Supplementary Information

Continuous Synthesis of Nanostructured Silica Based Materials in a Gas-Liquid Segmented Flow Tubular Reactor

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Table S1. Specifications of the different mesoporous silica particles.

Sample	V_{TEOS} /V_{OTMS}	V_{TEOS}+V_{OTMS} vol.%	Shell thickness [nm]	Total pore volume [$cm^3\ g^{-1}$]	BET Surface Area [$m^2\ g^{-1}$]
SiO_2@mSiO_2-18	2.5	1.06	17.9±2.7	0.09	125
SiO_2@mSiO_2-60	2.5	2.5	60.3±7.0	0.33	283
mSiO_2	2.5	3.6	340.9±53[a)]	0.65	627

[a)] total diameter.

Buoyancy

For the calculation of the approximate critical diameter, the dimensionless number (Bo) introduced by Bretherton[5b] is used. In the calculation, only the density and surface energy of ethanol were considered, due to the following facts: (i) ethanol is the main component (EtOH/Water = 5.2 vol vol^{-1}) in the reaction mixture and (ii) it leads to the smallest critical diameter, due to its lower surface tension compared to water. Applying these assumptions for the calculation of the critical diameter, we ensure that we are working in a regime below the critical threshold value.

$$Bo = \frac{\rho * g * d^2}{\gamma} < 3.368 \tag{S1}$$

$$\sqrt{\frac{\gamma * Bo}{\rho * g}} = d \tag{S2}$$

$$d = \sqrt{\frac{22.2202 * 10^{-3}\,{}^{N}/_{m} * 3.368}{0.7894 * 10^{3}\,{}^{kg}/_{m^3} * 9.8065\,{}^{m}/_{s^2}}} = 0.003109\ m \cong 3.1\ mm \tag{S3}$$

ρ	density	[kg m^{-3}]
g	gravitation	[m s^{-2}]
d	diameter	[mm]
γ	surface tension	[N m^{-1}]

Continuous synthesis of SiO_2 (Stöber) spheres

Before studying the continuous synthesis of advanced silica spheres (SiO_2@mSiO_2 and mSiO_2), we optimized the setup parameters and reaction compositions for the simpler synthesis of SiO_2 (Stöber) silica particles. In particular, we evaluated the influence of two different parameters: residence time and ammonium hydroxide concentration.

Residence Time

In order to investigate the necessary residence time in the aging tube, the flow rates of the liquid and gas supply were individually adjusted to result in residence times ranging from 15 min up to 120 min. The samples were collected and measured by means of dynamic light scattering (DLS) directly after the synthesis and for each sample after an additional aging time of 24 h. The results (Figure S1) indicate that the particle growth was brought to completion after a residence time of 90 min inside the aging tube: the additional growth in the following 24h was less than 10%.

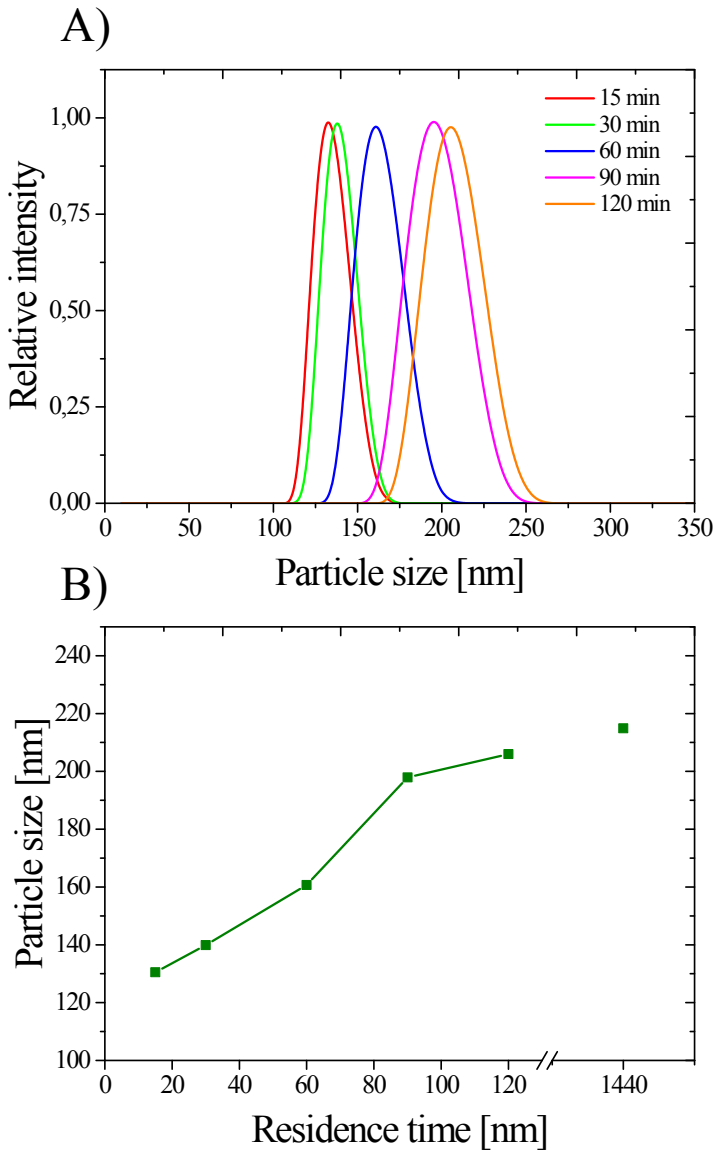

Figure S1. A) Relative intensity measured with DLS over particle size for increasing residence times in the aging tubing. B) Particle size over residence time in the tubing. The size reached by

each collected reaction mixture after an additional aging time of 24 h is shown in the right part of the graph (1440 h).

Variation of the ammonium hydroxide concentration

It is known that in the Stöber synthesis ammonia acts as catalyst in the TEOS hydrolysis-condensation reaction. As reported in literature,[20] the final size of the spherical particles can be tuned by varying the amount of ammonia used in the initial reaction mixture. Typically, the average diameter of the collected silica spheres is expected to increase proportionally to the concentration of ammonia. We decided to investigate the possibility to tune the size of the product – as it is possible in the classical batch process – by using different ammonia concentrations in the feeding reaction mixture.

The concentration was varied between 0.15 mol L^{-1}, 0.25 mol L^{-1} (regular synthesis) and 0.4 mol L^{-1}. The resulting particles size was measured by TEM (see **Figure S2**) and it was shown to be directly proportional to the ammonia concentration, without any noticeable change in the particle morphology. Therefore this parameter could be applied to fine tune the resulting mean particle size.

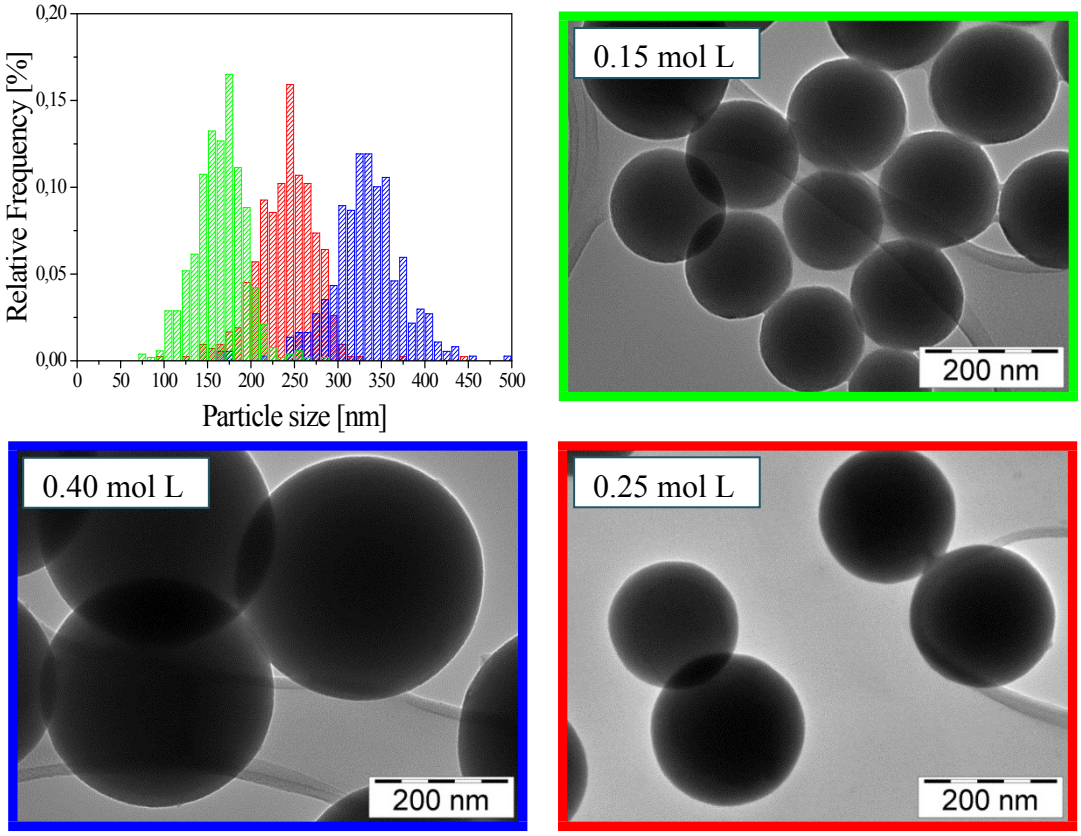

Figure S2. Variation of the particle size as function of $NH_{3(aq)}$ concentration. (Upper-left figure) Particle size histograms. TEM micrographs of the different concentrations. (green 0.15 mol L^{-1}; red 0.25 mol L^{-1}; blue 0.40 mol L^{-1})