Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supporting Information

for the manuscript

Hierarchical Nanoporous Melamine Resin Sponges with Tunable Porosity - Porosity Analysis and CO_2 Sorption properties.

*Antje Wilke[1], and Jens Weber[1,]**

1) Max-Planck-Institute of Colloids and Interfaces, Department of Colloid Chemistry, Science Park Golm, D-14424, Potsdam, Germany

Contact:

Tel: +49-331-5679569

Fax: +49-331-5679502

e-mail: jens.weber@mpikg.mpg.de

Experimental Section

Materials

Methylated Poly(melamine-co-formaldehyde) solution in butanol (84 wt.-%), LUDOX HS-40 and phosphoric acid were purchased from Aldrich and used as received.

Methods

Elemental Analyses were done with a varioMicro elemental analysis instrument from Elementar Analysensysteme.

Thermogravimetric analyses were performed in synthetic air with a NETZSCH TG209 F1 instrument at a heating rate of 10 K/min.

Fourier transform infrared spectra (FTIR) were collected using a BIORAD FTS 6000 FTIR spectrometer under attenuated total reflection (ATR) conditions.

SEM measurements were carried out in a LEO 1550-Gemini electron microscope (acceleration voltage: 3 kV) and TEM using a Zeiss EM 912Ω (acceleration voltage: 120 kV). Samples for ultrathin cuts were embedded in LR white resin. For SEM measurements the samples were coated with a thin gold layer.

Nitrogen sorption experiments were conducted at 77 K using a Quadrasorb and Autosorb from Quantachrome instruments. Before the experiment, the samples were outgassed overnight at 363 K under vacuum. The surface characterization parameter (surface area, pore size distribution, pore volume) were determined by means of different methods in the Quantachrome program AS1win.

SAXS measurements were performed using a rotating anode machine (Cu-Kα radiation, 0.154 nm) with a two-dimensional MARCCD detector. 1-D profiles were obtained by azimuthally averaging using the FIT2D software. The patterns were corrected for 3D electron density fluctuations (except the in-situ gelation monitoring).

Polymer Synthesis

Typical procedure: In a 10 mL glass flask 2.5 g of the precursor solution was mixed with 2 mL ethanol. After adding 0.5 mL of 85 % phosphoric acid, the LUDOX HS-40 dispersion and water was added dropwise to form a homogeneous mixture.

The glass flask was sealed and heated up to 60 °C for 20 h. In the opened glass the material was heated up to 75 °C for 6 h and finally to 90 °C for 20 h. After the heating period the

hybrid material was grinded and stirred for at least 4 days in 1 M sodium hydroxide solution to remove the template. The etched material was washed with water, ethanol and acetone and dried overnight in a vacuum oven at 40 °C.

Table S1. Precursor, ethanol, phosphoric acid, LUDOX HS 40 and water quantities for the synthesis of melamine resins

SiO_2 [wt.-%]	**precursor [g]**	**EtOH [mL]**	**H_3PO_4 [mL]**	**Ludox HS-40 [g]**	**H_2O [mL]**
32	2.5	2	0.5	2.5	2.10
40	2.5	2	0.5	3.5	1.30
46	2.5	2	0.5	4.5	0.57

Analytical Data

Table S2. Elemental analysis of etched resins, cured at 90 and 250 °C

T_{cure} [°C]	SiO_2 [wt.-%]	N [%]	C [%]	H [%]	Sum [%]	molar C/N
90	32	40.84	33.43	4.76	79.18	0.96
90	40	40.34	33.88	4.85	79.54	0.98
90	46	40.10	34.13	4.81	79.13	0.99
250	32	48.14	34.28	4.95	87.36	0.83
250	40	49.51	34.00	4.87	88.37	0.80
250	46	48.99	34.34	4.78	88.10	0.82

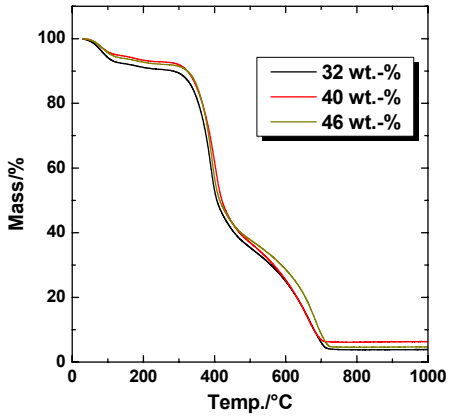


Figure S1. Thermogravimetric analysis (synthetic air atmosphere) of etched MF-resins cured at 250 °C

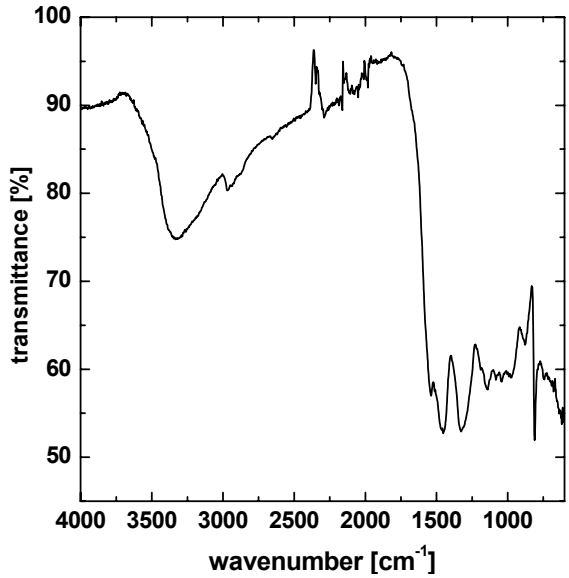


Figure S2. Representative FTIR spectrum of etched MF resins: Bands at 1540 cm^{-1}, 1462 cm^{-1} and 1328 cm^{-1} can be attributed to the triazine ring. The huge band around 3200 cm^{-1} indicates the presence of physisorbed water in the sample. The strong water adsorption behavior is in accordance with the results of TGA measurement and sorption. Bands at 1690 cm^{-1} according to NH_2-group (deformation) and at 1140 cm^{-1} according to ether-groups are not found in the spectra.

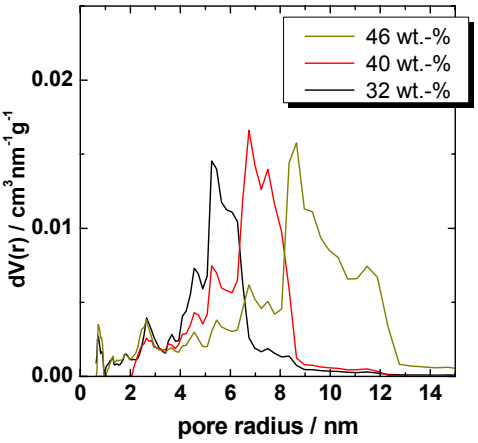


Figure S3. PSD of etched MF resins cured at 90 °C, NLDFT N_2@C, slit/cylindrical pores, equilibr. model

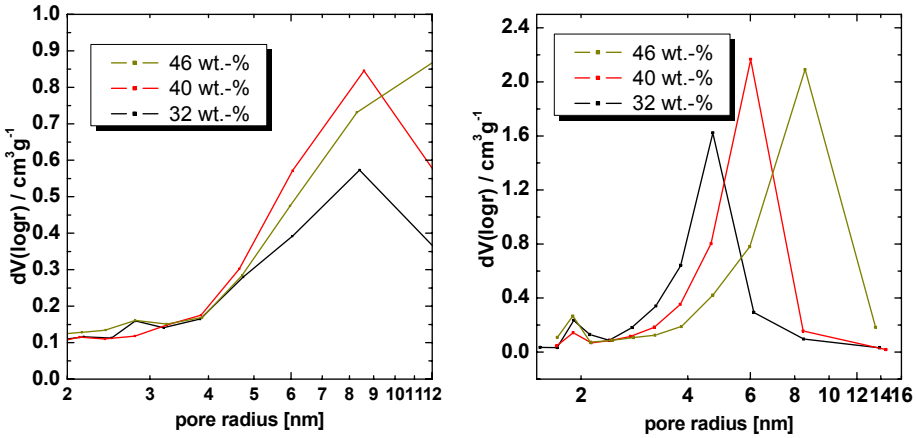


Figure S4. PSD of etched MF resins cured at 90 °C, BJH from adsorption branch (left-hand side) and desorption branch (right-hand side)

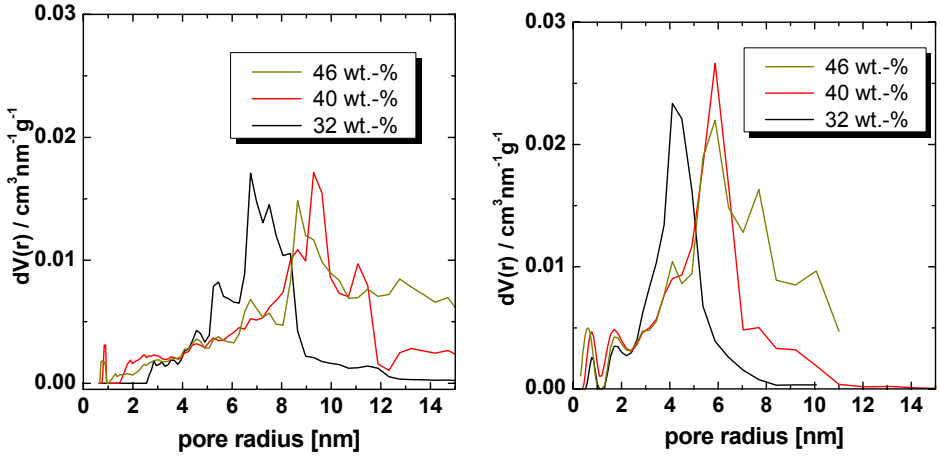


Figure S5. PSD of etched MF resins cured at 250 °C, NLDFT N_2@C, slit/cylindrical pores, equilibr. Model (left-hand side) and b) QSDFT, N_2@C, slit pores, equilibr. Model (right-hand side)

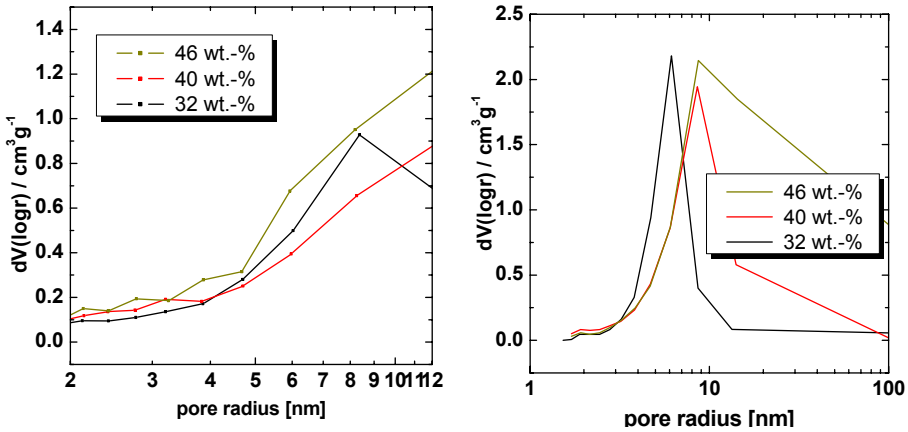


Figure S6. PSD of etched MF resins cured at 250 °C, BJH from adsorption branch (left-hand side) and desorption branch (right-hand side)

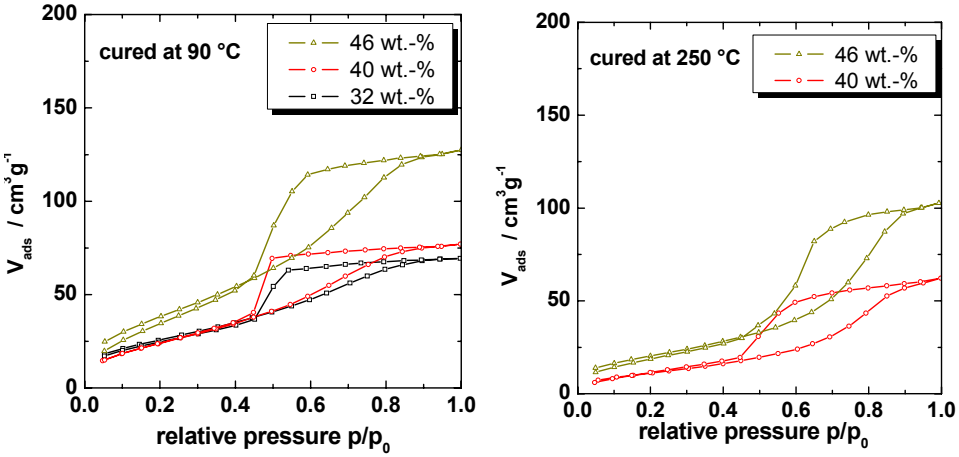


Figure S7. a) N_2 sorption isotherms of the hybrid material cured at 90 °C and b) at 250 °C

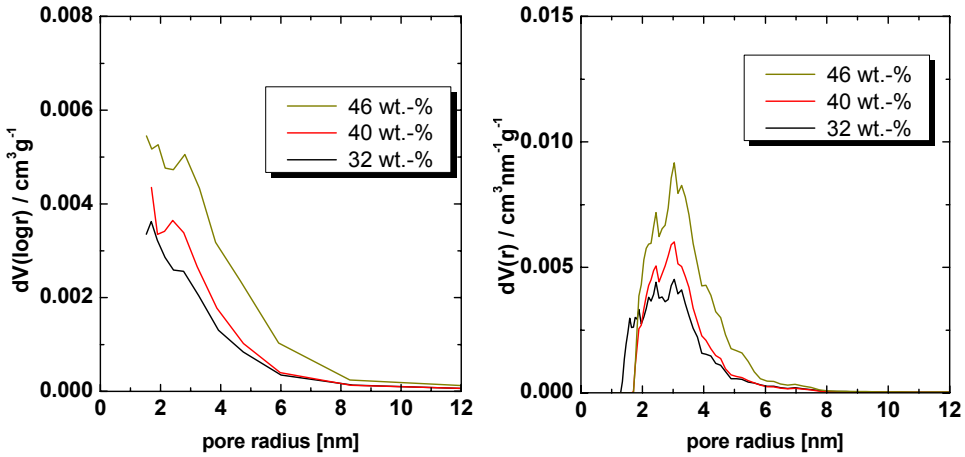


Figure S8. a) PSD of the hybrid material cured at 90 °C, BJH, adsorption branch (left-hand side) and b) NLDFT, N_2 @SiO_2, cylindrical pores, adsorption branch (right-hand side)

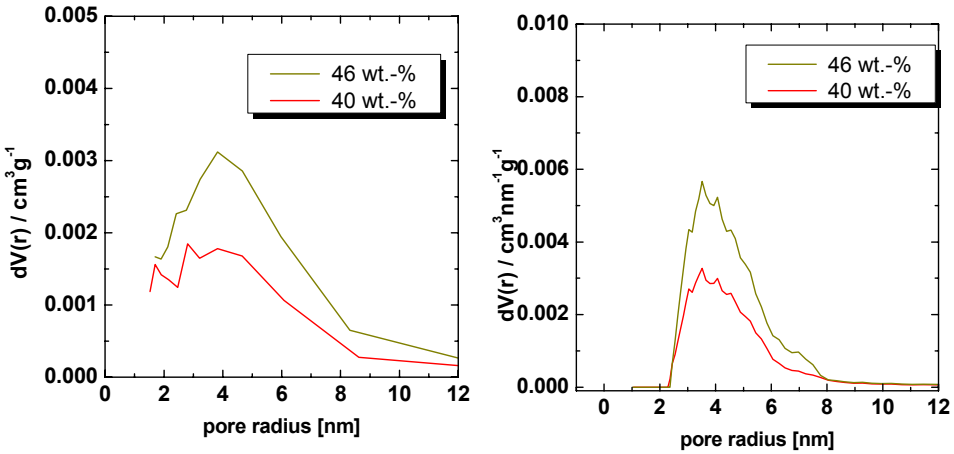


Figure S9. a) PSD of the hybrid material cured at 250 °C, BJH, adsorption branch (left-hand side) and b) NLDFT, N_2 @SiO_2, cylindrical pores, adsorption branch (right-hand side)

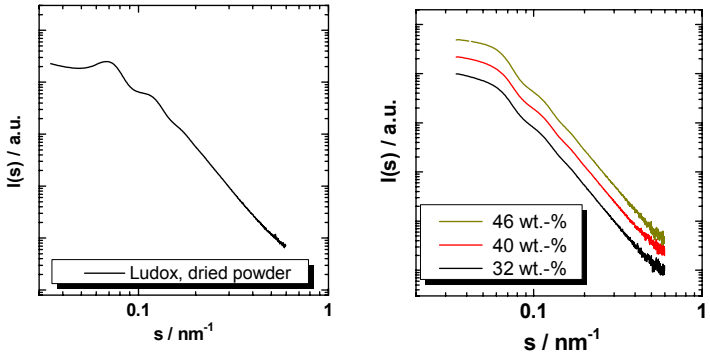


Figure S10. SAXS pattern of the template Ludox-HS40 and the hybrid materials, cured at 90 °C, plotted without vertical offset

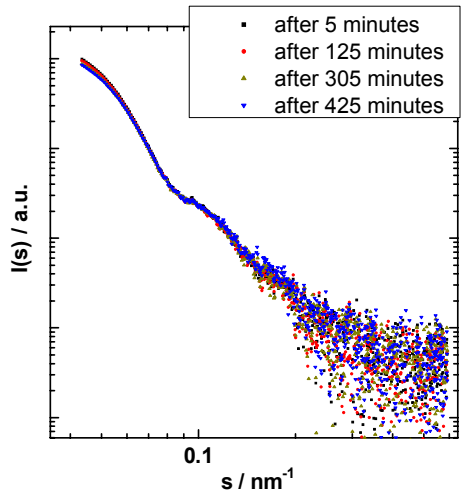
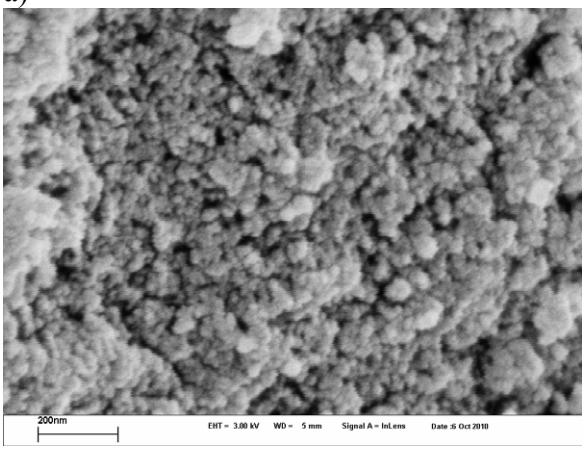
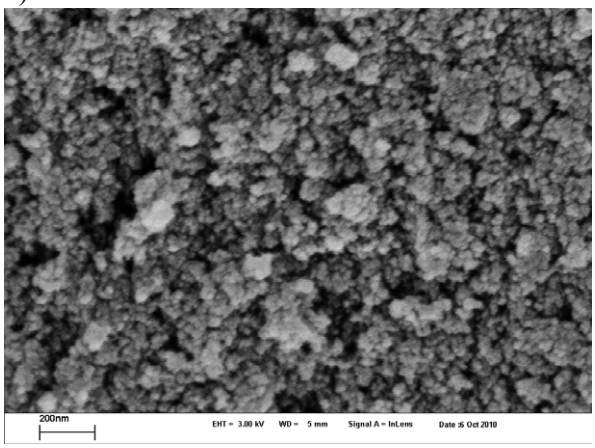


Figure S11. in-situ monitoring of the gelation process by SAXS measurements, no change in the scattering patterns can be found during gelation, which indicates that no aggregation of silica particles (phase separation) takes place, i.e. the silica particles stay well-dispersed upon gelation; patterns were not corrected for 3D electron density fluctuations

a)



b)



c)

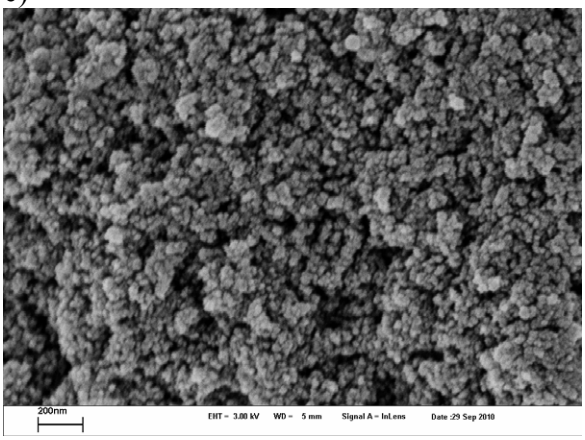


Figure S12. a) SEM micrograph of etched MF resin, cured at 90 °C, SiO_2 32 wt.-%, b) SiO_2 40 wt.-% and c) SiO_2 46 wt.-%

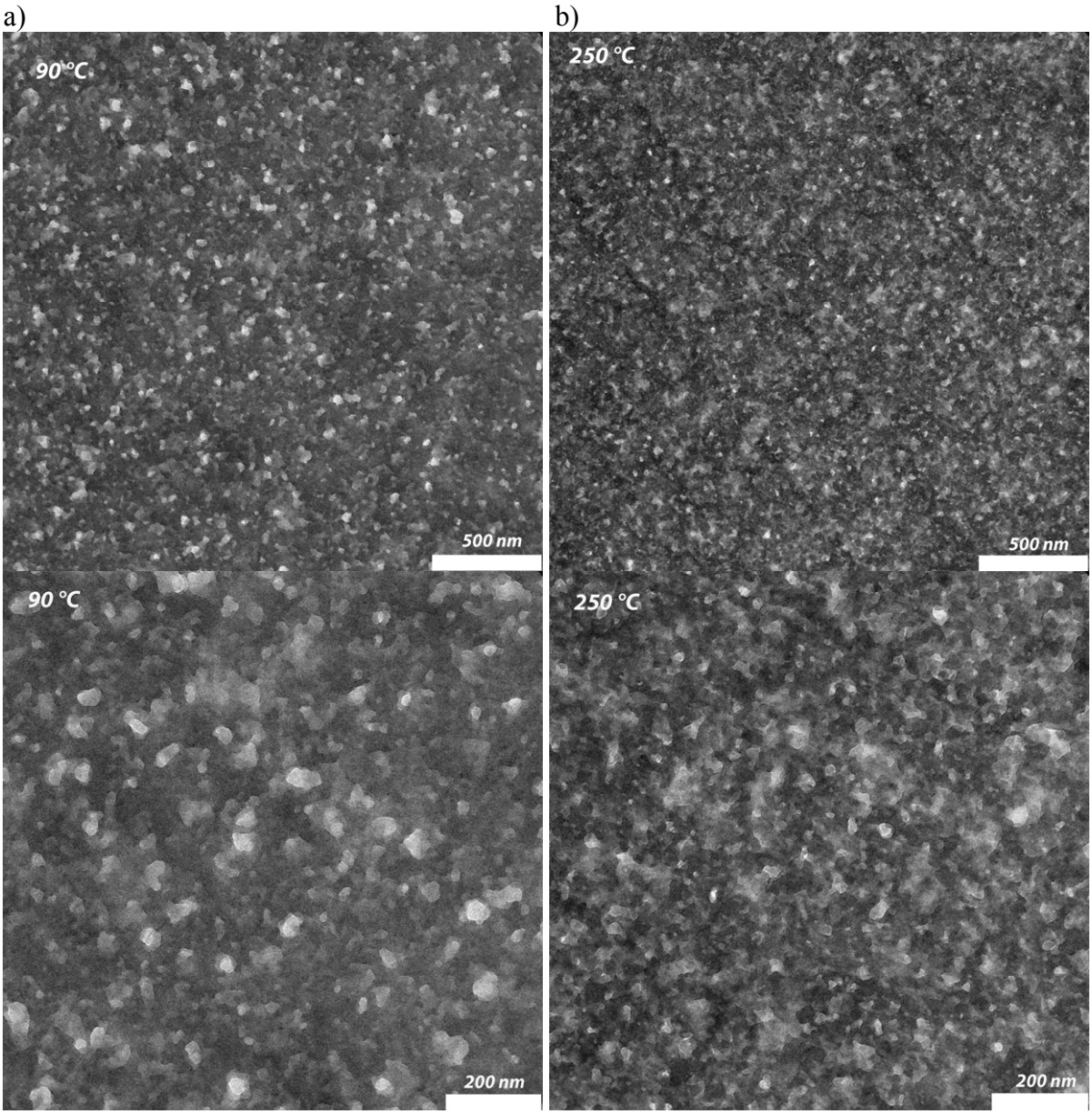


Figure S13. a) TEM micrograph of an etched MF resin, cured at 90 °C, SiO_2 40 wt.-% and b) 250 °C, SiO_2 40 wt.-%. The micrographs were obtained from ultramicrotomed samples

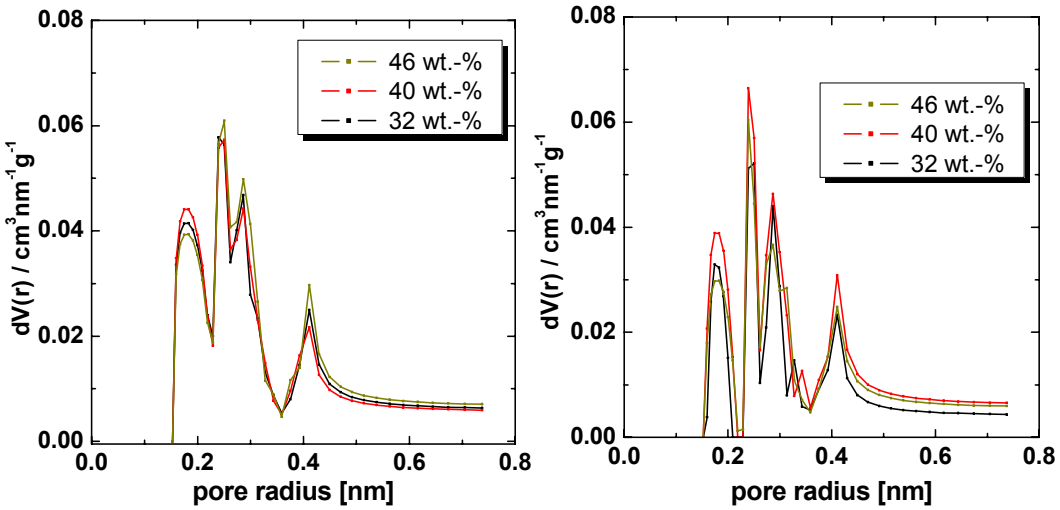


Figure S14. a) PSD of the etched MF resin, CO_2 sorption@273K, NLDFT, cured at 90 °C (left-hand side) and b) 250 °C (right-hand side)

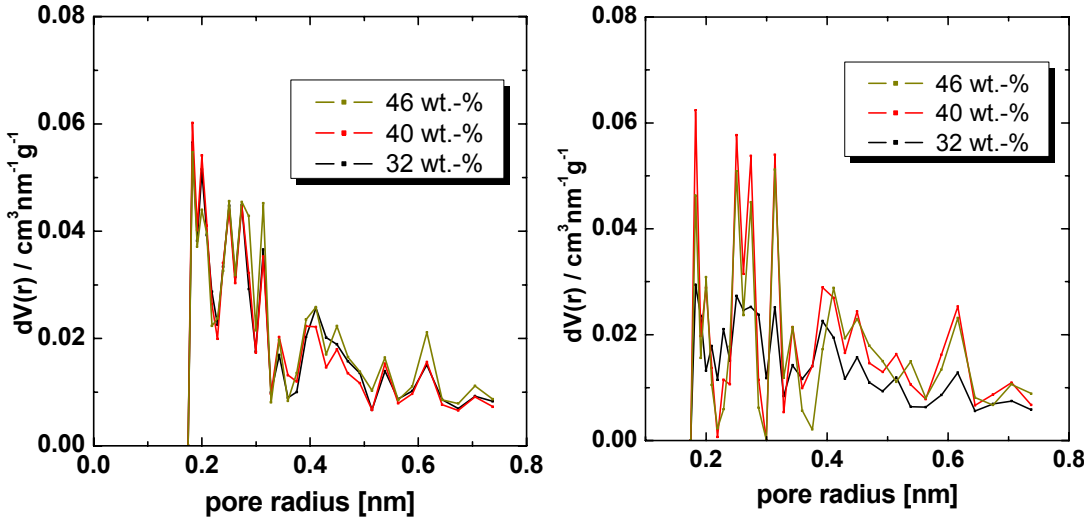


Figure S15. a) PSD of the etched MF resin, CO_2 sorption@273 K, GCMC, cured at 90 °C (left-hand side) and b) 250 °C (right-hand side)

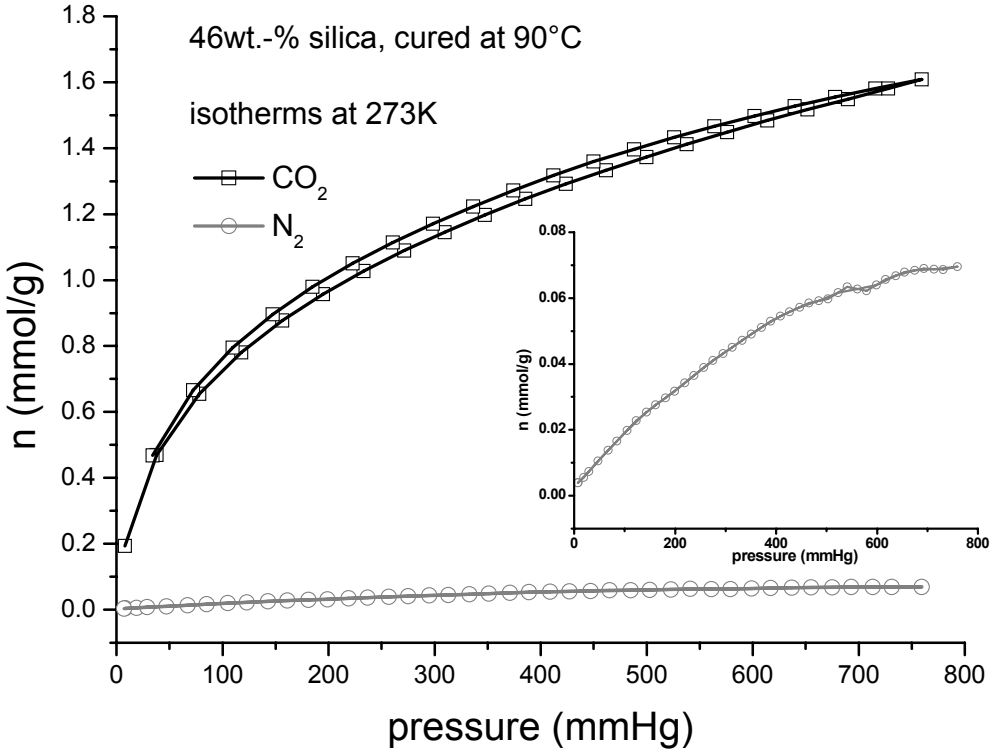


Figure S16. CO_2 and N_2 adsorption/desorption isotherms of MF resin (46 wt.-% silica, cured at 90 °C), inset: N_2 sorption data

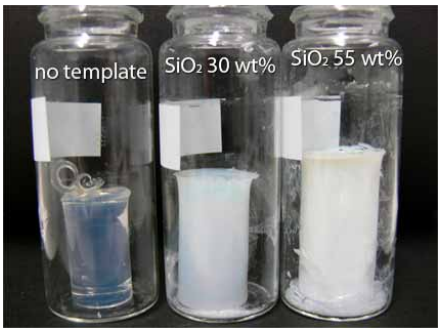


Figure S17. Exemplary photograph to demonstrate the shrinkage of typical hybrid materials after heating to 90 °C. The shrinkage is significantly higher in the absence of silica nanoparticles. Please not that the picture is just exemplary and does not depict the samples actually discussed but reproductions of slightly different silica/polymer ratios