Supplementary Information

Growth and Galvanic Replacement of Silver Nanocubes in Organic Medium

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Figure S1. Low-magnification TEM image of Ag nanocubes obtained with 0.6 mmol AgNO₃, 6 mmol oleylamine and 0.44 mole dichlorobenzene. The inset shows a representative HRTEM image.



Figure S2. HRTEM image of Ag NPs obtained after 1 hr of reaction time, showing multiple twinning. (Experimental parameters: 0.6 mmol AgNO₃, 6 mmol oleylamine, 0.44 mol DCB)



Figure S3. Population distribution of twinned *vs.* single crystalline Ag NPs (single crystalline polyhedral and nanocubes) with respect to reaction time.



Figure S4. TEM images of Ag nanocubes obtained under nitrogen atmosphere, while the other 80 experimental parameters were the same as indicated in Fig.S1. (0.6 mmol AgNO₃, 6 mmol oleylamine, 0.44 mole DCB).



Figure S5. TEM image of Ag nanoparticles obtained with 3 mmol (a) and 12 mmol (b) of oleylamine, keeping other reaction conditions the same as in Fig. S1 (0.6 mmol AgNO₃, 0.44 mol DCB).



Figure S6. Extinction spectra (a) and TEM images of silver nanoparticles obtained by using toluene (b), chlorobenzene (c), and (d) octadecene as solvents. Other reaction conditions were the same as in Fig. S1 (0.6 mmol AgNO₃, 6 mmol oleylamine).



Figure S7. Extinction spectra (a) and TEM images of Ag nanoparticles obtained using 0.22 (b), 0.44 (c) and 0.88 moles of dichlorobenzene, while keeping the amounts of other reactants the same as in Fig.S1 (0.6 mmol AgNO₃, 6 mmol oleylamine).



Figure S8. HRTEM image of a silver nanocube. The inset shows the corresponding FFT pattern, indicating highly symmetric spots of face-centred cubic silver.



Figure S9. Extinction spectrum (a) and low-magnification TEM image (b) of Ag nanocubes obtained using CF_3COOAg as precursor in 0.88 moles of dichlorobenzene (0.6 mmol AgNO₃, 6 mmol oleylamine).



Figure S10. Extinction spectrum (a) and TEM image (b) of Ag NPs obtained using CH₃COOAg as precursor in 0.88 moles of dichlorobenzene (0.6 mmol AgNO₃, 6 mmol oleylamine).



Figure S11. HRTEM image of a Au-Ag nanocage obtained after titrating Ag nanocubes with 0.25 mL of HAuCl₄ solution ([Au:[Ag]=15 mol %), indicating monocrystallinity.



Figure S12. EDS spectrum of Au-Ag nanocages obtained after titrating with 0.25 mL of $HAuCl_4$ solution ([Au]:[Ag] = 15 mol%), indicating that they contain Ag and Au.



Figure S13. TEM image (under low magnification) of the Au-Ag alloy nanocages obtained after titrating Ag nanocubes with 0.35 mL of $HAuCl_4([Au]:[Ag] = 21 \text{ mol}\%)$.



Figure S14. (a, b) TEM images (at two different magnifications) of fragmented Au NPs obtained after titrating Ag nanocubes with 0.8 mL of $HAuCl_4([Au]:[Ag]=50 \text{ mol}\%)$.



Figure S15. Extinction spectra (a) and TEM images of nanocube dispersions before (b) and after (c-f) the galvanic replacement reaction with different volumes of HAuCl₄ (0.2, 0.35, 0.5, 0.7 mL with final [Au]:[Ag] molar ratios of ~12%, 21%, 30%, 43%, respectively) at room temperature.



Figure S16. Extinction spectra of nanocube dispersions before and after the galvanic replacement reaction with different volumes of HAuCl₄ (0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4 and 0.8 mL with final [Au]:[Ag] molar ratios of ~6%, 9%, 12%, 15%, 18%, 21%, 24%, 50%, respectively) at 100 0 C.