

## Electronic Supplementary Information (ESI)

### 1 Experiment section

#### 1.1 Chemicals and Instrumentation:

Aerosol OT (AOT) (96 %, Shanghai Aladdin industrial Co., Ltd.), Sodium chloride (99 %, Shanghai Aladdin industrial Co., Ltd.), Benzene (99 %, Shanghai Aladdin industrial Co., Ltd.), Silver nitrate (99 %, Shanghai Aladdin industrial Co., Ltd.), N-octylamine (99 %, Shanghai Aladdin industrial Co., Ltd.), Hydrazine hydrate (80%, Jiangsu Qiangsheng Co., Ltd.), Isooctane (99 %, Shanghai Aladdin industrial Co., Ltd.), Polyvinyl Pyrrolidone (PVP) (99 %, Shanghai Aladdin industrial Co., Ltd., MW = 10000), Ethanol (99 %, Shanghai Aladdin industrial Co., Ltd.), 4-nitrophenol (99 %, Shanghai Aladdin industrial Co., Ltd.), 4-aminophenol (98 %, Shanghai Aladdin industrial Co., Ltd.), sodium borohydride (98 %, Shanghai Aladdin industrial Co., Ltd.).

X-ray powder diffraction (XRD) patterns were recorded on a D/MAX 2500/PC powder diffractometer (Rigaku) using a  $\text{CuK}\alpha$  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  $\text{AgNO}_3$  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.<sup>10</sup> 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  $\text{AgNO}_3$  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,  $\text{AgCl}@NaCl$  was obtained and then 2ml hydrazine hydrate was added dropwise, forming  $\text{Ag}@NaCl$  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<sub>3</sub> 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

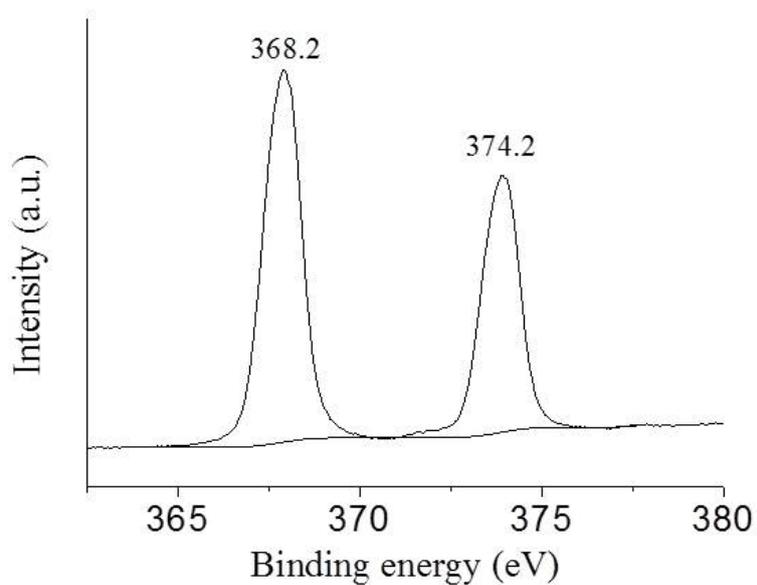


Fig. S1 Ag<sub>3d</sub> XPS spectra of the AgNCs-AD.

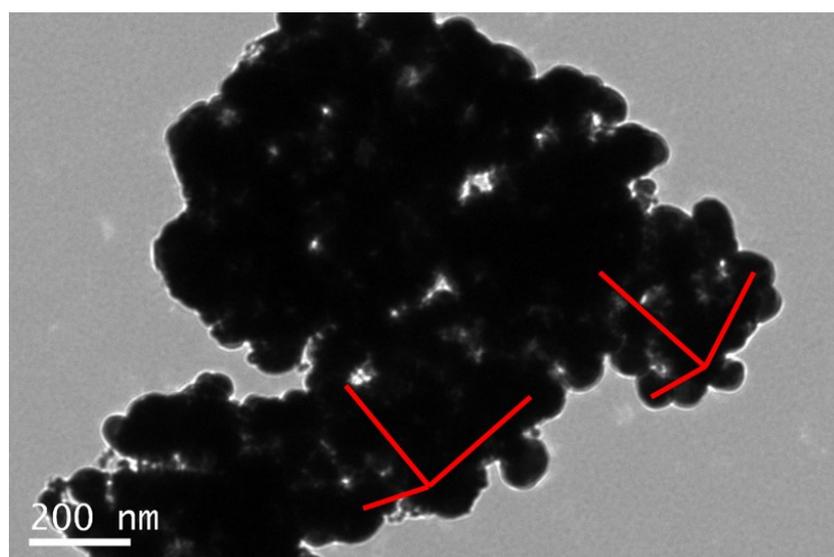


Fig. S2 Typical TEM image of AgNCs-AD. TEM image revealed their hollow interiors, but they failed to keep their intact cubic morphology under intense electron beam irradiation.

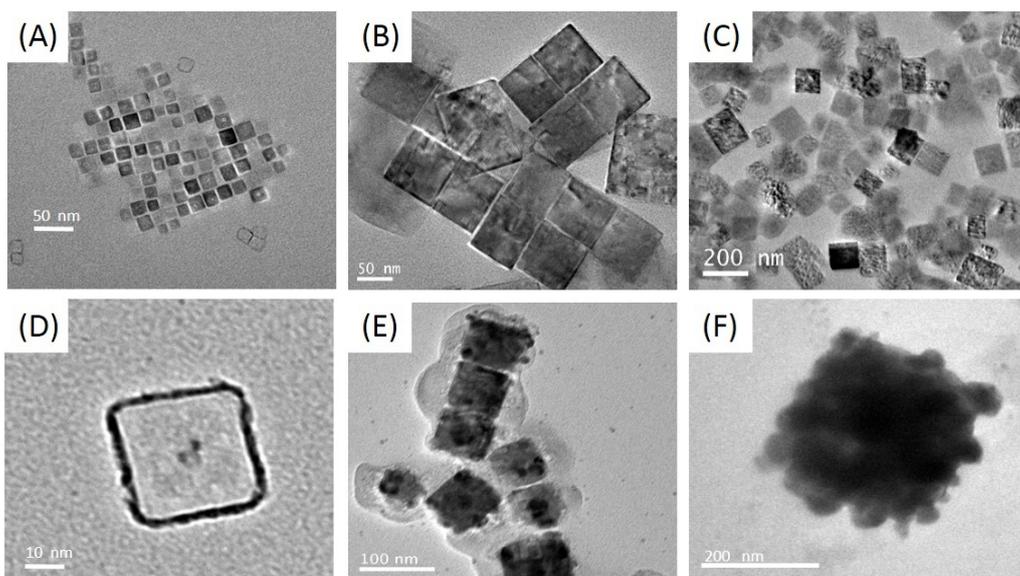


Fig. S3 TEM images of as-synthesized NaCl crystals (A, B, C) and Ag@AgCl nanocubes (D, E, F,) using azeotropic distillation (AD) assisted method with different mass ratio of water and AOT: (A, D) 5 : 1; (B, E) 10 : 1; (C, F) 20 : 1.

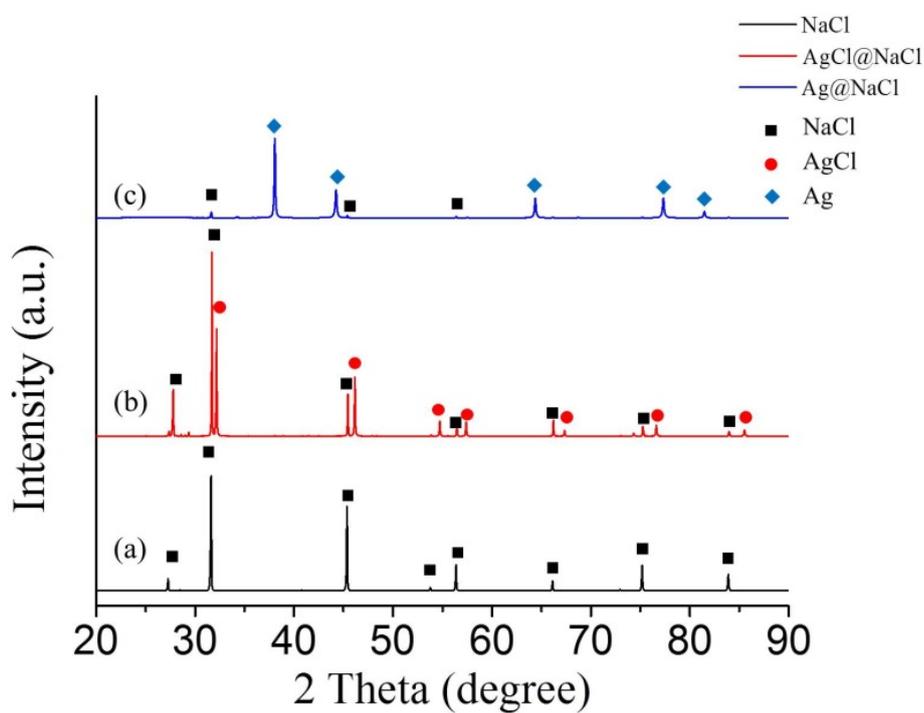


Fig. S4 XRD patterns of the as-prepared (a) NaCl, (b) AgCl@NaCl core-shell cubes, (c) Ag@NaCl core-shell cubes

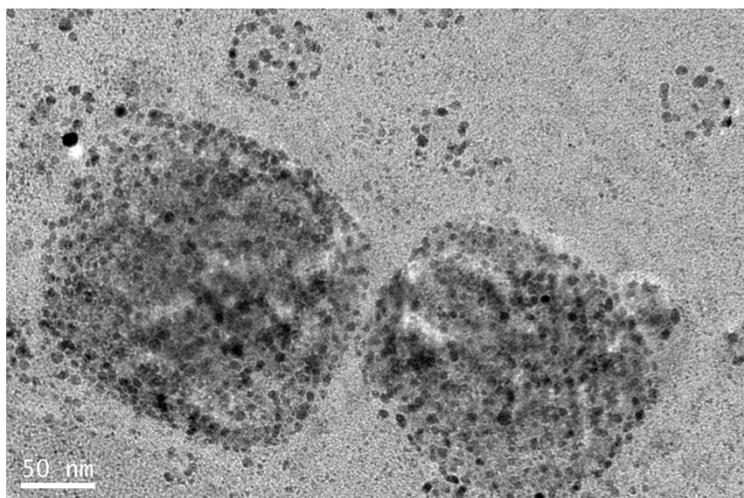


Fig. S5 TEM image of agglomerated Ag nanoparticles (NPs).