Supporting information

Dramatic Shape Transformation of Ag Nanoparticles with Concave Facets in a Solvothermal Process

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Experiment section.

Chemicals. Silver nitrate ($AgNO_3$, ≥99%), polyvinyl pyrrolidone (PVP, molecular weight = ~10000, 29000, and 55000 Da), ethylene glycol (EG, ≥99%), and L-ascorbic acid (≥99%) were purchased from Sigma-Aldrich (St. Louis, USA). Ethanol (AR) was obtained from Titan Corp. (Shanghai, China). Hyrochloric acid (HCl, AR) was purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). 1,4-benzenedithiol (1,4-BDT, 98%) was obtained from Alfa Aesar (Tianjing, China).

Synthesis of Ag nanocubes. 40-nm Ag nanocubes were firstly prepared according to the previous reported method.[1] Then the as-prepared 40-nm Ag nanocubes were used as seeds to synthesize 100-nm Ag nanocubes. In a typical procedure, 10 mL EG in 100-mL glass flask was pre-heated at 150 ^oC in an oil bath for 1 h under magnetic stirring; 2 mL PVP55K (20 mg/ml) in EG was added in the reaction solution; 2 min later, 0.4 mL of 40-nm Ag nanocubes (3.8×10^{15} particles/L) in EG was injected following with the addition of 2 mL $AgNO_3$ solution (282 mM) in EG. The reaction was stopped after 1 h reaction and quenched in an ice-water bath. The as-obtained Ag nanocubes were washed with acetone and DI water once and then stored in DI water for use.

Synthesis of cuboctahedra. Ag cuboctahedra were synthesized via a seed-mediated method. In a typical synthesis, 1 mL of ascorbic acid (10 mM) was added into 10 mL PVP55K (1 mM, in terms of the molecular weight) in DI water in a 100-mL flask followed by the addition of 0.1 mL 40-nm Ag nanocubes (3.8×10^{15} particles/L) under magnetic stirring. A certain amount of $AgNO_3$ (1 mM) solution was then injected into the reaction solution at a rate of 0.5 mL/min using a syringe pump. The as-prepared sample was washed with DI water and then stored for use.

Synthesis of Ag nanoparticles with concave facets. Ag nanoparticles with concave facets were synthesized via a solvothermal method. In a typical synthesis of Ag nanocubes with concave facets, 10 mL PVP29K (1 mM, in terms of the molecular weight) in ethanol was injected into a Teflon liner following with the addition of 0.3 mL of Ag nanocubes (2.2×10^{13} particles/L) in ethanol. The Teflon liner was then sealed in an autoclave and heated at 80 ^oC for 6 h. The UV-Vis spectra were recorded for the original reaction solution. 1 mL of the sample was centrifuged at 55000 rpm for 30 min to collect the solid and the supernatant, which was then measured for their

Ag content by inductively coupled plasma mass spectrometer (ICP-MS). Another 1 mL of the sample was centrifuged at 15000 rpm for 10 min and washed three times with ethanol for the characterization by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM).

Instrumentations and characterizations. TEM images were taken using a Hitachi microscope (HT7700, Hitachi, Japan) operating at an acceleration voltage of 100 kV. SEM images were captured using a SEM (S-4800, Hitachi, Japan) operated at 10 kV. The UV-Vis spectra were recorded by using a UV-Vis spectrometer (Cary60, Agilent Technologies, USA). The measurements of Ag contents were performed using an ICP-MS (NexION 300Q, Perkin-Elmer). A routine centrifuge (Eppendorf 5430) and a high-speed centrifuge (Max-XP Ultracentrifuge, Beckman Coulter Optima) was used for the collection and/or washing of the samples.

SERS measurement. In a typical preparation, 0.1 mL of Ag nanocubes (2.2×10^{13} particles/L) or Ag nanocubes with concave facets (2.2×10^{13} particles/L) in ethanol were incubated with 1mL of 1 mM 1,4-BDT at the room temperature for 1 h. The samples were then centrifuged and washed three times with DI water to remove free 1,4-BDT, and then were suspended in DI water. A homemade cuvette was used to hold the sample solution and covered by a glass coverslip to prevent evaporation. The SERS spectra were recorded using a Renishaw inVia confocal Raman spectrometer coupled to a Leica microscope with a 100 × objective (NA = 0.90). The 534-nm excitation source was obtained from an argon laser coupled to a holographic notch filter with a grating of 1200 lines per millimeter, and the 785-nm excitation source generated by a diode laser coupled to a holographic notch filter with a grating of 1200 lines per millimeter. Raman signals were collected on a thermoelectrically cooled (-60 °C) CCD detector. The Raman spectra were recorded in the range of 550-1750 cm^{-1} with a laser power of 10 mW and an accumulation time of 30 s.

References

1. Q. Zhang, W. Li, L.-P. Wen, J. Chen, Y. Xia, *Chem. Eur. J.*, 2010, **16**, 10234.

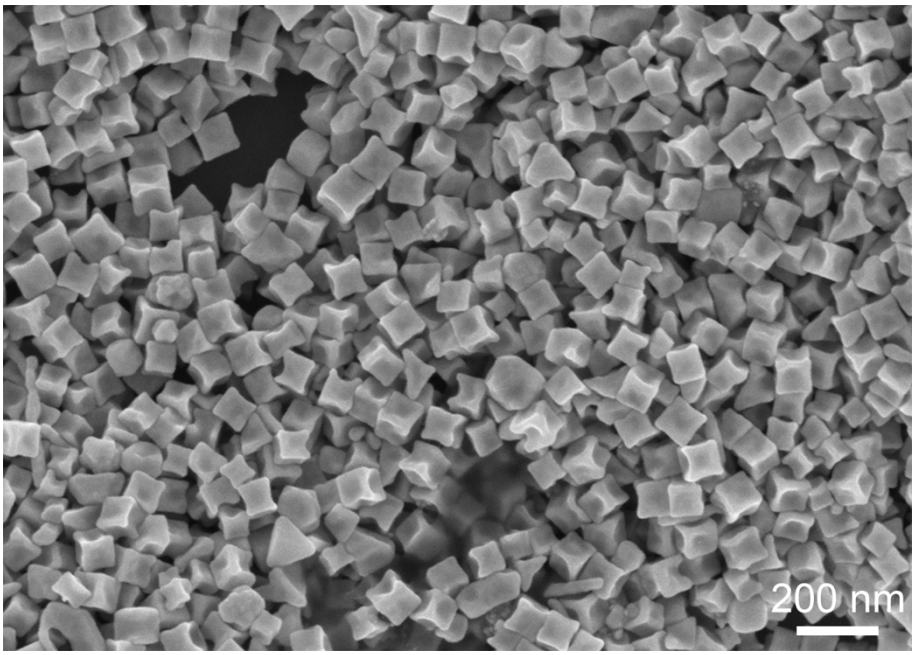

Fig. S1 Low magnification SEM image of Ag nanocubes with concave facets obtained from a typical synthesis stopped at a time point of 6 h.

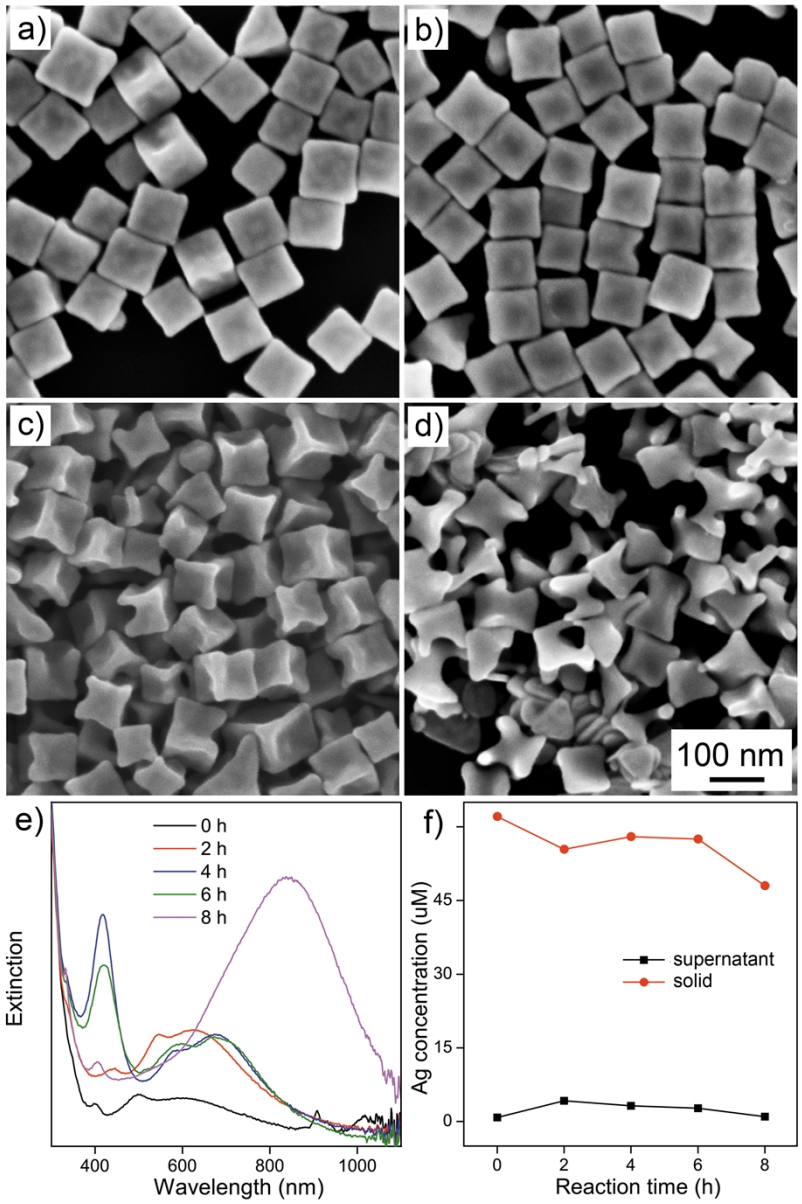

Fig. S2 a-d) SEM images of Ag nanoparticles obtained from the typical solvothermal syntheses terminated at different time points of a) 2, b) 4, c) 6, and d) 8 h, respectively. e) The corresponding UV-Vis spectra of the product shown in a-d). f) ICP-MS analysis of Ag content in the supernatant and the solid of fresh product collected at different reaction time points. The samples were also corresponding to that shown in a-d). The supernatant and solid were separated by centrifugation at 55000 rpm for 30 min.

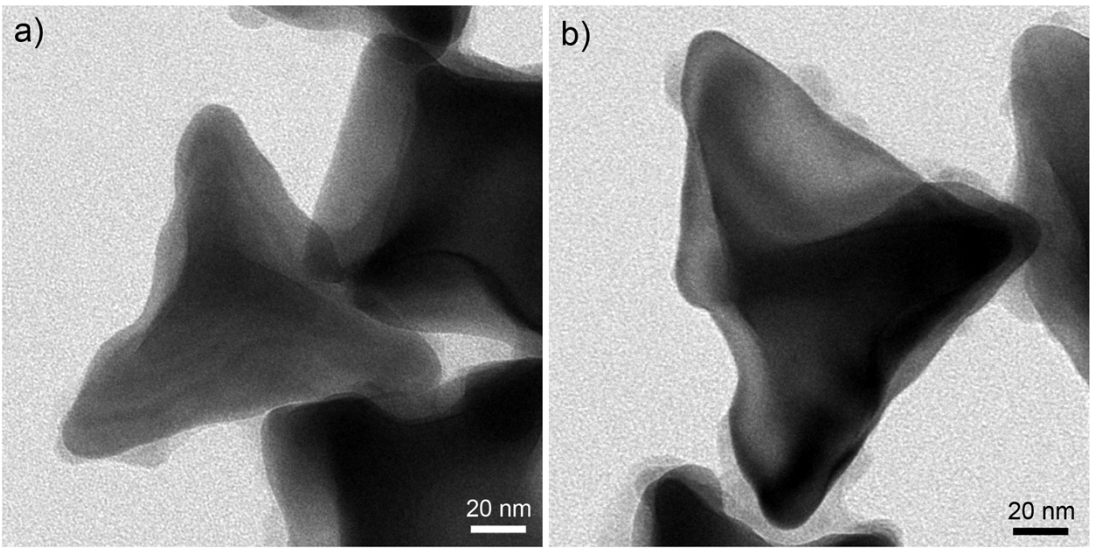

Fig. S3 TEM images of Ag bipyramids with concave facets as by-product obtained in the synthesis of Ag nanocubes with concave facets.

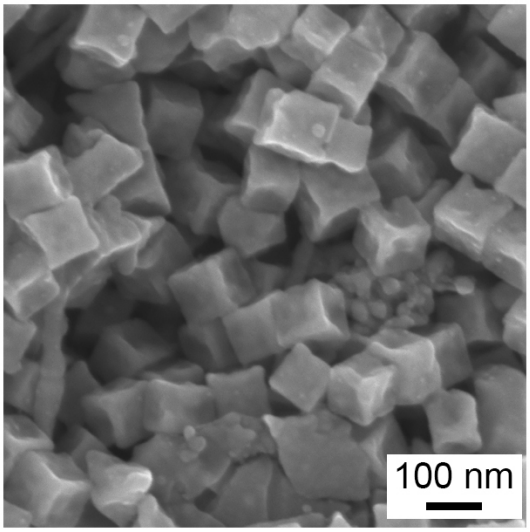

Fig. S4 SEM images of Ag nanoparticles obtained from a typical reaction heated under atmospheric pressure. The reaction was conducted in an opened flask that equipped with condensing pipe to prevent ethanol evaporation.

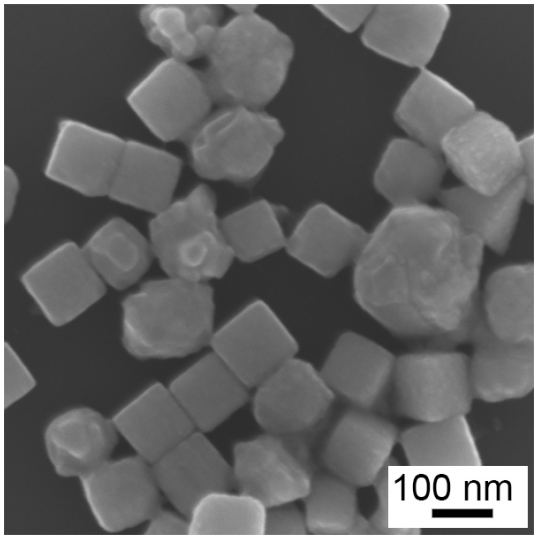

Fig. S5 SEM image of Ag nanoparticles obtained from a synthesis under the argon atmosphere at 80 ^{o}C for 6 h.

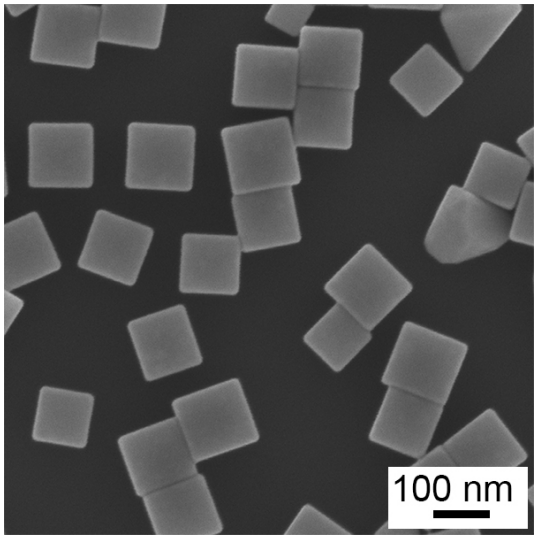

Fig. S6 SEM image of Ag nanoparticles obtained from a solvothermal treatment in ethanol without the addition of PVP29K.

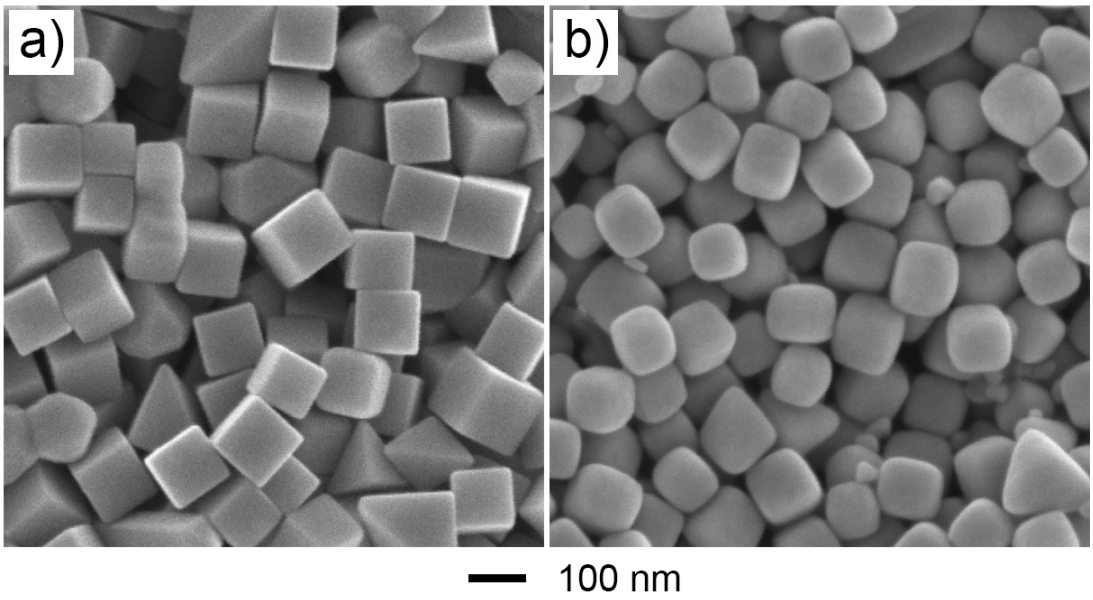

Fig. S7 SEM images of Ag nanoparticles obtained from the typical syntheses with the addition of a) PVP10K and b) PVP55K to instead of PVP29K. PVP with different molecular weight was added at the same mass concentration.

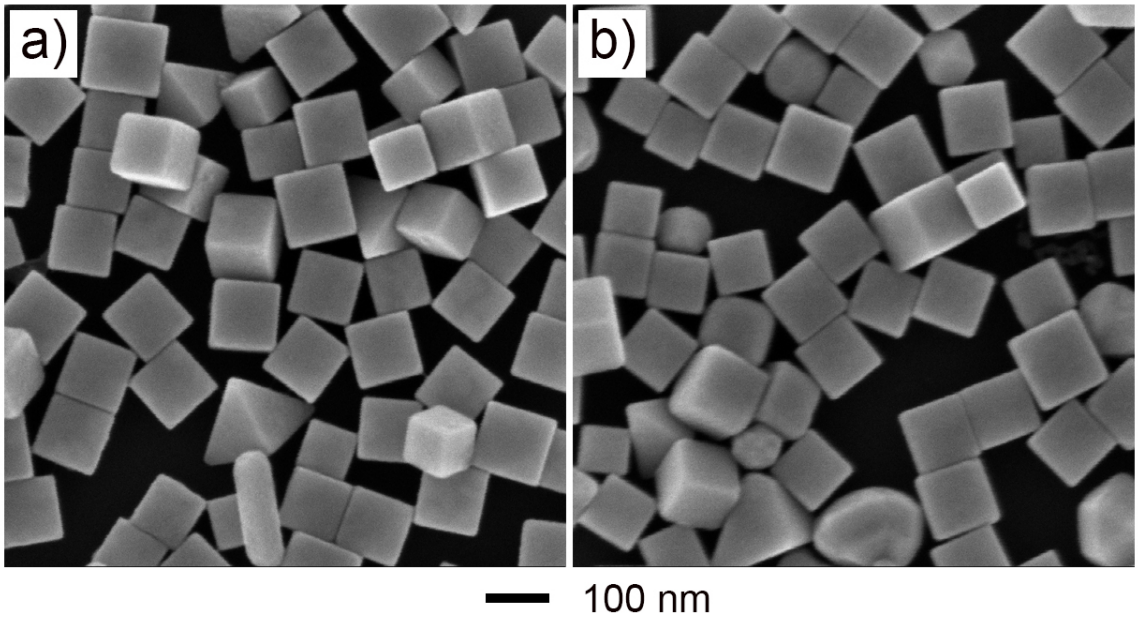

Fig. S8 SEM images of Ag nanoparticles obtained from the typical syntheses with the addition of a) 1mM ascorbic acid to instead of PVP29K, and b) 1mM ascorbic acid in the reaction with PVP29K.