride (CTAC, >95.0%) from Tokyo Chemical Industry, Japan. All reagents were dissolved in triply deionized water (≥18.2 MΩ) prepared by Milli-Q (from Millipore).

Synthesis of concentric PtAu@Ag nanorings

First, we prepared PtAu nanorings by following the experimental procedure in previously reported literatures.[1] We synthesized concentric PtAu@Ag nanorings by mixing 250 μL of Pt nanorings with 500 μL of 0.1 M CTAC, 0.2 mM $AgNO_3$ (100 μL, 200 μL, and 300 μL), 40 μL of 0.01 M ascorbic acid, and 20 μL of 0.05 M sodium hydroxide. After the reaction at 30 ℃ for 30 min, we washed the resulting solution with triply deionized water twice via centrifugation. The geometrical parameters of concentric PtAu@Ag nanorings was tuned by controlling the volume of 0.2 mM $AgNO_3$.

Synthesis of eccentric PtAu@Ag nanorings

We synthesized eccentric PtAu@Ag nanorings by mixing 250 μL of PtAu nanorings with 500 μL of 0.1 M CTAB, 0.2 mM $AgNO_3$ (40 μL, 60 μL, and 80 μL), 200 μL of 0.01 M ascorbic acid, and 200 μL of 0.05 M sodium hydroxide. After the reaction at 30 ℃ for 30 min, we washed the resulting solution with triply deionized water twice via centrifugation. The geometrical parameters of eccentric PtAu@Ag nanorings was tuned by controlling the volume of 0.2 mM $AgNO_3$.

Synthesis of PtAu@Au nanorings

We synthesized PtAu@Au nanorings by mixing 250 μL of PtAu nanorings with 200 μL of 0.05 M CTAB, 2 mM $HAuCl_4$ (20 μL, 30 μL, and 40 μL), 200 μL of 0.1 M ascorbic acid, and 20 μL of 0.1 M hydrochloric acid in the presence of iodide ion (50 μM). After the reaction at 30 ℃ for 30 min, we washed the resulting solution with triply deionized water twice via centrifugation. The geometrical parameters PtAu@Au nanorings was tuned by controlling the volume of 2 mM $HAuCl_4$.

Fabrication of the 2D monolayer of nanorings

We fabricated 2D monolayer of nanorings by Langmuir-Blodgett (LB) method.[2] We transferred 10 mL of nanoring solution into a Teflon bath, and added 2 mL of hexane at the top surface of nanoring solution to form a hexane-water interface. Then, we added 5 mL of ethanol dropwise at a rate of 30 mL/h. After ethanol transported nanorings from the aqueous solution to the hexane-water interface, hexane at the top surface of nanoring solution was evaporated. We collected a 2D monolayer of nanorings on the silicon wafer for FE-SEM and

surface-enhanced Raman spectroscopy (SERS) measurement.

Instrumentation

We obtained images of nanoparticles using Field-emission scanning electron microscopy (JSM-7100F, JEOL) and high-resolution transmission electron microscopy (JEM-ARM 200F-JEOL). We obtained ensemble SERS signals using confocal Raman microscopy (WiTec alpha 300R) equipped with a 633 nm He-Ne laser.

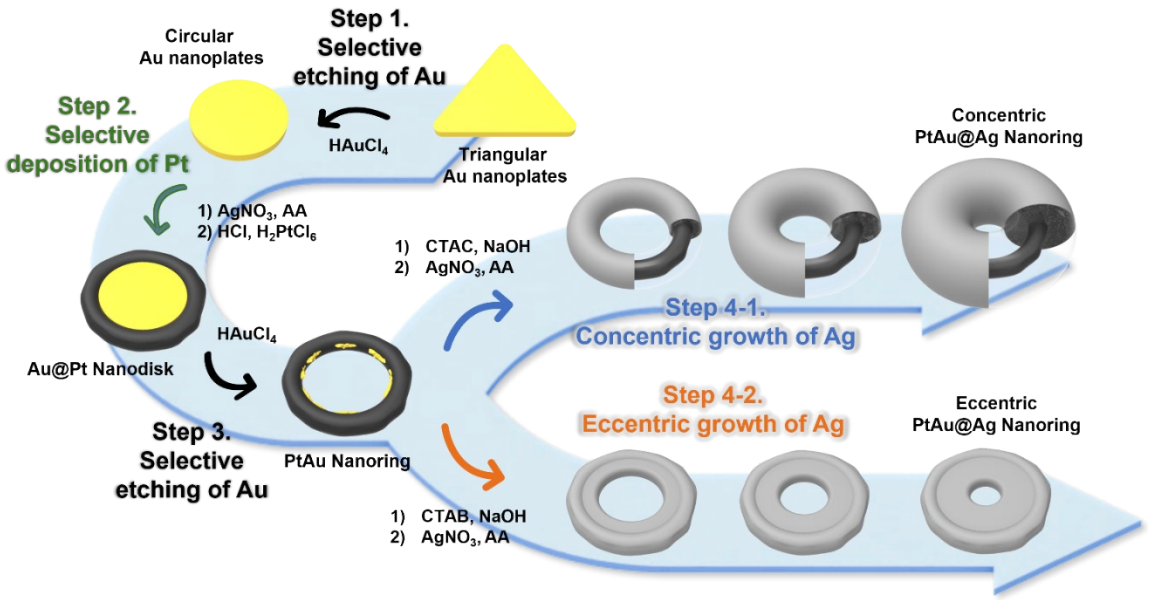

Figure S1. Schematic illustration representing synthetic procedure of concentric PtAu@Ag nanorings and eccentric PtAu@Ag nanorings. The multistep synthetic procedure for synthesizing PtAu@Ag nanorings included selective etching of Au, selective deposition of Pt, selective etching of Au, eccentric growth of Ag, and concentric growth of Ag.

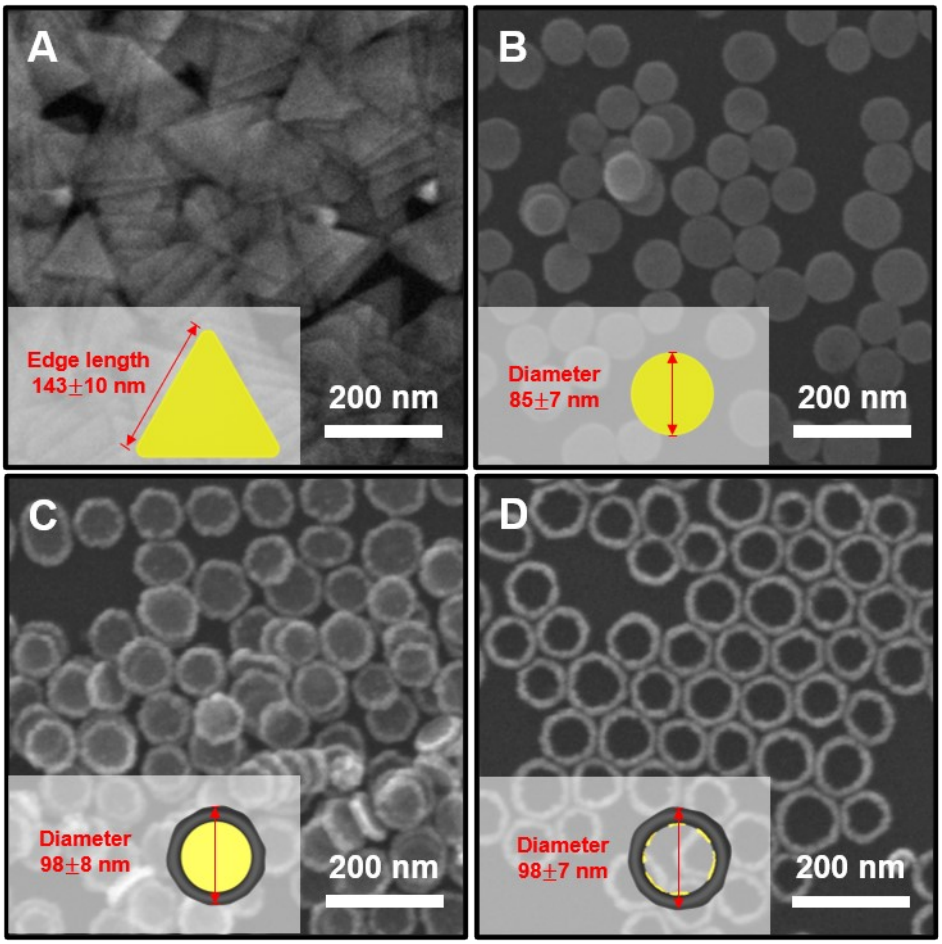

Figure S2. FE-SEM images of triangular Au nanoplates, circular Au nanoplates, Au@Pt nanodisks, and PtAu nanorings. (A-D) FE-SEM images of triangular Au nanoplates, circular Au nanoplates, Au@Pt nanodisks, and PtAu nanorings, respectively.

A

Concentric
PtAu@Ag nanoring

Element	Atomic %
Ag	91.49 %
Pt	6.07 %
Au	2.44 %
Total	100 %

B

Eccentric
PtAu@Ag nanoring

Element	Atomic %
Ag	84.37 %
Pt	9.99 %
Au	5.64 %
Total	100 %

Figure S3. Atomic fraction (Ag, Pt, and Au) data of a concentric PtAu@Ag nanoring and an eccentric PtAu@Ag nanoring obtained from energy-dispersive spectroscopy (EDS) analysis. (A) atomic fractions of Ag, Pt, and Au of a concentric PtAu@Ag nanoring were 91.49 %, 6.07 %, and 2.44 %, respectively. (B) atomic fraction of Ag, Pt, and Au of an eccentric PtAu@Ag nanoring were 84.37 %, 9.99 %, and 5.64 %, respectively.

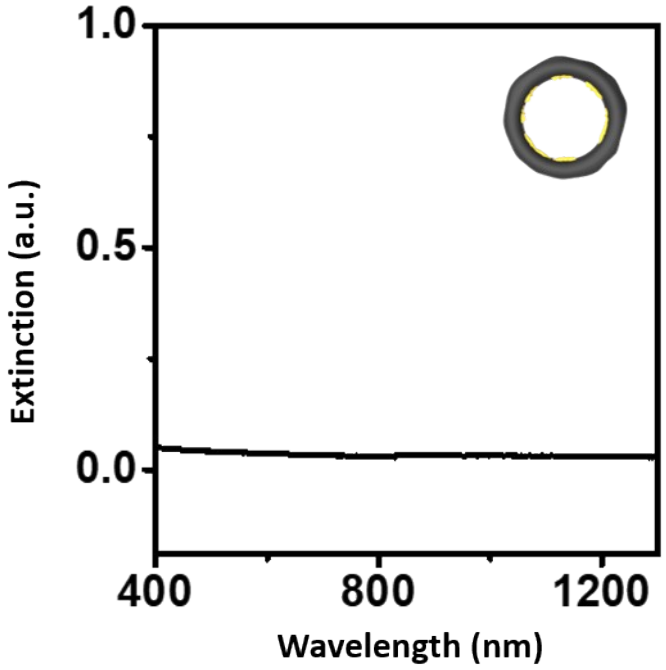

Figure S4. UV-vis-NIR spectrum of PtAu nanorings. UV-vis-NIR spectrum of PtAu nanorings showed no spectroscopic features.

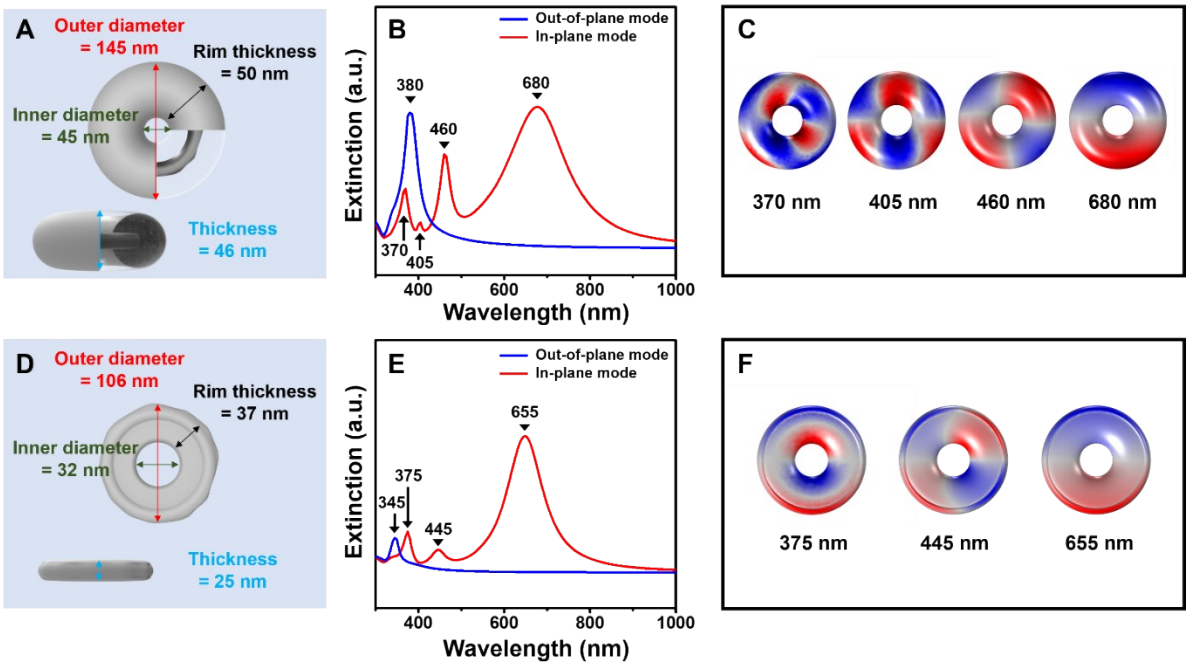

Figure S5. Theoretical simulation data of concentric PtAu@Ag nanorings and eccentric PtAu@Ag nanorings. Physical dimension utilized for theoretical simulation, theoretically simulated extinction spectra, and corresponding charge distribution analysis data of (respectively A, B, C) concentric PtAu@Ag nanorings and (respectively D, E, F) eccentric PtAu@Ag nanorings under the in-plane and the out-of-plane polarized wave.

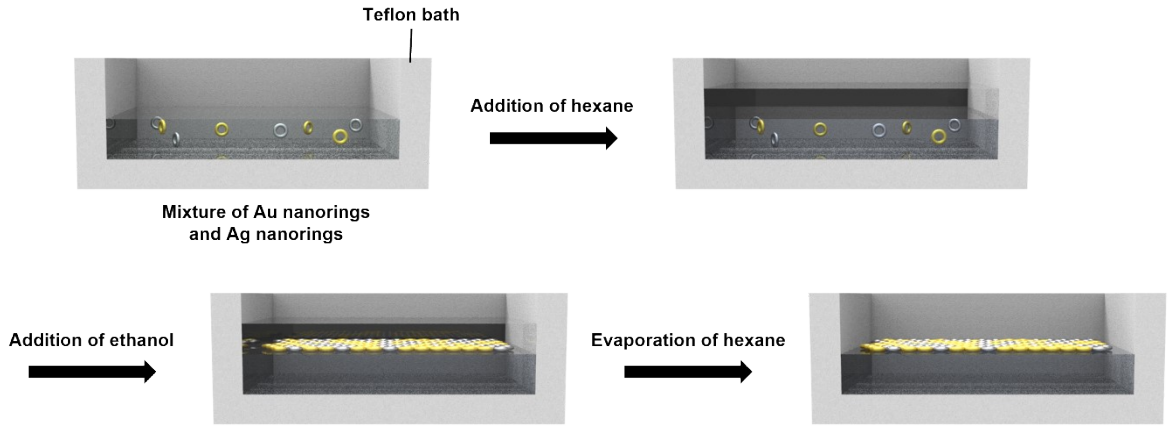

Figure S6. Schematic illustration representing methodology of fabricating 2D monolayer of Au and Ag nanorings. To fabricate 2D monolayer of nanorings, we added hexane on top of the mixture solution of Au and Ag nanorings. Then, we added ethanol to the water-hexane solution, which resulted in formation nanoring-monolayer assembly at the water-oil interface. After hexane evaporation, we collected 2D monolayer film of nanorings on the silicon wafer.

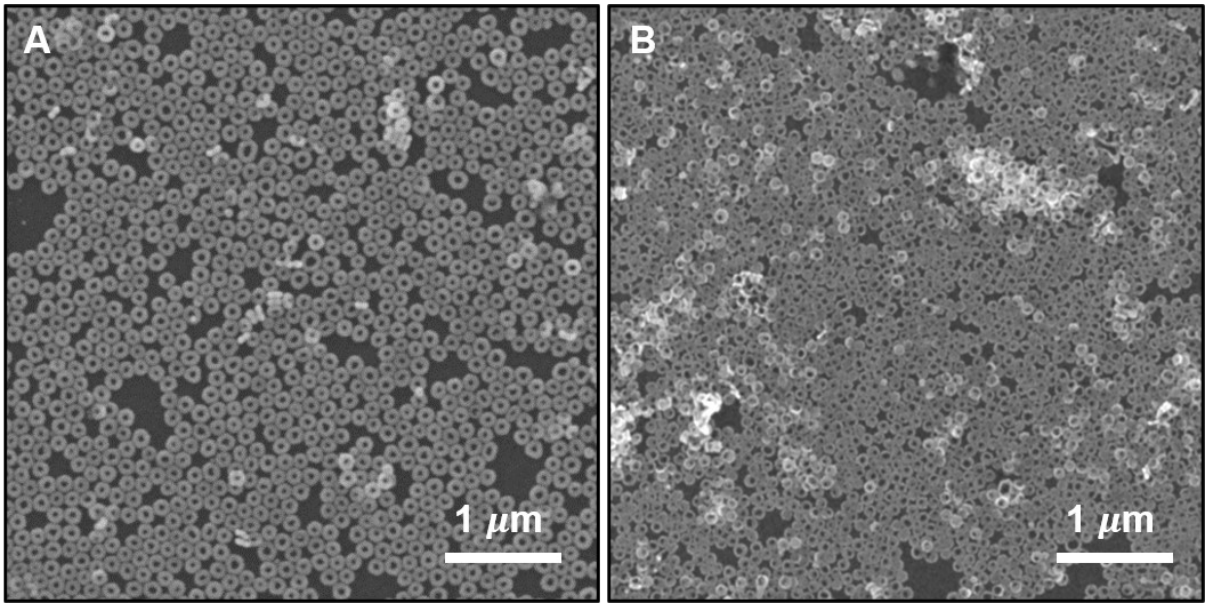

Figure S7. FE-SEM images of monolayer of Ag nanorings. FE-SEM images of monolayer of (A) concentric PtAu@Ag nanorings and (B) eccentric PtAu@Ag nanorings.

References

1. H. J. Jang, S. Ham, J. A. I. Acapulco, Y. Song, S. Hong, K. L. Shuford and S. Park, *J Am Chem Soc*, 2014, **136**, 17674-17680.
2. S. Yun, S. Hong, J. A. I. Acapulco, H. Y. Jang, S. Ham, K. Lee, S. K. Kim and S. Park, *Chem-Eur J*, 2015, **21**, 6165-6172.