Synthesis of Silver Nanoparticle Necklaces without Explicit Addition of Reducing or Templating Agents

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Supplementary Information

Materials and Methods

Chemicals. Silver nitrate (99%), ammonia (30%), sodium hydroxide standard solution (0.1 N), nitric acid standard solution (1 N) were purchased from Carl Roth GmbH + Co. KG (Germany). Ethanol (99.8%) was purchased from VWR International GmbH (Germany). Tetraethyl orthosilicate (TEOS 99%) was purchased from Merck KGaA (Germany). All chemicals were used as received and water was taken from a Millipore system.

Synthesis of silica particles. Silica particles were synthesized using the Stöber method.[25] Briefly, 51 mL of TEOS was added to a mixture of 629 mL ethanol, 62.9 mL water and 26.47 mL of ammonia under vigorous stirring. After five minutes the stirrer was set to a medium stirring rate and stirring was continued for four hours. The particles were washed three times with ethanol by centrifugation and redispersion and dried under vacuum at 90°C overnight. The silica particle size was determined by SEM to be 185 ± 9 nm.

Characterization. Scanning electron microscopy (SEM) analysis was carried out at 10 kV using an ULTRA 55 field emission SEM (Carl Zeiss AG, Germany). Transmission electron microscopy (TEM) was performed at 300 kV in diffraction contrast, high-resolution TEM (HRTEM) and high angle annular dark field scanning TEM (HAADF-STEM) modes using a Titan^3 80-300 instrument (FEI Company, Netherlands) equipped with a field emission gun and image side spherical aberration corrector. Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) analyses were performed with a SPECTRO CIROS-CCP spectrometer. The instrument was calibrated with solutions obtained by diluting commercial Si (1000 mg/L; Aldrich) and Ag (1000 mg/L; Bernd Kraft GmbH) standards, with a 0.01 M solution of ammonia. The latter solution was also used as blank. The samples were prepared by diluting 1.00 mL of supernatant to 10 mL, with bi-distilled water. A Zetasizer Nano instrument (Malvern Instruments Ltd., UK) was used to measure zeta-potential.

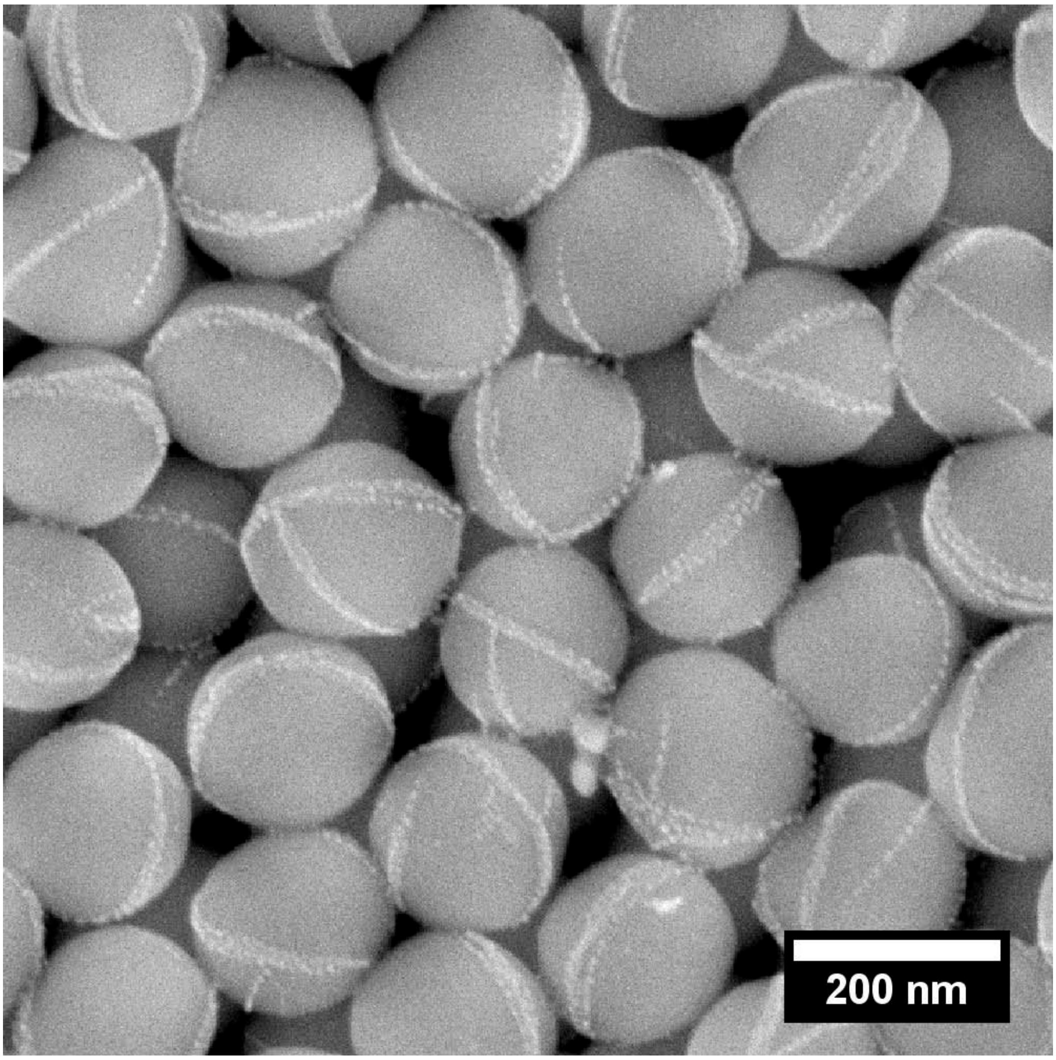


Figure S1. SEM image of silica spheres coated with long silver nanoparticle necklaces.

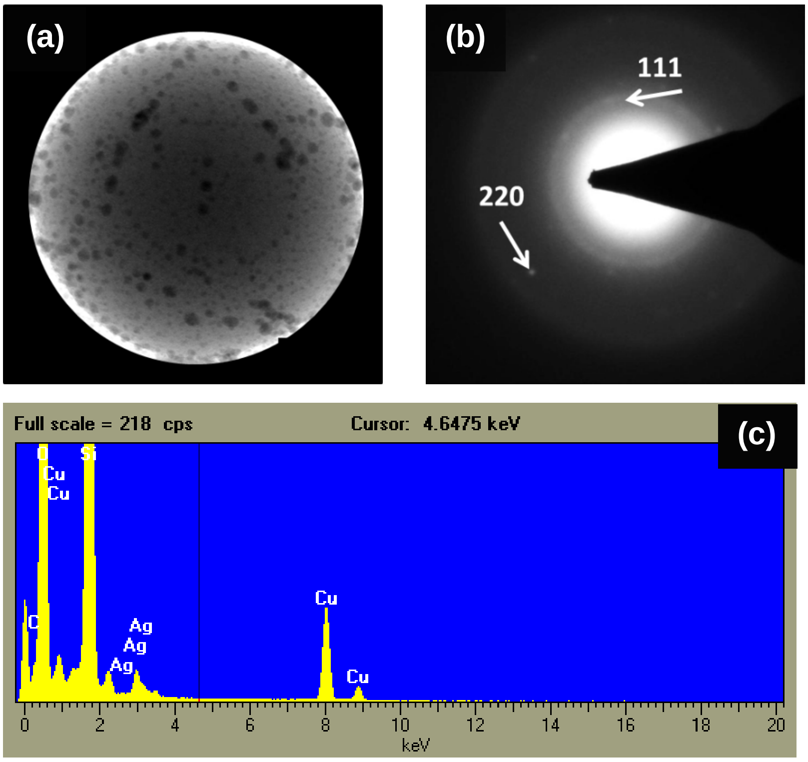
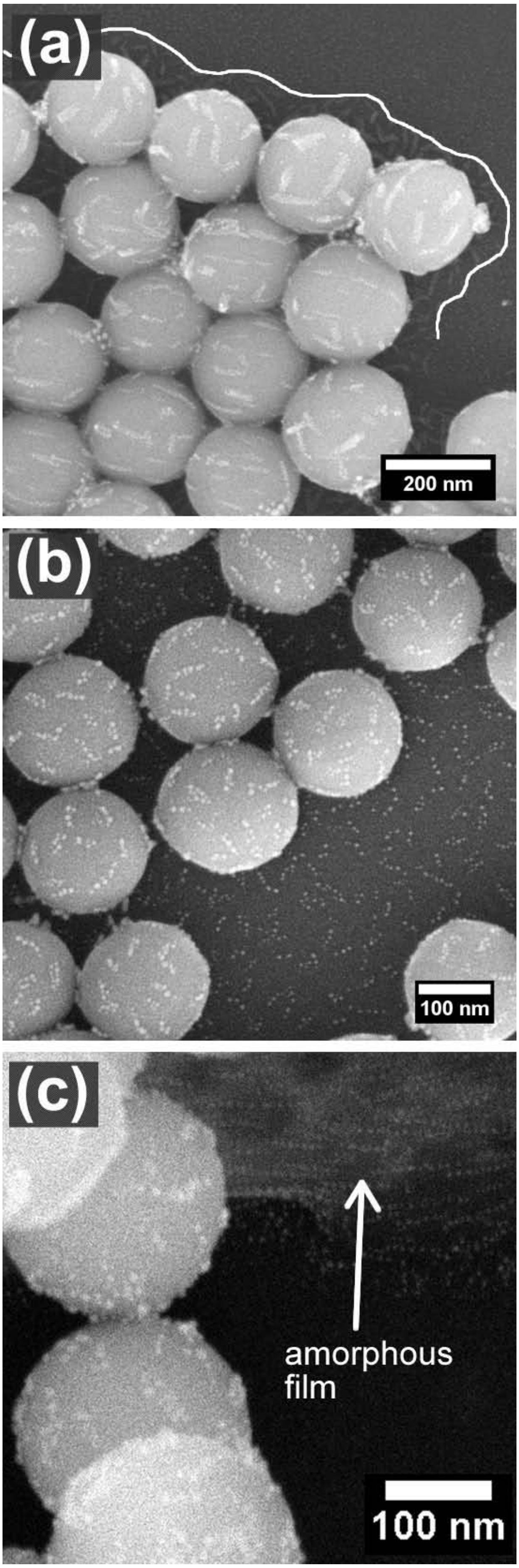


Figure S2. (a) Bright field TEM image of a silver nanoparticle necklace coated silica particle that was investigated by selected area electron diffraction (SAED). The selected area aperture is indicated. (b) SAED pattern corresponding to the particle in (a). The well-defined ring can be attributed to the (111) lattice plane of face centred cubic silver. Also indicated is a relatively strong reflection corresponding to the (220) planes possibly arising from a silver particle elongated in the [110] direction or from particles in a necklace with a shared orientation. (c) EDX spectrum of a silver nanoparticle necklace coated particle. The copper and carbon signal originates from the TEM grid support. Besides the silicon signal of the silica spheres, only silver can be detected.

Figure S3. SEM images of necklace formation on the silica spheres as well as on the nearby substrate for samples dried and aged on (a) a TEM grid and (b) a silicon wafer. The white line in (a) indicates the threshold between necklace formation and random silver precipitation.(c) SEM image of silver nanoparticle necklace formation within an amorphous film close to silica spheres.



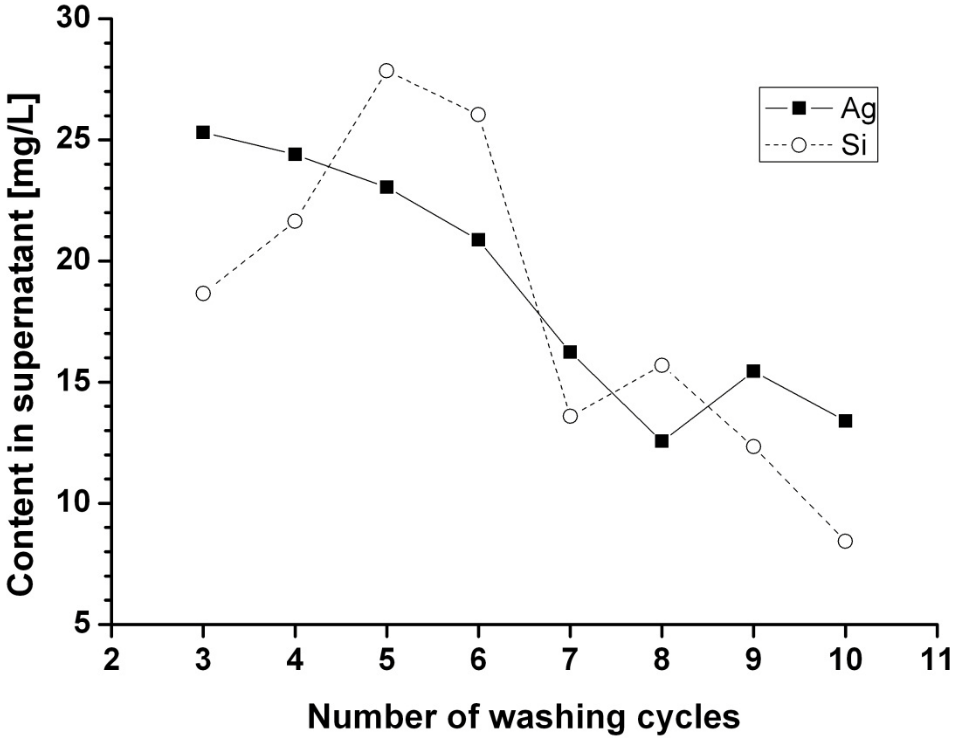


Figure S4. ICP-AES determined concentration of silver and silicon in the supernatant after certain numbers of cycles of washing and redispersion of ammoniacal silver complex treated silica spheres.

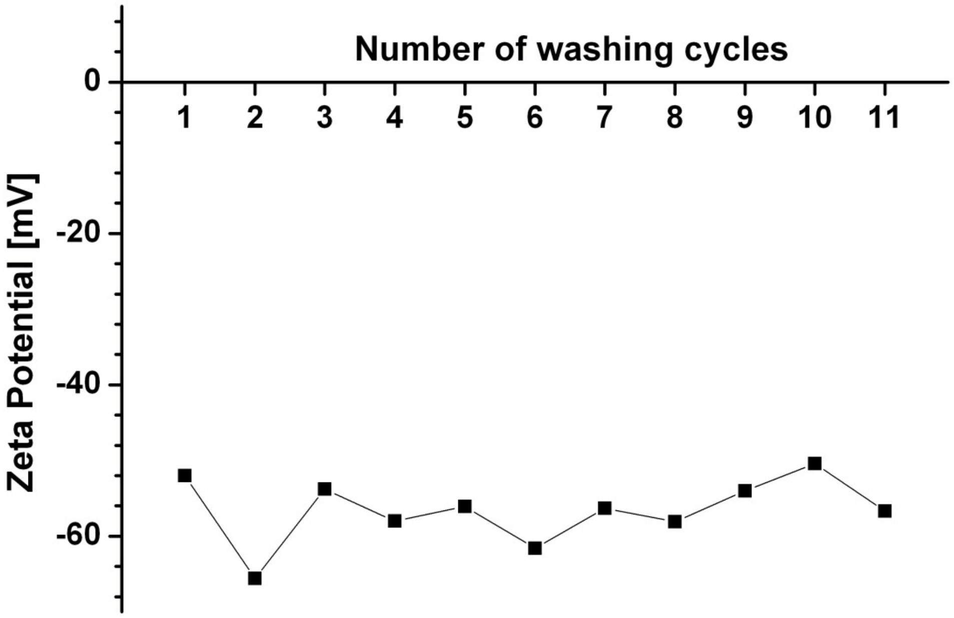


Figure S5. Zeta potential measurements of a dilute silica dispersion during repeated washing cycles following treatment with ammoniacal silver complex according to the standard procedure. The background electrolyte was 10 mM NaCl.

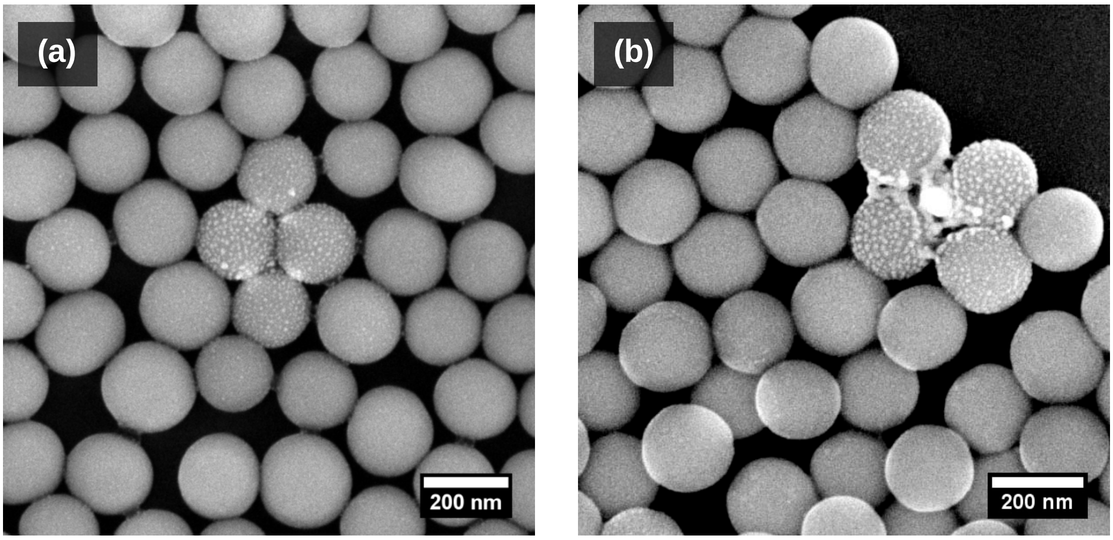


Figure S6. SEM images of a ammoniacal silver complex treated silica sample that was aged in an evacuated desiccator for 4 days following washing and deposition. Instead of nanoparticle necklace formation, silver precipitated randomly and formed larger aggregates.