ESI

Direct structural transformation of silver platelets into right bipyramids and twinned cube nanoparticles: morphology governed by defects

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Experimental

Reagents. Silver nitrate (99%), sodium citrate tribasic dihydrate (Aldrich 99+%), polyvinylpyrrolidone (PVP, M_w = 40K), and sodium borohydride (99%), all supplied by Aldrich, were used as received. High-purity deionized water (>18.4 MΩ·cm) was produced by Millipore A10 Milli-Q.

Transformation of silver platelets into cubes and bipyramids. The silver platelets were prepared using a standard procedure in aqueous solution reported in the literature.[1] Typical concentration of silver in the platelets was 0.15 mM, and their average dimensions were in a range from 20 to 50 nm in width (edge length for triangular platelets and the largest lateral dimension for truncated triangles and hexagons) and 4 to 10 nm in thickness. In a typical experiment of platelet transformation, 3-10 ml of platelet dispersions were used, to which 50 to 600 % of new silver relative to that present in the platelets was added in a form of silver nitrate. After that solutions were immediately rapidly brought to 95^0C or boiling and kept at this temperature for 3-4 minutes to complete the transformation. Heating was performed either using Heidolph MR3004 or domestic microwave (Panasonic NN-T685SF). Typical concentrations of PVP and citrate in transforming platelets were 0.1 mmol and 2 mmol respectively. Several series of experiments were performed to vary silver, PVP and citrate concentrations.

Characterization. Electron microscopy (both TEM and SEM) was performed using Hitachi S-5200. NP dispersions were deposited on carbon-coated formvar grid (EMS Corp.). Operating voltage was 30.0 kV. The average size and standard deviation were determined from SEM and TEM images by averaging diameters of at least 100 particles.

[1] G. S. Metraux and C. A. Mirkin, *Adv. Mater.* 2005, **17**, 412.

UV-Vis spectra were acquired with either Ocean Optics QE-65000 fibre-optic UV-Vis spectrometer or Cary 50Bio UV-Vis spectrophotometer. Raman spectra were recorded using R-3000QE fibre-optic Raman spectrometer equipped with 290 mW laser at 785 nm (RSI).

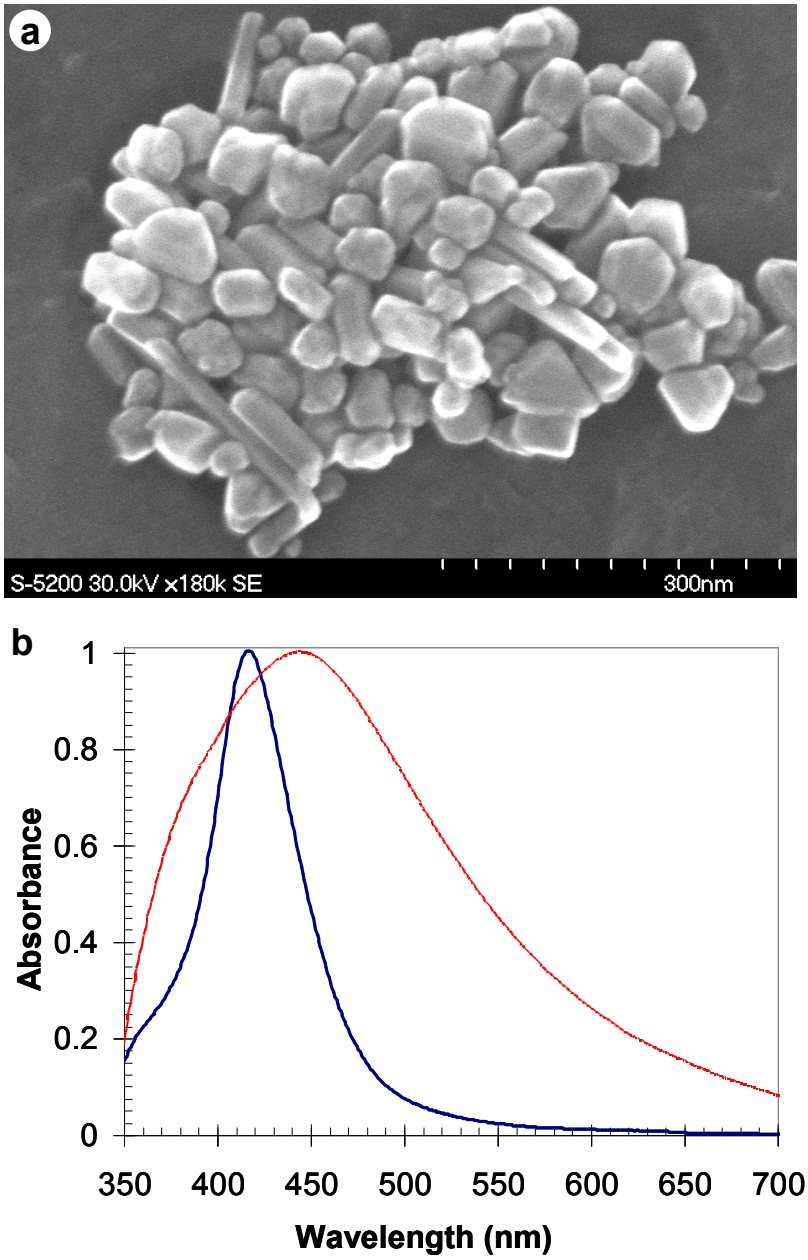

Figure S1. **a)** SEM images of AgNPs formed by heating silver nitrate in absence of platelets and otherwise similar conditions; b) Comparison of UV-vis spectra of NPs formed by silver nitrate heated in absence of platelets (broad red spectra) and platelets transformed using the same amount of silver (narrow blue spectra).

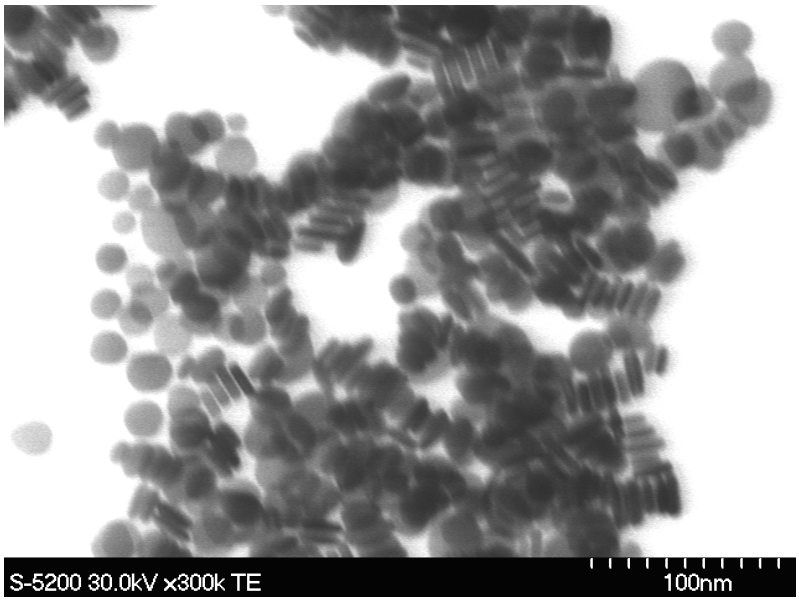

Figure S2. TEM images of silver platelets heated without silver in conditions similar to platelet transformation to cubes and bipyramids in presence of silver.

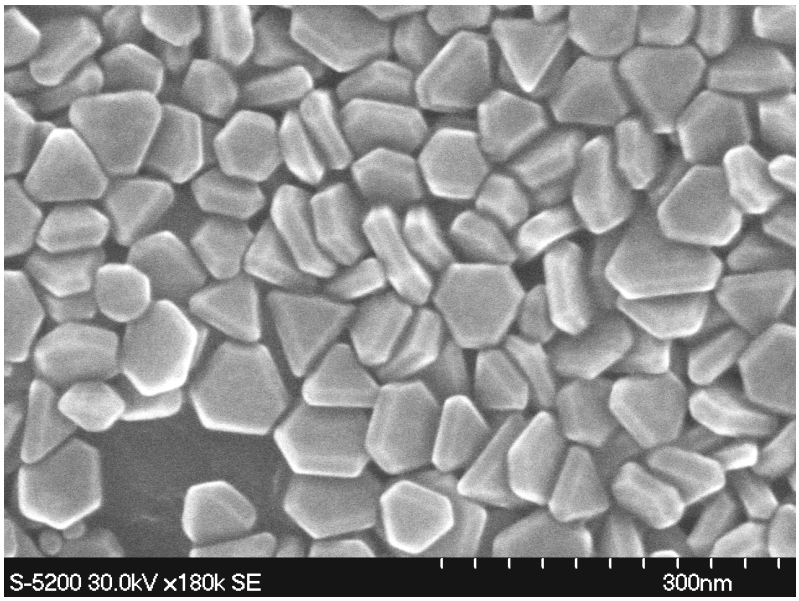

Figure S3. SEM images of thicker silver platelets during the earlier stages of platelet conversions to cubes and bipyramids. Note the large amount of truncated triangular (near hexagonal) platelets.

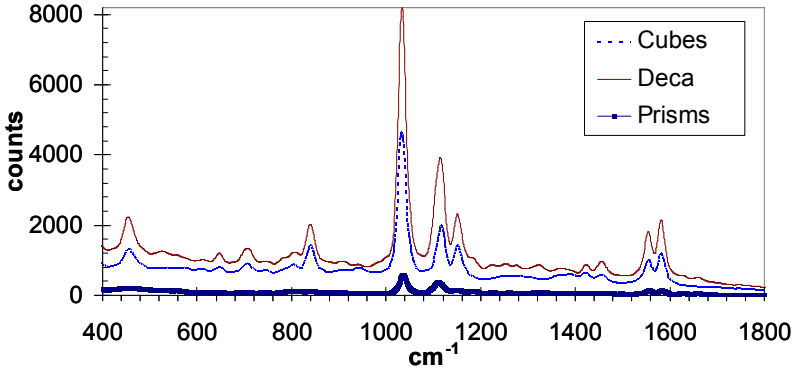

Figure S4. Comparison of SERS efficiency of several silver NPs including platelets (prisms), decahedra and mixture of cubes and bipyramids (with the same silver concentration and surface coverage of ca. 2 monolayers) serving as an active substrate for detection of thiosalicylic acid as an active molecule. Spectra were collected for 10 seconds at laser power of ca. 150 mW.