Electronic Supplementary Information

Setting Directions: Anisotropy in Hierarchically Organized Porous Silica

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Nitrogen adsorption analysis with in-situ dilatometry

The characteristics of the hierarchically organized porous silica were determined using nitrogen adsorption analysis at 77 K (ASAP2020, Micromeritics). Respective adsorption isotherms are shown in Figure S1. Prior to analysis the sample was degassed for 1 d at 110 °C and pressure < 10^{-3} mbar. The isotherms recorded were evaluated in terms of the total specific mesopore volume V_{meso} by applying the Gurvich rule.[1] In addition, the specific BET surface area S_{BET} was determined.[2] The average mesopore diameter d_{meso} was calculated assuming cylindrical mesopore geometry:

$$d_{meso} = \frac{4V_{meso}}{S_{BET}}.$$

With the density of the nonporous skeleton ρ_s = (1.76 ± 0.04) g/cm^3 as determined by He pycnometry and the specific mesopore volume, the average density $\rho_{strut} = 1/(V_{meso} + 1/\rho_s)$ of the mesoporous struts and the corresponding strut porosity $\phi_{strut} = 1 - \rho_{strut}/\rho_s$ were calculated.

Finally, the porosity of the macroporous strut network is given by $\phi_{net} = 1 - \rho/\rho_{strut}$, with ρ the bulk density of the hierarchical silica monolith determined from the mass and the geometric dimensions of a degassed monolith.

All results are given in Table S1.

Table S1. Comparison of structural data for reference and sheared samples as derived from bulk density ρ, skeletal density ρ_s and nitrogen adsorption data: density and porosity of the mesoporous struts ρ_{strut} and ϕ_{strut}, respectively, porosity of the strut network ϕ_{net}, specific mesopore volume V_{meso}, specific surface area S_{BET} and average mesopore diameter d_{meso}.

	ρ_{strut} [g/cm³]	ϕ_{strut}	ϕ_{net}	V_{meso} [cm³/g]	S_{BET} [m²/g]	d_{meso} [nm]
reference	1.18 ± 0.02	0.33 ± 0.01	0.65 ± 0.2	0.279 ± 0.01	215 ± 5	5.2 ± 0.2
sheared	1.18 ± 0.02	0.33 ± 0.01	0.65 ± 0.05	0.282 ± 0.01	211 ± 5	5.3 ± 0.3

The N_2 adsorption measurements of the sheared sample were complemented by *in-situ* dilatometry measurements utilizing a self-designed setup integrated into the commercial adsorption instrument. Detailed descriptions of the dilatometric setup can be found in refs [3,4]. The resulting (linear) strain isotherms in axial and radial direction of a cylindrical sample (length: 4.7 mm, diameter: 3.1 mm) are also shown in Figure S1.

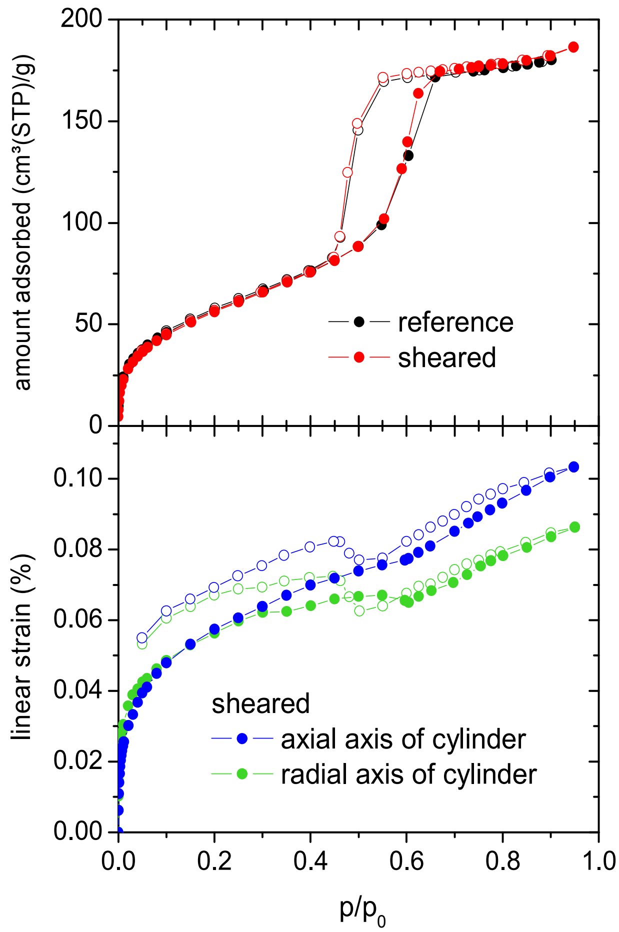

Figure S1. Upper panel: N_2 adsorption isotherms (77 K) of reference and sheared sample. Lower panel: linear dilatometric strain of the sheared sample during N_2 adsorption. Measurements were performed in axial as well as in radial direction of a cylindrical sample. Full symbols denote adsorption, open symbols desorption.

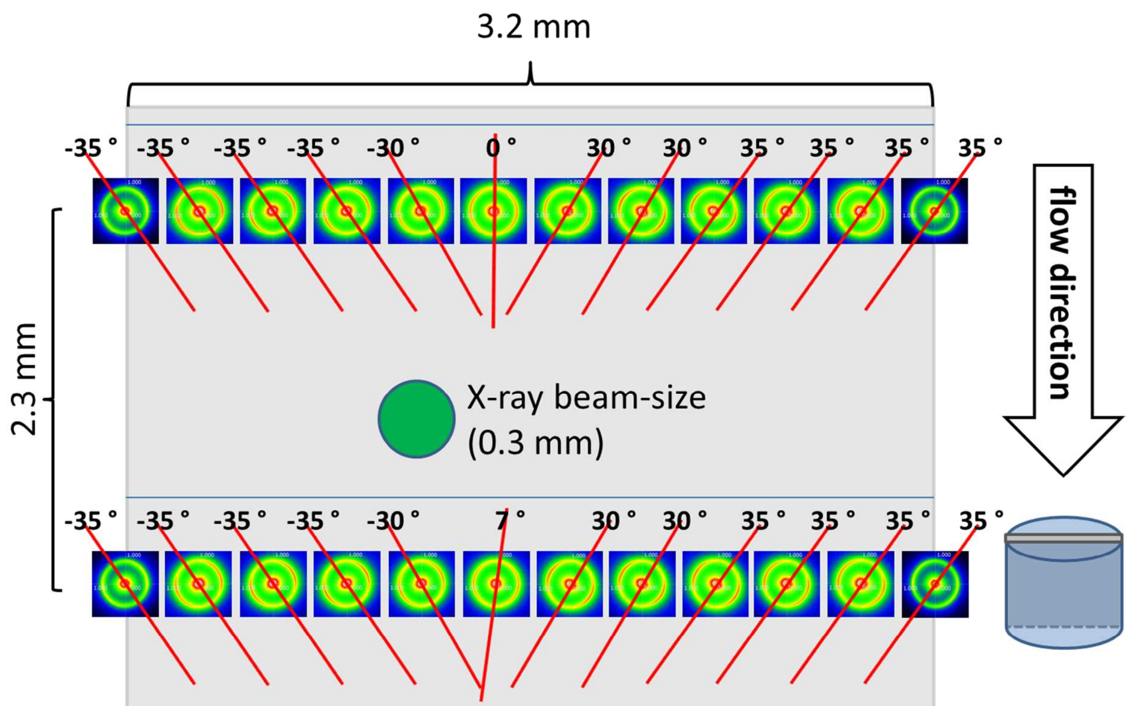

Figure S2. Position resolved SAXS patterns indicating that the main strut direction is at about 35° tilted with respect to the macroscopic flow direction, independent of position along the axis of the cylindrical sample, however with a clear symmetry in the direction perpendicular to the cylinder axis. The cylindrical sample axis which corresponds to the shear direction is vertical, beam size was about 0.3 mm and the step size was 0.2 mm

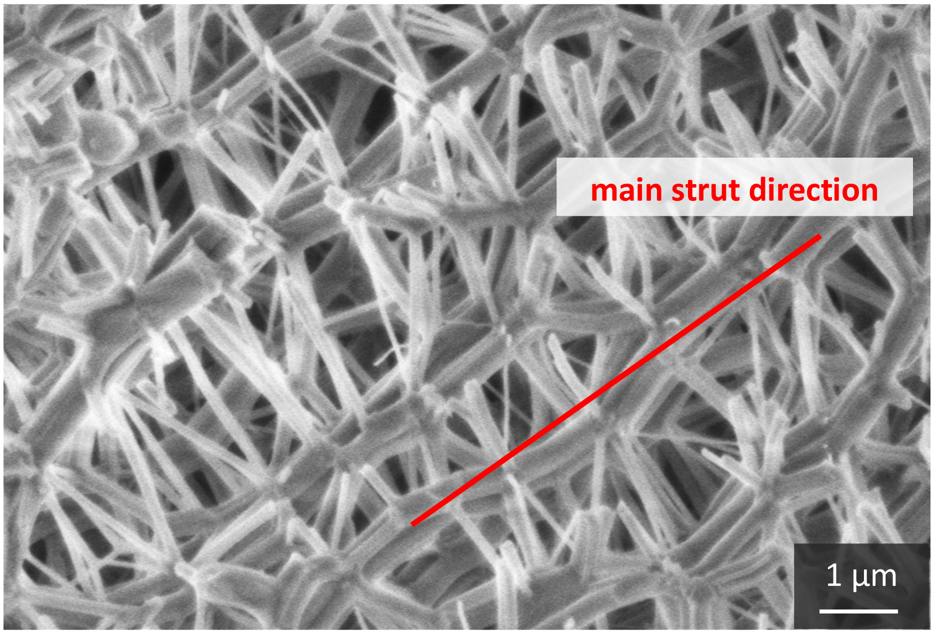

Figure S3. Representative SEM image of the sheared sample showing a major strut population oriented along the main strut direction (MSD) and a minor strut population oriented perpendicular to it. Struts of the latter population are considerably thinner compared to the major population.

Literature

1. L. Gurvich, *Zh. Russ. Fiz-Khim. Obshchestva Chem*, 1915, **47**, 805-827.
2. S. Brunauer, P. H. Emmett and E. Teller, *Journal of the American Chemical Society*, 1938, **60**, 309-319.
3. P. Kowalczyk, C. Balzer, G. Reichenauer, A.P. Terzyk, P.A. Gauden, A.V. Neimark, *Carbon* 2016**, 103**, 263-272.
4. C. Balzer, T. Wildhage, S. Braxmeier, G. Reichenauer, J.P. Olivier, *Langmuir* 2011, **27**, 2553−2560.