Electronic Supplementary Information for: Dynamically shaping the surface of silica colloids

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I. REACTION PROTOCOL FOR FIG. 1:

Initially, 2mL of ammonia at 25% v/v were added to 38mL of MilliQ water. 1mL of this solution was then added to 5.3mL of MiliQ while stirring at 500 rpm using an olive-shaped magnet of 10x20 mm in a 15mL flat glass flask. The desired amounts of TEOS and VTMS were sequentially added. The flask was sealed with a lid to prevent ammonia from evaporating. The quantity of VTMS and TEOS used for each r_{TEOS} are shown in Table S1. The reaction proceeded for 80 mins, after which the particles were washed 3 times by centrifuging at 1500 rpm for 10 mins and redispersing the particles in MilliQ water with the help of a bath sonicator.

The total volume of MilliQ water was always kept fixed at 6.3mL, even when the amount of ammonia was changed. All the volumes were measured with a pipette except for the ammonia at 25% v/v, which has a low viscosity and required a graduated glass measuring cylinder since for higher accuracy. Note: evaporation of ammonia from the aqueous stock solution may lead to different synthesis conditions. Caution should be exercised when repeating syntheses with older ammonia solutions.

To compute the concentration of the silane, the following formula is used: $C_{Si} = \frac{V_{Si} * d_{Si}}{M_{Si} V_{tot}}$ with V_{Si} the volume of the silane, d_{Si} the density of the silane, M_{Si} the molar weight of the silane and V_{tot} the total volume of the reaction. In our case, $d_{TEOS} = 0.933$, $M_{TEOS} = 208.33$ g/mol, $d_{VTMS} = 0.968$ and $M_{VTMS} = 148.23$ g/mol. To compute the concentration of the ammonia (NH_4OH), the following formula is used: $C_{NH_4OH} = \frac{V_{NH_4OH,H_2O} * d_{NH_4OH,H_2O}}{M_{NH_4OH} V_{tot}}$ with V_{NH_4OH,H_2O} the volume of the aqueous ammonia solution at 25% we used, $d_{NH_4OH,H_2O} = 0.91$ the density of the aqueous ammonia solution at 25%, $M_{NH_4OH} = 35.05$ g/mol the molar weight of ammonia and V_{tot} the total volume of the reaction.

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Table S 1. Different volumes of TEOS and VTMS (and their corresponding concentration) used for the different values of r_{TEOS} corresponding to the data of Fig. 1 in the main text. Different volumes of ammonia (and its corresponding concentration) used for the data of Fig. 1 in the main text.

r_{TEOS}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
V_{TEOS}(mL)	0	0.136	0.272	0.408	0.544	0.680	0.816	0.952	1.088	1.224
C_{TEOS}(mol/L)	0	0.08	0.16	0.24	0.32	0.4	0.47	0.55	0.63	0.71
V_{VTMS}(mL)	1.360	1.224	1.088	0.952	0.816	0.680	0.544	0.408	0.272	0.136
C_{VTMS}(mol/L)	1.15	1.04	0.92	0.81	0.69	0.58	0.46	0.35	0.23	0.12

V_{NH_4OH}(mL)	0.0125	0.025	0.050	0.100	0.200
C_{NH_4OH}(mol/L)	0.011	0.021	0.042	0.084	0.165

II.   PARTICLE SIZE MEASUREMENT:

The size of the synthesized particles was extracted from SEM images. To measure the size of the particles, a circle was manually drawn around each particle using Image J and the corresponding radius extracted. The average size, measured over at least 10 particles, is then reported in the different figures. Automatic sizing can also be carried out using the Matlab function *imfindcircles*, which accurately locates circular objects. However, this approach shows limitations when the particle is too elongated, as shown in Fig S1D. This limit is highlighted by the difference between the sizes measured with the two methods (see Table S2, Table S3, and Table S4).
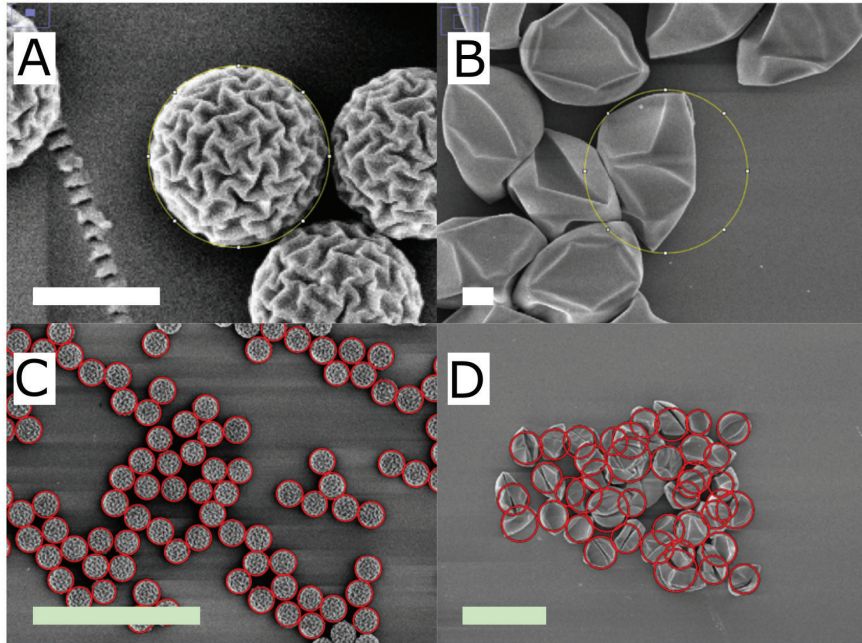

Fig. S 1.   A and B are two examples of the manual size measurement using ImageJ for particles of different shape. The white scale bars correspond to for 1 μm. C and D are two examples obtained when using Matlab's function *imfindcircles*, showing the conditions under which this approach works properly. The green scale bars correspond to 10 μm

Table S 2. Average measured sizes (in μm) using the *imfindcircles* function of Matlab and corresponding to the data reported in Fig. 1.

1.12	0.78	0.75	0.61	0.72	0.5	0.6	0.5		
1.33	1.46	1.41	1.05	1.00	0.89	0.6	0.8	0.86	
1.39	1.48	1.36	1.34	1.40	1.52	1.23	1.48	1.48	
2.2	2.4	2.2	2.2	1.87	1.95	2.40	2.25	2.46	1.92
3.65	4	3.1	2.8	3.7	2.8	2.7	3.2	3	2.7

Table S 3. Average measured sizes (in μm) obtained by manually fitting the particle profile with Image J and corresponding to the data in Fig. 1.

1.1	0.76	0.78	0.61	0.72	0.48	0.6	0.59		
1.33	1.46	1.41	1.05	1.00	0.93	0.63	0.86	0.91	
1.39	1.47	1.32	1.36	1.44	1.56	1.35	1.58	1.59	
2.39	2.55	2.28	2.38	1.96	2.56	2.86	2.57	2.72	2.27
4	4.24	3.19	3.14	5.05	3.21	2.88	3.33	3.24	2.75

Table S 4. Difference between Table S2 and Table S3 showing the shortcoming of the automatic fitting for non-circular objects.

-0.02	-0.02	0.03	0	0	-0.02	0	0.09		
0	0	0	0	0	0.04	0.03	0.06	0.05	
0	-0.01	-0.04	0.02	0.04	0.04	0.12	0.1	0.11	
0.19	0.15	0.08	0.18	0.09	0.61	0.46	0.32	0.26	0.35
0.35	0.24	0.09	0.34	1.35	0.41	0.18	0.13	0.24	0.05

Table S 5. Average measured sizes (in μm) obtained by manually fitting the particle profile with Image J and corresponding to the data in Fig. 2.

1.91	1.78	1.87	2.06
1.43	1.49	1.61	1.75
1.15	1.35	1.48	1.78
1.32	1.5	1.14	1.3

III. AFM TOPOGRAPHY MEASUREMENTS:

The following procedure is taken in order to characterize the topography of the particle surfaces from AFM images.

Initially, the surface of a sphere is subtracted from the AFM measurement of the particle height profile $Z_{AFM}(x,y)$ so that : If $x^2+y^2 > R_{part}^2$, $Z(x,y)= Z_{AFM}(x,y)$ and if $x^2+y^2 < R_{part}^2$, $Z(x,y) = Z_{AFM}(x,y) - \sqrt{R_{part}^2 - x^2 - y^2}$.

To determine d_{valley}, we count the number of local minima in a Gaussian-filtered image of the flattened topography. N1 is the number of local minima identified within the image and N2 is the number of local minima detected on the edge of the image (see Fig. S2F). A is the image size in pixels and r represents the conversion factor from nm to pixels. Thus, d_{valley} is defined as $d_{valley} = r\sqrt{\frac{A}{N1+\frac{N2}{2}}}$. The lowest d_{valley} that can be detected is determined by the resolution of the AFM images with $d_{valley} > 2$pixels.
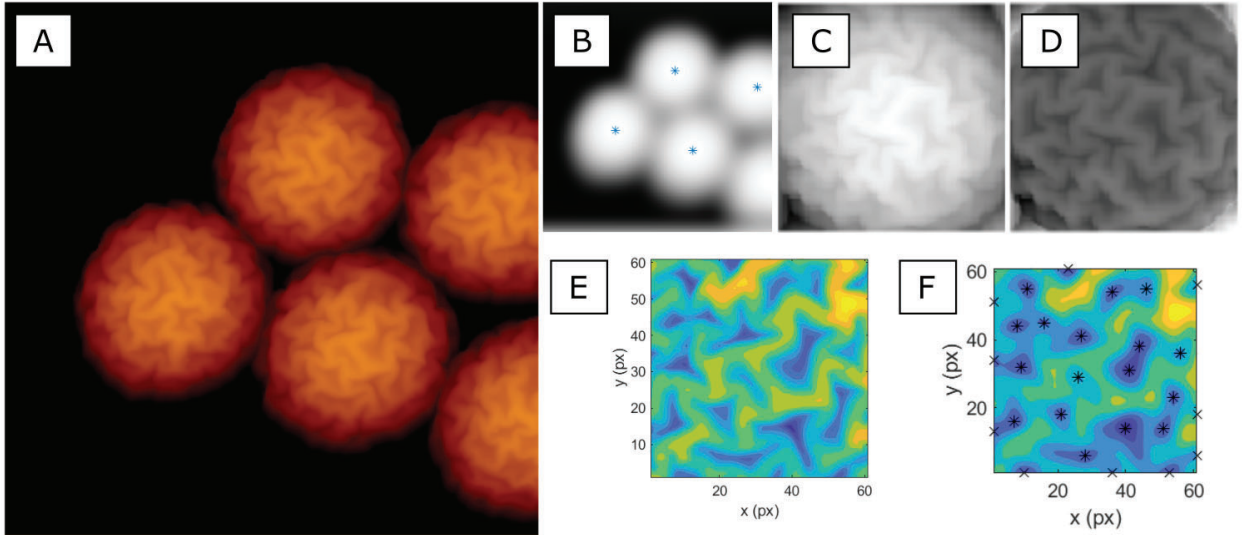
Fig. S 2.   (A) Original AFM image of 256 x 256 pixels (4μm x 4μm). (B) Gaussian-filtered image to locate particle centers, as indicated by the blue stars. (C) AFM image cropped around one of these points. (D) Surface topography after flattening by removal of the underlying spherical curvature. (E) Visualization of the surface height profile in the central part of the particle surface. (F) Detection of the local minima after application of a Gaussian filter. The black stars represent full local minima, while the black crosses represent the local minima on the edge of the image.

To obtain H_{10}, the difference between the 10% highest and 10% lowest values is computed.

These values are highly dependent on the diameter used to flatten the surface of the AFM measurements. In the example of Fig. S3, we can see that if the diameter is changed by $\pm$ 4 pixels from an ideal value of 98 pixels, the measured H_{10} value varies by $\pm$ 5%. Erroneous detection of the particle center can also lead to errors in the surface flattening procedure. As an example, a 20 nm offset leads to an error of 2% for a particle of diameter $D_{part} = 1$ μm.
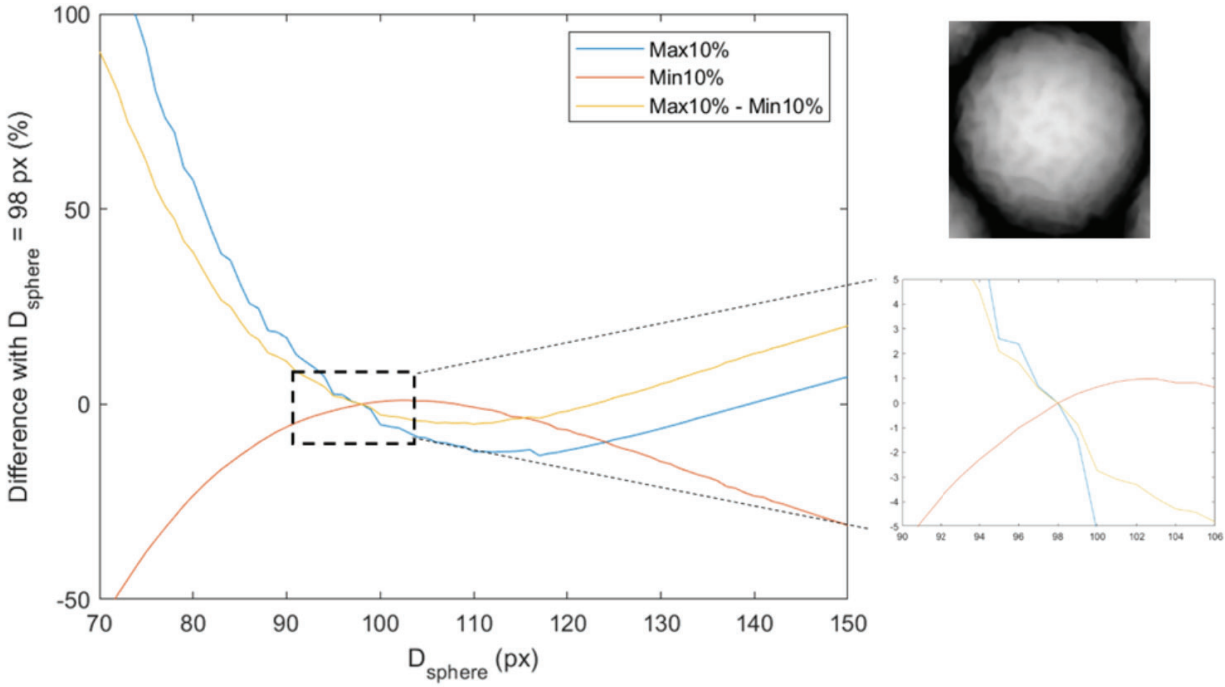

Fig. S 3.   Evolution of the values of the 10% highest pixels (Max 10%), of the 10% lowest pixels (Min10%) and corresponding $H_{10} =$ Max10% - Min10% computed when the diameter of the sphere used to flatten the surface is changed.

IV. VISUAL INSPECTION OF THE OUTCOME OF DIFFERENT MIXING OF SILANES
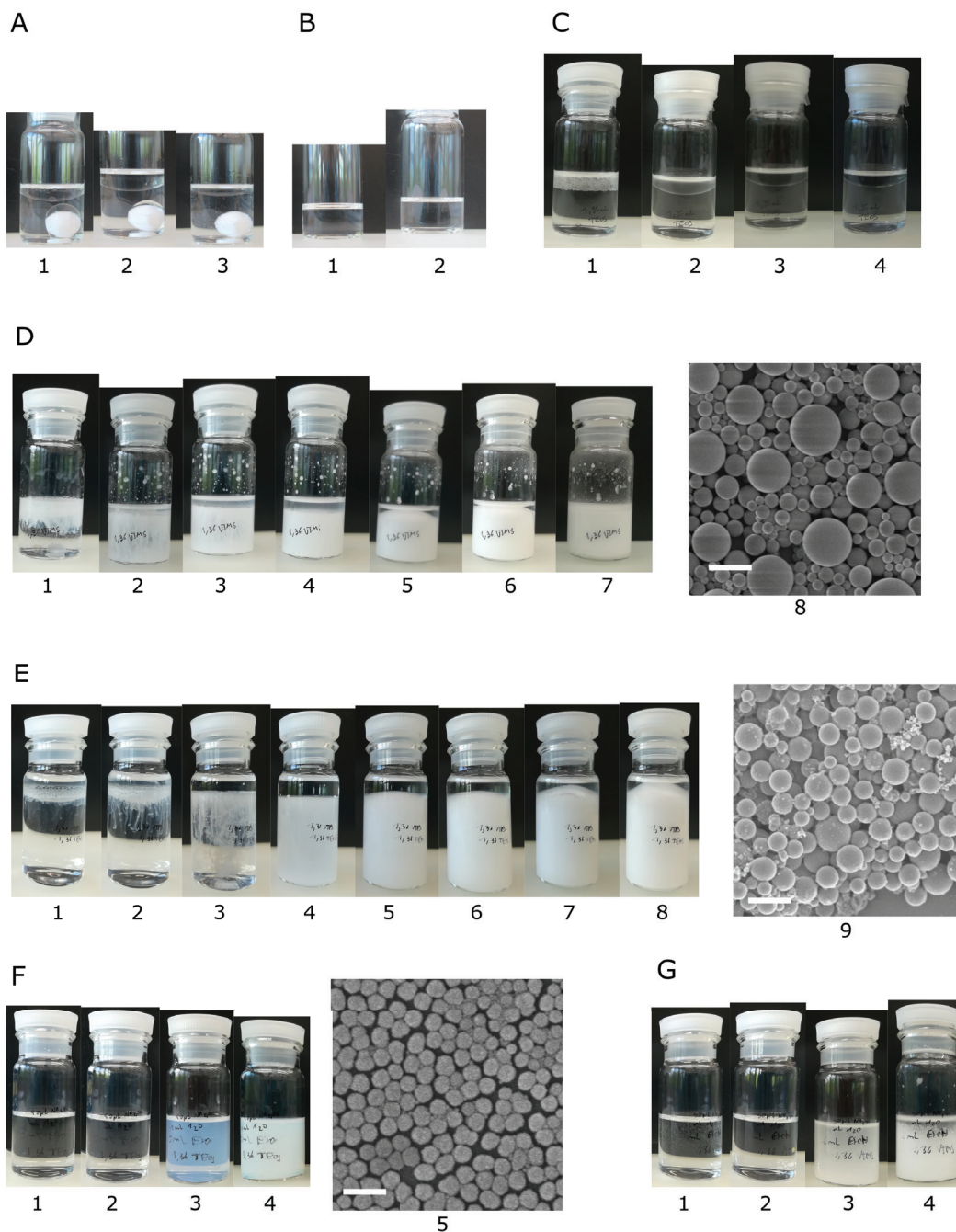
Fig. S 4. Overview of experiments to elucidate the effect of the mixing of silanes under different conditions, as described below. The scale bar for the SEM images D-8 and E-9 corresponds to 2 μm and the one for F-5 to 200 nm.

In order to clarify the role played by the two silica precursors, we have performed a range of experiments where the two silanes are added in different ways, as described below. The letters and numbers correspond to the various images in Fig. S4.

- A- Mixtures of 5.3 mL of MilliQ water with 1) 1.36 mL TEOS, 2) 1.36 mL TEOS and 1.36 mL VTMS, 3) 1.36 mL VTMS.

- B- Mixtures of 1 volume of VTMS for 4 volumes of TEOS (1) and 1 volume of TEOS (2).

- C- A suspension of 6.3 mL MilliQ water, 1.36 mL of TEOS and 50 μL of NH$_4$OH* was quickly mixed by hand before letting it rest. Images of the suspension just after mixing (1), 5 min later (2), 2 h later (3) ans 18 h later (4).

- D- A suspension of 6.3 mL MilliQ water, 1.36 mL of VTMS and 50 μL of NH$_4$OH* without any mixing. Image of the suspension just after gently adding the different compounds (1), after 40s (2), 1 min (3), 4 min (4), 22 min (5), 43 min (6) and 3 h (7). 8) shows an SEM image of the particles obtained. The white scale bar corresponds to 2 μm.

- E- A suspension of 12.6 mL MilliQ water, 1.36 mL of TEOS , 1.36 mL of VTMS and 100 μL of NH$_4$OH* without any mixing. Images of the suspension just after gently adding the different compounds (1), after 17s (2), 1 min (3), 5 min (4), 34 min (5), 1 h (6), 3 h (7) and 5 h (8). 9) shows an SEM image of the particles obtained six days later. The white scale bar corresponds to2 μm.

- F- A suspension of 6 mL EtOH, 1.36 mL of TEOS, 50 μL of NH$_4$OH* and 1 mL MillQ water was quickly mixed by hand before letting it rest. Images of the suspension just after mixing (1), after 28 min (2), 2 h (3) and 6 d (4). 5) shows an SEM image of the particles obtained. The white scale bar corresponds to 200 nm.

- G- A suspension of 6 mL EtOH, 1.36 mL of VTMS, 50 μL of NH$_4$OH* and 1 mL MilliQ water was quickly mixed by hand before letting it rest. Images of the suspension just after mixing (1), after 28 min (2), 2 h (3) and 6 d (4).

From the images shown in Fig. S4, we can conclude that TEOS, VTMS, or a mixture of both are not miscible in water. When we try to mix these silanes with water we obtain two

distinct phases (A). Furthermore, TEOS and VTMS are miscible with each other in different ratios. They form a unique phase when mixed together (B). In the reaction conditions for the synthesis of the rough particles, the reaction medium with only TEOS stays translucent over the course of few hours (C). In the case where both VTMS and TEOS are present, without mixing, we can see the phase separation between the silanes and the aqueous phase. Initially, the interface turns white and recirculation of a white fluid starts. After several minutes, the aqueous phase is completely white. In the end, from the SEM images, we can see that micron-sized silica particles were formed during the reaction (D). The same observations are made in the case of only VTMS as silane in the reaction (E). In order to obtain any particle nucleation in the sole presence of TEOS at this ammonia concentration, ethanol must be added. The suspension turns whitish after a few hours and after several days particles in the 100 nm range are formed (F). In comparison, the case of pure VTMS in ethanolic solutions produces larger particles (G). The reaction medium takes on a stronger white tinge earlier on, indicative of the generation of large solid particles, but VTMS still reacts slower in ethanolic solution than in water.

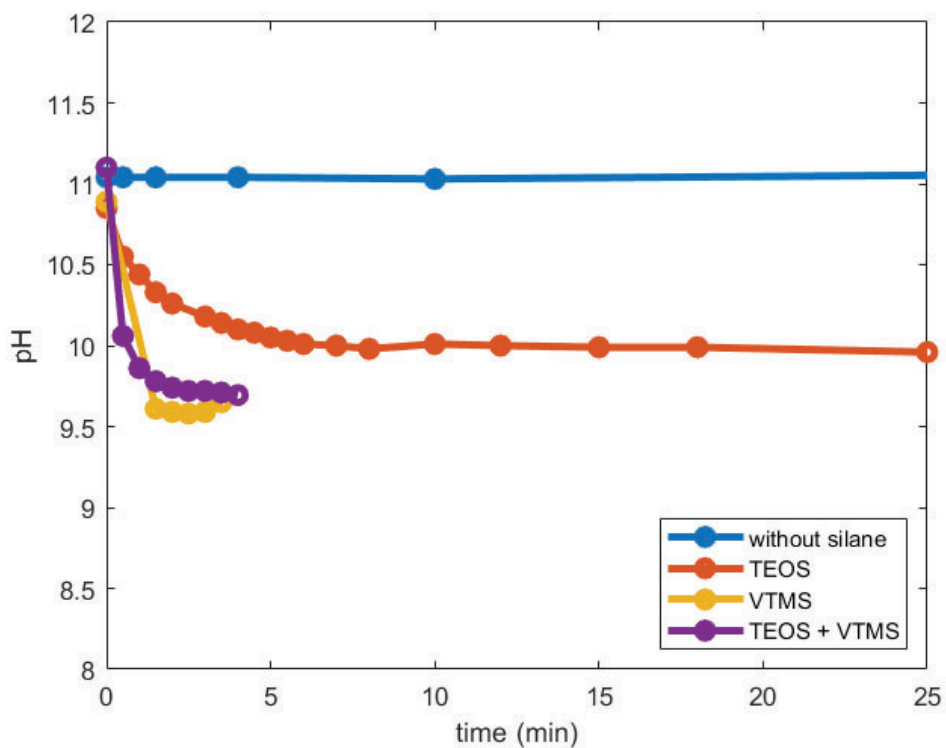## V. PH MEASUREMENT DURING THE REACTION

Fig. S 5. pH evolution during different reactions. To perform the pH measurements, 150 μL of NH4OH was added to 21 mL of MilliQ water under strirring. The pH electrode (InLab Routine Pro) was inserted in the solution and the pH value were measured at 1 minute intervals. The figure shows the case for: pure ammonia (blue), 2,04 mL of TEOS (brown), 2.04 mL of VTMS (yellow) and with 2.04 mL of TEOS and 2.04 mL of VTMS (purple). In the presence of VTMS, the measurement had to be stopped after 4 minutes due to the formation of silica on the electrode.

VI.   EFFECT OF AMMONIA CONCENTRATION:
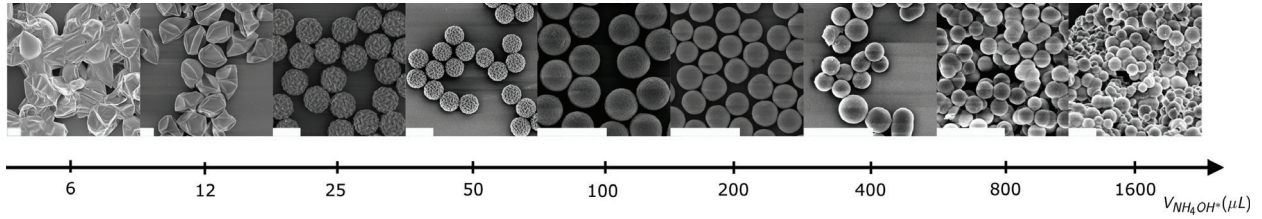
Fig. S 6.   SEM images of particles obtained by varying the amount of ammonia V_{NH_4OH*} beyond the range reported in the main text for a synthesis with 6.3mL of MilliQ water, 0.544mL of TEOS and 0.816mL of VTMS while stirring for 80mins before collecting. When using ammonia volumes lower than 12 μL big aggregates are formed. For ammonia volumes greater than 200 μL, non-spherical and poly-dispersed particles are obtained. For even higher concentrations, aggregates are again formed. The white scale bars correspond to 2 μm.

VII. FORMATION OF SPIKY PARTICLES
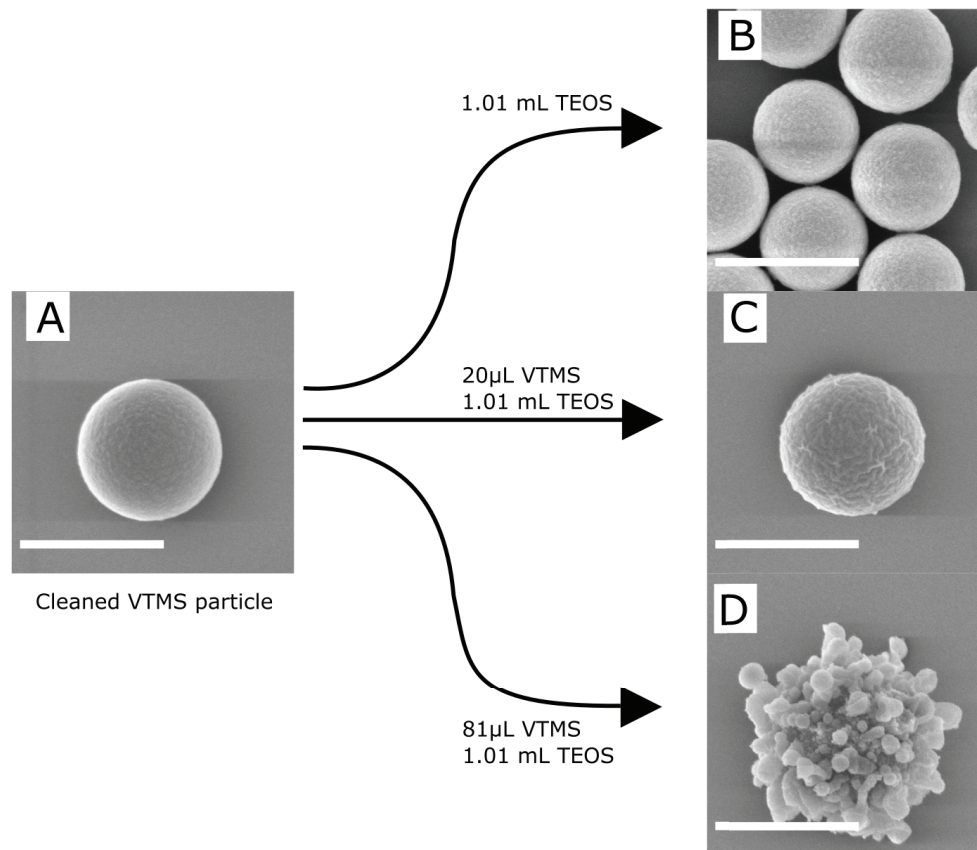
Fig. S 7. SEM images of particles obtained after adding 1.01 mL TEOS with no VTMS (B), with 20μL of VTMS (C), and with 81μL of VTMS (D) to a suspension containing 6.3 mL MilliQ water, 50 μL of NH$_4$OH*, and cleaned VTMS particles, which were previously made in a reaction with 6.3 mL MilliQ water, 50 μL of NH$_4$OH* and 272 μL VTMS (A). The white scale bars correspond to 1 μm. By adding a VTMS and TEOS at a large r$_{TEOS}$ to cleaned particles made of pure VTMS, spiky particles can be formed. By close inspection, the spikes appeared to be consisting of small, highly-buckled particles with similar shapes as the ones reported in Figure 1 with r$_{TEOS}$ = 0.9 and V$_{NH_4OH*}$ = 50 μL.

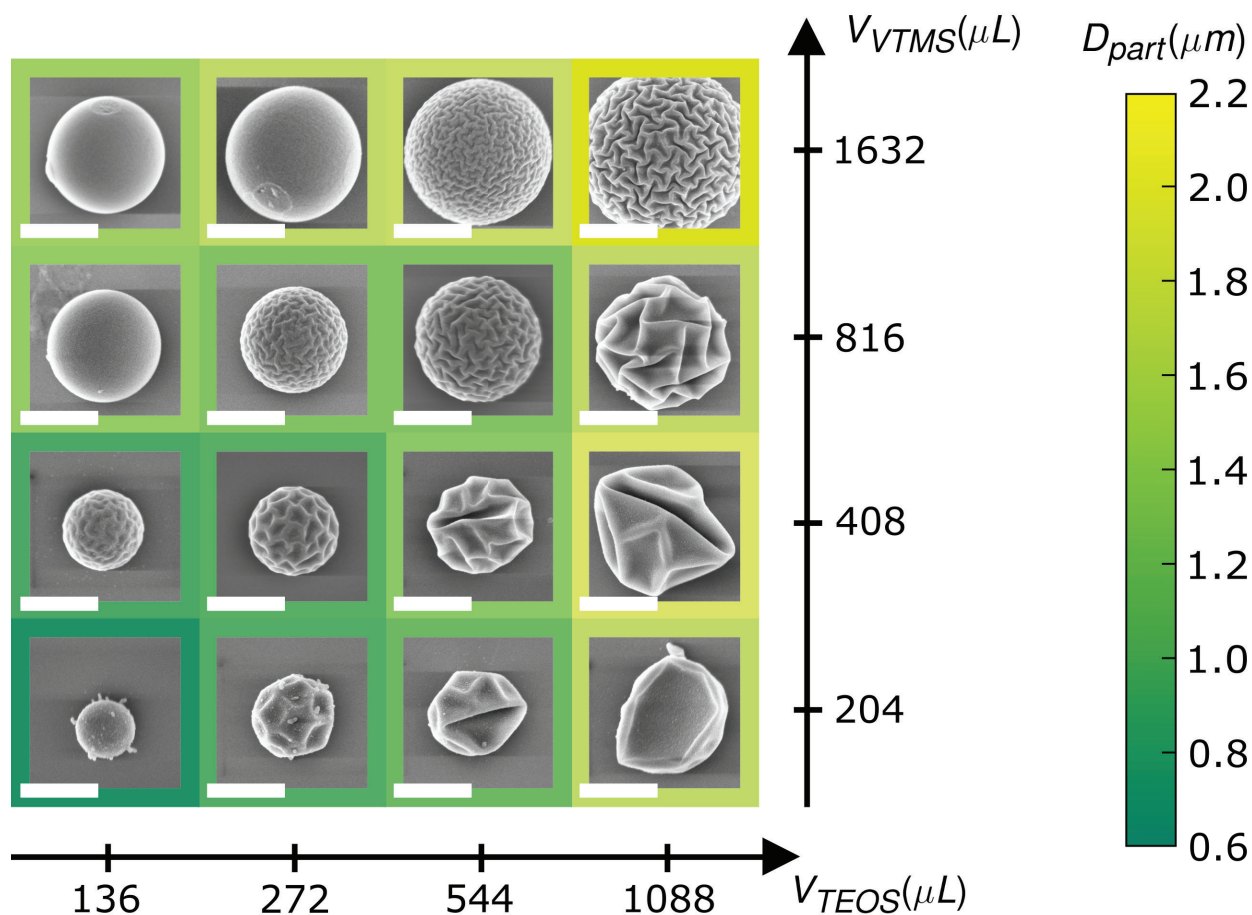# VIII. SYNTHESES WITH FIXED AMMONIA AND WATER VOLUMES:

Fig. S 8. SEM images of particles obtained by varying the volume of TEOS (V_{TEOS}) or the volume of VTMS (V_{VTMS}) for syntheses with 6.3mL of MilliQ water and $V_{NH4OH*} = 50\ \mu$L. The reactions were stirred for 80 mins. The white scale bars correspond to 1 μm.

Table S 6. Concentration of ammonia (A), TEOS (B) and VTMS (C) used for the Fig. S8. The values are in mol/L

A-

0.040	0.039	0.038	0.036
0.044	0.044	0.042	0.039
0.047	0.046	0.044	0.041
0.049	0.048	0.046	0.042

B-

0.08	0.15	0.29	0.54
0.08	0.16	0.32	0.59
0.09	0.17	0.33	0.62
0.09	0.18	0.34	0.64

C-

1.31	1.29	1.25	1.18
0.73	0.72	0.69	0.65
0.39	0.38	0.37	0.34
0.20	0.20	0.19	0.17

Table S 7. Concentration of TEOS and VTMS used in Figure 2. In this experiments, the concentration of ammonia C_{NH_4OH} was always 0.036 mol/L.

V_{TEOS} (mL)	0.136	0.272	0.544	1.088
C_{TEOS}(mol/L)	0.07	0.13	0.27	0.54
V_{VTMS}(mL)	0.204	0.408	0.816	1.632
C_{VTMS}(mol/L)	0.15	0.29	0.59	1.18

Table S 8. Particle sizes (in μm) manually measured with Image J corresponding to the syntheses in Fig. S8.

1.62	1.81	1.88	2.01
1.55	1.44	1.44	1.82
1.1	1.19	1.5	1.99
0.81	1.16	1.3	1.81

Table S 9. Variations of total reaction volumes between Fig. S8 and Fig. 2.

10%	9%	6%	0%
19%	18%	15%	9%
24%	22%	19%	13%
26%	25%	22%	16%

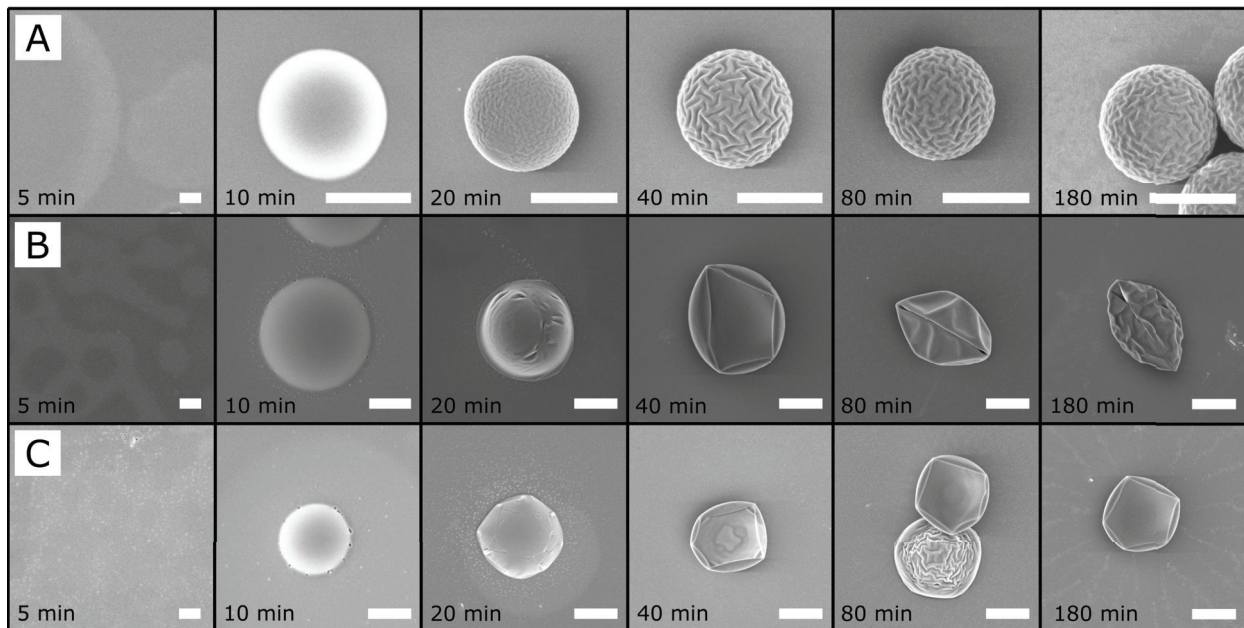# IX. TEMPORAL ANALYSIS OF PARTICLE MORPHOLOGY WITH V_{NH_4OH}= 12.5 μL:

Fig. S 9.   SEM images of the time evolution of the particles morphology. At each time point, 10 μL were removed from the synthesis suspension and added to 1 mL of H_2O before imaging. Synthesis conditions: V_{NH_4OH}= 12.5 μL and A) r_{TEOS} = 0.2; B) r_{TEOS} = 0.4; C) r_{TEOS} = 0.6. These conditions are similar the ones in Fig. 1 with corresponding values of r_{TEOS}. The white scale bars are 2 μm. The droplets formed at 5 minutes are not strong enough to withstand drying and will just explode, leaving an oily surface on the silicon wafer used as support for imaging. After 10 minutes, the particles show a spherical shape, with a soft shell than can deform, as shown in the images at 20 minutes. After 40 minutes, the particles show the first signs of buckling. As expected, the kinetics of the particle formation are slower than in the case where V_{NH_4OH}= 50 μL, as the particles appeared rigid already after 5 minutes. Moreover, the disk-shaped particles one can see in C-80 min are not generated during synthesis but are a consequence of drying during preparation for SEM imaging (see Fig. S 18).

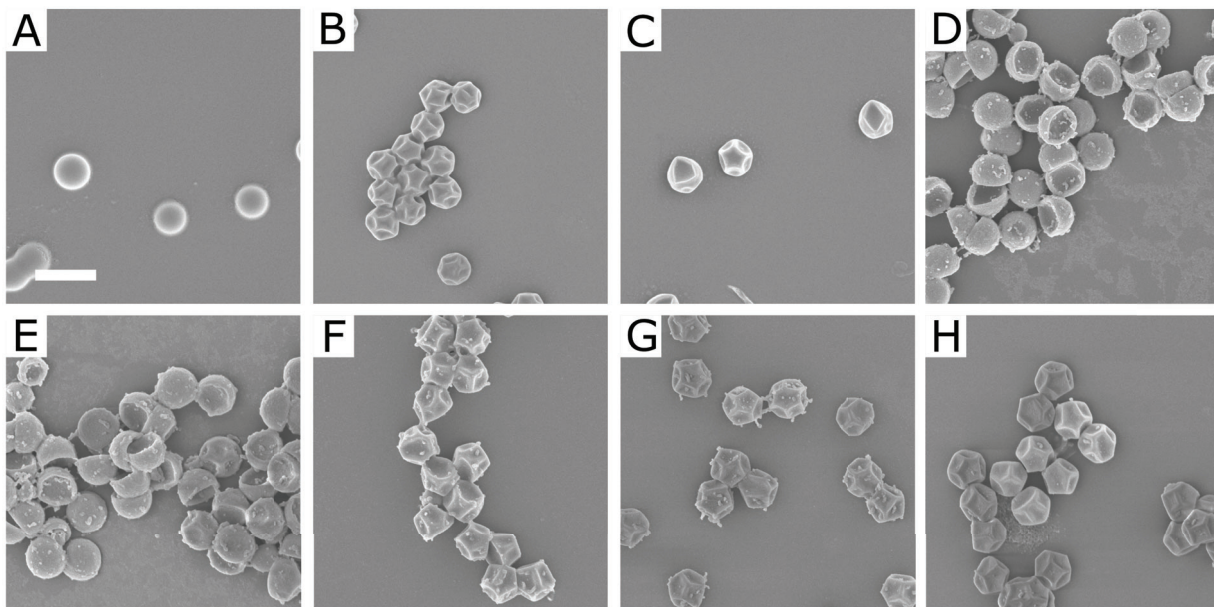# X. TEMPORAL ANALYSIS OF PARTICLE MORPHOLOGY WITH V_{NH_4OH}= 50 μL:

Fig. S 10. SEM images of particles obtained from a synthesis with 6.3 mL MilliQ water, 50 μL of NH$_4$OH*, 952 μL of TEOS, and 408 μL of VTMS. 20 μL of the reactions suspension was taken out and put in 1 mL of water after 3 min (A), 5 min (B) , 8 min (C), 12 min (D), 17 min (E), 40 min (F) and 80 min (G). H) shows an SEM image of the same suspension following centrifugation performed 80 min after the reaction's start. From these data, we can conclude that such a method does not represent a precise way to image the particle morphology. It rather conveys an image of the morphology of the particles after x minutes after being dispersed in excess water. Indeed, we observe an evolution from a sphere to a more buckled particle until a smooth "bowl-like" particle appears to be formed after 17 minutes (A–E). However, the same particles at 40 minutes and later appear less buckled than at 17 minutes. The particles size does not seem to change. The white scale bars correspond to 2 μm.

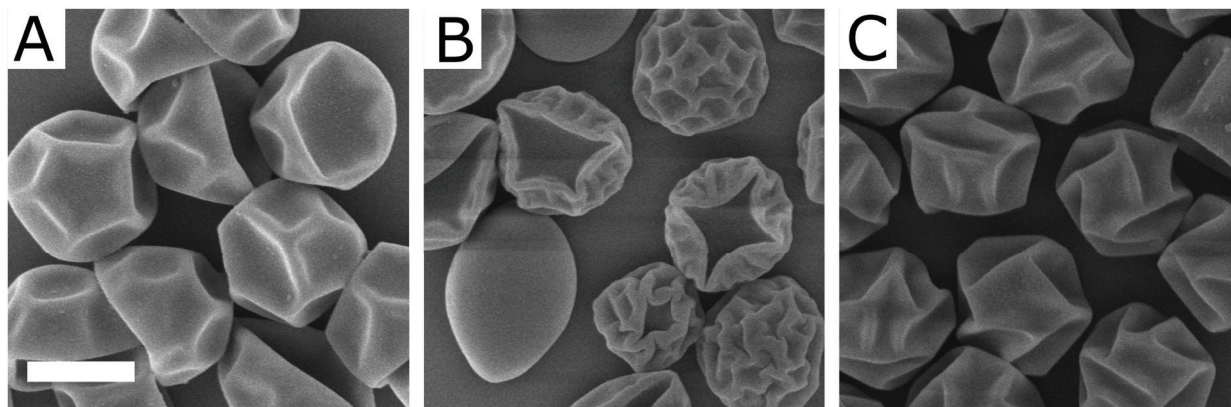## XI. INFLUENCE OF THE SOLVENT DURING CENTRIFUGATION.

Fig. S 11. SEM images of particles obtained from a synthesis where 952 μL of TEOS , 408 μL of VTMS, and 50 μL of NH$_4$OH* were added to 6.3 mL of MilliQ water. After 40 mins, 2 mL of the previous reaction medium was added to 13 mL of a solvent and centrifuged twice in it and then centrifuged twice more in water. A- SEM image of the particles when the solvent was MilliQ water, B- SEM image of the particles when the solvent was ethanol, C- SEM image of the particles when the solvent was toluene.The white scale bar corresponds to 1 μm. From these images, we conclude that after 40 minutes, the buckling process is still not complete. By dispersing the suspension in different solvents, the morphology is influenced.

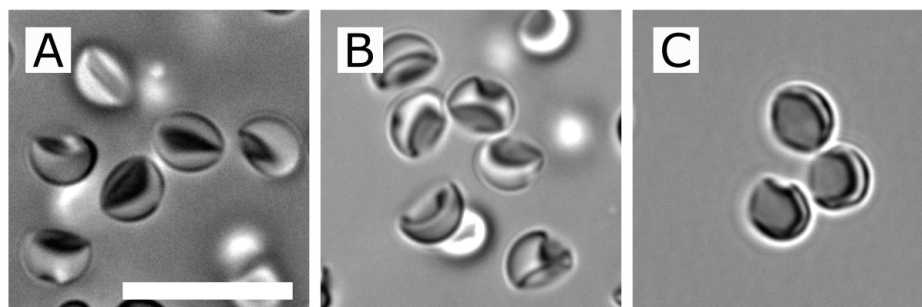# XII. *IN-SITU* STUDY OF THE PARTICLE MORPHOLOGY EVOLUTION WITH AN OPTICAL MICROSCOPE

Fig. S 12.   Optical microscopy images of particles obtained mixing 10 μL of a reaction suspension made of 6.2 mL of H_2O, 12.5 μL of NH_4OH^*, 544 μL of TEOS and 816 μL of VTMS either with 20 μL(A), 100 μL (B) or 1 mL (C) of MilliQ after 20 mins of reaction. All the images are at the same scale. The white scale bar in the top left image corresponds to 10 μm.
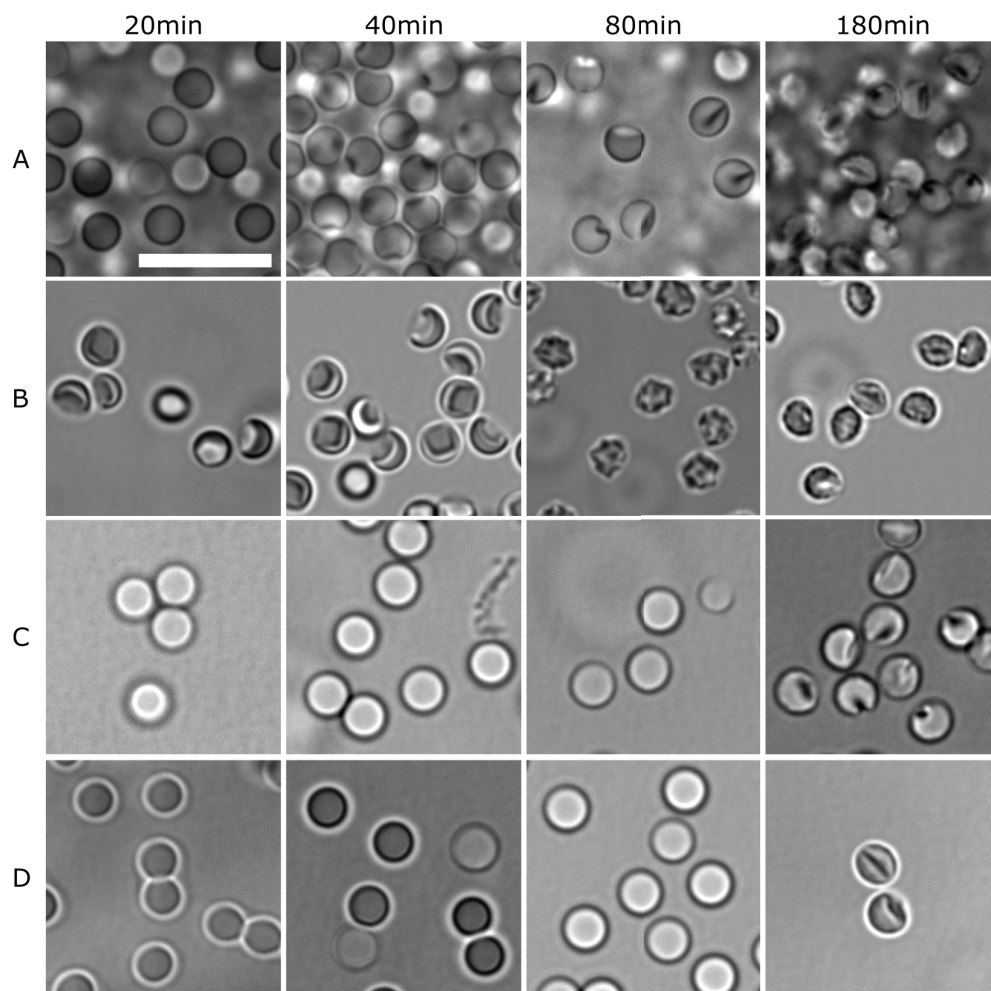
Fig. S 13. Optical microscopy images of particles as a function of time in different fluids. In row A, particles are imaged in the reaction mixture (6.2 mL of H_2O, 12.5 μL of NH_4OH^*, 544 μL of TEOS and 816 μL of VTMS - r_{TEOS}=0.4) as a function of time. In row B, particles from the same reaction mixture of A are transferred in MilliQ water after 20, 40, 80 and 180 minutes, respectively, (20 μL of the reaction mixture in 1 mL of MilliQ water) and imaged. In row C (respectively D), particles from the same reaction mixture of A are transferred to ethanol (methanol) (20 μL of the reaction mixture in 1 mL of ethanol or methanol) and imaged at the corresponding times. The scale is the same for all images and the white bar corresponds to 10 μm. To obtain the optical microscopy images, 5 μL of liquid is sealed with a spacer and a coverslip on a glass slide to avoid evaporation. These particles are slightly different from the ones in Fig. 5, due to a potentially lower ammonia concentration due to partial evaporation of the stock following intensive use of the solution overtime.

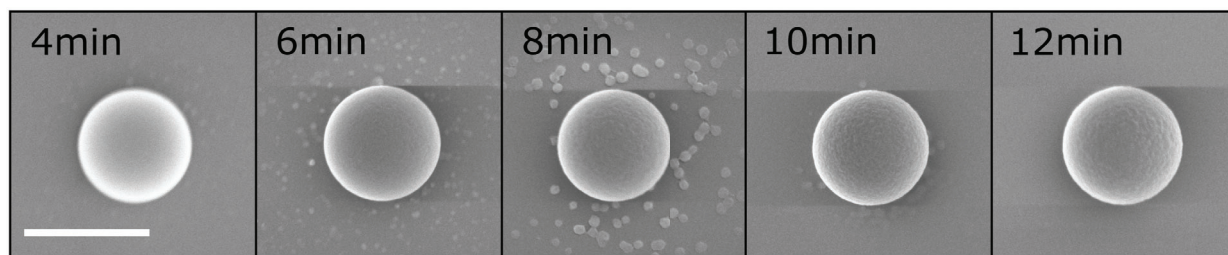## XIII.   TIME EVOLUTION OF PURE VTMS PARTICLES.

Fig. S 14.   Evolution of pure VTMS particles over time. The synthesis was carried out using 50 μL of NH$_4$OH* and 272 μL of VTMS in 6.3 mL of MilliQ water. The white scale bars correspond to 1 μm.
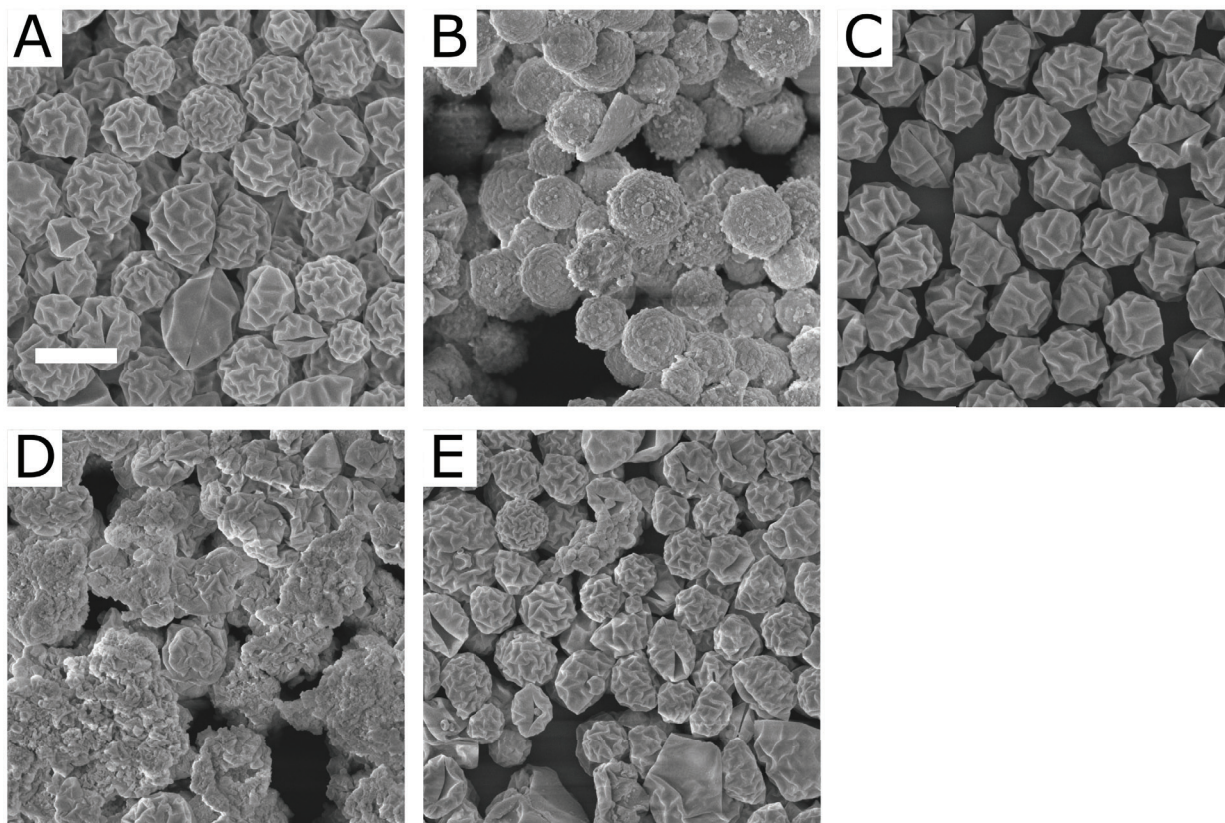
XIV. INFLUENCE OF THE MIXING METHOD

Fig. S 15. SEM images of particles obtained after adding 680μL TEOS and 680 μL VTMS to 6.3 mL MilliQ water and 50 μL NH$_4$OH. The reaction was performed for 80 min before centrifugation. Initially, the reactants were quickly mixed by hand (A), mixed at 80 rpm (B), mixed at 800 rpm (C), quickly hand-mixed before being put in a weak sonicator bath (D) or quickly hand-mixed before being put in a stronger sonicator bath (E). The white scale bar corresponds to 2 μm. From these observations, we conclude that the mixing method has a big influence on the resulting particle morphology. Hand-shaking produces more size- and shape-polydisperse particles than using mechanical stirring at high rpm. However, using a low speed in a rotary mixer leads to uncontrolled particles, since the silane phase is not well dispersed in the suspension, with larger droplets formed and attaching to the stirring bar. A similar problem can be seen when using a sonicator bath, which is not strong enough to create small droplets and break aggregates of particles.
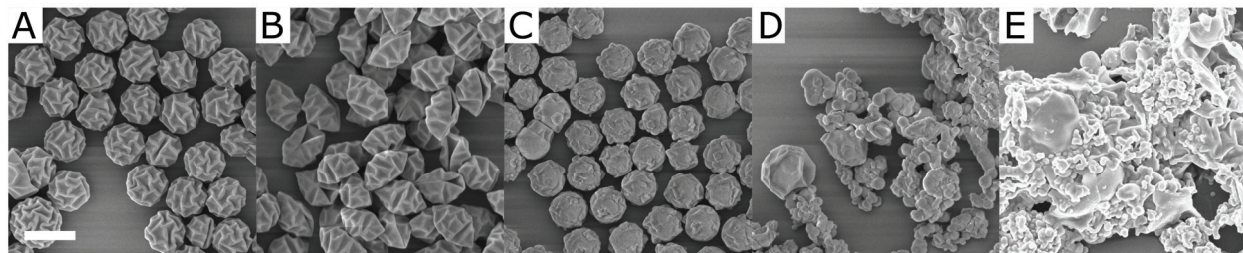
XV.   INFLUENCE OF THE INJECTION RATE OF THE SILANES:

Fig. S 16.   SEM images of the particles obtained by adding 544 μL of VTMS, 816 μL of TEOS, 50 μL of NH$_4$OH* to 6.3 mL of MilliQ water. The silanes were added together, either at once (A) or injected over 1 min (B), 8 min (C), 22 min (D) and 55 min (E). The white scale bar corresponds to 2 μm. The injection rate of the silanes has an influence on the result of the reaction. The slower the silanes are added, the more deformed the particles are. When the injection takes longer than tens of minutes, big aggregates are obtained.

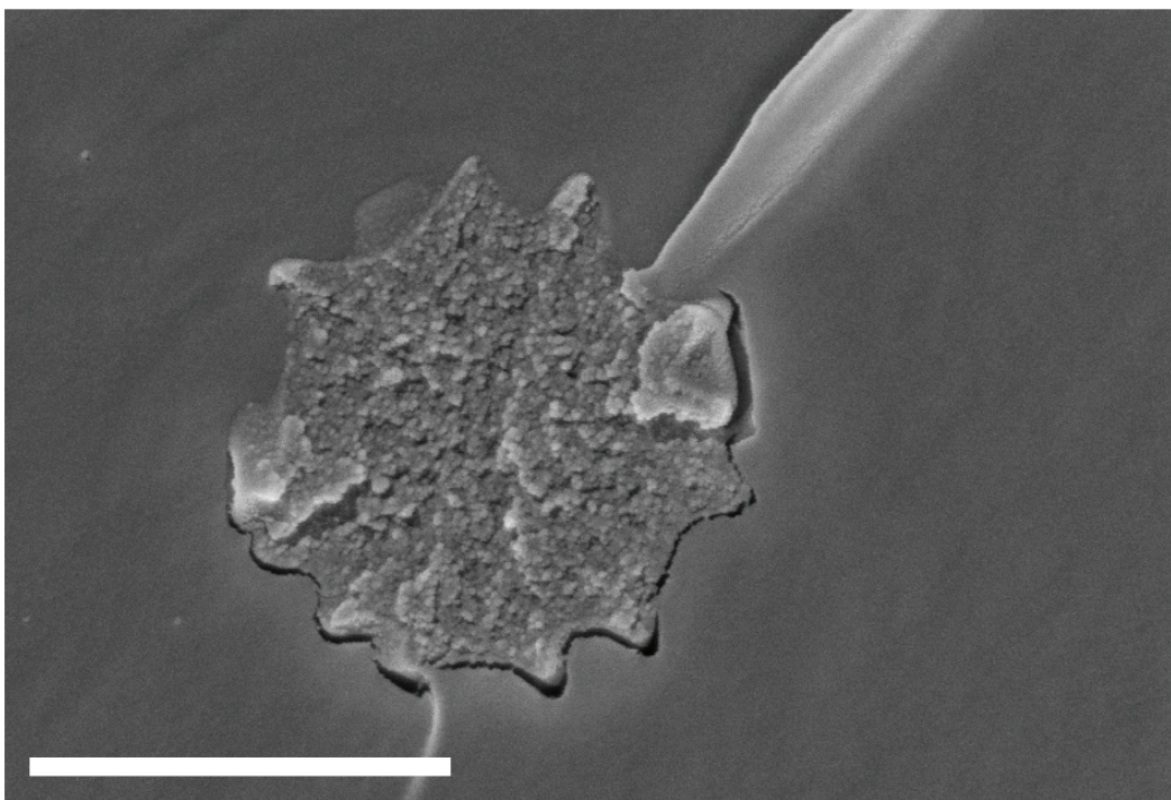# XVI. CRYO-SEM INVESTIGATION OF THE PARTICLE INTERIOR

Fig. S 17. Cross-section view of a particle from a synthesis with 50 μL NH$_4$OH, 6.3 mL MilliQ water, 544 μL VTMS and 816 μL TEOS as in Fig. 1. The particle was fractured and imaged with a cryo-SEM. The scale bar corresponds to 1 μm. For the cryo-sem images, samples were vortexed for 3s and 5μL were filled into a 6mm aluminium-planchette and a second filled aluminium-planchette was used as lid. The planchette sandwiches were frozen in a high-pressure freezer HPM 100 (Bal-Tec/Leica, AT) and stored in liquid nitrogen. Vitrified specimens were then transferred and mounted under liquid nitrogen on the cryo-holder and finally transferred under liquid nitrogen into a precooled (-120 C) freeze-fracturing system BAF 060 (Bal-Tec/Leica, AT) at 1×10^{-6} mbar. Coating was performed with 3nm tungsten at an elevation angle of 45° followed by 3nm at 90 degrees. Transfer to the precooled cryo-SEM was done under high vacuum ($< 5 \times 10^{-6}$ mbar) with an air-lock shuttle. Cryo-SEM was performed in a field emission SEM Leo Gemini 1530 (Carl Zeiss, DE) equipped with a cold stage to maintain the specimen temperature at - 120°C (VCT Cryostage, Bal-Tec/Leica, AT). Inlens-SE- and Everhart-Thornley SE-signals at an acceleration voltage of 2kV were used for image acquisition.

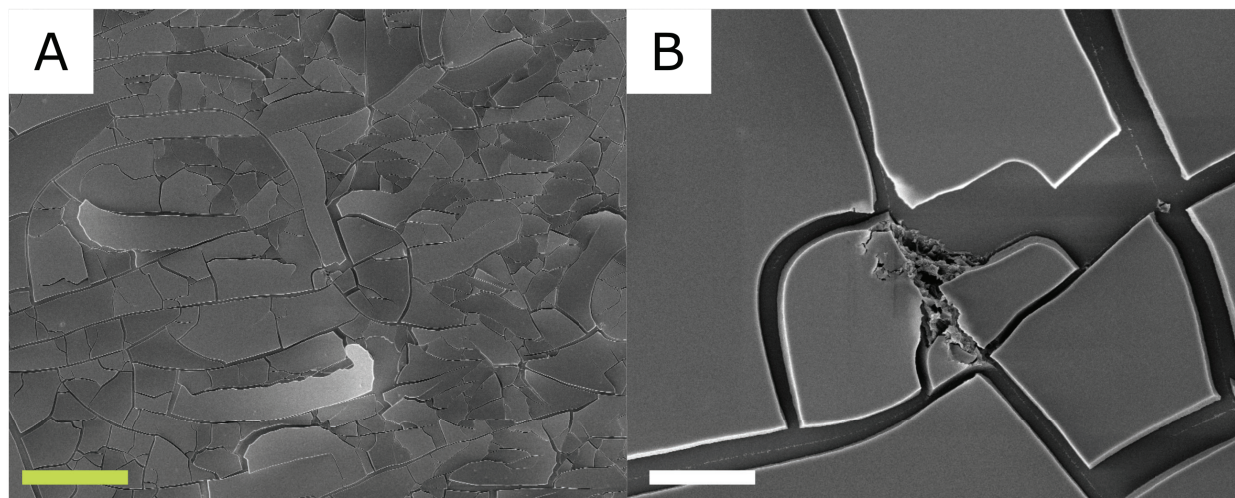## XVII.   DRIED SUPERNATANT AFTER FIRST CENTRIFUGATION

Fig. S 18.   SEM images of the dried supernatant obtained from the centrifugation of a particle suspension synthesized with 6.3 mL MilliQ, 0.05 mL NH4OH, 0.680 mL VTMS and 0.680 mL TEOS under stirring for 80 minutes. These films are also found together with particles if the suspensions are not cleaned by multiple centrifugation/redispersion cycles, but are no longer present after three cleaning cycles. The green scale bar in A corresponds to 40 μm, while the white scale bar in B corresponds to 4 μm.

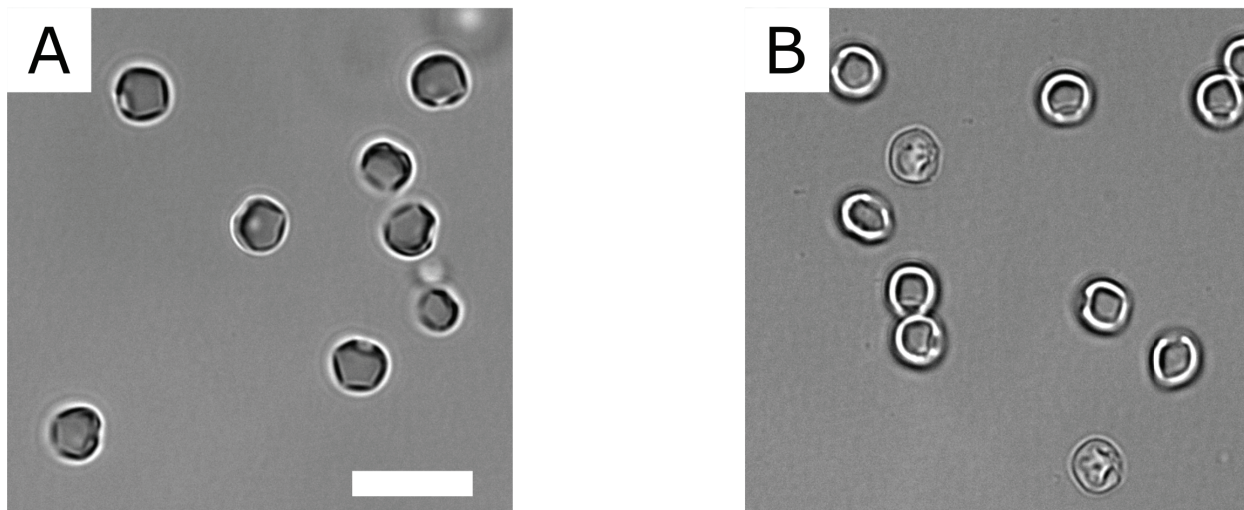## XVIII. FORMATION OF THE DISK-LIKE PARTICLES FROM DRYING.

Fig. S 19.   Optical micrographs of the suspension with the following synthesis parameters: V_{NH_4OH}= 12.5 μL and r_{TEOS} = 0.6. (A) 10μL of the suspension is quenched in 1 mL of water after 80 minutes and directly imaged. (B) Image of the same suspension after complete evaporation of the liquid. The white scale bar is 10 μm. While in (A) all particles are bowl-like particles, disk-like particles appear after liquid evaporation. Disk-like particles are therefore the result of drying and not of the synthesis itself.

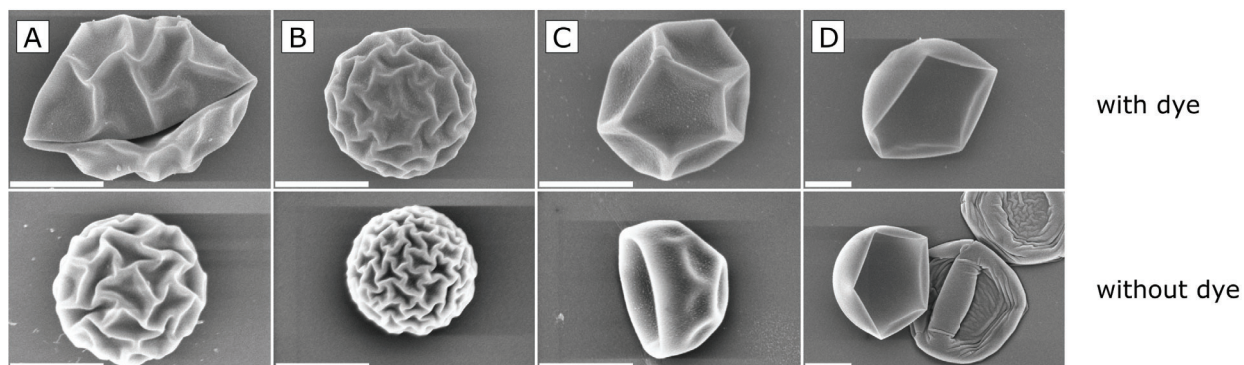# XIX. PARTICLE MORPHOLOGY WITH AND WITHOUT FLUORESCENT DYE:

Fig. S 20. SEM images of particles made by using A: $V_{VTMS} = 0.816$ mL, $V_{TEOS} = 1.088$ mL, $V_{NH_4OH*} = 50$ μL and $V_{H_2O} = 7.116$ mL, B: $V_{VTMS} = 0.544$ mL, $V_{TEOS} = 0.816$ mL, $V_{NH_4OH*} = 50$ μL and $V_{H_2O} = 6.3$ mL, C: $V_{VTMS} = 0.544$ mL, $V_{TEOS} = 0.816$ mL, $V_{NH_4OH*} = 50$ μL and $V_{H_2O} = 6.3$ mL, D: $V_{VTMS} = 0.544$ mL, $V_{TEOS} = 0.816$ mL, $V_{NH_4OH*} = 25$ μL and $V_{H_2O} = 6.3$ mL. For the particles with dye (first row), 50 μL of the solution (1mL EtOH, 1mg ATTO-495-NHS ester, 2.9 μL APTES) was added from the beginning. The dye was conjugated with APTES by dispersing 1mg of ATTO-495- NHS ester in 1 mL of EtOH, then 2.9 μL of APTES was added to the solution and stirred it overnight under N2 atmosphere. The white scale bars correspond to 1 μm.

XX. SUPPORTING MOVIE

Movie S1: Movie showing the effect of liquid exchange during shell formation in the conditions described in the text.