Electronic Supplementary Information

$LaFeO_3$-based nanopowders prepared by a soft-hard templating approach: the effect of silica texture

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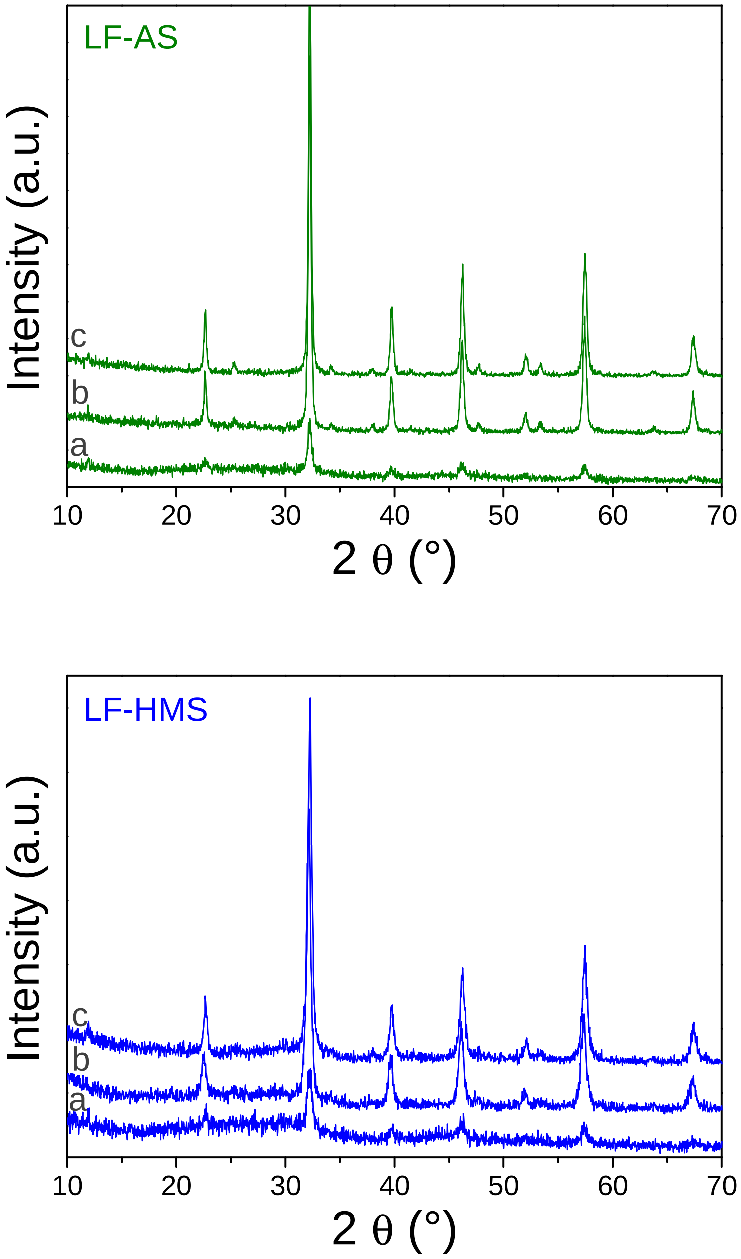

Fig. S1 XRD patterns of LF-AS and LF-HMS samples a) as-burned, (b) after calcinations at 700°C for 5h before etching and (c) after etching with NaOH.

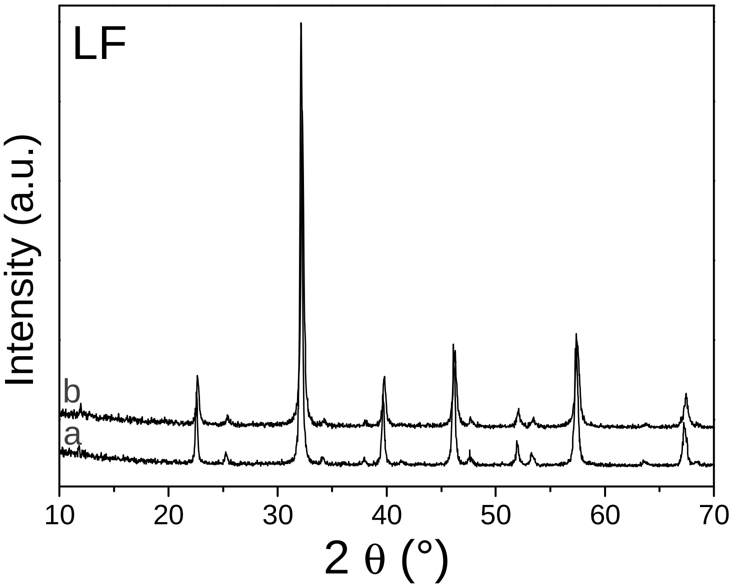

Fig. S2 XRD patterns of $LaFeO_3$ reference sample (a) just after combustion (as-burned) and (b) after thermal treatment at 700°C for 5h.

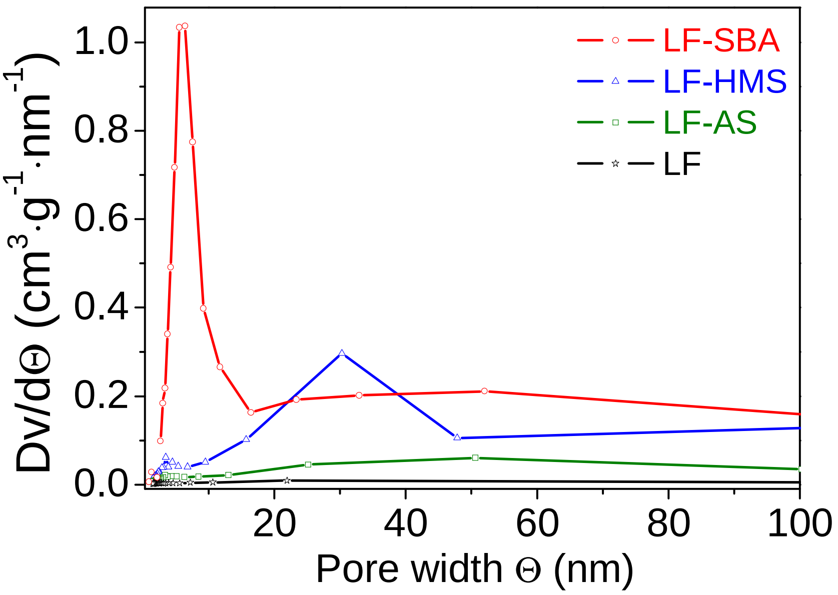

Fig. S3 Pore size distribution of the $LaFeO_3$-based nanopowders

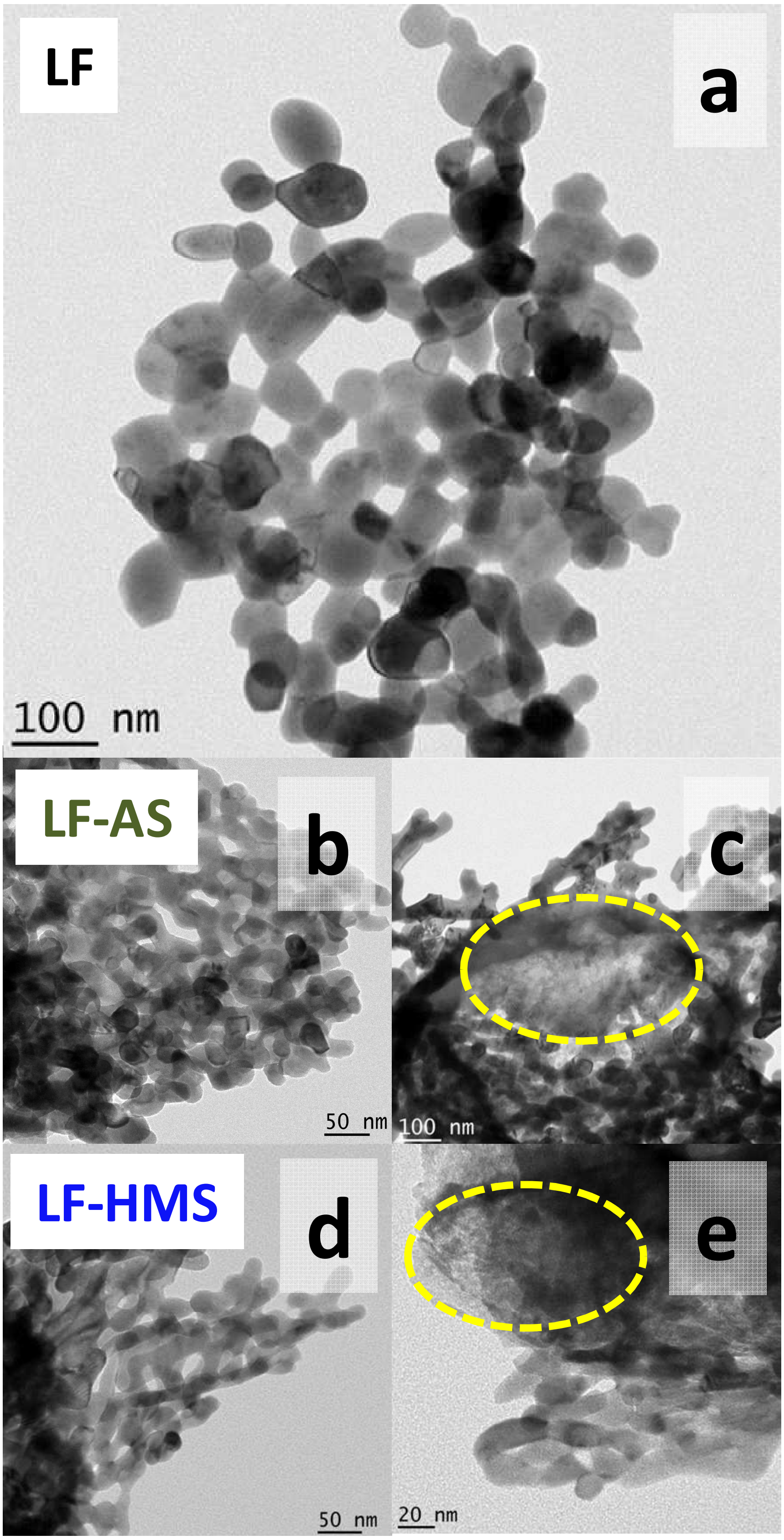

Fig. S4 TEM images of $LaFeO_3$-based nanopowders prepared without any silica template (a), with amorphous silica template (b, c) and with HMS silica template (d, e). The yellow dashed circles indicate the amorphous regions in the LF-AS and LF-HMS powders.

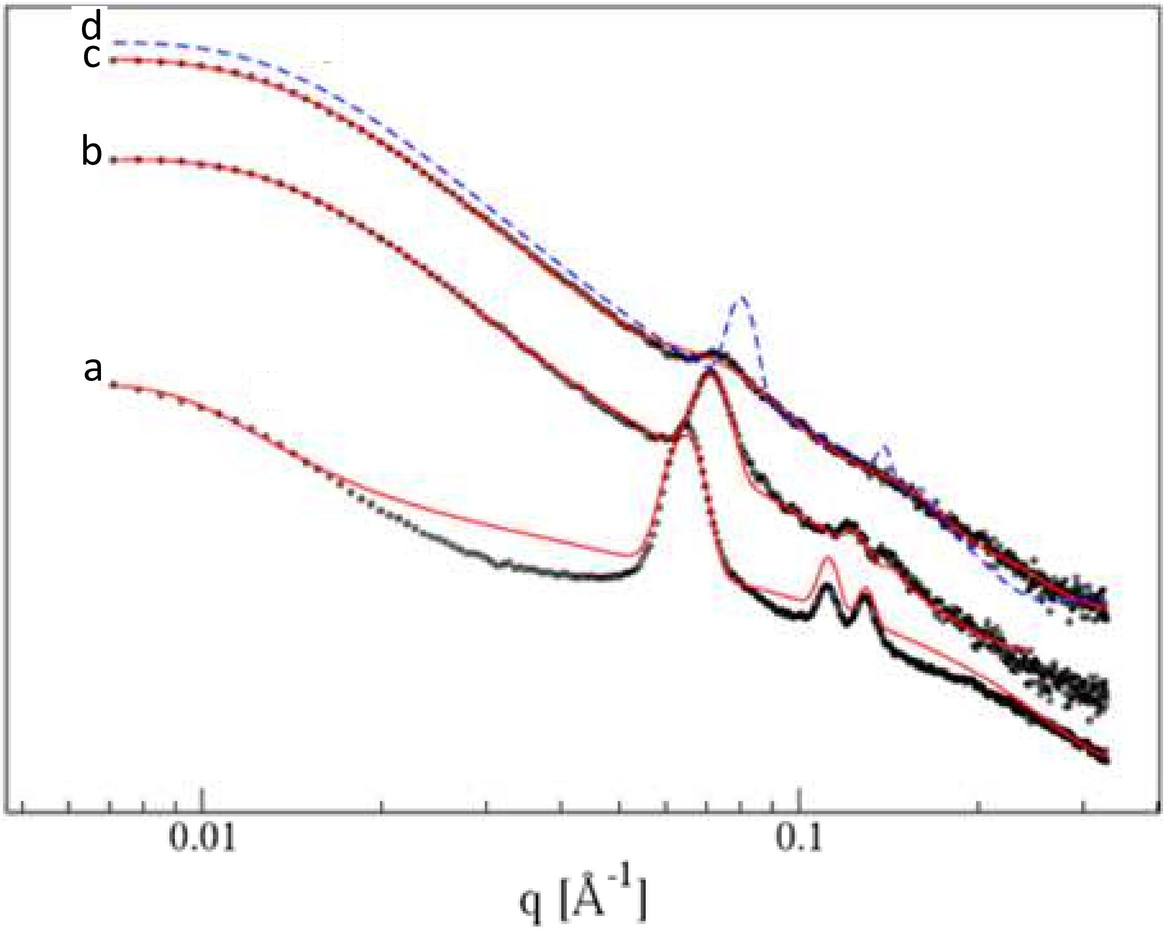

Fig. S5 Experimental data (black circles) and calculated SAXS pattern (red line) using the 2D-hexagonal packing of cylindrical pores for SBA-15 template (a), LF-SBA$_{BE}$ (b) and the liquid type model for the LF-SBA sample (c). The blue dashed line (d) simulates a 2D-hexagonal packing using the parameters obtained from the fitting of sample LF-SBA.

Description of the SAXS model

The scattering from a system of interacting parallel cylindrical pores is considered. In general the variation of the scattering intensity with scattering angle is governed by two factors. One arises from scattering from the geometrical shape of the particle and is called the form factor F(q), with the scattering vector $|\boldsymbol{q}| = |\mathbf{k}-\mathbf{k}_0| = 4\pi\cdot\sin\theta/\lambda$, in which θ is half of the scattering angle, and λ is the incoming wavelength. The second factor may occur if the particles are arranged in some kind of order, on a lattice or at least with a correlation between next neighbors. This contribution is called structure factor S(q).

Hence the main scattering function, which describes the intensity I (q) versus the scattering vector, is[s1]

$$I(q) = C \cdot \langle F(\vec{q}\,)\rangle^2 \cdot S(\vec{q}) + \langle F(\vec{q})^2\rangle - \langle F(\vec{q})\rangle^2 \qquad (1)$$

Note that the form factor is adimensional, and the volume of the particle is contained in the pre-factor C. The brackets < > refer to an ensemble or time average with respect to the scattering volume. The difference term on the right-hand side is usually called "Laue scattering". The constant is defined as $C = (be \cdot \Delta\rho_e \cdot V_P)^2 \cdot N$, with the electron density contrast $\Delta\rho_e$, the scattering length of electrons with respect for X-rays $b_e = r_e$(1+cos2 2θ 2)1/2 including the classical electron radius r_e, the volume of the particle V_P , and the number of particles N resulting in the unit of [m^2]. In the present work the intensity will be presented in arbitrary units.

If there is no structural correlation between the particles, the structure factor reduces to the value 1, which is the scattering intensity for randomly distributed particles:

$$I(q) = C \cdot \langle F(\vec{q})\rangle^2 \qquad (2)$$

In the following, a model function for the scattering of strictly parallel cylinders that are randomly distributed in 2D lattice, like parallel cylindrical pores, is showed. The form factor of a cylinder that is infinitely long in the *z* direction parallel to the X-ray beam and having a radius *r,* is given by the Fourier transform of:

$$\int \varrho(\vec{r}) \underset{0}{\overset{\infty}{\exp}}(i\vec{r}\vec{q})\,d\vec{r} \qquad (3)$$

where:

$\varrho(\vec{r}) = \varrho r \leq r$and 0 if $r_{xy} > r$. (4)

The result is the Fourier transform of a circle, given in terms of the Bessel function $J_1(rq_{xy})$, times a function in the z direction.

$$F(\vec{q}) = 2\pi \frac{\varrho}{q_{xy}} J_1(rq_{xy})\delta(q_z) \tag{5}$$

The δ function indicates that one can only see diffraction from an infinite cylinder if its axis is perpendicular to q. This has an important effect for powder specimens where each grain contains parallel pores but the grain orientation is random. If one collects diffraction data using a standard diffractometer (monochromatic incident beam and a single detector that scans in the horizontal plane), the measured intensity at a particular q comes only from those grains that are so oriented that their pores are perpendicular to q. If Δq_z is the vertical size of the resolution `window' of the diffractometer, the number of grains contributing to the measured intensity is directly proportional to the ratio (Δq_z=q), a factor that needs to be included in analyzing the data.

For a long but infinite-length cylinder, the I(q) function broadens into a Gaussian peak. In this discussion only parallel cylinders with respect to the incident X-ray beam are considered. Taking into account all the possible orientation, the I(q) for a cylinder system is given by:

$$I(q)_{cyl} = 2\pi \frac{\varrho}{q} \cdot \int_{0}^{\pi} [J_1(r \cdot \cos(\alpha)q)]^2 \cdot \frac{(\sin(q\cdot L\cdot\sin(\alpha)))^2}{(q\cdot L\cdot\sin(\alpha))}\, d\alpha \tag{6}$$

Experimentally, pores will have a variation of pore diameter. This radius distribution taken into account with the help of the normalized Weibull function:

$$D(r) = A \cdot (r/R)^{b-1} \cdot \exp{-r/R^b} \tag{7}$$

where A is the normalization factor R is the mean radius of the pores and b is the parameter which takes into account the poly-dispersion of the pores and tunes the width of the distribution. This function is similar to a Gaussian function for small widths compared to the average value but has the advantage that, for larger values of R, no unphysical negative radii contribute the average.

Then the I(q) becomes:

$$I(q)_{cyl} = 2\pi^2 \frac{\varrho}{q} \cdot \int_{0}^{\infty} D(r) I_{cyl}(r, R, b, \alpha) \cdot r^2 dr \tag{8}$$

Accordingly with the literature,[S2] the roughness of the pore walls, *i.e.* the smooth transition region from the electron density of the matrix to the core of the pore, has to be considered. This is realized by a convolution of the electron density distribution with a Gaussian function. The result is an additional decrease of the intensity I(q) with an exponential factor containing the scattering vector and the width of the transition region, both squared. This contribution was already considered earlier as an empirically chosen attenuation factor.[S3] Its effect is the decrease of intensity with increasing q:

$$I(q) = I_{cyl}(q) \cdot \exp{-\sigma_D^2 q^2} \tag{9}$$

As structure factor S(q), we consider the scattering from P6mmc structural arrangement, with 2D hexagonally ordered and strictly parallel cylindrical pores.[S4] The scattering is from a two-dimensional crystalline lattice with parameters in the nanometric length scale. Hence the principles of crystallography can be applied here. The crystalline structure results in a sum of Bragg peaks located at positions q^*_{hkl}. These positions q^*_{hkl} are the lengths of reciprocal lattice vectors and related to plane distances of the crystal in the real space. The sample consists of many domains of ordered cylindrical pores. The domains are rotated with respect to each other at arbitrary angles creating a two-dimensional powder. The scattering image will therefore be isotropic in the plane. The powder average leads to a factor proportional to 1/q for the scattering intensity in a 2D case. Hence for the case of a 2D hexagonal lattice, the structure factor results in:

$$S(\vec{q}) = \frac{c}{A} \cdot \exp(-q^2 \cdot \sigma_{DW}^2) \sum_{hk0}^{N} \frac{m_{hk0}}{(\sqrt{2\pi}\sigma_B)} \frac{1}{q} \exp\frac{[\vec{\mathrm{q}}_{\mathrm{hk0}} - \vec{\mathrm{q}}^2]}{(2\sigma_B^2)} \tag{10}$$

where A = a2√3/2 is the surface of the unit cell expressed in terms of the lattice parameter a, σ_{DW} is the Debye–Waller factor originating from imperfect structural order, m_{hk0} is the multiplicity, σ_B is the constant width of the Bragg–Peaks at the positions q^*_{hk0}, and c combines all further constant contributions. The set of q^*_{hk0} can be calculated for the P6mmc arrangement.

For the situation of less well-ordered or even randomly distributed pores, a structure factor liquid-type must be used to take the interference of scattering from different pores into account. For two-dimensionally ordered systems, such a structure factor was already proposed [S5] and successfully used in literature.[S2] In this case, the structure function depends from the concentration parameter h and k_c, which takes into account the real distance of the pores with respect to the hard sphere approximation.

References for the supplementary information

S1 A. Guinier, X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies (Dover, New York, 1994

S2 M. Engel, Be. Stühn, J. J. Schneider, T. Cornelius, M. Naumann (2009) Appl Phys A 97: 99–108;

S3 P. Gérard, K. Alexandr, (2001) Nucl. Instrum. Meth. Phys. Res. B 185, 198

S4 W. Ruland, B. Smarsly, (2005) Appl. Crystallogr. 38, 78,

S5 Y. Rosenfeld, (1990) Phys. Rev. A 42(10), 5978

Table S1 XRD results for the $LaFeO_3$-based nanopowders after thermal treatment at 800°C for 48h.

Sample name	$LaFeO_3$ Cell Parameters	Crystal size (nm)	Phase Composition
LF	a= 5.575 Å b=7.854Å c= 5.555 Å α=β=γ=90.0 ° V=243.2 $Å^3$	53	100 wt% $LaFeO_3$
LF-AS	a= 5.572 Å b=7.851 Å c= 5.561 Å α=β=γ=90.0 ° V=243.3 $Å^3$	49	88 wt% $LaFeO_3$ 6 wt% $La_6Si_6O_{21}$ 4 wt% $La_2Si_2O_7$ 2 wt% $FeSiO_3$
LF-HMS	a= 5.583 Å b=7.862 Å c= 5.554 Å α=β=γ=90.0 ° V=243.8 $Å^3$	31	61 wt% $LaFeO_3$ 17wt% $La_6Si_6O_{21}$ 10 wt% $La_2Si_2O_7$ 12 wt% $FeSiO_3$
LF-SBA	a= 5.584 Å b=7.857 Å c= 5.556 Å α=β=γ=90.0 ° V=243.8 $Å^3$	30	47 wt% $LaFeO_3$ 38 wt% $La_6Si_6O_{21}$ 15 wt% $FeSiO_3$

Table S2 XPS fitting results for the $LaFeO_3$ nanopowders. O1s, Fe 2p3/2 and La 3d 5/2 binding energy and XPS derived surface atomic ratio.

	O1s			**Fe2p**	**La3d**		**O (0.6)**^{c}	**Fe (0.2)**^{c}	**La (0.2)**^{c}	**Si/La**^{d}
	BE (eV)	(rel.%)^a	FWHM	BE (eV)	BE (eV)	α^{Ib}				
LF	529.8	(65%)	1.9	710.9	834.4	1.00	0.7	0.09	0.20	0.00
	532.1	(35%)	1.9		838.1					
LF-AS	529.6	(65%)	2.1	710.9	834.4	1.03	0.7	0.08	0.20	0.48
	532.1	(35%)	2.1		838.1					
LF-HMS	529.8	(57%)	2.3	710.7	834.5	1.03	0.7	0.05	0.15	0.77
	531.7	(42%)	2.3		838.1					
LF-SBA	529.9	(67%)	2.6	710.7	834.4	0.93	0.7	0.07	0.20	0.60
	532.2	(33%)	2.6		838.1					

(a) Relative percentage.

(b) α^I is defined as the ratio between La(3d5/2) and its satellite.

(c) Theoretical values.

(d) The theoretical value for the Si/La molar ratio is 0, if it is supposed that all silica has been removed by basic etching.

Table S3 Main results of the SAXS analysis. All the parameters are in Å. The bold case is used for non-fitting parameters.

	SBA-15[1]	***LF-SBA***$_{BE}$	***LF-SBA***	***LF-SBA***
			(simulation)[1]	***(liquid-type)***[2]
R	48.9(5)	43.2(8)	36.8(8)	10.5(8)
b	25.0(5)	25.0(5)	15.0(5)	10.0(5)
k_c	1.94(2)	2.02(3)	2.01(5)	3.77(5)
η	-	-	-	0.398(3)
a	95.0	87.3	74.0	-
σ_B	0.0036(2)	0.0040(4)	0.0080(4)	-
σ_{DW}	6.10(3)	8.90(5)	12.00(5)	-
σ_D	0.00024(5)	2.04(5)	9.04(5)	-
D	164.0(5)	88.0(5)	87.0(5)	87.00

[1] Parallel cylindrical pore model.
[2] Liquid type model.

R =mean radius of the pores; assuming that pores are in physical contact with each other

b =parameter which takes into account the poly-dispersion of the pores and tunes the width of the distribution (b values over 10 are indicative of monodispersion of the domain).

k_c = parameter which takes into account the real distance of the pores with respect to the hard sphere approximation.

η= a parameter which takes into account the packing of the liquid volume fraction

a= lattice parameter

σ_B = constant width of the Bragg–Peaks at the positions q^*_{hk0}

σ_{DW} = Debye–Waller factor originating from imperfect structural order

σ_D = pore coarsening correlated with the positional disorder of the pores

D= domains