Nanoparticle Stabilized Emulsions and Foams for EOR and LNG Spill Mitigation

Zhengdong Cheng

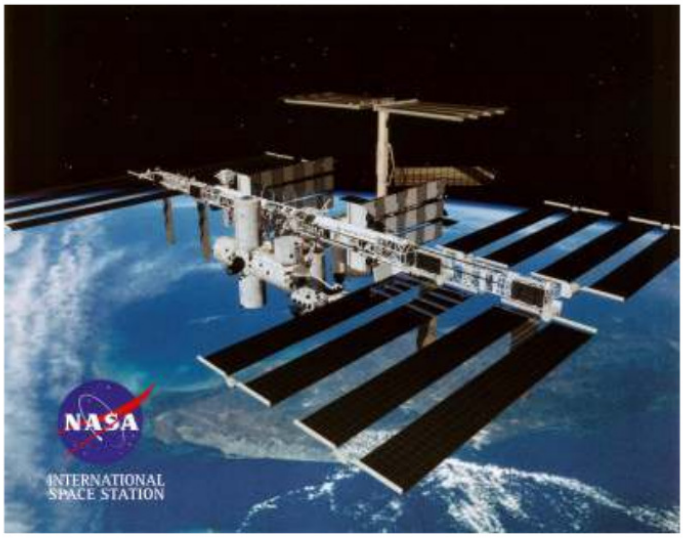
Artie McFerrin Department of Chemical Engineering
Texas A&M University



2nd World Congress on
Petrochemistry and Chemical Engineering
Oct 27-29, 2014
Las Vegas

Outline

- Amphiphilic platelets as nano-surfactants
- Reservoir on a chip
- Pickering foams as mitigation method for the accidental spill of LNG

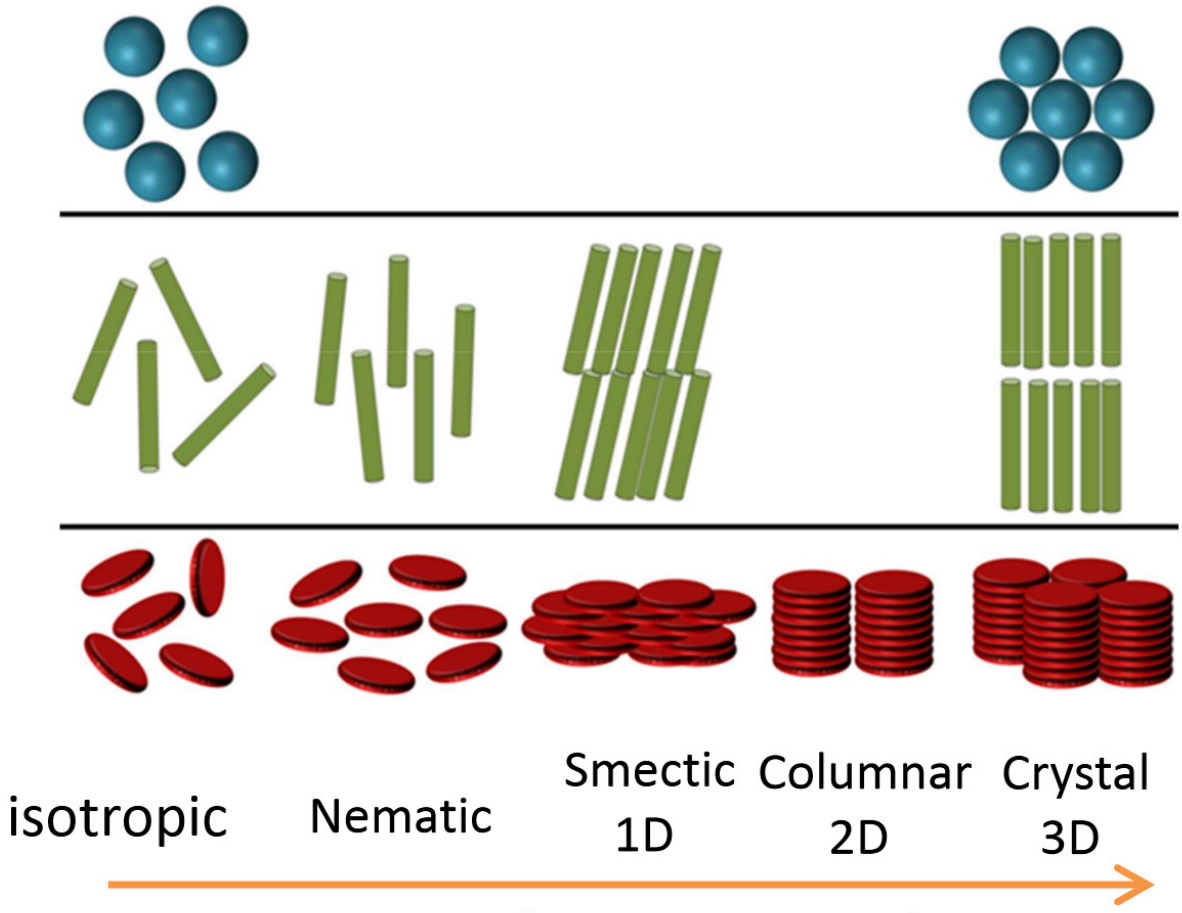




Emulsions
Foams

ickering Emulsions Stabilized by Amphiphilic Nano-sheets" A. F. Mejia, A. Diaz, S. ullela, Y. Chang, M. Simonetty (undergraduate), C. Carpenter, J. D. Batteas, M.S. Mannan, A. Clearfield, and Z. Cheng, 8, 2012, 10245-10253.

Stabilization of ickering Foams by High-aspect-ratio Nano-sheets" J. S. Guevara, A.F. Mejia, Y. Chang, M. Shuai, M.S. Sam Mannan, Z. Cheng, Soft Matter 9, 2013, 1327-1336.


isotropic
Nematic
Smectic
1D
Columnar
2D
Crystal
3D
ncrease in concentration



Clearfield, A.; Stynes, J. A.
117.
, 2007, 31, 39 - 43

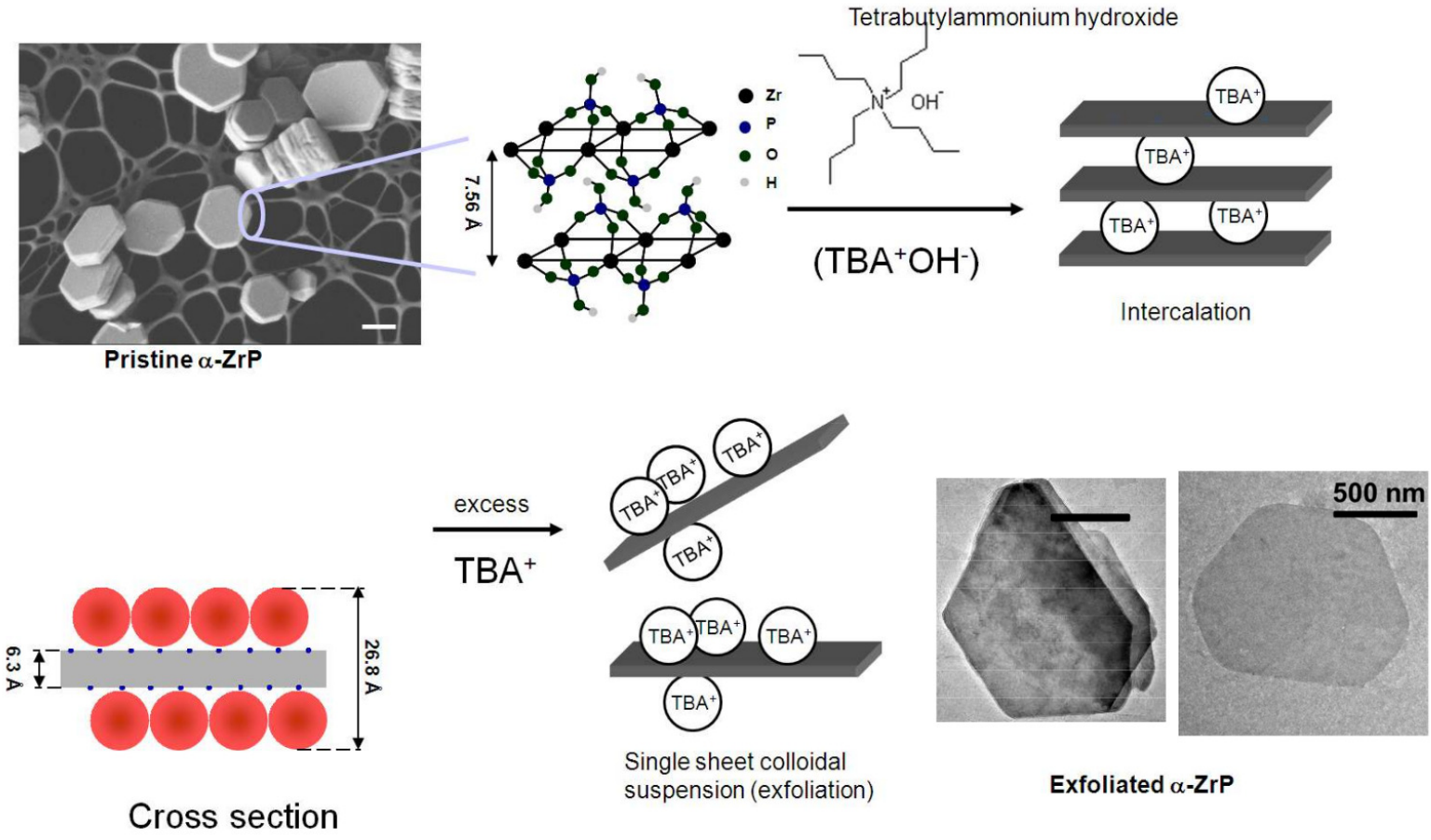
M. Shuai, A. F. Mejia, Ya-Wen (Winnie) Chang, Z. Cheng

Andres F. Mejia

CrystEngComm, 2013, 15,1970

Fabrication: How to obtain large aspect ratio plates?

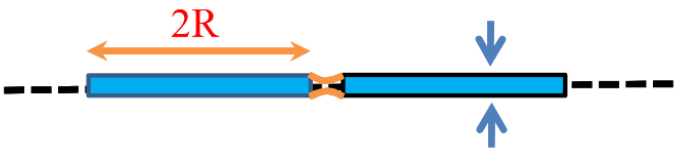
Exfoliation of layered crystals



L. Y. Sun et al. , , 39-43.

he need for Janus nanoplates (highest interface-“atomic” efficiency)

Nano plates have two dimensions: &



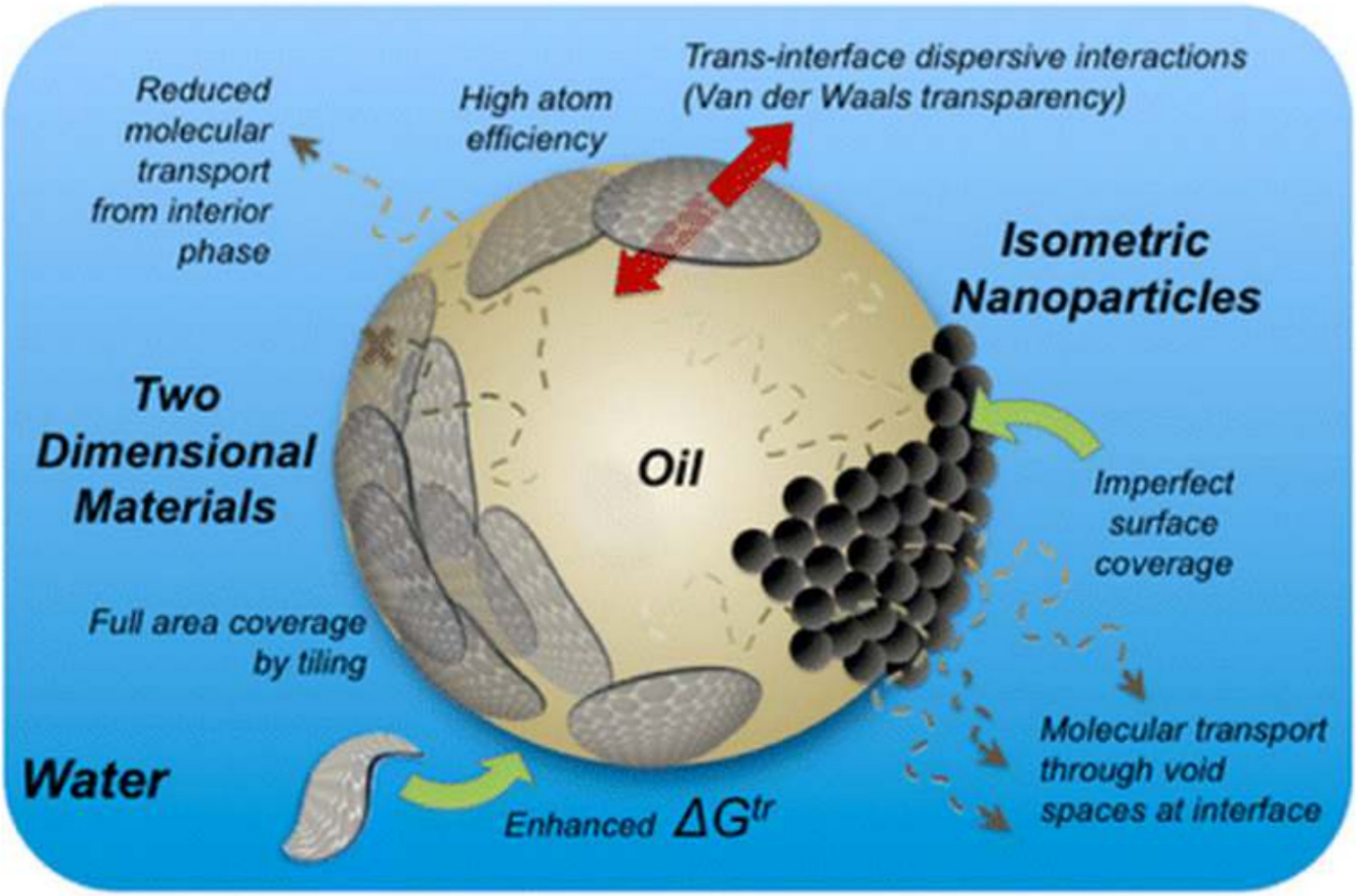
max ~ 2 : Thickness

~ 2 2 : Diameter

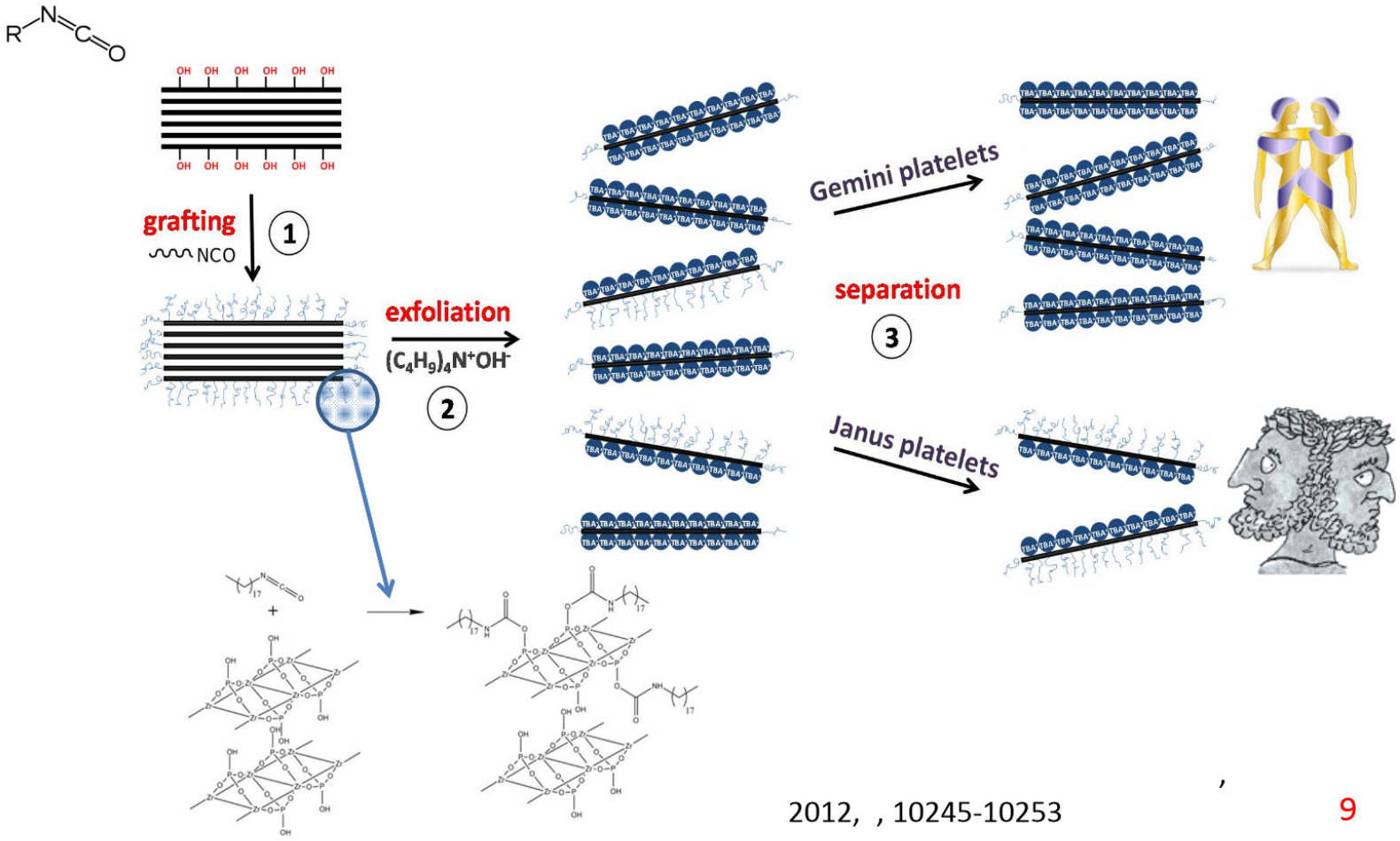
hinner platelets ( ) better hold emulsions apart.

Larger size ( ) harder to escape from the interface by thermal fluctuation.

_____ aspect ratio platelets are desired.

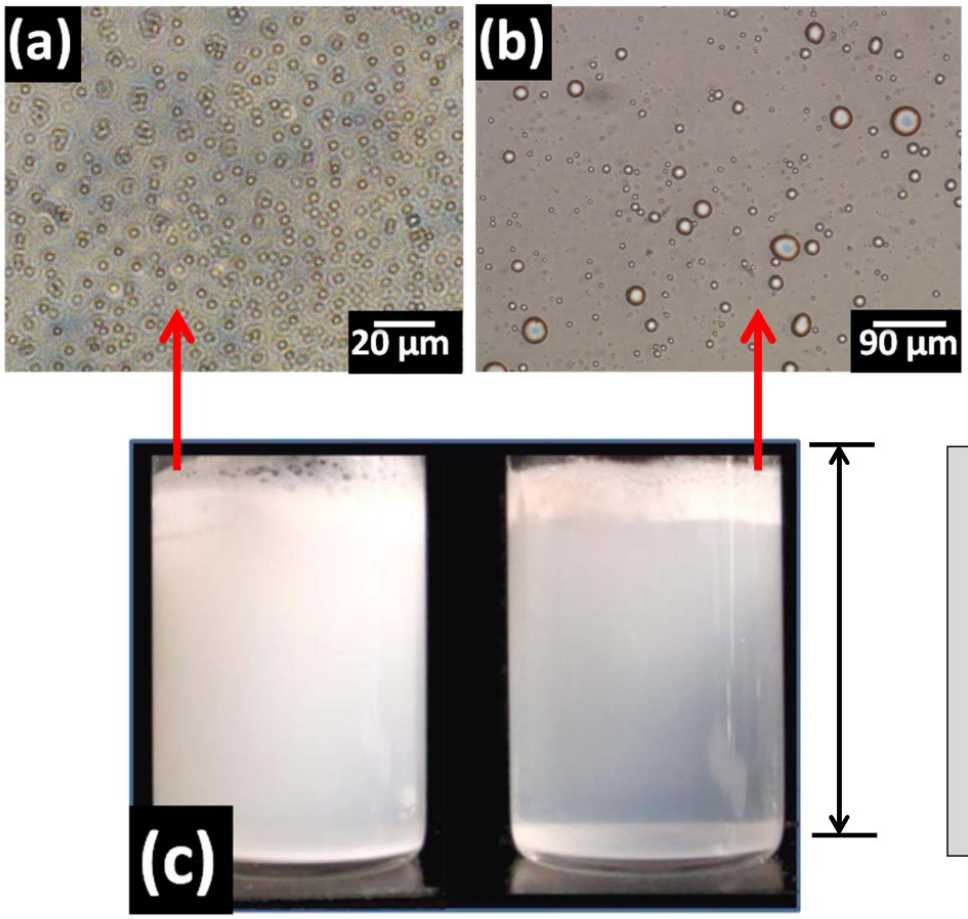


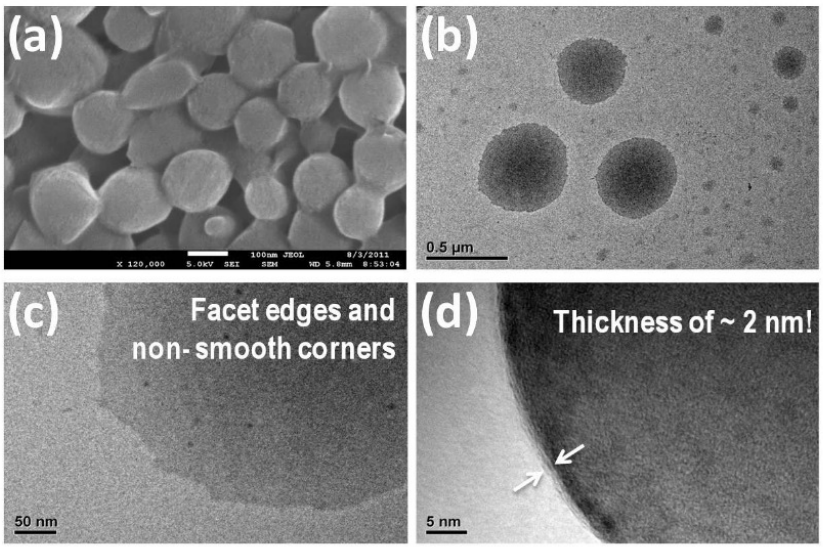
, , (13), pp 3687–3696

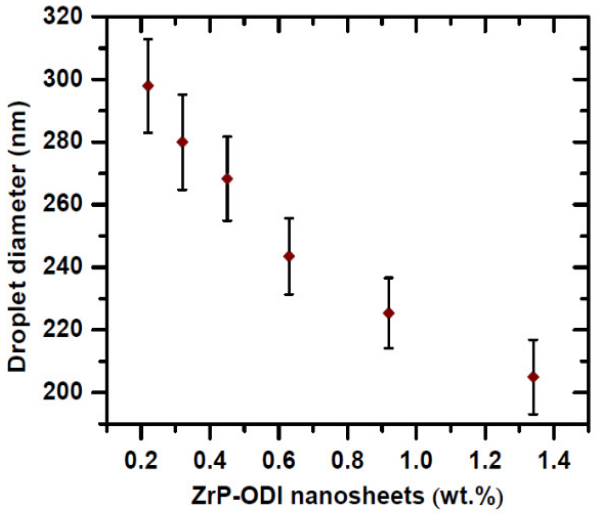


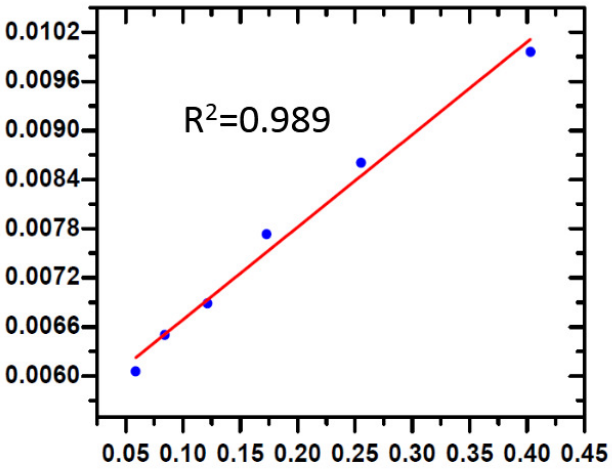
2012, , 10245-10253

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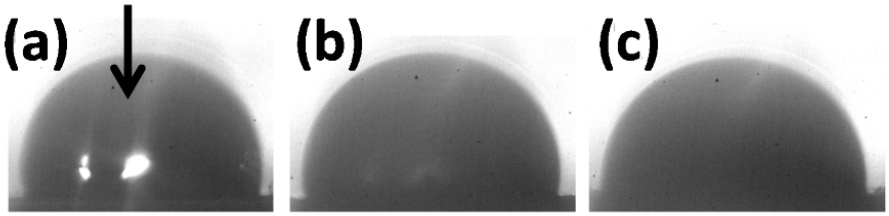

(a)
20 µm
(b)
90 µm
(c)

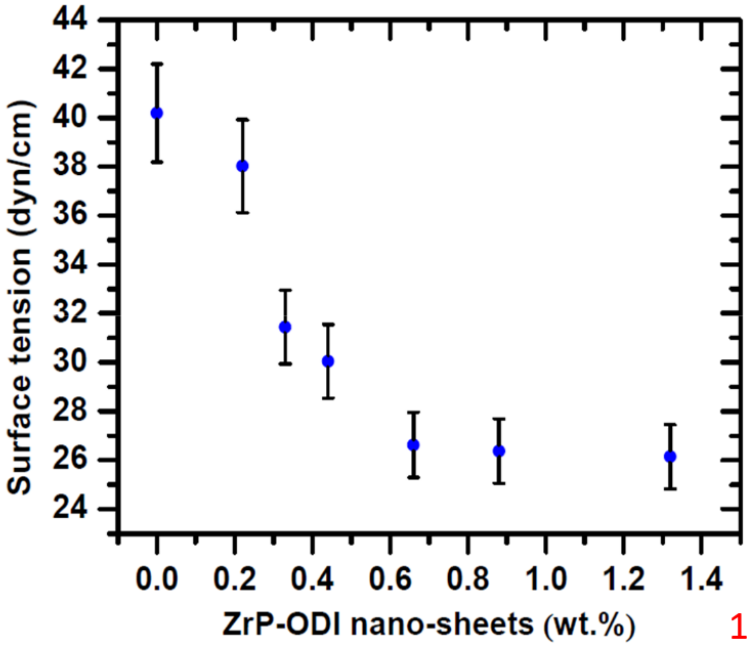




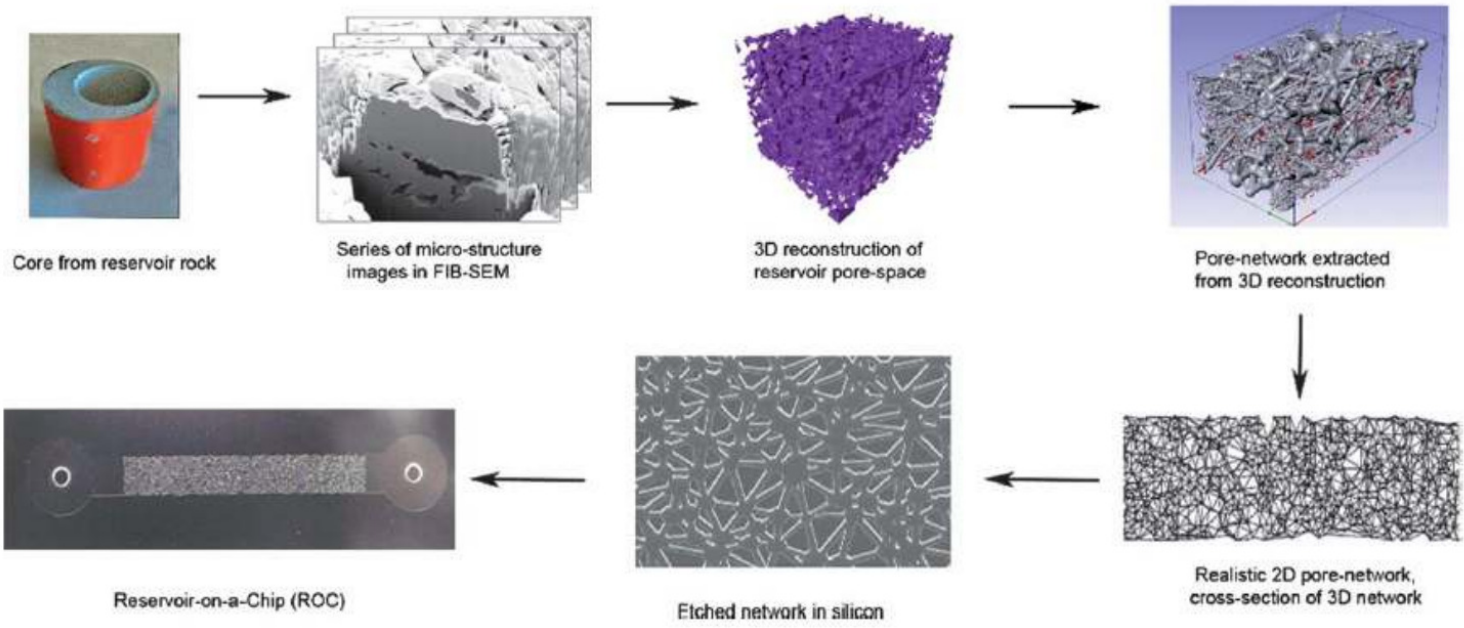


, 2012, , 10245-10253

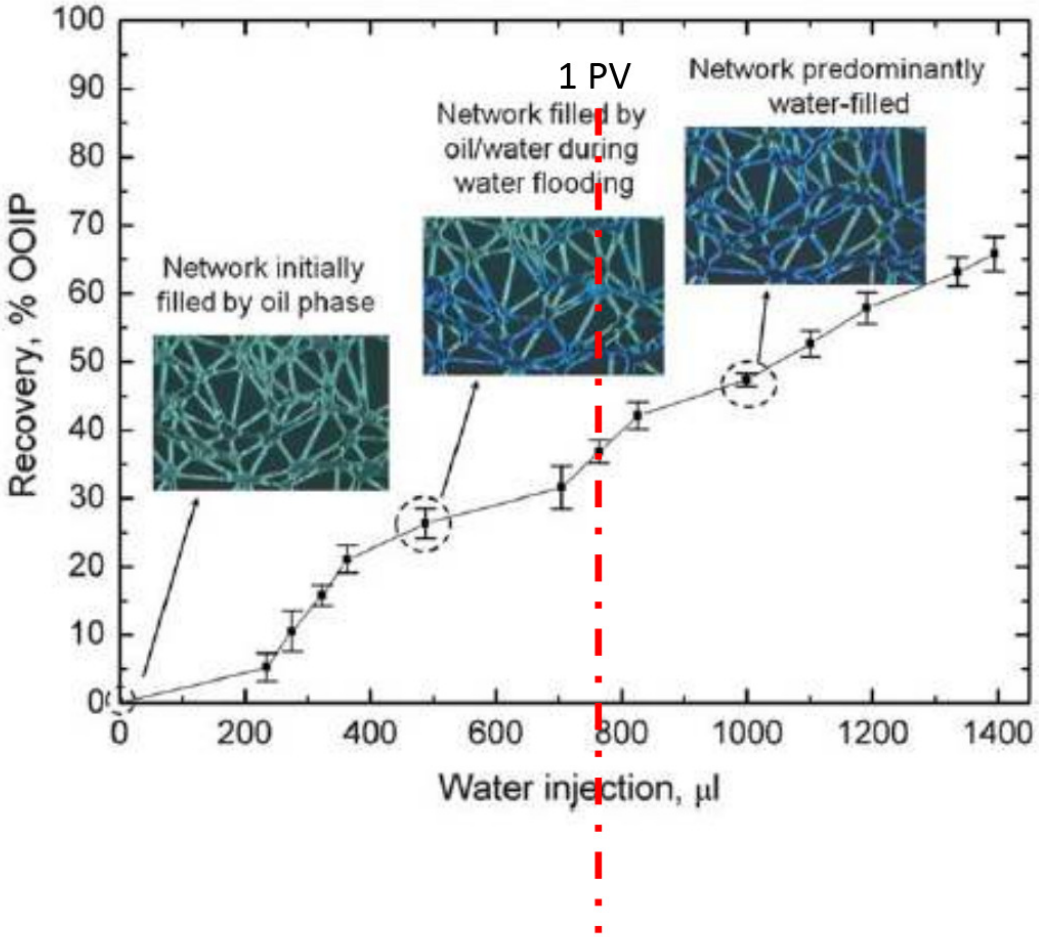

(a)
(b)
(c)


Surface tension (dyn/cm)
44
42
40
38
36
34
32
30
28
26
24
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
ZrP-ODI nano-sheets (wt.%)

Reservoir on a chip:
Fast and easy to evaluate performance of formulation



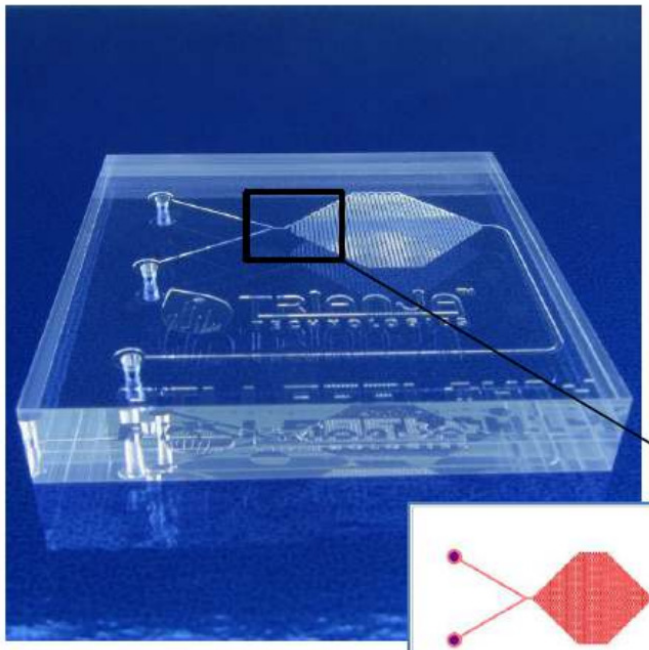
Lab Chip, 2011, 11, 3785–3792

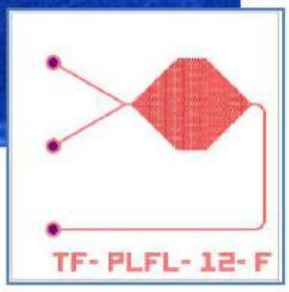


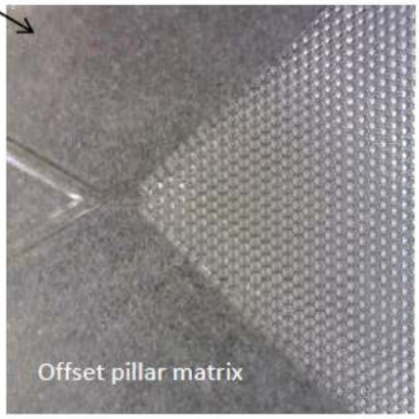
Lab Chip, 2011, 11, 3785–3792

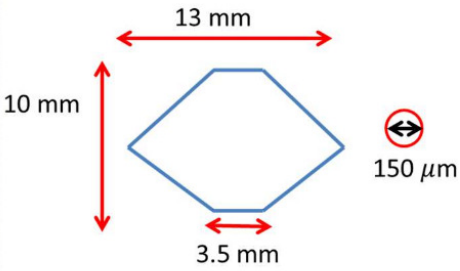
Product Number: TF-PLFL-12-F-D50-W150

Parameter	Unit	Dimension
Chip Size	mm	29 x 29
Channel Depth	µm	50
Channel Width	µm	200
Hexagon Width	mm	10
Hexagon Length	mm	13
Pillar Diameter (top)	µm	150
Pillar Pitch	µm	200



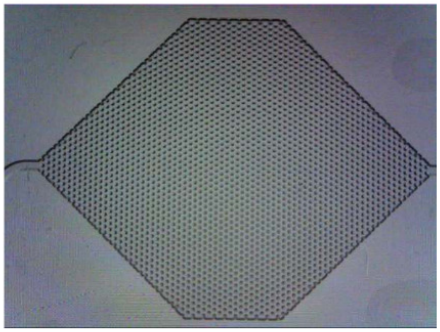




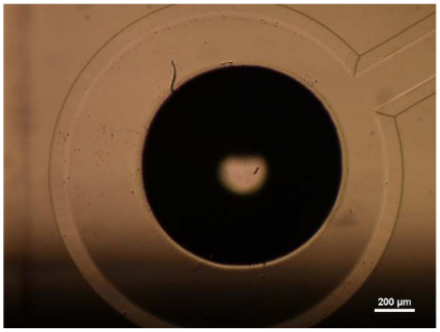


Channel depth is 50 µL

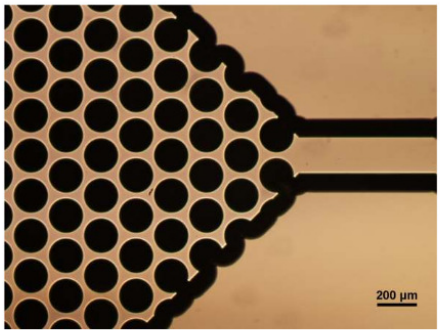
Hexagonal cell



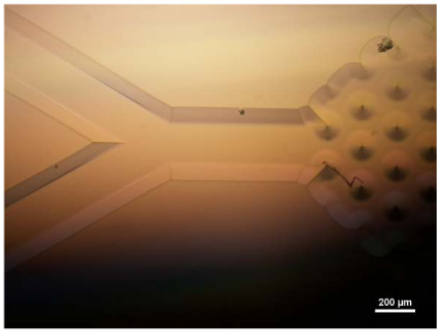
Entrance



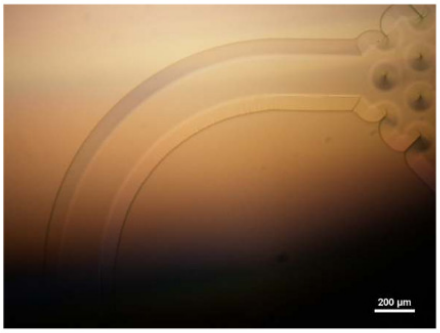
Bottom view



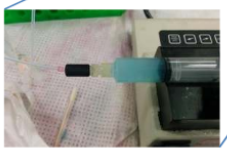
op view of inlet



op view of outlet



Experimental set-up



Syringe pump

Syringe pump

Microscope

Computer

Microfluidic chip

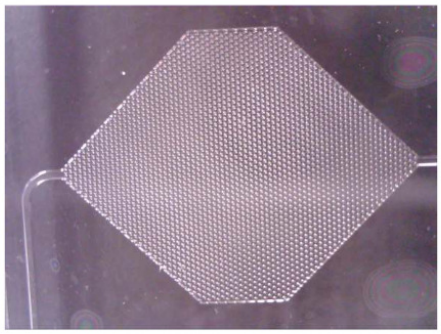
V = 4.1 μL

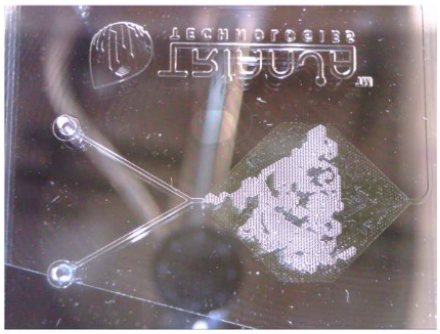
Waste

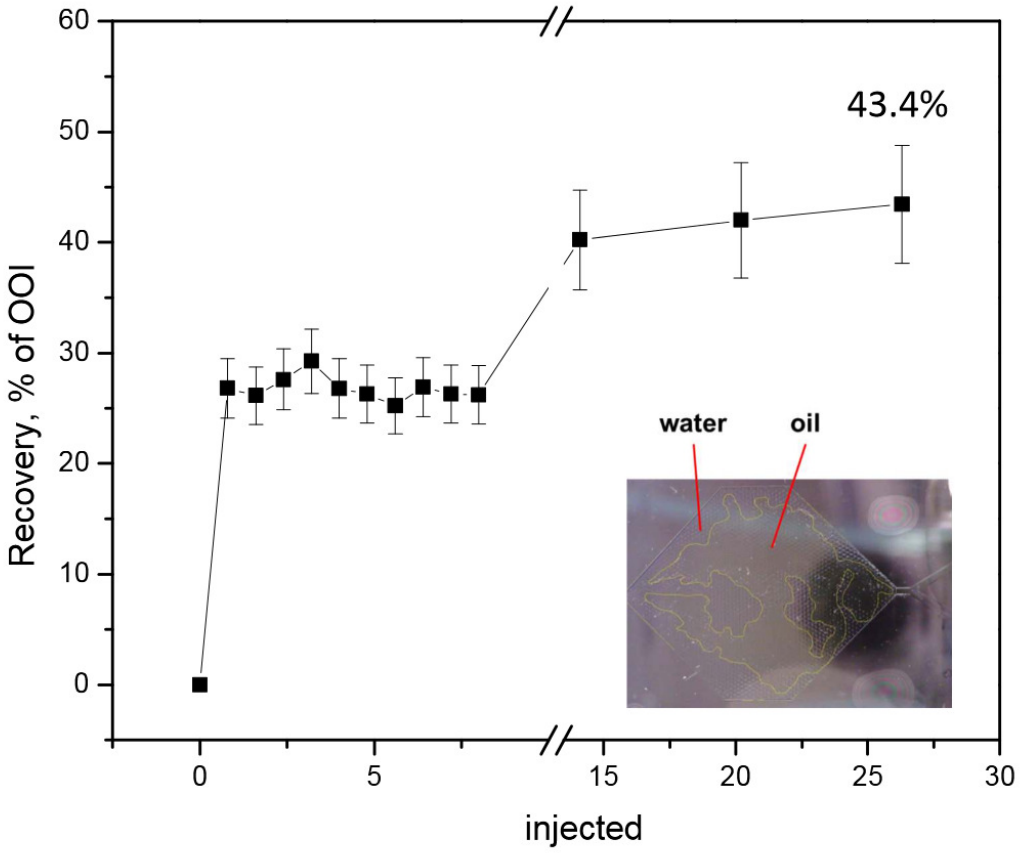
Dyed oil with nile red
Dyed aqueous solution with methylene blue

Flooding procedure

- Clean chip with D water
- Clean chip with ethanol
- Using air to remove ethanol
- Dried in oven
- Filled with oil and saturated chip overnight
- Flooding

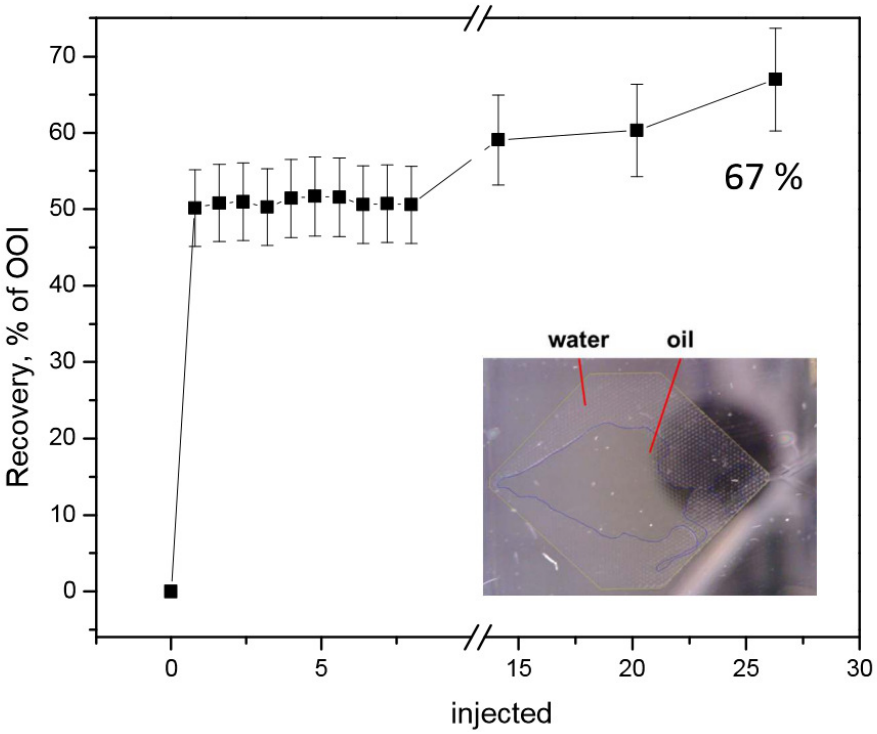




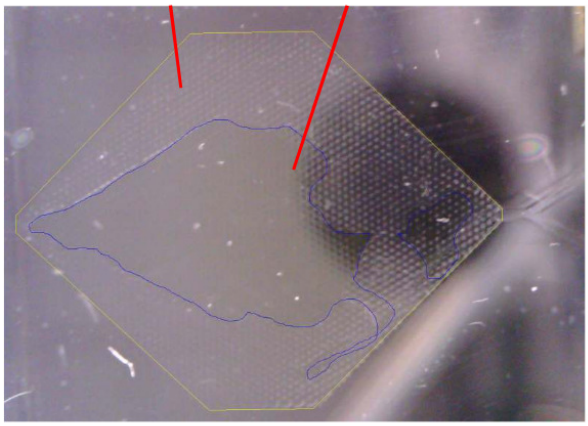


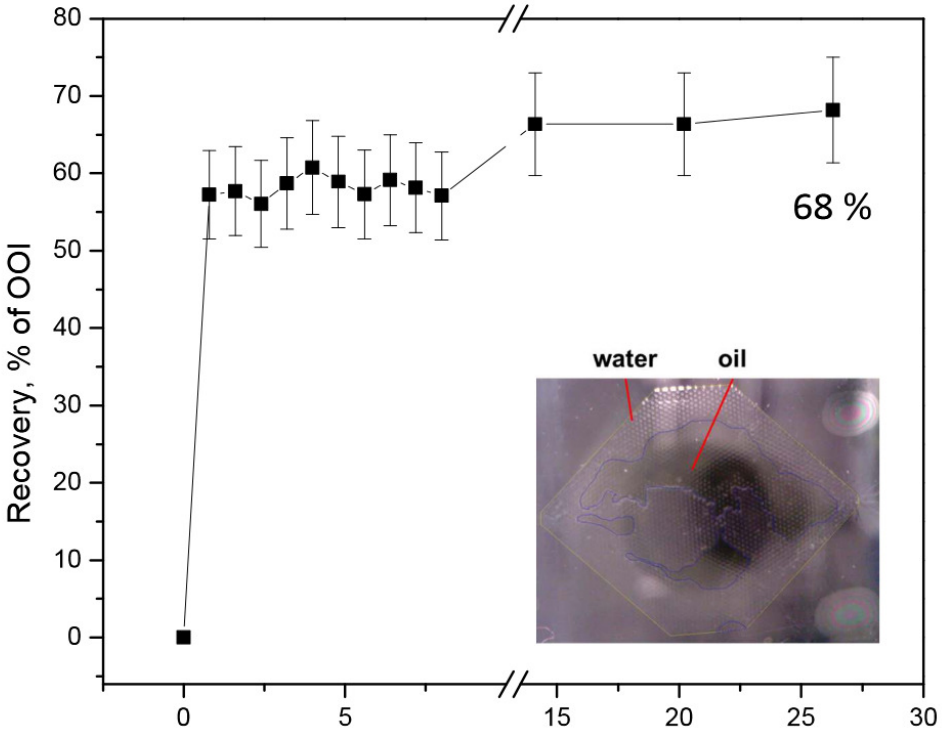
- 0.2 mL/hr
- 3 mL/hr
- ~43.4% oil was recovered



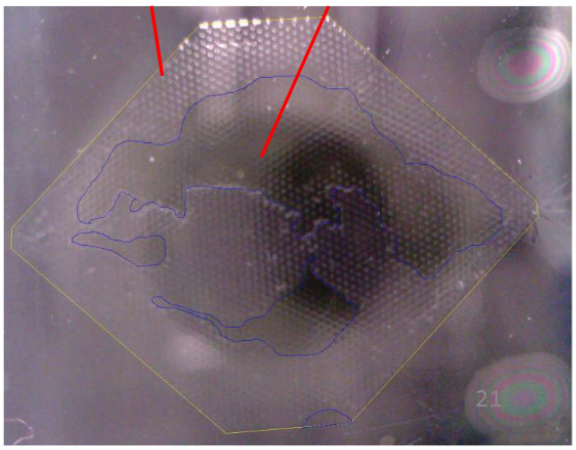


- 0.2 mL/hr
- 3 mL/hr
- ~67% oil was recovered

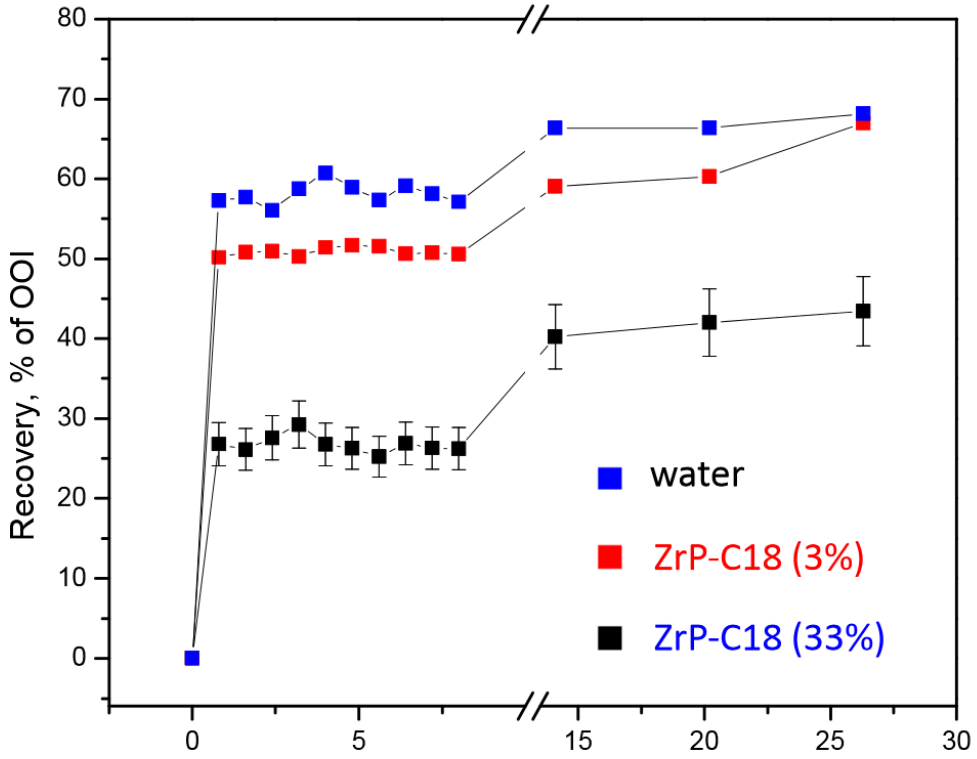




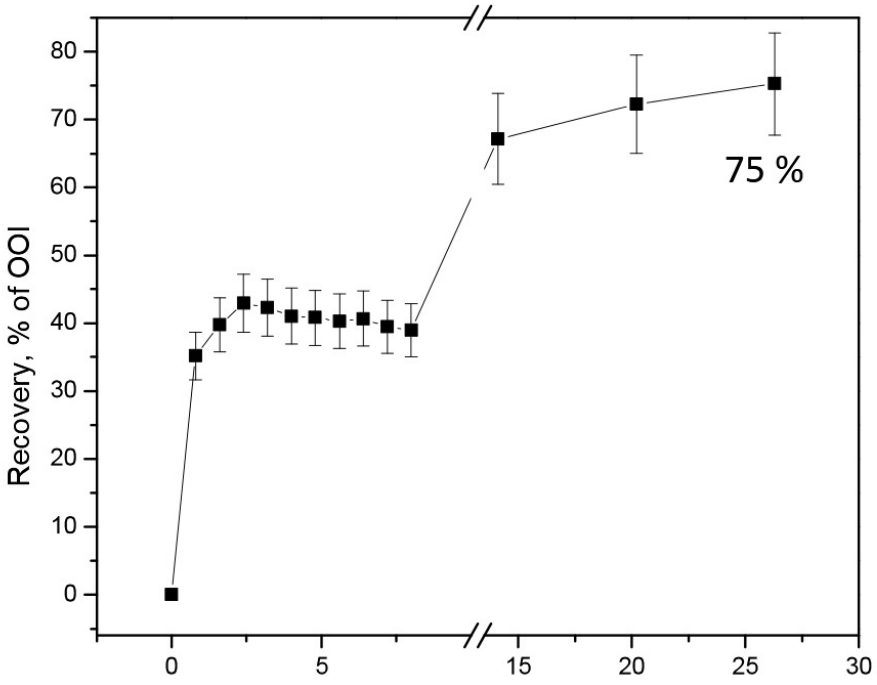
- 0.2 mL/hr
- 3 mL/hr
- ~68 % oil was recovered



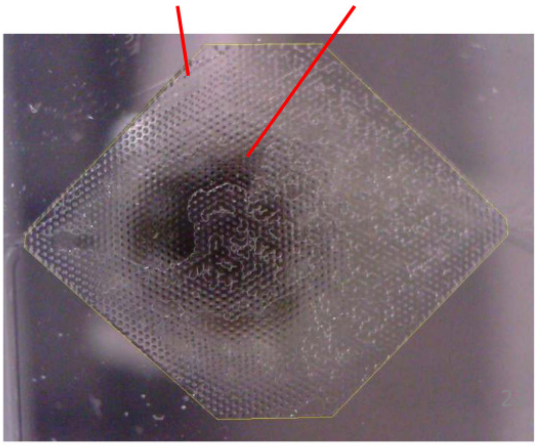
Black: water
Red: ZrP-C18 (3%)
Blue: ZrP-C18 (33%)

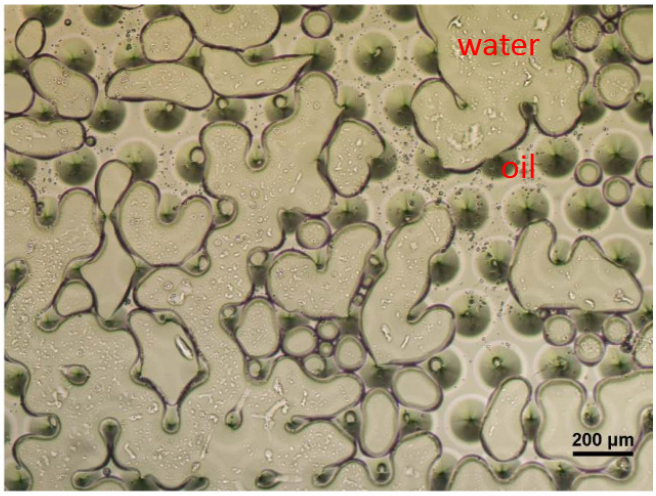


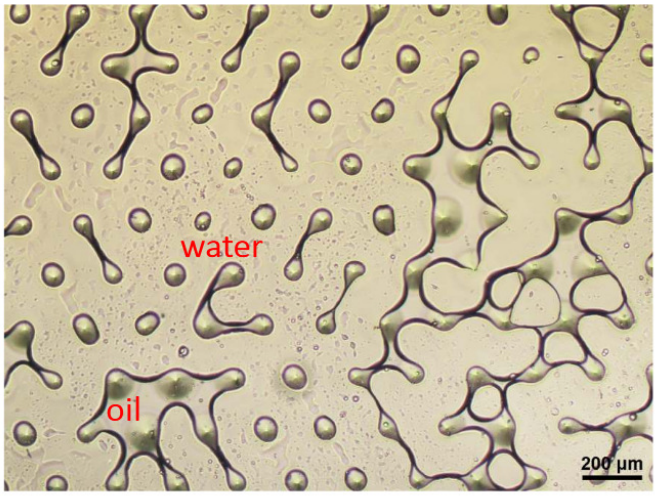
Synergy of co-surfactants

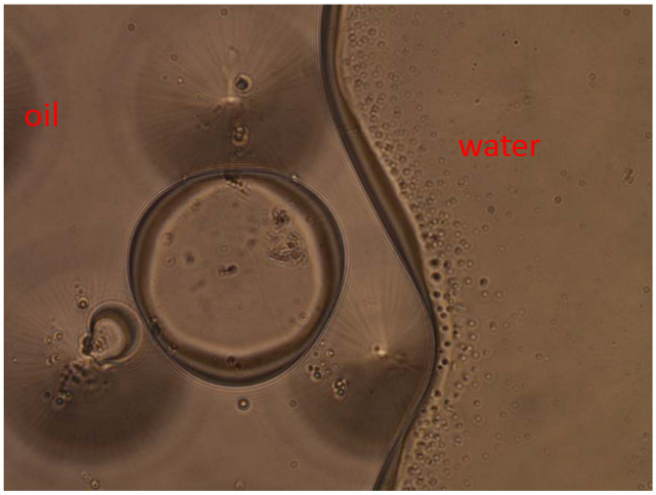


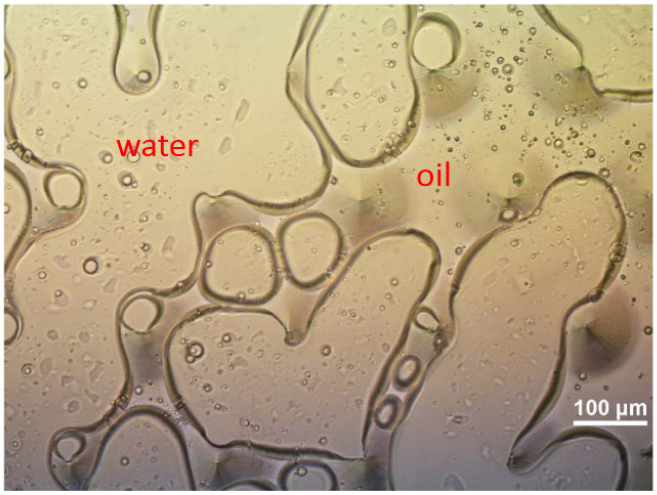
- 0.2 mL/hr
- 3 mL/hr
- ~75 % oil was recovered



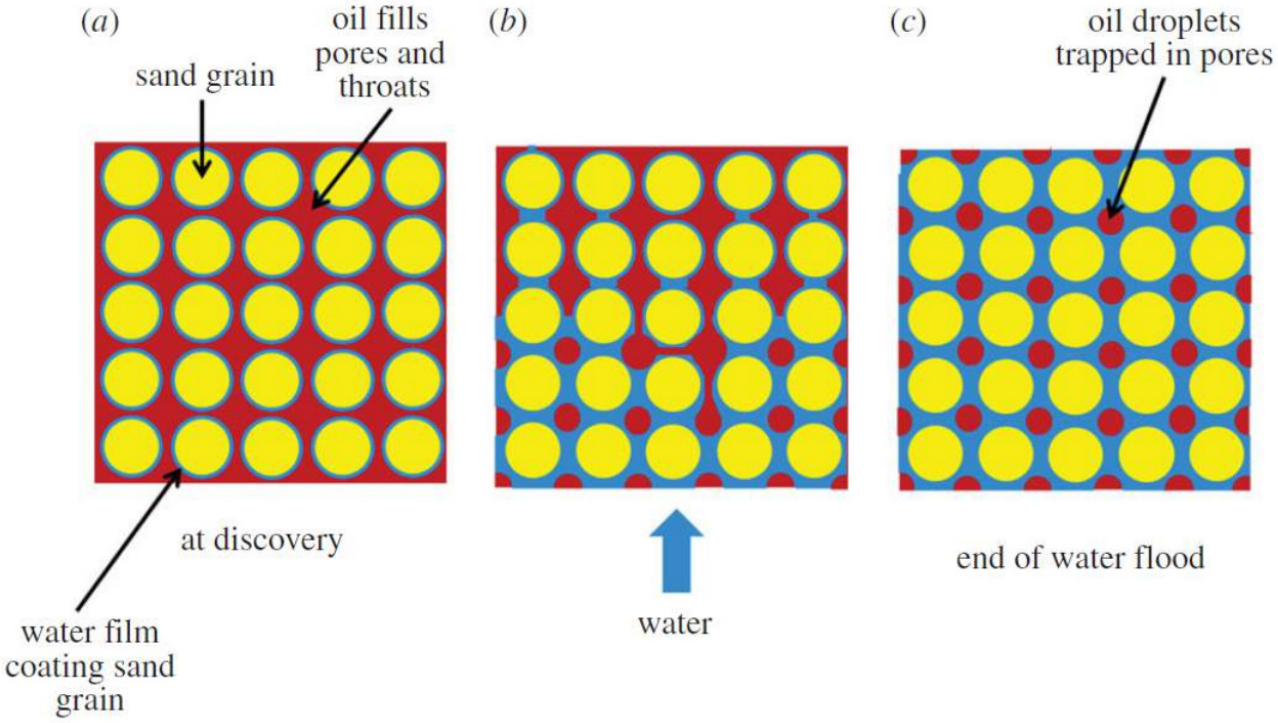

water
oil
200 µm


water
oil
200 µm


oil
water

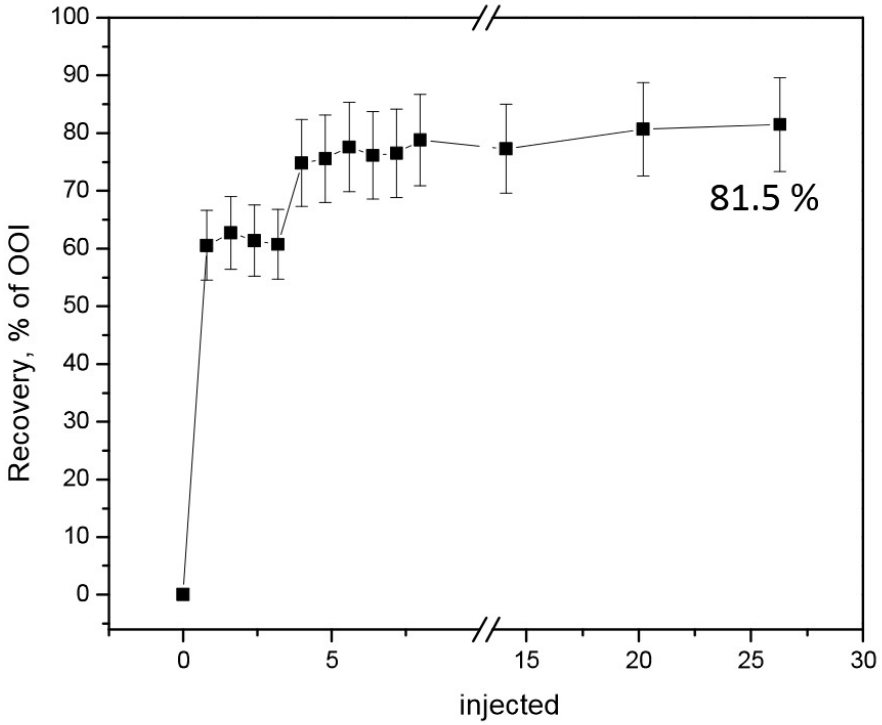

water
oil
100 µm

Wettability

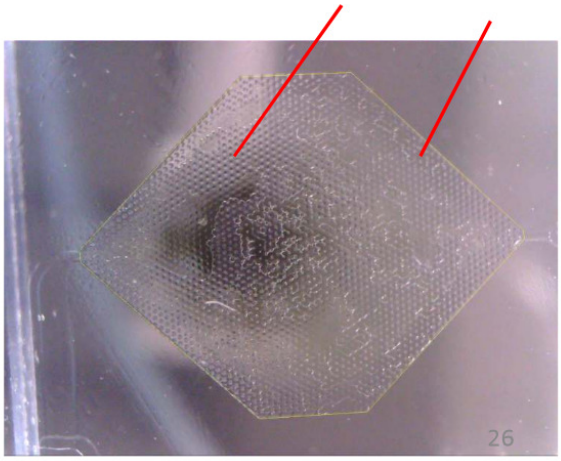


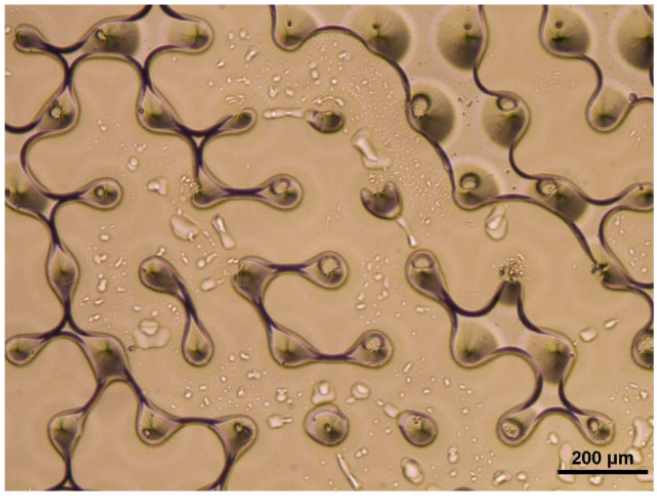
Similar to sandstones or carbonates

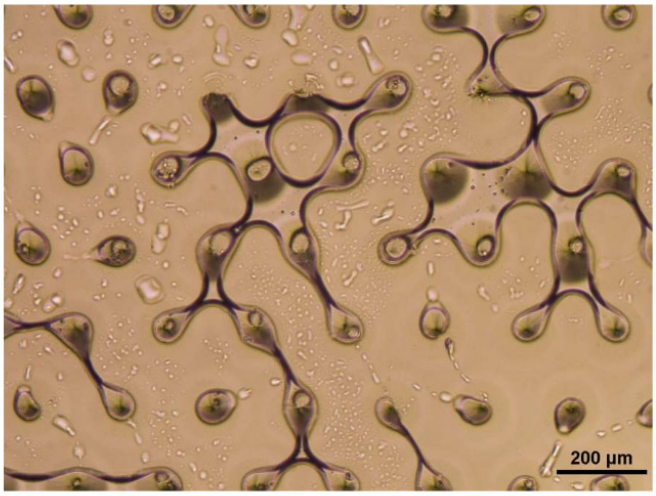
Muggeridge et al., 2014 , 20120320

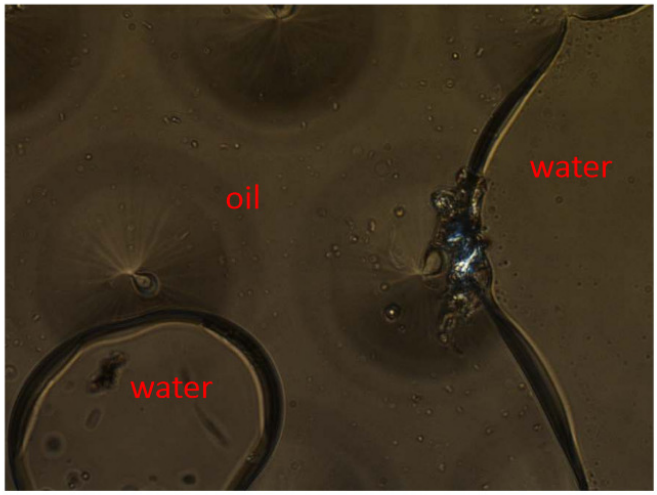


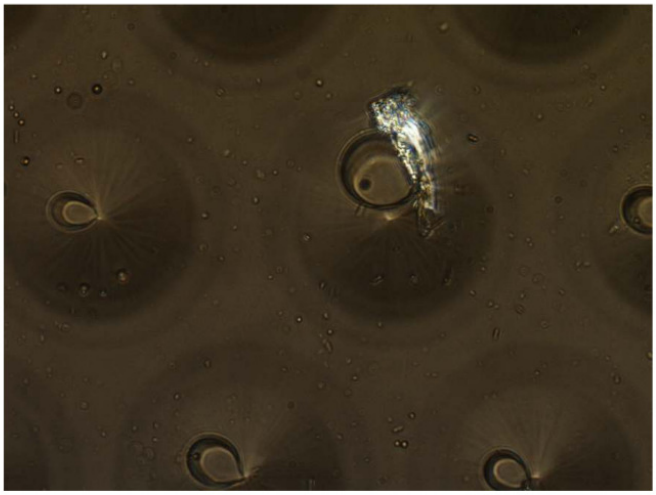
- 0.2 mL/hr
- 3 mL/hr
- ~81.5 % oil was recovered




200 µm

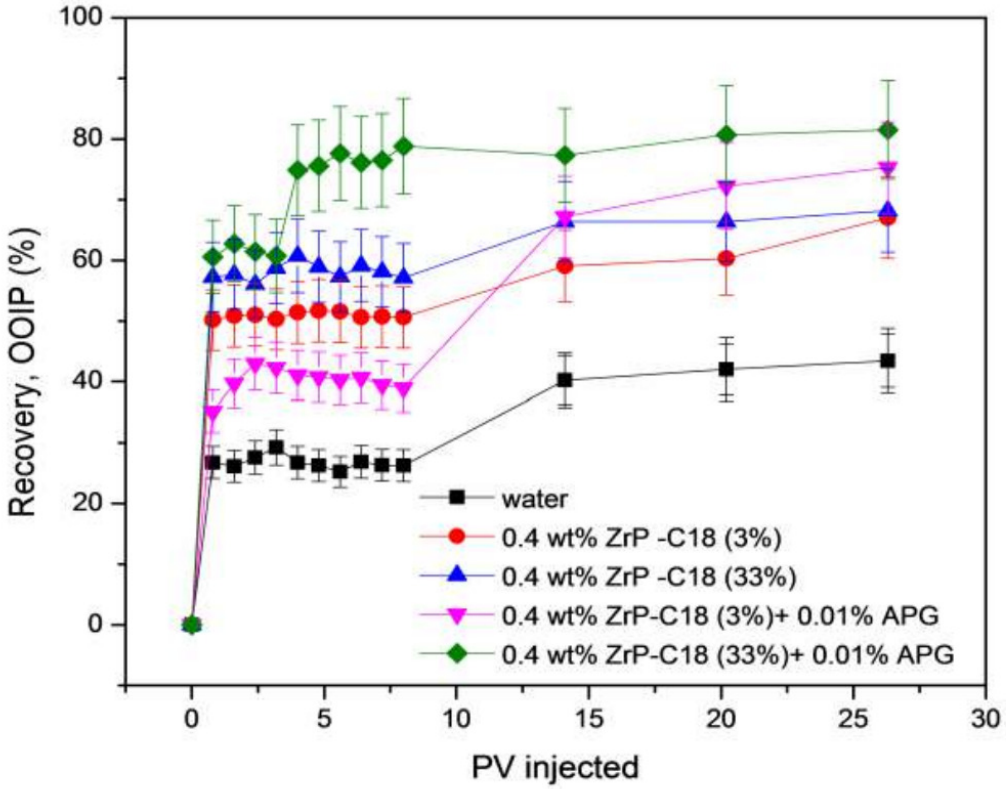

200 µm


oil
water
water

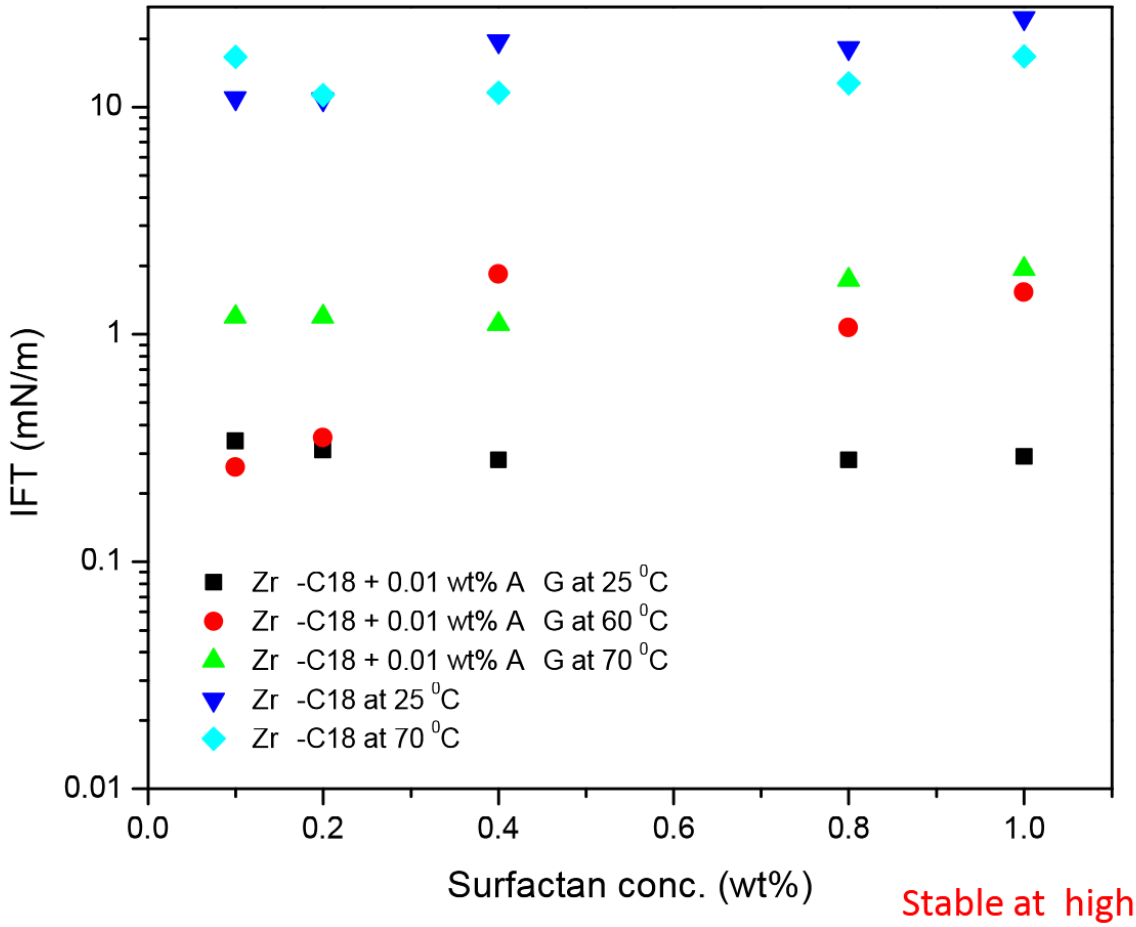




Overall flooding comparison



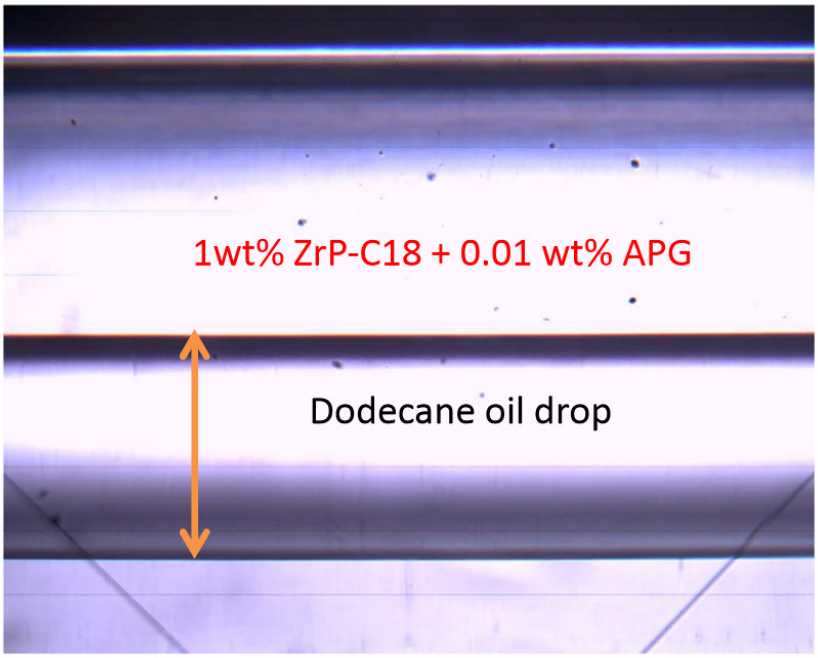
F comparison



Stable at high temperature

Co-surfactant synergy

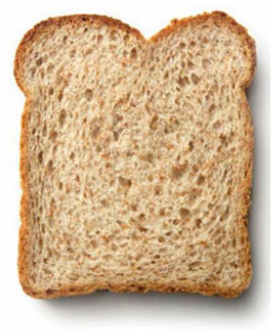
F image





Oil recovery

Pickering foams as mitigation method For the accidental spill of LNG





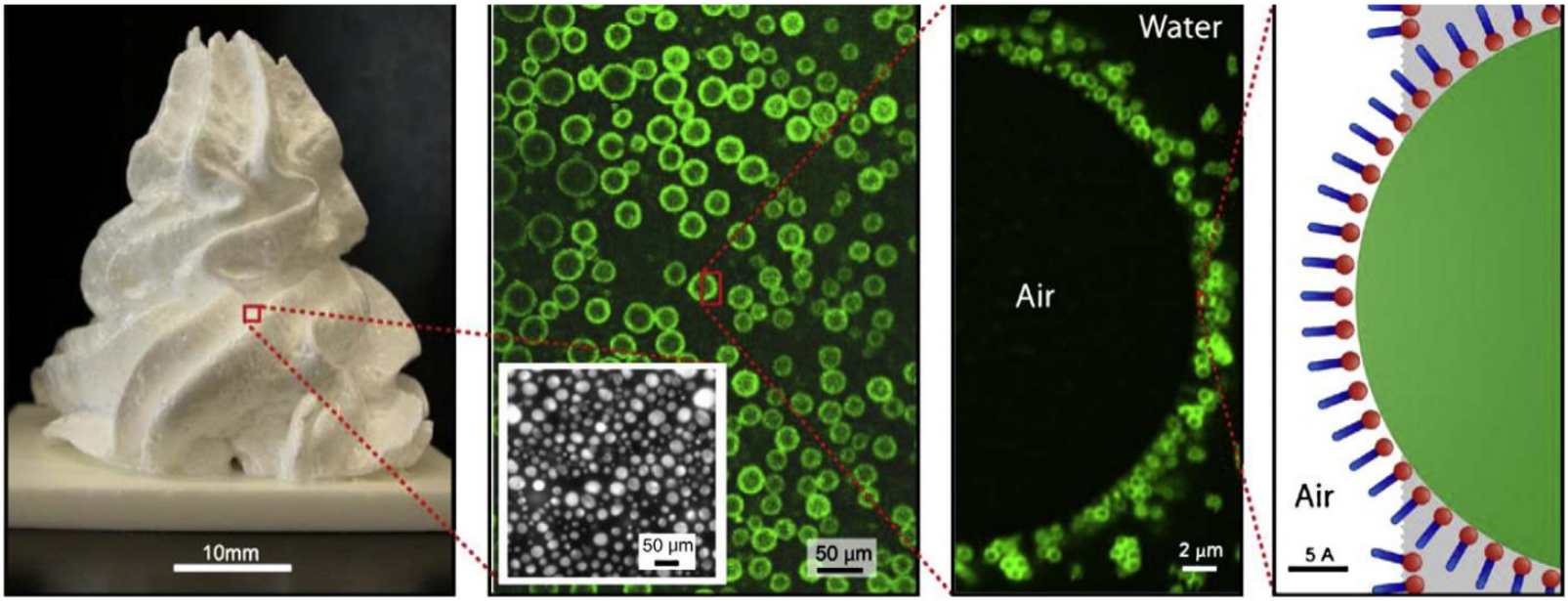








Pickering foams



Dickinson, E.,
Current Opinion in Colloid & nterface Science, 2009. (1-2):40-49.

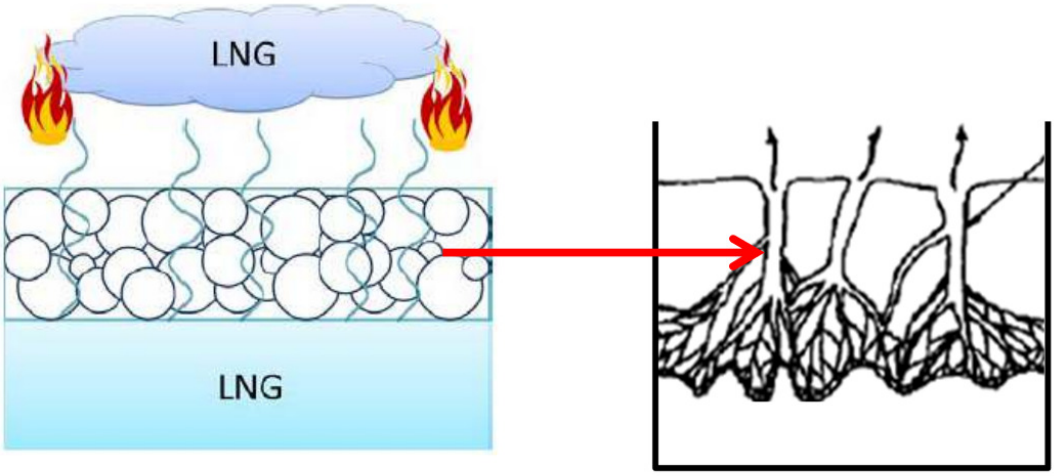
TEXAS A&M ENGINEERING

Mary Kay O'Connor Process Safety Center

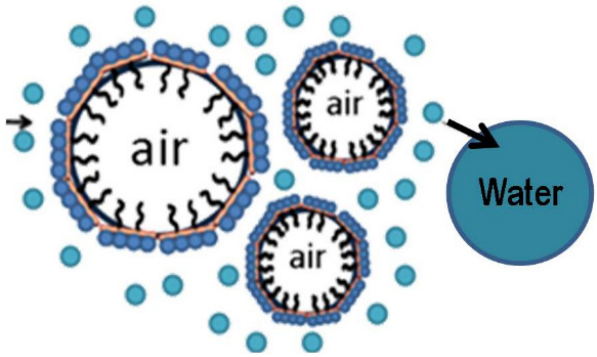
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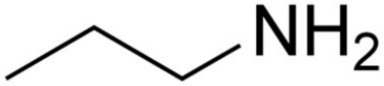


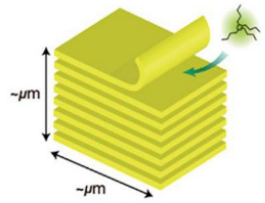


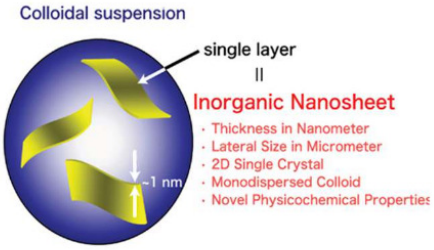

LNG
LNG



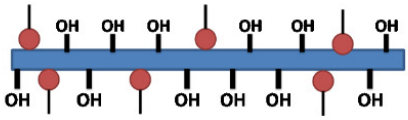

air
air
air
Water





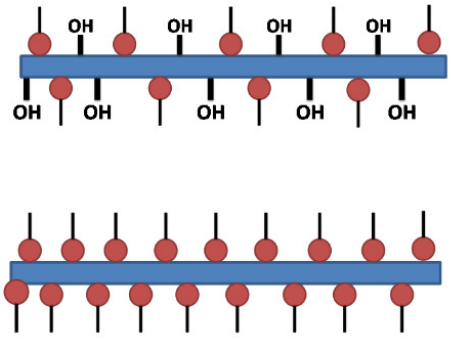


5082–5104 , , 1749–1754

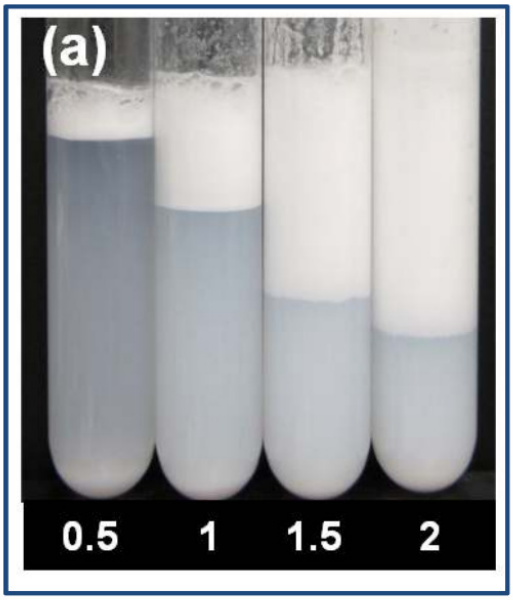


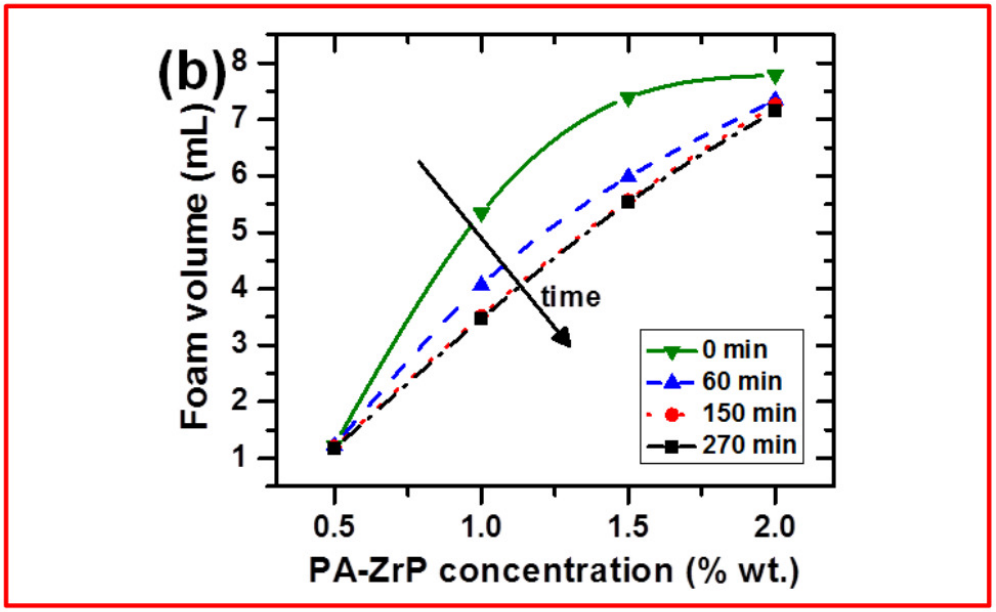
et. al

9, 2013, 1327-1336.



G. Alberti et al. JCIS , 256 (1985).



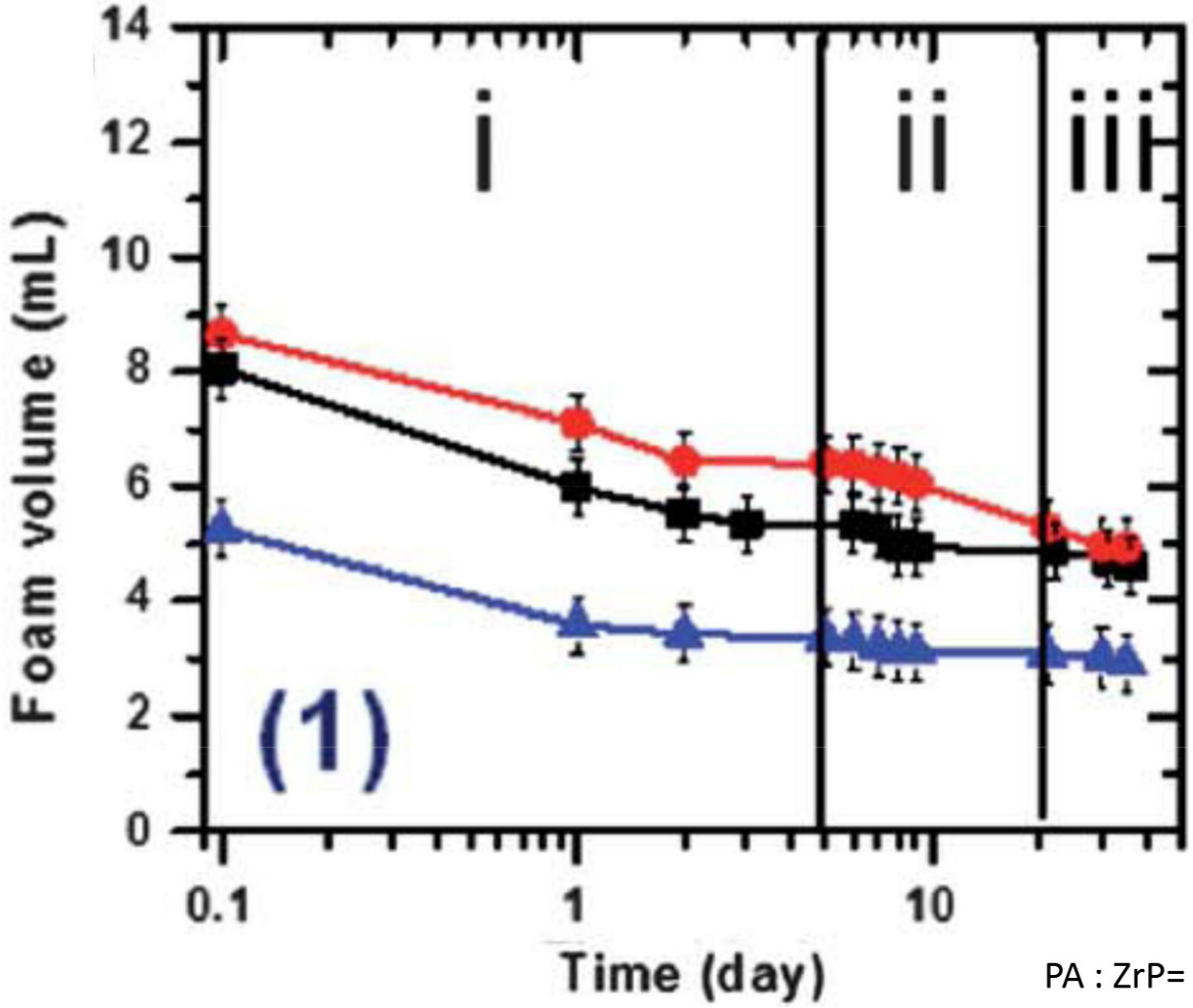


As nano-sheet concentration increases, foam volume increments

At equilibrium, the foam volume became linearly dependent on nano-sheet concentration

et. al

9, 2013, 1327-1336.



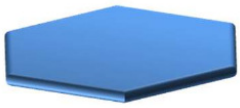
PA : ZrP= 2.16 0.05



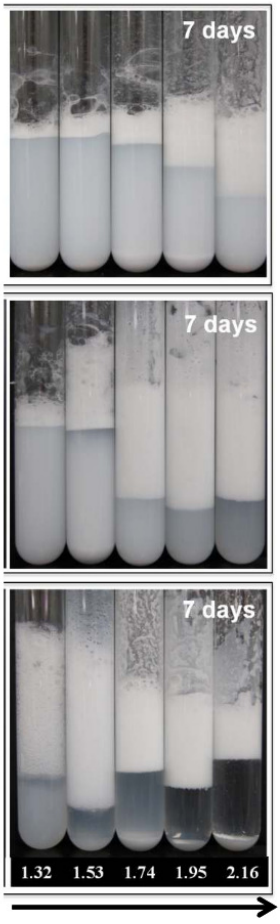
Batch A
(261 36 nm)

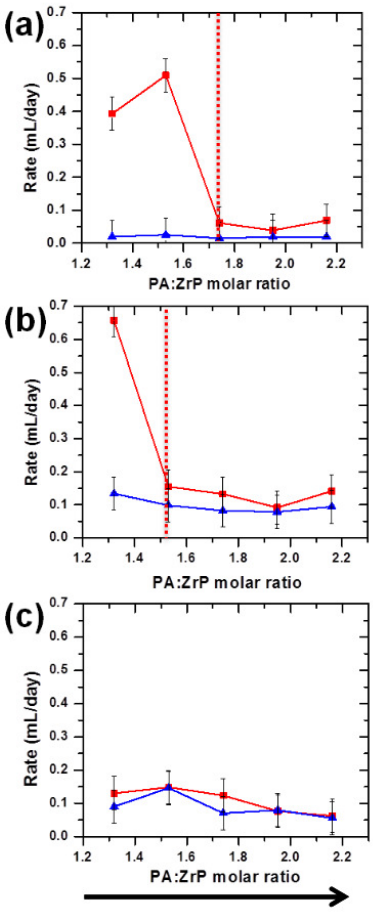


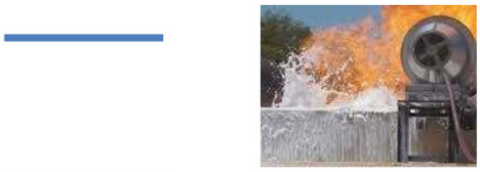
Batch B
(548 77 nm)

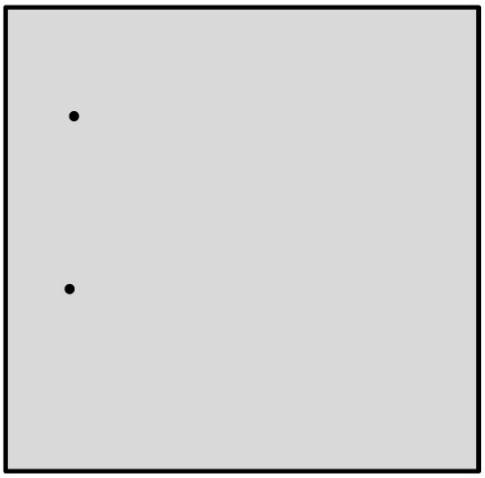


Batch C
(1142 305 nm)





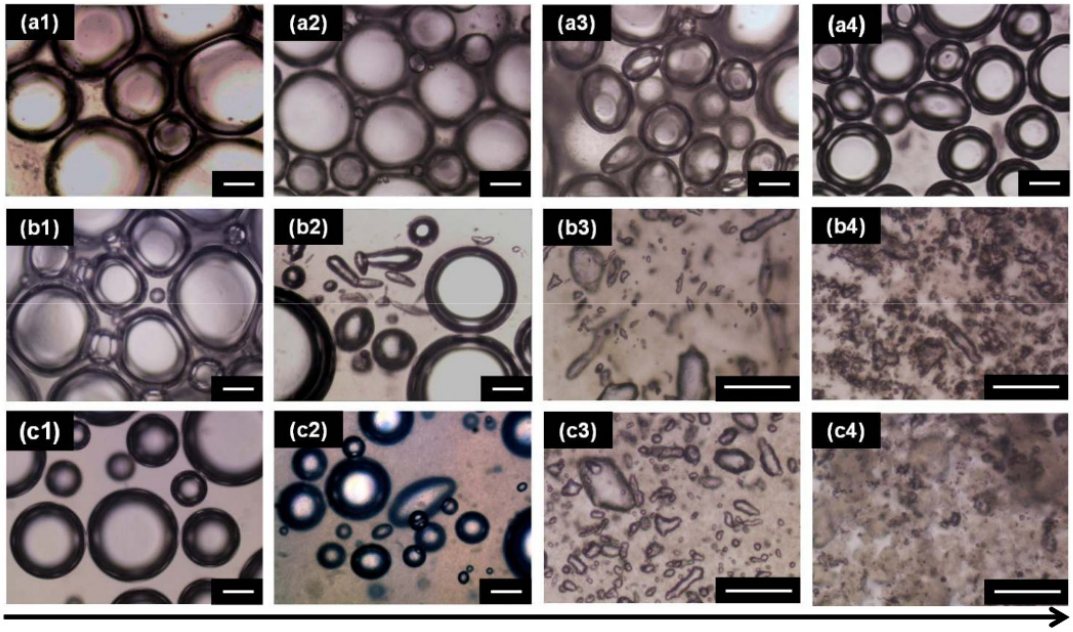




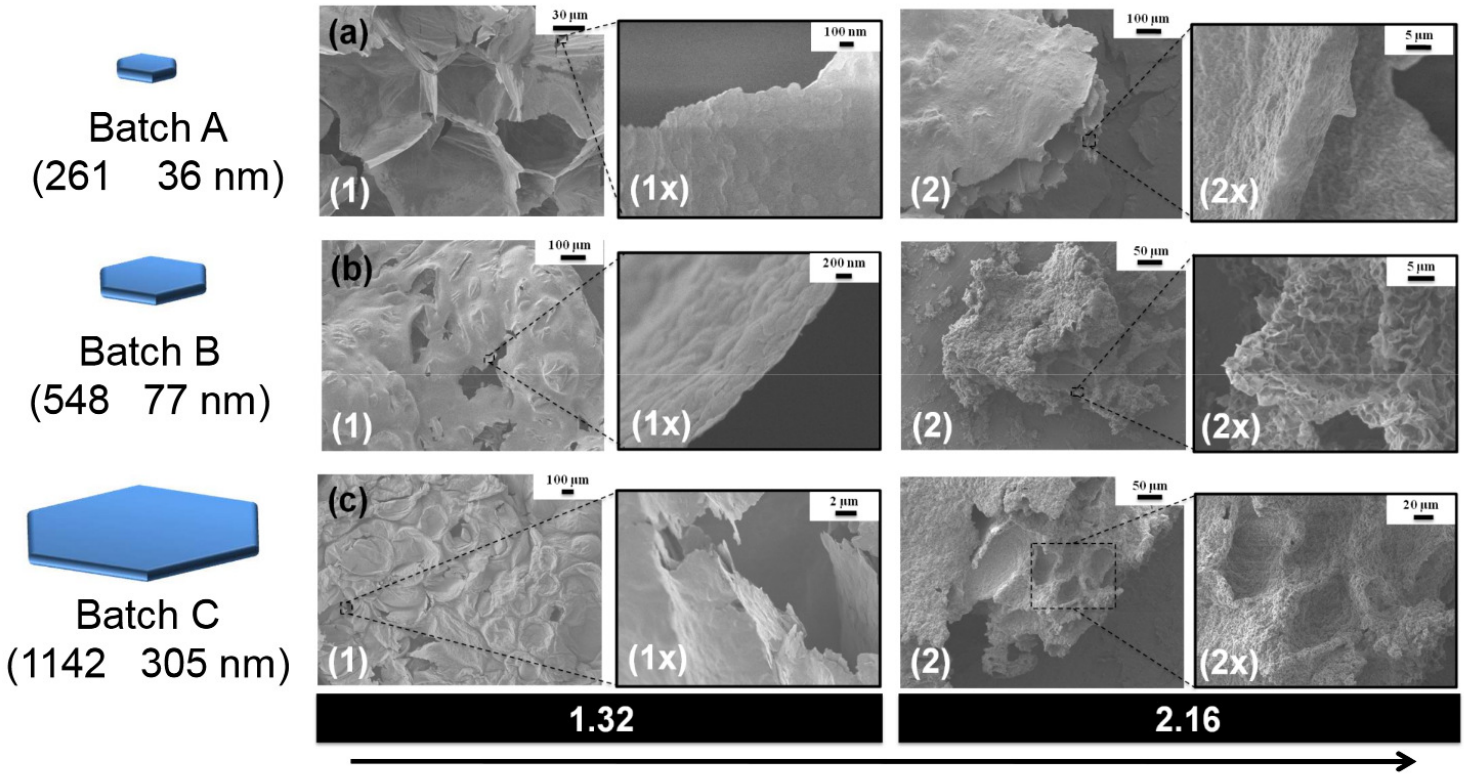
et. al

9,
2013, 1327-1336.





- Bubble size reduces as nano-sheet hydrophobicity increases
- At high nano-sheet aspect ratio and hydrophobicity, non-spherical bubbles were observed



Several layers of nano-sheets in a jammed-like structure stabilized each air bubble

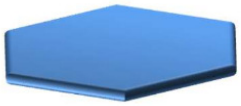
et. al 9, 2013, 1327-1336.



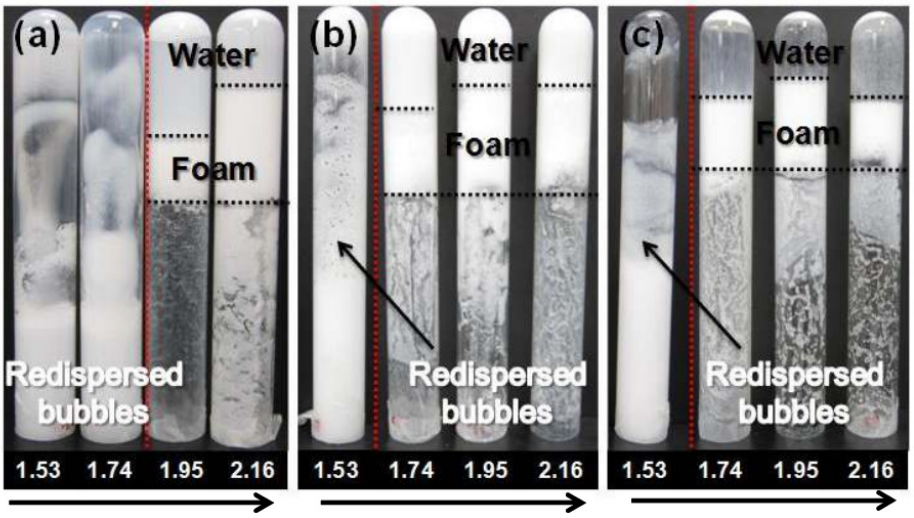
Batch A
(261 36 nm)



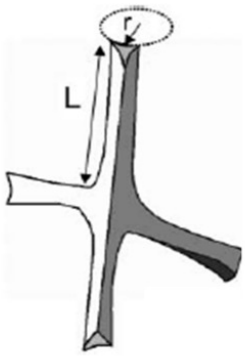
Batch B
(548 77 nm)



Batch C
(1142 305 nm)



Closed-packed rigid-structure created from the packing of nano-sheets at the air-water interface and in the plateau borders.



Water flow resistance (R)

$R \sim L/D^4$

After foam drainage,

$D << L$

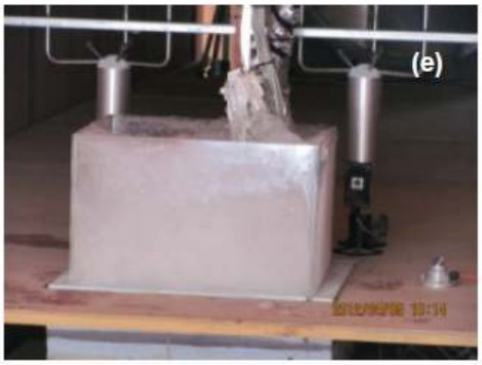
A. B. Subramaniam, M. Abkarian, L. Mahadevan, and H. A. Stone, Nature , 930 (2005).


(a)
FOMAX 7


(b)

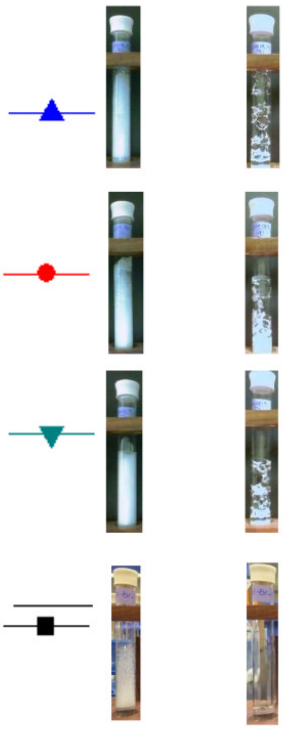

(c)

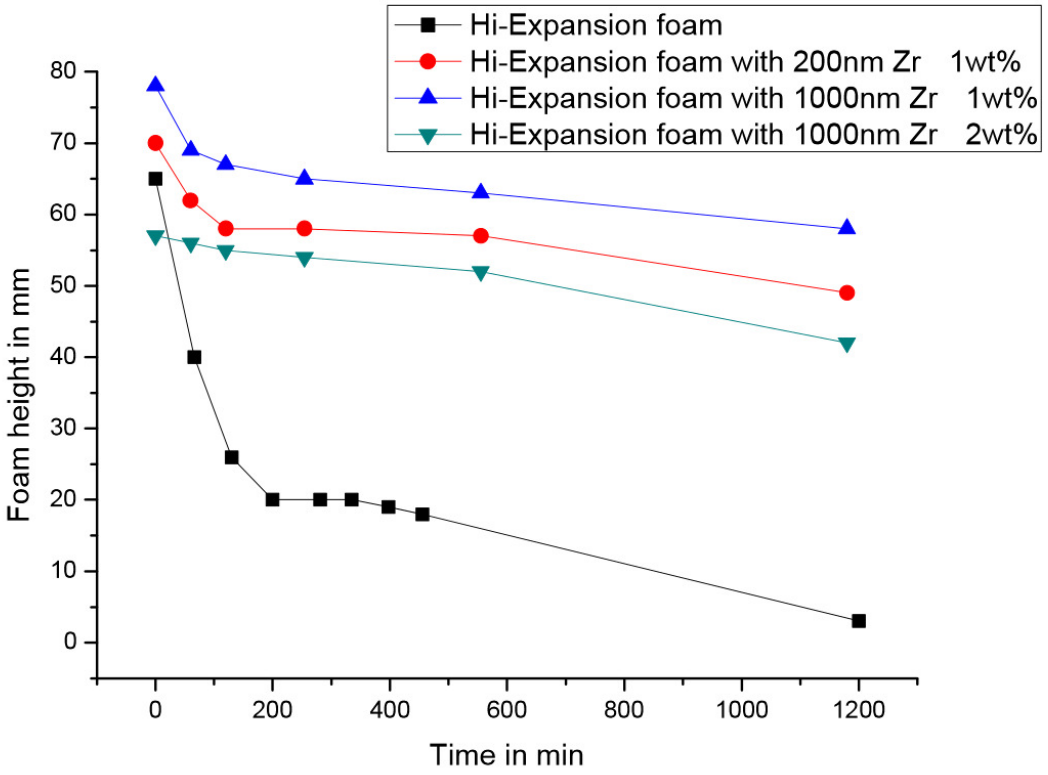

(d)
2012/05/08 14 54


(e)


(f)


(a)
Ultrasonic anemometers
Polystyrene box
Liquid nitrogen hose
(b)
Thermocouples
Plexiglas additional walls
Liquid nitrogen
(c)
Wind tunnel
Fan
Plexiglas additional walls
Polystyrene box
Balance
(d)





Foam height with time going with Hi-Expansion foam formula in market

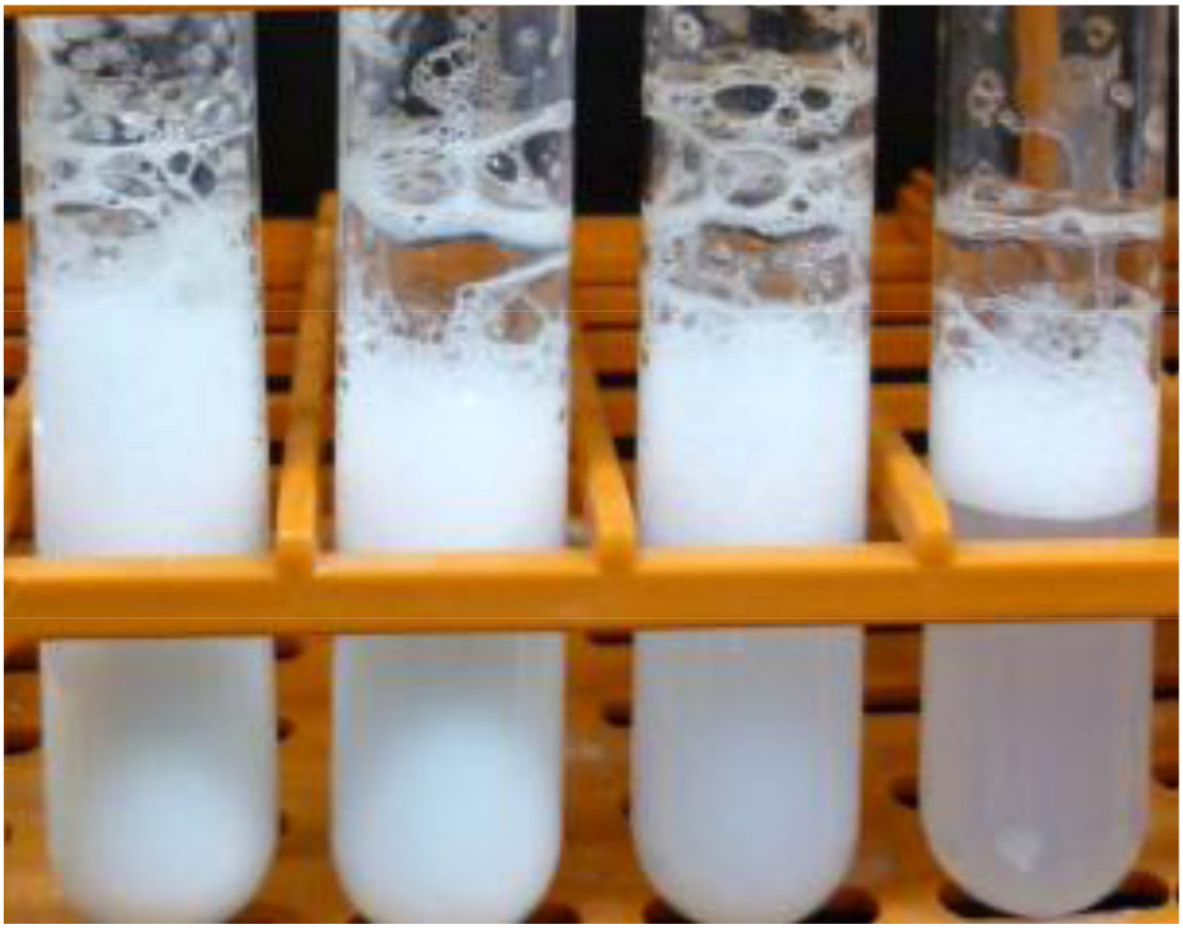
CO_2 FOAM

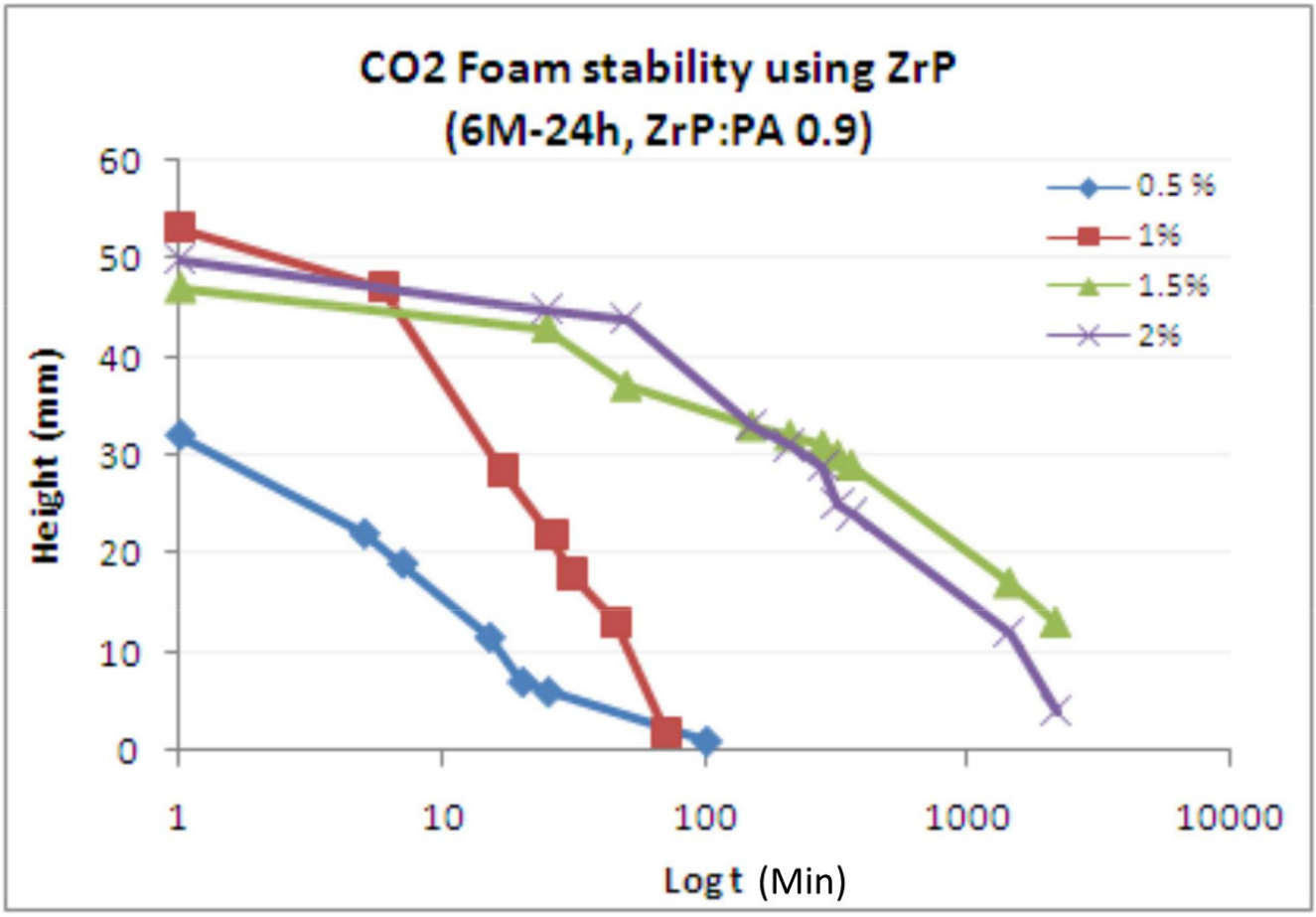


Dry ice








CO2 Foam stability using ZrP
(6M-24h, ZrP:PA 0.9)
Height (mm)
60
50
40
30
20
10
0
1
10
100
1000
10000
Log t (Min)
0.5 %
1%
1.5%
2%

Conclusion

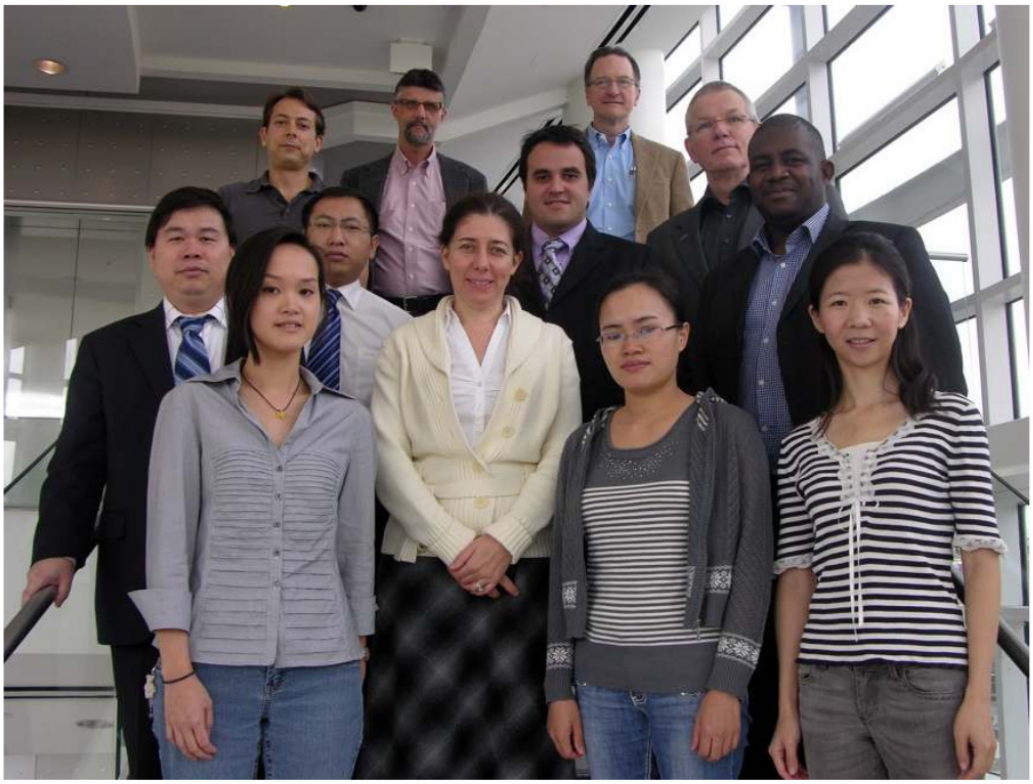
Nanoplate surfactants

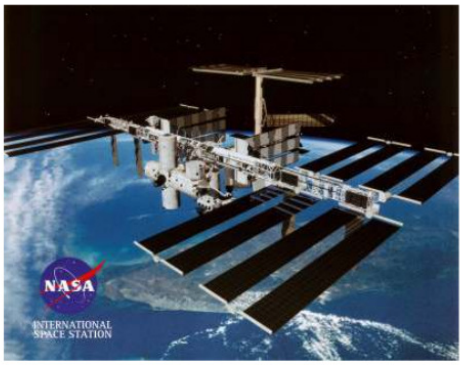
New method for emulsification and foams stabilization

Enhanced Oil Recovery

Chemical Process safety (LNG spill mitigation)

Acknowledgments





wintershall

BASF Group



DONG energy

Thanks for your attention!