Supporting Information

**Spreading-induced dewetting for monolayer colloidosomes with responsive permeability**

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**Experimental Section:**

1. Materials:

All chemicals were used as received without purification. N,N-Dimethylformamide (DMF) (99.9\%, anhydrous), ethanol (99\%) were from VWR. Tetraethyl orthosilicate (TEOS) (98\%), sulforhodamine B (75\%, $M_w \sim 580.66$), sodium chloride (99.5\%), L-arginine ((98\%), dichloromethane (99.8\%), oxalyl chloride (99\%), 1H,1H,2H,2H-perfluoroocylethoxysilane (FAS)(97\%), poly (vinyl alcohol) (PVA, $M_w \sim 13000$-$23000$, 87-89\% hydrolyzed), poly(ethylene glycol) (PEG, $M_w \sim 6000$), Pluronic L31 (PEO-PPO-PEO block copolymer $M_w \sim 1100$), poly(ethylene) diacrylate (PEGDA, $M_n \sim 700$), 2-hydroxy-2-methylpropionic acid (98\%), O,O’-bis(aminopropyl) polypropylene glycol-b-polyethylene glycol-b-polypropylene glycol (Jeffamine ED-900, $M_n \sim 900$) were purchased from Sigma-Aldrich. Ammonium hydroxide solution (28\%) was provided by Acros Organics. Commercially available Krytox 157-FSH (99.9\%, $M_w \sim 5000$) and HFE-7100 (99.5\%) were bought from Miller Stephenson Chemical and 3M, respectively.
Novec™ engineered fluid HFE-7500 (2-(trifluoromethyl)-3-ethoxydodecafluorohexane) was a kind gift from 3M. Heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane and 2-[methoxy(polyethyleneoxy)9-12 propyl]trimethoxysilane were both obtained from Gelest, Inc. Silica spheres of 100 nm were commercialized products bought from US research nanomaterials, Inc.

2. The generation of monodisperse double emulsions by capillary microfluidics

We generated double emulsion droplets using flow-focusing glass capillary device (Movie S2). The device comprised of two tapered cylindrical glass capillaries (World Precision Instruments, Inc.) inserted from opposite ends of a square capillary as illustrated in Fig. S1. The injection tube was aligned with the axes of collection capillary and the encountered cylindrical capillaries were medially placed in the square tube. Thus the inner flow of fluids was directed in injection channel and sheared successively by the middle fluids and outer fluids to form double emulsion droplets. The injection capillary was dipped into a 0.01 vol. % heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane in HFE-7500 solution to affiliate with the middle oil phase. The collection capillary was treated with 2-[methoxy(polyethyleneoxy) 9-12 propyl]trimethoxysilane to be hydrophilic.

The generated double emulsion droplets are stable due to the combination of Krytox-PEG-Krytox surfactant and fluoro-philic silica nanoparticles at the water-oil interfaces. F-Si nanoparticles stabilizes the single water-in-HFE-7500 emulsion droplets, and decreases the tension of the bare water-oil interface from 53 mN/m to 35 mN/m. However, the water-in-HFE-7500-in-water double emulsions cannot be stabilized by F-Si nanoparticles in the middle phase alone. Thus, we synthesize a Krytox-PEG-Krytox surfactant that significantly improves the stability of water-
in-HFE 7500-in-water double emulsions. The fluoro-philic Krytox and hydrophilic PEG blocks adsorb at the interfaces, decreasing its interfacial tension down to 5 mN/m. The resultant double emulsion remains stable for weeks in aqueous environment.

3. The biocompatible surfactant synthesis and characterization

The biocompatible surfactant PFPE-PEG-PFPE was synthesized in two steps: (1) The Activation of Krytox and (2) the Amidation of as-productions. The PFPE-PEG-PFPE surfactant is characterized using FTIR Spectrometer as shown in Supplementary Fig. 2.

In a typical reaction, 18.5 g perfluoro-polyether, Krytox 157-FSH was dissolved in an equal volume of fluorinated solvent, HFE-7100, in a round three-necked flask. One drop of anhydrous DMF was added as catalysis. The activation of perfluorinated carboxylic group was slowly initiated by introducing an excess amount of oxalyl chloride (4.65g) in HFE-7100. The reaction was kept under vigorous stirring in iced water bath. Subsequently, the cloudy yellow mixture was left stirring overnight at 85˚C and refluxing overnight under an argon atmosphere. Then, the remaining traces of unreacted oxalyl chloride and solvent were removed using a rotary evaporator at 65˚C. The activated Krytox was cooled down prior to use.

To incorporate the hydrophilic block part with the fluoro-philic product, a diamine PEG, Jeffamine ED900, was amidated with activated Krytox in the ratio 1:1. The activated Krytox 1 mmol was dissolved in 10 ml anhydrous dichloromethane, and 10 ml HFE-7100 was added subsequently. The mixture was chilled in iced water bath and then was added into pre-chilled Jeffamine ED900 in a dropwise manner. As the amidation was initiated by mixing, the bulk solution turned into milky color and was slowly heated to 65 °C under a nitrogen reflux for 2 days to form the crude product. By-product and solvent were removed using a rotary evaporator. The final product, a milky viscous fluid was obtained by centrifugation (14200rpm) and separation.
(1) The activation of Krytox

Krytox(Mw~5000) Oxalyl Chloride

(2) The amidation of as-productions

Kry-acylchloride PEG(M_w~900)

PFPE-PEG-PFPE block copolymers
4. The synthesis and characterization of as-synthesized silica nanoparticles

The synthesis methods of silica nanoparticles with various size are described herein. A modified stöber method\(^{38}\) was adopted for nanospheres larger than 100 nm. Two solutions with equal volumes were rapidly mixed to give a total volume of 250 ml, where one solution was ethanol and TEOS mixture, and the other was a mixture of ethanol, water and hydroxide ammonium. The reaction solution gradually turned into cloudy fluids and was stirred for 6 hours at room temperature. The mean diameter of the synthesized silica nanospheres was varied from 100 nm to 500 nm, by varying the ammonia concentration from 0.2 to 1.2 M. Meanwhile, the concentration of TEOS and water was kept constant at 0.2 M and 17.0 M respectively.

As stöber method is not suitable for the preparation of <50 nm silica nanospheres, we used L-arginine seed growth method to synthesize the needed silicananospheres ranging from 14 nm to 100 nm\(^{39}\). TEOS was added to the stirring L-arginine (1mM) aqueous solution (molar composition of the reactants was 1 TEOS: 0.02 Arg: 194 H2O), and the pH of the mixture system was tuned to be 9.4. The bulk solution was kept stirring for 24 hours at 343 K. To proceed the seed regrowth, a portion of the seed dispersion was added to the mixture of water, ethanol and L-arginine. Then, TEOS was introduced to the system and the reaction solution was kept stirring for another 24 hours at 343 K. The products were collected in powder form through freeze drying and preserved avoiding moistness.

The surface morphology and size of these silica nanoparticles are characterized using scanning and transmission electronic microscopy (SEM, TEM), as shown in Supplementary Fig. 3-1 and Supplementary Fig. 3-2, respectively.
Supplementary Figure 1. The schematic showing the experimental setup of capillary microfluidics.
Supplementary Figure 2. The IR spectrum of PFPE-PEG-PFPE surfactant. The appearance of 1637 cm\(^{-1}\) vibration peak corresponds to amide C=O stretch in the target product PFPE-PEG-PFPE.
Supplementary Figure 3-1. The SEM images of silica nanospheres in varied sizes: a) 14 nm, b) 100 nm, c) 220 nm, d) 315 nm.
Supplementary Figure 3-2. The TEM images of silica nanospheres in varied sizes: e) 14 nm, f) 36 nm, g) 65 nm.

Supplementary Movie S1. The spreading induced dewetting transition from the generated double emulsions to colloidosomes. The video is recorded at 10 frames per second. The playback speed is 2 times slower than real time.

Supplementary Movie S2. The generation of monodisperse double emulsion templates using capillary microfluidic devices. The inner aqueous phase is 6 wt% aqueous solution of Pluronic L31 with 2 mM dye sulforhodamine B. The middle oil phase consist of fluorinated oil (HFE-7500, 3M) with 2.5 wt% fluorinated silica NPs and 1.5 wt% PFPE-PEG-PFPE surfactant. The outer phase is 10 wt% aqueous solution of PVA. The flow rates of the inner, middle and outer phase are 0.6 ml/hr, 1.2 ml/hr, 3.5 ml/hr, respectively. The video is recorded at 1000 frames per second for 17 seconds. The playback speed 33.3 times slower than real-time speed.