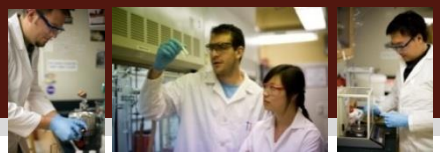
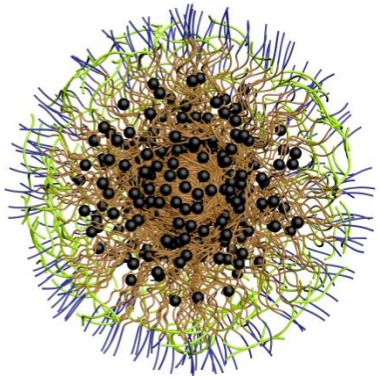
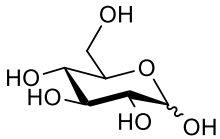


Environmental Remediation and Sustainability

Hybrid inorganic-organic nanoparticles to address environmental pollutants





Natural product-based building blocks for sustainability

Karen L. Wooley, Texas A&M University, wooley@chem.tamu.edu
Departments of Chemistry, Chemical Engineering, and Materials Science & Engineering

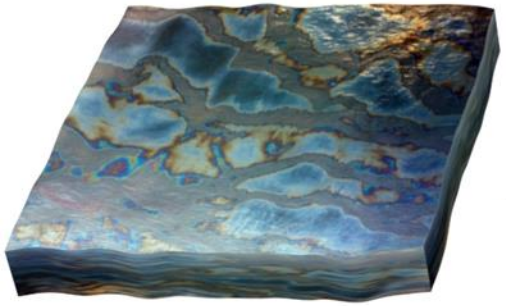
Oil Spill Response: Current methods of remediation

- Containment
  - Limits exposure
  - Facilitates recovery
- Bulk recovery
  - Current mechanical techniques
- Low concentrations
  - Sheen 0.04 to 50 µm on the water
- Current methods for sheen recovery

Images provided by Jonathan E. Sanders, MEC^{X,} L.P.

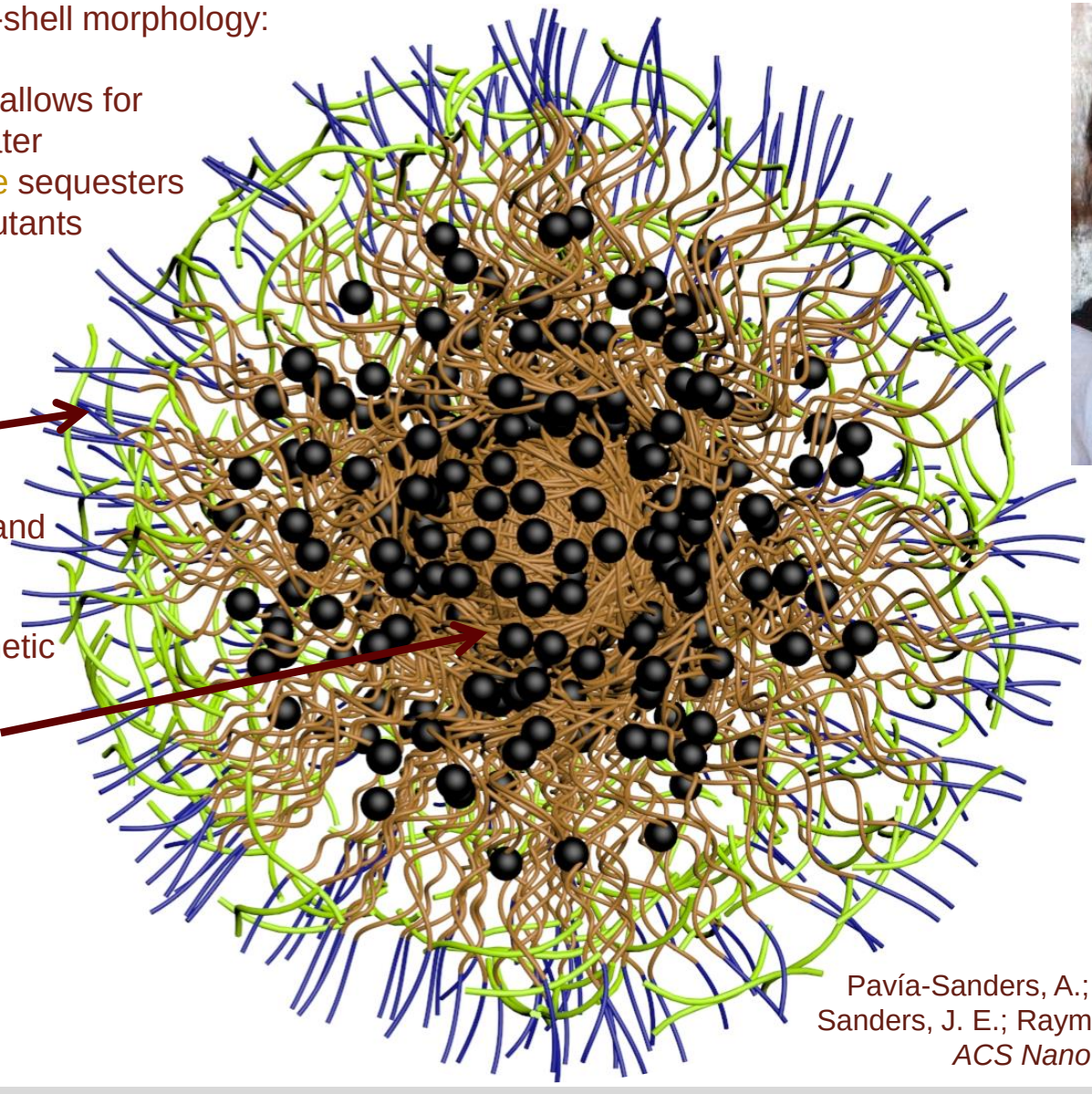
Identification of Oil on Water: Aerial observation and identification guide. A. M. S. Authority. (**2009**).

Mode of Recyclable Deployment of MSCKs



Magnetic Shell Crosslinked Knedel-like (MSCK) Nanoparticles Designed for Pollutant Recovery

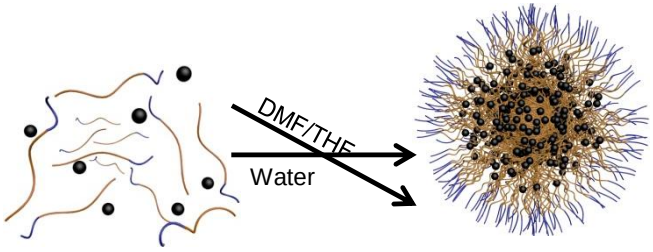
- Amphiphilic core-shell morphology:
- Hydrophilic shell allows for suspension in water
- Hydrophobic core sequesters hydrophobic pollutants



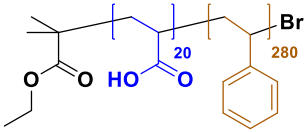
- Shell cross-linked protects micelles and stabilizes vessel
- Entrapped magnetic iron oxide nanoparticles
- High density NP loading

Pavía-Sanders, A.; Zhang, S.; Flores, J. A.; Sanders, J. E.; Raymond, J. E.; Wooley, K. L. *ACS Nano*, **2013**, *7*(9), 7552-7561.

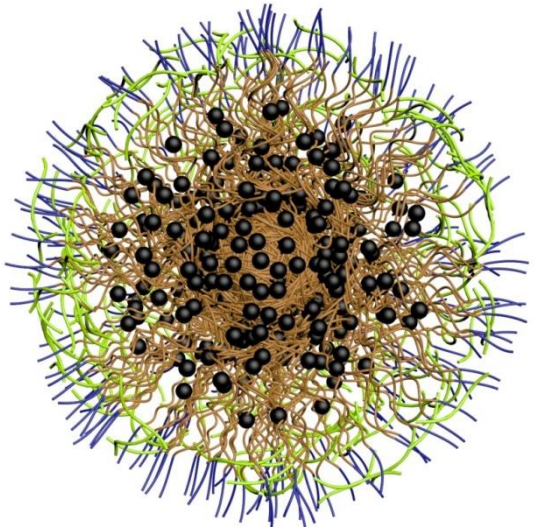
Crosslinking of Magneto Micelles



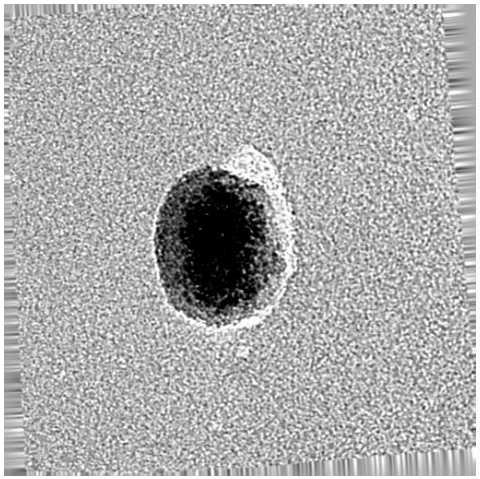
PAA_{20}-*b*-PS_{280}



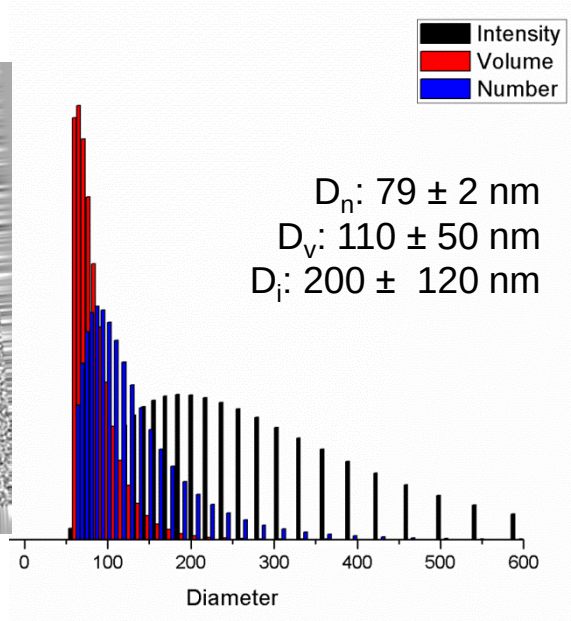
2,2′-(Ethylenedioxy) bis(ethylamine), EDCI



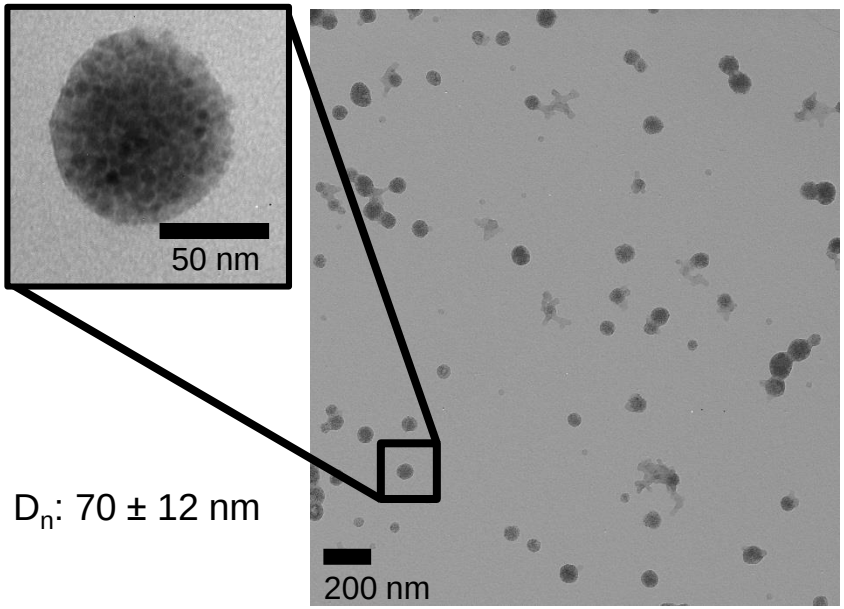
3D Tomography



Well defined core-shell morphology observed in 3D scan

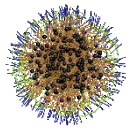


D_n: 79 ± 2 nm
D_v: 110 ± 50 nm
D_i: 200 ± 120 nm



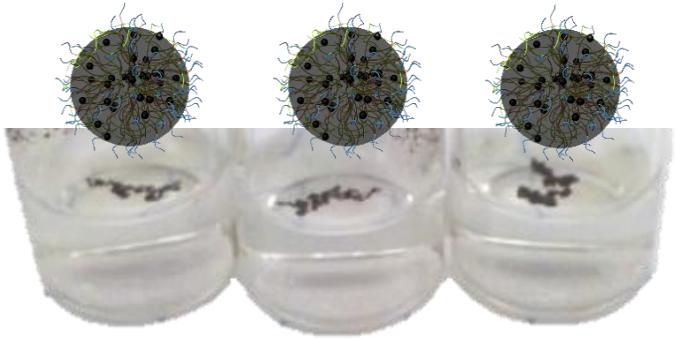
D_n: 70 ± 12 nm

MSCK-based Oil Recovery Procedure

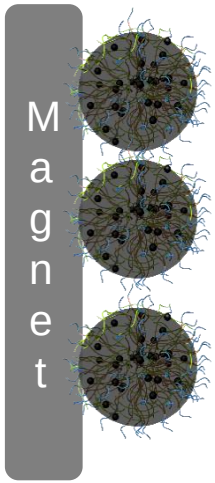


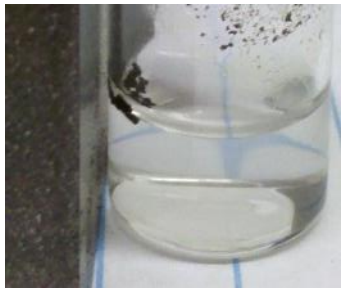
MSCKs

15-30 minutes →



Extraction *via* magnet →

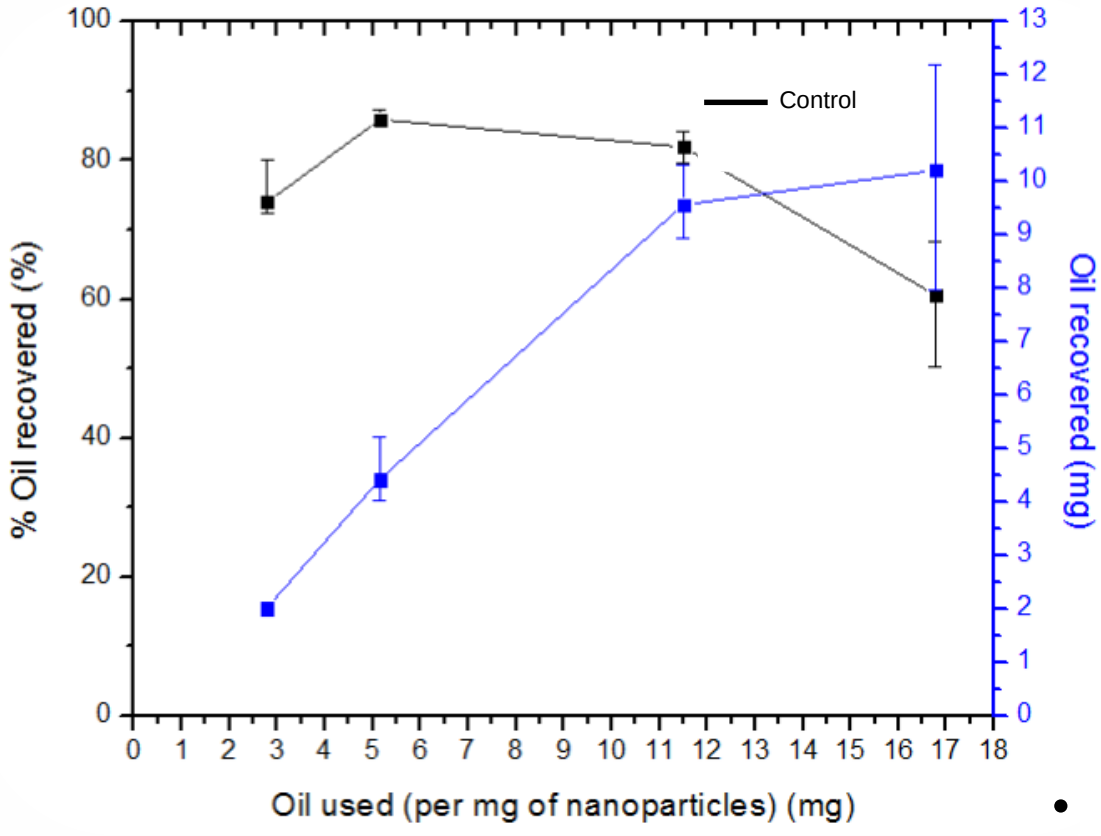




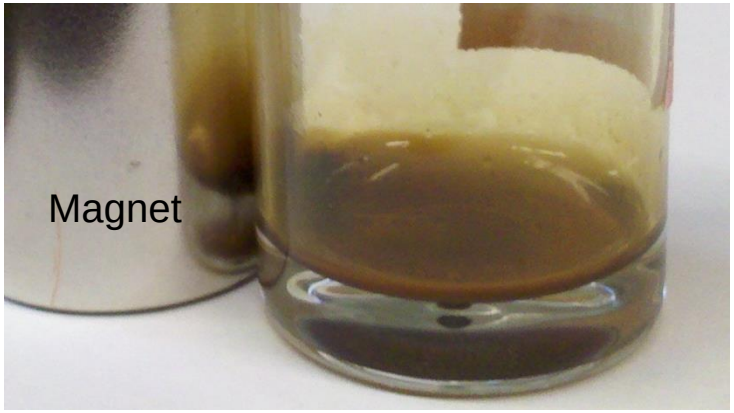
- Water and remaining oil in tests were decanted into vial to allow for extraction without the presence of MSCKs
- Extraction of oil with chloroform
- GPC used for quantitative analysis

Sequestration Data and Oil Evaluation

10X oil uptake



Initial MSCK: Oil	Recovery ratio	% oil recovered
1:2.8	1:2.1	74.0%
1:5.1	1:4.4	85.9%
1:11.5	1:9.6	81.2%
1:16.8	1:10.2	60.6%



- GC/MS analysis of extracted oil

Uptake of all oil fractions

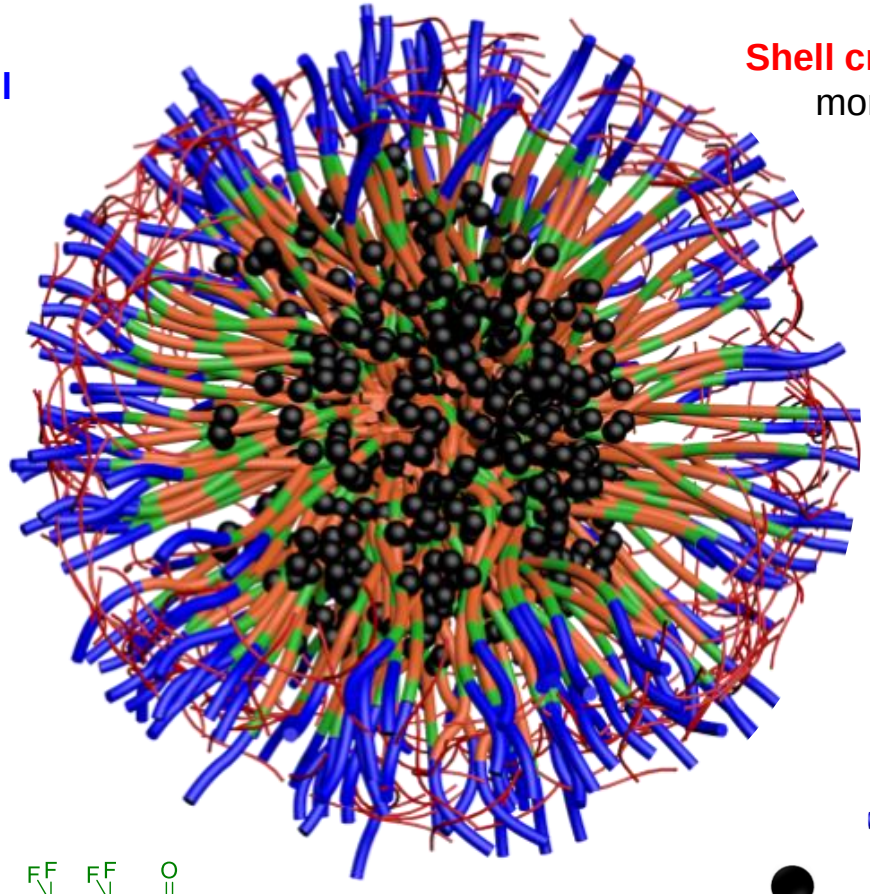
Design of Fluorinated MSCK (MSCK-F_9) Nanoparticles

Hydrophilic shell allows for particle suspension in water

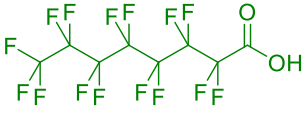
Shell crosslinks protect the morphological assembly while allowing for expansion and contraction

Fluorinated hydrophobic core facilitates nanoparticle assembly and provides an environment for capture of fluorinated and/or hydrophobic guests

Iron oxide nanoparticles entrapped in the core provide magnetic responsiveness



PFOA is an environmentally-and biologically-persistent pollutant

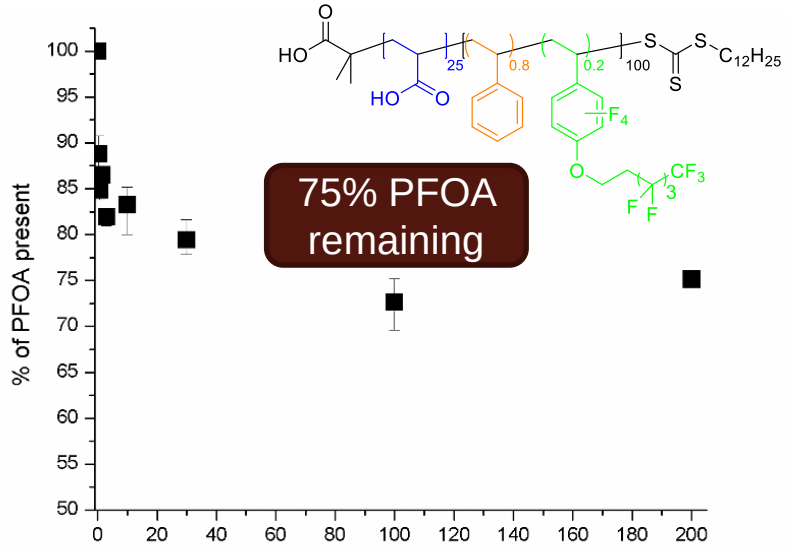


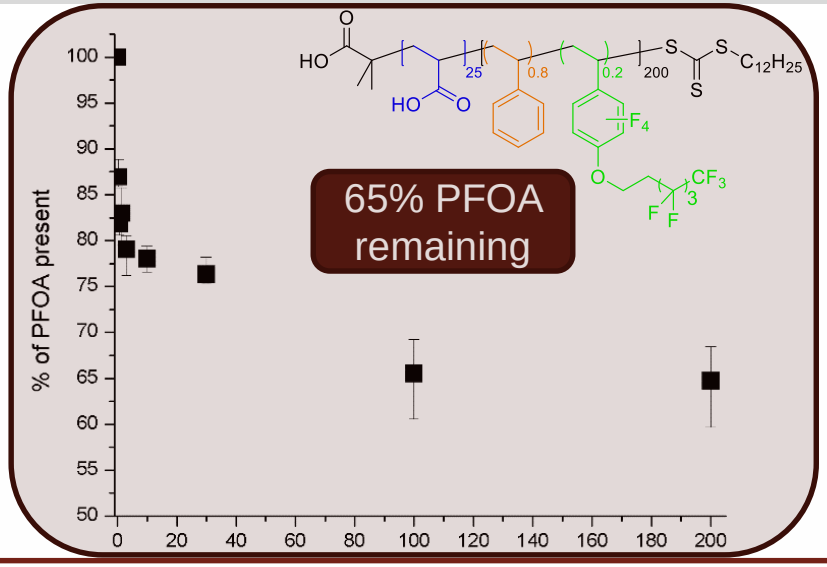
Iron oxide nanoparticle

Amphiphilic diblock copolymer

Pavía-Sanders, A.; Ward, S. M.; Jahnke, A. A.; Zigmond, J. S.; Smolen, J. A.; Wooley, K. L. "A Nanotechnological Device for Effective Capture of the Persistent and Ubiquitous Pollutant Perfluorooctanoic Acid (PFOA)", *Nature Nanotech.*, submitted

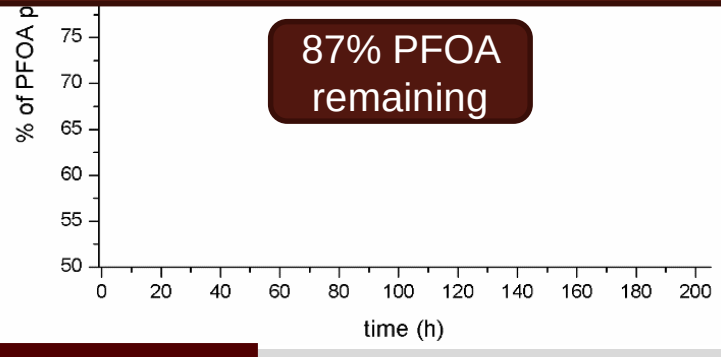
PFOA Sequestration Results

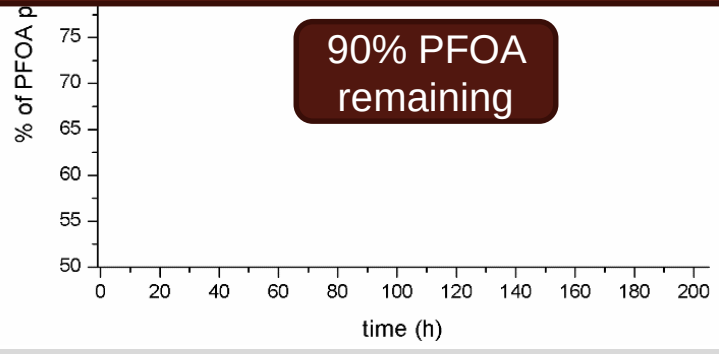




Hypothesis: Greater removal of PFOA due to size difference of nanoparticles *ca*. 60, 72, 40, and 42 nm in diameter.

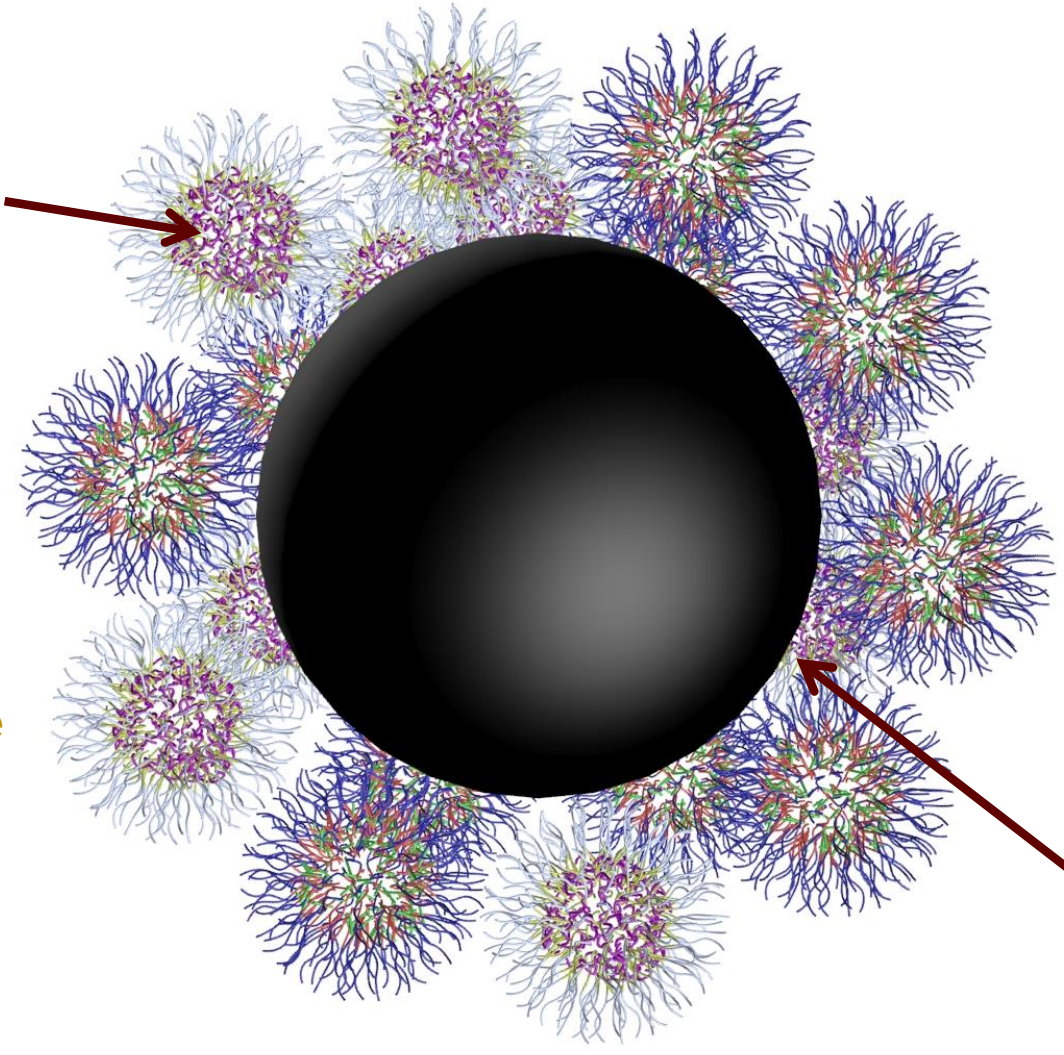
At 35% PFOA recovery, *ca*. 0.35 mg PFOA/mg MSCK-F_9, PFOA removal is two orders of magnitude better than other reported nanomaterials!





New Multi-compartment MSCK Nanoclusters

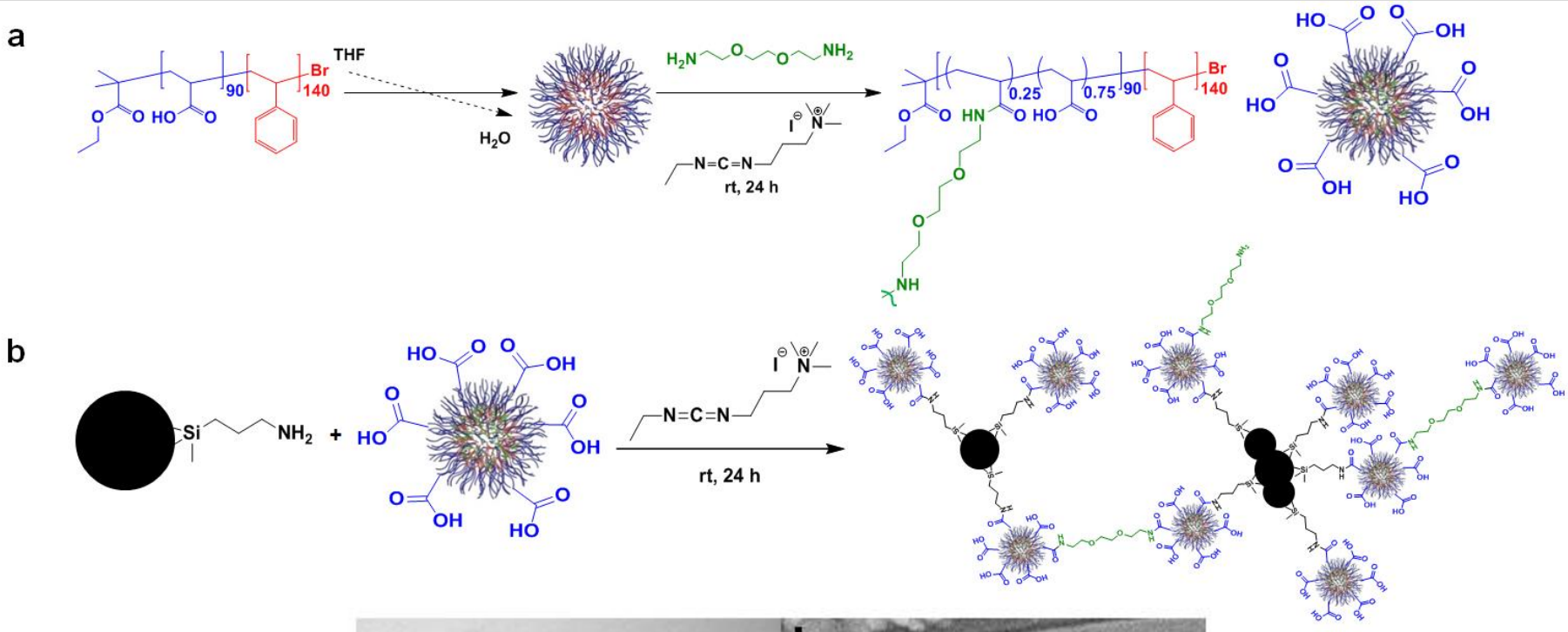
- Satellite amphiphilic shell crosslinked knedel-like (SCK) nanoparticles
- SCK hydrophilic shell allows for water solubility and covalent linkage to inorganic component
- Hydrophobic core preferentially sequesters hydrophobic pollutants

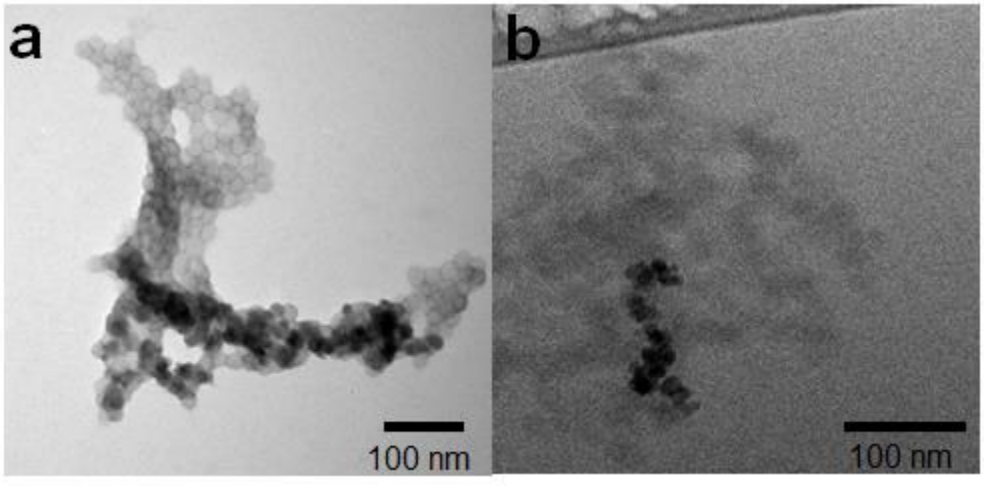


- Incorporating SCKs with differing compositions offers enhanced tunability of material for targeted remediation
- Large inorganic core for magnetic response of the material

Flores, J. A.; Pavia-Sanders, A.; Chen, Y.; Pochan, D. J.; Wooley, K. L. *Chem. Mater*. **2015**, *27*, 3775-3782.
Flores, J. A.; Jahnke, A. A.; Pavia-Sanders, A.; Cheng, Z.; Wooley, K. L. *Soft Matter,* **2016**, *12*(46), 9342-9354.

Magnetic Hybrid Networks (MHNs)



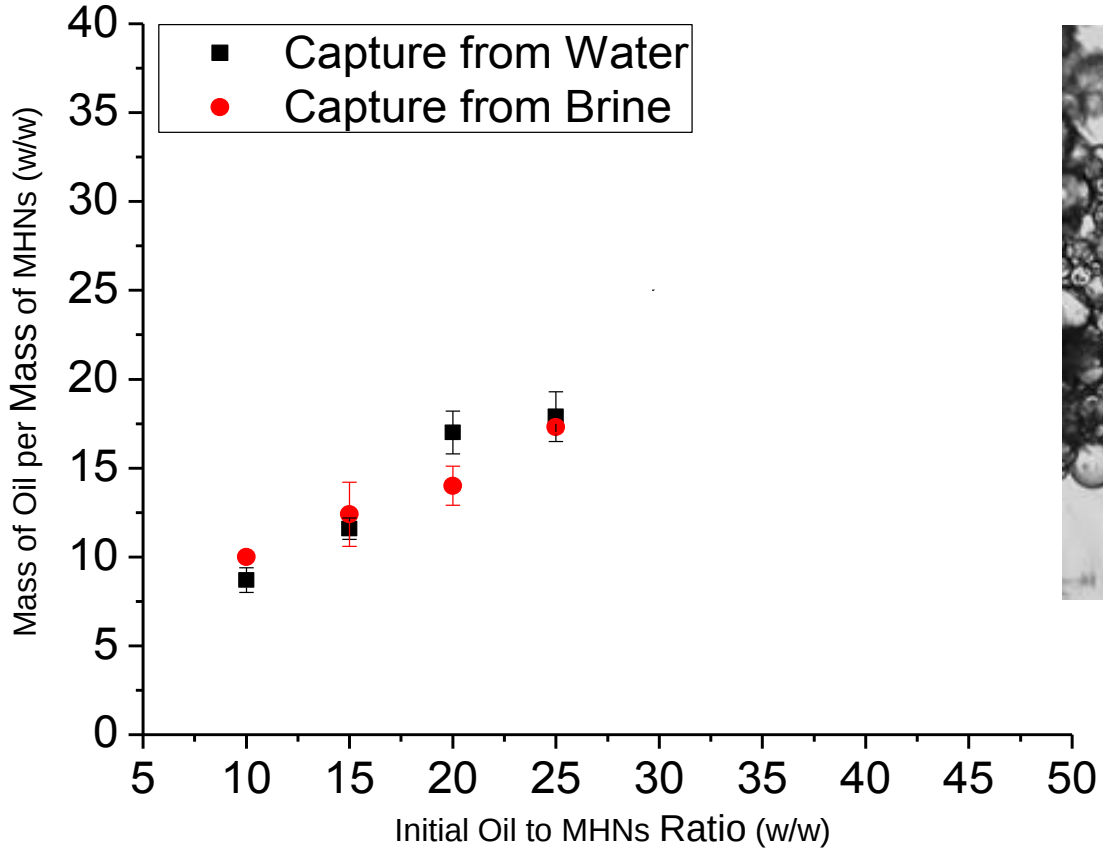


[Yingchao Chen w/Darrin Pochan]

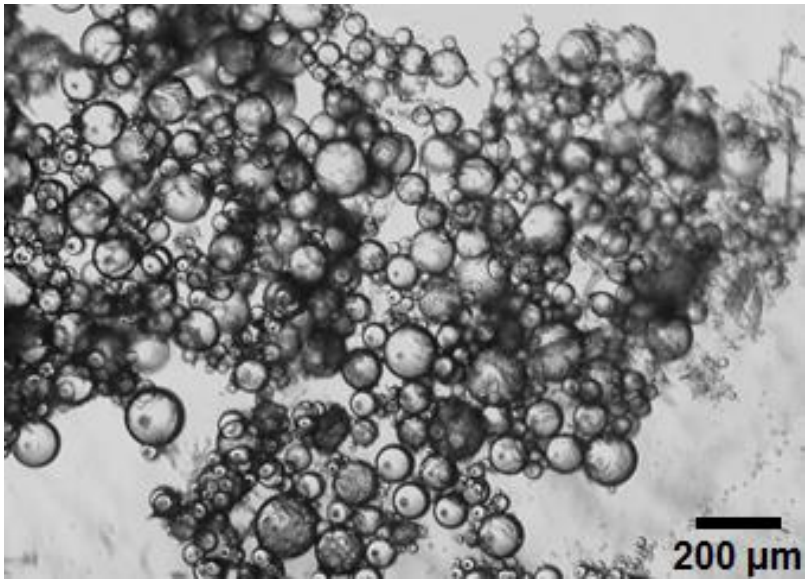
Performance of the MHNs is Compromised in the Presence of Brine

- Formation of an emulsion was observed upon hand-shaking of the water/dodecane/MHN mixture

Loading Capacity Ratio of the MHNs Towards Dodecane



MHNs Deployed in a Dodecane/water Mixture after Shaking

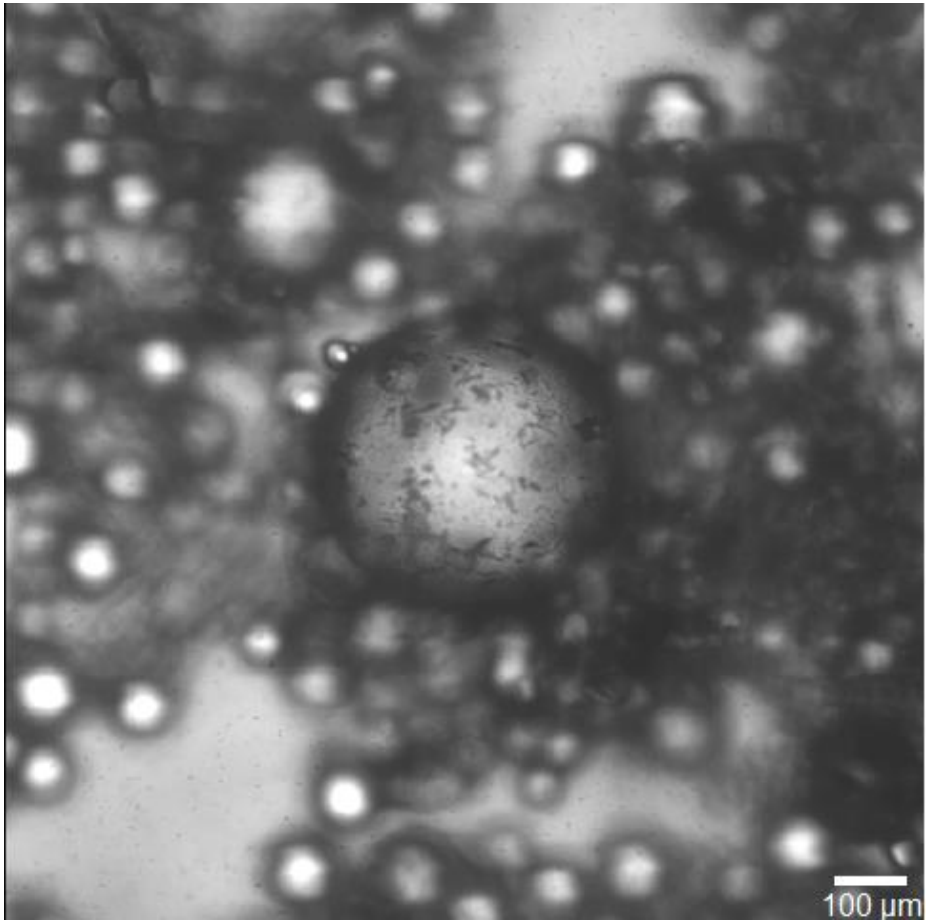


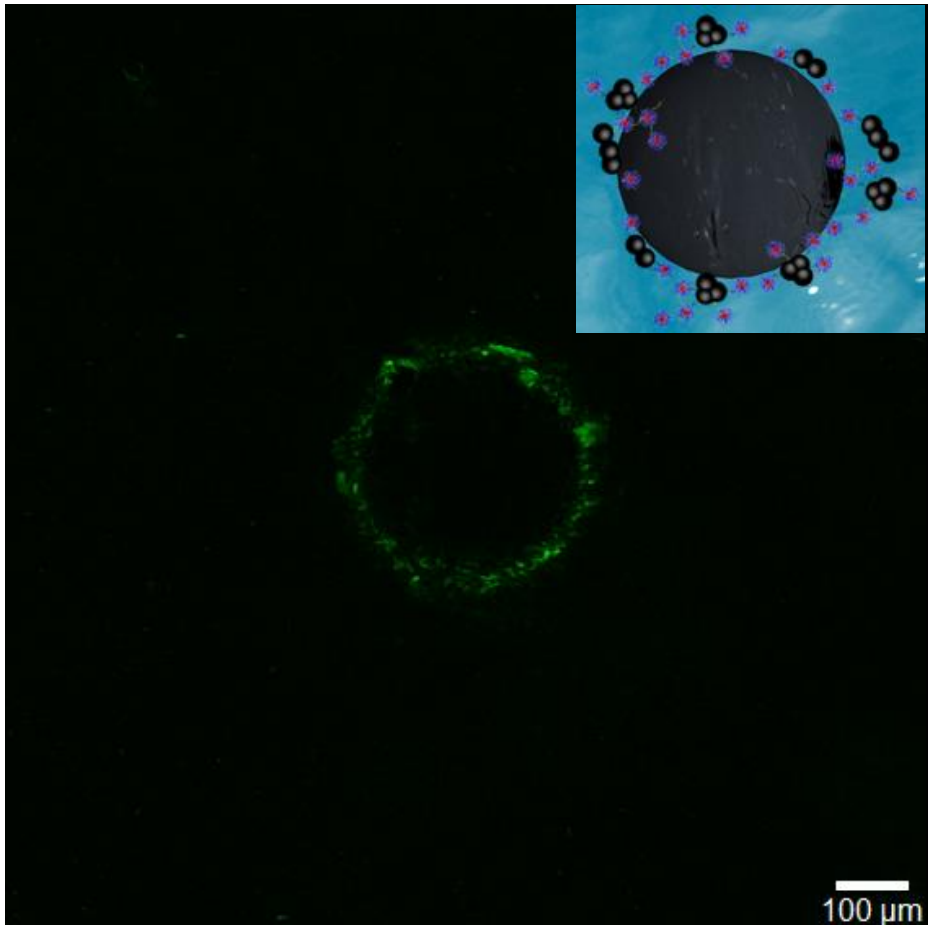
- Emulsification ability can be compromised in saline environments

- **Maximum Capacity in water = *ca.* 30 mg of dodecane per 1 mg of MHNs**
- **Maximum Capacity in brine = *ca.* 17 mg of dodecane per 1 mg of MHNs**

The MHNs Assemble at the Droplet Interface to Stabilize the Emulsion

- FITC was covalently bound to the MHNs

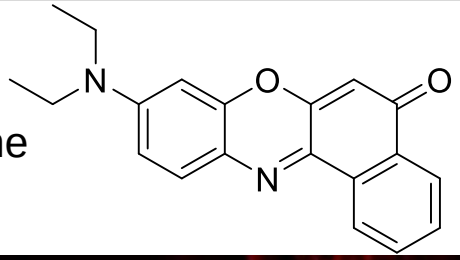




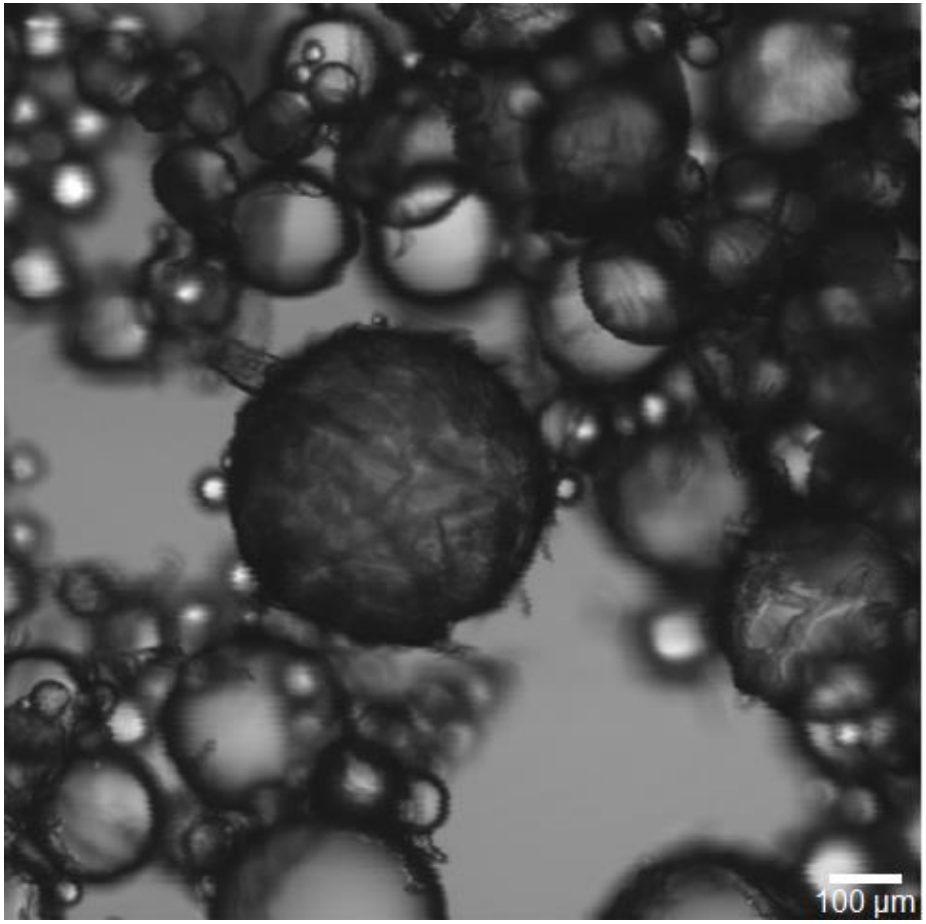
- Emulsions were formed by hand-shaking the dodecane/water/MHN mixture

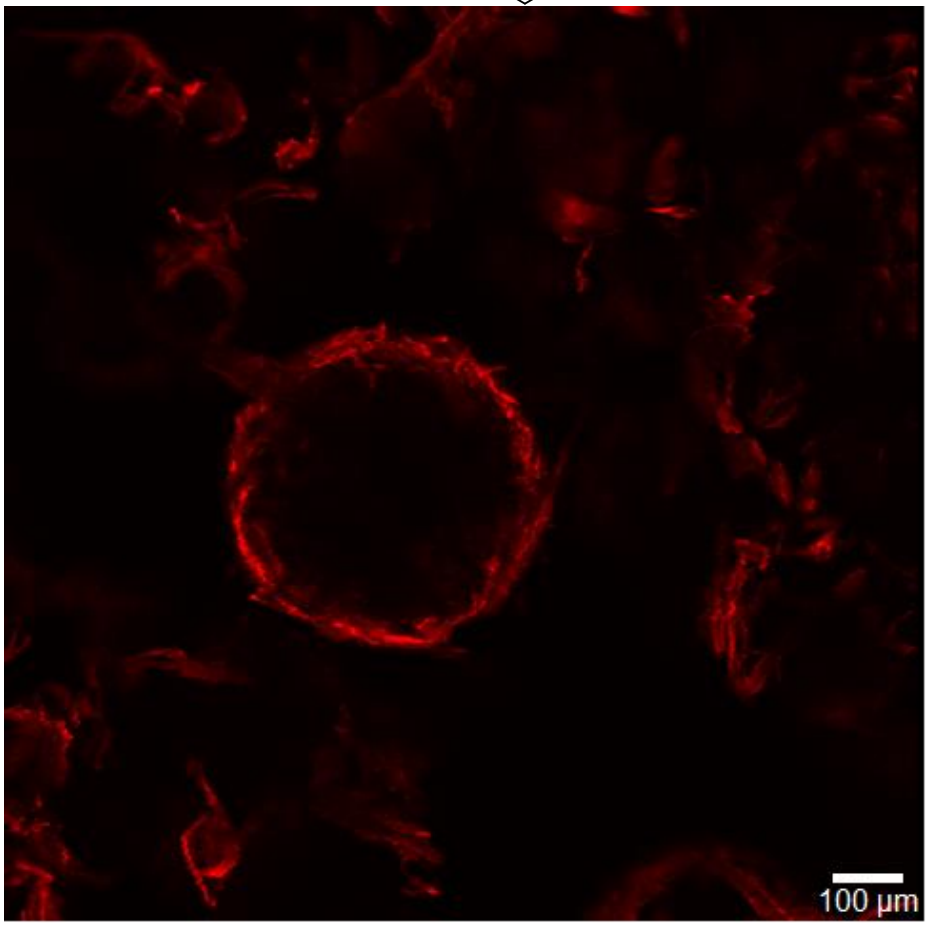
The MHNs Sequester the Hydrophobic "Pollutants"

- Nile red was dissolved in dodecane
- MHNs were not labeled with FITC
- Sample was excited with at a wavelength of 543 nm, the MHNs exhibit red fluorescence



Nile red

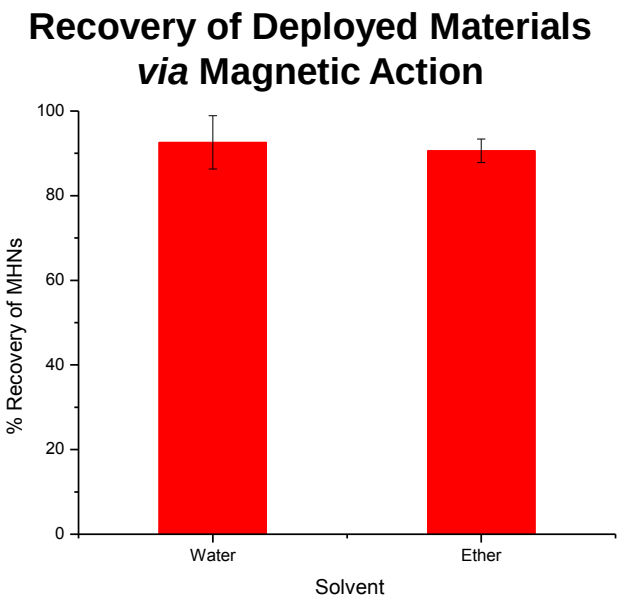




The Emulsion Droplets are Magnetically-active

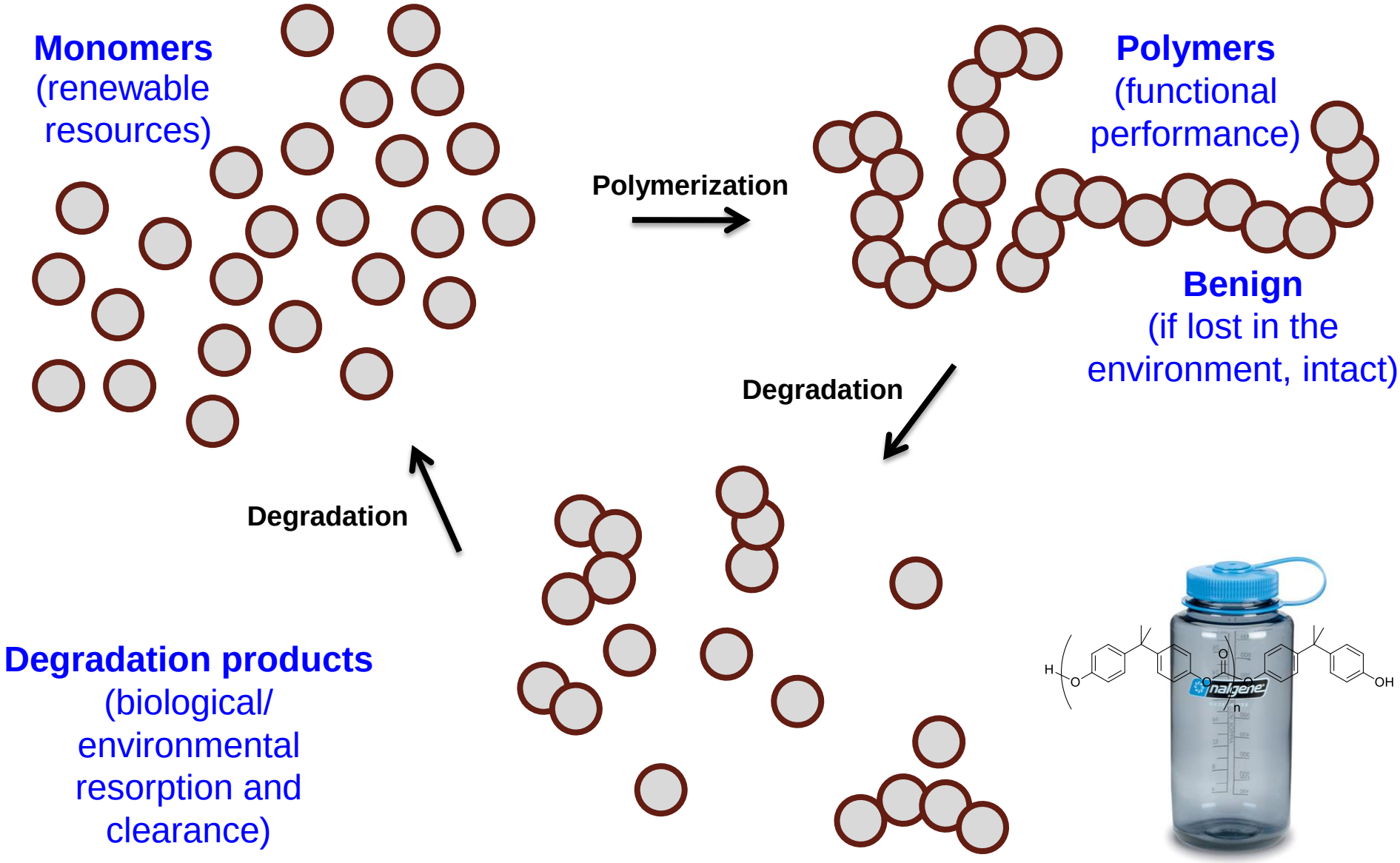
Flores, J. A.; Jahnke, A. A.; Pavia-Sanders, A.; Cheng, Z.; Wooley, K. L. *Soft Matter,* **2016**, *12*(46), 9342-9354

Potential Concerns with Unrecovered Nanoparticles



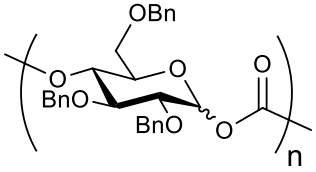
- *ca*. 93% recovery after deployment
- *ca.* 90% recovery after organic wash

Idealized Polymer Life Cycle

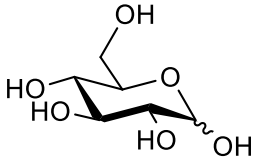


Current Status for Wooley Group Natural Product-based Polymers

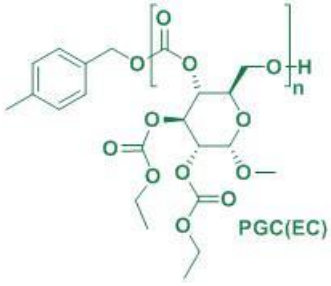
Linear Polycarbonates w/control Over Regiochemistry

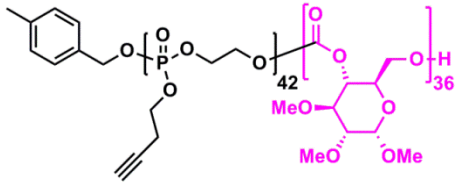


Glucose & other sugars



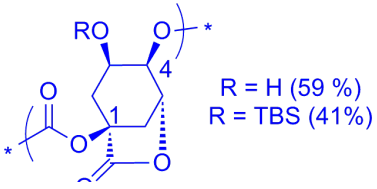
SUGAR PLASTICS™

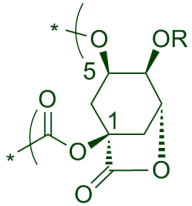


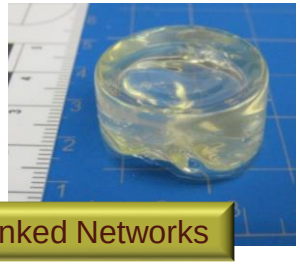


Linear Polycarbonates and Block Copolymers by ROPs

Quinic Acid

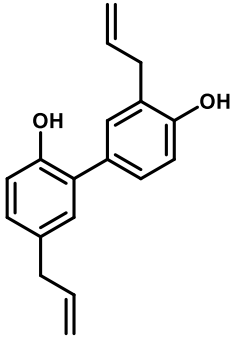




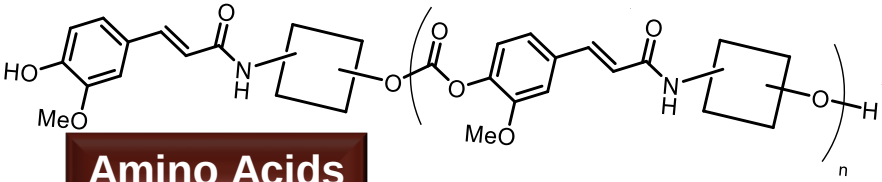


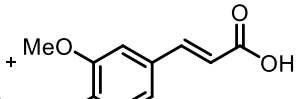
Crosslinked Networks

Honokiol

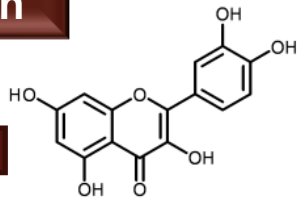


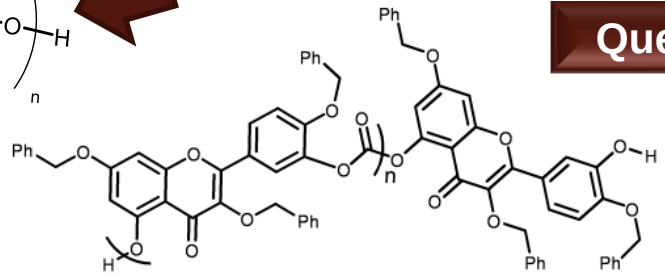
Ferulic Acid



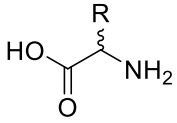


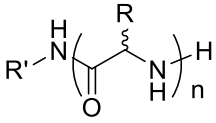
Quercetin





Amino Acids





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Kevin Wacker
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(A-0001)