

Supporting Information

Shaping Silica Rods by Tuning the Hydrolysis and Condensation of Silica Precursors

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Viscosity Measurements

In order to measure the viscosity of the continuous phase, the growth mixture was centrifuged and the supernatant was collected. The viscosity of the supernatant of the growth mixture, after sedimentation of the droplets, was measured using a Physica MCR 300 rheometer, fitted with a cone-plate geometry. The measurements were performed at shear rates in the range of 10-300 s^{-1} . The concentration of PVP was varied between 0.001 g/mL and 0.15 g/mL. The viscosity in the absence of citrate was measured by replacing the aqueous sodium citrate dihydrate solution with an equal volume of water. The mean diameter of the emulsion droplets was measured using a Malvern Nano ZS Zetasizer. The undiluted sample was placed in a plastic disposable cell for measurement.

To investigate this instability of the emulsion, we analyzed the size distribution of the droplets over time using dynamic light scattering. First, in order to obtain a precise value for the size of the water droplets, the viscosity of the continuous phase was measured. The total concentration of PVP was varied to determine its effect on the viscosity. After removal of the droplets by centrifugation, the viscosity was measured in the presence and also in the absence of citrate ions. The addition of sodium citrate in part of the water did not show a significant effect on the viscosity, as shown in Figure SI1a. Furthermore, the viscosity was found to remain constant with time, as shown in Figure SI1b. However, upon increasing the total PVP concentration the viscosity increased. The results of these measurements are shown in Figure SI1a and SI1b. The graph in Figure SI1c shows the mean diameter of the water droplets as a function of time. It is clear from this graph that the diameter of the droplets increased with time. If the droplet size increases in diameter over time, it is also likely that the rods that grow from the droplet obtain a larger diameter. Indeed, upon aging the emulsion before the addition of the reagent TEOS, one can see that the diameter of the silica rods increased with increasing size of the water droplets (Figure SI1c). A difference in trend was found between the rod-diameter and the droplet diameter. We believe that this difference was caused by the unavoidable homogenization step after the addition of TEOS or by polydispersity of the emulsion which highly affects the average droplet size as determined with dynamic light scattering as this measuring technique weighs larger droplets more strongly (volume squared). This step of shaking was not performed during the measurement of the droplet diameter.

Furthermore, during rod growth, slow dissolution of the water droplet as well as consumption of water by the hydrolysis reaction (1.80 mmol, 0.034 mL in total) attached to rods can cause the rod to become thinner with time. On the other hand, the hydrolysis reaction (1.80 mmol) releases ethanol and the condensation reaction (0.9 mmol per siloxane bond) releases water. Comparing this to the amount of ethanol (17.4 mmol) and water (28.6 mmol) present, we believe that the hydrolysis reaction and condensation reaction will not significantly alter the volume of the droplet, although the composition of the droplet can change significantly with time.

Water is a reagent in the hydrolysis of TEOS, which is catalyzed by the base ammonia. Therefore, the presence of water and ammonia is the main restriction on whether hydrolysis and therefore also the subsequent condensation reaction can take place in each phase. In the droplet, their concentrations are high and therefore the reaction will mainly take place from there. However, due to the non-zero solubility of water and ammonia in pentanol, hydrolysis and even condensation can also take place from the

continuous phase onto the water droplet and/or completely in the oil phase (nucleating spheres like in the Stöber process). The growth of silica from the oil phase was previously inferred by our group in literature previous paper.

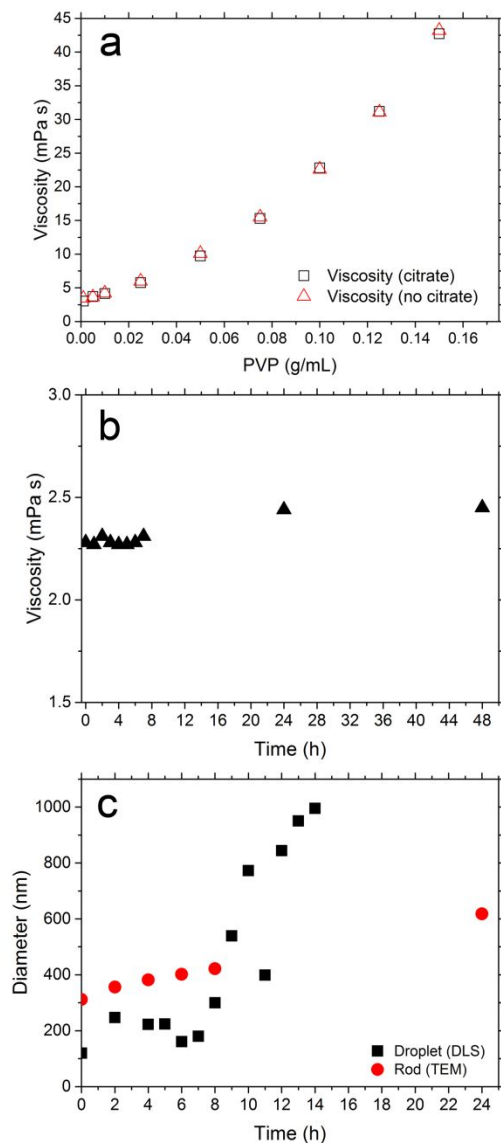


Figure S11 : (a) Viscosity of the continuous phase of the reaction mixture as a function of the PVP concentration. The squares represent the viscosity of the continuous phase in the presence of sodium citrate and the spheres show the viscosity in the absence of sodium citrate. (b) Viscosity of the supernatant as a function of time, in the presence of sodium citrate. (c) Dynamic light scattering measurements. The black squares represent the mean diameter of the droplets as a function of time. The red circles show the mean diameter of silica rods grown from solutions aged for different times. The difference in trend is very likely caused by the gentle shaking of the reaction mixture after the addition of TEOS in case of the rod diameter.

Cryo-SEM-EDX measurements

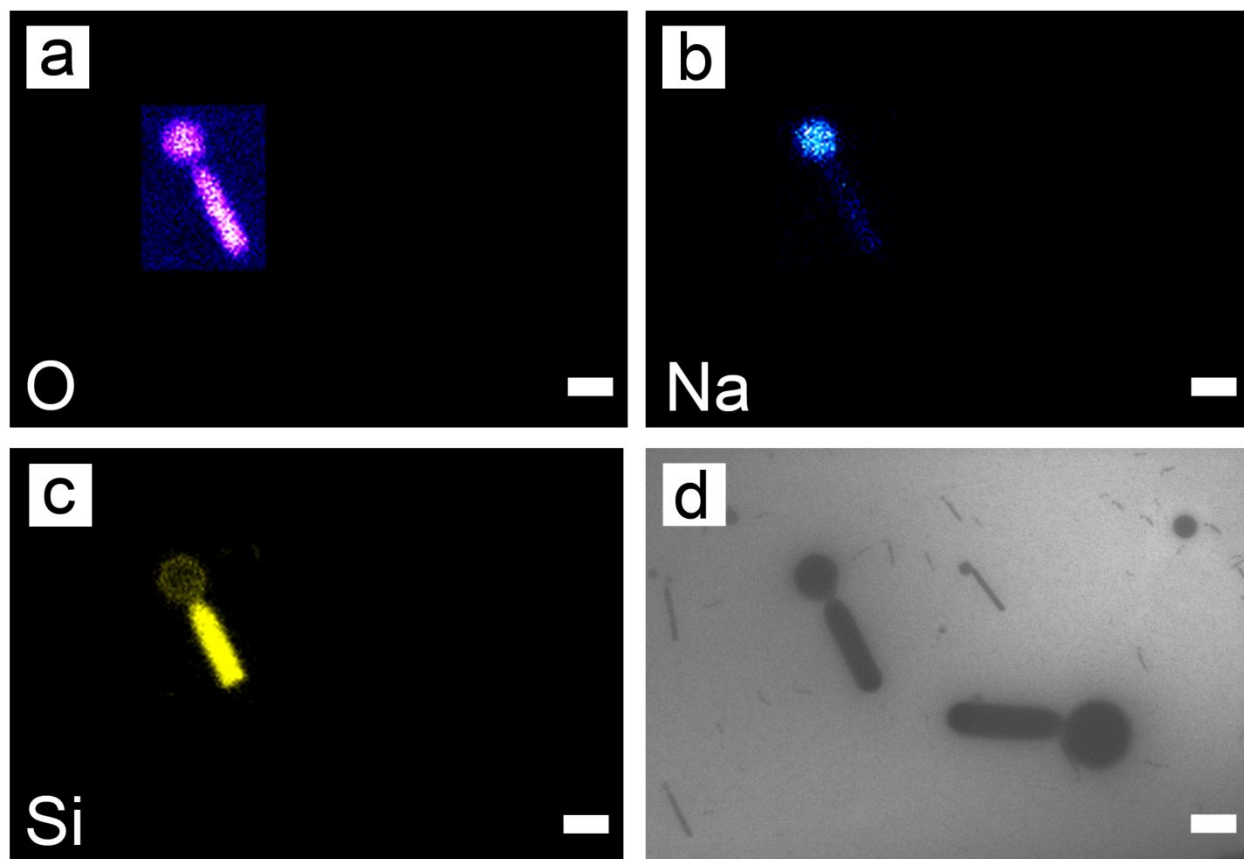


Figure S12 : cryo-SEM images of growing silica rods prepared using 14% (0.18 mmol) of partially pre-hydrolyzed TEOS. Panel (a), (b), (c) show the EDX map of oxygen, sodium and silicon, respectively. EDX was performed on a portion of the field. Panel (d) shows the SE image of the silica rods. Panel (b) shows the presence of sodium in the rounded tip. Scale bars indicate 2 μm .