Organic-Inorganic Hybrids for Energy & Environmental Applications

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Center for Energy and Sustainability

emc2 ENERGY MATERIALS CENTER at CORNELL

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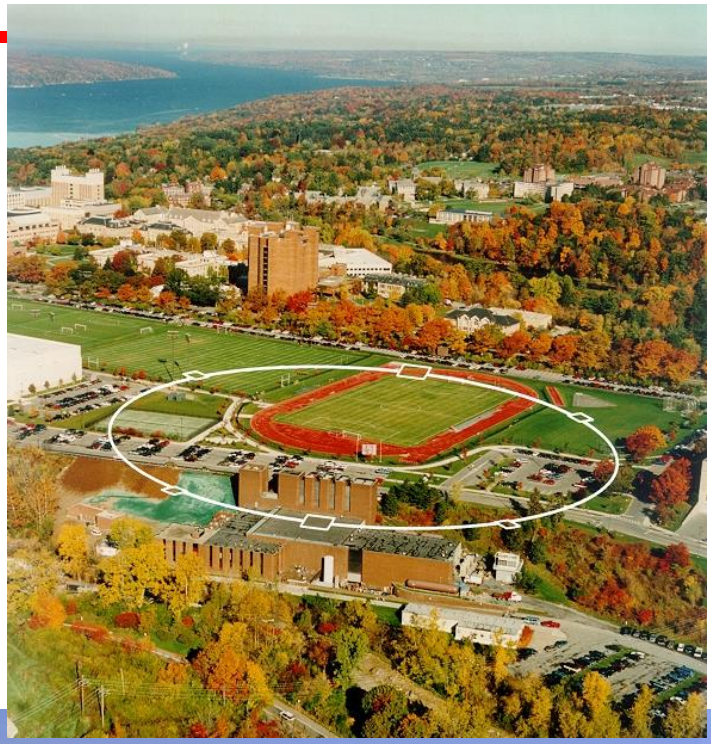
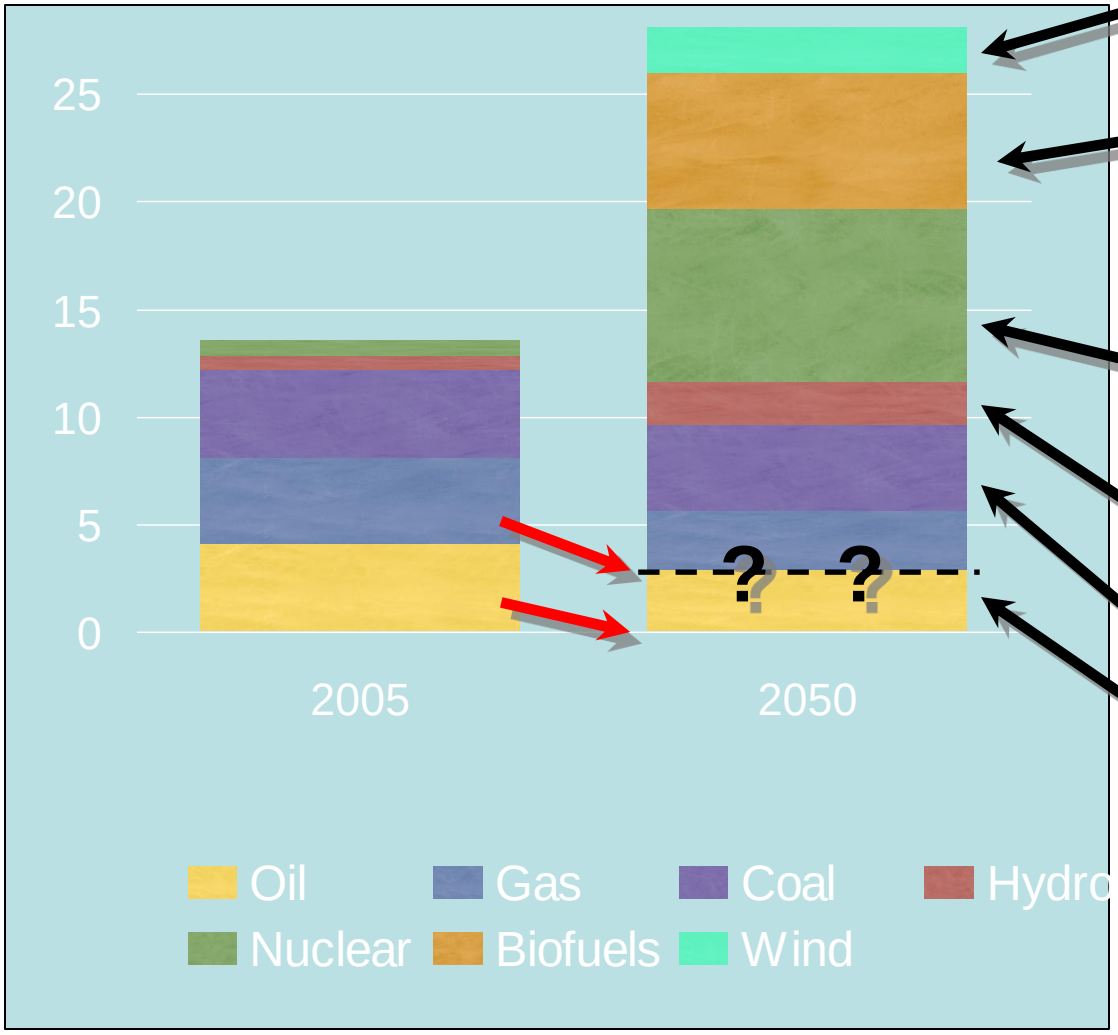


Energy Needs in 2050



If 4% of all class 3+ wind sites on planet is used

all arable land on the planet is used for biofuel production or food

8000 new nuclear plants (construct a new one every two days for next 45 years!)

Dam every river on the planet

same coal use as present

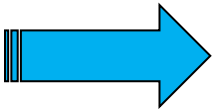
Traditional oil & gas production might be in decline

from Lewis & Nocera (2006, PNAS); Nocera (2006, Daedalus)

Polymer Nanocomposites: Opportunities

- **Synergy**
  - change of crystal phase/morphology of polymer
  - effect on structure/dynamics of polymer chains
  - "confinement" effects
  - …as opposed to simple mixtures

- **Interfaces**
  - behavior dominated by interfaces/synergy
  - …as opposed to weighted average of bulk properties



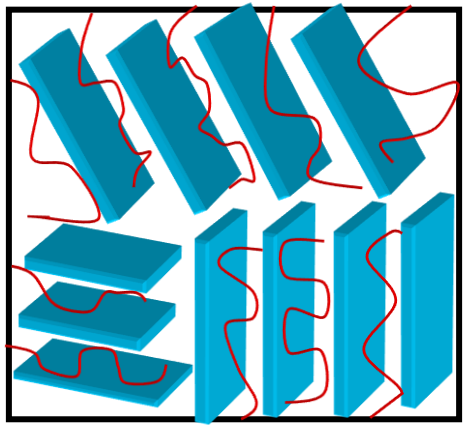
Overcome Tradeoffs in Materials Properties/Performance

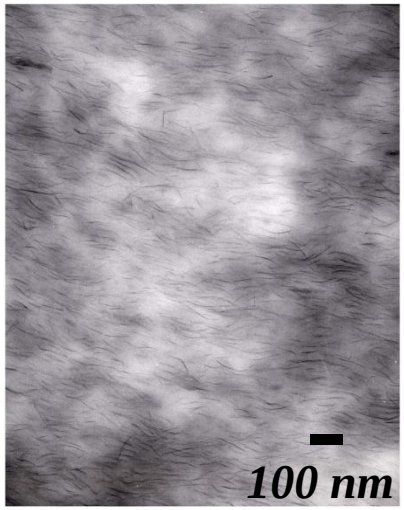
Polymer Nanocomposites

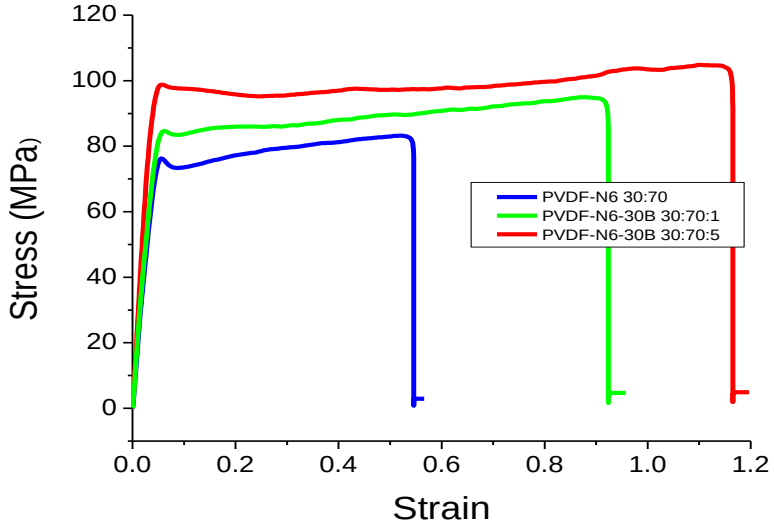
- **Widespread interest in *nanocomposites* has been motivated by the promise of unique performance, design flexibility, and lower cost**
  - **Market forecast for nanocomposites $800M by 2011 (24% pa)**

- **Persistent challenges with poor miscibility, dispersion and interfacial strength have prevented nanocomposites from realizing their full potential**

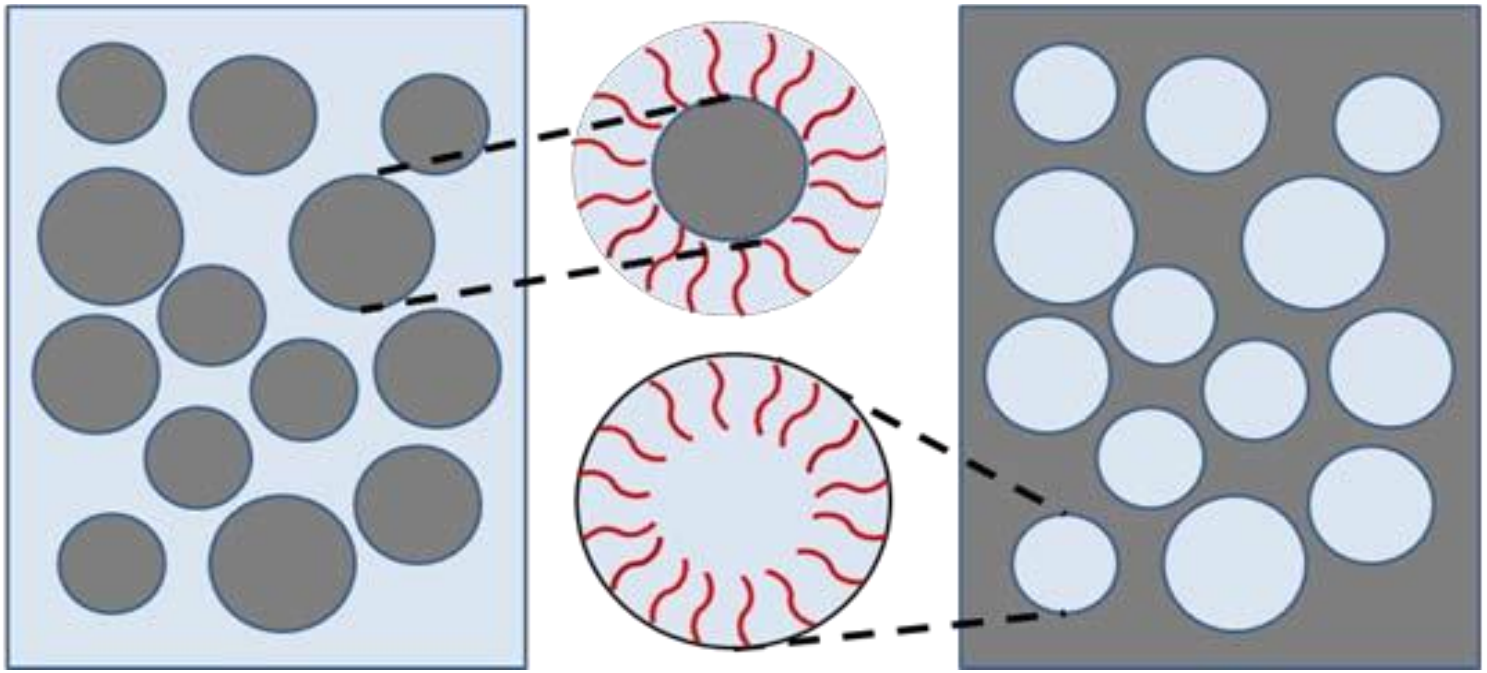
Clay Nanocomposites







New Nanocomposite Platforms

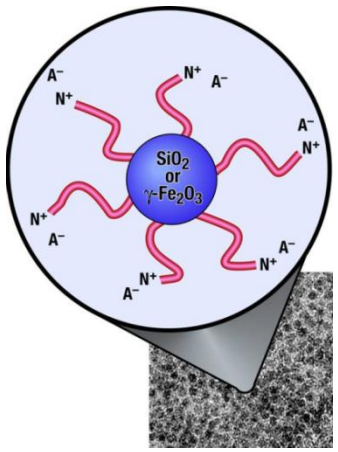


(a) (b)

a) Organic Molecules Tethered on Nanoparticles
b) Organic Molecules Tethered on a Porous Matrix

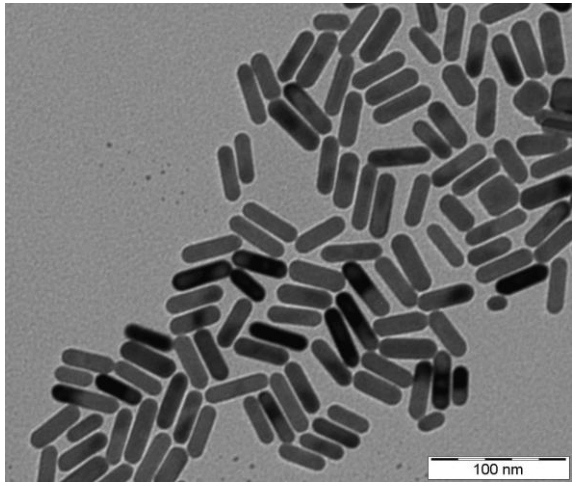
Opportunities: Science & Technology

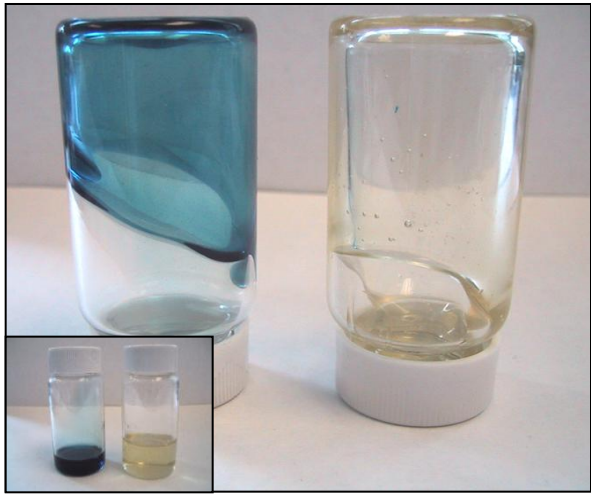
- **Particles carry solvent on their back**
  - No volatiles – environmentally friendly



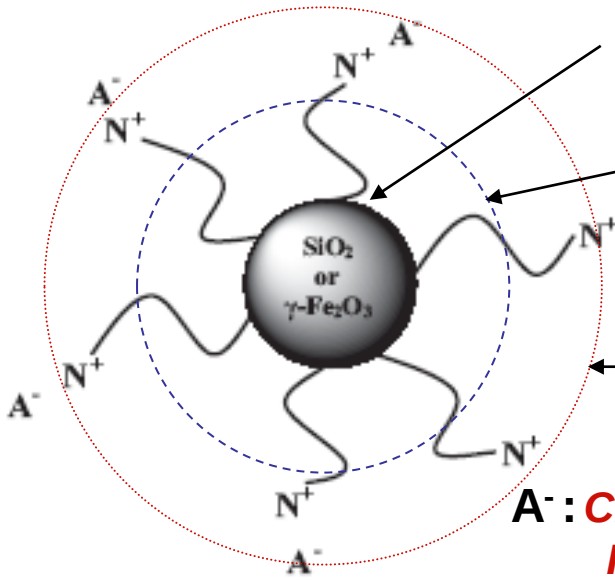
- **Tunable materials properties**
  - Fluidity (liquid, gels, LC, solid)
  - conductivity, magnetic susceptibility, refractive index

- **External fields can be used for assembly**





Gen-1 NIMs



inorganic core

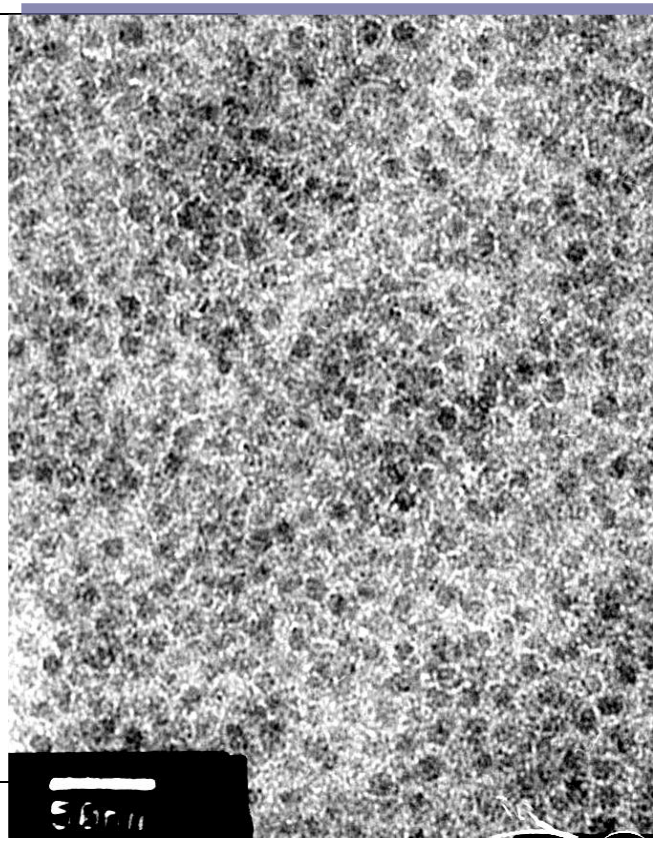
charged corona

canopy

A^- : Cl^-

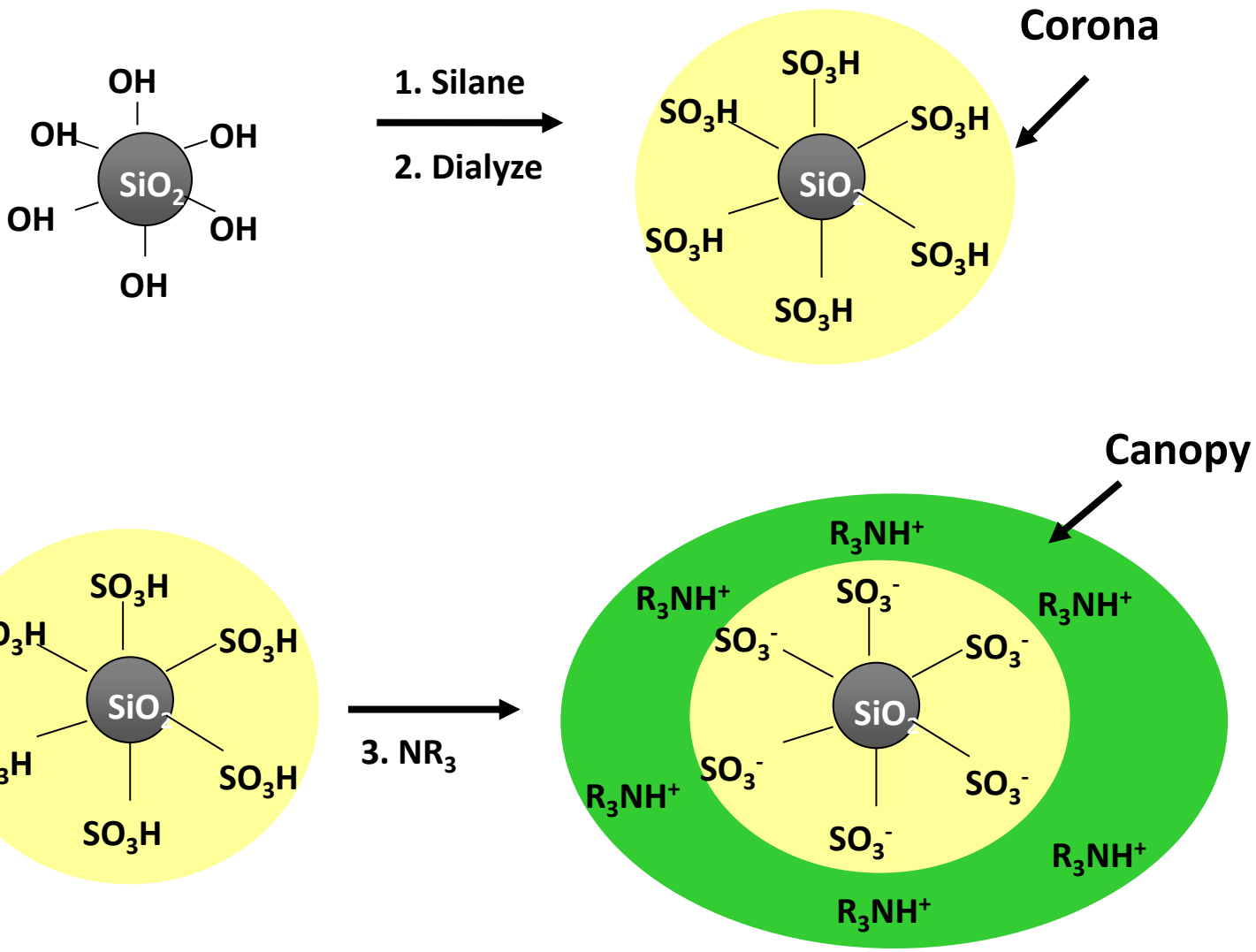
$R(OCH_2CH_2)_7O(CH_2)_3SO_3^-$

$CH_3(CH_3)CHCH_2(CH_2)_{12}CH_2COO^-$

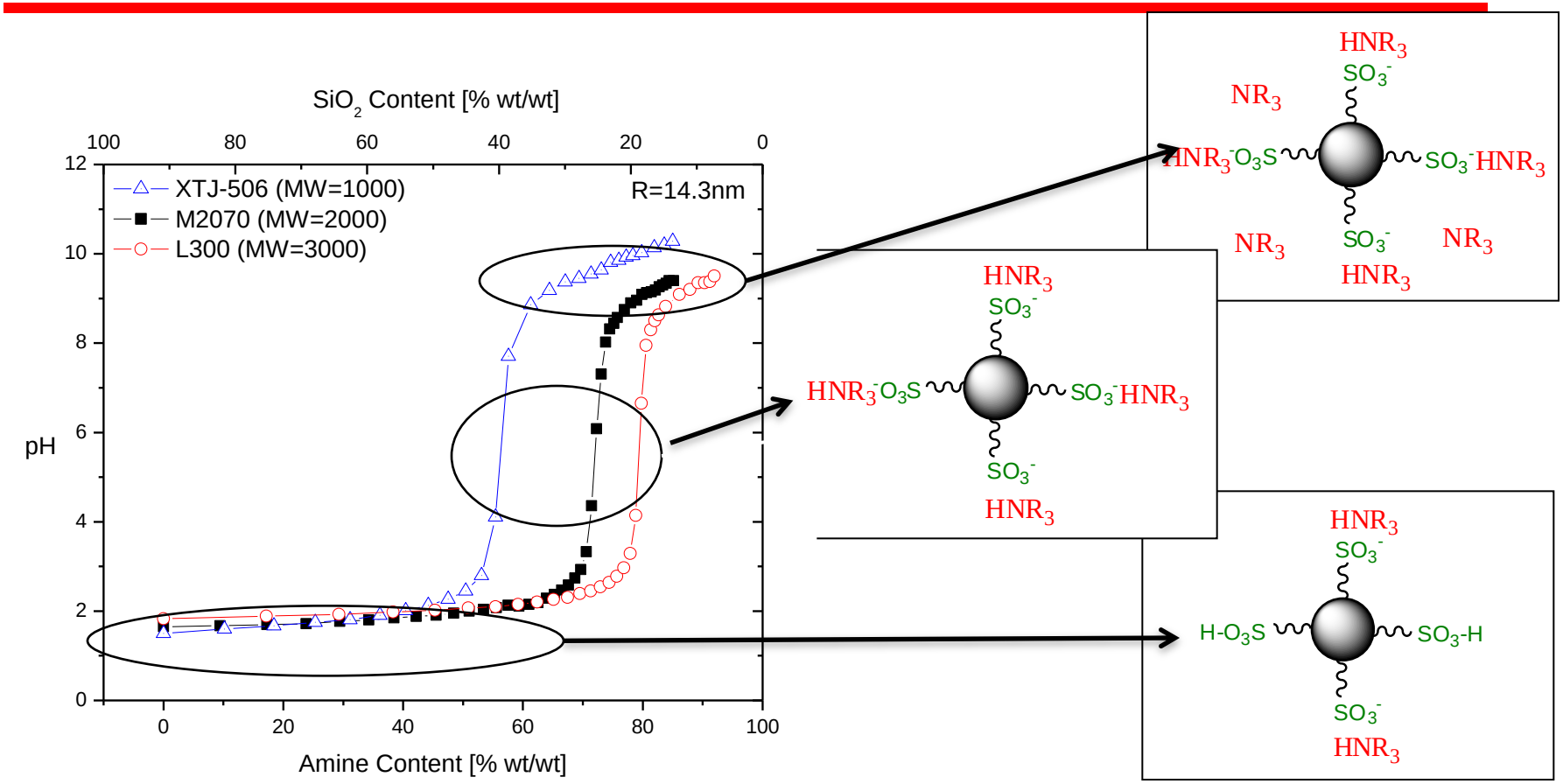


Nanoparticle *Cores*: SiO_2, TiO_2, γ–Fe_2O_3, *ZnO*, *Au*, *Ag*, *PbS*, CNTs, C_{60}

Gen-2 NIMs


OH
OH
OH
OH
OH
OH
SiO2
1. Silane
2. Dialyze
Corona
SO3H
SO3H
SO3H
SO3H
SO3H
SO3H
SiO2
3. NR3
Canopy
R3NH+
R3NH+
R3NH+
R3NH+
R3NH+
R3NH+
SO3-
SO3-
SO3-
SO3-
SO3-
SO3-
SiO2

Acid-Base Titration: NIMs Transition



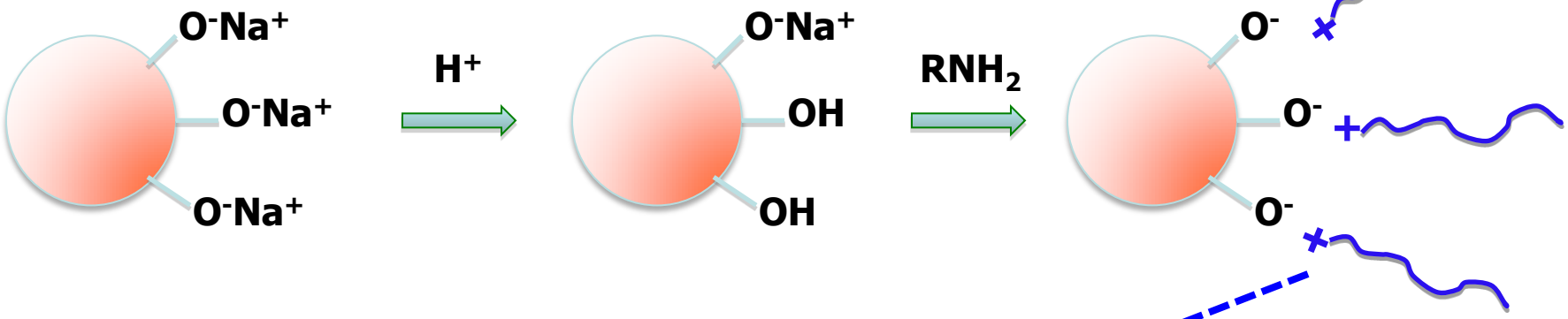
Amine	Theoretical	Experimental
XTJ-506 (MW=1000 g/mol)	40 % wt/wt	44 % wt/wt (32 % v/v)
M2070 (MW=2000 g/mol)	26 % wt/wt	27 % wt/wt (18 % v/v)
L300 (MW=3000 g/mol)	20 % wt/wt	21 % wt/wt (13 % v/v)

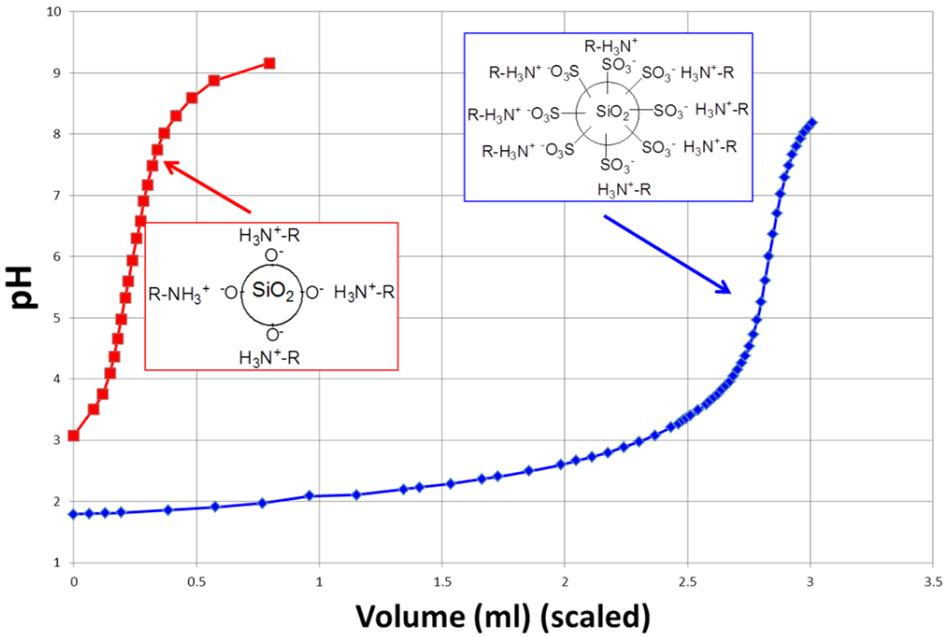
New Platform: NIMs Without Corona

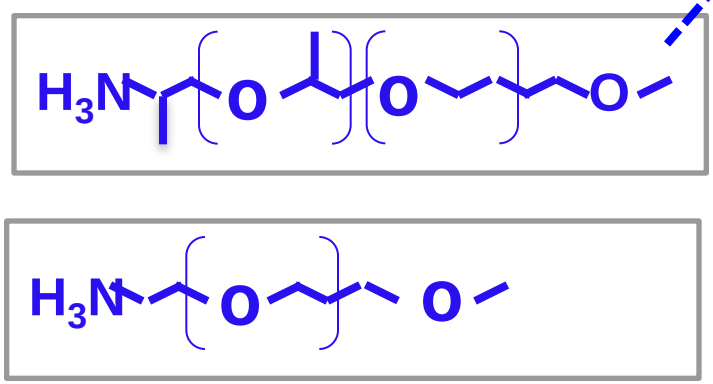
pH = 11, ζ=-30 mV

pH = 3, ζ=-5 mV

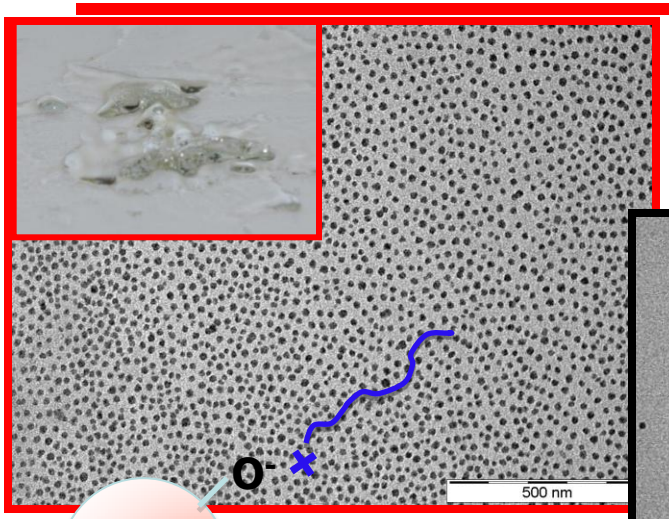
pH = 8, ζ=-17 mV

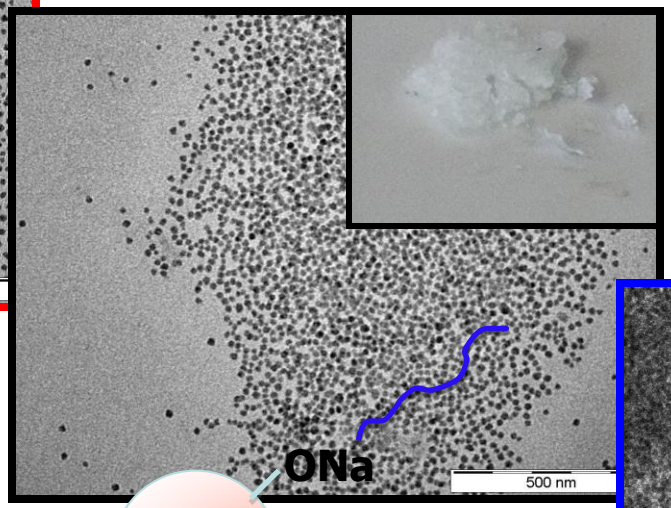


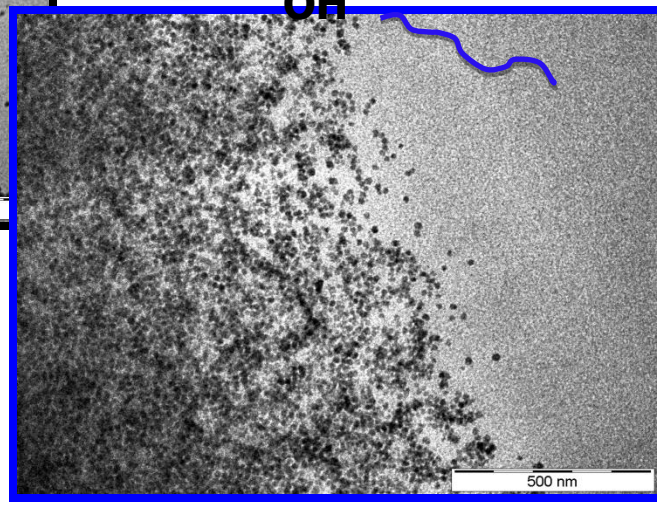


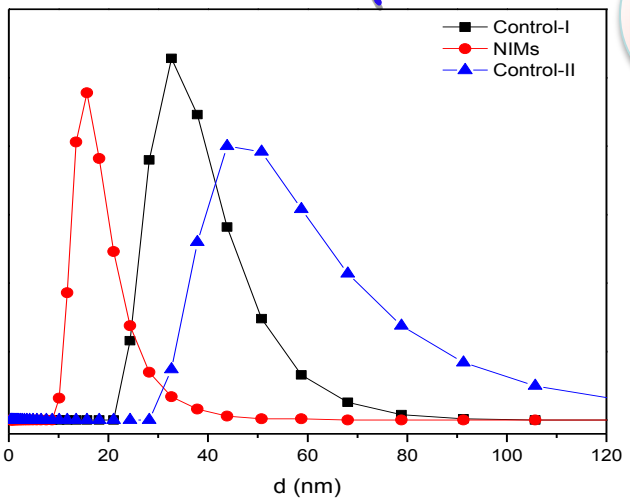


Dispersion of New NIMs

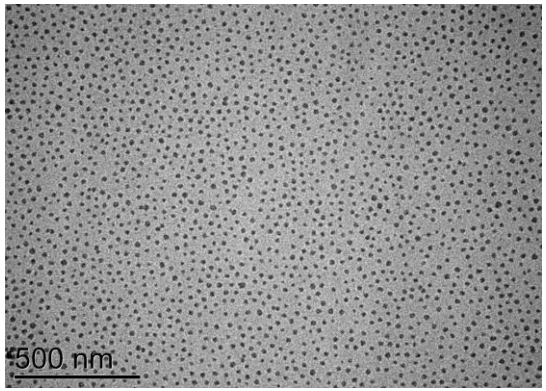




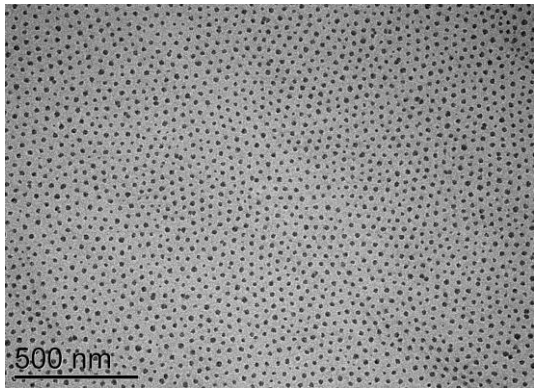




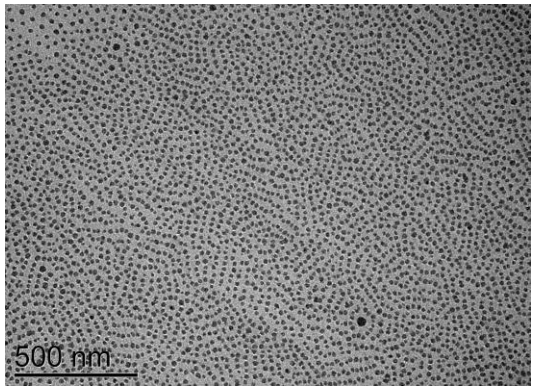
Structure: Experiment & Theory



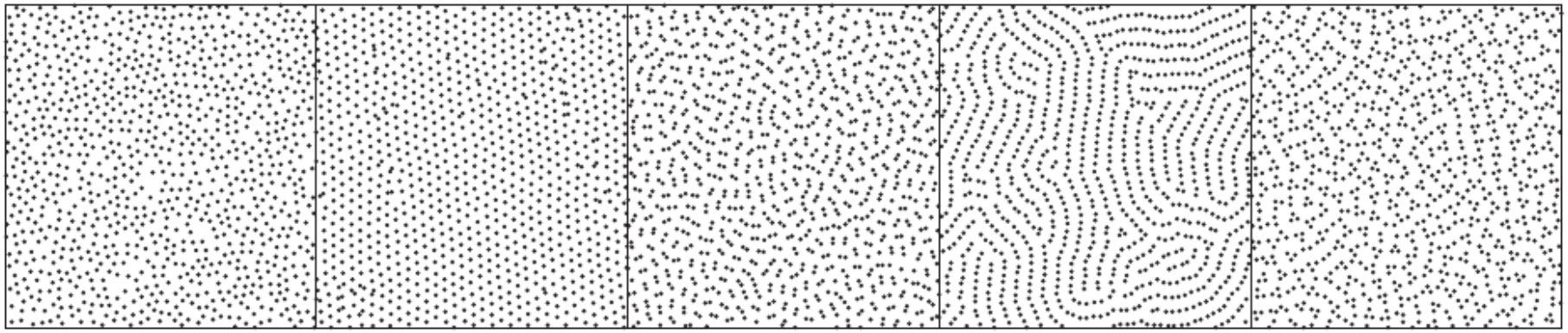
σ = 0.13



σ = 0.15

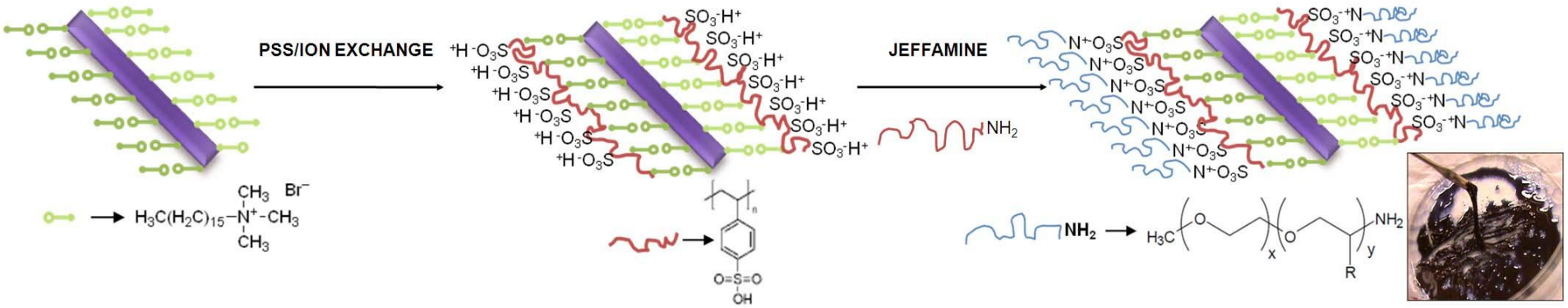


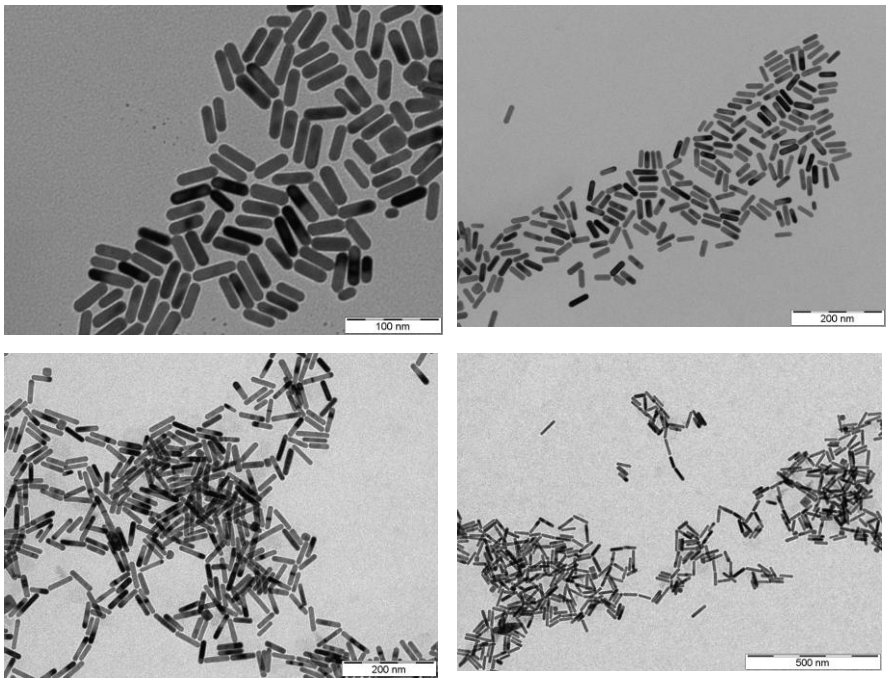
σ = 0.27

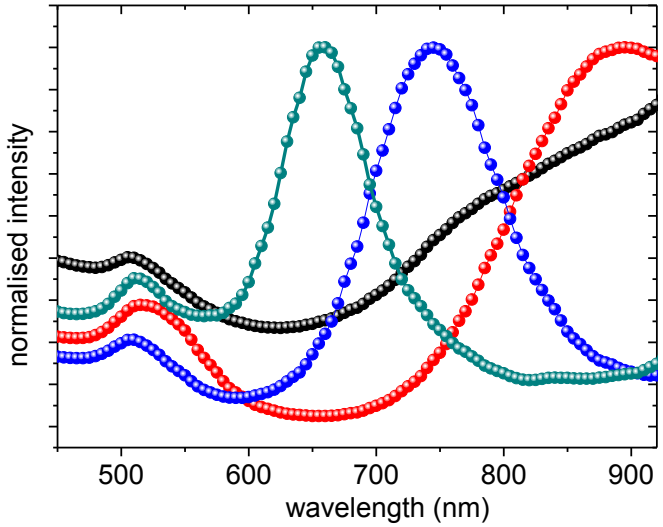


σ = 0.1 σ = 0.15 σ = 0.23 σ = 0.29 σ = 0.38

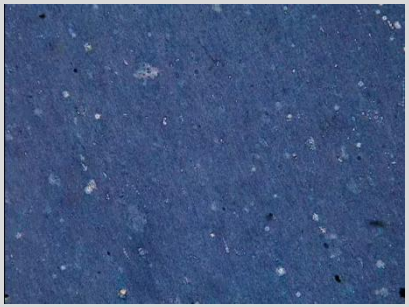
Au NIMS


PSS/ION EXCHANGE
JEFFAMINE
NH2

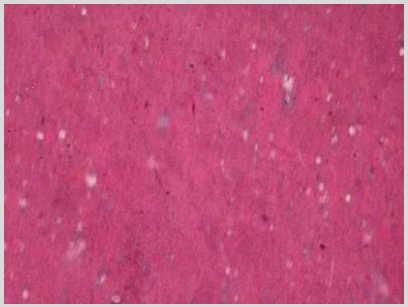

100 nm
200 nm
200 nm
500 nm


normalised intensity
500
600
700
800
900
wavelength (nm)

Modulating Optical Response

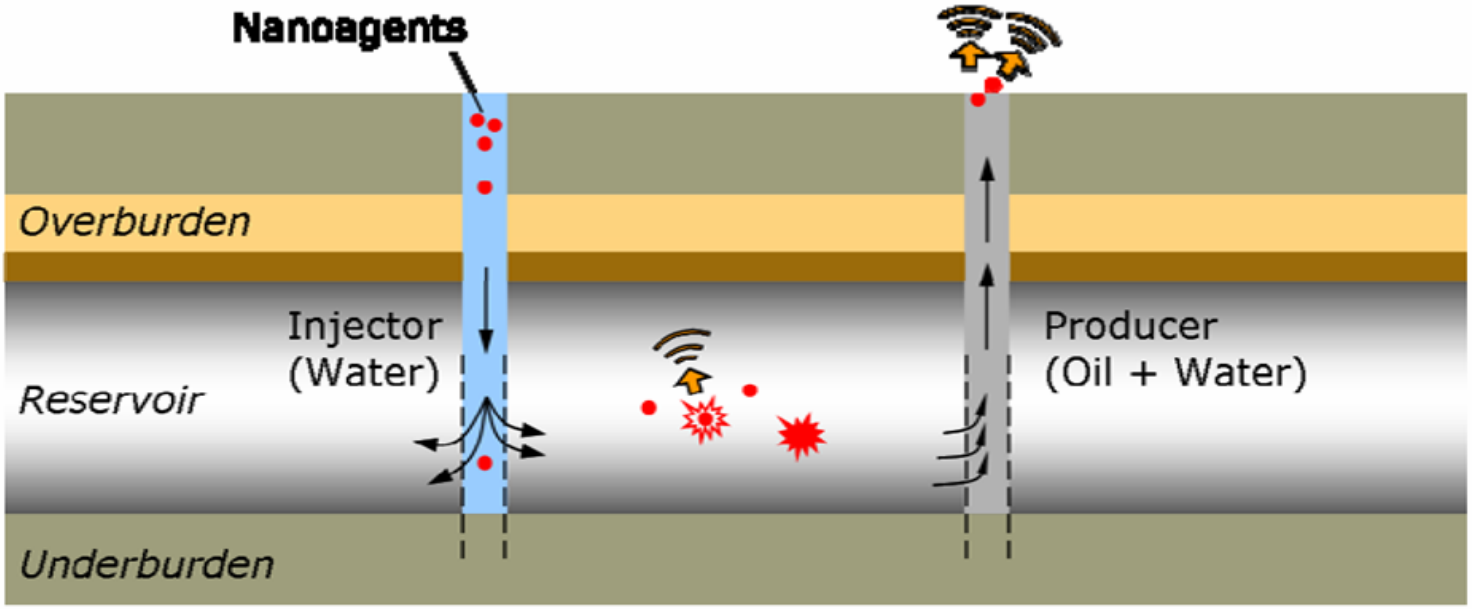


SHEAR



RELAX

Opportunities in Upstream Exploration and Production



- **Map the well connectivity in the field**
  What is the T, P, pH, salinity in the reservoir?

- **Map the oil-water interface**

- **Delivery of surfactants into the reservoir**
  are there surfactants that survive 100 ° C and 100 Kppm salinity (M^{2+}) ?

- **Estimate oil saturation**
  is oil present in droplets or big patches?

State of the Art for Nanoparticle Tracers

A large number of fluorescent tracers has been developed especially for biological systems

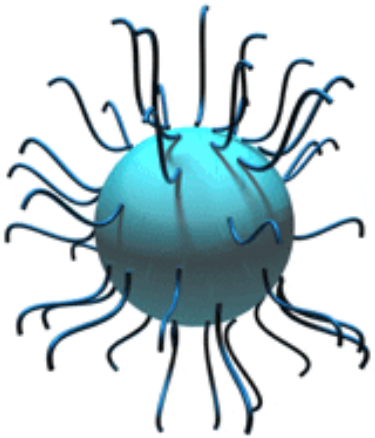
- **quantum dots**
- **encapsulated dyes**
- **…**

Stable particle suspensions is a well-known technology practiced in many different fields

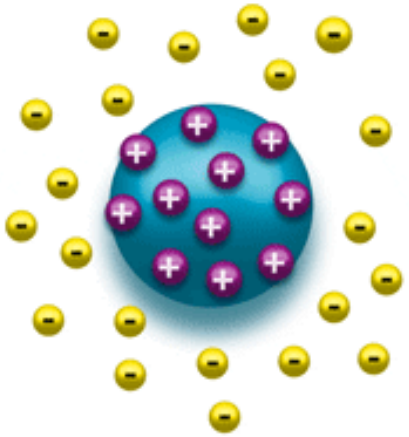
- **steric stabilization**
- **electrostatic stabilization**

Fluorescent nanoparticles that are stable at 100 ° C & 100 Kppm salinity (Ca^{2+}, Mg^{2+} and SO_4^{2-} ions) are required

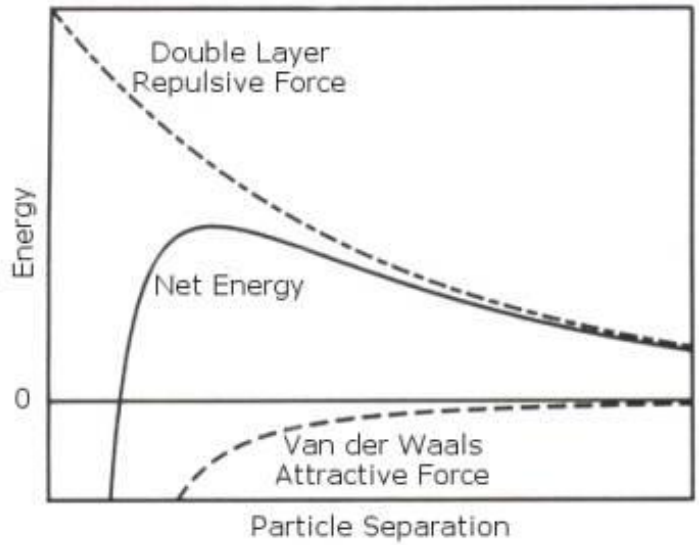
Stability of NP Suspensions



Steric stabilization



Electrostatic stabilization



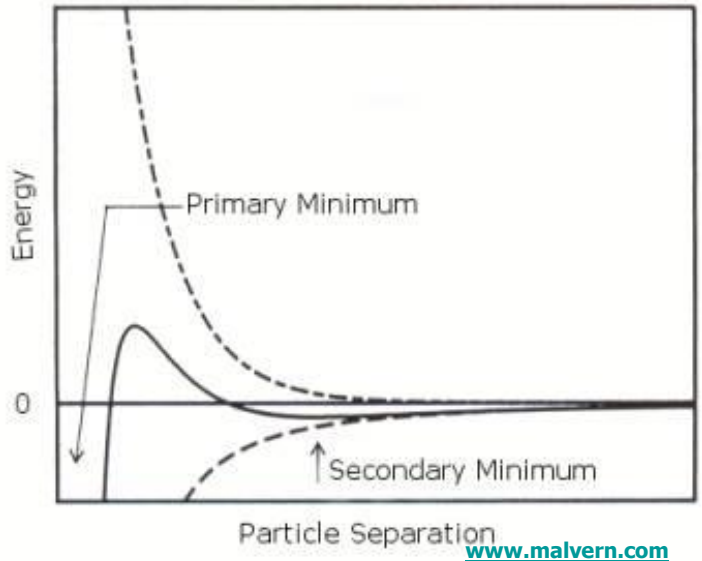
$$\psi = \psi_0 e^{-kx}$$

1/k = Debye Length

$$k^2 \sim z^2[c]$$

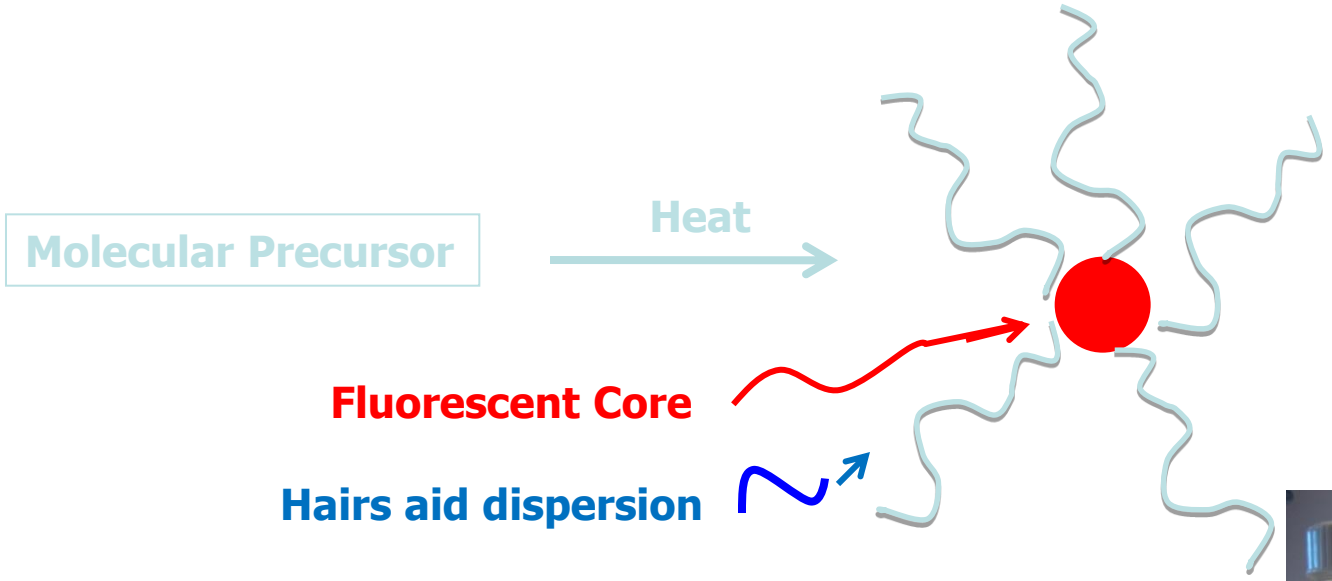
1/k ↓ as electrolyte concentration ↑

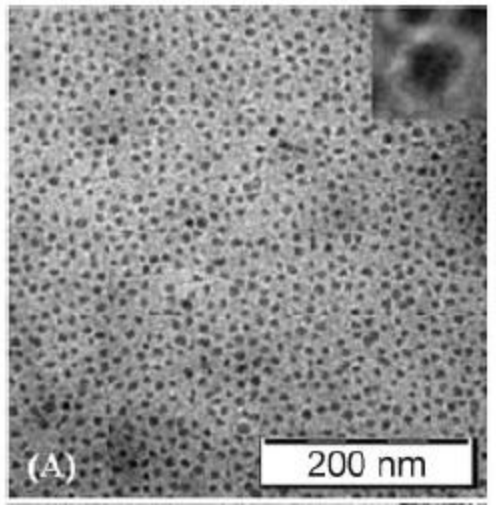
1/k ↓ as ionic charge ↑



www.malvern.com

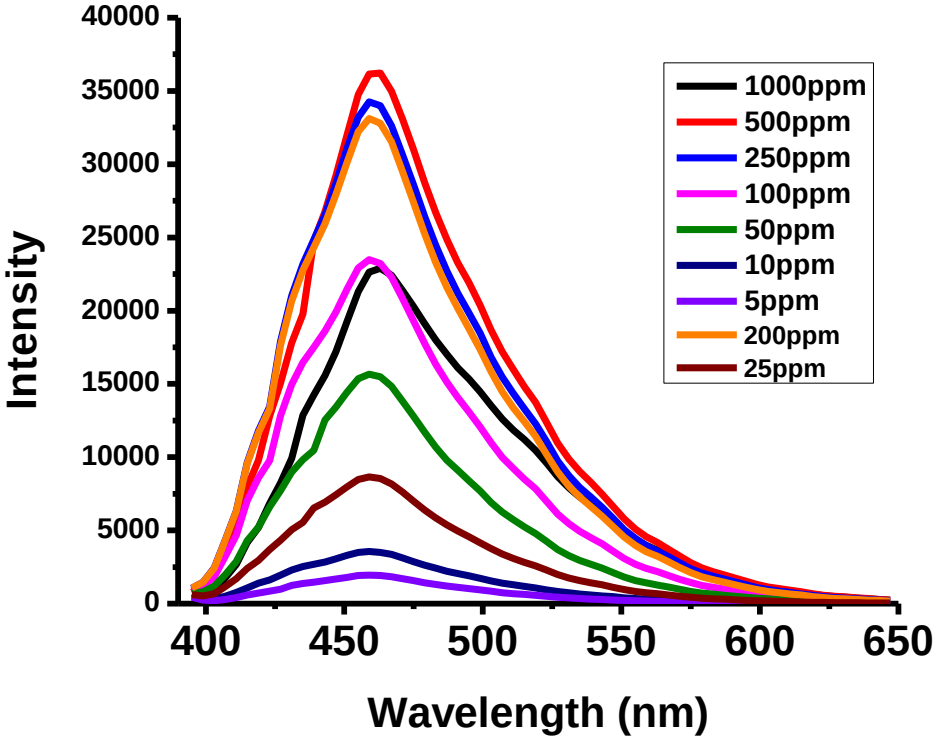
Fluorescent Nanoparticle Tracers

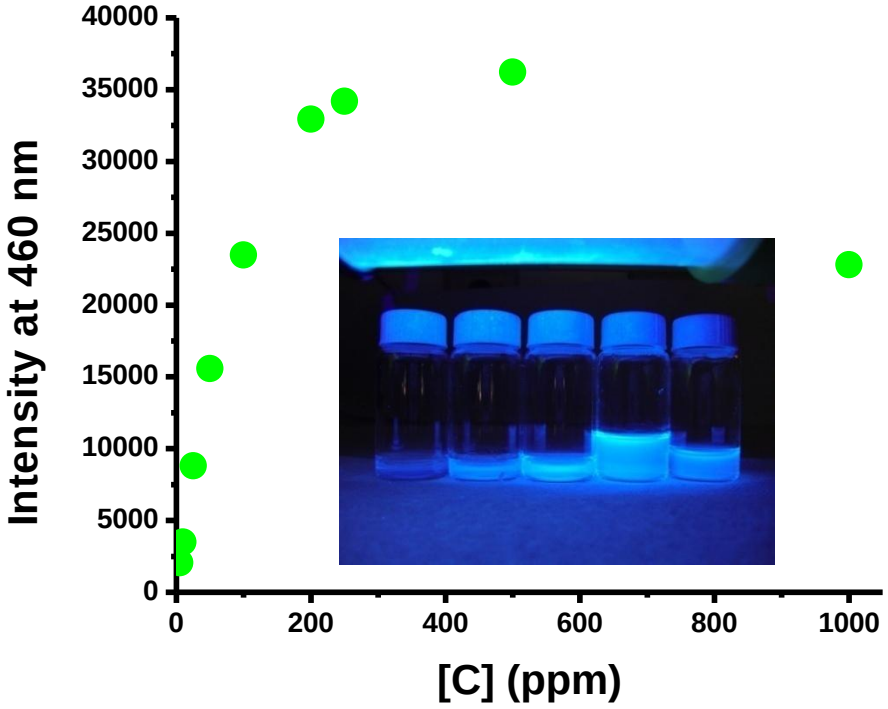




1. **Simple one-step, high-yield reaction**
2. **Uniform size nanoparticles**
3. **Nanoparticles disperse in water (or other solvents) chemistry/length of hairs can be readily controlled**
4. **Synthesis has been scaled-up to Kg**

Fluorescence Spectra of Nanoparticle Tracers





Tracers can be detected at 5 ppm level

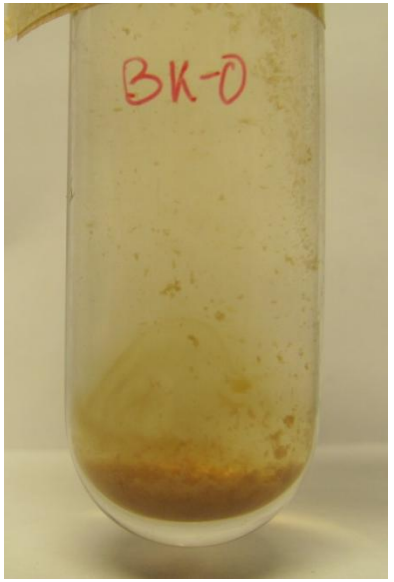
Saturation at concentrations larger than 200 ppm due to self-quenching

Stability of Nanoparticles in High Salinity

Stable Nanoparticles

16 hr at 150 ° C **56 hr at 150 ° C**

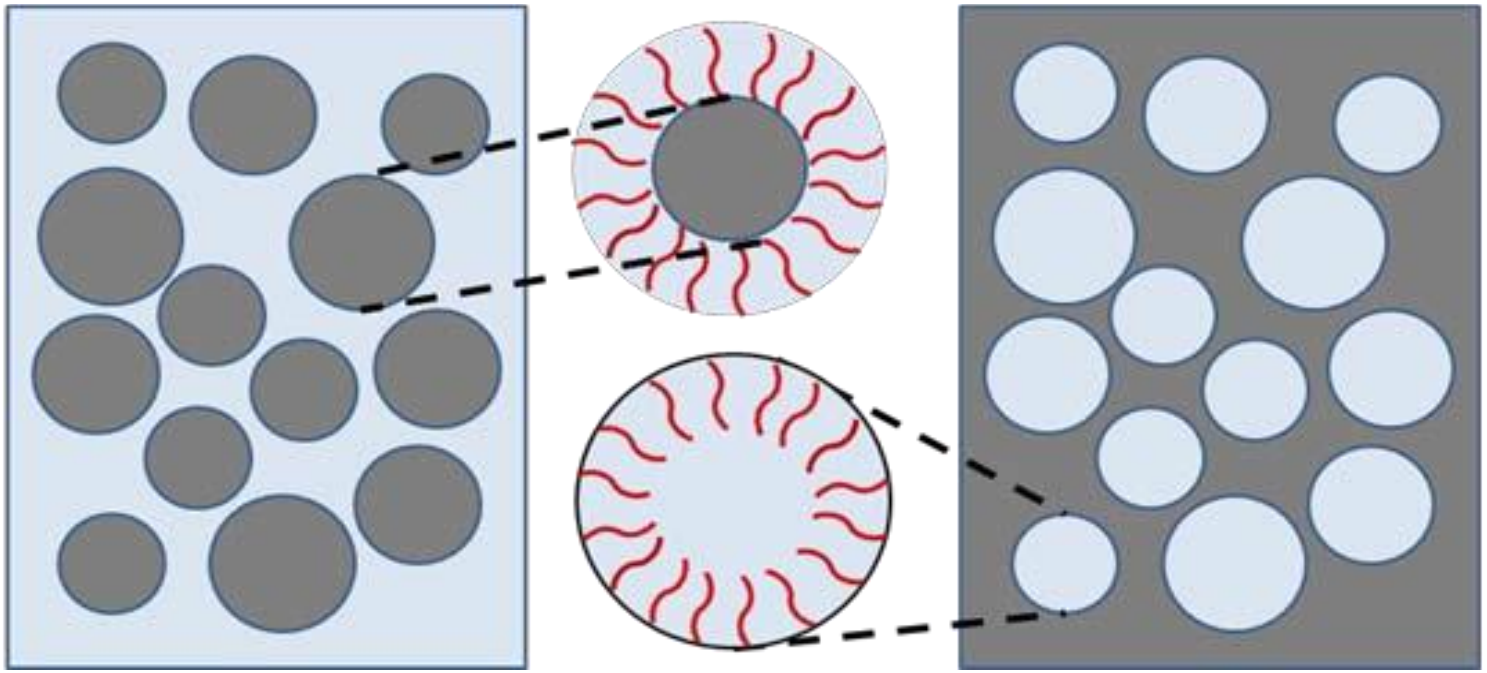
Unstable Nanoparticles



15 hr at 150 ° C **62 hr at 150 ° C**

Concentration: 1000 ppm

Nanohybrid Platforms



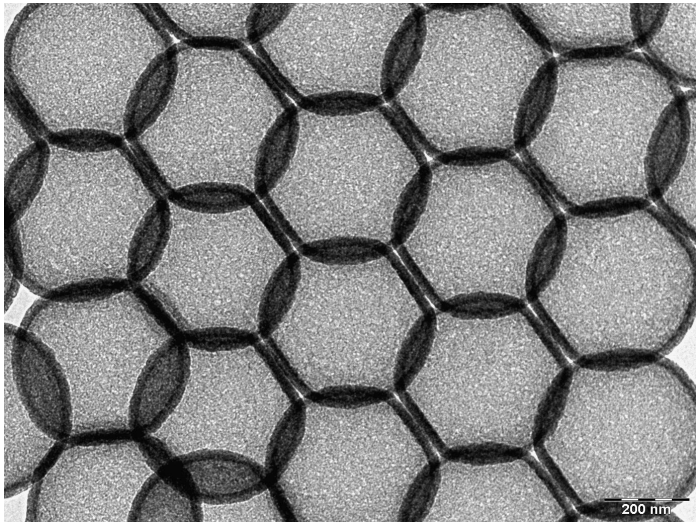
a) Organic Molecules Tethered on Nanoparticles

b) Organic Molecules Tethered on a Porous Matrix

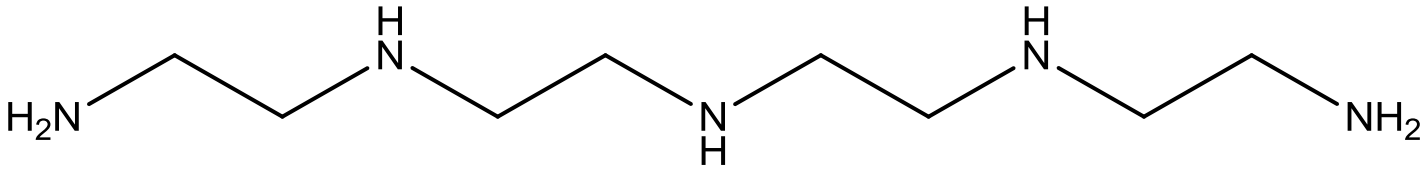
Carbon Dioxide Capture & Sequestration

- CO_2 is a greenhouse gas
- Post-combustion capture has the greatest near-term potential for reducing CO_2 emissions
- A challenge because of the scale of CO_2 to be captured
  - Low concentration of CO_2 in flue gas
  - Often with other gases including H_2O
- Simple amines such as MEA is the state of the art
  - Corrosive: increases construction cost
  - Evaporate and degrade: need to be replaced frequently
- Several carbon capture technologies under development

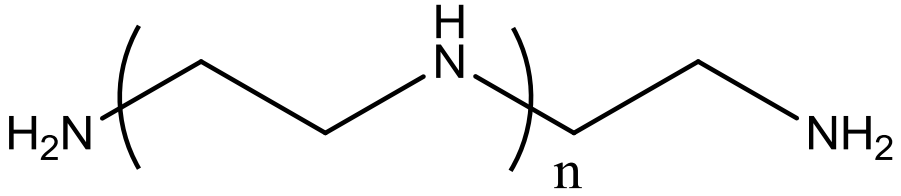
New CO_2 Capture Platform



Silica Capsules with Mesoporous Shell

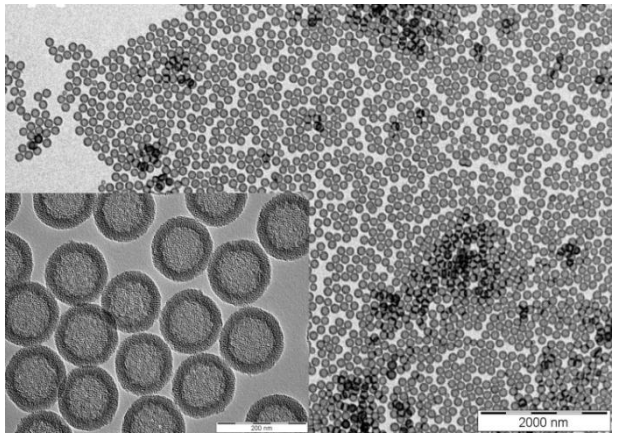


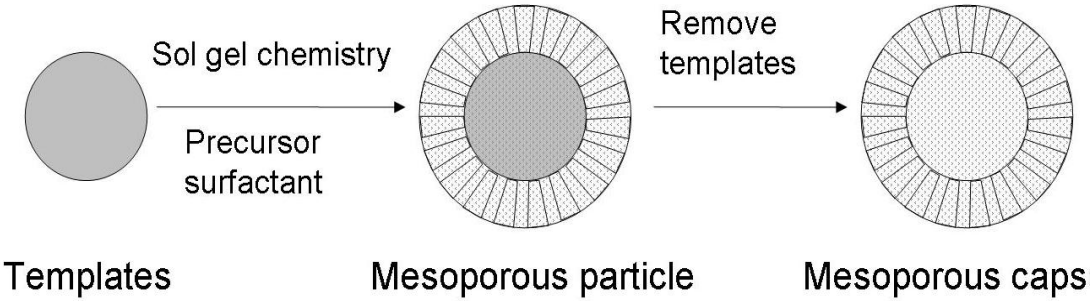
Tetraethylenepentamine (TEPA)

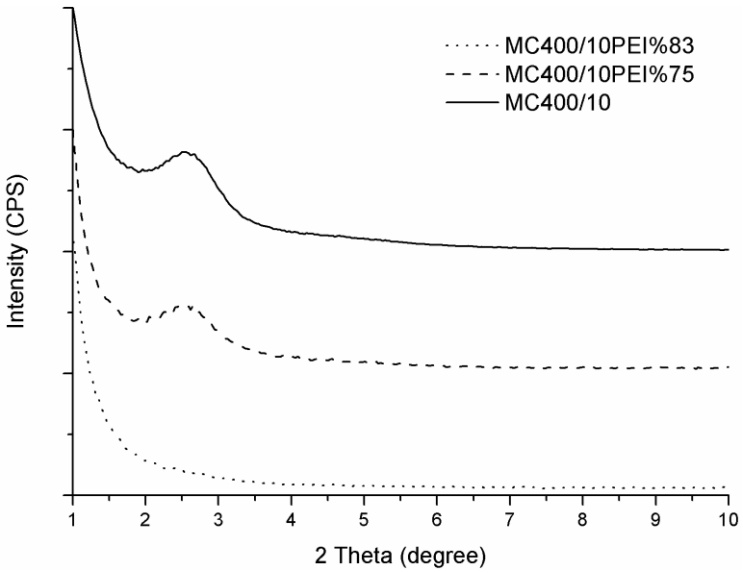


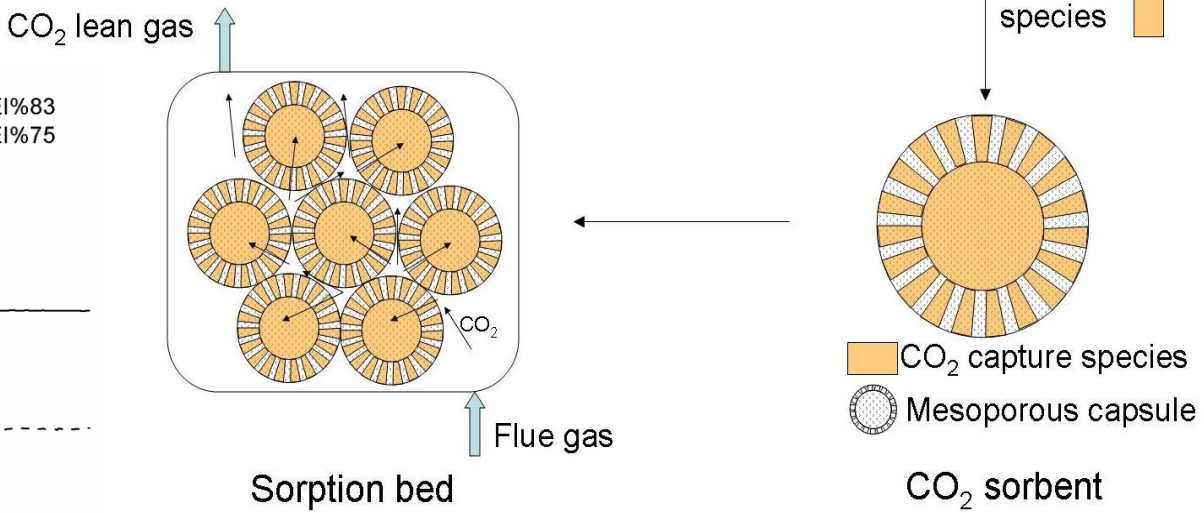
Polyethylenimine (PEI, Mn~430)

CO_2 Capture Platform





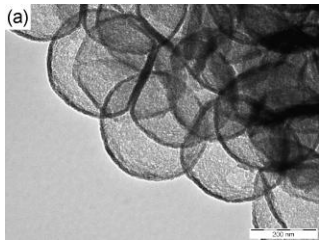


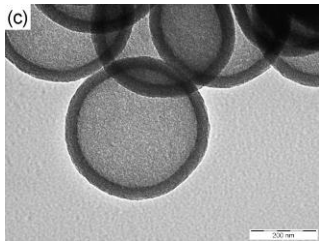


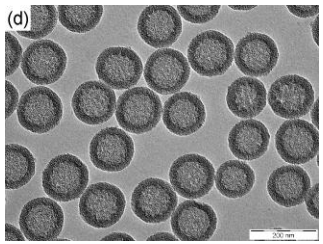
Benchmarking Between Sorbents

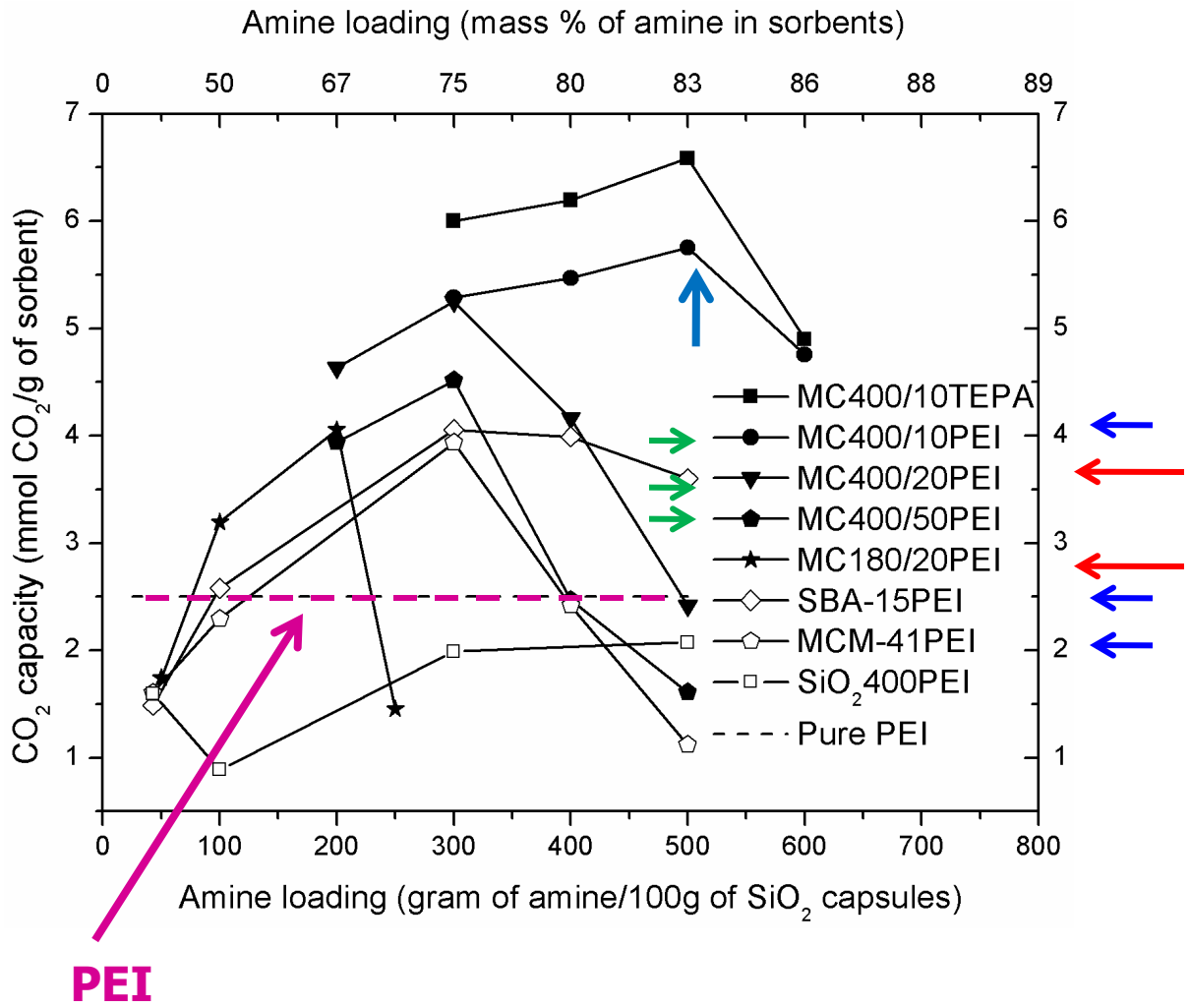
Maximum capacity at higher amine loadings with capsules

Capsules with thinner shell and larger size are better for capture

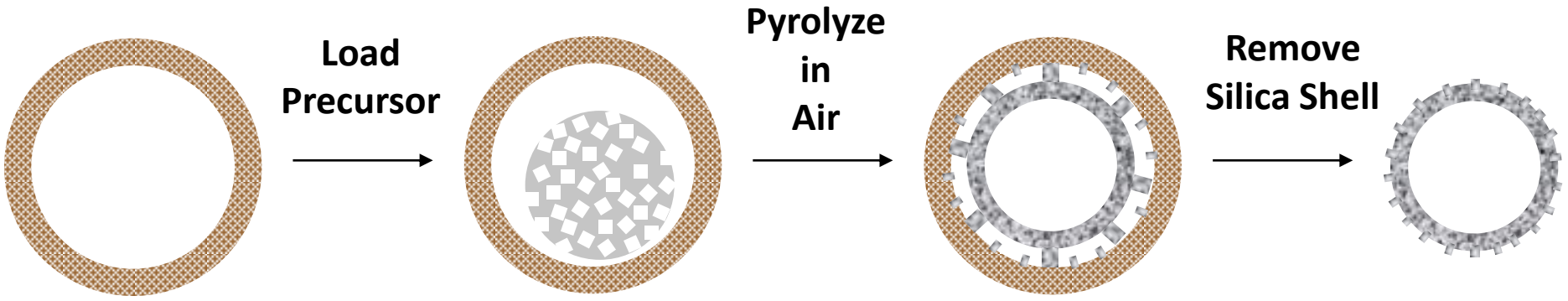


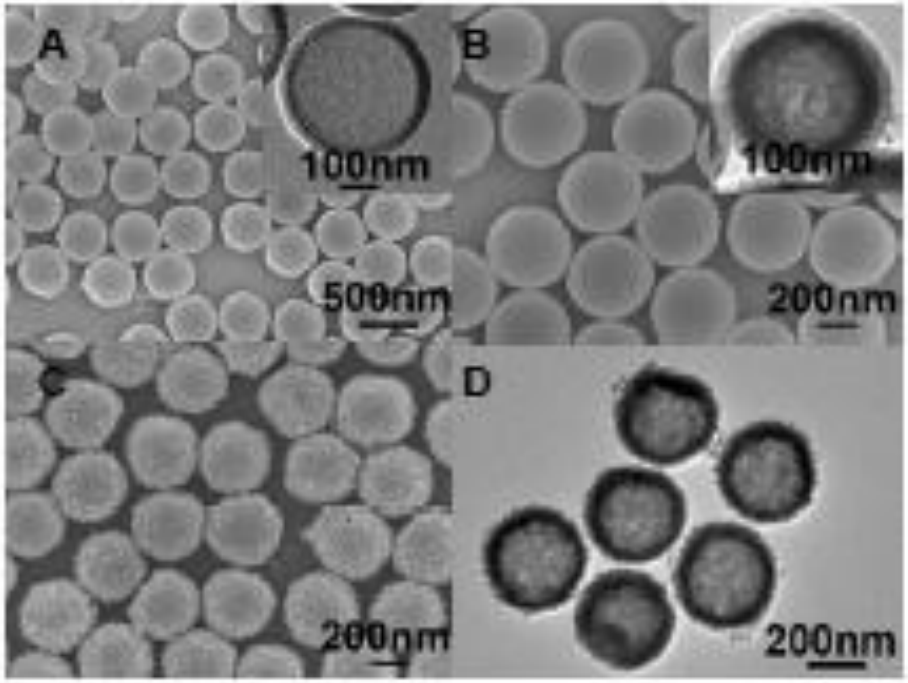


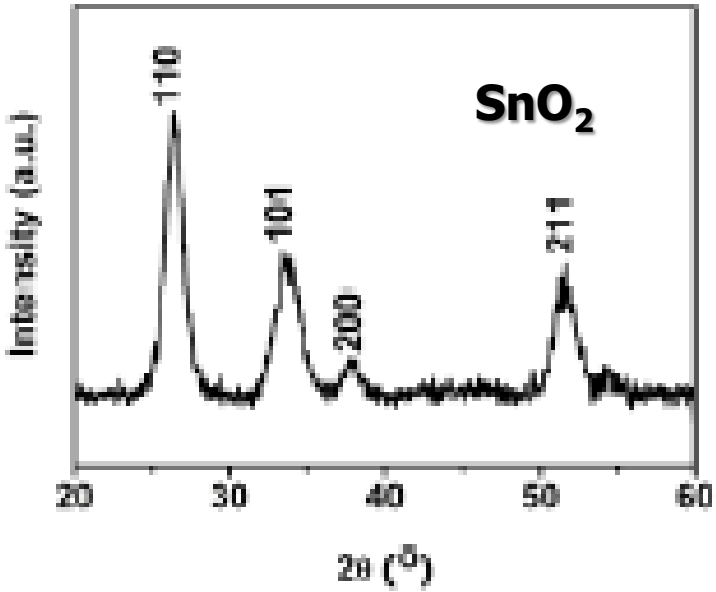




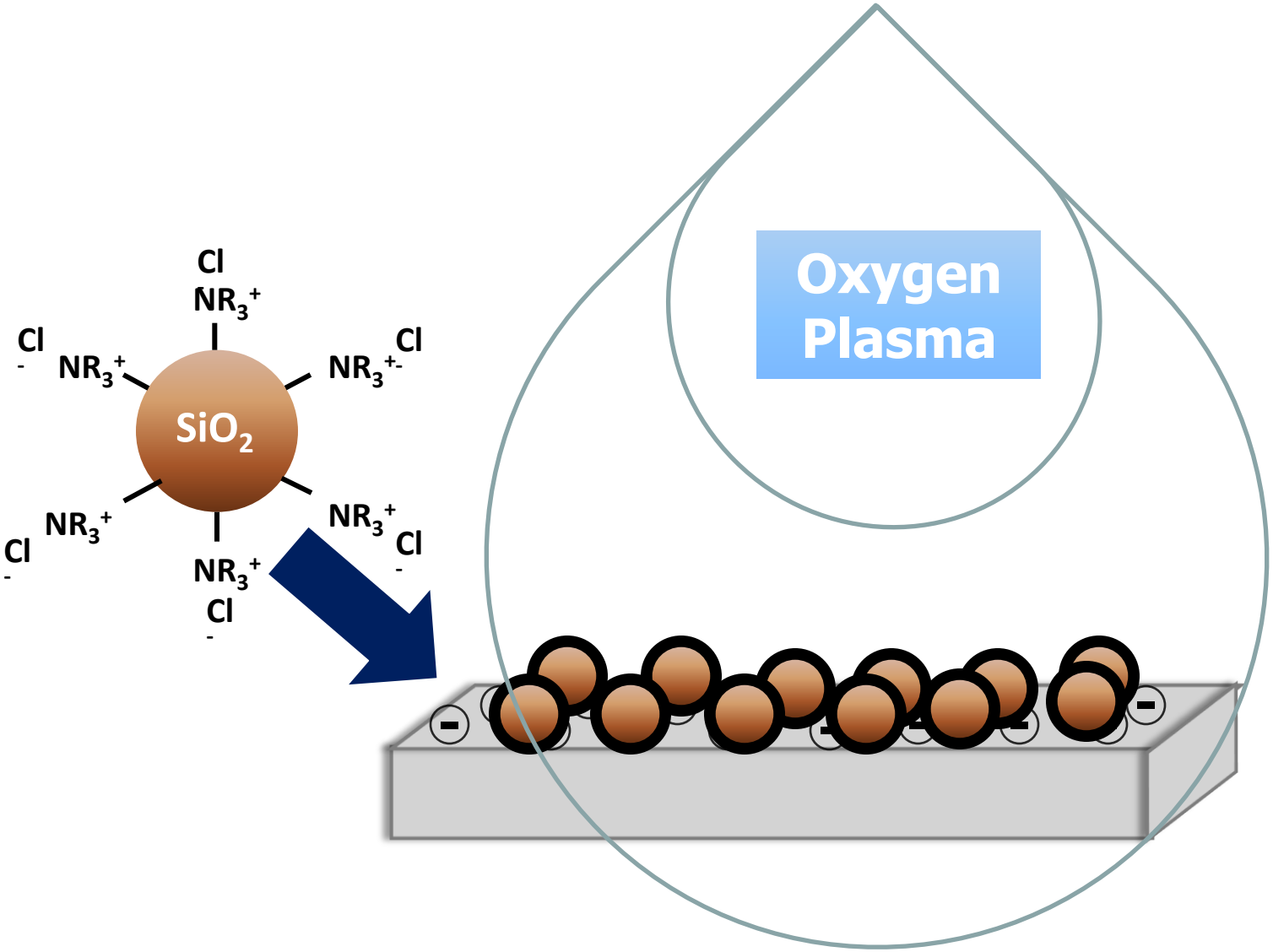
SnO_2 Capsules for Battery Anodes



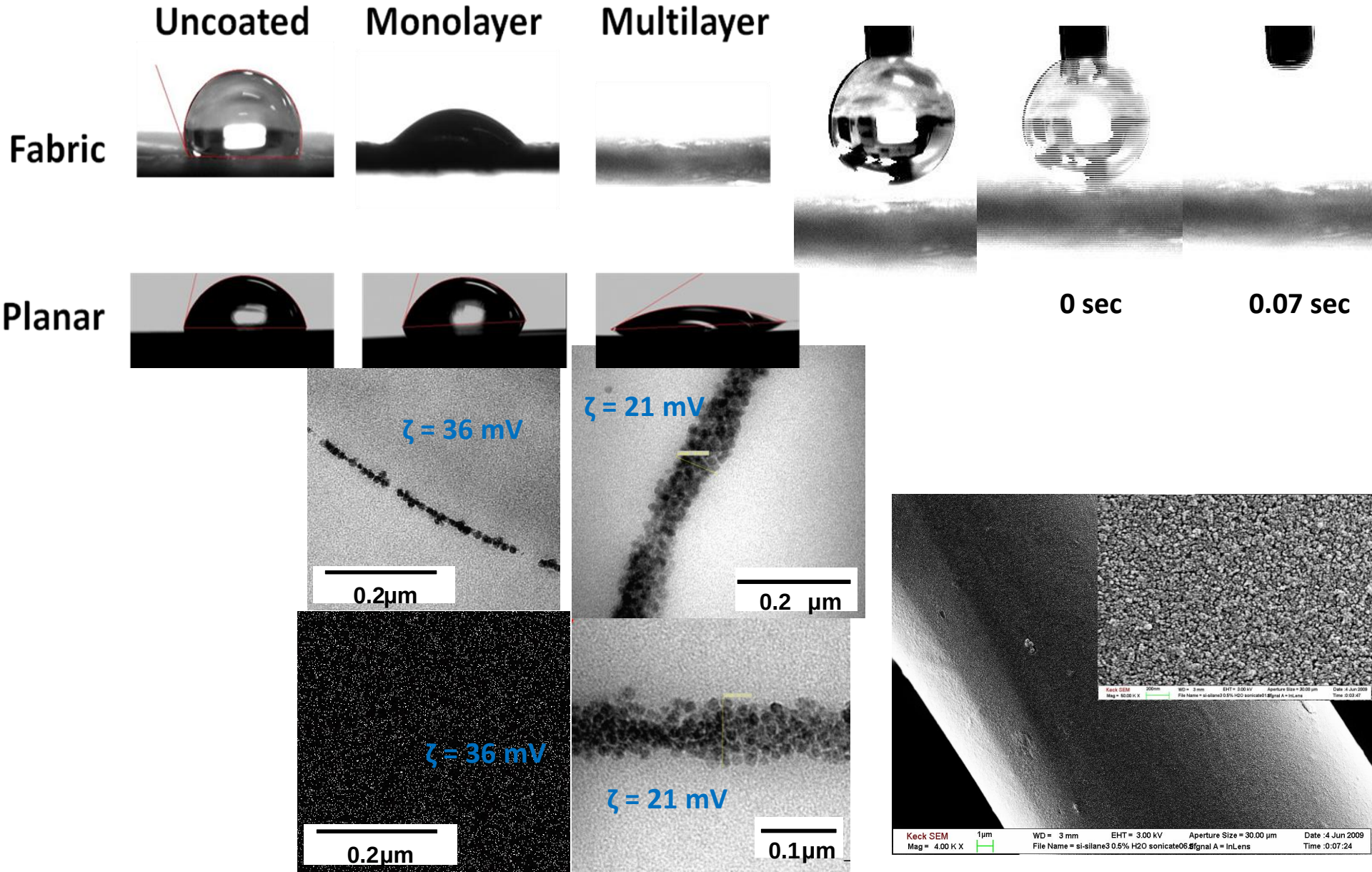




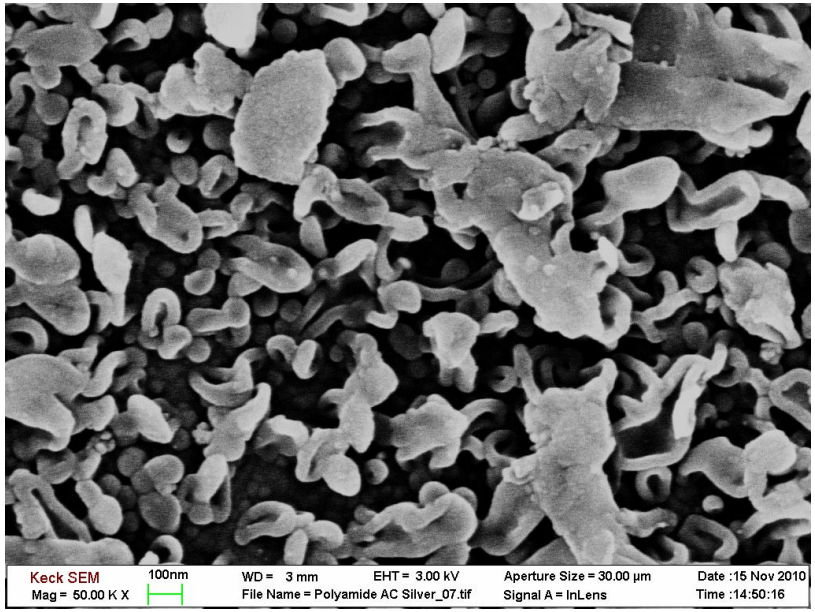
Surface Modification

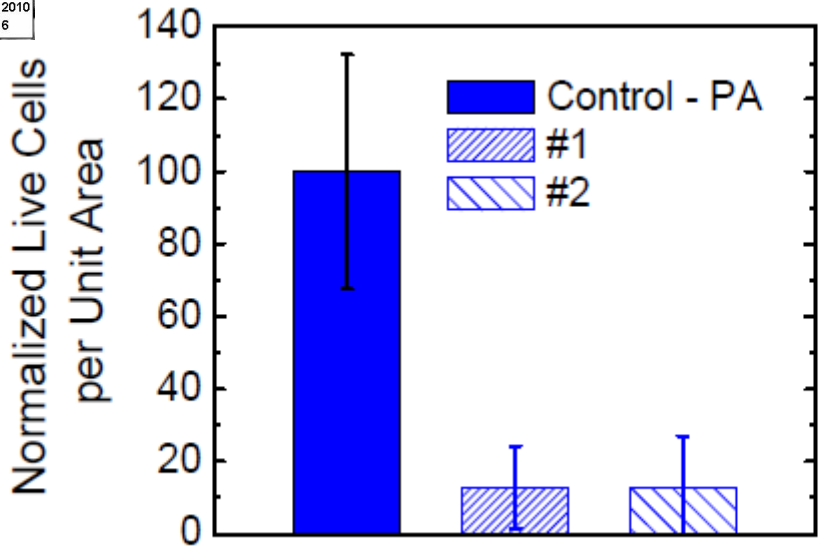


Controlling Surface Properties



RO/FO Thin-Film Composite (TFC) Membranes





Salt rejection rate and permeability of the membrane remained virtually unchanged

Battery Separators