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Writing Silica Structures in Liquid with Scanning Transmission Electron Microscopy

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Silica nanoparticles are imaged in solution with scanning transmission electron microscopy (STEM) using a liquid cell with silicon nitride (SiN) membrane windows. The STEM images reveal that silica structures are deposited in well-defined patches on the upper SiN membranes upon electron beam irradiation. The thickness of the deposits is linear with the applied electron dose. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) demonstrate that the deposited patches are a result of the merging of the original 20 nm-diameter nanoparticles, and that the related surface roughness depends on the electron dose rate used. Using this approach, sub-micrometer scale structures are written on the SiN in liquid by controlling the electron exposure as function of the lateral position.

1. Introduction

Conventional and cryogenic transmission electron microscopy (TEM) are key techniques for the real-space imaging of soft matter at the nanometer scale.^[1] Still, these techniques can only produce snapshots, and not reveal the true dynamics of a system that will give insight in the dynamic interactions between the different components.^[2] In contrast, the application of liquid phase TEM (LP-TEM), using 200–500 nm thick cells with electron transparent (generally Si₃N₄) windows allows the dynamic monitoring of events in liquid samples, thus avoiding the need for specimen preparation at every time point.^[3] To trigger (electrochemical) reactions in a closed environment liquid cells can contain electrodes,^[4]

or reactions can be initiated by slow evaporation.^[5] Also the electron beam can be used to initiate reactions, e.g., by the reduction of metal precursors.^[6] Recently, commercial flow cells have become available that allow to inject a reaction mixture, or even mix reactants in the liquid cell. As the electron mean free path in TEM is ~200 nm for water and organic samples, LP-TEM can probe thin specimens with sufficient resolution and contrast.^[7] Samples of up to several micrometers in thickness can be studied with high angle annular dark field (HAADF) STEM,^[8] e.g., for the tracking of nanoparticles in biological structures.^[9]

Currently LP-TEM still has some limitations,^[3,10] e.g. the interaction of the electron beam with the fluid is a matter of concern as it may induce free electrons in the liquid and also gradients in temperature and pH (due to water decomposition), and beam induced deposition of nanoparticles is also often observed. Indeed, many of the reported experiments so far have either a) used the electron beam to drive the processes under investigation,^[10a,11b] have imaged objects rather than processes,^[12] or c) reported on the effects of the electron beam on the events observed.^[10b,c,12b]

Here, we exploit these beam-sample interactions to write silica nanostructures in aqueous medium. By applying a focused electron beam in STEM mode we can control the localized deposition of fused silica nanostructures with defined thickness from a solution of monodisperse silica nanoparticles. The observed process could be useful in future

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Figure 1. Cryogenic transmission electron microscopy (cryo-TEM, FEG, 300 kV) of 20 nm-diameter silica nanoparticles imaged (a) at low (6500 $\times$, $4 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$, scale bar 200 nm), and (b) at high magnification (61 000 $\times$, $70 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$, scale bar 20 nm). Images were acquired with an exposure time of 1 second on a $2\text{k} \times 2\text{k}$ Gatan CCD camera.

work for the direct writing of three dimensional nanoscale silica structures in liquid.

2. Results and Discussion

Monodisperse silica nanoparticles with a diameter of $20 \pm 2 \text{ nm}$ (**Figure 1**) were synthesized by lysine-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in water at 60°C .^[13] CryoTEM analysis recently demonstrated that these nanoparticles formed by the agglomeration of nanometer-sized primary particles and that stable colloidal dispersions in water with concentrations up to of 5 vol% could be obtained without any signs of agglomeration, clustering or Oswald ripening for periods exceeding one year.^[14]

Samples for in situ liquid cell STEM were prepared by placing a $0.5 \mu\text{L}$ droplet of the nanoparticle suspension on a silicon microchip supporting a SiN membrane window.^[15] The microchip was positioned in a slot in the tip of a dedicated specimen holder for liquid samples.^[16] A second microchip was then placed with the SiN membrane facing down on the droplet. The second microchip contained a spacer layer of $0.5 \mu\text{m}$ in thickness, such that a liquid-filled gap was obtained between the two microchips (**Figure 2**). The tip of the specimen holder was then closed by a lid and tightening screws in the lid.

Immediately following sample loading, the liquid specimen holder was inserted into the electron microscope, the correct (eucentric) height of the stage was adjusted, and the STEM probe was focused. The microscope stage was then moved so that the electron beam illuminates a fresh/non-irradiated portion of the liquid, and the magnification was increased to 110 000 $\times$ such that individual silica nanoparticles became visible. Subsequently, the STEM probe was refocused and the stage again moved to a fresh position. Finally, the STEM probe was continuously scanned over an area of interest, with a pixel dwell time of $38 \mu\text{s}$, and a frame time of 3 s. Under these conditions most of the observed individual nanoparticles were moving while a few were stationary (see **Figure 3a** and Movie S1). Interestingly, the field of view became increasingly filled with silica nanoparticles upon continued exposure to the electron beam (see **Figure 3a–c** and

Figure 2. Schematic of the liquid cell for scanning transmission electron microscopy (STEM). A liquid containing silica nanoparticles is enclosed between two silicon nitride (SiN) membranes forming a liquid cell. The focused electron probe of STEM scans over the sample.

Movie S1). Switching to lower magnifications (9900 $\times$, see **Figure 4**) made clear that nanoparticles that were initially freely dispersed became immobilized on the SiN membrane within the area exposed to the electron beam. To study the influence of the electron beam on the deposition of the nanoparticles, we have analyzed the growth of the silica deposits in time within the irradiated area. The contrast of these deposits in STEM is approximately proportional to the mass $\times$ thickness of the material within the path of the electron beam,^[17] and therefore forms a direct measure for the amount of silica deposited in the observed area. This allowed us to use the integrated signals from the individual frames of the recorded movie (Movie S1) to accurately monitor the rate of the deposition process. For dose calculations, a flat field image was recorded (i.e. without the sample present) under the same STEM imaging conditions from which the electron dose ($28 \text{ e}^-/\text{nm}^2/\text{frame}$) and the total amount of electrons per image per second was determined (see Supporting Information). Analyzing these data showed that the silica deposition rate linearly depended on the exposure time, and hence on the cumulative applied electron dose only (**Figure 3d**).

2.1. Effect of Applied Electron Dose

The electron dose effects inducing deposition of the silica was further studied under different applied electron doses by imaging at different magnifications while keeping the dwell time of $38 \mu\text{s}$ constant. A first patch was created by exposing an area of the cell to an electron dose of $7 \text{ e}^-/\text{nm}^2/\text{frame}$ at a magnification of 56 000 $\times$ (pixel size 8.1 nm). Subsequently the magnification was increased to 79 000 $\times$ visualizing the newly deposited layer (**Figure 4a (i)**). By moving the sample and using various magnifications and exposure times during several repeated scans, three further patches of different dimensions were created (**Figure 4a (iii–v)**).

Figure 3. Electron beam induced immobilization of silica nanoparticles on a silicon nitride (SiN) membrane observed in-situ with liquid cell scanning transmission electron microscopy (STEM) using an annular dark field (ADF) detector. Probe current 2 pA, 200 kV, magnification 110 000 $\times$, pixel size 4.1 nm, pixel dwell time 38 μs , 28 electrons/ nm^2 /frame, image size 256×256 pixels. Scale bars represent 200 nm. (a) Selected image from a continuously recorded time lapse series. The image was recorded 21 seconds after this region was first imaged. (b) Image recorded 39 seconds after image a showing an increased number of immobilized nanoparticles. (c) Image recorded 42 seconds after image b. (d) Integrated total intensity per image frame from the time-lapse series as function of applied total dose.

For a further investigation of the deposited structures, the sample was removed from the liquid specimen holder, the two microchips were separated, dried, and imaged with both SEM and AFM. The topology of the same deposits shown in Figure 4 were located and then imaged with semi-contact mode AFM (Figure 4b) and SEM (Figure 4c). Figure 4 thus represents a correlative study of a sample with liquid cell STEM, and dry SEM and AFM. Both the top and bottom membranes were investigated. As expected, SEM showed that the silica nanoparticles were mostly deposited on the top window of the liquid cell membrane where the intensity of the electron beam was the highest. The SEM image in Figure 4c taken from a top-membrane shows details of the edge of a deposited silica patch and the background. Although silica had deposited on both the background and the exposed areas, a clear difference in density and size of the deposits between the two regions was observed.

Whereas the sizes of the nanoparticles deposited just outside to the exposed areas had similar sizes and shapes as the original 20 nm nanoparticles in solution, the objects in the exposed area reached diameters of up to 5 times this size (50–100 nm), suggesting that they must originate from the merging of deposited nanoparticles.

The observed spatial control over the silica deposition on the top SiN membrane contrasts what has been observed on the bottom membrane (see Figure S2). Here, the features appeared similar to those observed in unexposed areas of the top membrane with only a few agglomerated structures that are spatially not well correlated to the exposed areas. This effect is ascribed to the electron scattering within the liquid

Figure 4. Visualizing the formation of silica deposits in liquid using correlative Liquid STEM, scanning electron microscopy (SEM), and atomic force microscopy (AFM) (a) Liquid cell STEM images (9900 $\times$, pixel size 11.4 nm, frame size 1024×1024 , pixel-dwell time 20 μs , frame time 25.2 seconds, scale bar 1 μm) of five patches deposited by several repeated scans during STEM irradiation at higher magnifications using different electron doses; (i) total dose $315 \text{ e}^- \text{ nm}^{-2}$ (56 000 $\times$), (ii) total dose $420 \text{ e}^- \text{ nm}^{-2}$ (79 000 $\times$), (iii) total dose $952 \text{ e}^- \text{ nm}^{-2}$ (110 000 $\times$), (iv) total dose $960 \text{ e}^- \text{ nm}^{-2}$ (160 000 $\times$) and (v) total dose $5280 \text{ e}^- \text{ nm}^{-2}$ (320 000 $\times$). For more details, see Supporting Figure S4. (b) AFM semi-contact (scan velocity 7.23 $\mu\text{m/s}$, pixel size 17.61 nm) topography of corresponding areas shown in (a) (Scale bar 1 μm) with (d) corresponding height profiles and (c) SEM image (scale bar 200 nm).

cell: when the electron beam is focused on the top membrane the electrons will scatter through the liquid to giving rises to a broadened electron beam at the bottom with a lowered current density. The difference in morphology between the deposits in the exposed areas of the top membrane and those in the back ground and on the bottom membrane suggests that the deposition and subsequent merging of the silica nanoparticles depends on the local electron dose rate/current density.

Using an unexposed area as a reference, AFM provided information about the height of the deposits (Figure 4b and d). Line scans revealed a low surface roughness for the unexposed area and a very high roughness for two patches (Figure 4b (iii and iv)) which were prepared with different magnifications (and therefore different dose rates per exposed area: $28 \text{ e}^-/\text{nm}^2/\text{frame}$ and $60 \text{ e}^-/\text{nm}^2/\text{frame}$, respectively) but with the same total electron dose ($\sim 950 \text{ e}^-/\text{nm}^2$, see also Figure S4) by applying different exposure times. Indeed, AFM showed that the two deposits had similar heights: $39 \pm 10 \text{ nm}$ and $45 \pm 13 \text{ nm}$, respectively. However, AFM images also showed that the high surface roughness of the patches was mainly due to the presence of non-spherical features covering the upper surface of the deposits. These flattened features were more pronounced on the patch generated at $60 \text{ e}^-/\text{nm}^2/\text{frame}$ and not observed in the unexposed areas of the silicon nitride top membrane, supporting the above proposition that the morphologies of the deposits depend on the applied electron dose rate and the associated merging of the original silica nanoparticles.

2.2. Patterning

The electron beam induced deposition of silica structures from a solution of nanoparticles can be readily employed to construct well-defined patterns by controlling the local distribution of the electron dose. **Figure 5** demonstrates that silica nanoscale structures can be generated by a pre-defined movement of the electron beam writing on the SiN mem-

Figure 5. Dark field STEM image ($28\,000\times$, pixel dwell time $20 \mu\text{s}$, pixel size 4.05 nm , frame size 1024×1024 pixels) of patterning with silica deposits by controlling the electron beam position in lateral direction. The electron beam was located on each position for several seconds until deposition became visible. Scale bar is 500 nm .

brane in the liquid phase. The letters were written by moving the focused beam in spot mode slowly over the sample. During this procedure, the magnification was held constant ($28\,000\times$, pixel size 17.2 nm) and the beam was located on each spot for several seconds until deposition became visible. The immobilized and deformed silica particles agglomerate according to the applied electron dose pattern. Interestingly, the letters deposited in this manner had dimensions of 100 nm in width and 500 nm in length, while the diameter of the STEM beam was only 3.5 nm (see Supporting Figure S4). By locating the beam, the exposure time per pixel increased from microseconds to seconds. Consequently, the dose per area increased six orders of magnitude and electron scattering effects by both the membrane and the liquid played a more significant role. As a result, silica deposition is significantly extended beyond the irradiated area.

Depending on the manufacturing and pre-treatment procedure of the SiN membranes, silanol and silanolate groups are present on the surface of these membranes.^[18] This will certainly be the case in our experiments, in which the membranes were made hydrophilic by oxygen plasma treatment. This will result in a high affinity of the membrane for the surface silanols on the silica nanoparticles. In addition electron beam exposure will cause the local reduction of water to form hydroxide ions, leading to a local pH increase. As a result, locally the silica solubility increases and bond rearrangement at the nanoparticles surface will take place, aiding the adhesion of the particles to the membranes as well as to neighboring particles through the formation of siloxane (Si-O-Si) bonds. Through the use of STEM the water reduction ($2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + 2 \text{ OH}^-$) is a highly localized process, which explains that no hydrogen formation was observed. In addition, the generation of secondary electrons from the interaction of the electron beam with the SiN membrane is known to lead to local reduction sites, as is commonly used for the immobilization of different materials in traditional electron beam induced deposition (EBID) techniques.^[19] We propose that the secondary electrons produced in the liquid generate reactive, charged silicate species such that chemical bonds can be formed^[20] and the nanoparticles become chemically linked both to each other as well as to the Si_3N_4 membrane. This results in agglomeration of the nanoparticles into the observed solid deposits.

Our results indicate that the observed smoothing of the silica structures is a result of the fusion of the deposited nanoparticles due to their interaction with the electron beam. Rearrangement of the siloxane bonds broken under the influence of the electron beam will lead to surface smoothing as the system will try to reduce the total surface energy. Moreover, it is likely that this rearrangement of bonds also increases the mechanical properties of the silica structures.^[21] The observation that the silica deposits formed at lower dose rate have smoother surfaces than those formed at higher electron doses may be due to a continuous deposition of new nanoparticles at higher dose rate that render these surfaces rough compared to the situation at lower dose rates where smoothing successfully competes with deposition. Hence the shape of the structures is determined

by the path of the electron beam at the (sub-)micron scale, but also by the amount of clustering nanoparticles and the rate at which they agglomerate and rearrange their chemical bonds at the nanoscale. This process is limited by the area over which the hydroxyl ions can diffuse while still being able to induce silanolate formation and the area over which the silica nanoparticles can diffuse before being immobilized on the surface. Since the patterning process involves the immobilization, assembly and merging of individual nanoparticles as induced by exposure to the electron beam, the smallest possible dimensions are ~ 100 nm, i.e. the size of several nanoparticles.

3. Conclusion

We demonstrated that the exposure of a dispersion of 20 nm silica nanoparticles in water to a focused electron beam led to the deposition of silica structures on one of the liquid enclosing SiN membranes. The thickness of the observed deposits depended linearly on the cumulative electron dose, while their surface roughness depends on the electron dose rate. By correlative STEM, SEM, and AFM it was found that the silica nanoparticles first immobilized on the SiN membrane, and then fused upon the exposure to an increased electron dose. Silica structures can be written on the SiN membrane in the liquid phase by controlling the electron dose as function of the lateral position. Depending on the irradiated area, structures can be obtained in the sub-micrometer range. We anticipate that the formation of silica deposits directly in a liquid will open new possibilities for creating three dimensional nanoscale structures.

4. Experimental Section

Preparation of Silica Nanoparticles: Silica nanoparticles were prepared by the slow diffusion of tetraethyl orthosilicate (6 mL, TEOS, Merck Hohenbrunn, Germany) in distilled water (100 mL) in presence of lysine (0.1 g, SigmaAldrich). The mixture was continuously stirred for 7 hours at 60 °C. After completion of the reaction, the pH is 8.5 and the final concentration of SiO_2 is 16 mg/mL.^[14] At these conditions, an aqueous solution of colloidal silica particles was obtained since the solubility limit of $\text{Si}(\text{OH})_4$ is ~ 130 ppm with a ethanol content of at most 5 wt%.

Cryo TEM: Analysis of silica nanoparticles was performed using cryo TEM (cryoTITAN, FEI, OR, USA) at 300 kV with a Gatan $2\text{k} \times 2\text{k}$ CCD camera. The sample vitrification procedure was performed using a freezing device (Vitrobot Mark III, FEI, OR, USA). A 3 μL drop of the suspension of silica in water was applied to a this foil grid (Quantifoil, Germany) in the environmental chamber (100% relative humidity) of the freezing device, and the grid was blotted with two filter papers to remove the excess liquid. Subsequently, the grid was plunged into liquid ethane that was maintained at approximately -180 °C using liquid nitrogen. The vitrified sample was then transferred to the electron microscope, and maintained at cryogenic temperature during observation. Images were taken at 6,500 $\times$ (defocus: -30 micrometer) and 61 000 $\times$ (defocus: -1 micrometer) with an exposure time of 1 second.

Liquid Cell STEM Equipment: STEM experiments were carried using a liquid flow TEM/STEM sample holder (Protochips Inc., NC, USA). The liquid cell consisted of two silicon microchips (Protochips Inc., NC) supporting electron transparent silicon nitride (SiN) membrane windows of 50 nm thickness. The dimensions of the window were $20 \times 200 \mu\text{m}^2$. One microchip had a spacer structure of 0.5 μm thickness made of SU8 material to create a sample space between the SiN windows once the microchips were assembled together. The windows on both chips were oriented perpendicular, such that an overlapping window area of $20 \times 20 \mu\text{m}^2$ was available once both microchips were assembled as liquid cell.

The sample was loaded in the specimen holder with the following procedure. One microchip was placed in in the specimen holder with its SiN surface facing up. A 0.5 μL droplet of the silica nanoparticles suspension was placed on the SiN surface with a micropipette (Eppendorf). The second microchip, one with a spacer of SU8 material of 0.5 μm thickness, was positioned on top of the first chip but with its SiN surface facing downward. The tip of the specimen holder was then closed, and inserted in the micro-scope within 2 minutes.

Liquid Cell STEM: STEM (Tecnai G2 TEM/STEM, FEI, OR, USA) experiments of liquid specimens were carried out at 200 kV. Images were recorded using the annular dark field detector (ADF) with a camera length of 52 mm. The image size was 256×256 pixels with pixel sizes varying between 4.1 nm and 16.2 nm. Time-lapse image series were acquired with a pixel dwell time of 38 μs and a frame time of 3 seconds. The electron dose was determined in two different ways. First, a flat field image of the STEM beam was taken (probe size 4.2 nm) were the total photon counts on the CCD camera were directly measured and related to the total electrons on the camera. This is resulted in 475 electrons per pixel per frame, corresponding to a probe current of 2 pA. The fluorescent screen was used for direct current measurements under STEM imaging conditions at lower spot sizes (1 – 5) and extrapolated to the used spot size 9, since spot sizes >5 were not measurable in this way directly on account of the low probe current. This resulted in the same value (see supporting info Figure S2).

AFM: Measurements of the height profiles were performed on dismantled microchips with dried SiN membranes after liquid cell STEM with AFM (SMENA-NTEGRA, NT-MDT, Russia) with a gold-coated NSG 03 tip from (NT-MDT, Limerick, Ireland) in semi-contact mode with a scan velocity of 7.23 $\mu\text{m/s}$ and a pixel size of 17.61 nm.

SEM: After AFM analysis, the stubs were sputter-coated with chromium to prevent beam damage. After the dismantling of the liquid cell, the microchips with SiN membranes were glued onto aluminum stubs with conductive carbon tape. The Cr layer was deposited with a lower grain size than the SEM resolution with a Turbo Sputter Coater K575X (Quorum Technologies, United Kingdom) dual for 20 seconds at 100 mA. Dried samples were studied with SEM (Quanta 3D FEG, FEI, OR, USA) at an acceleration voltage of 5 to 15 kV.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. It includes a liquid cell STEM membrane

window analysis; dose analysis, detailed description of patch deposition.

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