ELECTRONIC SUPPLEMENTARY INFORMATION

for the manuscript:

Waterborne Colloidal Polymer/Silica Hybrid Dispersions and their Assembly into Mesoporous Poly(Melamine-Formaldehyde) Xerogels

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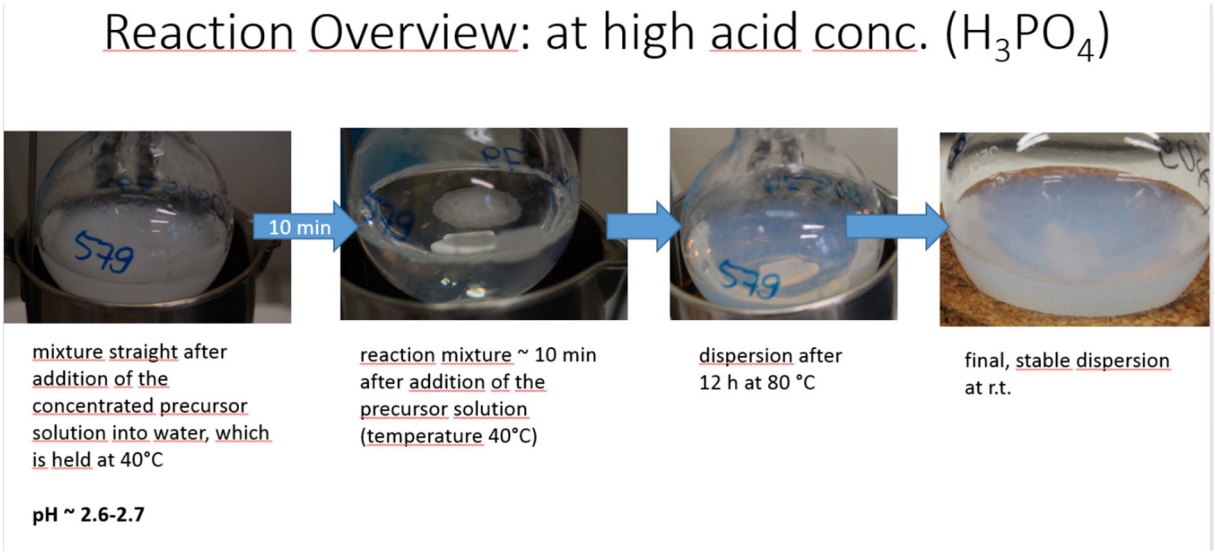
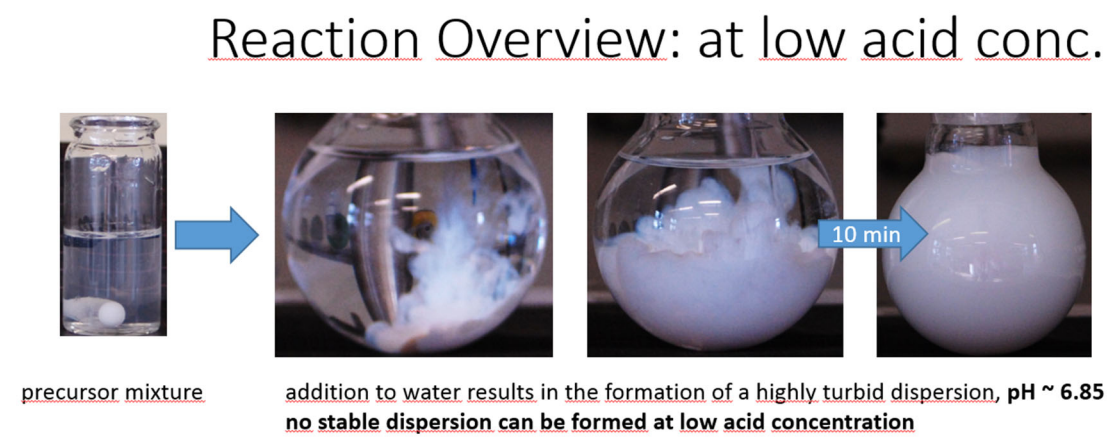
Content

1. Photographs of the reaction mixtures obtained at high (upper panel) and low (lower panel) acid concentrations:





Photograph of the compacted gel, which was obtained from the above dispersion (high acid conc.) after destabilization by EtOH and compaction:

2. Microscopic Analysis

Figure S1: AFM imaging of the dispersion (diluted, on Mica support)

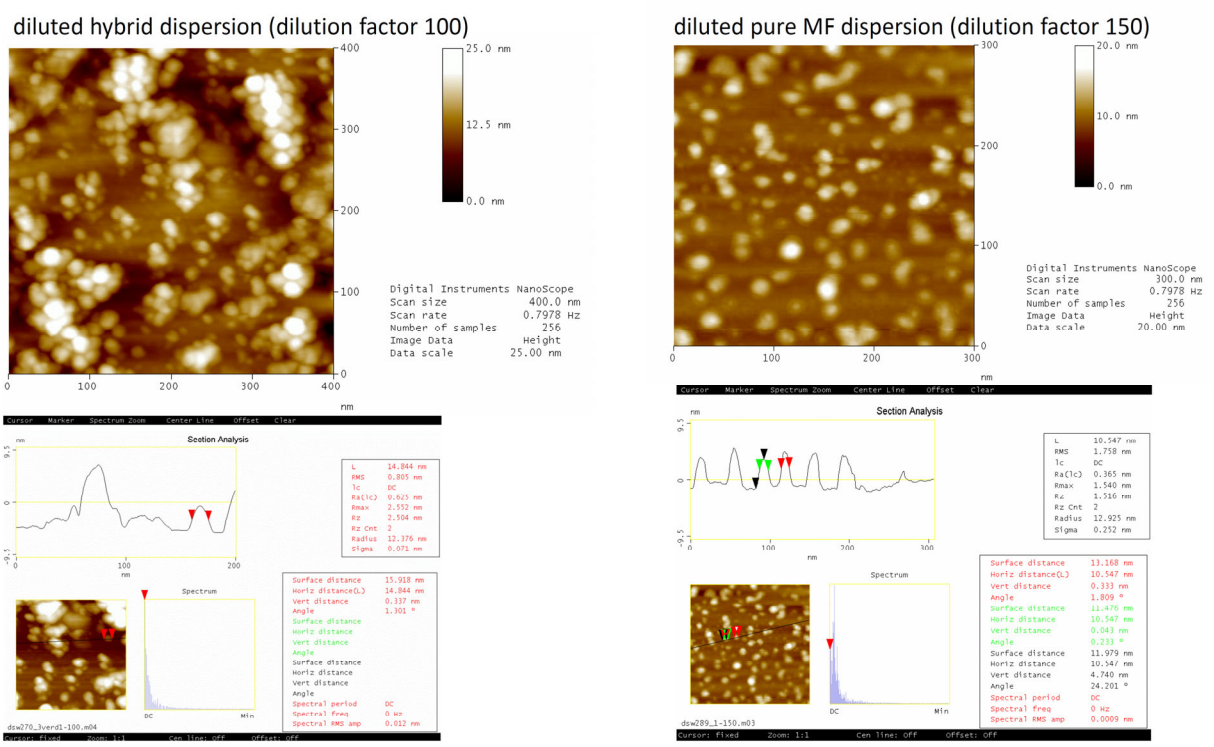


Figure S2: AFM imaging of the hybrid dispersion showing formation of dense coating (low dilution factore, on Mica support)

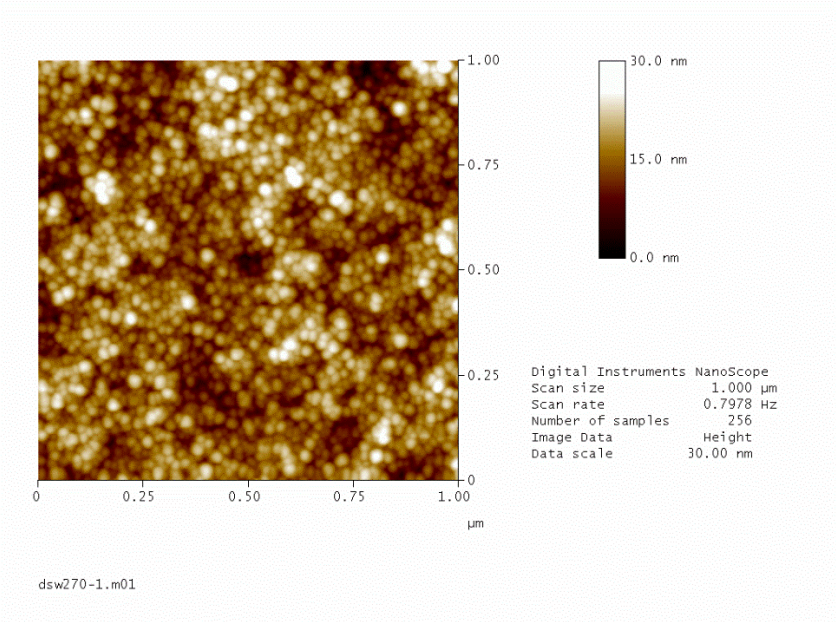


Figure S3: AFM imaging of the Ludox HS-40 dispersion (on Mica)

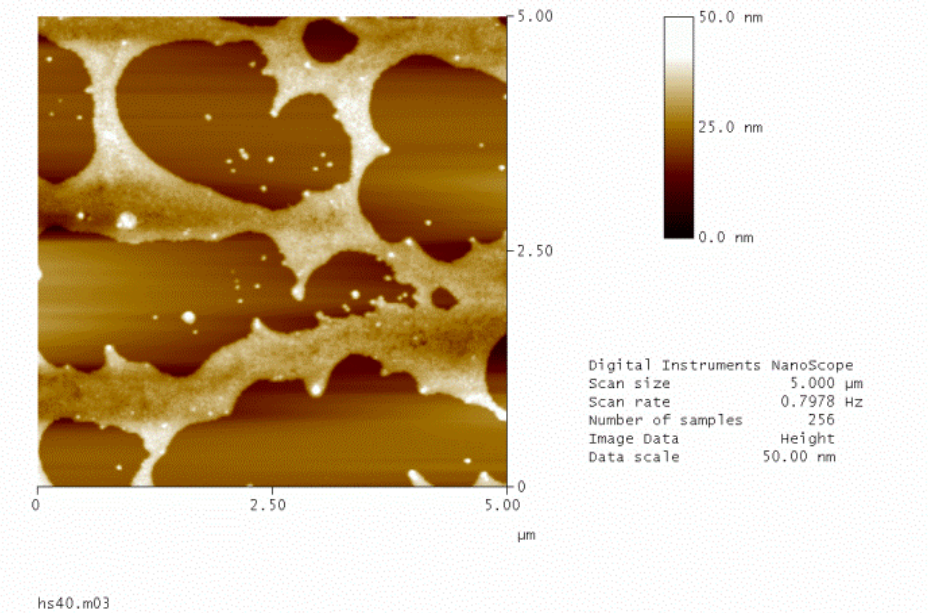
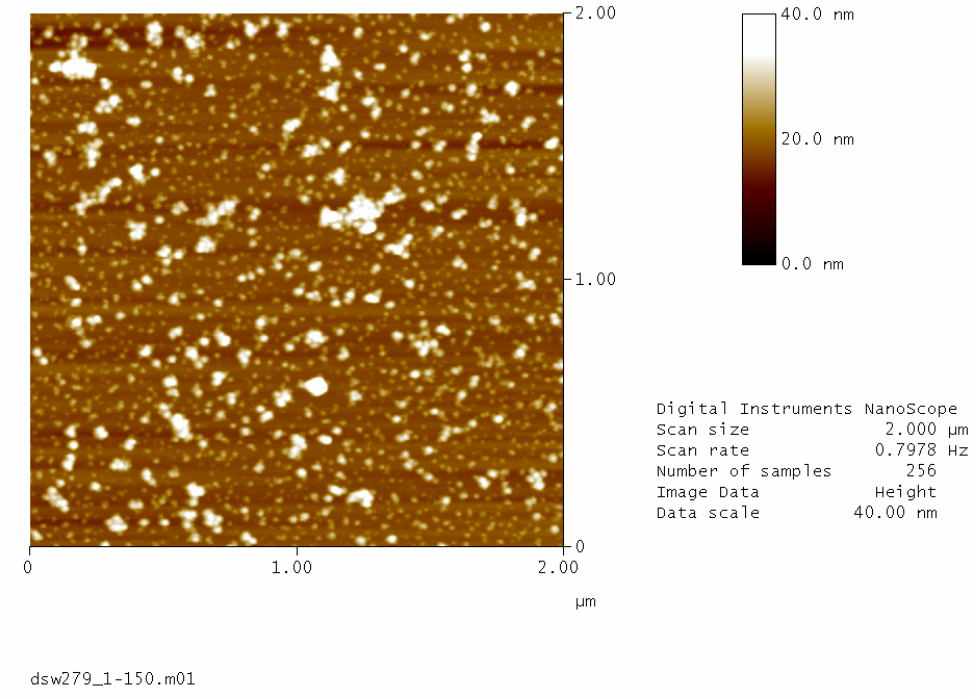


Figure S4: comparative AFM imaging of the hybrid dispersion (support: Mica vs. positively charged Mica (PEI treated), both at the same dilution factor): There are obvious differences in the ability of the particles to adhere to the surface, it seems that the MF colloids are repelled from the positively charged surface and are missing.



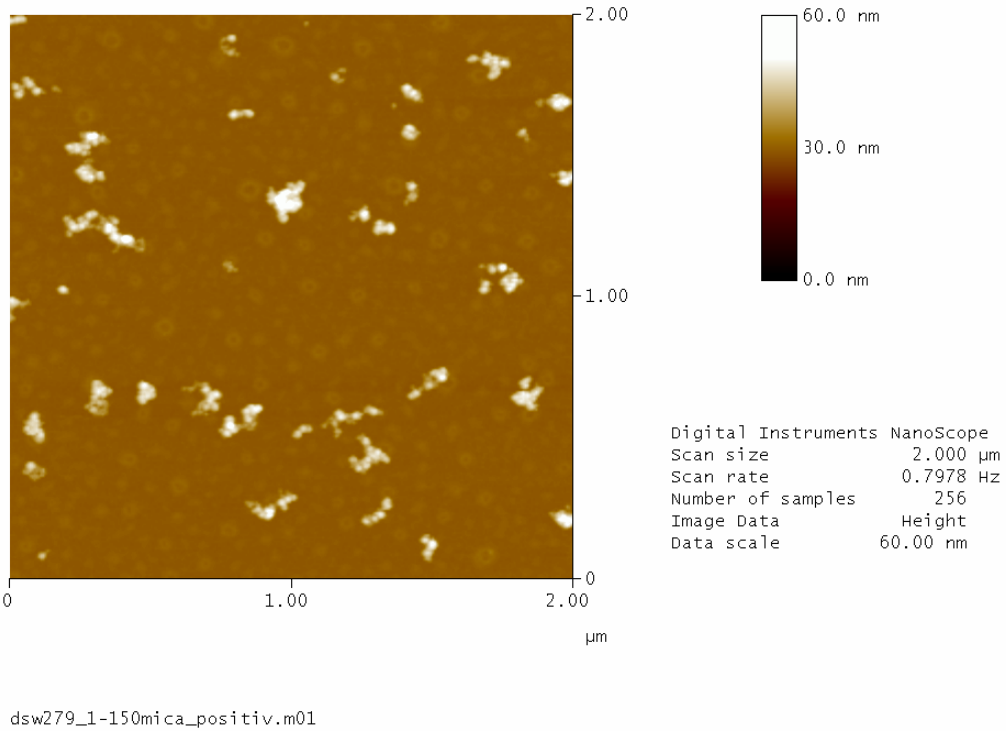


Figure S5. Additional TEM micrographs; left-hand side: hybrid dispersion obtained at strongly reduced PMF content; right-hand side: hybrid dispersion obtained after 20 h at 40°C (without heating to 80°C); scale bars 200 nm (upper panels) and 100 nm (lower panels)

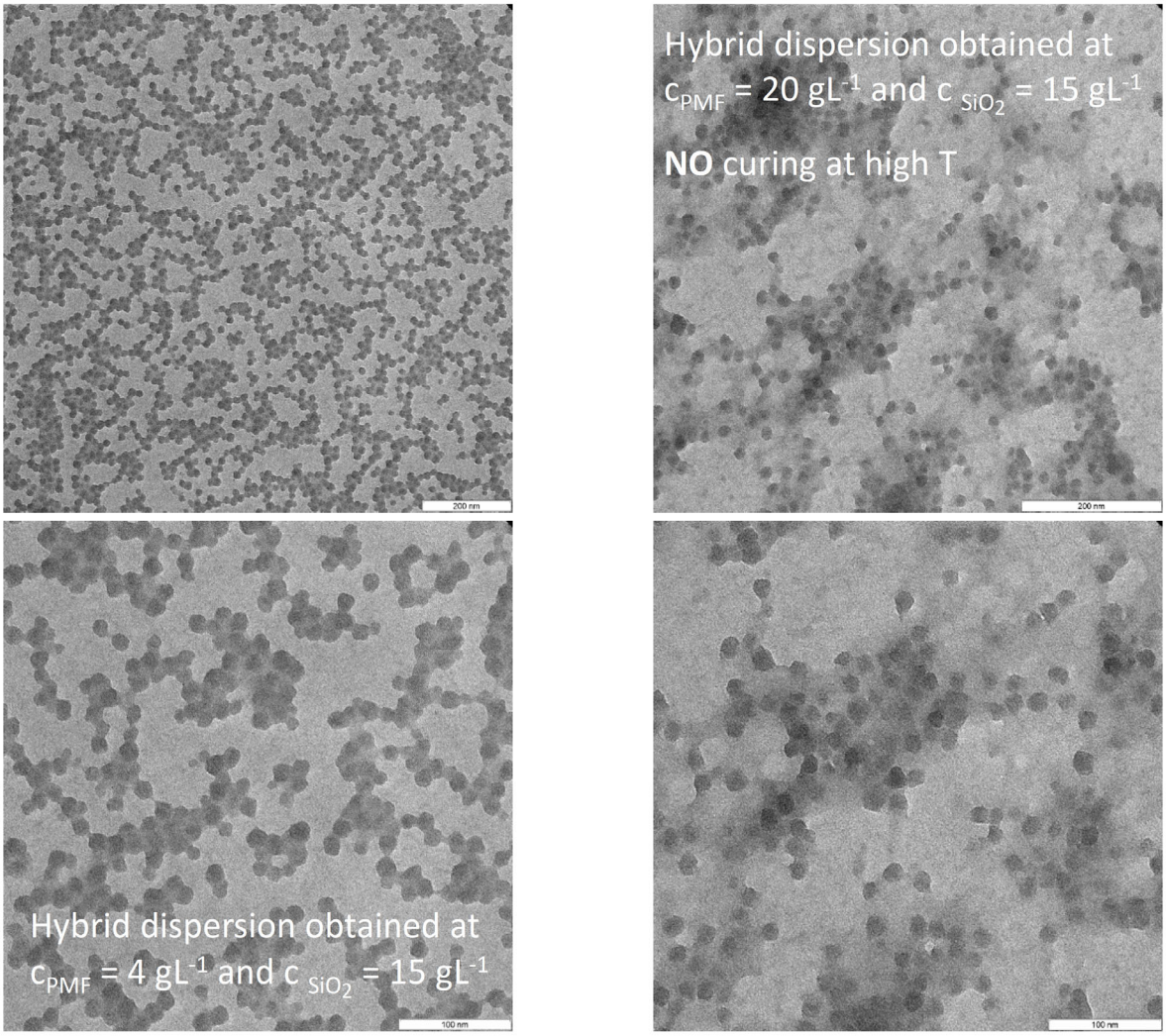
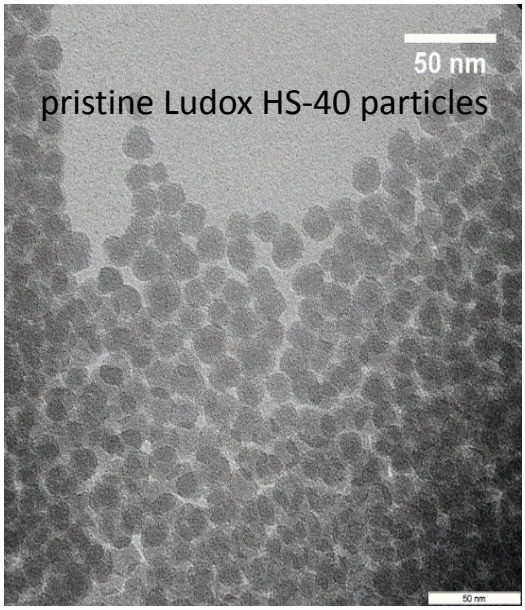


Figure S6. Additional TEM micrograph of the pristine Ludox HS-40 particles used for the synthesis



3. Additional analytical data of the dispersion/xerogels

Figure S7: Exemplary zeta potential curves in dependence on the pH of the dispersion.

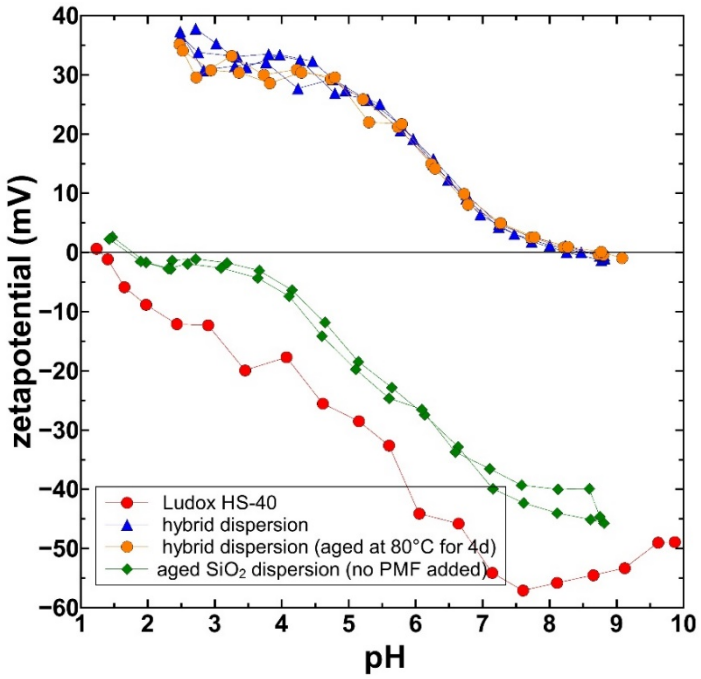


Table S1: Elemental analysis data, elements are given in wt %, C/N ratio is calculated as molar ratio.

	N [%]	H [%]	C [%]	S [%]	Ratio C/N	Residue
Hybrid xerogel	8.2	1.7	6.6	0.0	0.94	83
Polymer xerogel (after etching)	51.1	4.4	36.1	0.0	0.82	8
Pure PMF	36.5	4.2	27.0	0.0	0.86	38
Pure MF (washed with NaOH)	38.6	4.6	28.6	0.7	0.86	28

Figure S8: FTIR spectrum of the PMF xerogel

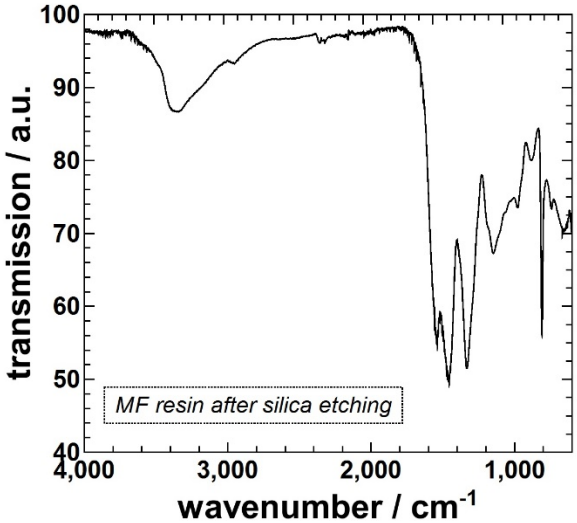


Figure S9: Thermogravimetric analysis of xerogels.

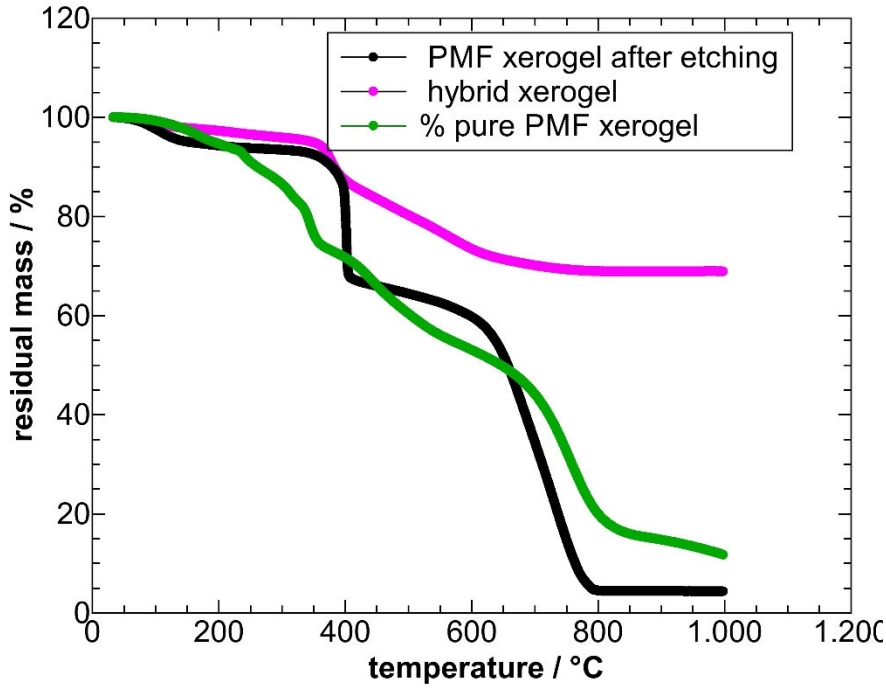
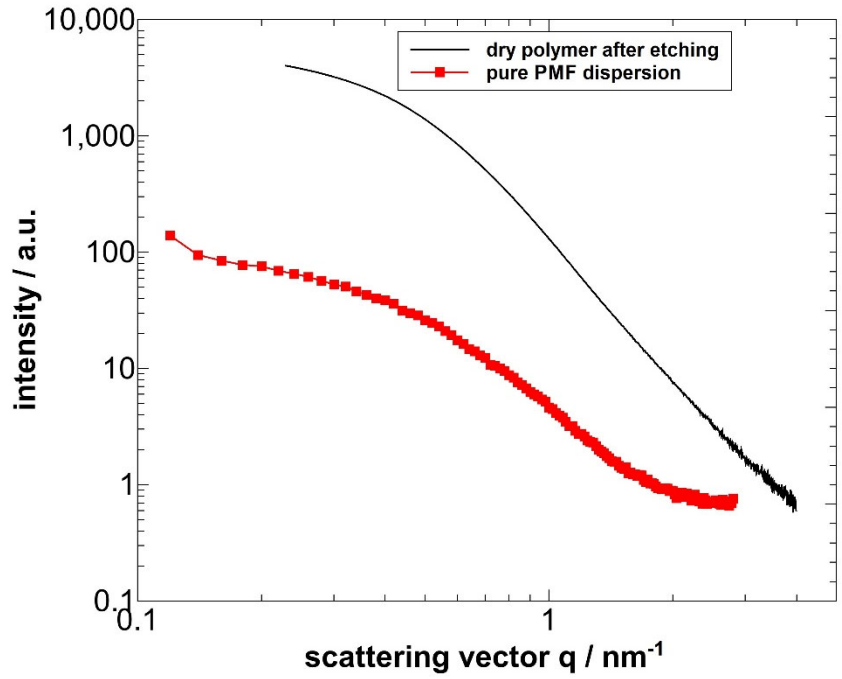
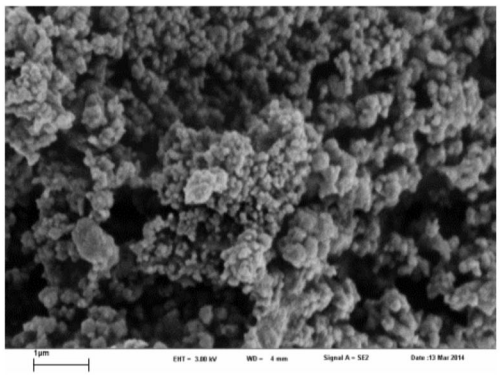


Figure S10. SAXS pattern of pure PMF dispersion (line) and PMF xerogel (after etching). Both patterns show the featureless patterns of small colloidal particles without well-defined morphology. The porous xerogel shows also the characteristic Porod-decay ($I(q) \sim q^{-4}$) of porous two-phase structures.



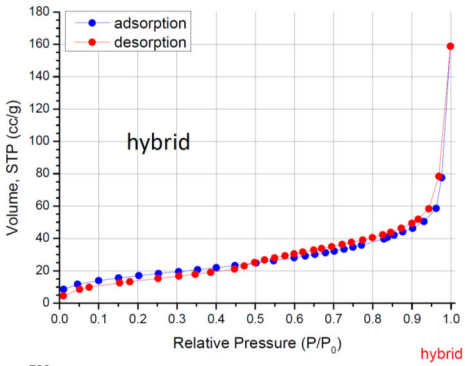
4. “Low” acid concentration – Results:

Scheme S1: Exemplary summary on the morphology and porosity of particles obtained under diluted acid concentrations (0.005M, phosphoric acid – upper panel, hydrochloric acid - lower panel). The obtained morphology and porosity of the hybrid and polymeric particles (which do not form a stable dispersion, see photograph below) are very much comparable to those obtained under oxalic acid concentration (low conc) in a previous study: Schwarz and Weber, Macromol. Mater. Eng. 2015, DOI: 10.1002/mame.201400330

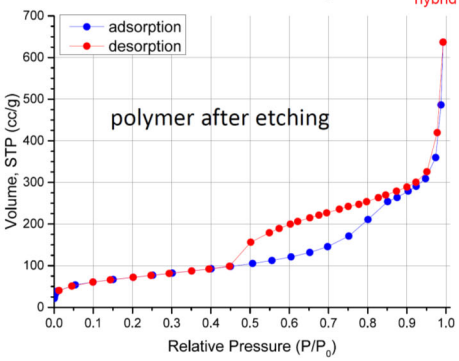


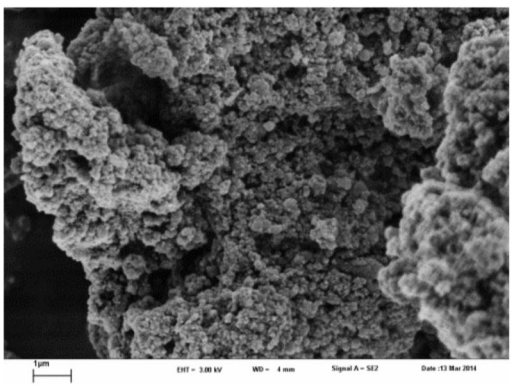
2.5 g polymelamin-co-formaldehyde
2 mL ethanol
0.5 mL **H_3PO_4** (1M)
4.0 g Ludox HS40® (40% Silica)
in **100 mL** H_2O (90 °C)

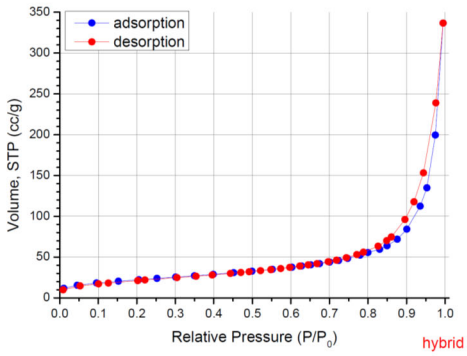
BET: Hybrid (DSW 172) 61 m²/g
PMF (DSW 172-1) 253 m²/g



hybrid

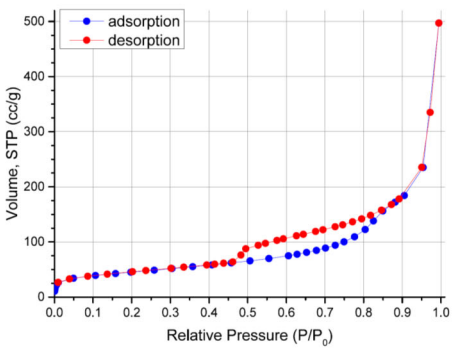






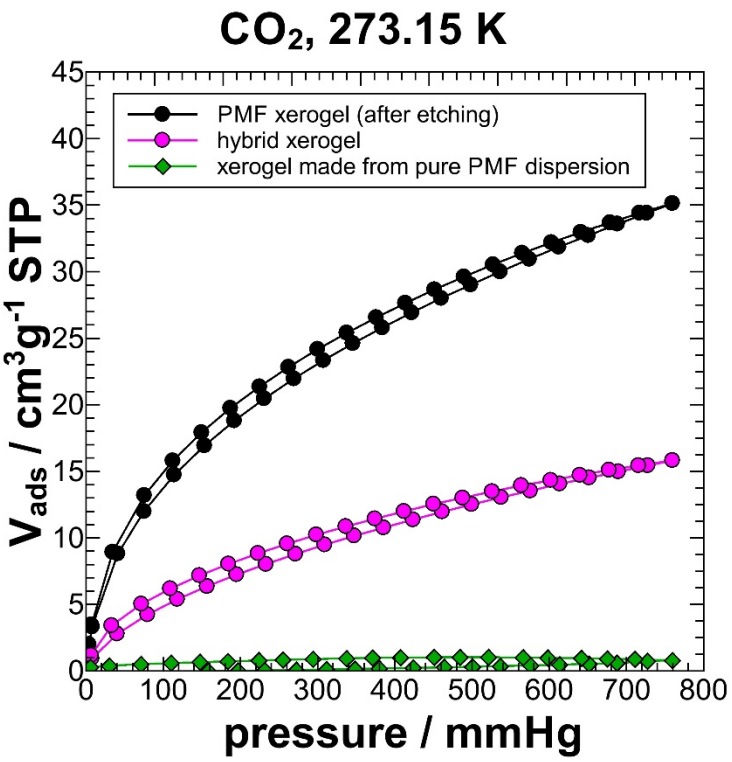
hybrid

2.5 g polymelamin-co-formaldehyde
2 mL ethanol
0.5 mL **HCl** (1 M)
4.0 g Ludox HS40® (40% Silica)
in **100 mL** H_2O (90 °C)
BET: Hybrid (DSW 176) 80 m²/g
PMF (DSW 176-1) 158 m²/g



5. CO_2 adsorption

Figure S11. CO_2 adsorption/desorption isotherms obtained at 273 K:



6. Preparation of a “mixed” hybrid dispersion based on mixing of a pure PMF dispersion with Ludox-HS-40:

A pure PMF dispersion was prepared according to the main protocol using following parameters/protocols:

m_{OMF} = 2.5g; V_{EtOH} = 2 mL; V_{H3PO4} (85%) = 0.5 mL; dissolved in 100 mL water, 2 hours at 40 °C; 20 hours at 80 °C, cooling down to room temperature.

4.0 g Ludox HS40 were added to the dispersion and the mixture was stirred for 1 hour at room temperature. The “mixed hybrid dispersion” was gelled by the addition of ethanol. The gel was compacted by using a centrifuge (8,500 rpm, 5 min). After drying, the xerogel was washed with aceton, ethanol and water. The dried hybrid xerogel is etched by the addition of NaOH (1M) and purified with water.

Porosity analysis of the obtained materials gave:

S(Hybrid) = 201 m²/g $V(d_{pore})$ = 0.19 cm^3g^{-1} (p/p0 = 0.99)

S(Polymer) = 387 m²/g $V(d_{pore})$ = 0.47 cm^3g^{-1}

Figure S12: isotherms (N2, 77.4 K) and PSD calculated based on N_2 adsorption at 77.4K on carbon (slit/cylindrical/spherical pores, QSDFT adsorption branch data model)