Addressable morphology control of silica structures by manipulating the reagent addition time

P. Datskos, a and J. Chen, b and J. Sharma a

a Energy and Transportation Science Division, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA
b Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA

S1.

Chemicals: Polyvinylpyrrolidone (PVP, MW = 40,000) was purchased from Sigma Aldrich. Absolute ethanol (C2H5OH, 200 proof), sodium citrate, pentanol (C5H11OH), tetraethyl orthosilicate (TEOS), and ammonium hydroxide (NH4OH, 28–30 %) were purchased from Fisher Scientific. Required solutions were made by mixing the above chemicals.

Silica structure (rod) washing: The as synthesized rods were centrifuged at 5000 rpm for 15 minutes, and discarded the supernatant. Washed the rods with ethanol by centrifuging at 3000 rpm three times and discarded the supernatant every time. Finally centrifuged the rods at 1500 rpm for 15 minutes.

SEM studies: SEM samples were prepared by depositing the purified rods on silicon wafers. Silicon wafers were employed to minimize the charging of the silica samples. SEM studies were performed using Merlin 200 instrument at 1.67 kV.

TEM studies: TEM experiments were performed at 120 kV with an emission current of 4 µA in order to minimize electron-beam-caused microstructural change or sample damage. TEM samples were prepared by mixing PVP, pentanol, sodium citrate, ammonium hydroxide, and water in the absence and presence of ethanol (no TEOS was added). The concentrations and volumes were same as provided in the main manuscript text.

DLS studies: DLS samples were prepared by using standard volume and concentration of reagents as explained in the main manuscript text. Everything else, except ethanol and TEOS in sample a. For sample ‘b’ 300 µL ethanol was added to the 1 mL of sample a.

DLS measurements were made using Zeta Potential/Particle Sizer (Nicomp™ 380 ZLS) at channel width = 200 µsec., using pentanol refractive index 1.409, and viscosity as 4 cP.
**Fig. S1:** SEM image of silica rods obtained when ethanol is added with other reagents in the beginning.
Fig. S2: TEM images showing round aggregates instead of rod like templates in both cases a) without ethanol, and b) with ethanol. Note all other reagents (PVP, citrate, water, pentanol, ammonium hydroxide, and no TEOS) are of same concentration and volume as given in the main manuscript text.
S2: Rod growth in the presence and absence of ethanol.

Reaction is completed within 48 hrs. (48 hrs. are given for complete TEOS consumption, though almost no change was observed even after 24 hrs.).

<table>
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<th>Ethanol is added</th>
<th>Ethanol is added</th>
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<td>in the beginning</td>
<td>after 5 hrs.</td>
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| % amount of TEOS deposited in 5 hrs. | ≈67% | ≈62% |
| % amount of TEOS deposited in next 43 hrs. | ≈33% | ≈38% |

It must be noted that the calculation of exact amount of TEOS is difficult due to the polydispersity in rod length and diameter, and the values given are the average numbers. Even assuming 5% error in calculations, it appears that ethanol is not playing a significant role in enhancing the hydrolysis and hence TEOS deposition.
**Fig. S3:** SEM image showing the rods grown without ethanol but by addition of another equivalent amount of TEOS after 7 hrs. of initial reaction.

**Fig. S4:** SEM image showing the shrinkage of diameter on extra ethanol addition to already growing rods.
S3.
To see the effect of related change in pH or decrease in TEOS concentration by ethanol addition, we prepared sample B (everything same but replaced ethanol with pentanol). No change in diameter or shape was observed on addition of pentanol (B), while diameter shrinkage was observed on addition of ethanol (C).

Similarly, to keep the concentration of TEOS same, before and after ethanol or pentanol addition, we added an equivalent amount (1.62 µL TEOS / 170 µL of ethanol or pentanol). We observed that the length of structures (rods) increased for both pentanol (D) and ethanol (E) addition. But no change of diameter in case of pentanol (D), while diameter shrinkage similar to C, but with longer rod segment was observed in case of ethanol (E).

Above experiments showed that the related change in solution pH or TEOS concentration on addition of ethanol did not cause the diameter change of growing structures. It is the ethanol that played an active role in decreasing the diameter.

**Fig. S5:** SEM images showing effect (if any) of pH or TEOS concentration on addition of ethanol. A. no ethanol; B. 170 µL of pentanol; C. 170 µL of ethanol; D. 170 µL of pentanol + 1.62 µL of TEOS; E. 170 µL of ethanol + 1.62 µL of TEOS. Scale bar = 200 nm

Note. Additions for B, C, D, and E were made to 2 mL of sample A after 3 hrs. of initial growth. Amounts of ethanol or TEOS are calculated according to the standard reaction conditions given in the main manuscript. SEM images were taken after 24 hrs. of ethanol or pentanol addition.
S4: Maximum achievable shrinkage of rod diameter before emulsion droplet detaches.

Initial rod sample was prepared by dissolving 1.0 g PVP (MW=40,000) in 10 mL of pentanol in a glass vial. 280 µL H₂O, 100 µL sodium citrate (0.18 M), 950 µL absolute ethanol, and 200 µL NH₄OH (28–30%) were added to it. 100 µL of TEOS was added to the above solution followed by vortexing. Reaction was allowed to proceed for 2 hrs.

After 2 hrs., took three aliquots from the above solution, and by adding more ethanol made the final ethanol concentration a) 200 µL ethanol / 1 mL reaction mixture, b) 293 µL ethanol / 1 mL reaction mixture, and c) 366 µL ethanol / 1 mL reaction mixture.

Fig. S6: SEM images showing shrinkage of rod diameter and emulsion droplet detachment. a) 200 µL ethanol / 1 mL reaction mixture, b) 293 µL ethanol / 1 mL reaction mixture, and c) 366 µL ethanol / 1 mL reaction mixture.
Some more SEM images

More SEM images of rods a) made by two subsequent additions of ethanol and shown in Fig. 3c, b) made by three subsequent ethanol additions and shown in Fig. 3d.
SEM image when ethanol is added after one hour to the growing structures.

SEM image when ethanol is added after two hours to the growing structures.
SEM image when ethanol is added after three hours to the growing structures.

SEM image when ethanol is added after four hours to the growing structures.
SEM image when no ethanol is added to the growing structures.