

Electronic Supplementary Information

One-step preparation of hydrophilic-hydrophobic asymmetric bilayer microcapsules via photopolymerization

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1. Materials and Methods

1.1 Materials

Dichloromethane (DCM, 99.5%), n-hexadecane (99%), poly(vinyl alcohol) (PVA, $M_w \sim 85$ kDa, 87%–89% hydrolysed) and benzoic acid (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai China). Photoinitiator (1173) and polyurethane acrylate with 4 functionality (PUA, 6170) were provided by Eternal chemical Co., Ltd (Taiwan China). Epoxidized soybean oil acrylate (AESO, RY1202) was purchased from Jiangsu Kailin Ruiyang Co., Ltd (Changzhou China). Water-based epoxy resin (LLA-10) and curing agent (LLG-119) was supported by Jiangsu Lanling Chemical Group Co., Ltd (Changzhou China). Deionized water was obtained from Jiangnan University. All chemical reagents were used without further purification.

1.2 Preparation of hydrophilic-hydrophobic asymmetric bilayer microcapsules

Firstly, 0.5 g of hydrophilic shell-formation material (PUA), 0.5 g of hydrophobic shell-formation material (AESO), 1 g of n-hexadecane (core material), 3 g of DCM (solvent) and 0.02 g of photoinitiator (1173) were mixed to form a homogeneous oil phase. Then the oil phase was added into 40 mL of PVA aqueous solution (2 wt%), and the mixture was placed on a homogenizer and stirred at 10000 rpm for 2 min to obtain initial emulsion. Subsequently, the initial emulsion was added into a beaker and stirred at 40°C for 4 h to remove DCM, which was followed by exposure to ultraviolet light irradiation (365 nm) for 10 min. After washing with deionized water three times and drying at room temperature, the hydrophilic-hydrophobic asymmetric bilayer microcapsules were obtained. Monolayer microcapsules were prepared with the identical method, in which only a single type of UV-curable prepolymer (PUA or AESO) was selected as the shell-formation material.

1.3 Characterization

The morphology of microcapsules was investigated using scanning electronic microscope (HITACHI, S-4800). The particle size and distribution of microcapsule were measure by ImageJ. The element content of individual shell was characterized by EDS. The water contact angle of microcapsule was investigated by optical contact angle measuring system (LAUDA, OCA15EC), where 5 μ L water was dripped on the surface of compacted microcapsule samples at room temperature. To investigate the dispersibility of microcapsules in water, microcapsules (5 wt%) were added in water and dispersed by ultrasonic cleaner for 5 min. The dispersion of microcapsule in water was observed by optical microscope (NIKON, E200). For microcapsules dispersed in water-based epoxy resin, a high-speed dispersion machine (FLACKTEK, DAC 330-100 SE) was used, where the speed was 3000 rpm and the time was 2 min. After curing at 70 °C for 12 h, the water-borne epoxy coating with 5 wt% microcapsules suffered brittle fracture, and the cross section was observed by scanning electronic microscope (HITACHI, S-4800). The water-resistance property of microcapsule was characterized by UV-Vis spectrophotometer (PERSEE, TU-1950). Microcapsules were prepared with an extra 2.5 mg of benzoic acid in the oil phase. 0.5 g of microcapsules were dispersed in 60 mL of water. 3 mL supernatant was periodically collected, and the absorbance at 227 nm was tested by UV-Vis spectrophotometer, while an equal volume of pure water was added. The mechanical properties of the microcapsules were characterized qualitatively and quantitatively by pressing and nanoindentation respectively. Microcapsule dispersions were added dropwise to slides, then it was covered with coverslips and pressed by a 500 g standard weight. The breakage of the microcapsules was observed through optical microscope (NIKON, E200). The hardness and Young's modulus of the microcapsules were tested by nanoindentation (BRUKER, Hysitron TI980) with Berkovich indenter (TI -0039), where the compression force was set as 500 μ N and the indentation time was 2 s. The solvent resistance of microcapsule was tested with acetone as the solvent. The microcapsules were soaked in acetone for 10 min followed by filtering, and the morphology changes were observed by scanning electronic microscope (HITACHI, S-4800) after drying. The chemical structure of microcapsules was characterized by Fourier-transform infrared spectrometer (FTIR, Nicolet 6700) in the range of 4000-400 cm^{-1} . The core material loading capacity and thermal stability of microcapsule was characterized using thermogravimetric analyzer (METTLER, 1100SF), where the samples were heated from 50 °C to 600 °C under a nitrogen atmosphere, and the heating rate was 20 °C/min. The molecular weight of UV-curable prepolymer was characterized by GPC (TOSOH, HLC-8320GPC). The yield

of microcapsules was calculated according to the following formula:

$$Yield (\%) = \frac{M_{microcapsule}}{(M_{PUA} + M_{AESO})} \times 100\%$$

where $M_{microcapsule}$ was the mass of the obtained microcapsule, M_{PUA} was the feeding mass of PUA, and M_{AESO} was the feeding mass of AESO.

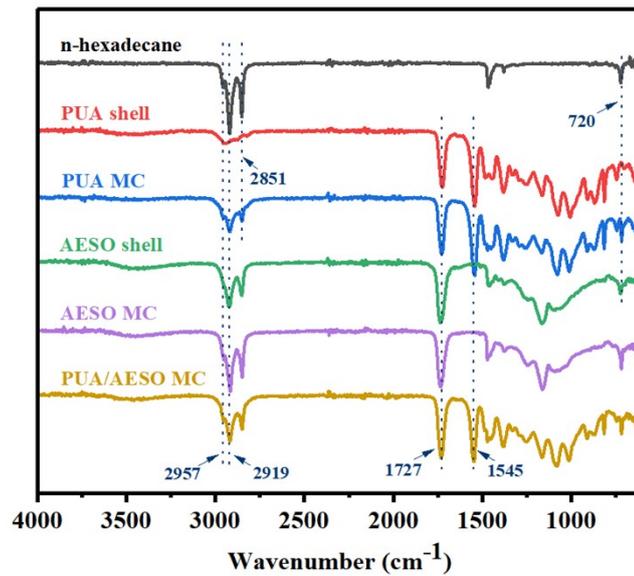


Fig.S1 FTIR spectra of pure n-hexadecane, monolayer PUA microcapsule, AESO microcapsule and PUA/AESO bilayer microcapsules.

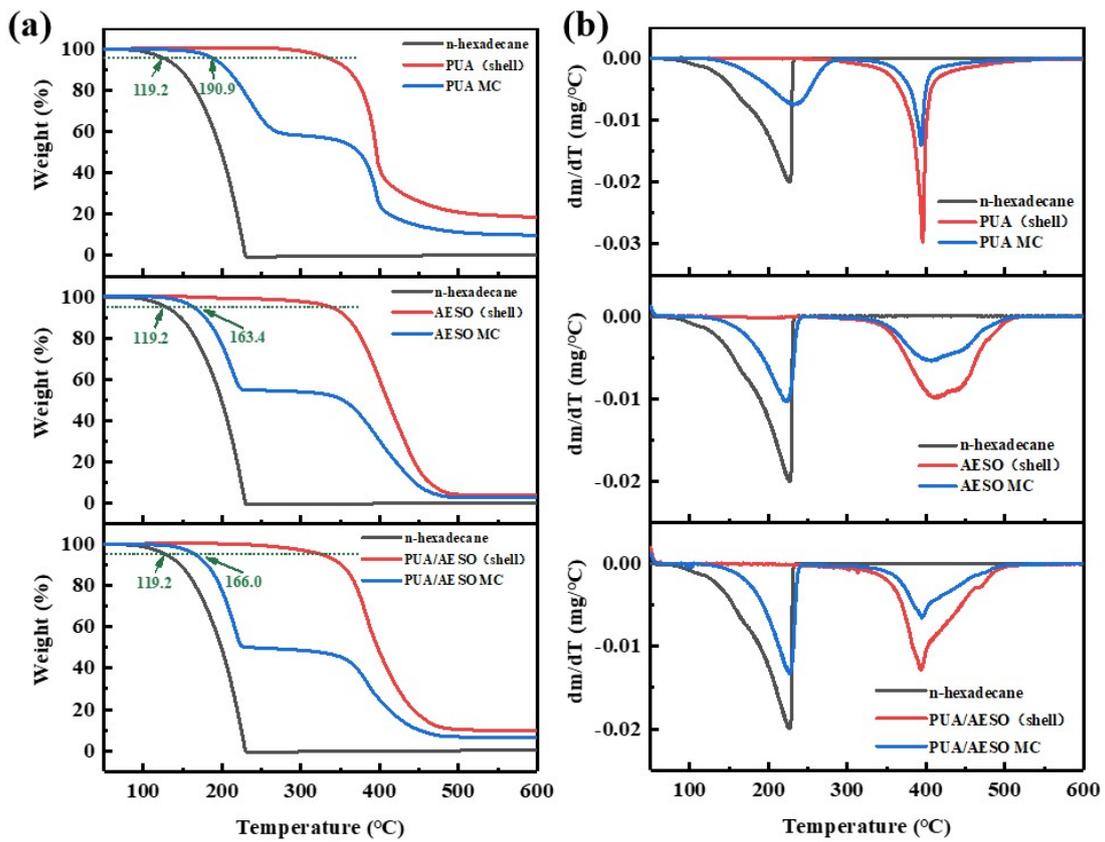


Fig. S2 The TGA (a) and DTG curves (b) of pure n-hexadecane, monolayer PUA microcapsule, AESO microcapsule and PUA/AESO bilayer microcapsules.

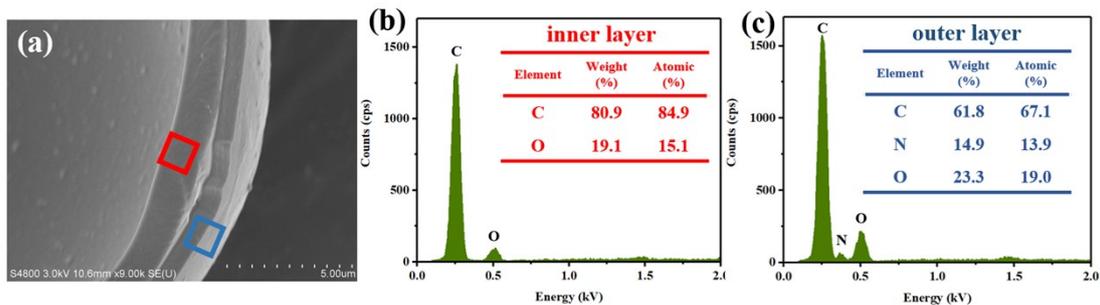


Fig. S3 (a) SEM images of the broken PUA/AESO bilayer microcapsules. EDS spectra of the inner shell (b) and outer shell (c) of the microcapsules. Inset: the content of each element.

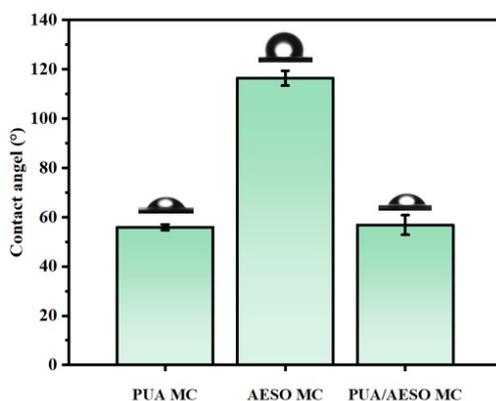


Fig.S4 Water contact angle of monolayer PUA microcapsules, monolayer AESO microcapsules and PUA/AESO bilayer microcapsules.

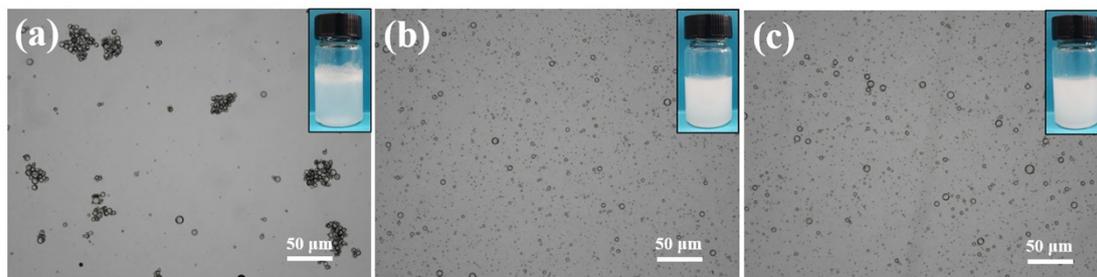


Fig.S5 Optical microscope images of water dispersed with microcapsules (5 wt%). Inset: the digital photograph of the microcapsule dispersion after standing for 5 min.

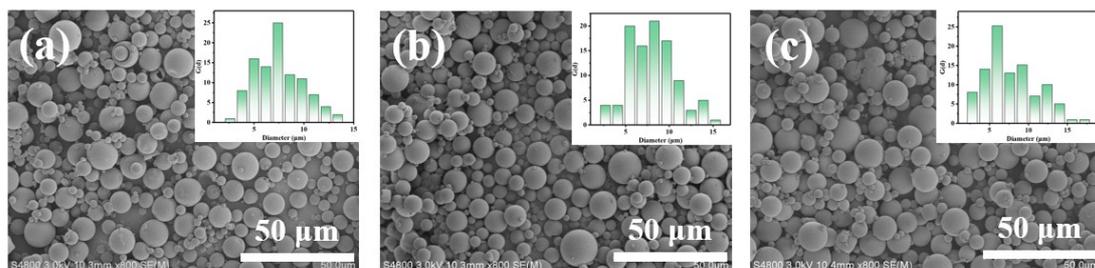


Fig. S6 SEM images of bilayer microcapsules prepared with different PUA/AESO ratios. Inset:

the particle size distribution of microcapsule. (a) PUA/AESO=2:1, (b) PUA/AESO=1:1, (c)
PUA/AESO=1:2

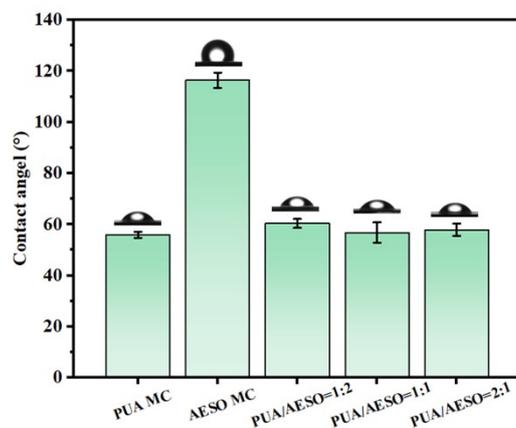


Fig. S7 Water contact angles of monolayer PUA microcapsule, monolayer AESO microcapsule and bilayer microcapsules with different thickness ratios of PUA shell/AESO shell.

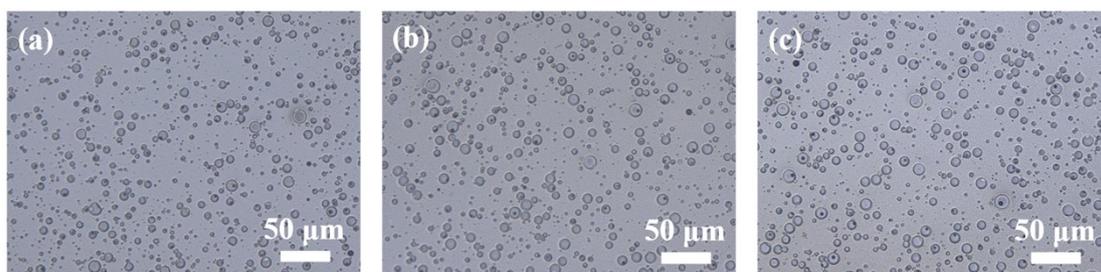


Fig. S8 Optical microscope images of water dispersed with bilayer microcapsules (5 wt%). (a) PUA/AESO=2:1, (b) PUA/AESO=1:1, (c) PUA/AESO=1:2

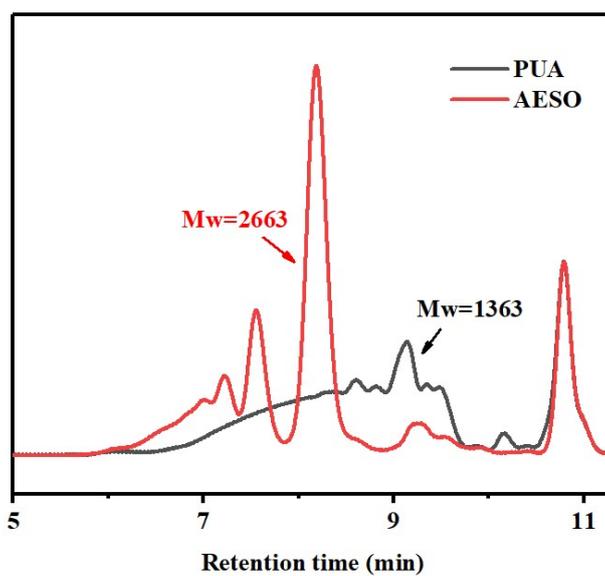


Fig. S9 GPC curves of PUA and AESO.

Table S1 The shell thickness of microcapsules with different PUA/AESO ratios

	Shell thickness (μm)			The ratio of outer and inner shell
	Total shell	Outer shell	Inner shell	
2:1	1.29	0.83	0.46	1.80:1
1:1	1.41	0.68	0.73	0.93:1
1:2	1.65	0.63	1.02	0.62:1