Supplementary Information (SI) for Nanoscale.

Electronic Supplementary Information

Controlling the Formation of Fast-Growing Silver Nanocubes in Non-Polar Solvents

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Experimental Section

Synthesis details

Nanoparticle purification. The temperature of the solution was kept at 50 °C prior to every centrifugation step to ensure the removal of all organic residues. At ambient temperature, some organic material (*e.g.*, oleylammonium chloride (OlAmoCl)) can solidify and precipitate with the nanoparticles.

The solution was filled into a 50 mL centrifugal tube (polypropylene, Labsolute) and centrifuged at 800*g* for 15 min. The supernatant was removed, and the nanoparticles were redispersed in 25 mL hexane by sonication for 5 min. The second centrifugation step was performed at 500*g* for 5 min. The redispersion was carried out according to the first step. The nanoparticles were centrifuged for a third time at 300*g* for 3 min, the supernatant was removed, and the nanoparticles were finally redispersed in 10 mL hexane.

Experiments with dimethyldistearylammonium chloride (DDAC). In the case where DDAC was used instead of OlAmoCl, 365-440 mg DDAC was added to the mixture of 20 mL dibenzyl ether (DBE) and 2.6 mL oleylamine (OlAm). 365 mg DDAC was used in a static argon atmosphere, while an increasing argon flow was used with increasing amounts of DDAC. Additionally, the chloride precursor was kept at 260°C for 20 min (constant gas flow) or 10 min in a static argon atmosphere to give the DDAC enough time to react and another 10 min with an argon flow (~2 L/h) to remove water from the mixture. Other than that, the synthesis was carried out as described in the experimental section of the main publication.

Chloride variations. For the experiments in which the Cl:Ag ratio was varied, the amount of silver was kept constant at 0.6 mmol. The amount of OlAmoCl solution used was varied between 0.4 and 1.14 mL. OlAm was then added up to a total volume of 2.6 mL.

Solvent exchange. To examine the role of DBE, it was exchanged with 1-octadecene (ODE). In addition, $FeCl_3 \cdot 6H_2O$ was dissolved in acetone to receive a 1 g/L solution. 0.3 mL of this solution was dried in an argon flow in the reaction vessel before the addition of the other components.

Influence of nitrate. The influence of nitrate on the oxidative etching of the multiple twinned Ag nanoparticles was tested with two different experiments. In the first experiment, $AgNO_3$ was replaced by the same amount of Ag acetate (31.73 M solution in OlAm). In the second experiment, NH_4NO_3 was added to the $AgNO_3$-OlAm precursor solution to increase the amount of nitrate by a factor of 1.5. The resulting NH_4NO_3 concentration was 15.87 M in the precursor solution.

Characterization

Infrared spectroscopy (IR). IR spectra were recorded with a JASCO FT/IR-4100 IR spectrometer. The measurement range was 4000-600 cm^{-1} with a step size of 4 cm^{-1}. The samples were applied as a liquid on the attenuated total reflectance (ATR) crystal.

Thermogravimetric analysis (TGA). The determination of organic residues in the final particle samples was performed using a Netzsch TG209 F1 libra with the external cooling system Julabo F32-MA. After a 10 min equilibration period, 2-6 mg of dried sample was heated in an Al_2O_3 crucible up to 600 °C at a rate of 10 K/min. A nitrogen gas flow of 20 mL/min was used during the measurement.

Scanning electron microscopy (SEM). SEM images were recorded on a Hitachi SU 5000 Schottky field emission scanning electron microscope in the secondary electron (SE) mode with an electron acceleration voltage of 15 kV and a spot intensity of 30. The working distance was set to 3 mm. The nanoparticle dispersion in hexane was dropped undiluted onto an uncoated copper grid (Cu 400 mesh, Plano GmbH) and dried before the measurement. The software FIJI was used to evaluate the particle size for at least 300 particles per synthesis on three or more images from different spots. The same software was also used to determine the number of multiply twinned and single crystalline nanoparticles. For this purpose, a total of 6000-10000 particles per sample were analyzed on at least five different images from different spots.

Transmission electron microscopy (TEM). TEM investigations were conducted on a conventional Tecnai $G^2$20 S-TWIN transmission electron microscope (FEI/TFS Company, USA) with a LaB_6 emitter, operated at 200 kV. For image acquisition, a US1000 CCD camera and the DigitalMicrograph software (both: Gatan Inc., USA) were used. The samples were prepared on carbon-coated copper grids (carbon-coating type A, 6-10 nm thickness, Cu 400 mesh, Plano GmbH) from the undiluted nanoparticle dispersion in hexane.

Energy-dispersive X-ray analysis (EDX). The SEM was equipped with an EDAX X-ray detector (Octane Elect Plus) to analyze the elemental composition of the samples. During the measurements, the SEM was operated with an acceleration voltage of 15 kV and a spot intensity of 50. The working distance was set to 10 mm. The resolution of the detector was 126.2 eV. The samples were deposited on uncoated copper grids in a layer several micrometers thick and measured on a STEM holder. Areas of 2x2 mm^2 were measured at three different locations of the sample with 200 s accumulation time. The results for chlorine and silver were corrected by measurements with standards.[1]

X-ray diffraction spectrometry (XRD). The samples were prepared by drying 2-3 mg of silver nanoparticles on a glass slide (76x26 mm, Elka). The samples were measured in Bragg-Brentano geometry with a fixed sample stage and movable X-ray source and detector arm. A Bruker D8 Eco X-ray diffractometer was used equipped with a LYNXEYE XE-T detector and a Cu Kα1 radiation source (25 kV, 40 mA) with a radiation wavelength of 0.15405 nm. The angular range of the measurements was 25-80° 2θ with a step size of 0.025°. The measurements were performed right after sample purification.

Additional Data

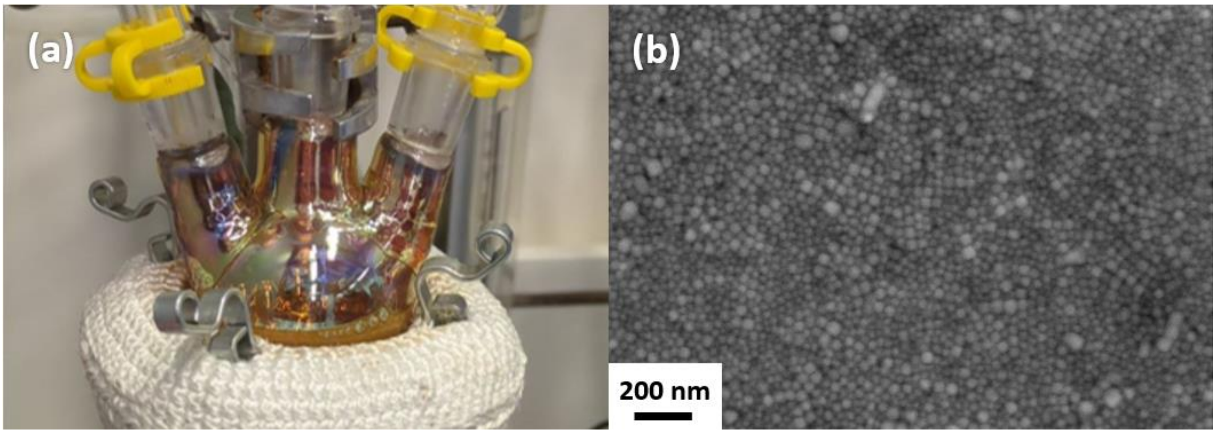

Figure S1: (a) Photograph of the occasionally occurring silver mirror and (b) SEM image of the resulting Ag nanoparticles.

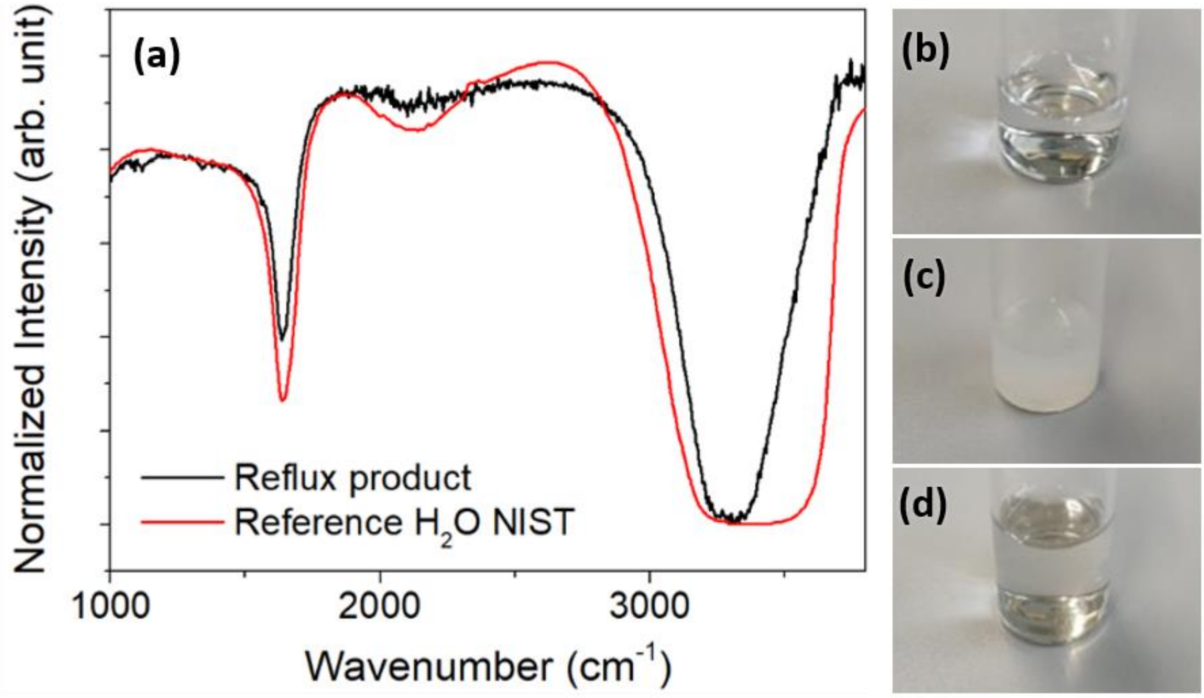

Figure S2: (a) IR spectrum of the reflux product and the reference spectrum of water from the NIST database as well as photographs of the chloride detection reaction: $AgNO_3$ solution (b) before and (c) after the addition of the reflux product and (d) after a 25 % NH_3 solution was added to the solution shown in image (c).

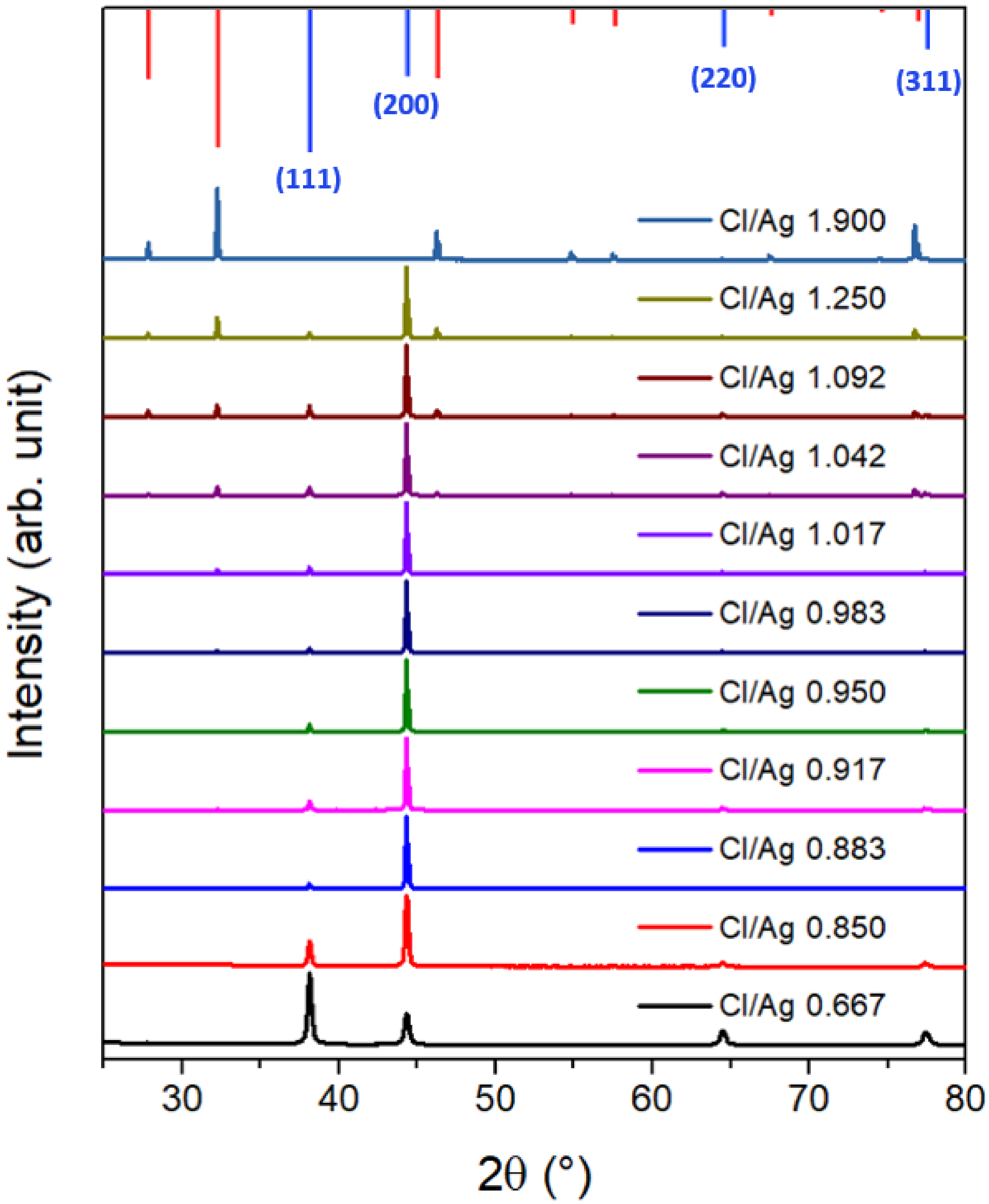

Figure S3: X-ray diffractograms of several samples from silver nanocube syntheses with different Cl:Ag ratios. The diffraction pattern for AgCl (COD: 9011666) is displayed in red on the top of the image, the pattern for Ag (COD: 9008459) is displayed in blue.

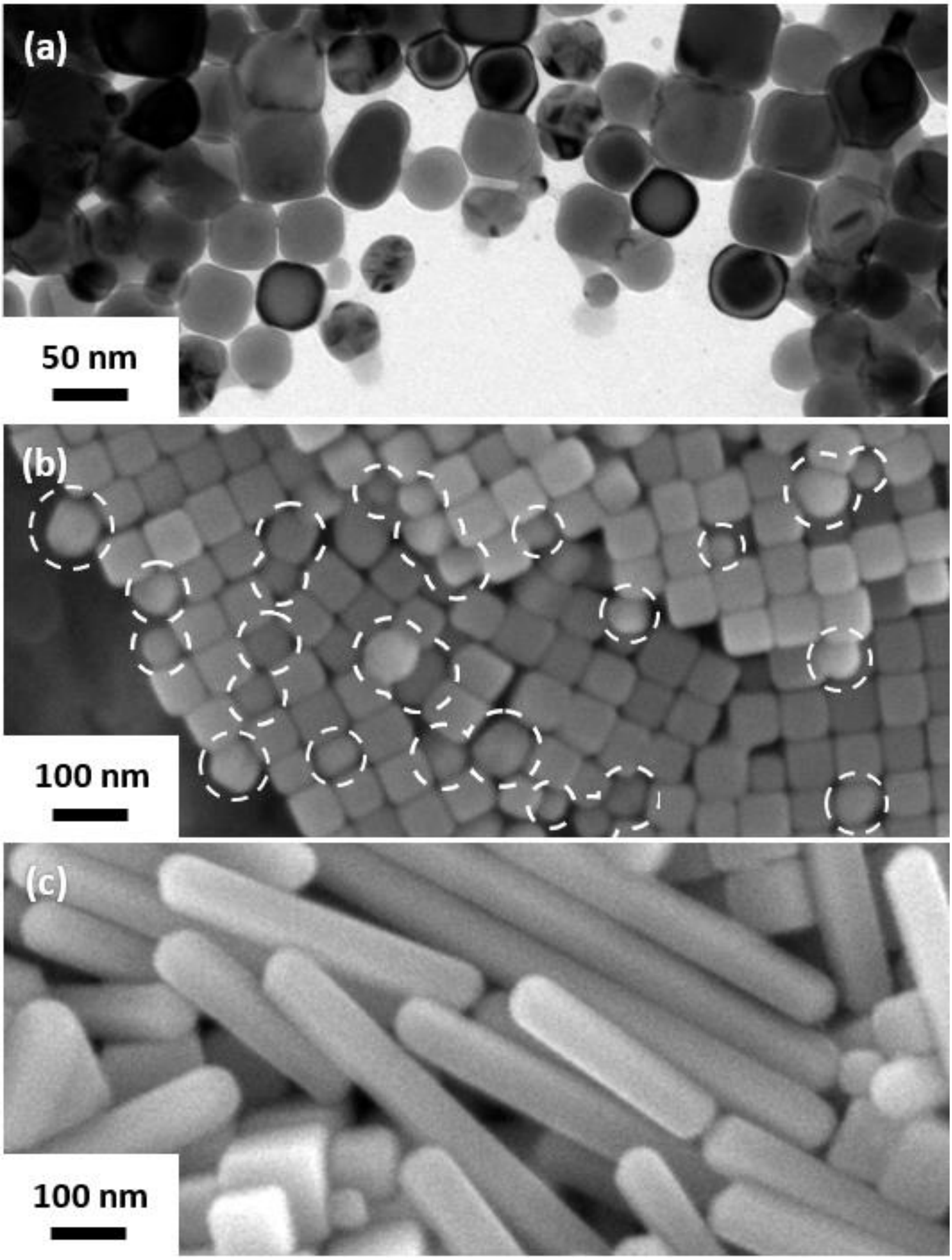

Figure S4: EM images of multiple twinned (MT) nanoparticles alongside single (SC) crystalline nanocubes: (a) TEM image showing a uniform contrast for SC nanocubes and a blotchy contrast for MT nanoparticles, (b) SEM image of medium-sized nanocubes and MT nanoparticles (in white dashed circles) and (c) SEM image of nanorods at high magnification.

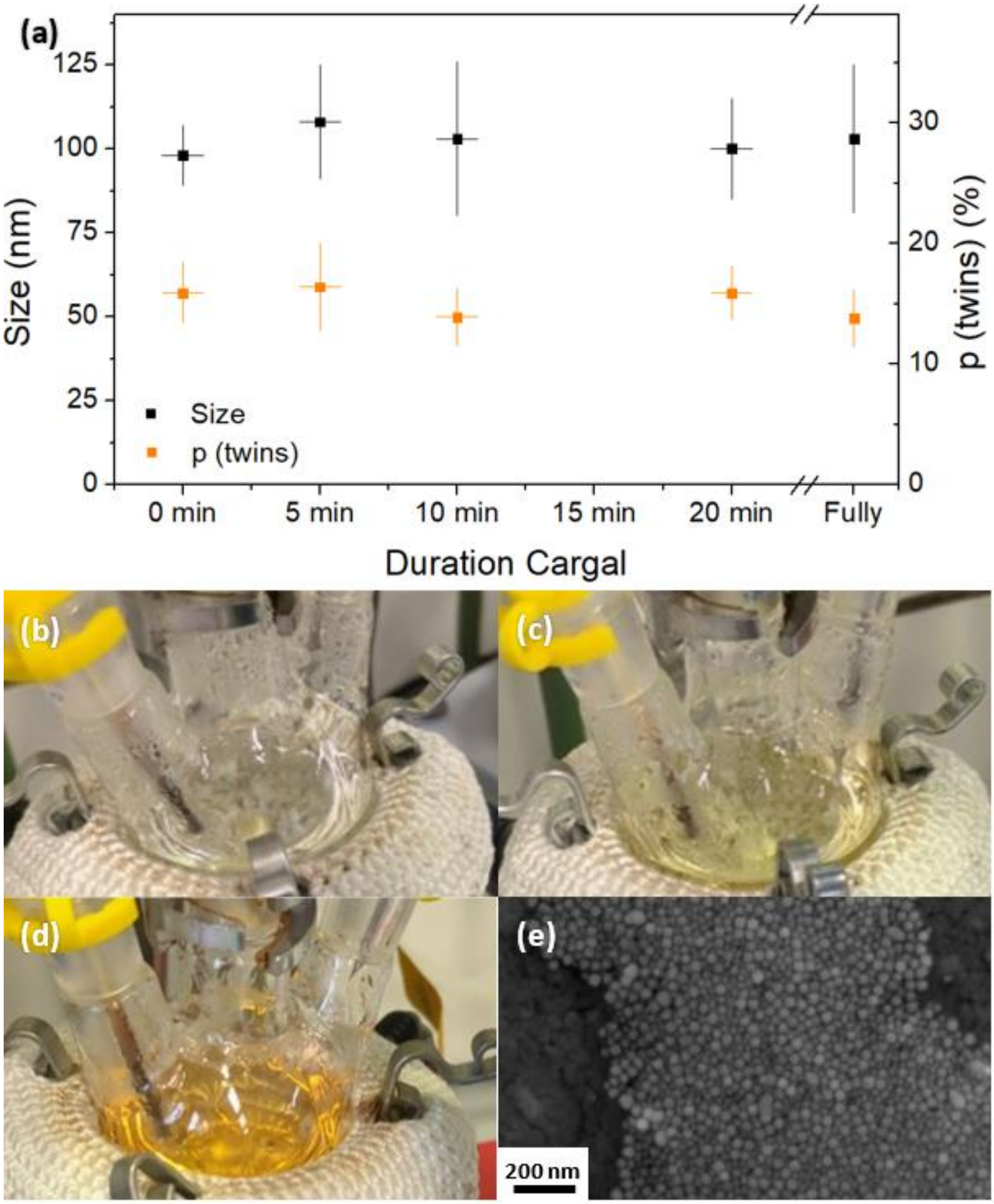

Figure S5: Study on the influence of oxygen. (a) edge length of the nanocubes and number of MT Ag nanoparticles in the product as a function of the Cargal flow duration, (b) – (d) photographs of the reaction solution before injection of the Ag precursor at different levels of oxygen exposure: (b) no exposure, (c) synthesis performed completely under Cargal atmosphere, and (d) synthesis performed under ambient atmosphere, and (e) SEM image of the nanoparticles obtained from the synthesis performed under ambient atmosphere.

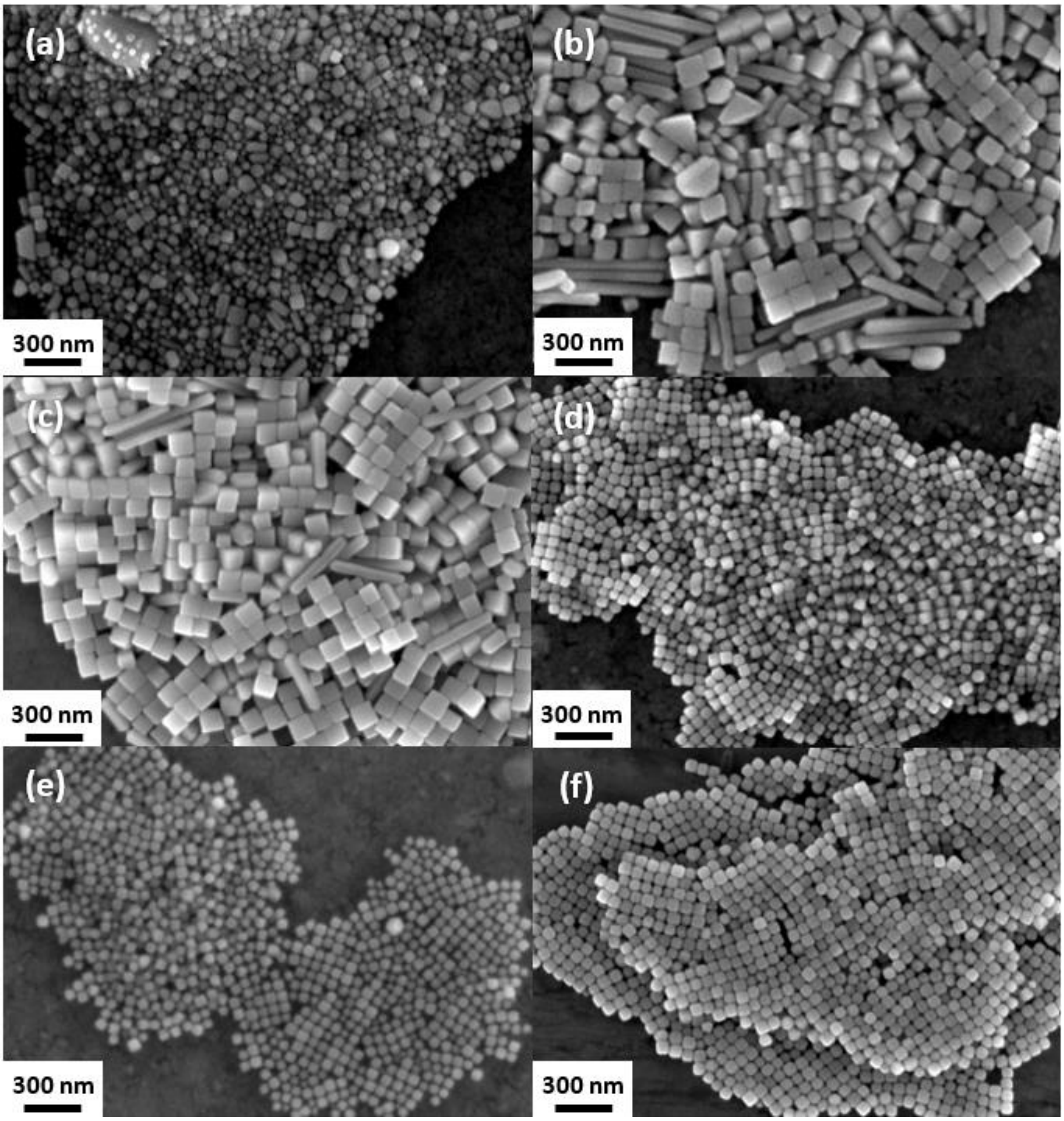

Figure S6: SEM images of the nanoparticles obtained at different temperatures: (a) 0.525 mmol Cl^- at 220 °C, (b) 0.525 mmol Cl^- at 240 °C, (c) 0.525 mmol Cl^- at 260 °C, (d) 0.525 mmol Cl^- at 270 °C, (e) 0.525 mmol Cl^- at 280 °C, and (f) 0.55 mmol Cl^- at 290 °C.

References

1 Mausz, J., EDAX AMTEK, personal communication, **2024**.