Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

A simple ternary nonionic templating system for preparation of complex hierarchically meso-mesoporous silicas with 3D interconnected large mesopores

Electronic Supplementary Information

Table S1

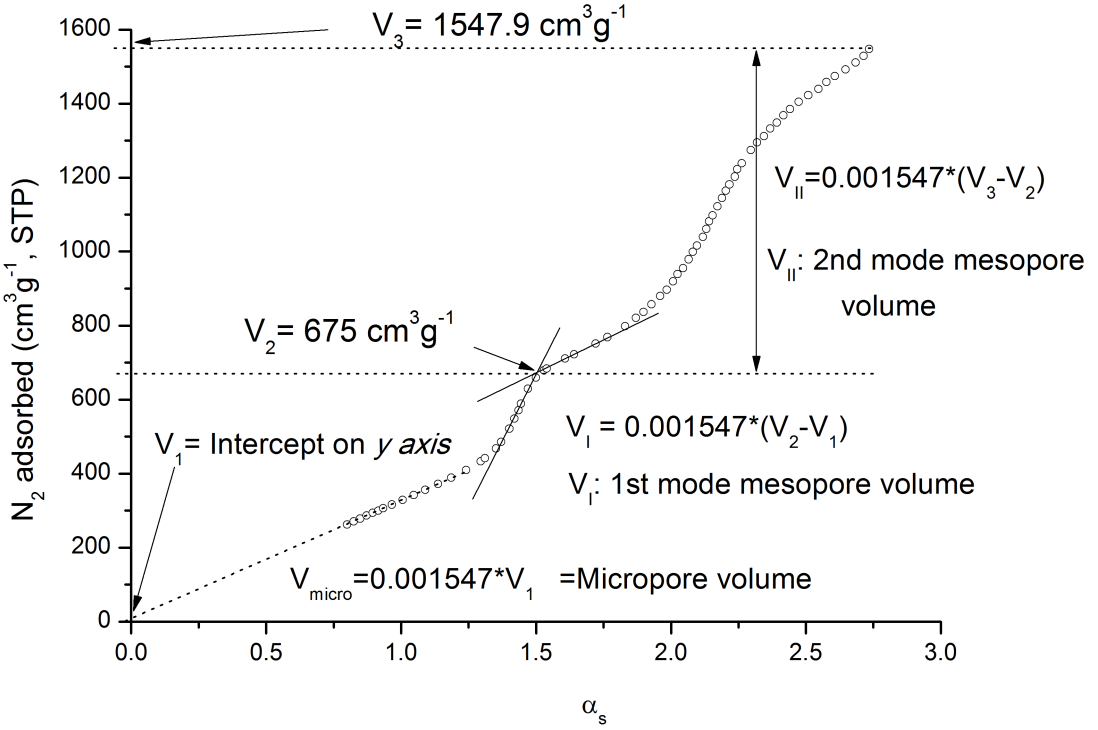
Physico-properties of meso-silicas prepared via the PCSA process based on TEOS

Places of the samples appeared	Sample No.	BET /m^2g^{-1}	V_{total} /cm^3g^{-1} [a]	V_{mi} [b]	V_I [c]	V_{II} [d]	D_I /nm [e]	D_{II} /nm [f]	Φ [g]
Fig. 1& Fig. 4	T5-1.5h-5@43H6.15	758	1.00	0.06	0.94	0	9.0	0	0
	T5-2.5h-5@43H6.15	760	1.15	0.06	1.11	0	9.4	0	0
	T5-3.5h-5@43H6.15	769	1.60	0	0.87	0.73	8.3	26.4	0.84
	T5-4.5h-5@43H6.15	915	2.37	0	1.04	1.34	8.8	32.4	1.30
	T5-5.0h-5@43H6.15	807	1.69	0	1.00	0.69	9.5	23.1	0.69
Fig. 5 & Fig. 4	T3-3.5h-7@43H5.95	747	1.09	0.05	1.05	0	9.6	0	0
	T4-3.5h-6@43H5.95	1011	1.49	0.05	1.46	0	10.5	0	0
	T5-3.5h-5@43H5.95	871	1.53	0	1.0	0.53	8.2	17.8	0.53
	T6-3.5h-4@43H5.95	858	1.86	0	1.09	0.77	9.6	23.3	0.71
	T7-3.5h-3@43H5.95	753	1.10	0.03	1.07	0	9.5	0	0
Fig. 4	T5-1.5h-5@43H5.95	899	1.16	0.05	1.11	0	8.0	0	0
	T5-2.5h-5@43H5.95	857	1.25	0.04	1.21	0	8.5	0	0
	T5-3.0h-5@43H5.95	738	1.21	0	0.82	0.39	8.5	18.6	0.48
	T5-4.0h-5@43H5.95	763	1.25	0	0.84	0.41	7.9	16.2	0.49
	T6-1.5h-4@43H5.95	666	0.99	0.04	0.96	0	9.2	0	0
	T6-2.5h-4@43H5.95	779	1.38	0.04	0.97	0.36	10.0	25.5	0.37
	T6-3.0h-4@43H5.95	719	1.48	0.01	0.87	0.6	8.9	26.7	0.69
	T6-4.0h-4@43H5.95	816	1.61	0.02	1.01	0.58	9.5	23.3	0.58
	T4-3.0h-6@43H5.95	1003	1.41	0.05	1.36	0	10.2	0	0
	T4-4.0h-6@43H5.95	948	1.48	0.06	1.42	0	9.7	0	0
	T5-3.0h-5@43H6.15	767	1.51	0.02	0.89	0.6	9.0	28.0	0.67
	T5-4.0h-5@43H6.15	760	1.70	0.01	0.89	0.8	9.2	28.2	0.9
	T4-4.5h-6@43H6.15	781	1.32	0.02	0.95	0.35	9.2	23.0	0.37
	T6-4.5h-4@43H6.15	777	1.26	0	0.85	0.41	7.9	16.6	0.48
	T6-2.5h-4@43H6.15	886	1.49	0	1.07	0.42	9.4	18.9	0.39
	T6-3.0h-4@43H6.15	794	1.58	0	1.02	0.56	9.7	22.7	0.54
	T6-3.5h-4@43H6.15	887	1.38	0.01	1.02	0.35	8.9	17.3	0.34

	T6-4.0h-4@43H6.15	804	1.54	0.03	1.01	0.49	9.3	27.3	0.49
	T5-4.5h-5@40H6.15	808	1.49	0	0.94	0.55	8.5	23.1	0.58
	T5-4.5h-5@43H6.35	889	1.48	0	0.99	0.49	8.5	20.1	0.49
	T5-4.5h-5@40H5.95	892	1.66	0	1.04	0.61	8.2	22.4	0.6
	T5-4.5h-5@46H5.95	793	1.25	0	0.87	0.38	8.5	18.2	0.44
	T5-4.5h-5@46H6.15	833	1.23	0	0.85	0.38	7.7	16.8	0.45
	T5-4.5h-5@46H6.35	802	1.16	0	0.80	0.36	7.5	16.3	0.44

[a] V_{total} is the total pore volume at relative pressure 0.995; [b-d] The calculation of micropore volume, 1st mode mesopore and 2nd mode mesopore volumes can be found in Fig. S1 (Supporting Information) ; [e-f] The most probable pore size distributions were calculated according to the KJS method. [g] The Φ is defined as the ratio of 2nd mode pore volume to the 1st mode pore volume.

Fig. S1



The calculation of the micropore volume (Vmicro), 1st mode and 2nd mode mesopores were give in the text in this figure.

Note: (1) The 0.001547 is density conversion coefficient for nitrogen. (2) Because the pore volumes derived from KJS calculations show slight overestimation, we did not use this method to calculated different pore volumes. (3) The particle sizes obtained are micron-sized, we assumed that the contribution from interparticles volumes is negiligible in nitrogen sorption measurement.

Fig. S2

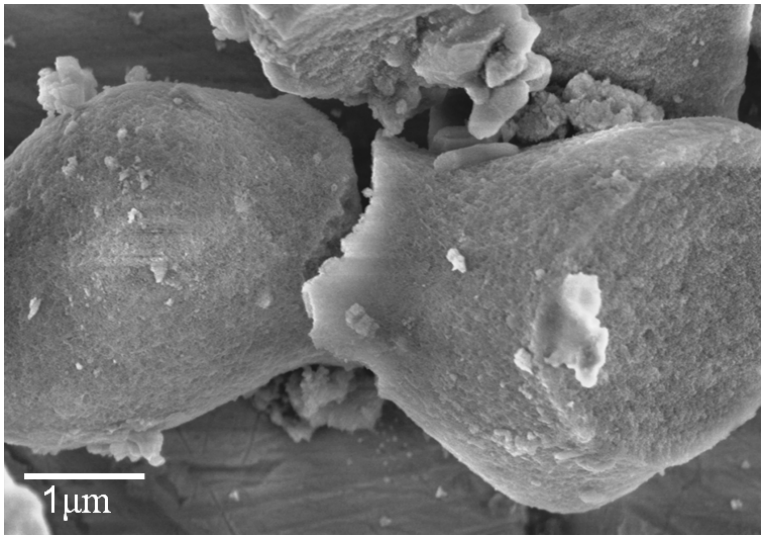


Fig. S2 SEM of T5-1.5h-5@43H5.95 with monomodal mesostructures

Fig. S3

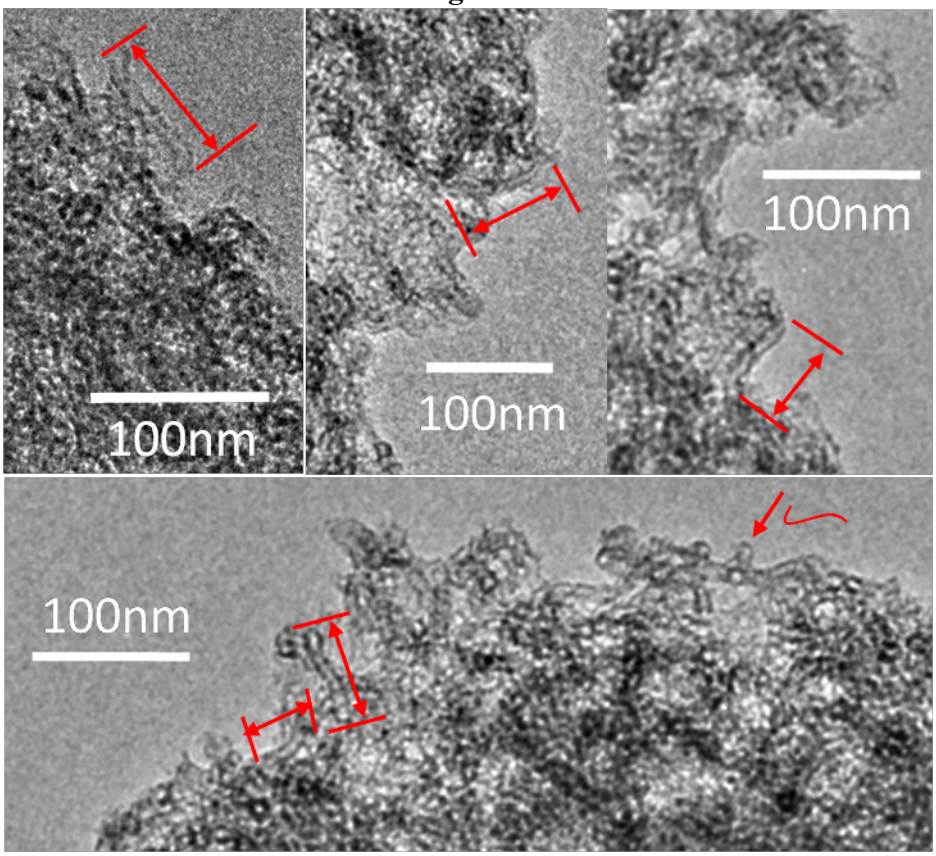


Fig.S3 TEM image showing the presence of short channels of the 1st mode mesopores of TS5-4.5h-5@43H6.15.

Fig. S4

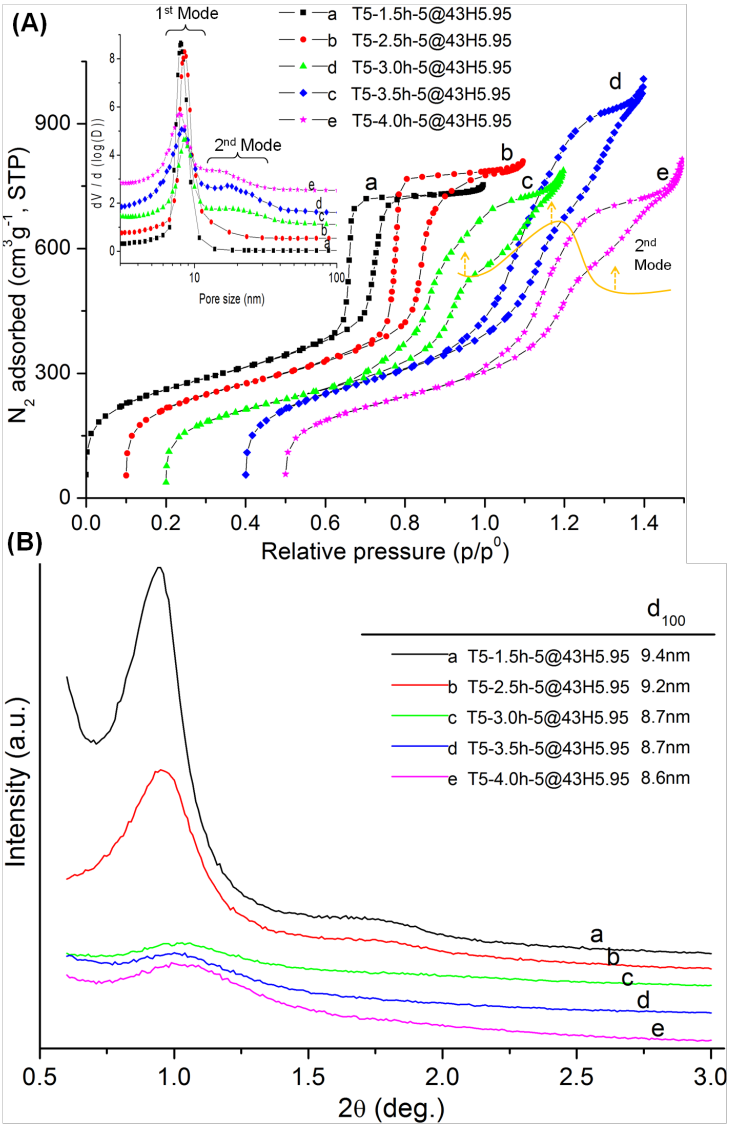


Fig. S4 (A) nitrogen adsorption-desorption isotherm curves and pore size distributions (inset) of HMS prepared with fixed addition combination but varying interval time. The isotherm curves of (b-d) were shifted horizontally to avoid overlap. The N_2 adsorbed due to the 2nd mode mesopores (above the brown line for curves c-e) and their pore sizes distributions were also marked. (B) Corresponding low-angle XRD patterns and calculated d_{100} spacing (inset table in (B)).

Fig. S4-A shows the nitrogen sorption results depicting the influence of interval times on mesostructures. Mesoporous silica prepared with interval time of 1.5h (T5-1.5h-5@43H5.95) shows to possess type-IV adsorption-desorption isotherm curves and H1 hysteresis loops, suggeting the formation of cylindrical (though not 100 %) mesopores. When the interval time is in excess of 2.5h, the adsorption-desorption curves show an interesting feature: at high p/p^0, an extra capillary condensation/evaporation steps (above the dotted brown line) are observable, corresponding to the presence of the 2nd mesopore system, which can also be seen from the PSDs shown in Fig. S4-A (inset). The higher step is attributed to the formation of second mode of mesopores with pore size of about 18 nm (p/p^0~0.85) (Fig. S4-A). The well-defined HMM structure forms with the interval time of 3.5h,

while further increase in the interval time (T5-4h-5@43H5.95) did not led to an improvement in the 2nd mode mesoporosity. In Fig. S4-B, low-angle XRD patterns also show progressively broadened and lowered low-angle XRD peaks when the interval times fall in the ragne from 1.5h to 4.0 h, indicative of the progressive deterioration in the meso-ordering.

All these resutls are in good agreement with those observed for T5-xh-5@43H6.15 series in Section 3.1 in the manuscript.

Fig. S5

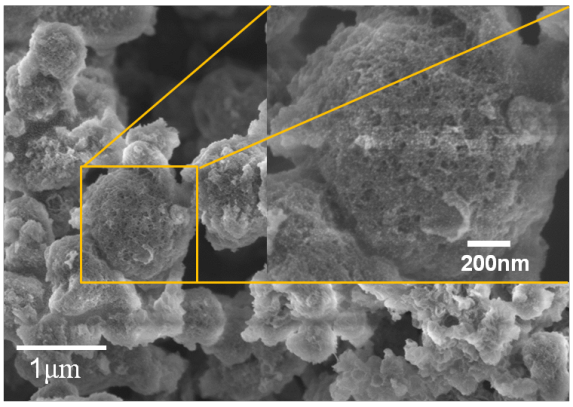


Fig. S5 FE-SEM images of T5-3.5h-5@43H5.95. Inset is the FE-SEM image taken at higher magnification.

Fig. S6

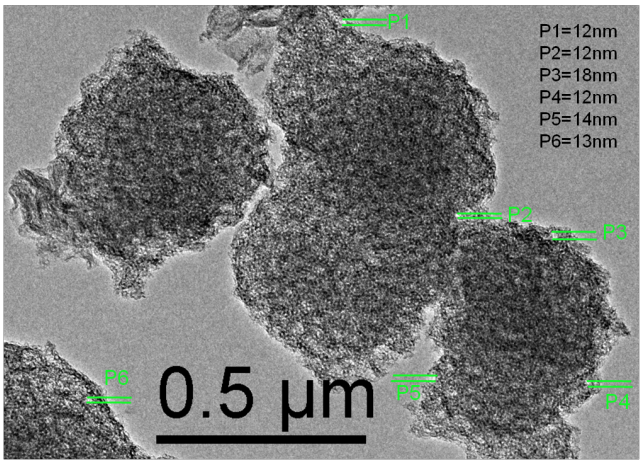


Fig. S6 Representative TEM images of T5-3.5h-5@43H5.95 showing the presence of hierarchical mesoporous structures. The pore size of discernible 2nd mode mesopores were also marked and listed.

Similar ‘fluffy clew’ feature can be observed for T5-3.5h-5@43H5.95 from Fig. S5-S6 , which are also consistent with those reported in the maunscript (Fig. 3).

Fig. S7

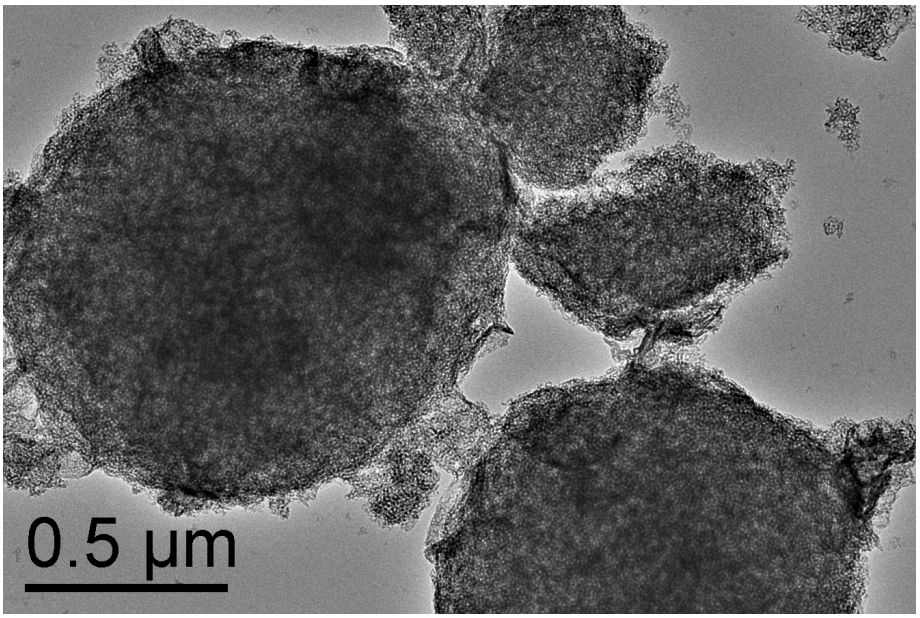


Fig. S7 TEM image of TS6-3.5h-4@43H5.95 shows the presence of small 1st mode mesopores and 2nd mode mesopores (light areas) too, which are similar to that shown in Fig. 3 in the manuscript.

Fig. S8

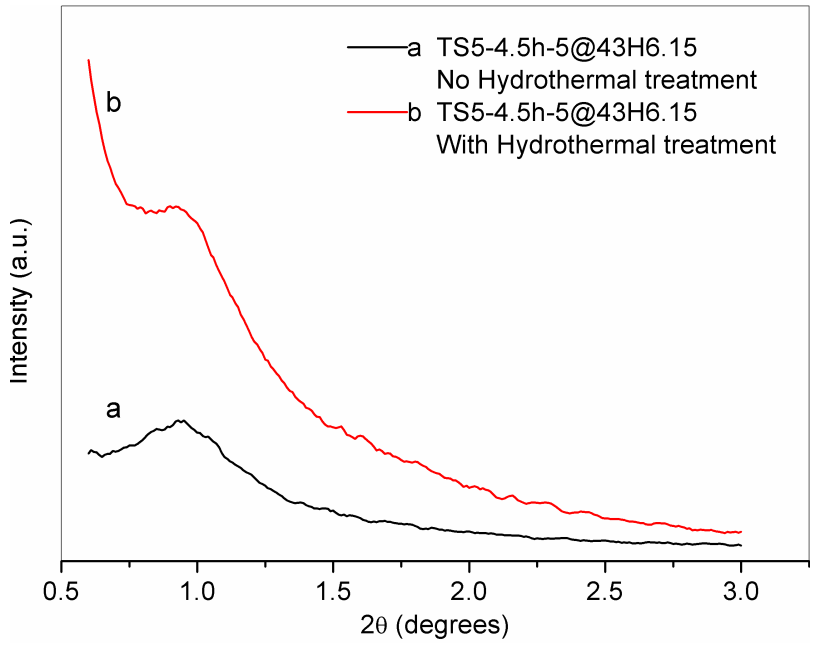


Fig.S8 low-angle patterns of as-prepared TS5-4.5h-5@43H6.15 without (a) and with (b) hydrothermal treatment.