Supporting Information

Hybrid mesoporous microspheres from aqueous droplets containing silica nanoparticles-polymer network in W/O suspension

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Contents

Scheme S1 Reaction scheme of MAPTS and DMAA.

Figure S1 ¹H NMR spectra of pSiDm (A) and pDMAA (B); FT-IR spectra of both polymers (C).

 Table S1 Different experimental conditions for the synthesis and appearance of different microspheres.

Figure S2 Optical micrographs to observe the effect of APS.

Figure S3 Summary of outcomes for microspheres preparation with homopolymer and SiPs of different size.

Figure S4 SEM image after calcination of M4 microspheres.

Figure S5 Microspheres obtained from SiPs (40-50 nm) and APS (2 mL).

Table S2 Data obtained from elemental analyses of M3 microspheres in situ preparation at different time of stirring.

Figure S6 Comparison of TGA curves of hybrid microspheres with bare polymer (*p*SiDm) and bare SiPs.

Thermo-gravimetric Analysis (TGA)



Scheme S1 Reaction scheme of MAPTS and DMAA.



Fig. S1¹H NMR spectra of pSiDm (A) and pDMAA (B); FT-IR spectra of both polymers (C).

	Oil phase Aqueous phase				
	(mL)				
Experiment No.	APS	10 wt% <i>p</i> SiDm solution	10 wt% SiP suspension (8-11nm)	10 wt% SiP suspension (40-50nm)	microspheres
1	0	0	5 (100 %)	0	No
2	0.5 (50 %)	0	5 (50 %)	0	No
3	1 (66.7 %)	0	5 (33.3 %)	0	No
4	2 (80 %)	0	5 (20 %)	0	No
5	0.5 (50 %)	0	0	5 (50 %)	No
6	1 (67.7 %)	0	0	5 (33.3 %)	No
7	2 (80 %)	0	0	5 (20 %)	Agglomerated microspheres
8	2 (67.7 %)	0	0	10 (33.3 %)	No
9	0	5 (50 %)	5 (50 %)	0	No
10	0.5 (33.3 %)	5 (33.3 %)	5 (33.3 %)	0	No
11	1 (50 %)	5 (25 %)	5 (25 %)	0	No
12	2 (66.7 %)	5 (16.7 %)	5 (16.7 %)	0	No

Table S1 Different experimental conditions for the synthesis of microspheres; the first parenthesis indicates the fraction of solid input in the preparation; the oil phase consists of Silicone oil (100 mL) and APS (different composition).

Observation of the effects of APS as an endcapping agent:

Here, the 10% aqueous solution of pSiDm was mixed with 10% SiPs (40-50 nm) suspension in equal ratio and poured in silicone oil containing no APS with vigorous stirring. Although some transient microspheres were observed during stirring, upon washing no microspheres could be collected as they all agglomerated (M1 in Fig. S2). However, addition of APS in silicone oil prior to the addition of the aqueous part results in independent spherical particles (M3 in Fig. S2).



Fig. S2 Optical micrographs to observe the effect of APS. Scale bars =100 μ m.

Summary of outcomes for microspheres preparation with homopolymer and SiPs of different size:

Use of homopolymer instead of copolymer results as a layer of dried thin film, whereas SiPs (8-11 nm) gives some agglomerated particles (Fig. S3). Only copolymer and SiPs of 40-50 nm with exact amount of APS can avoid agglomeration (c, Fig. S3).



Fig. S3 Pictorial view of the dried product obtained from (a) homopolymer + SiPs (40-50 nm) + APS, (b) copolymer + SiPs (8-11 nm) + APS, (c) copolymer and SiPs (40-50 nm) + APS.



Fig. S4 SEM image after calcination of M4 microspheres.



Fig S5 Agglomerated microspheres obtained from SiPs (40-50 nm) and APS (2mL). [Run 7 from Table S2].

Thermo-gravimetric Analysis (TGA)

TGA were performed on a SII EXSTAR 6000 TG/DTA 6200 thermo-balance in static air from 30 to 700 °C at a heating rate of 10 °C/min. using an empty Platinum cell as a reference. The heating process was carried out up to 700 °C, which has been demonstrated to be sufficiently high to degrade all surface-bonded organosilanes. From Fig. S6 it can be seen that there is an initial loss of weight at a temperature below 100 °C for all samples. This is attributed to the removal of physically adsorbed water and/or any minor solvent residues remaining from the particle modification procedures. Physically adsorbed water is removed completely by further heating to about 100 °C. Inspection of the TGA trace for the bare silica reveals a small, but obvious, thermal event in the wide range from 100 to 700 °C. This can be attributed to dehydroxylation of the silica surface, in which silanol groups condense to siloxanes, a process known to occur in this thermal region. On the other hand, the modified particles showed distinct thermal events. The weight loss of the modified particles beyond 100 °C was comparable to that of the bare SiPs and bare *p*SiDm.



Fig. S6 Comparison of TGA curves of hybrid microspheres with bare polymer (pSiDm) and bare SiPs.

Time of stirring (hours)	N%	С%	Н%	C/N Value
2	5.8	27	5.39	4.65
4	6.65	26.1	4.6	3.92
6	6.65	25.8	4.49	3.88
8	6.6	25.7	4.34	3.89

Table S2 Data obtained from elemental analyses of M3 microspheres in situ preparation at different time of stirring