Electronic Supplementary Information

Facile, controlled, large scale fabrication of novel capsule clusters

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Experimental:

Hydrophilic modified amorphous fumed silica (N20) and hydrophobic modified amorphous fumed silica (H30) are a gift from Wacker-Chemie GmbH, whose primary particles are approximately spherical of diameter between 5 and 30 nm. PPG-TDI (mean degree of polymerization is 34 according to the supplier), IPDI, DBP, toluene were used as received.

Preparation of the melamine-formaldehyde pre-polymer solution (pre-MF):[1] 1.75 g of melamine and 3.5 mL of 37.0 wt % formaldehyde aqueous solution were mixed in a 50-mL two-necked round bottom flask connected to a reflux condenser and equipped with stirring rod. Then, the pH value of the solution was adjusted to 9.0-9.5 by 2.5 mL of triethanolamine (TEA) under mechanical stirring. The mixture was heated to 55-60 °C. After 30 min, the MF pre-polymer solution was obtained.

Preparation of Fe_3O_4 nanoparticles:[2] A mixture of 1.0144 g of $FeCl_3 \cdot 6H_2O$ and 0.3732 g of $FeCl_2 \cdot 4H_2O$ dissolved in 10 mL of water was added to a 50 ml three-necked round bottom flask pre-immersed in an oil bath at 343 K and the reaction was allowed to proceed for 2 h after quickly adding dropwise 4 mL 16.5% $NH_3 \cdot H_2O$ under vigorous stirring. The resulting black precipitate was washed and centrifugalized with anhydrous ethanol several times, then dried at room temperature. Finally, Fe_3O_4 nanoparticles powder was obtained.

Preparation of graphene oxide (GO):[3] GO was prepared from natural graphite using the modified Hummers and Offema method. In brief, 1 g of the natural graphite powder, 0.5 g of $NaNO_3$, and 23 mL of H_2SO_4 were added to a 250 mL beaker under stirring in an ice-bath. 3 g of $KMnO_4$ was added slowly to the beaker under stirring. The ice bath was removed 5 min later and the mixture was heated at 35 ^{o}C for 30 min. 30 mL of water was slowly added to the mixture and was stirred for another 15 min. Then, the temperature rose to 95~100 ^{o}C and kept for 30min. 15 mL of H_2O_2 aqueous solution was added to reduce the residual $KMnO_4$ until the bubbling was disappeared. The mixture was cooled to room temperature and washed with 5 wt % HCl and water for 3 times. Finally, GO powder was obtained after drying in a vacuum oven for 3 d.

Characterization

The Pickering emulsion droplets and capsule clusters were observed with an optical microscope (Carl Zeiss, Germany), and the average diameter was estimated by counting 150 beads. FTIR spectra were recorded using a Bruker Vector-33 FTIR spectrometer under ambient conditions. The samples were grinded with KBr and then compressed into pellets. The spectra were taken from 400 to 4000 cm^{-1}. TGA was performed using a NETZSCH TG 209F3 instrument under a nitrogen atmosphere and a heating rate of 10 ^{o}C min^{-1} from 30 to 700 ^{o}C. Morphology of the capsule clusters and their inner structure (cutting by a razor blade on a quartz wafer) were analyzed via SEM, which was carried out with a Zeiss EVO 18 electron microscope equipped with a field emission electron gun. The air-dried or vacuum freezing dried samples were sputter-coated with gold prior to measurement. Raman spectra were recorded on a Renishaw in plus laser Raman spectrometer with λ_{ex} of 785 nm.

Table S1 Parameters of $O_1/W/O_2$ Pickering emulsion templates for capsule clusters.

Entry	O_1			W		O_2	O_1/W Emulsion[a]		$O_1/W/O_2$ Emulsion[b]	
	DBP (mL)	PPG-TDI (g)	IPDI (mL)	Pre-MF[c] (mL)	Water (mL)	toluene (mL)	O_1:W (v/v)	D_1[d] (μm)	$(O_1+W):O_2$ (v/v)	D_2[d] (μm)
1	2.4	0.24	0.6	0.9	2.1	18	1:1	67±23	1:3	197±76
2	1.6	0.16	0.4	1.8	4.2	24	1:3	35±18	1:3	235±99
3	0.8	0.08	0.2	1.8	4.2	21	1:6	24±7	1:3	202±69
4	0.4	0.04	0.1	1.5	3.5	16.5	1:10	13±3	1:3	206±99
5	1.6	0.16	0.4	1.8	4.2	8	1:3	35±18	1:1	509±85
6	1.6	0.16	0.4	1.8	4.2	48	1:3	35±18	1:6	140±81
7	1.8	0.16	0.2	1.8	4.2	18	1:3	-	1:3	-
8	1.2	0.16	0.8	1.8	4.2	18	1:3	-	1:3	-
9	1.6	0.16	0.4	1.2	4.8	18	1:3	-	1:3	-
10	1.6	0.16	0.4	2.4	3.6	18	1:3	-	1:3	-

[a] The stabilizer for O_1/W emulsions is 1 wt % hydrophilic silica nanoparticles N20 with respect to water (W), which is dispersed in water (W).

[b] The stabilizer for $(O_1/W)/O_2$ emulsions is 1 wt % hydrophobic silica nanoparticles H30 with respect to O_2, which is dispersed in O_2.

[c] The content of pre-MF in the pre-MF stock solution is 50 wt %.

[d] The average diameters were determined by dynamic light scattering (DLS).

Entries 1-4

O_1:W (v/v): 1:1, 1:3, 1:6, 1:10, respectively; the other conditions are the same.

Entries 5, 2, 6

$(O_1+W):O_2$ (v/v): 1:1, 1:3, 1:6, respectively; the other conditions are the same.

Entries 7, 2, 8

The content of IPDI in O_1: 10, 20, 40 vol %, respectively; the other conditions are the same.

Entries 9, 2, 10

The content of pre-MF in W: 10, 15, 20 wt %, respectively; the other conditions are the same.

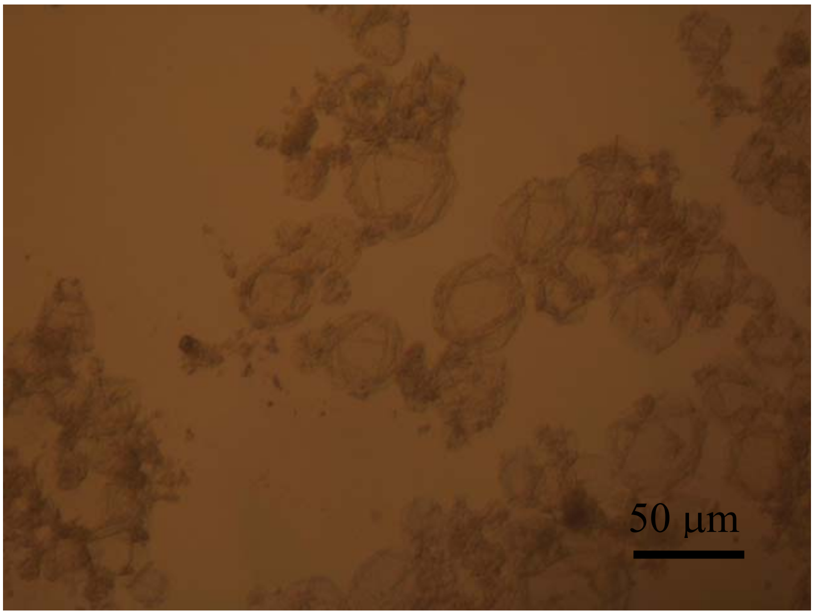

Figure S1 Optical microscopic image of the air-dried O_1/W emulsion droplets (Entry 2 in Table S1).

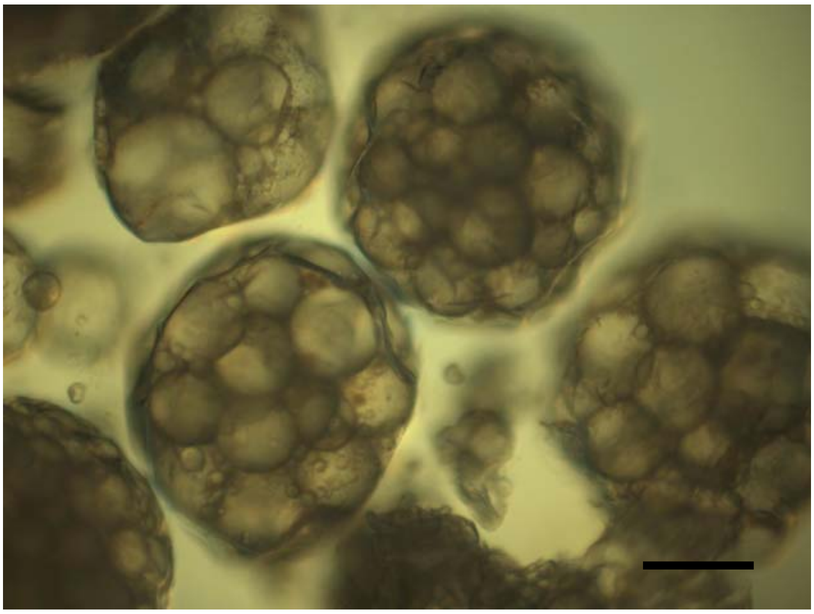

Figure S2 Representative optical microscopic image of capsule clusters in toluene (Entry 1 in Table S1).

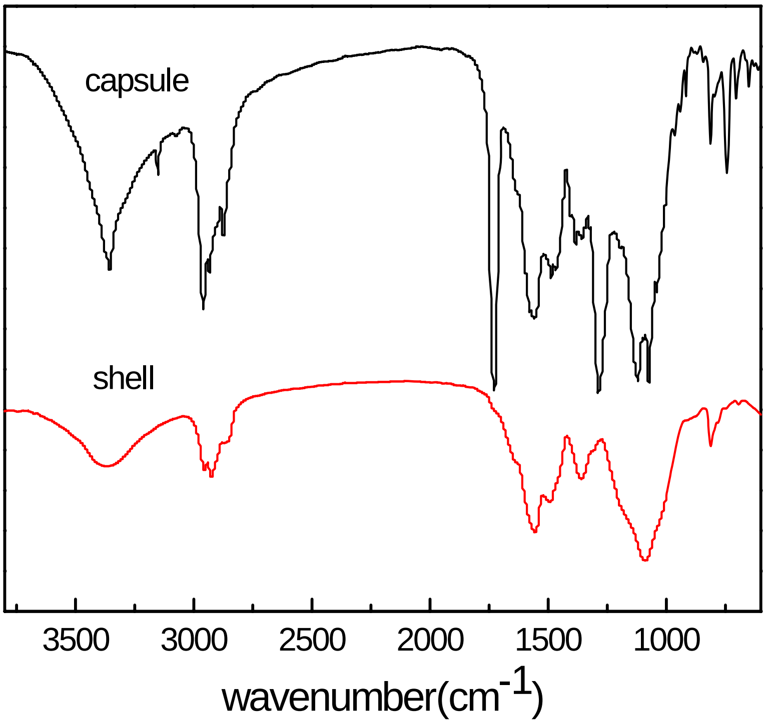

Figure S3 FTIR spectra of capsule clusters and the shells without DBP oils (Entry 1 in Table S1).

The spectrum of PMF shell exhibits broad stretching vibration peaks of N–H and O–H at about 3360 cm^{-1}, stretching of C–N and C=N at 1366–1556 cm^{-1}, and stretching of triazine ring at 814 cm^{-1}. The stretch of NH-CO at 1601 cm^{-1} confirmed the existence of the PU shell. The DBP-loaded capsule clusters also perform obvious absorbing peak at 1736 cm^{-1}, representing the C=O groups. The absence of stretching of –NCO at 2200-2280 cm^{-1} indicates that no IPDI and PPG-TDI remain in the core liquids.

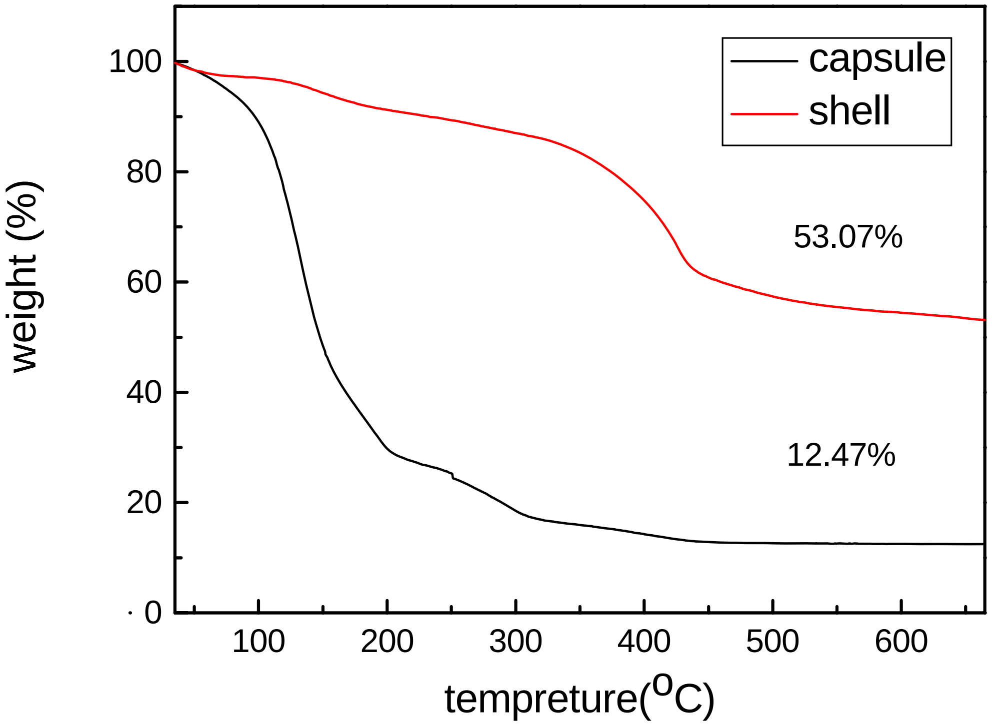

Figure S4 Thermal decomposition behaviors of capsule clusters and the cluster shells without DBP oils by TG (Entry 1 in Table S1).

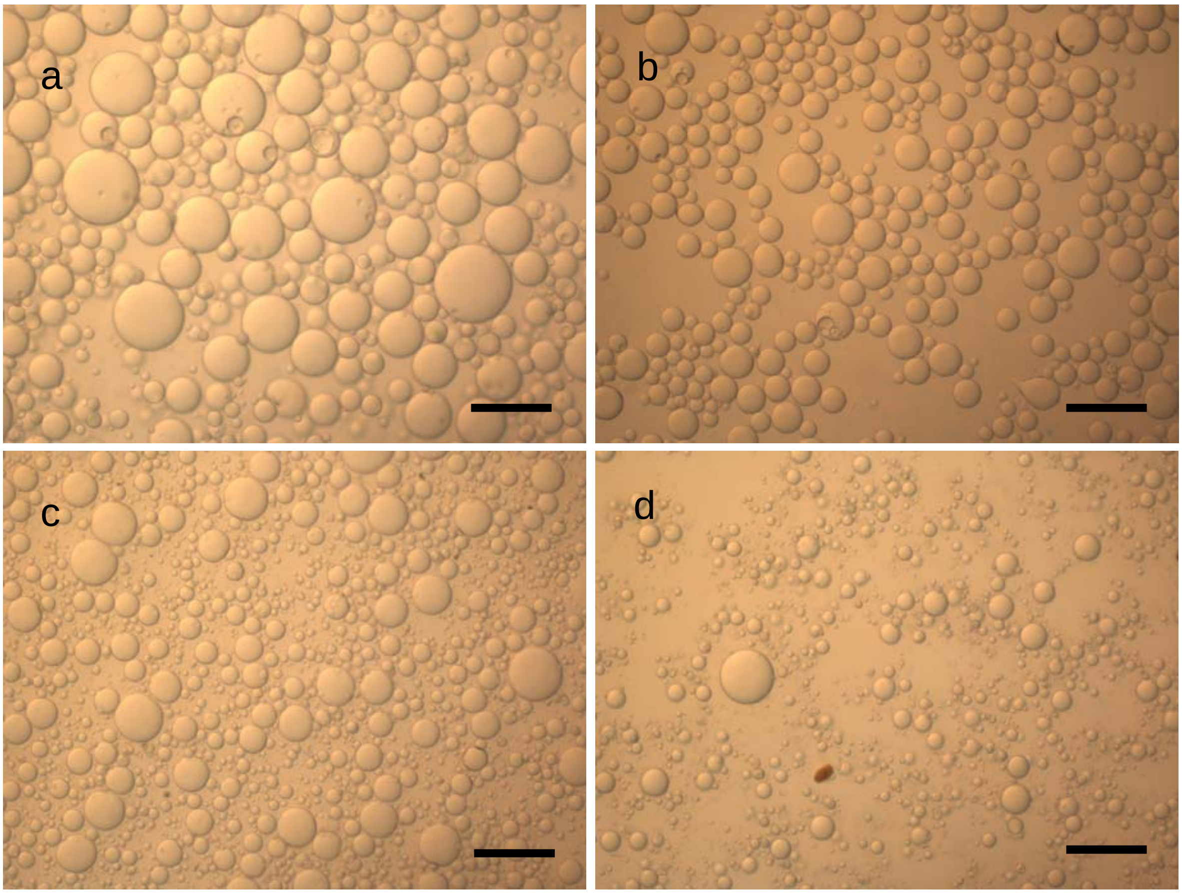

Figure S5 Optical microscopic images of DBP-in-water Pickering emulsions with different volume ration of O:W: (a) 1:1, (b) 1:3, (c) 1:6, and (d) 1:10. The stabilizer is 1 wt % N20 with respect to water. The scale bars are 100 μm.

Four emulsions are polydisperse. The average diameters are: 67 μm for O/W of 1:1, 35 μm for 1:3, 24 μm for 1:6, 13 μm for 1:6. The size of droplets decreases with the decrease of O:W due to the increasing amount of particles used for stabilization.

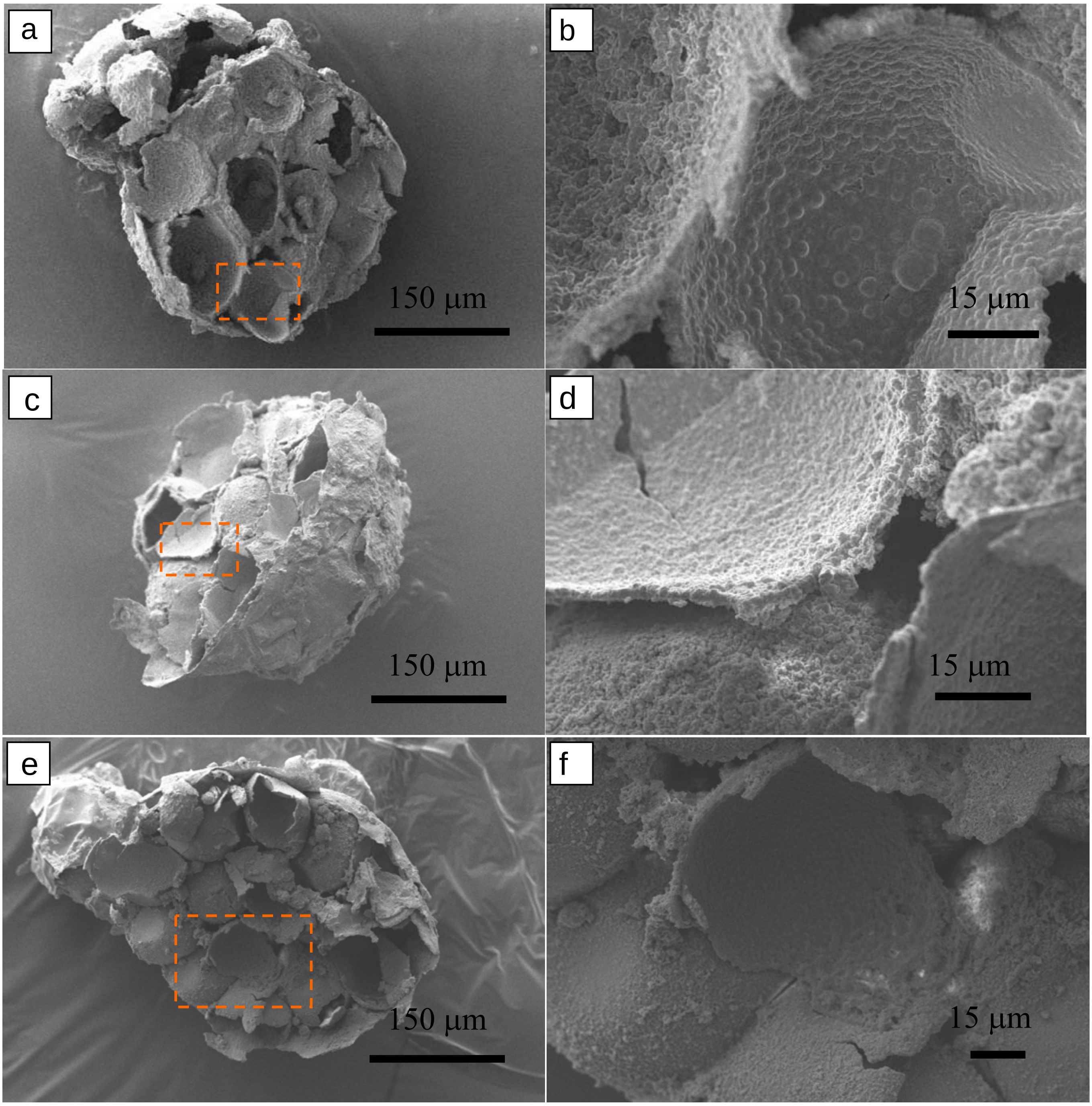

Figure S6 SEM images of the capsule clusters: (a, b) Entry 8 in Table 1S; (c, d) Entry 2; (e, f) Entry 7. The contents of pre-MF in the water phase is fixed and the contents of IPDI in the inner oil phase (O_1) from Entries 8 to 2 to 7 decrease successively.

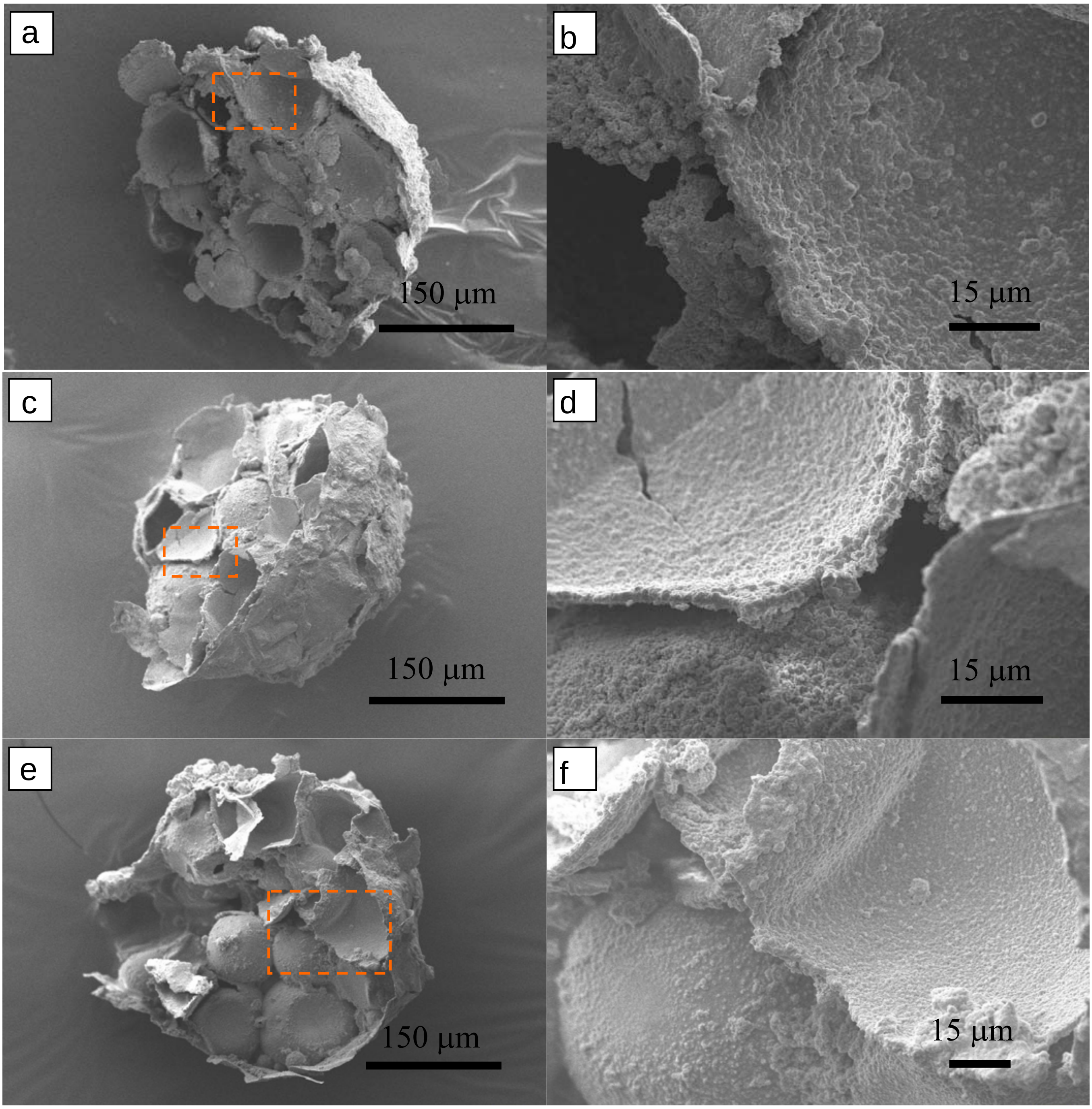

Figure S7 SEM images of the capsule clusters: (a, b) Entry 9 in Table 1S; (c, d) Entry 2; (e, f) Entry 10. The contents of the contents of IPDI in the inner oil phase (O_1) is fixed and the contents of pre-MF in the water phase (W) from Entries 9 to 2 to 10 decrease successively.

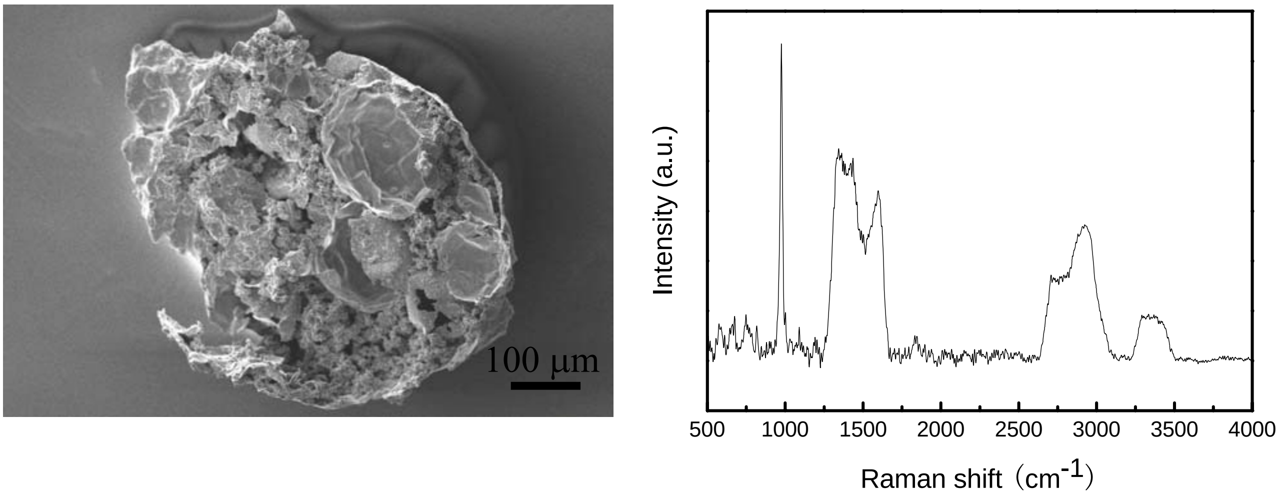

Figure S8 SEM image (left) and Raman spectrum (right) of the capsule cluster with graphene oxide. The cluster with graphene oxide exhibited a similar structure of the cluster with Fe_3O_4, appearing to be a large degree of debris filling in the interspaces between the inner capsules and the outer PMF shells. The Raman spectrum shows that the existence of the D (1350 cm^{-1}), G (1602 cm^{-1}), and 2D (2700 cm^{-1}) bands for graphene oxide.

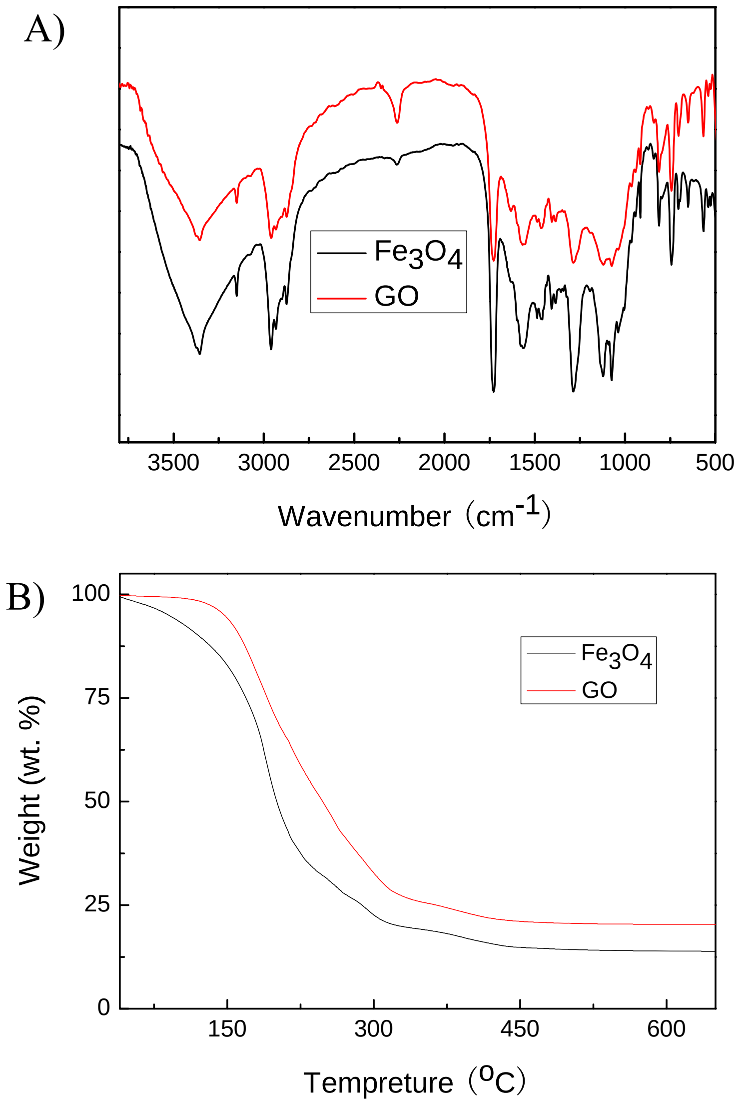

Figure S9 (A) FTIR spectra of capsule clusters filled with Fe_3O_4 nanoparticles (red line) and capsule clusters filled with GO nanoparticles (balck line). (B) Thermal decomposition behaviors of capsule clusters filled with Fe_3O_4 nanoparticles (black line) and capsule clusters filled with GO nanoparticles (red line) by TG.

References

[1] H. P. Wang, Y. C. Yuan, M. Z. Rong, M. Q. Zhang, *Colloid Polym. Sci.* **2009**, *287*, 1089-1097.

[2] Y. S. Kang, S. Risbud, J. F. Rabolt, P. Stroeve, *Chem. Mater.* **1996**, *8*, 2209–2211.

[3] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339.