Electronic Supplementary Information (ESI)

1 Experiment section

1.1 Chemicals and Instrumentation:


   X-ray powder diffraction (XRD) patterns were recorded on a D/MAX 2500/PC powder diffractometer (Rigaku) using a CuKα radiation source operated at 40 kV and 200 mA. Transmission electron microscope (TEM, JEOL JEM-2100) and energy-dispersive X-ray spectroscopy (EDS) were applied for the detailed microstructure and composition information. Scanning electron microscopic (SEM) analyses were carried with a Zeiss SUPRA 55 field emission scanning electron microscope. UV-vis absorption spectrum was measured by Shimadzu UV-3600 Uv-vis-nir spectrophotometer.

1.2 Synthesis of AgNCs-AD

   A typical synthesis of AgNCs-AD was performed as follows: sodium chloride (NaCl) aqueous solution (1.4 M, 10 ml) and 0.2 g AOT were added into benzene solution (100 ml), forming a reverse microemulsion (water in oil) after ultrasonic treatment for 20 min and medium speed magnetic stirring for 3 hours at 60 °C. Then, the resulted emulsion was treated by an azeotropic distillation process for about 8 hours, and cubic and monodisperse NaCl crystals were produced. On this basis, 10 ml 0.1 M AgNO₃ solution (dissolve in N-octylamine) was added to form a cubic core-shell structure of an AgCl shell layer encasing the cubic crystal. Further reduction using 2 ml hydrazine hydrate formed an Ag shell layer encasing the cubic salt crystal NaCl. Remaining AOT was washed by iso-octane and NaCl was removed from the Ag shell by water extraction, respectively. And then the product was obtained.

1.3 Synthesis of AgNPs-SCT

   The synthesis of AgNPs-SCT is according to the SCT method.¹⁰ Ethanol (10 ml) was added dropwise to NaCl aqueous solution (1.4 M, 10 ml) with continuous stirring, and a white precipitate NaCl was formed immediately, and then 0.17 g AgNO₃ and 0.2 g PVP (dissolve in 10 ml water) was added into the above solution with continued vigorous stirring. After stirring for one hour, AgCl@NaCl was obtained and then 2ml hydrazine hydrate was added dropwise, forming Ag@NaCl cubic cages. After the reaction, the product was centrifuged and washed in de-ionised
water (DI Water) for three times, and then dried in oven at 70 °C.

1.4 Synthesis of AgNPs

A typical synthesis of AgNPs was performed as follows: 0.17 g AgNO$_3$ and 0.2 g PVP was dissolved in 20 ml water, and then 10 ml 20 wt. % hydrazine hydrate was added slowly into the solution under vigorous stirring, forming AgNPs. The product was centrifuged and washed in DI-Water for three times, and then dried in oven at 70 °C.

2 Additional Figures

![Diagram](image1)

**Fig. S1** Ag3d XPS spectra of the AgNCs-AD.

![Image](image2)

**Fig. S2** Typical TEM image of AgNCs-AD. TEM image revealed their hollow interiors, but they failed to keep their intact cubic morphology under intense electron beam irradiation.
Fig. S3 TEM images of as-synthesized NaCl crystals (A, B, C) and Ag@AgCl nanocubes (D, E, F,) using azeotropic distillation (AD) assisted method with different mass ratio of water and AOT: (A, D) 5 : 1; (B, E) 10 : 1; (C, F) 20 : 1.

Fig. S4 XRD patterns of the as-prepared (a) NaCl, (b) AgCl@NaCl core-shell cubes, (c) Ag@NaCl core-shell cubes
Fig. S5 TEM image of agglomerated Ag nanoparticles (NPs).