Supplementary Information

Electron beam induced chemistry of gold nanoparticles in saline solution

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Methods:

HPLC-grade ethanol, acetone and water were used for all experiments (Roth, Germany). Citrate coated gold nanoparticle (AuNP) dispersions with nanoparticle (NP) sizes of 5, 15 and 30 nm diameter were purchased from BBInternational. The thiolated chitosan (TCHIT) capped AuNP dispersion was purchased from Nanopartz (Loveland, CO, USA). Before use AuNP mixtures in a ratio of 1:1:1:3 (5 nm Au : 15 nm Au : 30 nm Au : water) were prepared. 1 N HCl and 1 N NaOH were obtained from AppliChem and Fluka, respectively, NaCl (cell pure grade), H_2SO_4 and Na_2HPO_4 were bought from Roth, and NaH_2PO_4 from Sigma Aldrich. Solutions of different salt molalities were prepared by dissolving NaCl in HPLC-grade water. The pH was adjusted by adding HCl and H_2SO_4, respectively, or NaOH.

Liquid STEM experiments were conducted using a liquid flow transmission electron microscopy (TEM) holder (Poseidon system, Protochips Inc. NC, USA). In this setup, the liquid is situated between two silicon microchips with electron transparent 50x450 µm wide SiN-membranes of 50 nm thickness in the centre. One of the two chips featured spacers of 0.5 or 2 µm thickness. Except for the contrast, we did not notice differences resulting from differences in the liquid thickness. Prior to their use, the microchips were cleaned following a procedure described elsewhere.[1] In short, the photoresist that covered the microchips was removed by subsequent 5 min washes in in acetone and ethanol. Dried microchips were further cleaned and hydrophilized by a 5 min plasma treatment in an O_2/Ar-plasma.

A sample was applied by placing a 1 µL droplet of the AuNP mixture on the microchip and allowing it to dry up. This procedure was repeated once more. Subsequently, a 2 µL droplet of water was placed on the SiN membrane and was removed with a clean tissue after 10 seconds in order to wash off salt remainders. This procedure was repeated once. Then, the microchip was placed facing up in the tip of the liquid flow TEM holder, and a 0.3 µL droplet of a saline solution with the desired composition was added. After that the lid was closed and a solution with the desired composition was flushed through the holder for 10 min.

During the experiments, the saline solution was continuously pumped through the liquid TEM holder with a flow rate of 2 µL/min. When the liquid was changed within an experiment, pumping for 15 min (with a flow of 30µL) guaranteed a full exchange of the liquid.

A C_S-aberration corrected JEOL ARM 200F in STEM mode was utilized for the experiments. The microscope was operated at an acceleration voltage of 200 kV, and a probe current of approximately 100 or 45 pA (spot size 4c, condenser lens apertures of 20 or 30 µm diameter, respectively.) The

probe current was calculated using the current readout of the phosphorous screen of an electron beam in vacuum with the respective condenser lens aperture inserted. An ADF-detector with an acceptance semi angle ranging from 34 to 140 mrad at 8 cm camera length was employed for imaging. Pixel dwell times applied during continuous recording were between 1 and 2 µs. Movies were recorded by either using a screen recorder or saving image sequences.

The dose *D* introduced per recorded frame was calculated according to the following equation:

$$D = \frac{\mathrm{I} \times \tau}{e \times \mathrm{s}^2}$$

(with the current *I*, the pixel dwell time *τ*, the pixel size *s*, and the electron charge *e*). The dose rate (dose per time unit) was calculated by dividing *D* by the time per frame.

Most images recorded exhibited a weak gradient in the background intensity from one side to the other, caused by liquid thickness variations due to bulging of the SiN membranes. Sudden or moving changes in the background intensity, which indicate the presence of gas bubbles formed during the experiment, were not observed. The liquid thickness varied between 0.6 and 0.8 µm for chips with 0.5µm spacers, and 2.0 and 3.1 µm for chips with 2 µm spacers depending on the position at the window. The liquid thickness was calculated from the ratio of the measured current density on the phosphorous screen with and without the sample inserted I_{screen}/I_0 according to the following equation:[2, 3]

$$\frac{I_{screen}}{I_0} \cong exp\left(-\left(\frac{t_{SiN}}{l_{SiN}} + \frac{t_{water}}{l_{water}}\right)\right)$$

t_{SiN} and t_{water} represent the thicknesses of the amorphous silicon nitrate membranes and the thickness of the water layer, respectively. The mean free path length for a detector opening angle of 34 mrad was determined to be t_{SiN} = 0.79 µm and t_{water} = 3.0 µm.

Data analysis

Images and movie stills of the experiment were analysed using both Matlab and ImageJ routines. First the recorded images were smoothed using a Gaussian filter and the background was subtracted using top-hat filtering with a disk shaped structuring element in order to remove background variations due to bulging of the SiN membrane. The AuNPs and areas covered by nanoparticles were automatically identified by applying maximum entropy thresholding. The evolution of the total area covered by Au NPs was determined from the binarised images. As magnifications and hence the total number of particles within the field of view varied strongly, relative areas were used for further analysis.

Supporting Online Material

Movie S1: Time series of ADF STEM images recorded of 5, 15 and 30 nm diameter citrate-capped AuNPs in 10% phosphate buffered saline. The speed of the movie was increased by a factor of 6 with respect to the original data.

Movie S2: Time series of ADF STEM images recorded of 5, 15 and 30 nm diameter citrate-capped AuNPs in an aqueous solution containing 2 mol/kg sodium chloride at an initial pH of 7. The speed of the movie increased by a factor of 4 with respect to the original data.

Movie S3: Time series of ADF STEM images recorded of 5, 15 and 30 nm diameter citrate-capped AuNPs in an aqueous solution containing 2 mol/kg sodium chloride at an initial pH of 12. The speed of the movie increased by a factor of 6 with respect to the original data.

Movie S4: Time series of ADF STEM images recorded of 5, 15 and 30 nm diameter thiolated-chitosane stabilized AuNPs in an aqueous solution containing 0.2 mol/kg sodium chloride at an initial pH of 7. The speed of the movie increased by a factor of 25 with respect to the original data.

References:

1. E. A. Ring, D. B. Peckys, M. J. Dukes, J. P. Baudoin and N. De Jonge, *J. Microsc.*, **2011**, 243, 273-283.
2. L. Reimer and H. Kohl, *Transmission Electron Microscopy: Physics of Image Formation*, Springer, **2008**.
3. N. de Jonge, N. Poirier-Demers, H. Demers, D. B. Peckys and D. Drouin, *Ultramicroscopy*, **2010**, 110, 1114-1119.