

Scalable synthesis of smooth PS@TiO₂ core-shell and TiO₂ hollow spheres in the (sub) micron size range: understanding synthesis and calcination parameters

Supporting Information

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Particle diameter evaluation

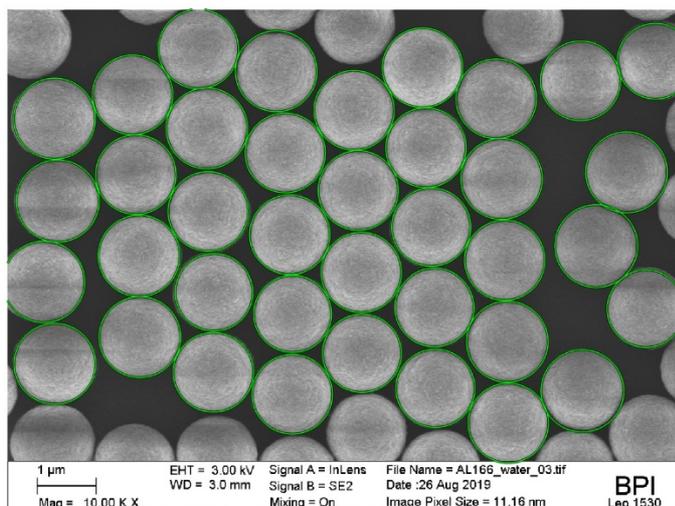


Fig. S1 Output of SEM image after MATLAB circle detection method. The green circles indicate the particles that were included in the evaluation

PS particle histograms

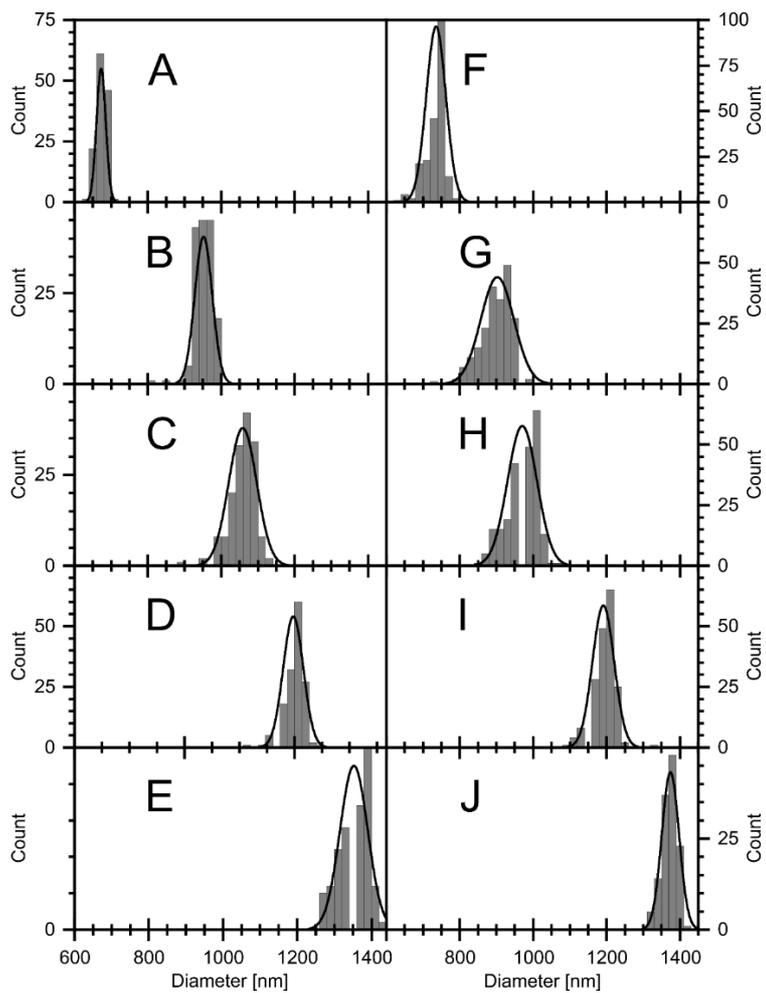


Fig. S2 Histograms of the polystyrene particles A-J

PS particle surface area per mL dispersion

Table S1 Calculation of total surface area (A_{tot}) per ml PS particle dispersion, assuming the density of PS being 1040 kg/m^3 . First, the number (n) of particles is calculated from the mass (m) of a single particle and the concentration (c) of the dispersion. A_{tot} is determined by multiplying n with the surface area of one particle. The total surface area per ml does not change significantly.

	d (SEM) [nm]	m (particle) [mg]	c [mg/ml]	n (particle) per ml	A (particle) [m ²]	A_{tot} per ml
A	673	1.66E-10	6.50E+01	3.92E+11	1.42E-12	5.57E-01
B	952	4.70E-10	9.00E+01	1.92E+11	2.85E-12	5.45E-01
C	1059	6.47E-10	1.10E+02	1.70E+11	3.52E-12	5.99E-01
D	1196	9.32E-10	1.34E+02	1.44E+11	4.49E-12	6.46E-01
E	1353	1.35E-09	1.58E+02	1.17E+11	5.75E-12	6.74E-01

Single IR spectra

Fig. S3 shows the single IR spectra of the STA measurements of pure PS and PS@TiO₂ particles shown in Fig. 4. The spectra were exported after the first baseline correction. At the first baseline correction, the measured signal is divided by a baseline measurement that is taken before the sample measurement starts. Since the baseline varies with increasing temperature, this can lead to transmittance values larger than 1. This effect was visible in the PS sample. Furthermore, an intensity shift is visible with increasing temperature. The effect is larger for the PS@TiO₂ sample and is caused by the increasing temperature of the measured gas, which is not considered in the first baseline correction. The OPUS software tries to cancel this effect out by the rubberband baseline correction.

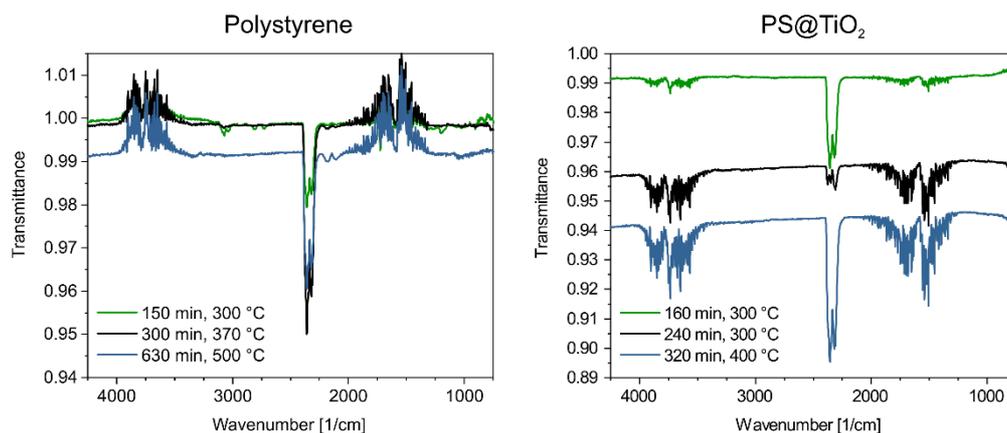


Fig. S3 Single IR Spectra of STA measurements at positions 1, 2 and 3 of Fig. 4. The spectra were taken before the rubberband baseline correction.

Particle shrinkage inert calcination

The left column of figure S4 shows the STA data from inert calcination of PS@TiO₂ particles A. In the TG (a) and DSC (b) curves three events are visible. The first step happens during the first heating ramp to 300 °C and may be due to loss of adsorbed water and loss of low molecular weight residues. The DSC signal reveals a jump at the onset of the isothermal step (2). In contrast to calcination in air, we observe only a minimum mass loss during this isothermal step. The last step (3) happens at the second heating ramp to 400 °C. During this heating ramp a rapid mass loss to the expected value of about 35 % happens. Owing to the inert atmosphere the IR signal shows only spectra of aromatic hydrocarbons and no CO₂ in this range. The decomposition occurs in this case via an endothermic decomposition in contrast to the exothermic combustion in air.

From the SEM images on the right column (d-f) it can be seen that the particle shrinkage in inert calcination atmosphere is less than in air calcination. In the case of inert calcination, the mass loss is 10 % until the precondensation starts. In the case of core-shell particles A, the diameter shrinkage is 12 % in the case of inert calcination and 18 % in the case of air calcination. This underlines our observation that the first degradation and size reduction of the PS template particle strongly affects the size of the final TiO₂ hollow particles.

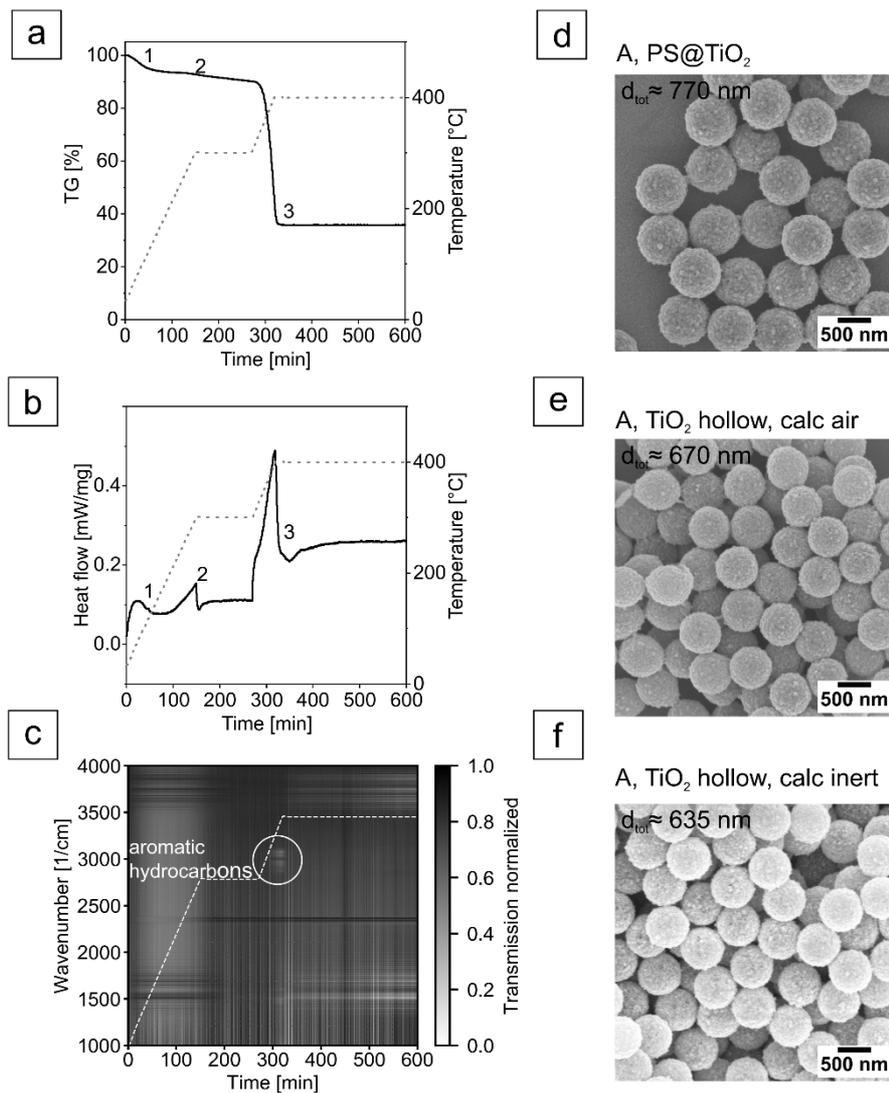


Fig S4 TG (a), DSC (b), and IR (c) measurements of inert calcination of PS@TiO₂ particles A. The right column shows SEM images of the core-shell (d) particles, hollow TiO₂ particles calcined in air (e) and hollow particles calcined in inert atmosphere (f)

Influence of calcination ramp on particle stability

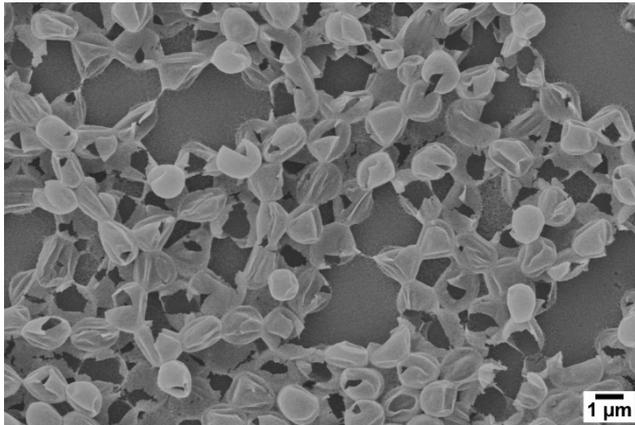


Fig S5 Particles that collapsed during calcination to 500 °C with 2 K/min without isothermal steps