Supporting Information

Mechanistic Studies on the Galvanic Replacement Reaction between Multiply Twinned Particles of Ag and $HAuCl_4$ in an Organic Medium

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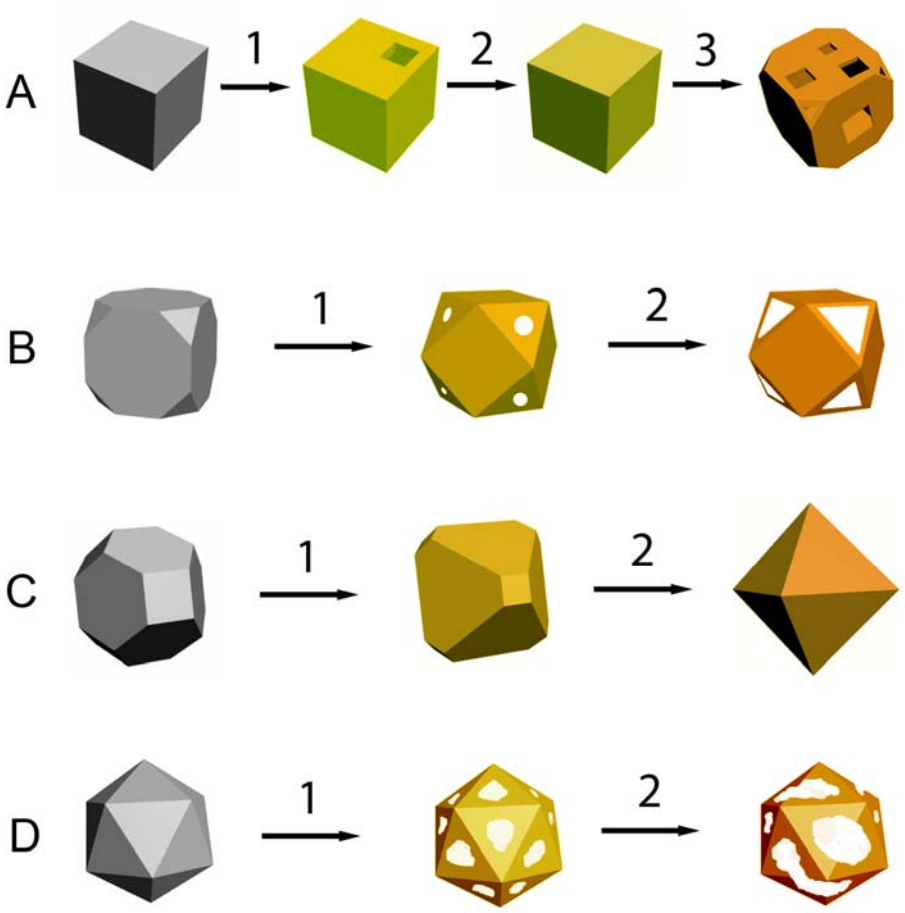

Figure S1. A comparison of all four different mechanisms that have been observed for the galvanic replacement reaction between $HAuCl_4$ and Ag template in the form of (A) single-crystal nanocubes with sharp corners (ref. 21); (B) single-crystal nanocubes with truncated corners (ref. 17c); (C) single-crystal cubooctahedrons (ref. 23); and (D) multiple twinned particles (the present work). For the Ag nanocube with sharp corners, the reaction starts by pitting (Step 1) on one of the six faces. Through an alloying and dealloying process, pin-hole free nanoboxes with hollow interior (Step 2) and porous nanocages (Step 3) can be obtained along the reaction process. For the Ag nanocube with truncated corners, the reaction initiates from all the corners and cubic nanocages with holes at the corners are obtained. For the single-crystal cubooctahedron, the replacement reaction and consumption of Ag preferentially take place on the {111} faces while the deposition of Au tend to occur on the {100} and {110} faces (Step 1), resulting in faceted growth which could form rhomboidal-shaped hollow particles eventually (Step 2). For the Ag MTP, the reaction initiates from the {111} facets rather than ridges and apexes, leading to the formation of a nanoring and nanocage.

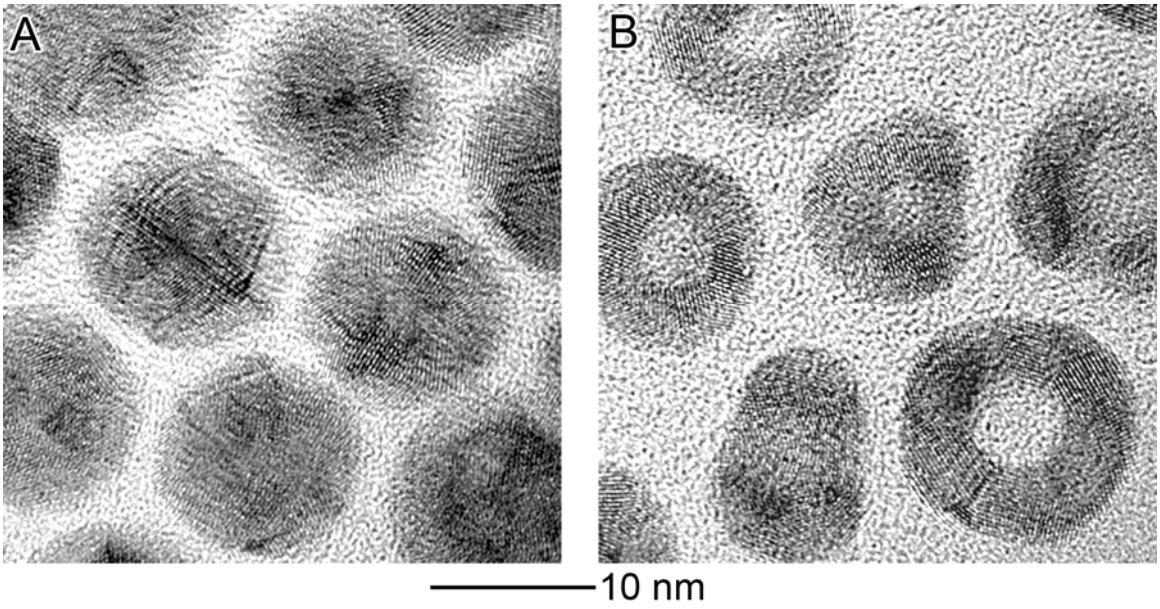

Figure S2. HRTEM images of 11-nm Ag MTPs synthesized with oleylamine as the capping agent: (A) before and (B) after galvanic replacement reaction. Before the replacement reaction, the particles were decahedral and icosahedral in shape and exhibited a multiply twinned structure. The hollow particles obtained after the replacement reaction with 2.6 mL of 0.5 mM $HAuCl_4$ solution in $CHCl_3$ showed polycrystallinity with a ring-type structure.

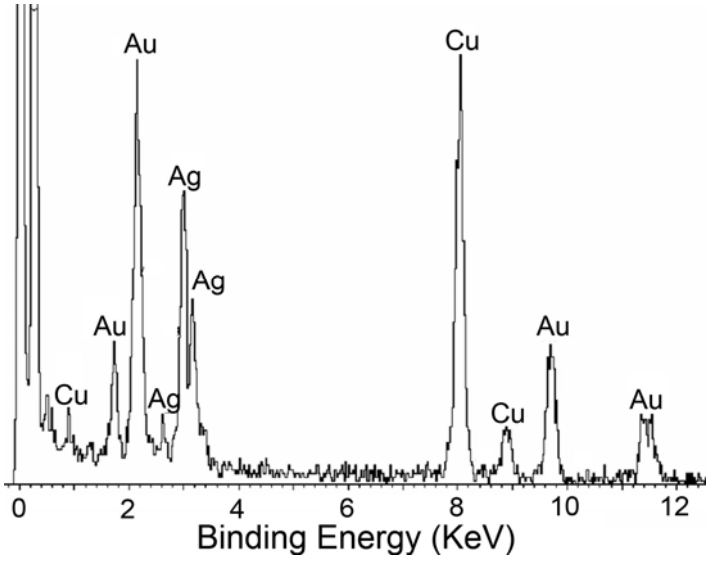

Figure S3. Typical EDS for hollow nanoparticles derived from oleylamine-capped Ag MTPs by reacting with 2.6 mL of 0.5 mM $HAuCl_4$ solution in $CHCl_3$. The molar ratio of Ag to Au was 2:1. The peaks of Cu and Si were from the copper grid and Si substrate used to support the nanoparticles. Note that there was no signal from Cl, indicating that the sample was free of AgCl.

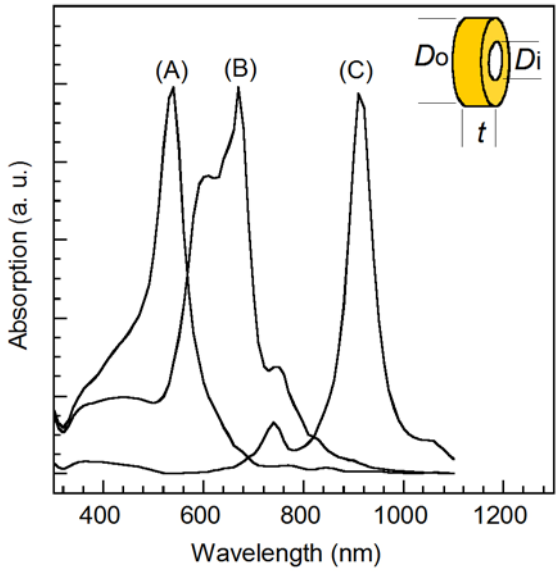

Figure S4. Extinction spectra calculated using DDA method for Ag-Au alloy (Ag:Au=2:1) nanorings with different particle sizes (outer diameter D_o, inner diameter D_i) and ring thicknesses (t): (A) D_o = 10 nm, D_i = 2 nm, t = 4 nm, showing SPR peak at 540 nm; (B) D_o = 10 nm, D_i = 4 nm, t = 3 nm, showing a major peak at 670 nm; and (C) D_o = 16 nm, D_i = 10 nm, t = 3 nm, showing a major peak at 910 nm. It is worth noting that such a ring can only be considered as a rough model of the ring shown in Figure 1D, where the thickness (t) varies across the ring.

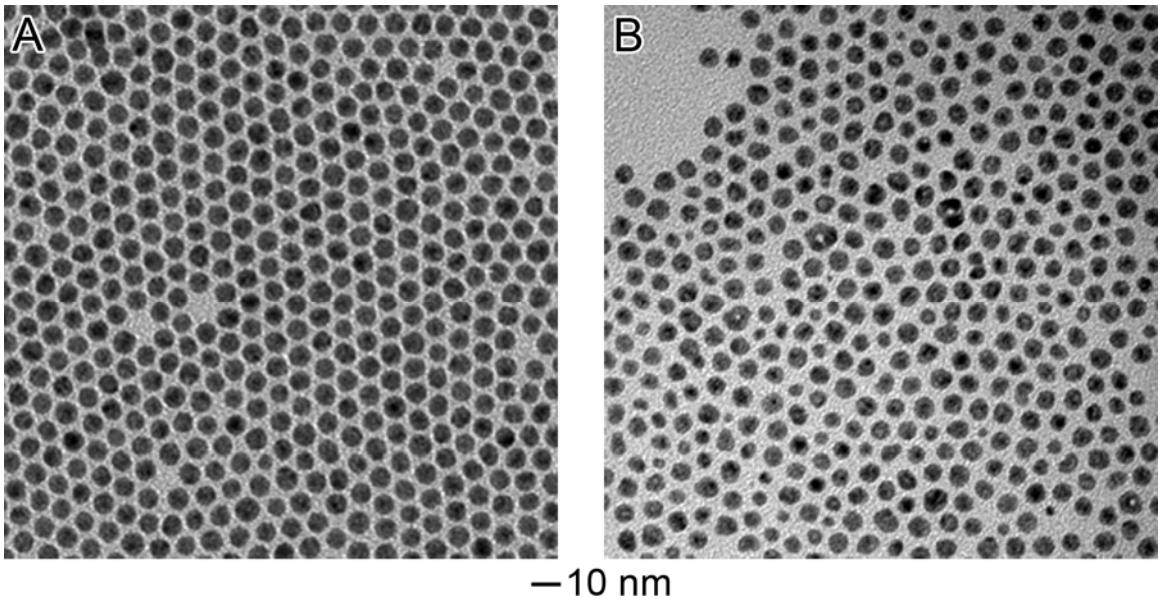

Figure S5. Ag nanoparticles synthesized with oleic acid as the capping ligand: (A) before and (B) after galvanic replacement reaction. In contrast to the oleylamine-capped Ag MTPs, which exhibit void inside most of them (Figure 1B), less than 10% of the oleic acid-capped particles showed any hollow feature after reacting with 2.6 mL of 0.5 mM $HAuCl_4$ in $CHCl_3$. The size distribution changed significantly from 6% to 18% before and after the replacement reaction.