Supplementary Information

Top-down and Bottom-up Reconstruction of Matter in Charged Water Microdroplets

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Experimental section

Materials

Silver powder (APS 4–7 µm, 99.9% metal basis) and copper powder (APS 10 µm, 99.9% metal basis) were purchased from Thermo Scientific, USA. Silver flakes (≤10 µm, ≥99.9% trace metal basis) and gold powder (≥99.9% trace metal basis) were purchased from Sigma-Aldrich, USA. In contrast, silver acetate (AgOAc, ≥99%) and gold(III) acetate ($[Au(OAc)_3]$, ≥99%) were purchased from Sigma-Aldrich, India. Copper acetate monohydrate ($[(CH_3COO)_2Cu\cdot H_2O]$, ≥98%) was purchased from Merck Specialities, India. Methylene blue was also purchased from Sigma-Aldrich, India. All products were used as received without further purification. Ultrapure water (resistivity > 18.2 MΩ·cm) was used for all aqueous solution preparations.

Preparation of precursor suspensions and solutions

For the top-down approach, 0.5 mg of metal powder was weighed and suspended in 1 mL of ultrapure water, and the freshly prepared suspension was loaded into a Hamilton syringe for electrospray. For the bottom-up approach, 5 mM solutions of silver acetate and copper acetate were prepared in water; in contrast, gold acetate was prepared in acetonitrile by sonicating for 30 min, then centrifuging, and the supernatant was collected for experiments. These freshly prepared solutions were loaded into n-ESI glass electrospray emitters (inner diameter 25-30 µm).

Electrospray deposition setup

For the top-down experiments, a custom-built electrospray ionization (ESI) setup was employed to generate microdroplets. A gastight Hamilton syringe (0.5 mL) fitted with a 22-gauge needle (inner diameter: 413 µm) was connected to a fused-silica capillary (50 µm inner diameter) using a union connector. The syringe needle was electrically connected to a high-voltage power supply, while a carbon-coated copper TEM grid (300 mesh) placed on the plate collector served as the grounded counter-electrode (carbon-coated copper TEM grids were used for silver and gold experiments, while carbon-coated gold TEM grids were used for copper experiments). The flow rate of 0.1 mL h^{-1} was precisely controlled using a stepper motor with 400 steps per rotation, and deposition experiments were carried out under ambient conditions for 30 min. The polyimide-coated fused-silica capillary was obtained from Polymicro Technologies™ (Molex, USA), while the union connector, PEEK tubing, and ferrules were purchased from IDEX Health & Science (USA).

For bottom-up experiments, a custom-built nanoelectrospray ionization (nESI) source was mounted on a burette stand. The emitter was positioned 2 cm from the ground electrode, and a potential of approximately 2.5 kV was applied to induce electrospray from the emitter. TEM grids, cleaned and placed on an indium tin oxide (ITO)-coated glass slide, were used as the ground electrode.

Characterization

To image the morphology of the parent metal powders, a Thermo Fisher Scientific Verios G4 UC high-resolution field-emission scanning electron microscope (FESEM) was used at an accelerating voltage of 10 kV and an emission current of 0.10 nA. For nanoparticle imaging, a Thermo Fisher Scientific Talos™ F200i transmission electron microscope (TEM) was used at 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) were employed for elemental mapping of nanoparticles. To remove surface impurities and render the carbon-coated TEM grids more hydrophilic, a glow discharge was performed using a Quorum GloQube Plus. Lattice fringes in HRTEM images were measured using Gatan Microscopy software. UV–visible spectra were recorded using a PerkinElmer Lambda 365 spectrophotometer. XPS was performed using an ESCA probe TPD spectrometer (Omicron) with polychromatic Al kα (hν = 1486.6 eV) X-ray source to comprehend the chemical oxidation states of elements.

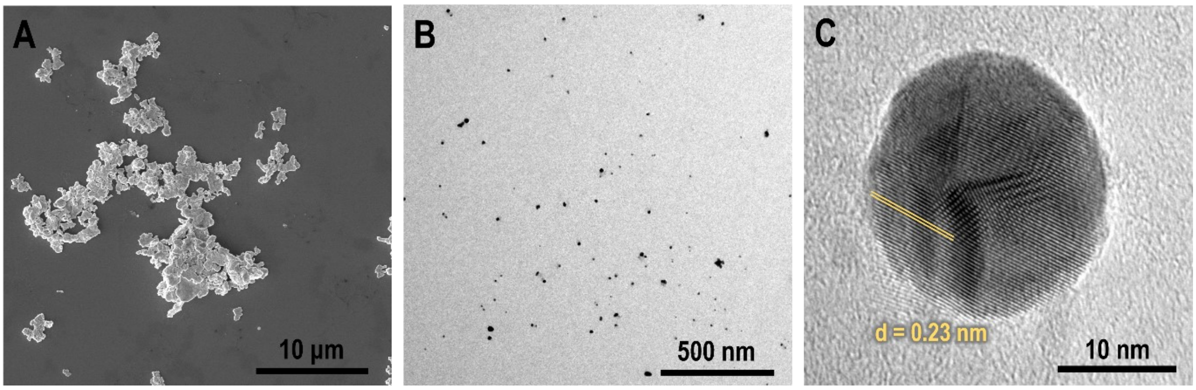

Figure S1. Experimental data obtained for the top-down fragmentation of silver flakes. A) SEM image of the parent silver flakes. B) Large-area TEM image of the fragmented nanoparticles. C) HRTEM image of a representative nanoparticle.

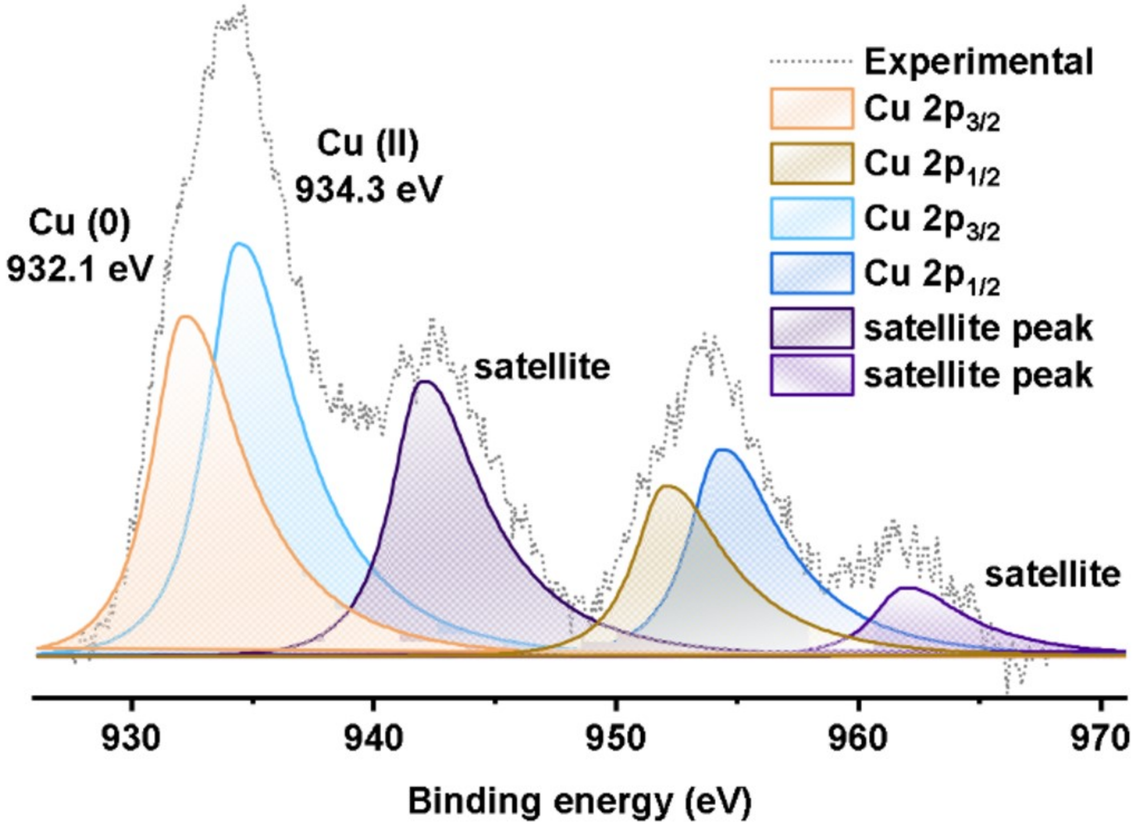

Figure S2. XPS spectrum of copper nanoparticles formed by the top-down approach.

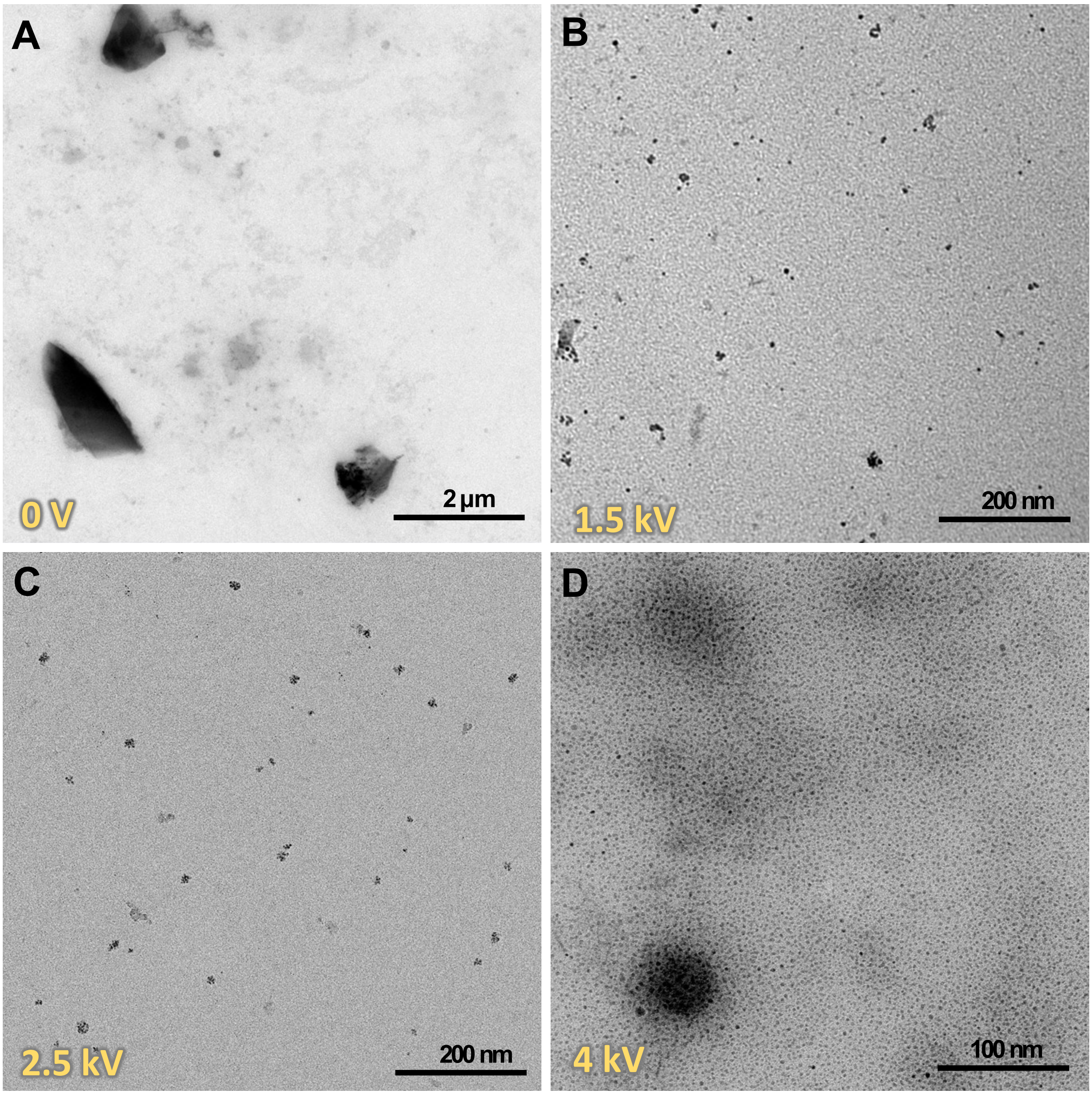

Figure S3. TEM images demonstrating voltage-dependent Cu particle disintegration, A) 0V, showing partial disintegration due to mechanical stress generated by the gas pressure of 50 psi. B-D) 1.5, 2.5, and 4 kV of applied potential demonstrating progressive size reduction in the resulting nanoparticles.