Utilizing AgCl:Ag and AgCl Mesostructures as Solid Precursors in the Formation of Highly Textured Silver Nanomaterials via Electron-Beam Induced Decomposition

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Experimental Section.

Chemicals

Ethylene glycol (EG, J. T. Baker), poly(vinyl pyrrolidone) (PVP, Mw ≈ 5.5 × 10^4), Sodium hydrosulfide (NaSH nH2O), Rhodamine 6G (R6G, 95%), Silver trifluoroacetate (CF_3COOAg, 99.999%) were all obtained from Aldrich. All chemicals were used as received.

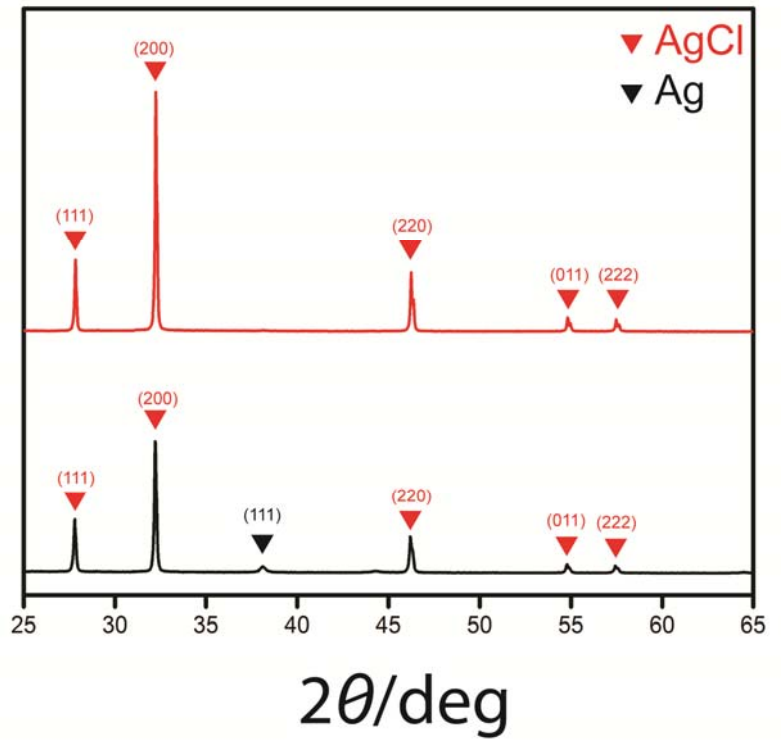
AgCl:Ag, and AgCl nanostructure synthesis:

In a typical procedure for the generation of AgCl:Ag, or AgCl nanostructures, 5 mL of Ethylene Glycol (EG) was injected into a vial with a Teflon-coated stir bar and heated in air at 150^{o}C for 30 minutes. Subsequently, 60 µL of a 3 mM NaSH solution in EG was then added to the hot EG. After two minutes 0.5 mL of 3mM HCl in EG and 1.25 mL of PVP (20 mg/mL in EG, Mw≈5.5x10^4) were added and allowed to heat for an additional two minutes. Finally, 0.4 mL of a 282 mM CF_3COOAg solution followed immediately by 0.4 mL of 208 mM R6G (AgCl:Ag) or HCl (AgCl) solution. The reaction mixture

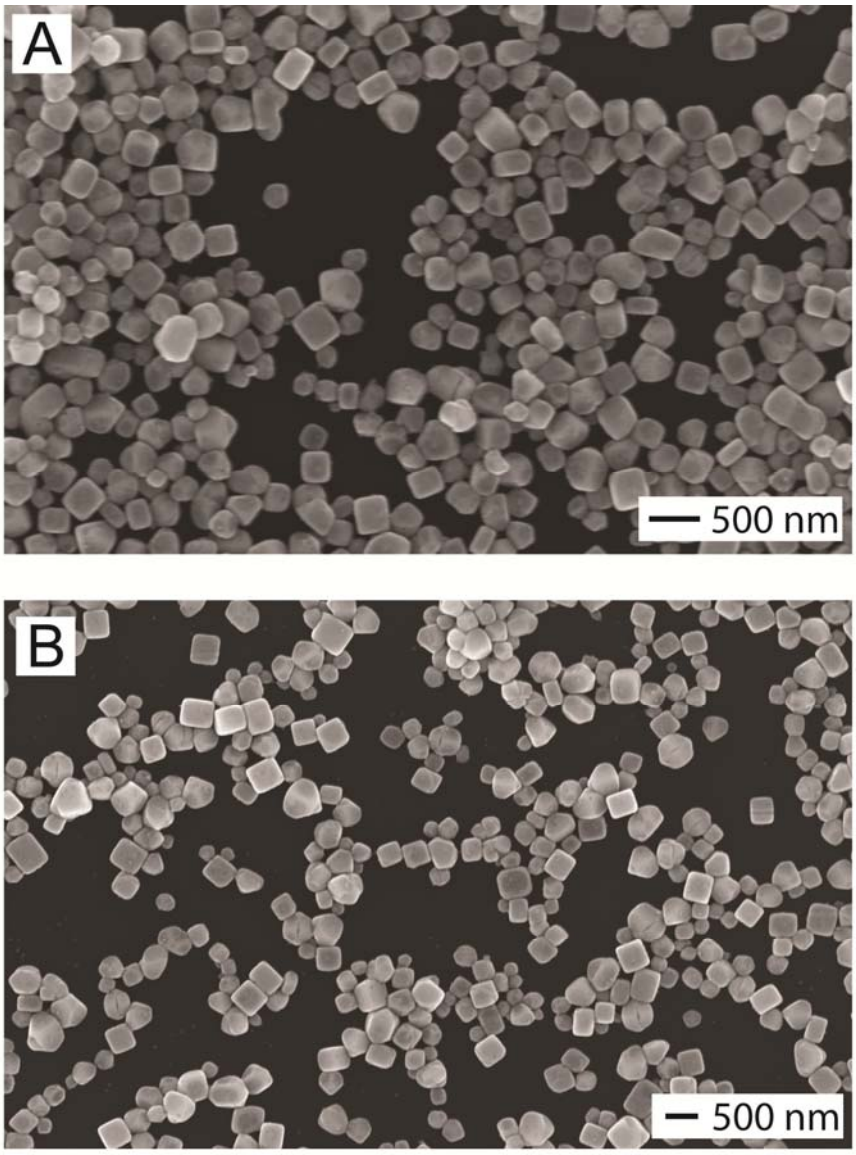
was continuously heated at 150^{o}C in air for 80 minutes. The solution was then washed with acetone and 18 MΩ D.I. water to remove excess organics.

Characterization

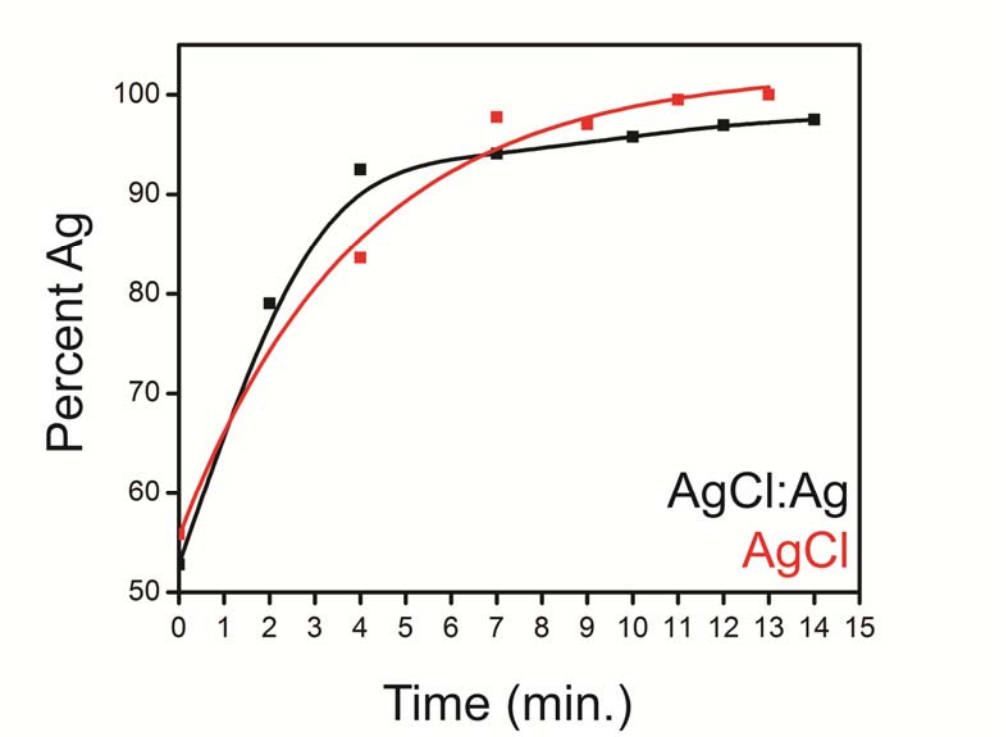
Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDAX) samples were prepared by drop casting a dispersion of the nanostructures onto a Si chip and allowing them to dry in air. SEM and EDAX analysis were performed with a Carl Zeiss Merlin FE-SEM operated at 20 kV with a working distance of 6.1 mm. Powdered X-ray diffraction pattern (PXRD) measurements were performed at a PANalytical X' pert PRO 2-circle X-ray diffractometer with a Cu Kα radiation (λ ≈ 1.5418 Å). The scan range is from 2θ 5˚ to 90˚. Raman spectra were recorded with a Renishaw system 1000 Raman spectrometer equipped with an integral microscope (Leica DMLMS/N). The laser line of 632.8 nm from a 25-mW air-cooled He-Ne laser (Renishaw) was used as an excitation source. Raman scattering was collected with a dry objective in 180° configuration. With a holographic grating and a 50-ím slit, a spectral resolution of 1 cm^{-1} was obtained. A silicon wafer with a Raman band at 520 cm^{-1} was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm^{-1}. For SERS characterization an ethanol solution containing a known concentration of 0.1 mM rhodamine 6G chloride (R6G) was used. Laser power was at 100% and 25% for AgCl and AgCl:Ag samples respectively.



S1: XRD pattern of AgCl:Ag (Black) and AgCl (Red) cubic nanostructures



S2. SEM of the different stages of a AgCl:Ag standard synthesis that used 208 mM R6G removed at (a) 10 and (b) 20 minutes which have average edge length of ~250 and ~350 nm respectively.



S3. EDAX measurements of a singular AgCl:Ag (Black) and AgCl (AgCl) with respect to time under the electron beam.