Supporting information for

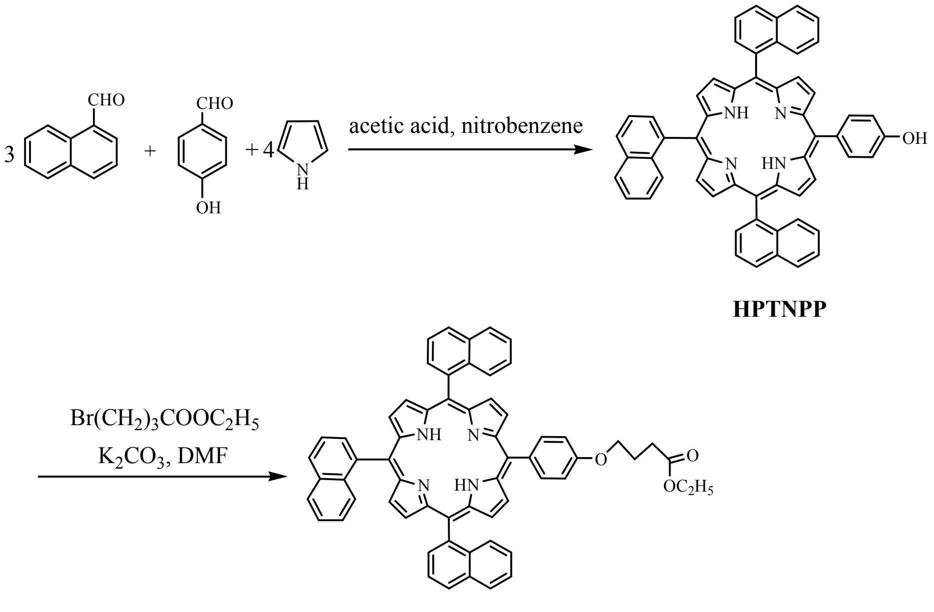
Simultaneous Synthesis/Assembly of Anisotropic Cake-shaped Porphyrin Particles toward Colloidal Microcrystals

Ting Wang,† Minxuan Kuang,† Feng Jin, Jinhua Cai, Lei Shi, Yongmei Zheng, Jingxia Wang,*and Lei Jiang

1. Experimental

1.1 Synthesis of 5-(4-(ethylcarboxypropoxy)phenyl)-10,15,20-tri(naphthyl) porphyrin (CPTNPP)

CPTNPP was prepared by the scheme S1.



CPTNPP

Scheme S1. Synthetic procedure of CPTNPP

Firstly, HPTNPP was synthesized by the method similar to the literatures.[1] In detailed, 4.7 g naphthalaldehyde (30 mmol) and 1.2 g 4-hydroxybenzaldehyde (10 mmol) were dissolved in a mixture of acetic acid (120 ml) and nitrobenzene (60 ml). 2.7 g pyrrole (40 mmol) was added into the system followed by the temperature of system was raised to 120°C, and the system was kept at 120 °C for 1.5 h. Finally, the solution was then allowed to cool to room temperature and purple residues were obtained by filter. The crude material was purified on a silica gel chromatograph using $CHCl_3$ as an eluent. The second band was collected and the solvent was evaporated. Purple solid HPTNPP was obtained in 2.6% yield.

ESMS [$CHCl_3$, *m*/*z*]: 781 ([HPTNPP]$^+$).

1H NMR (300MHz, $CDCl_3$): 8.56-8.58 (d, 8H, β-pyrroles),8.04-8.07 (d, 2H, 2,6-phenyl), 8.43-8.47(d, 6H, 2,8- naphthyl), 8.12 (s, 3H, 4- naphthyl), 7.53-7.57(d, 6H, 3,5- naphthyl), 7.45-7.49(d, 6H, 6,7- naphthyl), 7.11 (d, 2H, 3,5-phenyl), −2.36 (s, 2H, NH, pyrrole).

CPTNPP was synthesized by esterification reaction of HPTNPP. A mixture of 0.3902 g HPTNPP, 1.8 g K_2CO_3 and 50 mL N,N-Dimethylformamide(DMF) was stirred at 90 °C. 2mL ethyl 4-bromobutyrate dissolved in 5ml DMF was added dropwise. After 10 h, the mixture was washed with H_2O several times to neutrality, drying over anhydrous Na_2SO_4 and concentrating via rotary evaporation, the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. The first band was collected and the solvent was evaporated. Purple solid CPTNPP was obtained in 85% yield.

ESMS [$CHCl_3$, *m*/*z*]: 895.3([CEPTNP]$^+$).

1H NMR (300MHz, $CDCl_3$): 8.53-8.57 (d, 8H, β-pyrroles), 8.05-8.07 (d, 2H, 2,6-phenyl), 8.41-8.46(d, 6H, 2,8- naphthyl), 8.10 (s, 3H, 4- naphthyl), 7.76-7.78(d, 6H, 3,5- naphthyl), (7.41-7.47(d, 6H, 6,7-naphthyl), 7.18 (d, 2H, 3,5-phenyl), 4.16-4.26 (s, 4H, C–CH_2–O), 2.26(s, 2H, C-CH_2-C=O), (1.51 (s, 2H,C- CH_2-C), 1.29 （d, 3H, CH_3-C-）−2.39 (s, 2H, NH, pyrrole).

1.2 Substrate preparation

Hydrophobic silicon wafers **(FAS-modified Si)** were obtained by FAS-treated of hydrophilic silicon wafer. After being blown dry with a flow of high purity argon, the hydrophilic silicon wafers were then placed in a desiccator together with a vial containing liquid 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FAS-17) (Alfa Aesar). The desiccator was evacuated, and the sample was kept in the desiccator for 12 h at 85°C. Finally, the sample was taken out and baked in an oven at 60°C for 1 h. The water CA of the FAS-modified silicon wafer is 110.8±1.5°。

1.3 Self-assembled of cake-shaped colloidal crystals

Cake-shaped colloidal crystals were fabricated by three steps: firstly, CPTNPP suspension is prepared by dispersing the CPTNPP chloroform solution (10^{-6} ~ 10^{-5} mol/L) into IPA in a changing volume fraction from 75%, to 66.7%, to 50%, to 33.3%, to 25%. Secondly, after being ultrasonicated for 0.5 h at room temperature, the mixing dispersion is casted onto the previously-prepared hydrophobic substrate, followed by the formation of water droplet template owing to solvent evaporation. Accompanied with the encapsulation of water droplet template by CPTNPP suspension and solvent evaporation, the cake-shaped porphyrin colloidal crystals were fabricated. The shape of the cake-shaped colloidal crystals can be modified based on the change of the solvent ratio in CPTNPP suspension.

1.4. Characterization

The cake-shaped assemblies were characterized by SEM (S-4800, Japan Hitachi) operating at 5.0 kV. Transmission electron microscopy (TEM) images of latex spheres were obtained with a H800 transmission microscopic (JEM2010, Japan). AFM images were acquired using an Agilent 5500 AFM (Agilent Corp). UV-vis spectra were collected using a Hitachi U-4100. The morphologies of samples were also characterized by using a polarized optical microscope equipped with a charge-coupled device camera (Panasonic Super Dynamic II WVCP460). Reflection spectra were measured from FTIR (Bruker, VERTEX 70, 36×, NA = 0.5). The apparent water contact angle, sliding angles and the θ_R were measured on an OCA20 machine (DataPhysics, Germany) at ambient temperature. The surface tension of liquids and liquid-liquid interface tension of liquids were determined on an OCA20 machine (Data-Physics, Germany) at ambient temperature, the value was calculated from the shape of the pendant droplet in air or being surrounded by the aqueous phase. Particle distribution of the CPTNPP vesicles is characterized by Malvern Lazer Particle analyzer.

2. Characterization of cake-shaped porphyrin colloidal crystals

2.1 The confirmation of CPTNPP vesicles in the dispersion

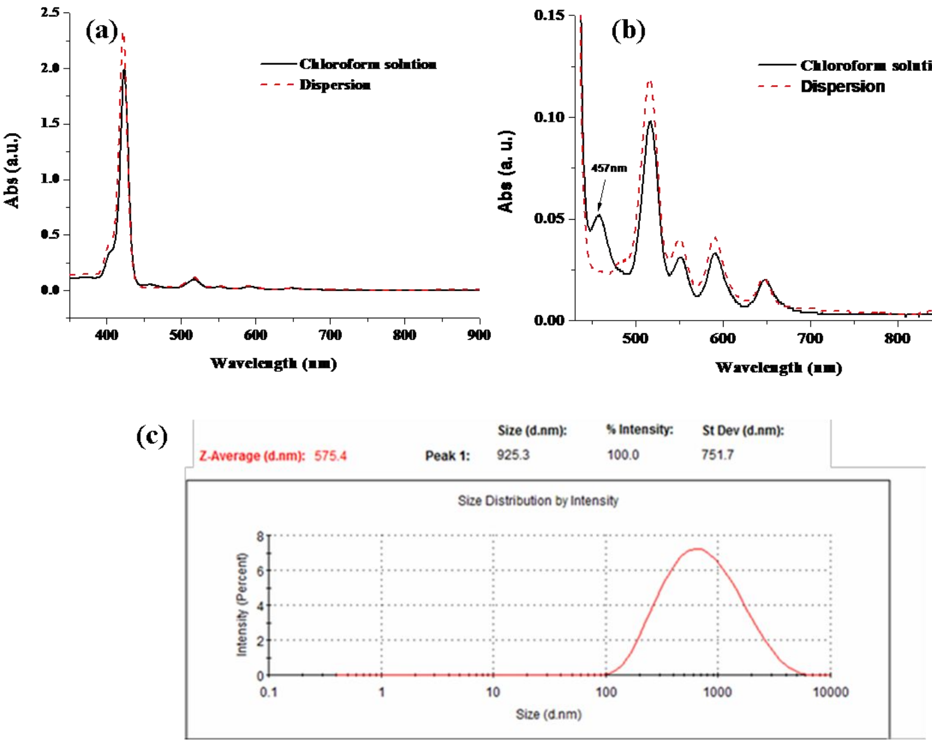


Figure S1. (a, b) UV-vis absorption spectra of the chloroform solution of CPTNPP and the CPTNPP dispersion obtained by mixing its chloroform solution and IPA at the volume ratio of 1:1. (c) Dynamic light scattering data of the CPTNPP dispersion from Malvern Lazer Particle Analyzer.

Figure S1a, b show UV-vis absorption spectra of chloroform solution of CPTNPP and the CPTNPP dispersion. Comparing the spectra of monomeric CPTNPP in chloroform solution, the peak centered at 457.0 nm disappears, and new peak centered at 871 nm emerges for the spectra of CPTNPP dispersion. These phenomena suggest the formation of vesicles in the CPTNPP dispersion.

The data in **Figure** S1c is obtained from dynamic light scattering of Malvern Lazer Particle analyzer for the CPTNPP dispersion. It was found that the as-formed vesicle has average size of 575.4 nm, indicating the presence of the CPTNPP vesicle in the dispersion.

2.2 The orientated arrangement of the porphyrin molecule around the vesicles with hydrophilic ether group toward the exterior and hydrophobic porphyrin core toward the interior.

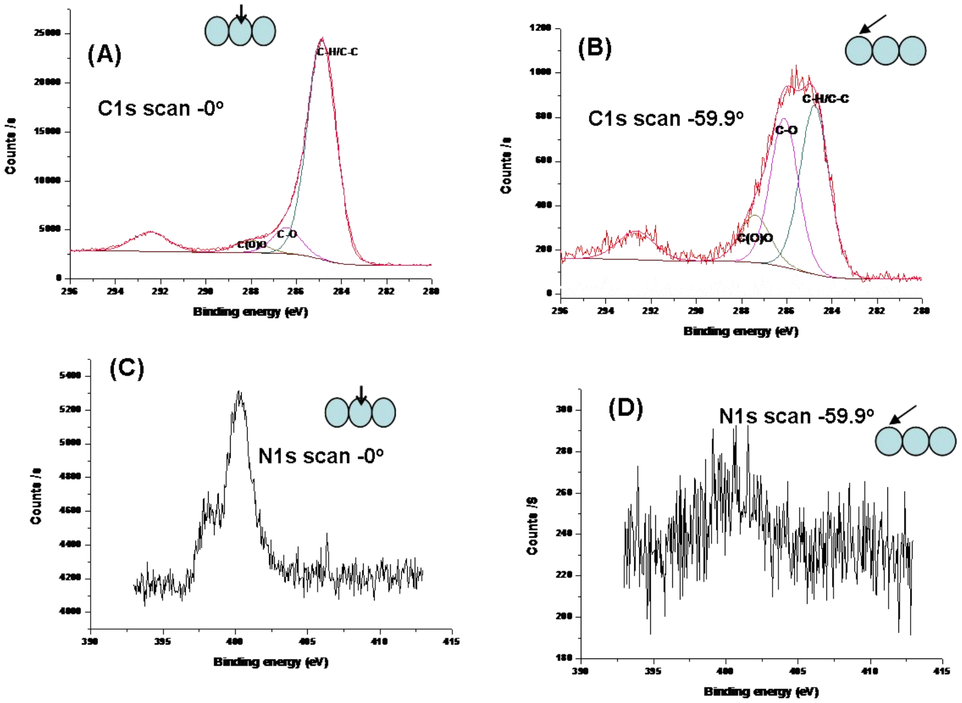


Figure S2. XPS analysis for the as-fabricated cake-shaped colloidal crystals, with measuring angle of (A, C) 0° and (B, D) 59.9°. The inserted cartoon indicates the detecting position of the detecting probe on the sample.

XPS analysis is used to clarify the change of chemical component distribution of the surface of the hole-shell particles. **Figure** S2 presents the XPS result measured at 0° (with detecting probe normal to the surface as indicated in Figure S2A, 2C) and

59.9° (Figure S2B, 2D) for the film assembled from hole-shell particles. There is a broad carbon peak with several kinds of binding energies of 284.7, 286.4, and 287.6 eV, which correspond to functional groups of CH_2, C–O, and C(O)O, respectively.[4]

The comparative results of Broad/strong peaks of C–O and C(O)O (Figure S2B) and trace peak for C-O and C(O)O (**Figure** S2A) confirm that the hydrophilic carboxyl groups mainly are located at the surface of the vesicle. Simultaneously, the decreased N content in the surface of (Figure S2D) particles compared to the interior (**Figure** S2C) is consistent to the distribution of the hydrophobic porphyrin core toward the interior of the vesicle.

2.3 The CPTNPP aggregate

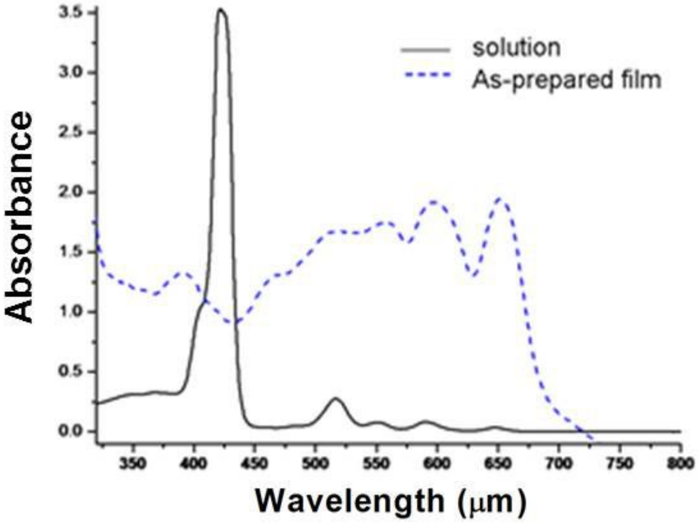


Figure S3. Comparative results of UV-Vis spectra of the CPTNPP solution and as-prepared CCS.

Figure S3 presented UV-Vis spectrum of the as-prepared porphyrin aggregate, indicating the possible aggregate mode of porphyrin molecuels. Compared to the Soret-band of the monomeric CPTNPP dispersed in chloroform (centered at ca. 420 nm), the cake-shaped assemblies display a spitted blue-shifted Soret-band at ca. 391 nm (**Figure S3**) and part red-shifted Soret-band at 464 nm, suggesting that most of the CPTNPPs therein are possibly organized as J-like aggregates.[16] It is worth-noting that, this adsorbent band (~ 650 nm) manifests itself with a relatively sharper profile compared to the broad Q band of the monomeric CPTNPP in **Figure S3**, preliminarily implying the formation of well-orientated aggregation: with the hydrophilic group toward the outside, while the hydrophobic porphyrin core toward the interior. That can be confirmed in XPS result in Figure S2.

2.4 Morphology of cake-shaped colloidal crystals

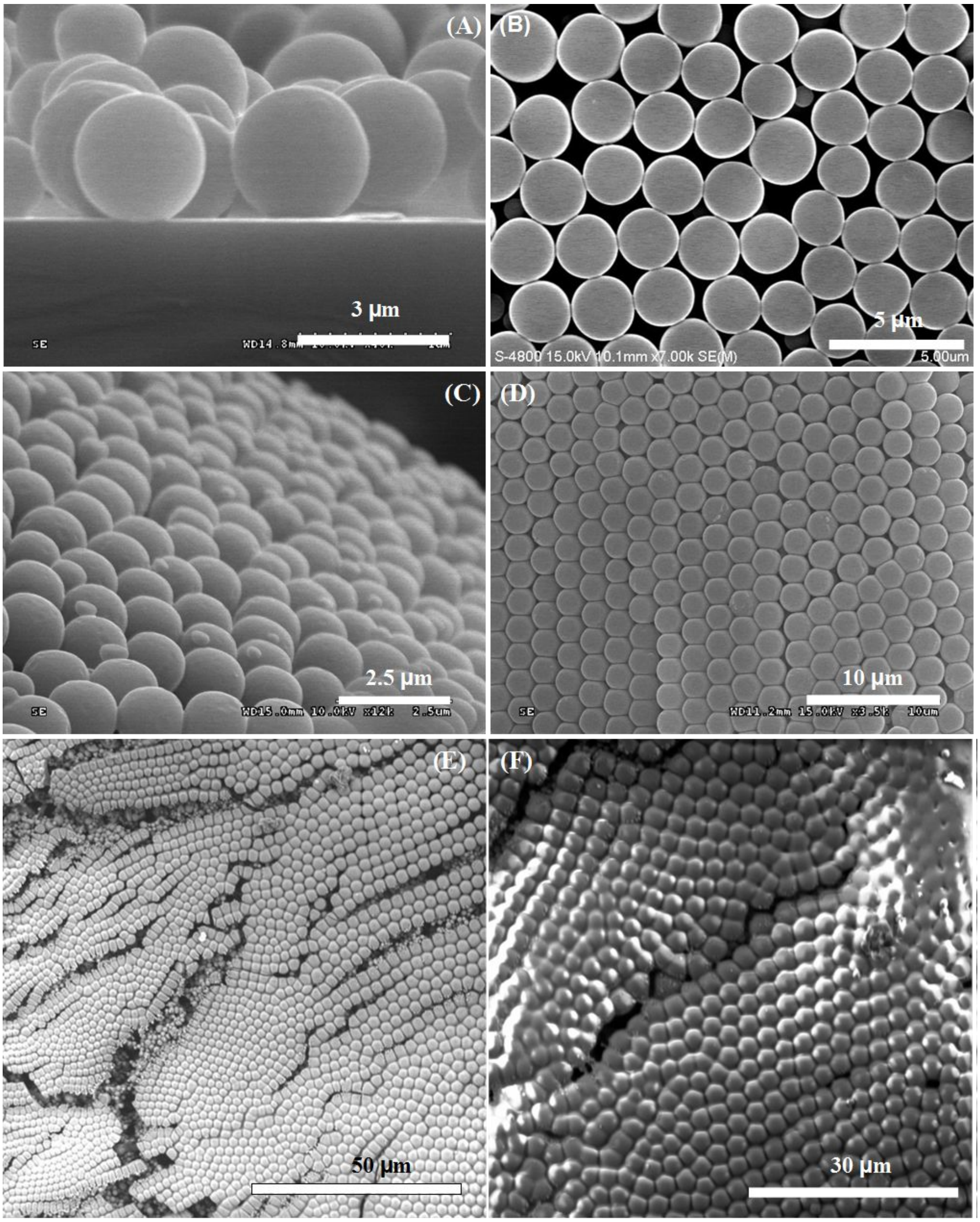


Figure S4. SEM images of the films obtained from porphyrin suspension with volume fraction of IPAof 25% in the CPTNPP suspension. h/D of the particles is 1.

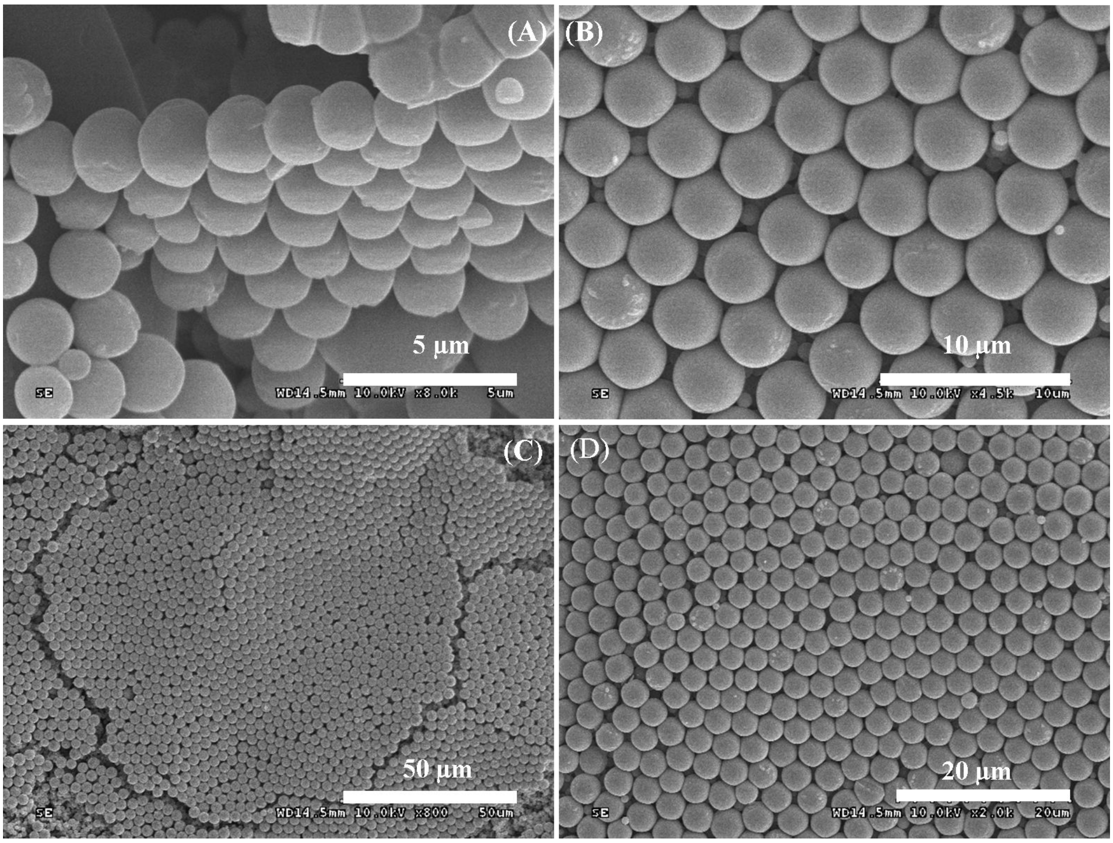


Figure S5. SEM images (A-D) of the films obtained from porphyrin suspension with IPA fraction of 33.5% in the CPTNPP suspension. h/D of the particles is 0.8.

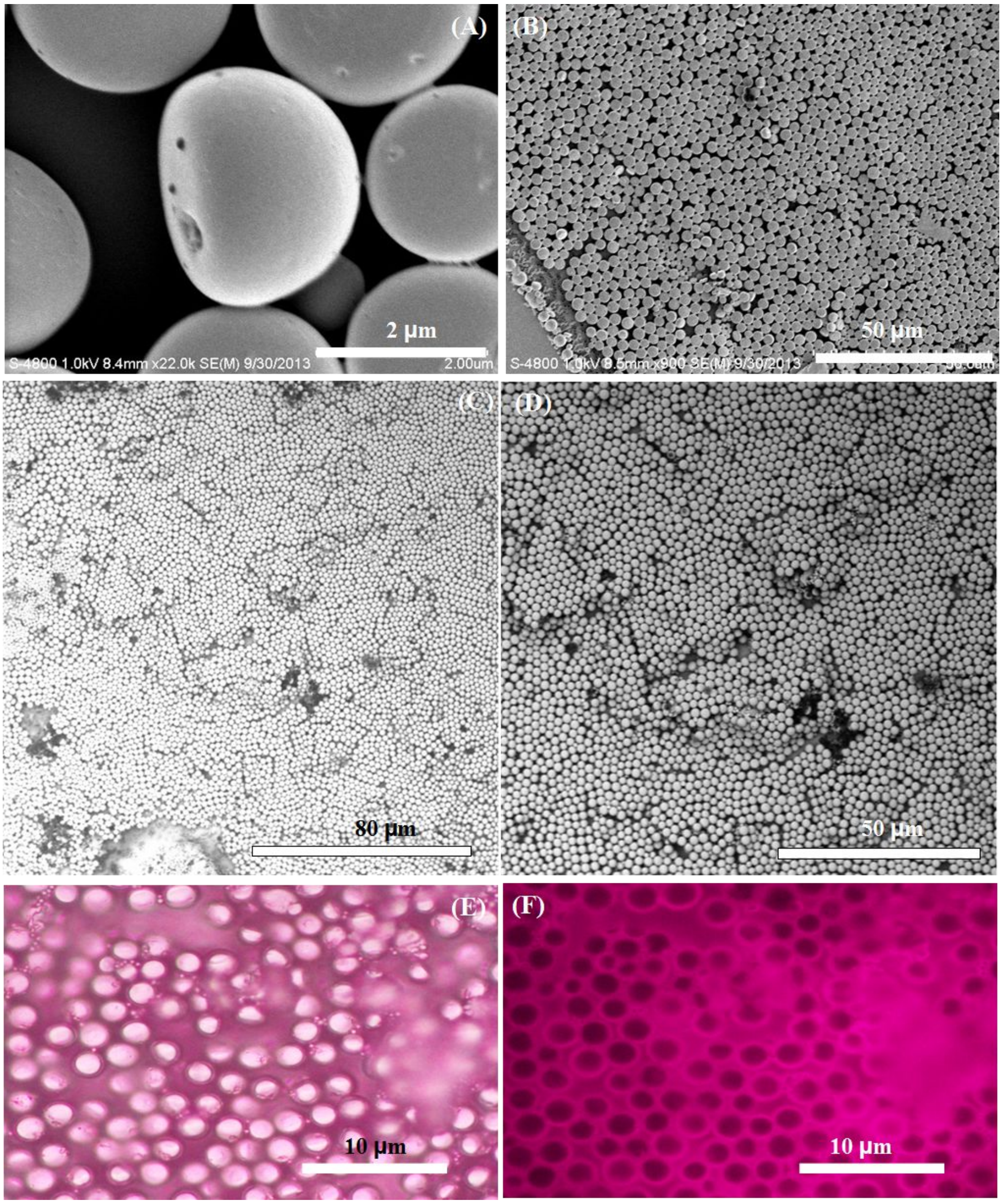


Figure S6. SEM images (A-D) optic image (E), and fluoresent image of the films obtained from prophyrin suspension with IPA fraction of 66.5% in the CPTNPP suspension. The dark image in fluoresent images images the cavity structure in the particles. h/D of the particles is 0.6.

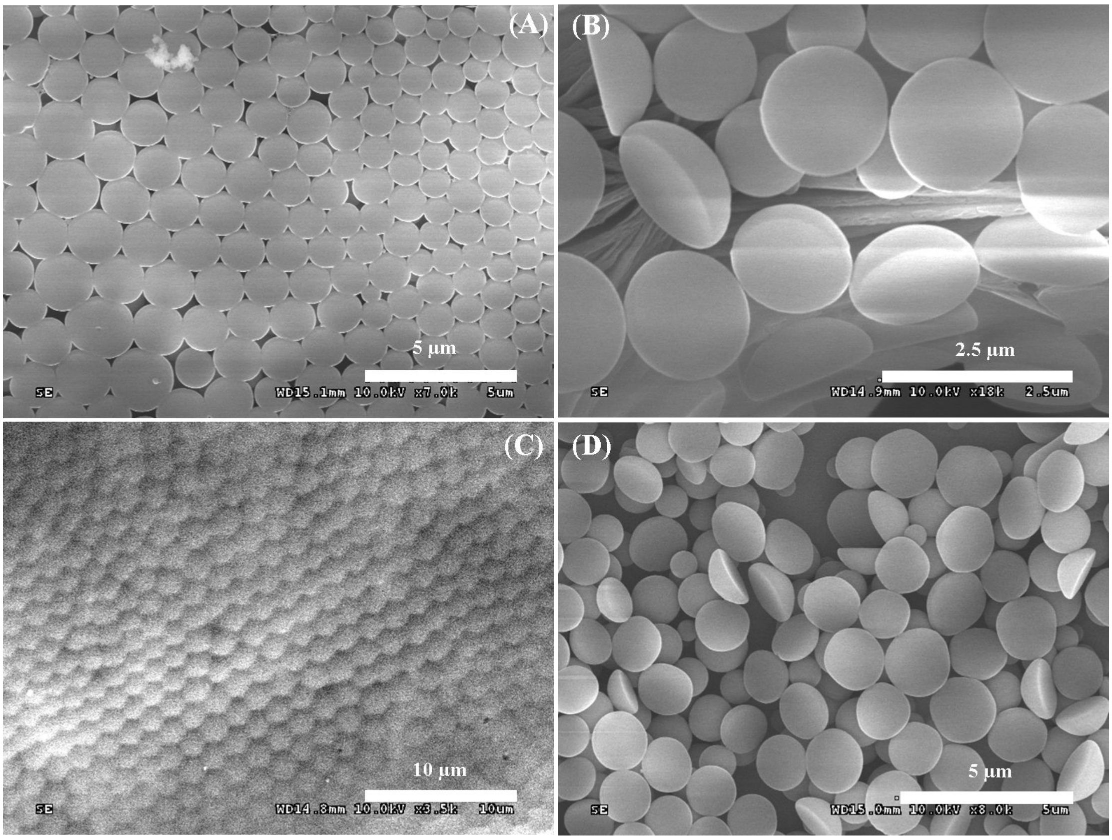
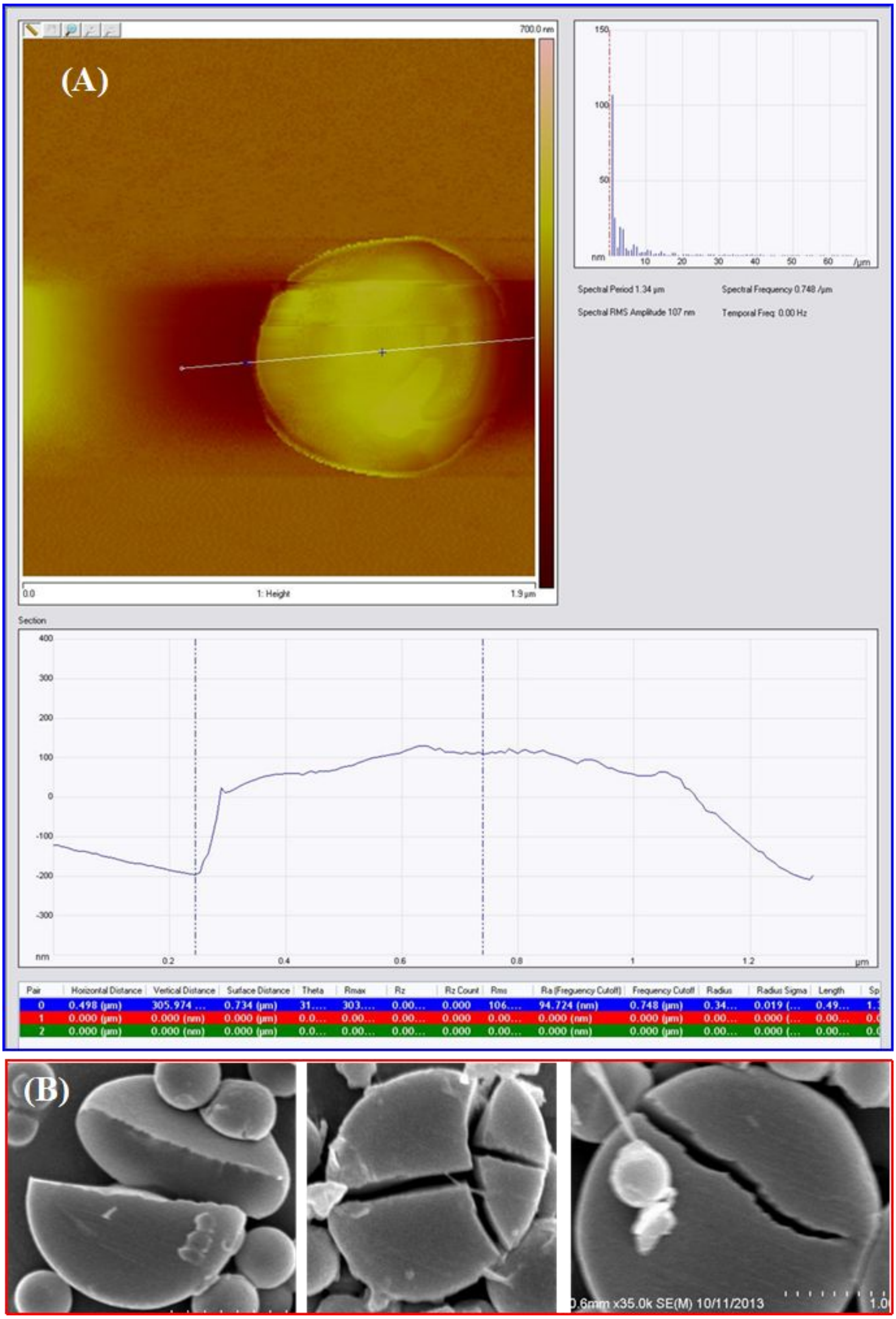


Figure S7. SEM images of the films obtained from prophyrin suspension with IPA fraction of 75% in the CPTNPP suspension. h/D of the particles is 0.33.

(A)



Spectral Period 1.34 µm
Spectral Frequency 0.748 /µm
Spectral RMS Amplitude 107 nm
Temporal Freq: 0.00 Hz

Pair	Horizontal Distance	Vertical Distance	Surface Distance	Theta	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius Sigma	Length	Sp
0	0.498 (µm)	305.974 ...	0.734 (µm)	31....	303....	0.00...	0.000	106....	94.724 (nm)	0.748 (µm)	0.34...	0.019 (...	0.49...	1.
1	0.000 (µm)	0.000 (nm)	0.000 (µm)	0.0...	0.00...	0.00...	0.000	0.00...	0.000 (nm)	0.000 (µm)	0.00...	0.000 (...	0.00...	0.0
2	0.000 (µm)	0.000 (nm)	0.000 (µm)	0.0...	0.00...	0.00...	0.000	0.00...	0.000 (nm)	0.000 (µm)	0.00...	0.000 (...	0.00...	0.0

Figure S8. (A) AFM and (B) SEM images of the cake-shaped CPTNPP particles obtained from CPTNPP suspension with IPA fraction of 75%. H/D of the particles is 0.33.

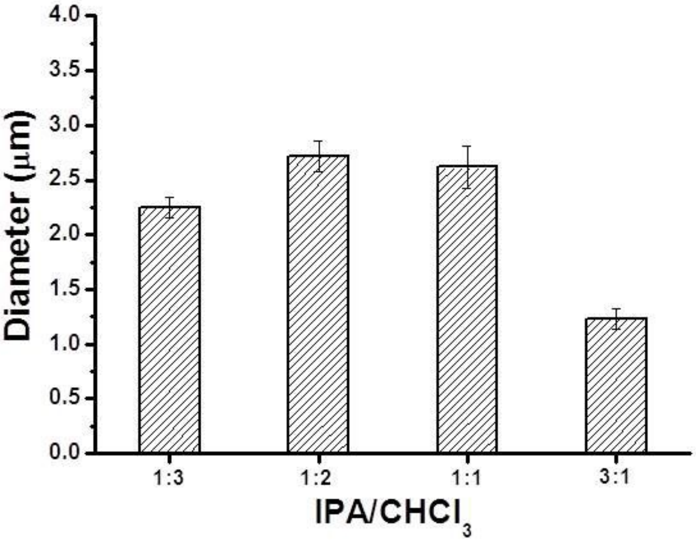


Figure S9. Diameters of as-prepared particles produced from solvent with different ratio of IPA/$CHCl_3$.

3. Prediction of the cake-shaped particles based on the shape of critical water droplet

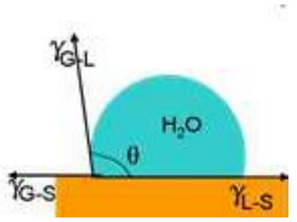


Figure S10. Schematic illustration of water contact angle formed by three phase contact line.

When water droplet sits on the substrate as shown in **Figure S10**, its contact angle(θ) can be calculated by the Young's equation[3] (1).

$$\cos\theta = \frac{\gamma_{s-g} - \gamma_{l-s}}{\gamma_{l-g}} \qquad \text{-----(S1)}$$

Wherein, $\gamma_{s\text{-}g}$ is the surface energy of the substrate, γ_{l-s} is the adhesion energy of the liquid on the substrate. γ_{l-g} is the surface tension of the water.

When water droplet is condensed onto the surface of porphyrin suspension as shown in **Figure S11**, part of IPA would penetrate into the water droplet, forming aqueous phase, and the other IPA left in the porphyrin disperion act as oil phase. With the solvent evaporation, the porphyrin vesicles would encapsuate around the aqueous phase, forming the W/O system in Figure S11c. the porphyrin vesicles would encapsulated around the water droplet template owing to the solvent evaporation.

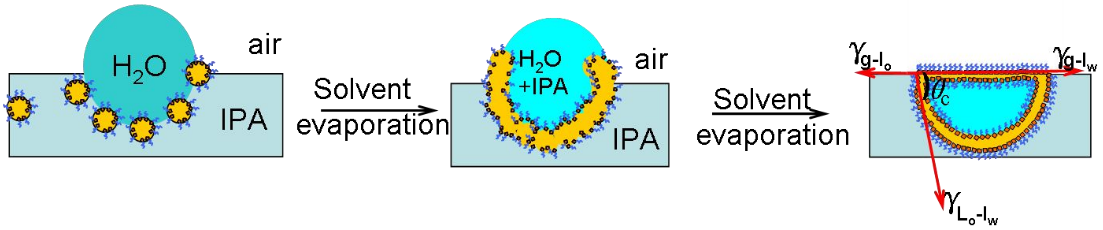


Figure S11. Evolution process of water droplet after condensed onto the interface of air and porphyrin suspension.

When the TCL of the water droplet stop receding,[1] approaching the critical water droplet, its contact angle (θ_c) can be calculated based on the modified Young's equation.

$$\cos\theta_c = \frac{\gamma_{g-lo} - \gamma_{g-lw}}{\gamma_{lw-lo}} \qquad \text{-----(S2)}$$

Wherein, *lw* is aqueous phase, *lo* is oil phase. (here, we neglect the effect of CPTNPP on the system to simplify calculation). γ_{w-g} and γ_{o-g} are the surface tension of aqueous phase and oil phase in air respectively. γ_{lw-lo} is the aqueous/oil interfacial tension.

The definition of H/D by the critical contact angle

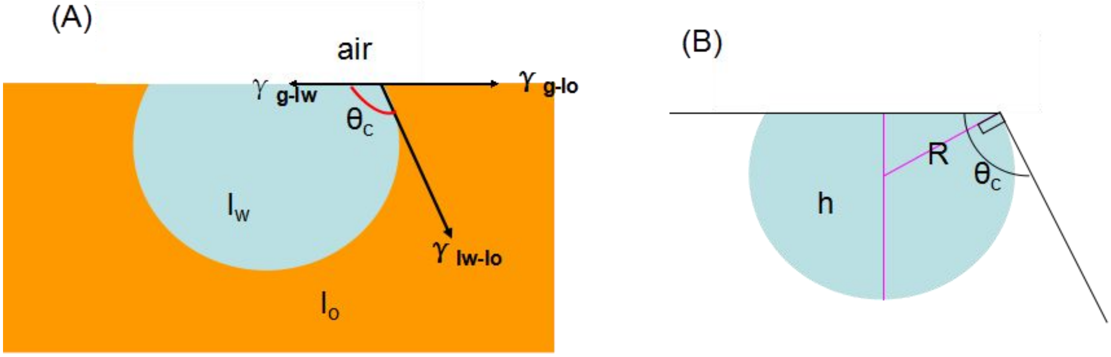


Figure S12. Schematic illustration for the definication of the *h/D* of the cake-shaped particles by critical contact angle.

$$\frac{h}{D} = \frac{\left[1 + \sin(\theta_c - \frac{\pi}{2})\right]R}{2R} = \frac{1 - \cos\theta_c}{2} \qquad \text{----------------(S3)}$$

Table S1. The surface tension of the oil phase

IPA fraction in oil phases (vol%)	0	5	15	25	35	45	55
Surface tension (Nm/S)	26	25	24.5	24	22	21	20

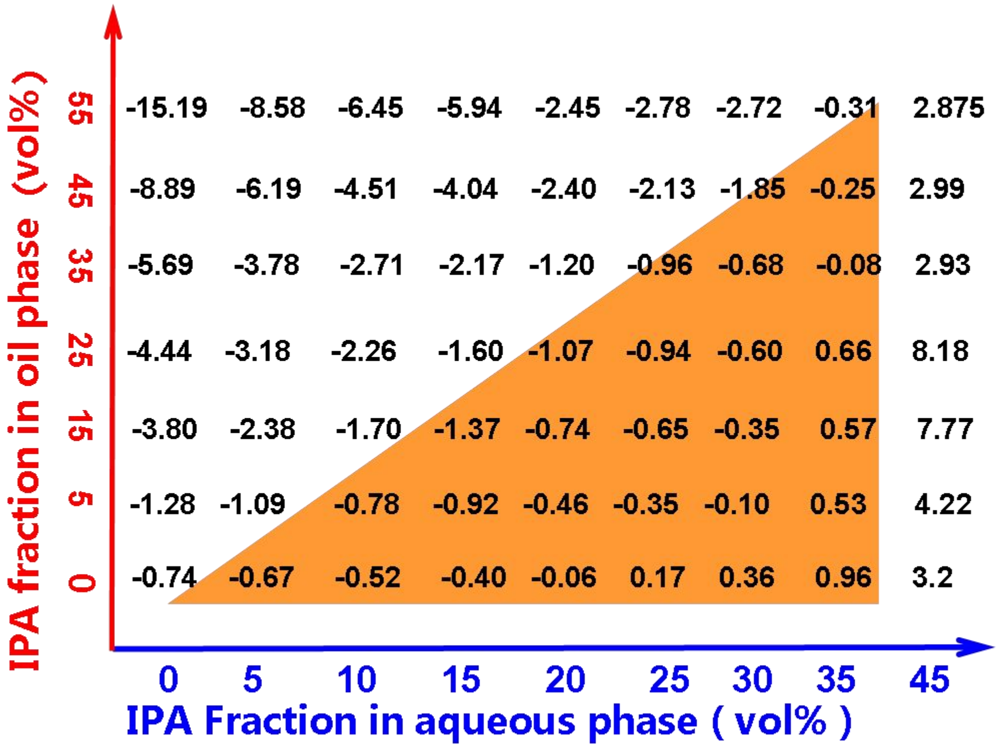
Table S2. The surface tension of the aqueous phase

IPA fraction in aqueous phases(vol%)	0	5	10	15	20	25	30	35	45
Surface tension (Nm/S)	72	49.5	42.5	37.4	36.6	29.5	23.6	22	21.7

Reference:

[1] Xu, J.; Xia, J. F.; Hong, S. W.; Lin, Z. Q.; Qiu, F.; Yang, Y. L. Self-Assembly of Gradient Concentric Rings via Solvent Evaporation from a Capillary Bridge, *Phys. Rev. Lett.*, **2006**, 066104

Table S3. The cosθ_c calculated from equation S2



	0	5	10	15	20	25	30	35	45
55	-15.19	-8.58	-6.45	-5.94	-2.45	-2.78	-2.72	-0.31	2.875
45	-8.89	-6.19	-4.51	-4.04	-2.40	-2.13	-1.85	-0.25	2.99
35	-5.69	-3.78	-2.71	-2.17	-1.20	-0.96	-0.68	-0.08	2.93
25	-4.44	-3.18	-2.26	-1.60	-1.07	-0.94	-0.60	0.66	8.18
15	-3.80	-2.38	-1.70	-1.37	-0.74	-0.65	-0.35	0.57	7.77
5	-1.28	-1.09	-0.78	-0.92	-0.46	-0.35	-0.10	0.53	4.22
0	-0.74	-0.67	-0.52	-0.40	-0.06	0.17	0.36	0.96	3.2

Table S3 presents the calculated cosθ_c from equation S6 based on data of surface tension (from **Table** S1, S2). It can be found that only data in orange red region is valid. This indicates that the chloroform vesicle can stably encapsulate around water droplet (W/O system), is suitable for the formation of hole-shell assembly.

Table S4. The CA of the the aqueous phase, oil phase and CPTNPP suspension on FAS-substrate with varying IPA suspension

IPA fraction in aqueous phases(vol%)	0	5	10	15	20	25	30	40	50
Water CA(°)	115	110	90	88	86	80	78	70	68
IPA suspension in oil phase	0	5	15	20	25	30	40	45	50
Water CA(°)	65	60	54	50	48	47	46	42	38

It can been taken from Table S4 that the water CA of the sample decreased when increased the IPA fraction in the solution, which indicates that the increase of IPA fraction in the liquid will lead to increased spreading area and rapid evaporation rate.