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Supplementary Information

Structural discrimination of nanosilicas particles and mixed-structure silica by multivariate analysis applied to SAXS profiles in combination with FT-IR spectroscopy

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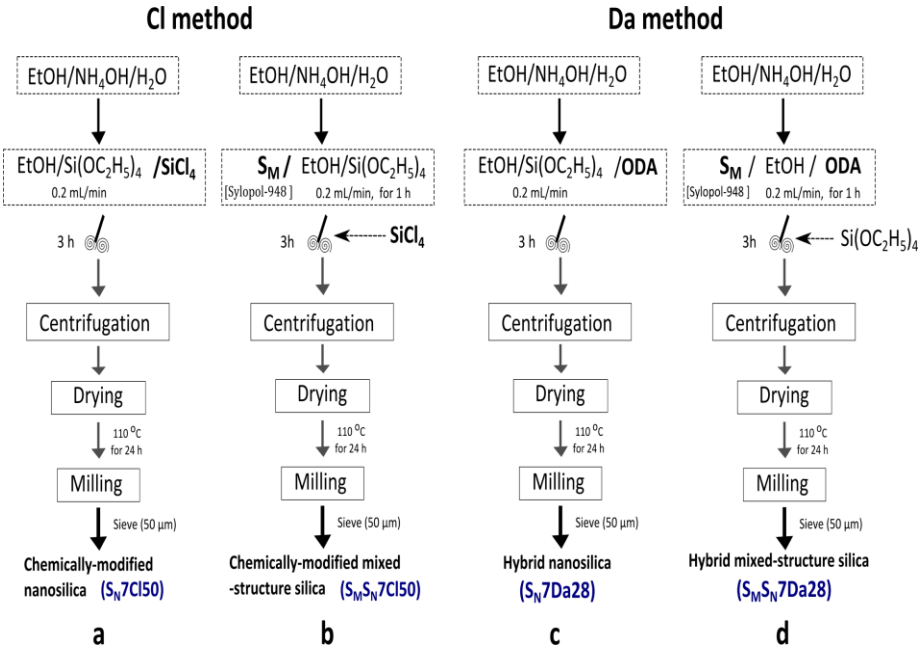
1. Methodology

The steps involved in the synthesis of nanomaterials. Scheme S1 depicts the steps involved in the synthesis of nanosilicas S_N7Cl50 (Scheme S1a) and S_N7Da28 (Scheme S1c), mixed silicas S_MS_NCl50 (Scheme S1b), and S_MS_N7Da28 (Scheme S1d), as well as the explanations for the corresponding abbreviations. For example, S_MS_N7Cl50 refers to S_MS_NCl prepared with a TEOS/ethanol molar ratio of 0.07 and a TEOS/$SiCl_4$ molar ratio of 5.0 (Scheme 1b), and S_MS_N7Da28 refers to S_MS_NDa prepared with a TEOS/ethanol molar ratio of 0.07 and an ODA molar amount of 0.0028 (Scheme 1d).



Scheme S1. Steps employed for the synthesis of S_N7Cl50 (a), S_MS_N7Cl50 (b), S_N7Da28 (c), and S_MS_N7Da28 (d) using a TEOS/ethanol molar ratio of 0.07, a TEOS/$SiCl_4$ molar ratio of 5.0, and 0.0028 mol of ODA.

Infrared Fourier transmission spectroscopy. An analysis of the absorbance modes was performed by co-adding 32 scans with 4 cm^{-1} of resolution. The characteristic spectral bands of the harmonic vibrations of the silica material networks [$\nu_{as(Si\text{-}O(\text{-}Si))}$] were studied by FT-IR in the region of 1300-1000 cm^{-1}. [1, 2] The broad band between 1300 - 1000 cm^{-1} was deconvoluted via Gaussian functions into the following four independent components: two (TO_4 and TO_6) associated with the transverse-optic (TO) modes and two (LO_4 and LO_6) with

the longitudinal-optic (LO) modes of Si-O-Si using a non-linear least-squares fitting method.[3] The percentage of six-fold siloxane rings ($(SiO)_6$) in the silica network was estimated using the following ratio of fitted areas: [2, 3]

$$\%((SiO)_6) = \frac{[A(LO_6) + A(TO_6)\,]}{[A(LO_6) + A(TO_6) + A(LO_4) + A(TO_4)].} * 100 \qquad (S1)$$

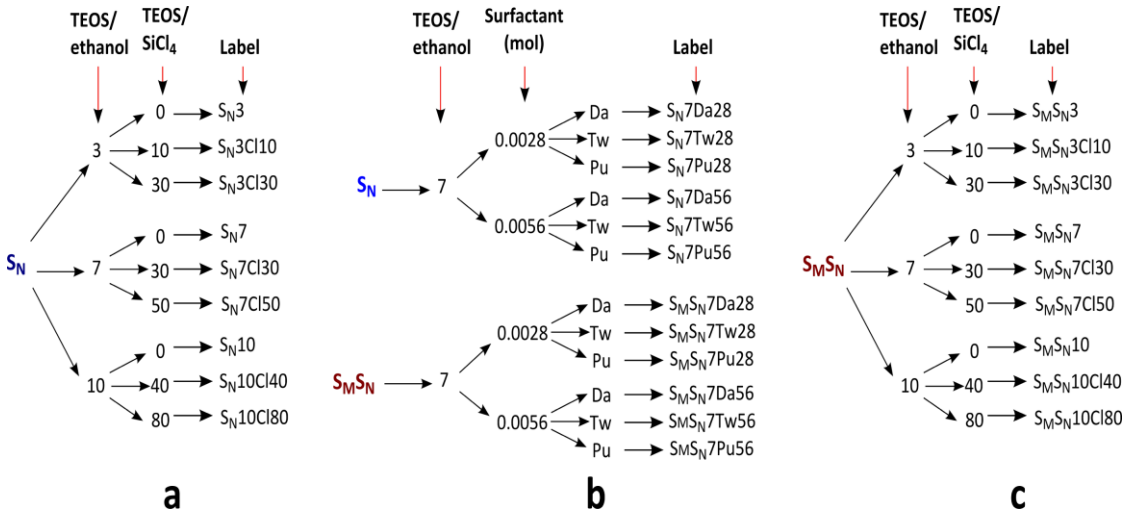
According to Fidalgo et al.,[4] LO mode is particularly sensitive to the introduction of chemical groups or organic molecules into the silica network. In this paper, the longitudinal-optical (LO) percentage in the silica network (% LO) was estimated as the following ratio of fitted areas: [3, 4]

$$\%(LO) = \frac{[A(LO_6) + A(LO_4)\,]}{[A(LO_6) + A(TO_6) + A(LO_4) + A(TO_4)]} * 100 \qquad (S2)$$

The proportion of silanol groups in S_MS_N versus S_M was estimated using the ratio of integrated areas (A) of the bands related to silanol [A(Si-OH)] and the silica backbone [$A(\nu_{as(Si\text{-}O(\text{-}Si))})$], [$A(\nu_{s(Si\text{-}O(\text{-}Si))})$] (Eq. (3)): [2-4]

$$\%(Si-OH) = \frac{A(\nu_{(Si-OH)})}{A\left(\nu_{as(Si-O(-Si))}\right)+A\left(\nu_{s(Si-O(-Si))}\right)+A(\nu_{(Si-OH)})} * 100 \qquad (S3)$$

2. *Nested Design*



Scheme S2. The experimental approach for the syntheses of silica samples.[5]

3. The N_2 adsorption-desorption isotherms.

Table S1. BET isotherm parameters (S_{BET}, V_p, and Dp_{BJH}), structural parameters of the SAXS profiles, Rg_H and $P_H = 4$ from the high-*q* region, Rg_M and P_M from the mid-*q* region and P_L from the low-*q* region obtained through a unified fit.

Sample	S_{BET}	Vp_{BJH}	Dp_{BJH}	High-*q* region		Mid-*q* region			Low-*q* region
				Rg_H [a]	Rp_H [b]	Rg_H	Rp_H	P_H [c]	P_L
	($m^2.g^{-1}$)	($cm^3.g^{-1}$)	(nm)	(nm)	(nm)	(nm)	(nm)		
S_M	272 ± 6.7	1.47 ± 0.5	15.7 ± 0.9	1.06	1.37 ± 0.3	5.73	7.39 ± 1.2	4.2	2.3
S_{N3}	337 ± 24.0	0.73 ± 1.0	10.6 ± 0.7	0.40	0.50 ± 0.0	5.40	7.00 ± 1.2	4.0	2.8
S_N7	369 ± 19.3	0.96 ± 0.1	9.3 ± 0.3	0.36	0.47 ± 0.0	7.28	9.39 ± 1.4	3.9	2.8
S_N10	326 ± 17.1	0.95 ± 0.0	11.3 ± 0.2	0.41	0.53 ± 0.2	9.64	12.44 ± 1.2	4.0	2.0
S_MS_N3	210 ± 7.0	1.03 ± 0.5	11.0 ± 1.2	0.40	0.50 ± 0.5	6.60	8.50 ± 0.2	4.0	2.6
S_MS_N7	313 ± 7.4	0.87 ± 0.0	9.4 ± 1.4	0.36	0.47 ± 0.0	7.55	9.74 ± 0.1	3.9	2.9
S_MS_N10	298 ± 27.0	1.15 ± 0.1	14.2 ± 0.3	0.41	0.53 ± 0.2	12.57	16.21 ± 1.6	4.0	1.8
S_N3Cl10	545 ± 20.0	0.16 ± 0.0	2.6 ± 0.1	0.40	0.60 ± 0.0	4.80	6.20 ± 2.1	3.0	3.8
S_N3Cl30	731 ± 14.0	0.42 ± 0.2	2.8 ± 0.3	0.40	0.61 ± 0.0	2.10	2.70 ± 0.0	3.5	3.7
S_N7Cl30	714 ± 10.4	0.17 ± 0.0	2.6 ± 0.0	0.76	0.98 ± 0.0	3.05	3.93 ± 0.1	4.0	3.8
S_N7Cl50	522 ± 2.0	0.11 ± 0.0	2.6 ± 0.1	0.40	0.50 ± 0.0	2.40	3.00 ± 0.2	4.0	3.8
$S_N10Cl40$	588 ± 21.4	0.08 ± 0.0	3.5 ± 0.6	0.42	0.55 ± 0.0	2.58	3.33 ± 0.3	4.0	3.8
$S_N10Cl80$	620 ± 27.1	0.10 ± 0.0	2.6 ± 0.8	0.41	0.53 ± 0.0	2.43	3.14 ± 0.1	4.0	3.8
S_MS_N3Cl10	517 ± 16.0	0.23 ± 0.0	4.0 ± 0.1	0.40	0.60 ± 0.1	5.30	6.80 ± 0.3	3.4	3.5
S_MS_N3Cl30 [d]	375 ± 17.0	0.32 ± 0.0	5.8 ± 0.3	0.50	0.60 ± 0.0	5.60	7.20 ± 0.3	3.8	3.1
S_MS_N7Cl30	567 ± 8.3	0.25 ± 0.3	4.3 ± 0.2	0.44	0.56 ± 0.2	5.42	7.00 ± 1.1	3.6	3.3
S_MS_N7Cl50	231 ± 2.0	0.74 ± 0.1	9.5 ± 0.7	0.80	1.10 ± 0.0	5.70	7.40 ± 1.0	4.0	3.3
$S_MS_N10Cl40$	405 ± 17.1	0.11 ± 0.1	3.8 ± 0.0	0.33	0.43 ± 0.1	6.67	8.61 ± 0.2	4.0	2.5
$S_MS_N10Cl80$	308 ± 21.7	0.11 ± 0.1	4.0 ± 0.1	0.43	0.55 ± 0.1	5.89	7.61 ± 1.1	3.5	3.7
S_N7Da28	286 ± 18.0	0.42 ± 0.0	5.0 ± 0.3	0.34	0.44 ± 0.0	8.21	10.59 ± 4.0	3.6	3.0
S_MS_N7Da28	179 ± 11.0	0.35 ± 0.5	7.1 ± 0.5	0.25	0.33 ± 0.1	10.31	13.30 ± 2.2	3.9	2.5
S_MS_N7Da56	212 ± 6.0	0.72 ± 0.1	10.1 ± 1.0	2.00	2.58 ± 1.0	6.41	8.27 ± 1.4	3.7	2.2
S_N7Tw28	39 ± 2.0	0.17 ± 0.0	14.6 ± 2.2	0.93	1.20 ± 0.0	22.18	28.61 ± 4.3	3.9	2.4
S_MS_N7Tw28	150 ± 7.5	0.60 ± 0.1	12.6 ± 1.6	0.79	1.02 ± 0.1	7.97	10.29 ± 1.1	3.6	2.4
S_MS_N7Tw56	127 ± 11.4	0.64 ± 0.0	16.4 ± 1.0	0.65	0.84 ± 0.1	16.86	21.76 ± 1.5	3.9	1.7
S_N7Pu28	204 ± 16.3	1.21 ± 0.3	19.5 ± 2.6	0.93	1.20 ± 0.0	10.92	14.09 ± 2.1	3.7	2.7
S_MS_N7Pu28	153 ± 10.7	0.60 ± 0.1	11.9 ± 1.1	0.65	0.84 ± 0.2	6.58	8.49 ± 1.3	3.5	2.2
S_MS_N7Pu56	138 ± 5.5	0.75 ± 0.0	14.2 ± 1.9	0.43	0.52 ± 0.1	13.77	17.81 ± 1.1	4.0	2.8

a) Rg is the radius of gyration of the particles in each region. Rg_H at high-*q* region, Rg_L at low-*q* region, and Rg_M at mid-*q* region; b) and c) Rp and P are the radius of the particle and Power-law exponent decay extracted in each region, respectively. $P_H = 4.0$ at high-q region [2, 3]. d) Cl30 corresponds to TEOS/$SiCl_4$ molar ratio of 3.0.

4. Molecular structural characteristics

Table S2 shows the band assignments for the different investigated systems**.**

Table S2. Band assignments for the FT-IR spectra (region of 4000 - 400 cm^{-1}), and the correlation between the parameters % $(SiO)_6$, % LO and (% Si-OH) for a selected sample, obtained by deconvolution of the band from 1300 - 1000 cm^{-1}.

Sample	Assignments [6,4,7,8], wavenumber (cm^{-1})									$(SiO)_6$ (%)	LO (%)	(Si-OH) (%)
	$\nu_{(OH)}$	$\nu_{as(Si-O(-Si))}$	$\nu_{(Si-Od)}$	$\nu_{s(Si-O(-Si))}$	$\nu_{(Si-O)}$	$\nu_{as((C)-CH2)}$	$\nu_{s((C)-CH2)}$	$\nu_{s(C=O)}$	COO^-			
S_M	3434	1104	954	800	468	2926	2904	-	-	42.6	73.8	12.5
S_N7	3423	1095	953	796	461	2984	2906	-	-	23.7	66.3	11.6
S_MS_N7	3425	1099	955	799	458	2987	2904	-	-	49.9	51.0	13.1
S_N7Cl30[a)]	3416	1079	958	796	460	-	-	-	-	65.9	56.2	16.3
S_N7Cl50[b)]	3423	1075	952	795	462	-	-	-	-	46.9	51.5	20.0
S_MS_N7Cl30	3443	1086	954	799	458	-	-	-	-	51.9	45.9	20.9
S_MS_N7Cl50	3440	1092	956	799	464	-	-	-	-	50.3	47.3	18.1
S_N7Da28	3444	1096	957	804	461	2924	2852	-	-	26.1	64.5	10.8
S_MS_N7Da28	3457	1100	958	802	465	2924	2853	-	-	45.4	41.1	15.6
S_MS_N7Da56	3448	1108	967	798	459	2920	2850	-	-	69.0	42.7	21.1
S_N7Tw28	3429	1091	952	800	460	2935	2876	1732	1651	34.8	45.2	14.9
S_MS_N7Tw28	3443	1094	953	803	457	2936	2893	1728	1645	44.1	38.9	29.2
S_MS_N7Tw56	3436	1097	961	802	463	2940	2890	1725	1640	47.5	36.1	10.4
S_N7Pu28	3438	1098	957	801	461	2978	2956	1727	1636	47.1	52.4	8.2
S_MS_N7Pu28	3428	1097	952	796	465	2985	2941	1728	1641	55.2	40.0	3.5
S_MS_N7Pu56	3441	1101	959	801	459	2983	2960	1722	1643	53.6	37.2	12.4

a) Cl30 and b) Cl50 correspond to TEOS/$SiCl_4$ molar ratio of 3.0 and 5.0, respectively.

4. TGA and DTGA curves, and X-Ray diffraction spectra

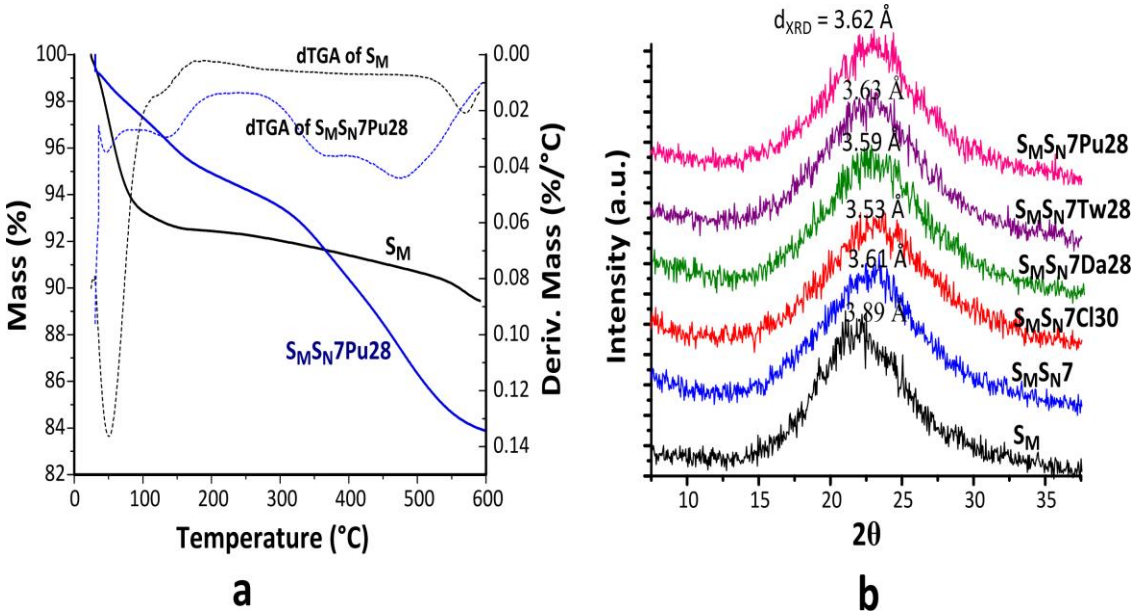


Fig. S1 (a) TGA and DTGA curves of S_M (black) and S_MS_N7Pu28 (blue); heating 20 ºC.min^{-1}. (b) X-Ray diffraction spectra of S_M compared with S_MS_NCl30, S_MS_N7Da28, S_MS_N7Tw28, and S_MS_N7Pu28.

5. TEM image of S_MS_NTw28

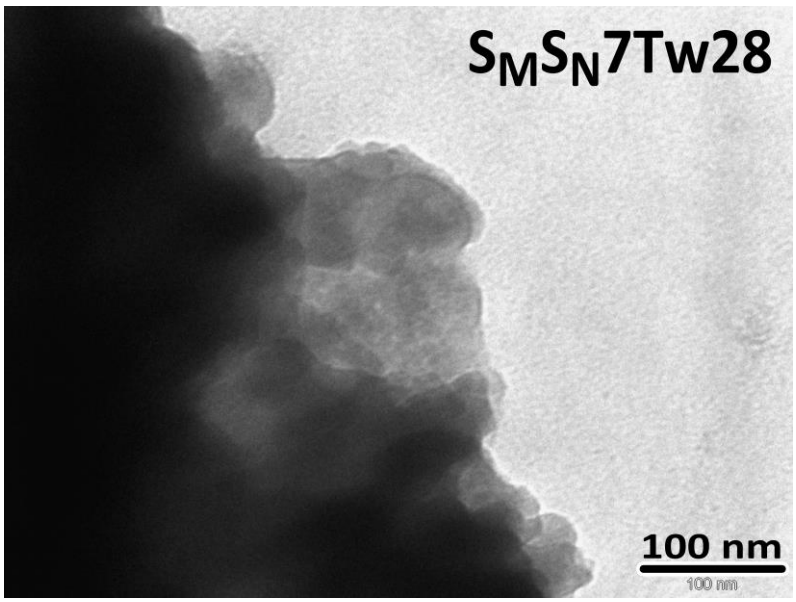


Fig. S2 TEM images of hybrid mixed-structure silicas using Tween®80, S_MS_NTw28.

6. Zeta potential measurments

Table S3. Zeta potential of synthesized silicas according to different employed methods to prepare the samples.

Sample	ZP (mV)
S_M	0.06
S_N**7**	-15.03
S_MS_N**7**	-25.80
S_N**7Cl30**	-10.60
S_N**7Cl50**	-22.90
S_MS_N**7Cl30**	-9.00
S_MS_N**7Cl50**	-17.80
S_N**7Da28**	-26.50
S_MS_N**7Da28**	-0.05
S_MS_N**7Da56**	--
S_N**7Tw28**	-20.70
S_MS_N**7Tw28**	-19.53
S_MS_N**7Tw56**	--
S_N**7Pu28**	-25.53
S_MS_N**7Pu28**	-28.34
S_MS_N**7Pu56**	--

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