

Supplementary Information for:

Polymer-inorganic hybrid microparticles with hierarchical structures formed by
interfacial instabilities of emulsion droplets

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Supplementary data:

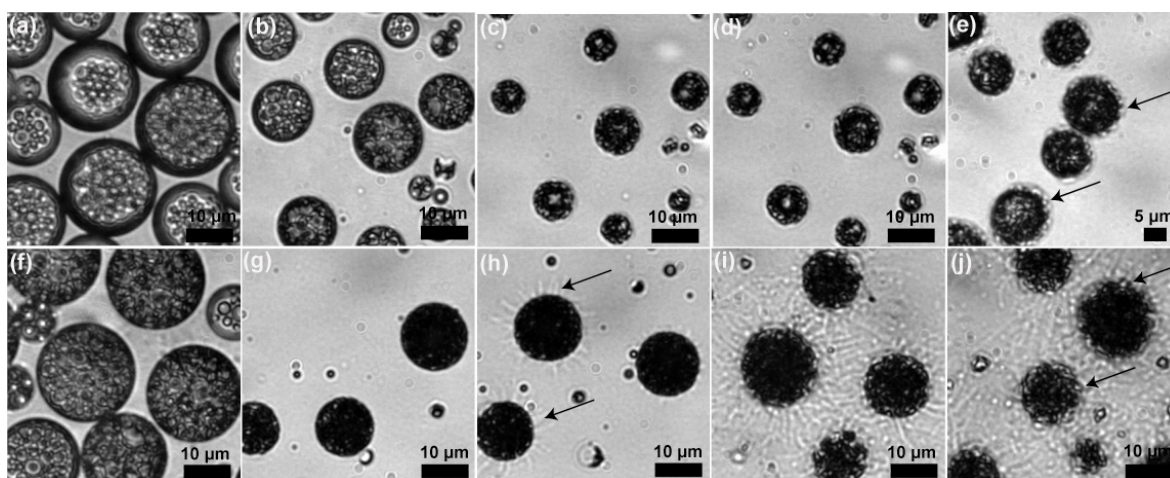


Fig. S1. (a-e and f-j) Optical micrographs showing the evolution of the emulsion droplets during chloroform evaporation. The time elapse for the images of (a-e) is (a) 0 min, (b) 11 min, (c) 17 min, (d) 19 min, and (e) 30 min. The time elapse for the images of (f-j) is (f) 0 min, (g) 71 min, (h) 132 min, (i) 157 min, and (j) 212 min. Water layer height in the evaporation device (h) varied from ~ 1.4 (a-e) to ~ 5.5 mm (f-j). The emulsion droplets consist of 10 mg mL^{-1} PS_{38k}-PEO_{11k} and 0 mg mL^{-1} TEOS. 5 mg mL^{-1} PVA was added to the aqueous phase, where $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to adjust the pH value to 10.

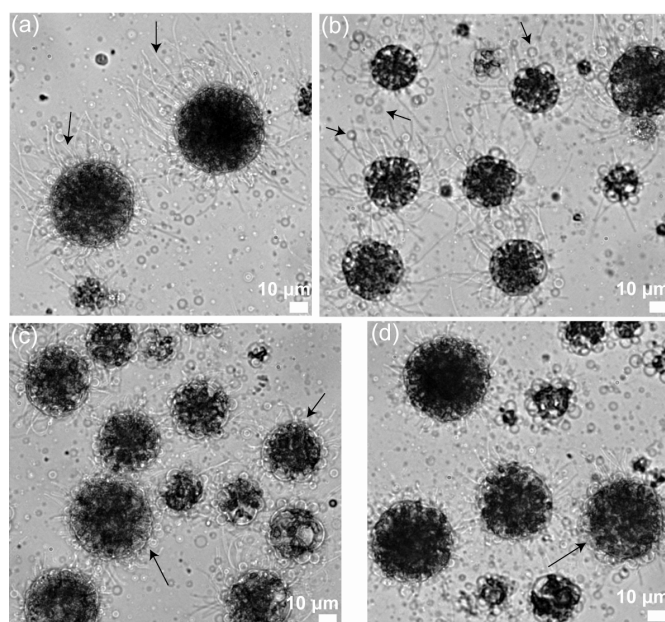


Fig. S2. Optical microscopy images of the early stages of the budding vesicles formation for the emulsion droplets containing 10 mg mL^{-1} PS_{38k}-PEO_{11k} and 0.3 mol L^{-1} TEOS at pH=10. Particles with spines (length: $\sim 5\text{--}50 \text{ }\mu\text{m}$) were observed, as indicated by arrows in (a) for the spines. Isolated small vesicles were also observed, as indicated by arrows in (b). Arrows in (c) and (d) indicate the tied spines and the possible transition from spines to vesicles. Water layer height in the evaporation device (h) was set to $\sim 5.5 \text{ mm}$.

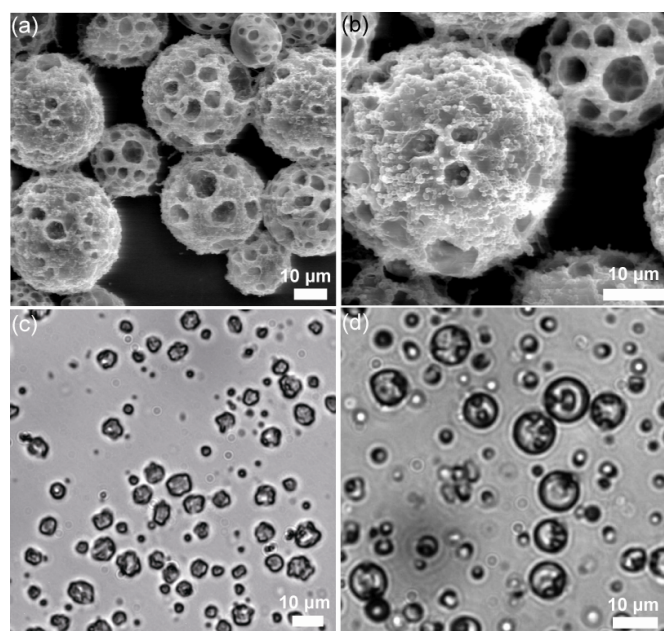


Fig. S3. (a, b) SEM images of the neat PS_{38k}-PEO_{11k} budding vesicles which were formed in a control experiment without TEOS addition, wherein solvent evaporation of emulsion droplets containing 10 mg mL⁻¹ PS_{38k}-PEO_{11k} at pH=10 with h of ~ 5.5 mm. (c, d) Optical micrographs show the microparticles formed from emulsion droplets containing (c) 0.3; (d) 0.6 mol L⁻¹ TEOS without PS-PEO addition at pH=10.

It is worth noting that we can not exclude the possibility that PVA templates the formation of silica shell at oil-water interfaces. The pendent hydroxyl groups in the repeating units of PVA are expected to produce strong interactions with any untreated $-\text{OC}_2\text{H}_5$ group from silica or residual silanol groups generated from hydrolysis-condensation reaction of TEOS (H. Zou, S. S. Wu and J. Shen, *Chem. Rev.*, 2008, 108, 3893). This hypothesis has been confirmed by the control experiment which indicated that collapsed hollow particles can also be obtained from the emulsion droplets containing TEOS without PS-PEO addition (Fig. S3c and S3d). However, hierarchical particles decorated with budded vesicles could not be obtained in the absence of the interfacial instabilities induced by the PS-PEO.

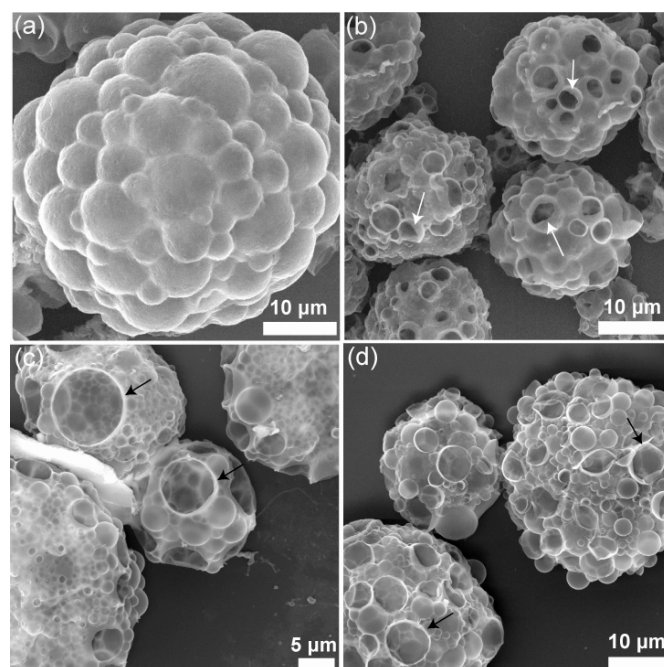


Fig. S4. SEM images of the hybrid budding vesicles formed from emulsion droplets containing 10 mg mL^{-1} PS_{38k}-PEO_{11k} and 0.75 mol L^{-1} TEOS at pH=10. h was set to $\sim 5.5 \text{ mm}$. Clearly, vesicles on the surface of the microparticles were preserved during analysis although part of the bigger vesicles (above $\sim 5 \text{ }\mu\text{m}$) was broken (as indicated by arrows) in (b-d).

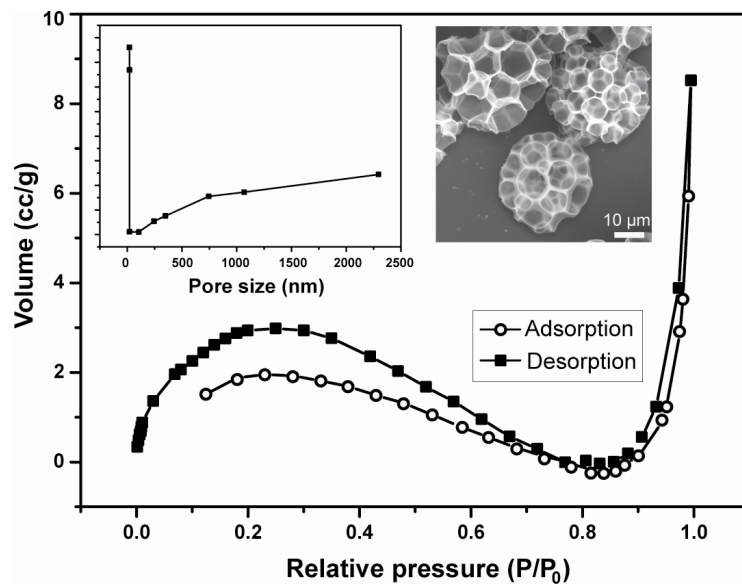


Fig. S5. Nitrogen adsorption-desorption isotherms, pore size distribution (left inset), and the SEM (right inset) image of the microparticles which were formed from emulsion droplets containing 10 mg mL^{-1} PS_{38k}-PEO_{11k} and 0.3 mol L^{-1} TEOS at pH=10.

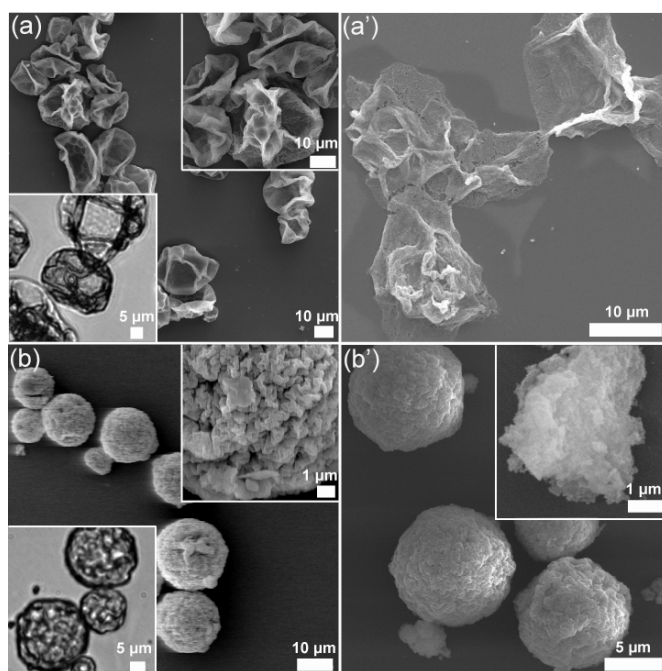


Fig. S6. SEM images of the hybrid aggregates formed from emulsion droplets containing 10 mg mL^{-1} PS_{38k}-PEO_{11k}, 0.3 mol L^{-1} TEOS, and 1.5 μmol L^{-1} TBOT with different pH value: (a) pH=1, microparticles with collapsed surfaces; (b) pH=7, microparticles with rough surfaces; (a', b') are the SEM images of the corresponded microparticles after calcination at 400 °C for 4h. In all the samples, h was set to $\sim 5.5 \text{ mm}$. Insets in the upper right are the enlarged SEM images while insets in the lower left are the corresponded optical micrographs of the particles.

Clearly, in an acidic aqueous solution, collapsed hollow particles were obtained, as shown in Fig. S6a. Presumably, TBOT has a fast hydrolysis rate and thin inorganic shell will form at the relatively early stage of the evaporation. The formed hollow capsules with thin shell will collapse during sample preparation. Yet, in the neutral aqueous system, the TBOT can be hydrolyzed quickly into titanium oxide, cross linking with silicon oxide, to form a solid shell on the surface of the emulsion droplets. In this case, no obvious interfacial instability can be observed under optical microscopy investigation, and microparticles with rough surface were obtained, as shown in Fig. S6b.

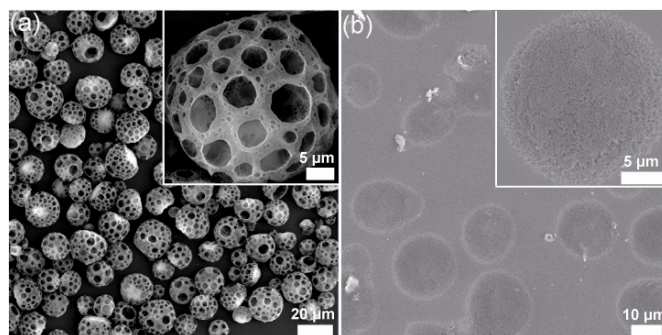


Fig. S7. SEM images of the cage-like microparticles (a) before and (b) after calcinations at 400 °C for 4h. The microparticles were formed from emulsion droplets containing 10 mg mL⁻¹ PS_{38k}-PEO_{11k}, 0.1 mol L⁻¹ TEOS, and 1.5 μmol L⁻¹ TBOT at pH value of 10. *h* was set to ~ 5.5 mm. Similar cage-like microparticles (as compared to the microstructures in Fig. 2a in the text) with thin shell and macropores were formed when fairly lower concentration of TEOS (0.1 mol L⁻¹) and TBOT (1.5 μmol L⁻¹) was added to the initial polymer solution (see Fig. S7a). However, the microparticles were collapsed and can not keep their intact after calcination, as displayed in Fig. S7b.

Supplementary Movies:

Movie S1: Evolution of the morphology of emulsion droplets containing 10 mg mL⁻¹ PS_{38k}-PEO_{11k} and 0.3 mol L⁻¹ TEOS as chloroform evaporation. 5 mg mL⁻¹ PVA was added to the aqueous phase to stabilize the emulsion droplets while pH value of the aqueous solution was adjusted to 10 by adding ammonium water. Fast solvent evaporation rate was achieved by setting *h* to ~ 1.4 mm. During solvent evaporation, emulsion droplets will shrink first, interfaces of the solvent/water become rough, tiny vesicles appear, grow, ultimately yielding budding vesicles. The movie was speeded up for 60 times to clearly show the evolution of the emulsion droplets.

Movie S2: Evolution of the morphology of emulsion droplets containing 10 mg mL⁻¹ PS_{38k}-PEO_{11k} and 0.3 mol L⁻¹ TEOS as chloroform evaporation. 5 mg mL⁻¹ PVA was added to the aqueous phase to stabilize the emulsion droplets while pH value of the aqueous solution was adjusted to 10 by adding ammonium water. Slow solvent evaporation rate was achieved by setting *h* to ~ 5.5 mm. During solvent evaporation, emulsion droplets will shrink first, interfaces of the solvent/water become rough; spines will appear, grow, retract back and tie up, ultimately yielding budding vesicles. The movie was speeded up for 60 times to clearly show the evolution of the emulsion droplets.