Aggregation and Deposition Behavior of Carbon-Based Nanomaterials in Aquatic Environments

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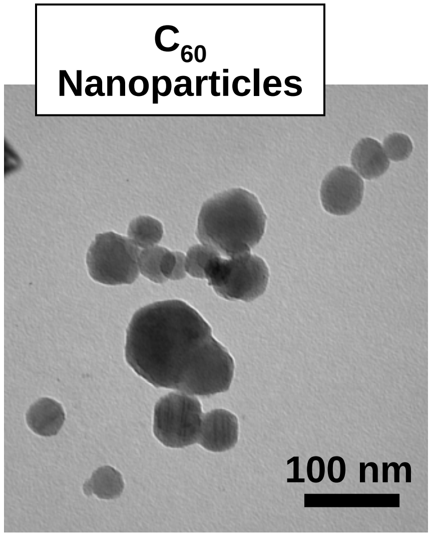
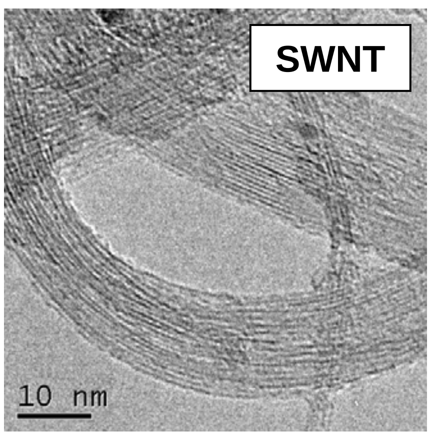
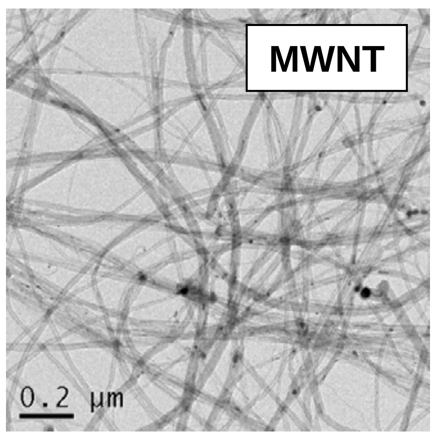
Engineered Carbon-Based Nanomaterials

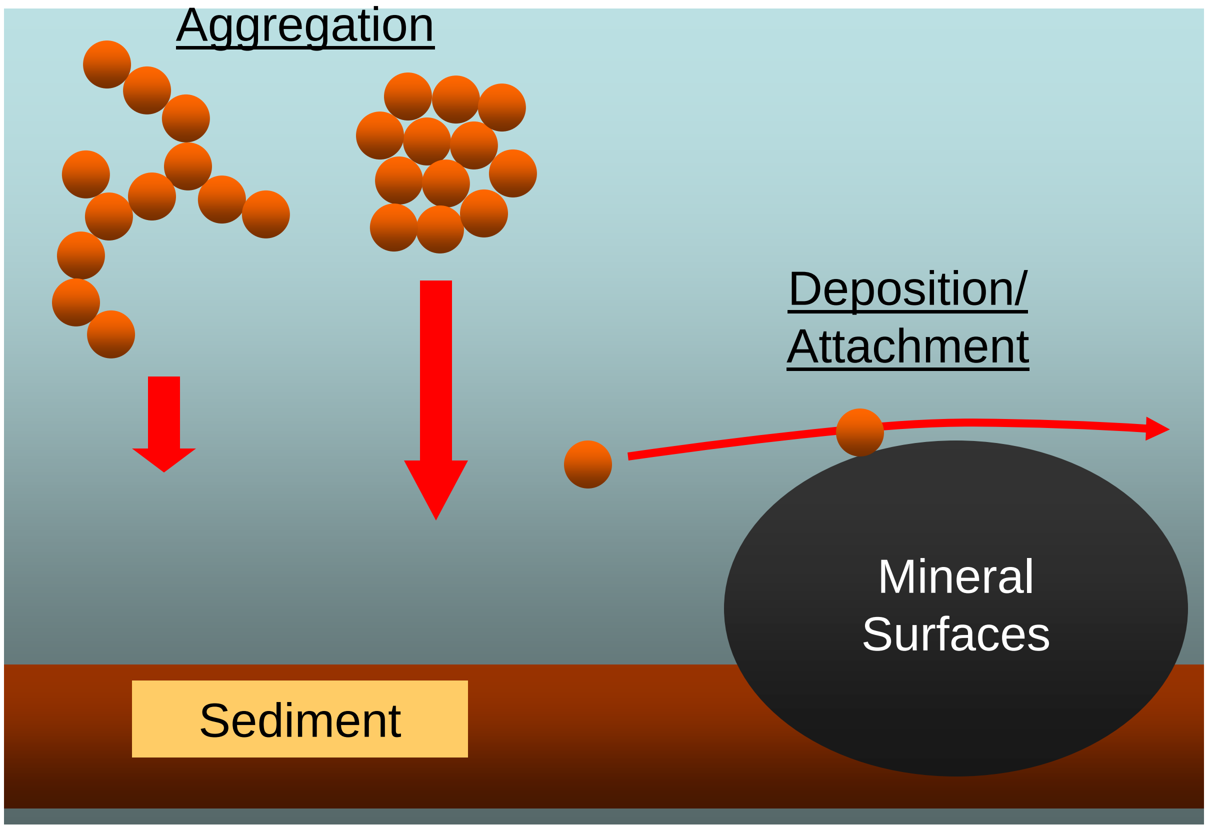






- Exponential growth in production and potential applications
- Unique properties (shape, surface charge, reactivity)
- Environmental and health impacts are not known

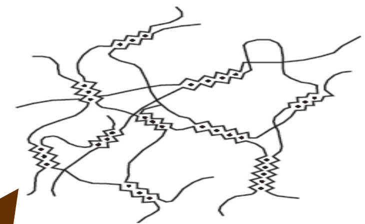
Aggregation and Deposition Behavior Determines Fate and Transport



- Influences rate of settling and transport
- Removal from aqueous phase
- May influence reactivity and toxicity

Complex Interactions in Aquatic Systems

NOM, biomolecules, minerals/suspended solids



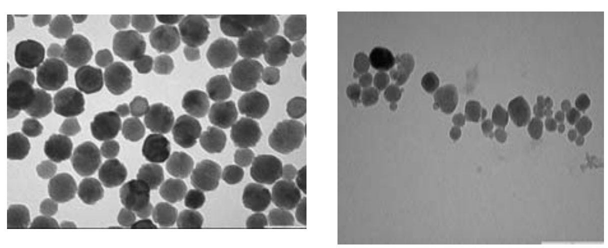
<u>Ions</u>

Na^+

Cl^-

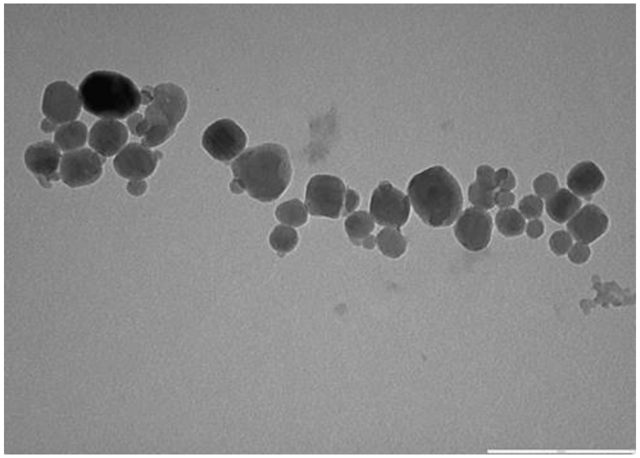
Ca^{2+}

Mg^{2+}



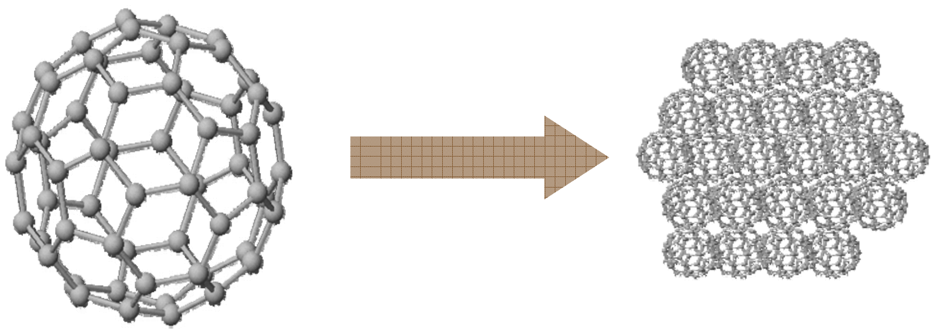
Nanomaterials

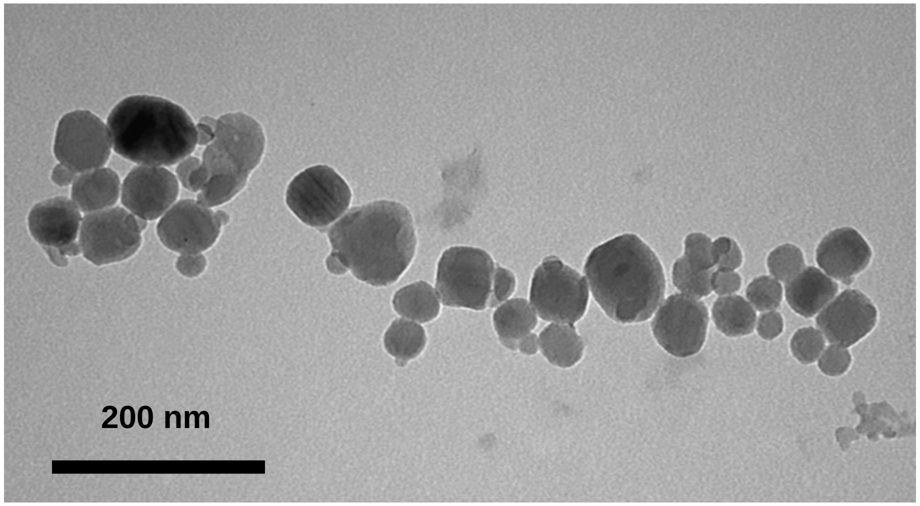
Aggregation Kinetics of Fullerene Nanoparticles



Fullerene Nanoparticles

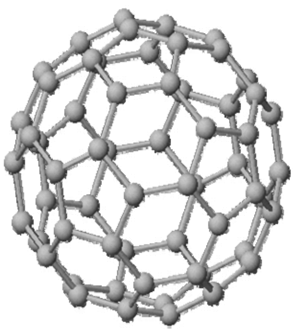
Buckminsterfullerene C_{60} nC_{60}



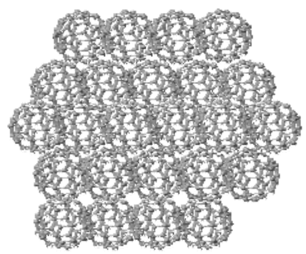


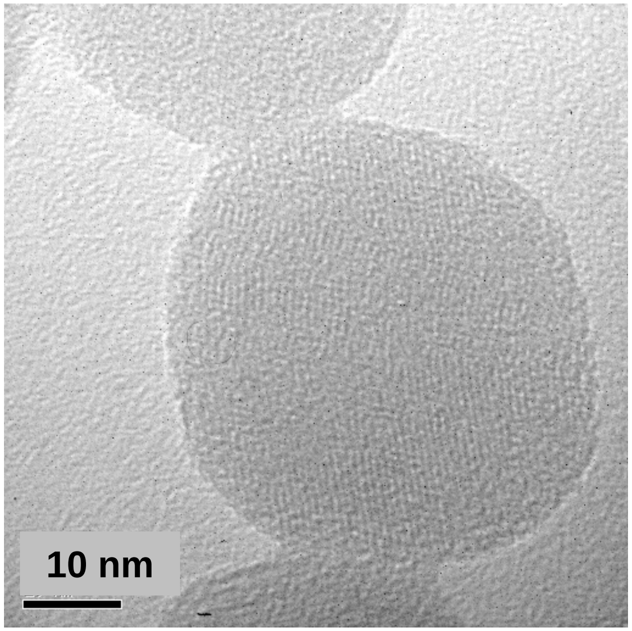
Ordered Structure of C_{60} Molecules

Buckminsterfullerene C_{60}



nC_{60}





Two Synthesis Methods

- **Sonicated C_{60} Nanoparticles (Son-C_{60})**

Fullerene
(99.9% purity)

Dissolve
fullerene in
toluene

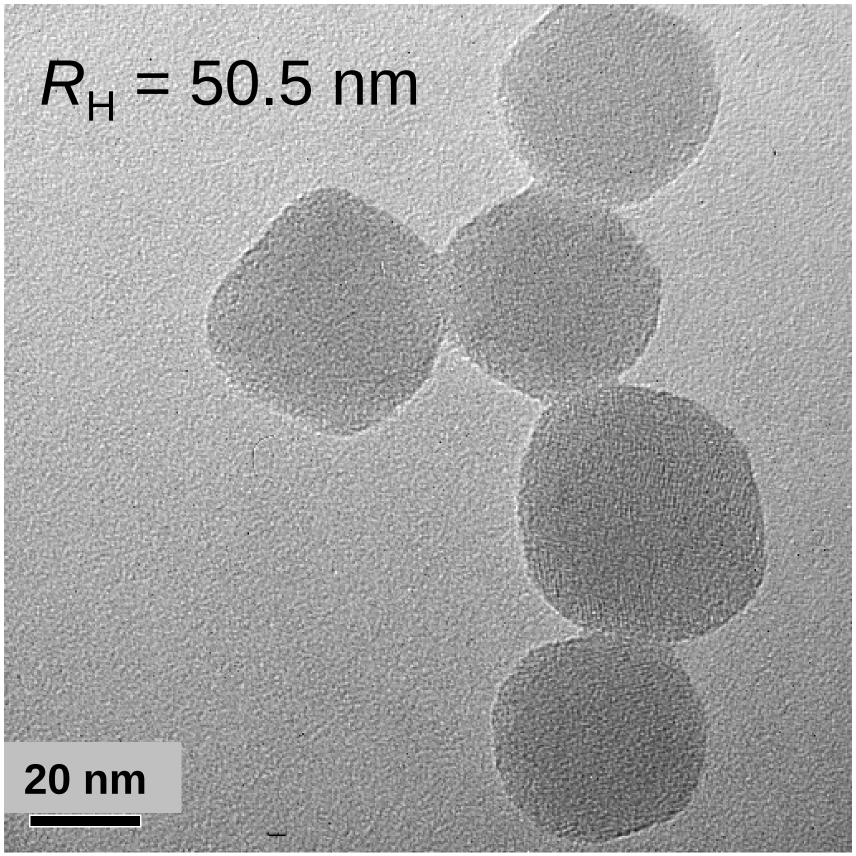
Sonicate with
water and
ethanol for 3 hr

Filter with
0.45 then 0.2
µm filters

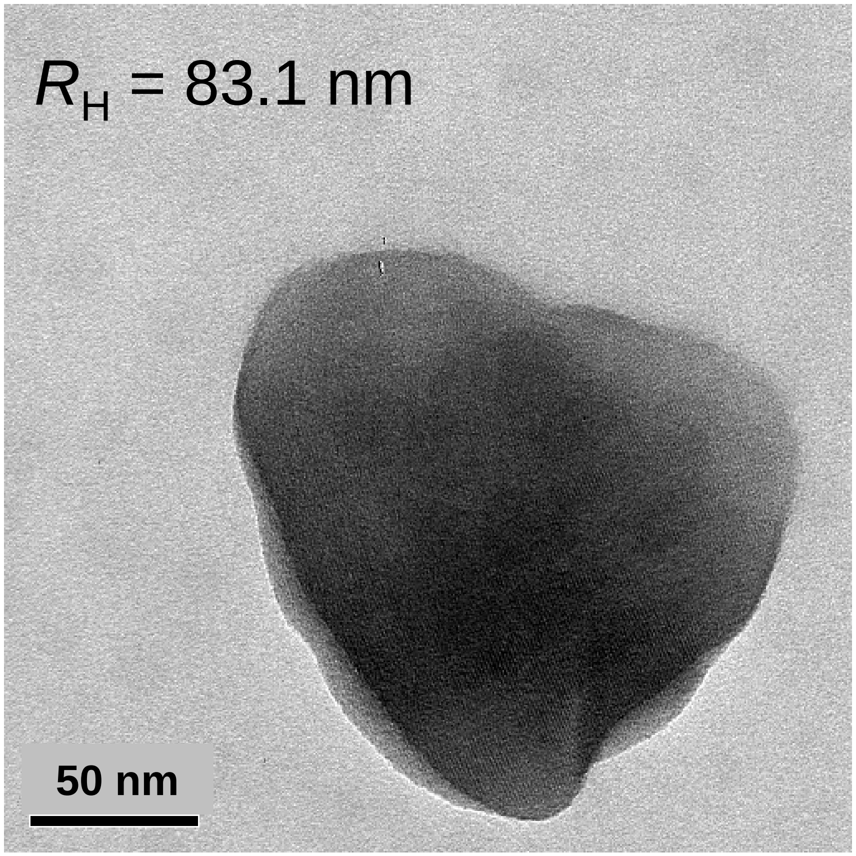
- **Aqueous C_{60} Nanoparticles (Aq-C_{60})**
Stirring fullerene in deionized water for 40 days before filtration

Physical Characterization

Son-C_{60}

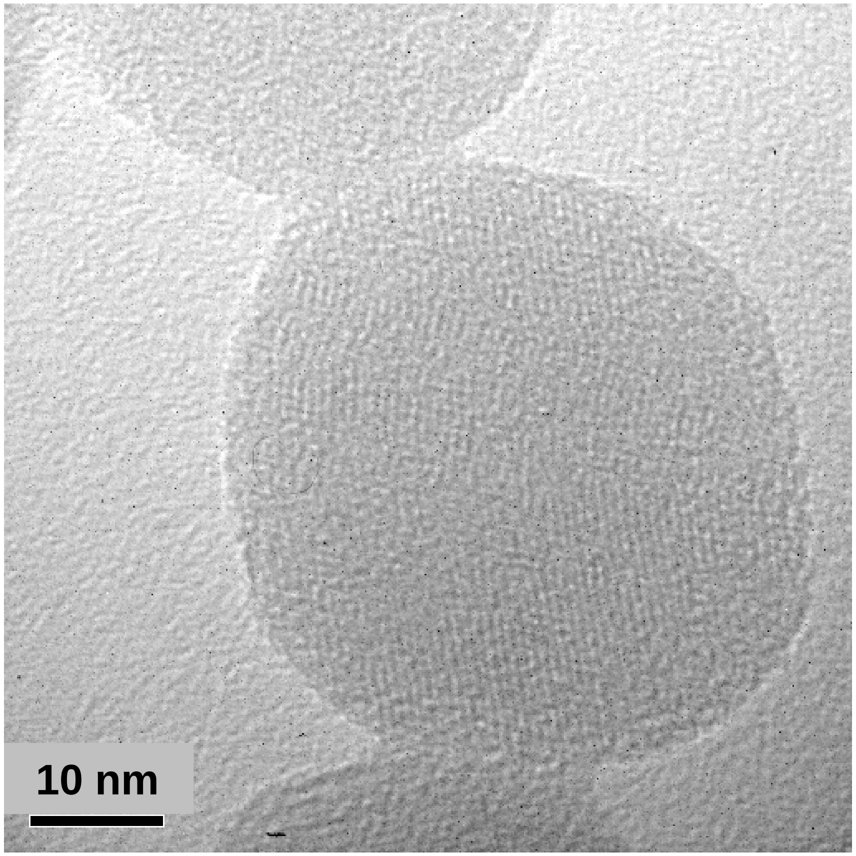


Aq-C_{60}

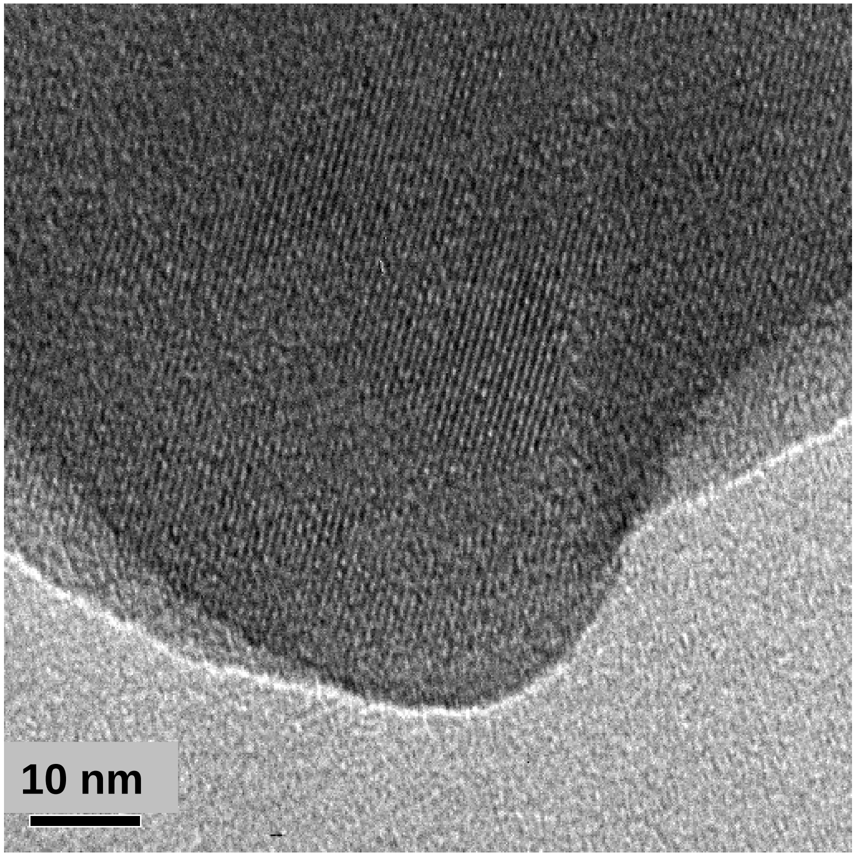


Physical Characterization

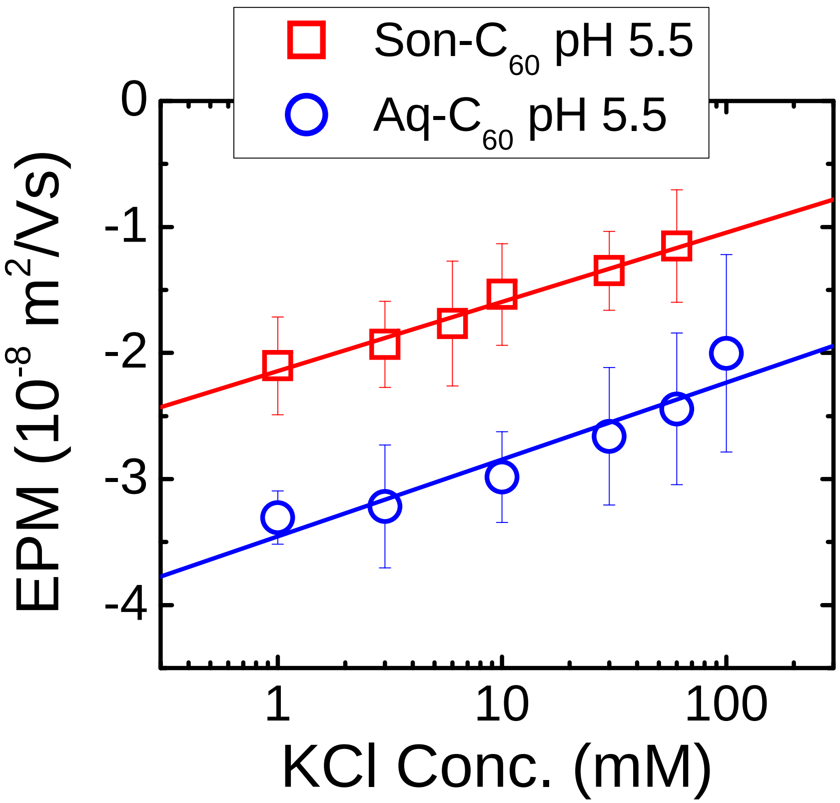
Son-C_{60}



Aq-C_{60}



Electrophoretic Mobility (EPM) in KCl

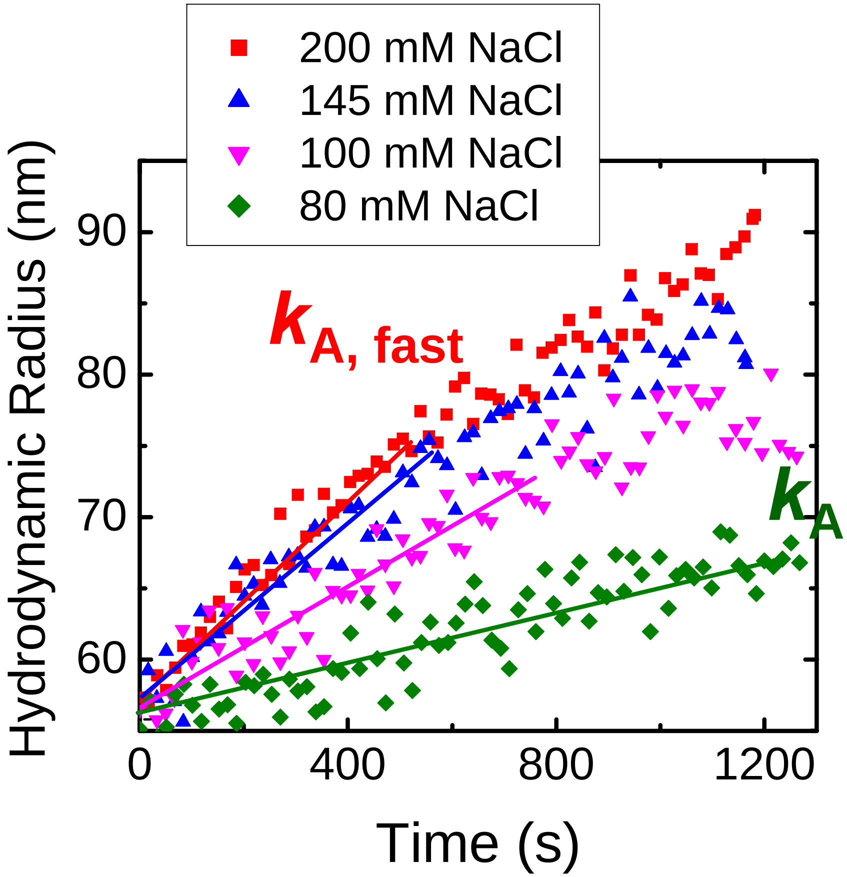


- Negatively charged
- Aq-C_{60} more negatively charged than Son-C_{60}
- EPM becomes less negative as KCl concentration increases

ALV Light Scattering Setup

- Dynamic light scattering to derive hydrodynamic radius
- YAG laser with wavelength of 532 nm
- Scattered light intensity measured at 90° from incident beam

Time-Resolved Dynamic Light Scattering



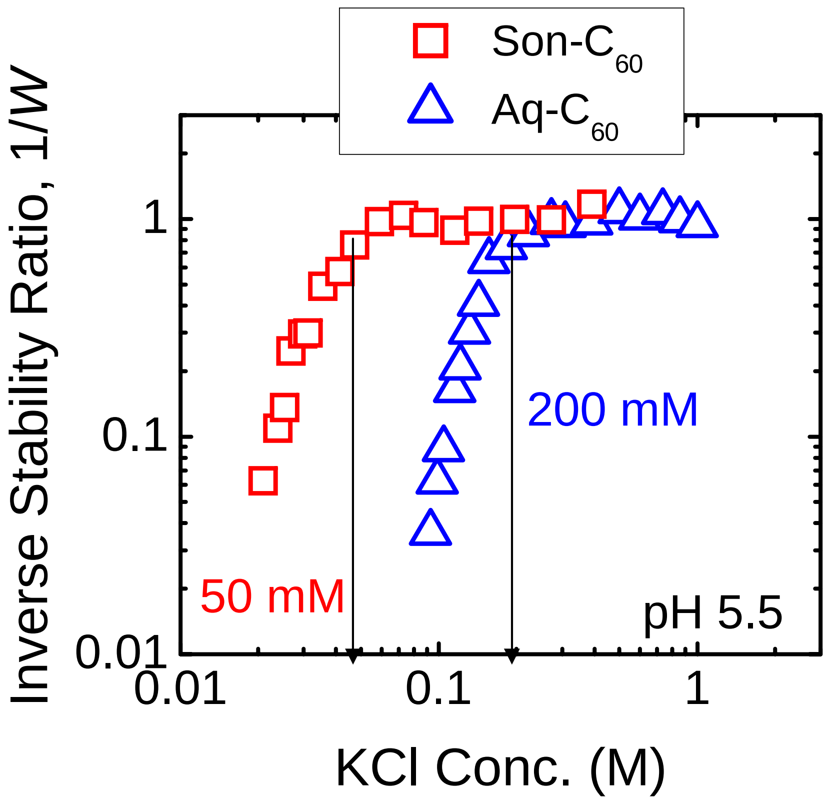
Initial aggregation kinetics:

$$k_A \propto \left(\frac{dr_h(t)}{dt} \right)_{t \to 0}$$

Attachment Efficiency or Inverse Stability Ratio:

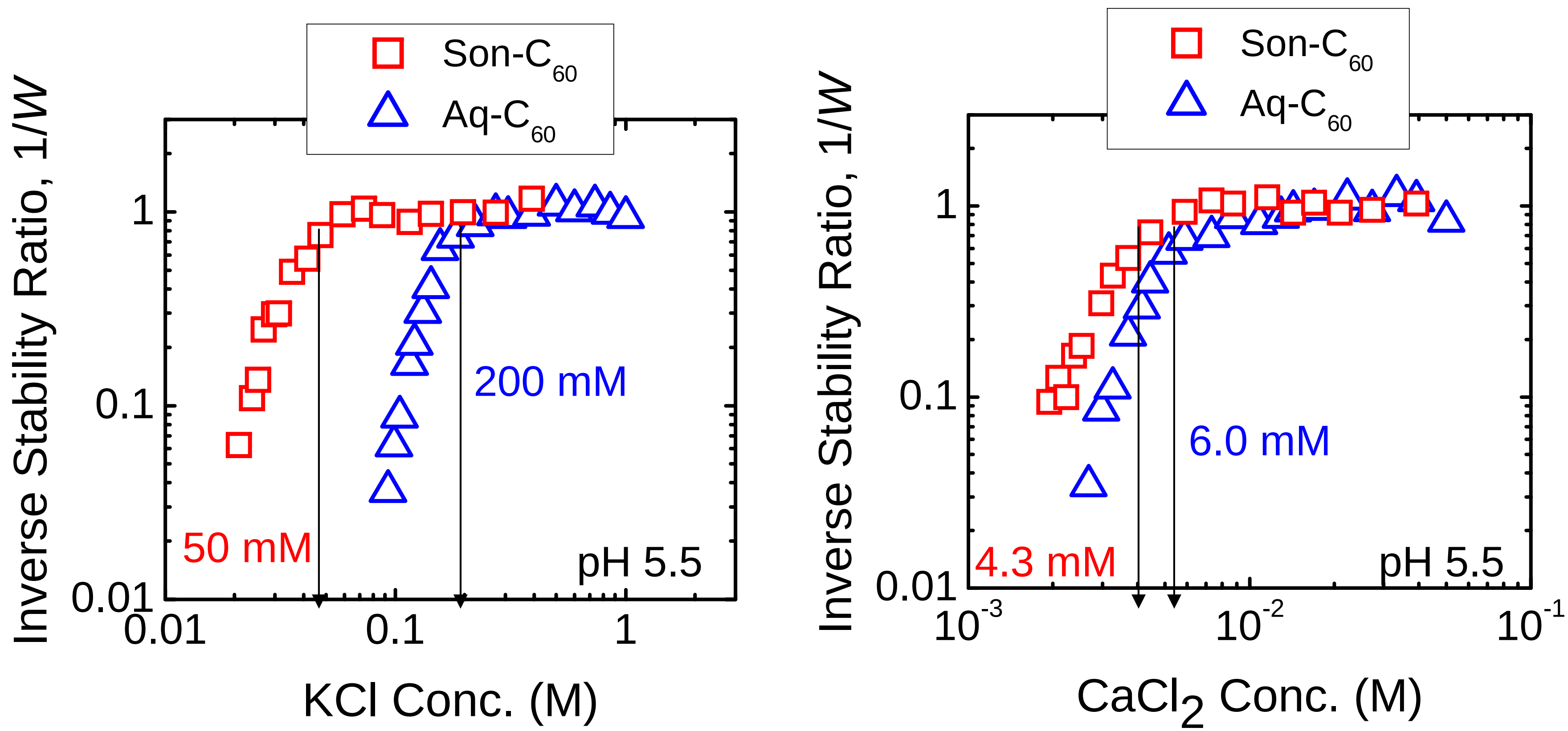
$$\boxed{\alpha = 1/W = \frac{k_A}{k_{A,\, fast}}}$$

Aggregation Kinetics in KCl

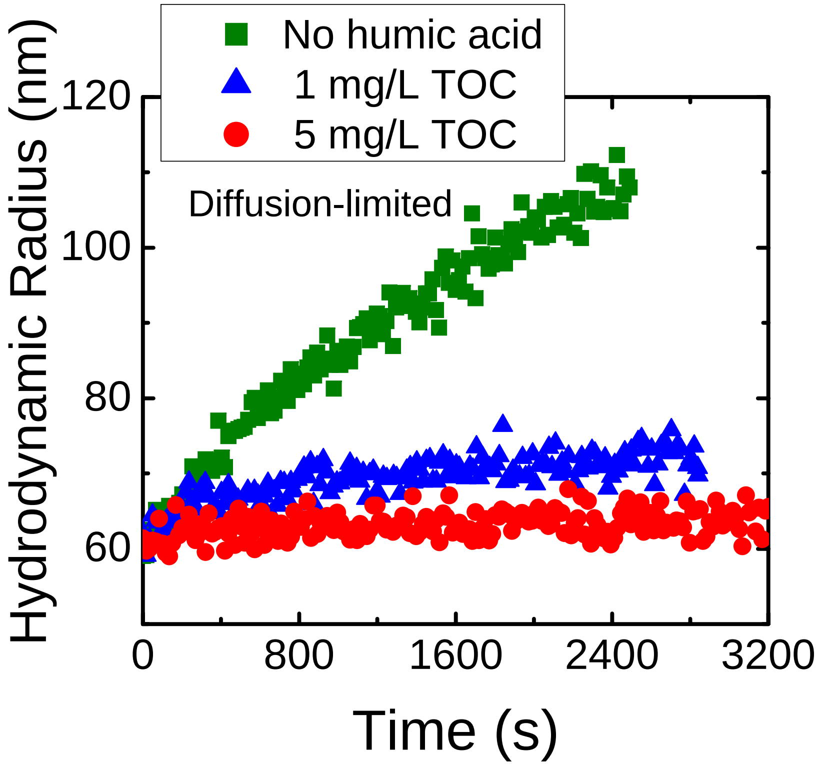


- Classic slow and fast aggregation regimes
- Aq-C_{60} are much more stable (CCC of 200 mM)

Aggregation Kinetics in KCl and $CaCl_2$



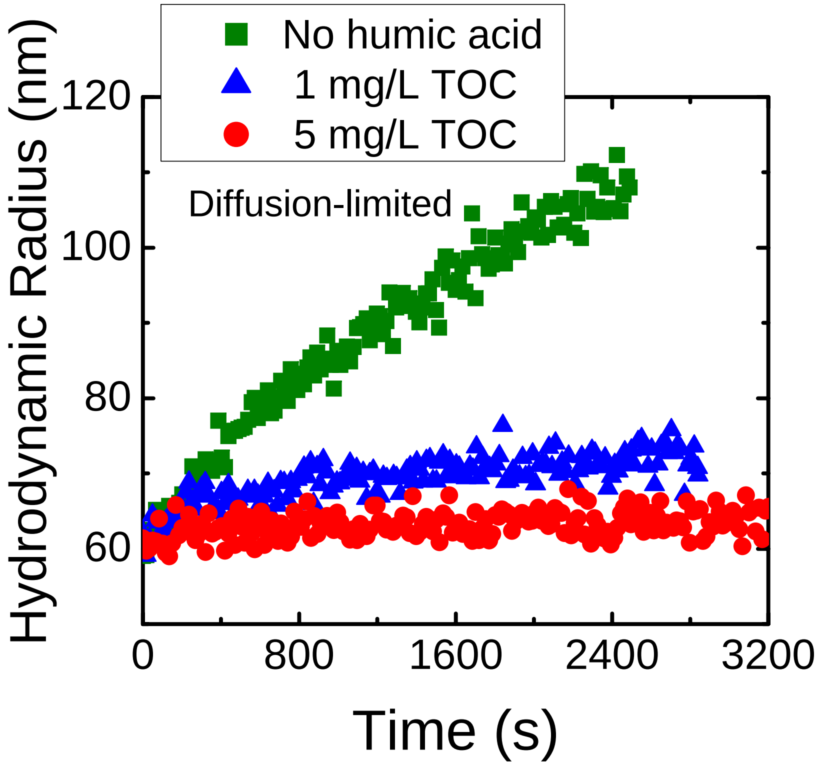
Increased Stability in Humic Acid with NaCl

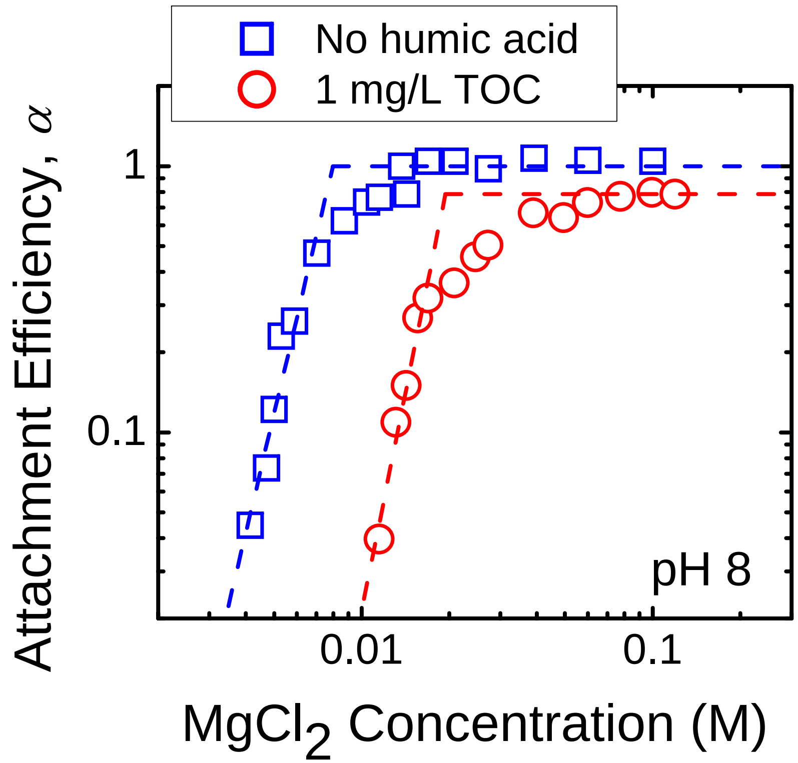


- NaCl concentration = 650 mM
- pH 8

Chen and Elimelech, *J. Colloid Interface Sci.* **2007,** *309,* 126-134

Increased Stability in Humic Acid with NaCl and $MgCl_2$



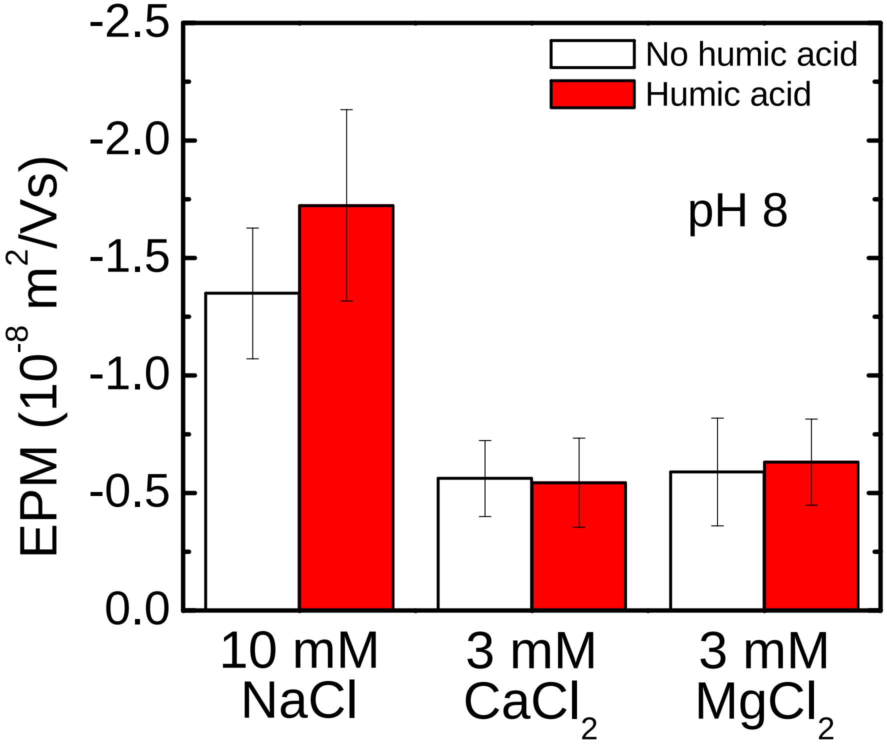


- NaCl concentration = 650 mM
- pH 8

- CCC increases in humic acid

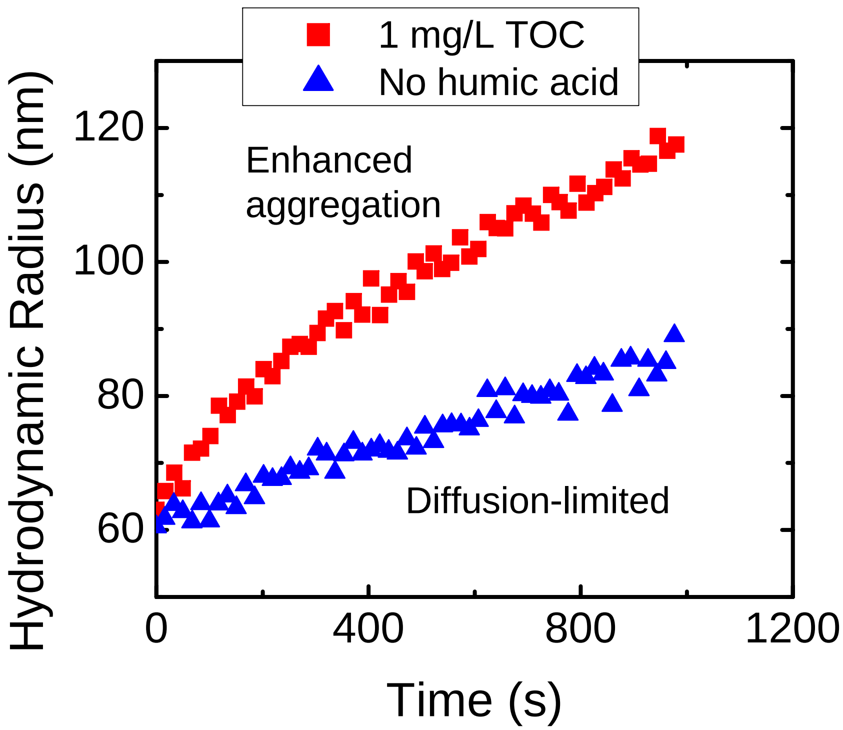
Chen and Elimelech, *J. Colloid Interface Sci.* **2007,** *309,* 126-134

Steric Stabilization with Humic Acid in NaCl and $MgCl_2$



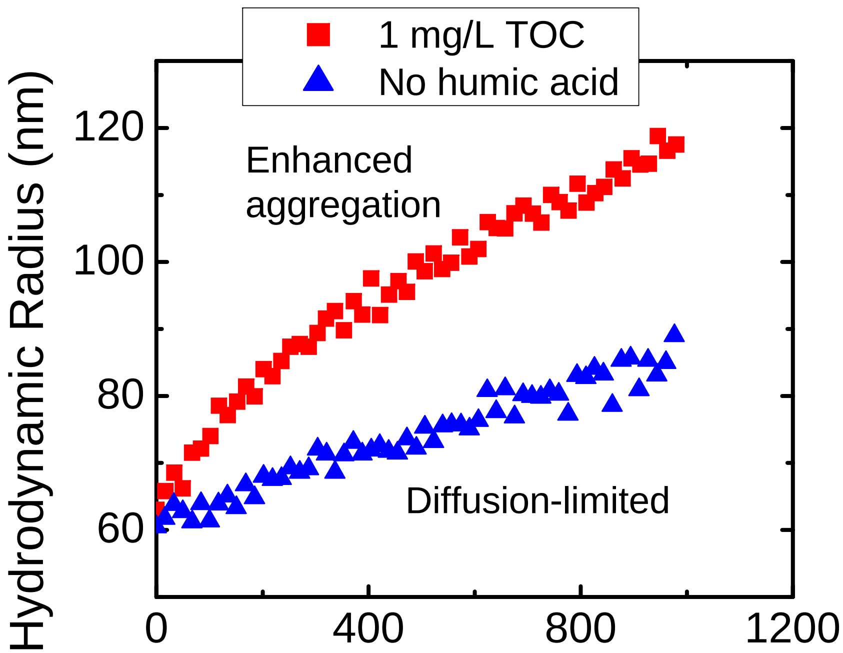
- Electrophoretic mobility (EPM) similar with and without humic acid
- Indication of steric stabilization

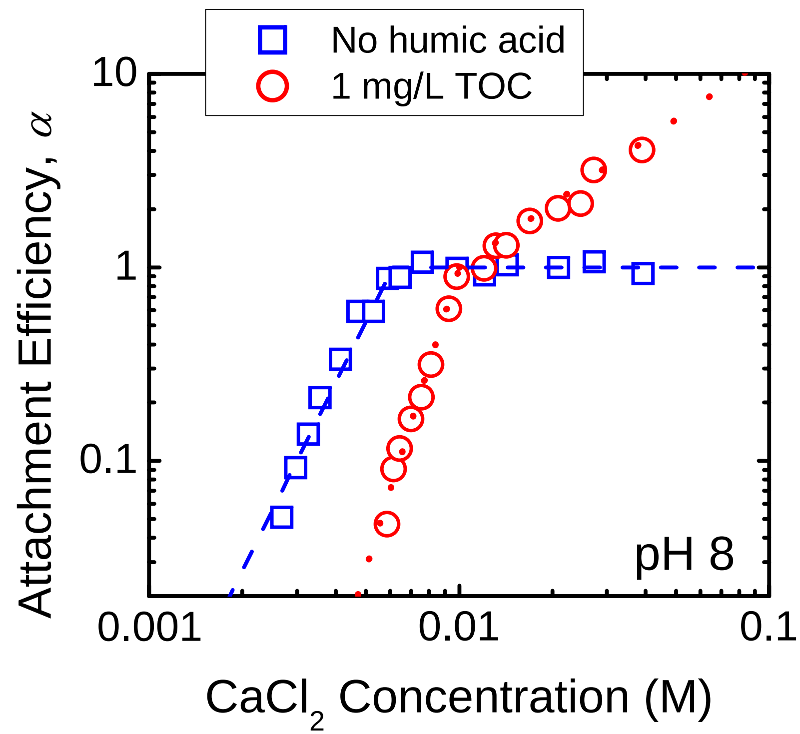
Enhanced Aggregation at High $CaCl_2$ Concentrations



- $CaCl_2$ concentration = 40 mM
- pH 8

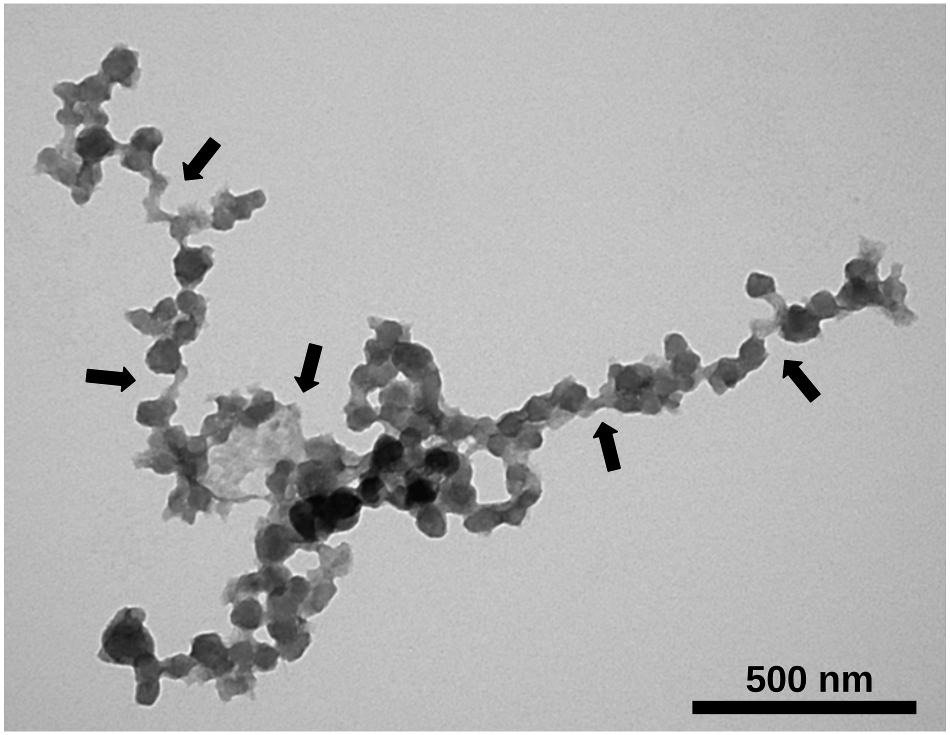
Enhanced Aggregation at High $CaCl_2$ Concentrations



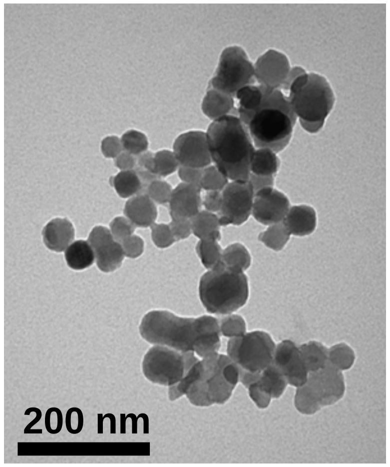


- At 1 mg/L TOC, enhanced aggregation occurs above 10 mM $CaCl_2$

Humic Acid Clusters Bridge Fullerene Nanoparticles

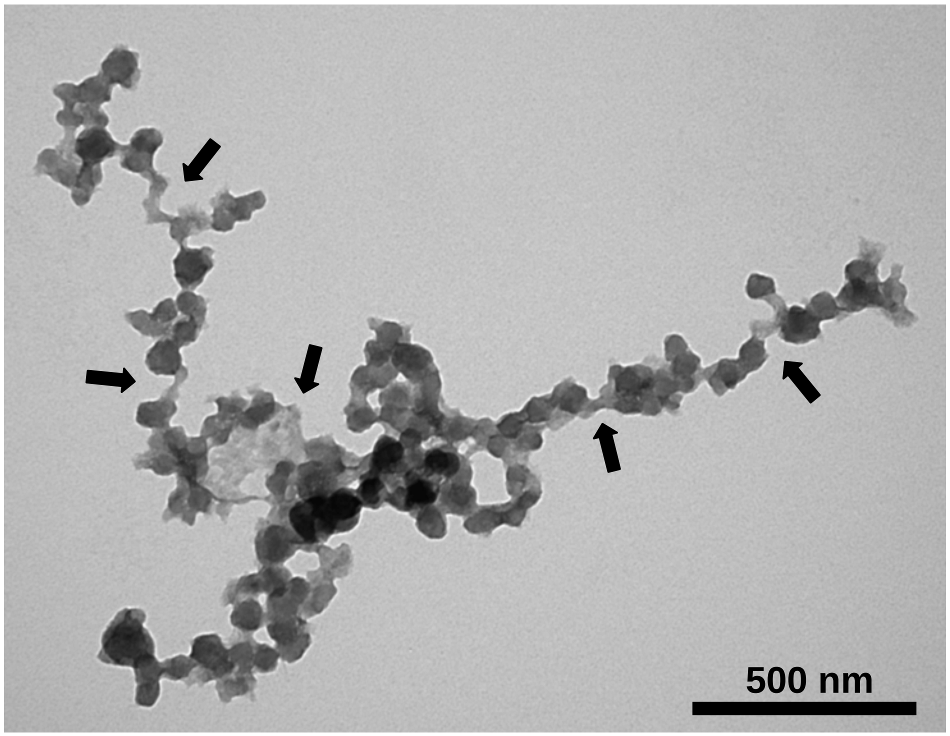


40 mM $CaCl_2$

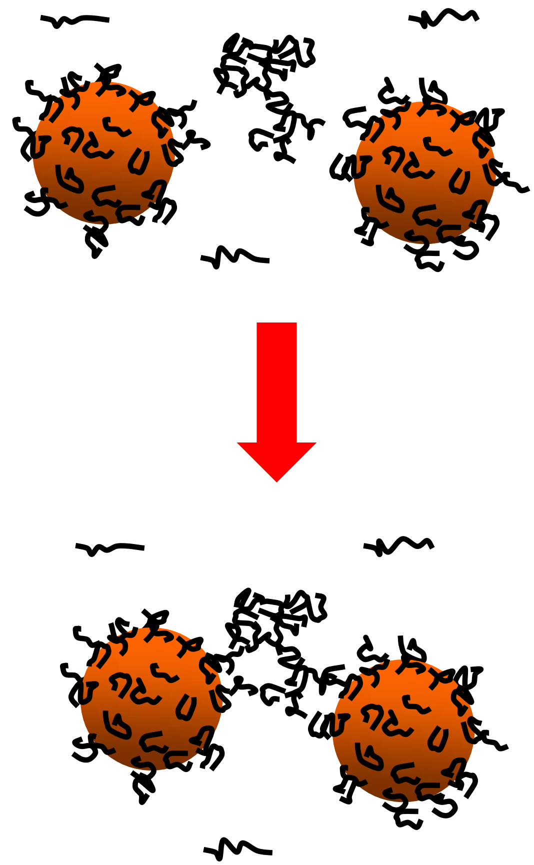


100 mM $MgCl_2$

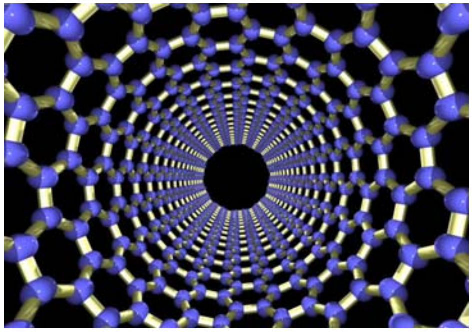
Humic Acid Clusters Bridge Fullerene Nanoparticles

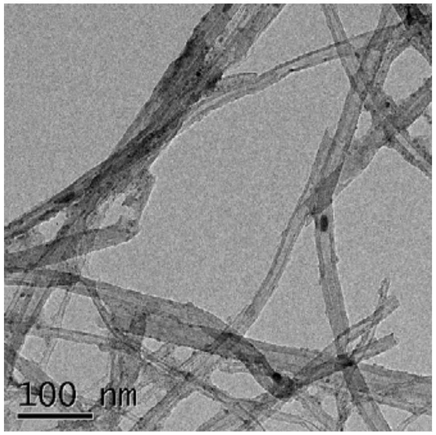


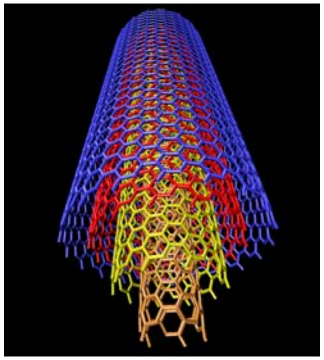
40 mM $CaCl_2$



Aggregation Kinetics of Multi-Walled Carbon Nanotubes (MWNTs)





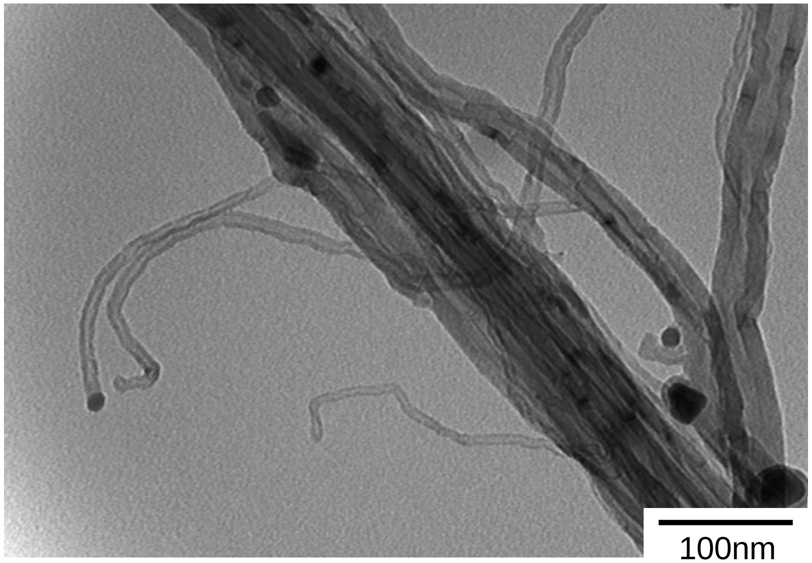


MWNT Sample Preparation

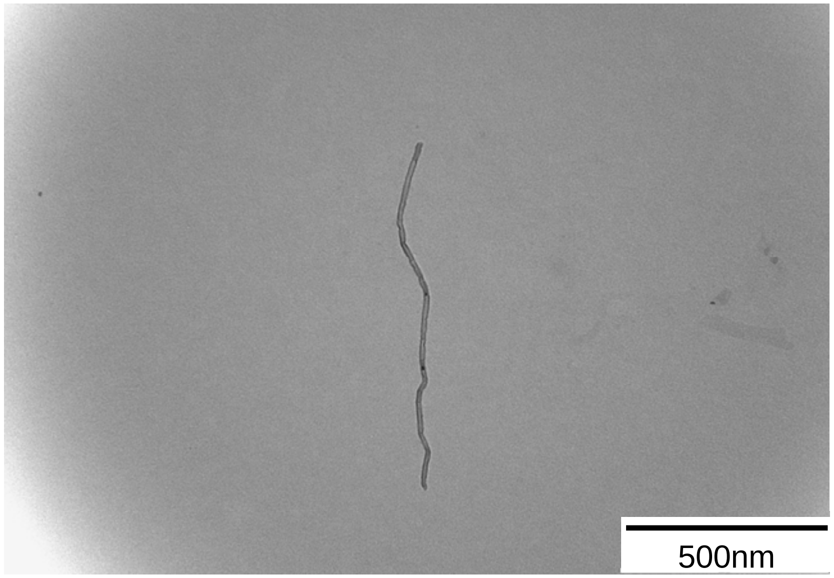
- 10 mg MWNTs added to 100 mL DI water
- Sonicated for 30 minutes using ultrasonicating probe
- Supernatant collected
- Re-sonicated for 5 more cycles (30 minutes each) to obtain final sample

TEM Images of Untreated and Treated MWNTs

Untreated

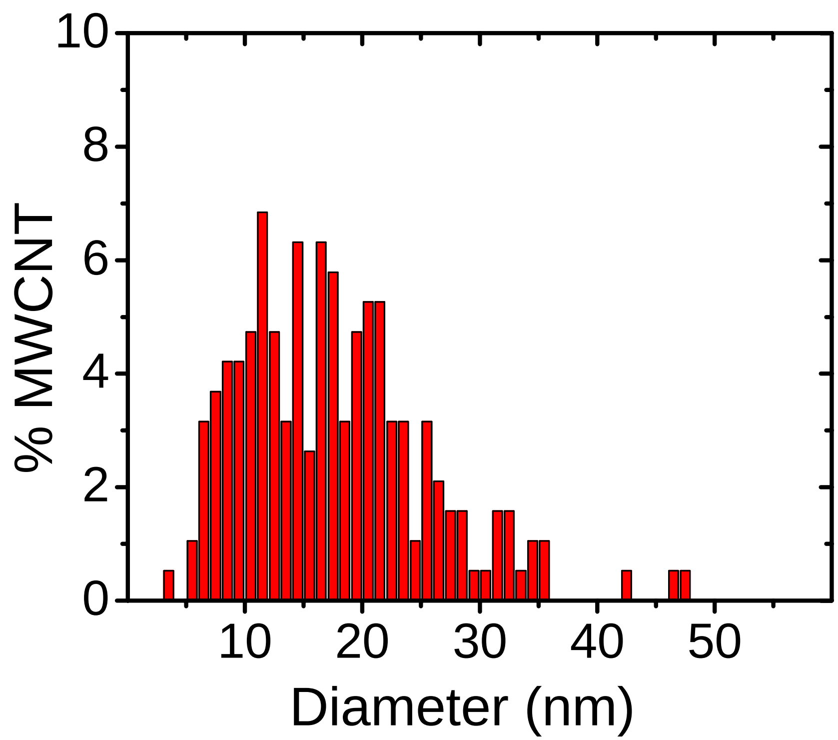


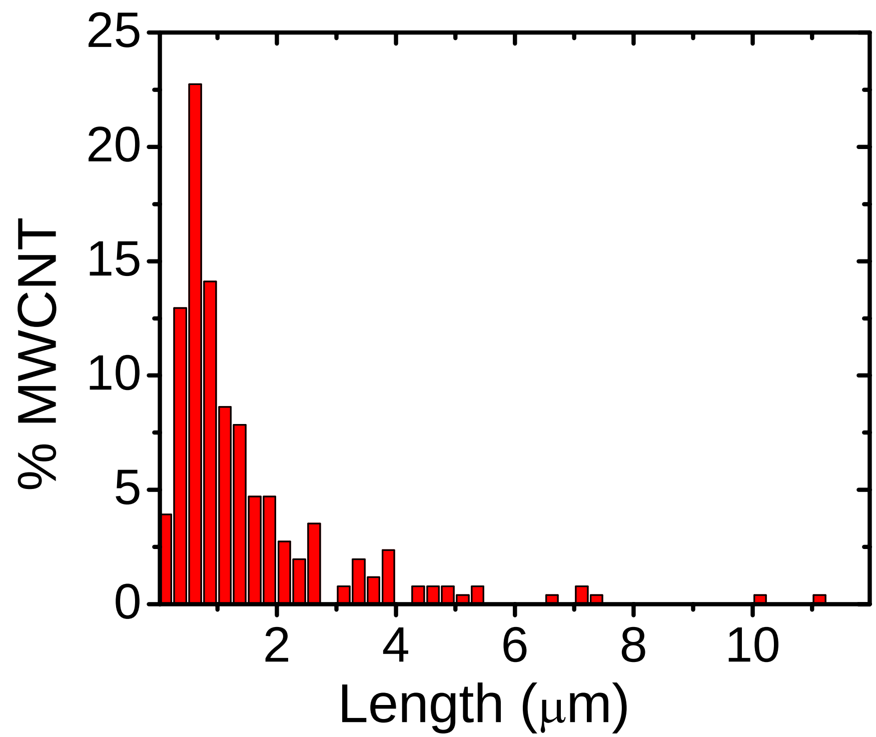
Treated



- Tubes are bundled and long before treatment
- Sonication debundles and reduces average length

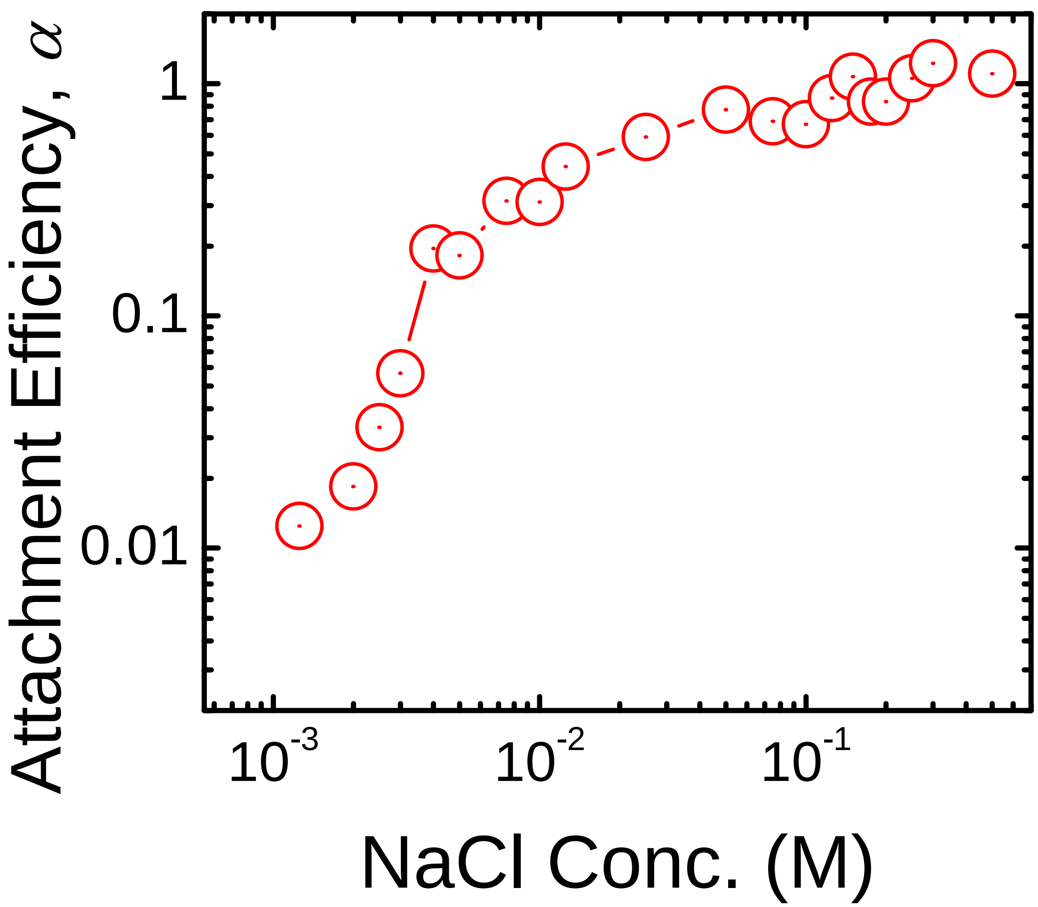
Diameter and Length Distributions of Treated MWNTs



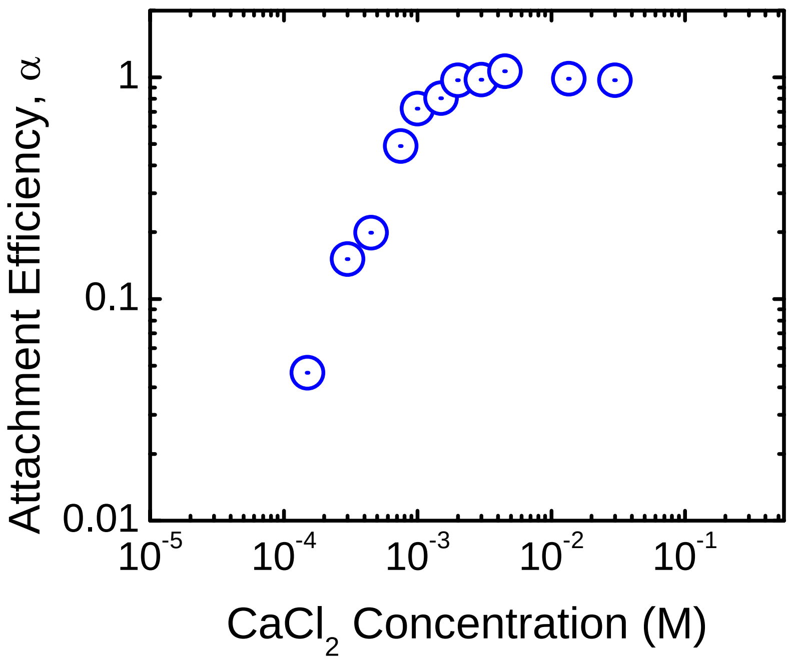


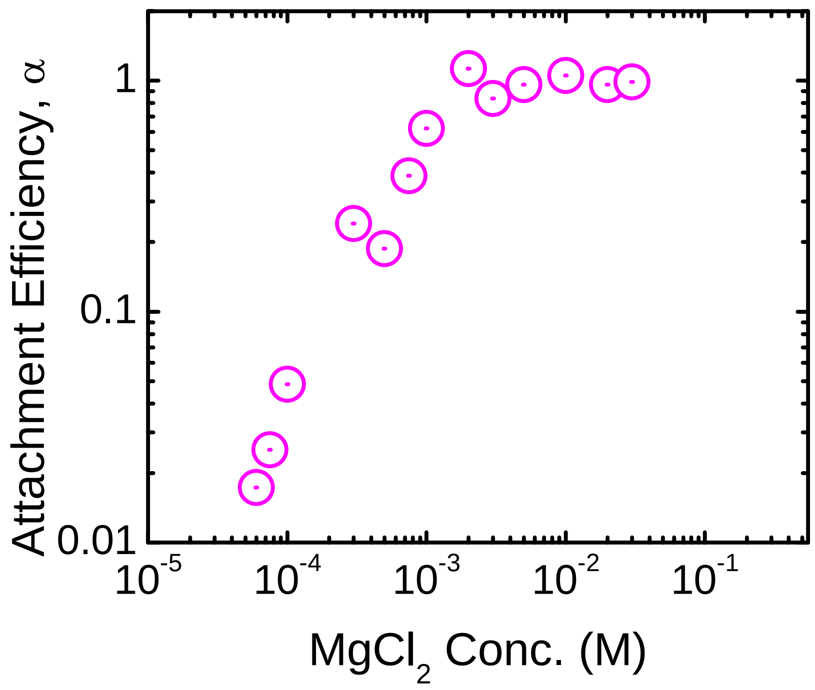
- Diameter and length distributions are obtained with TEM
- Average diameter 18 nm and average length 1.5 μm

Aggregation Kinetics with Monovalent Salt (NaCl)



Aggregation Kinetics with $CaCl_2$ and $MgCl_2$

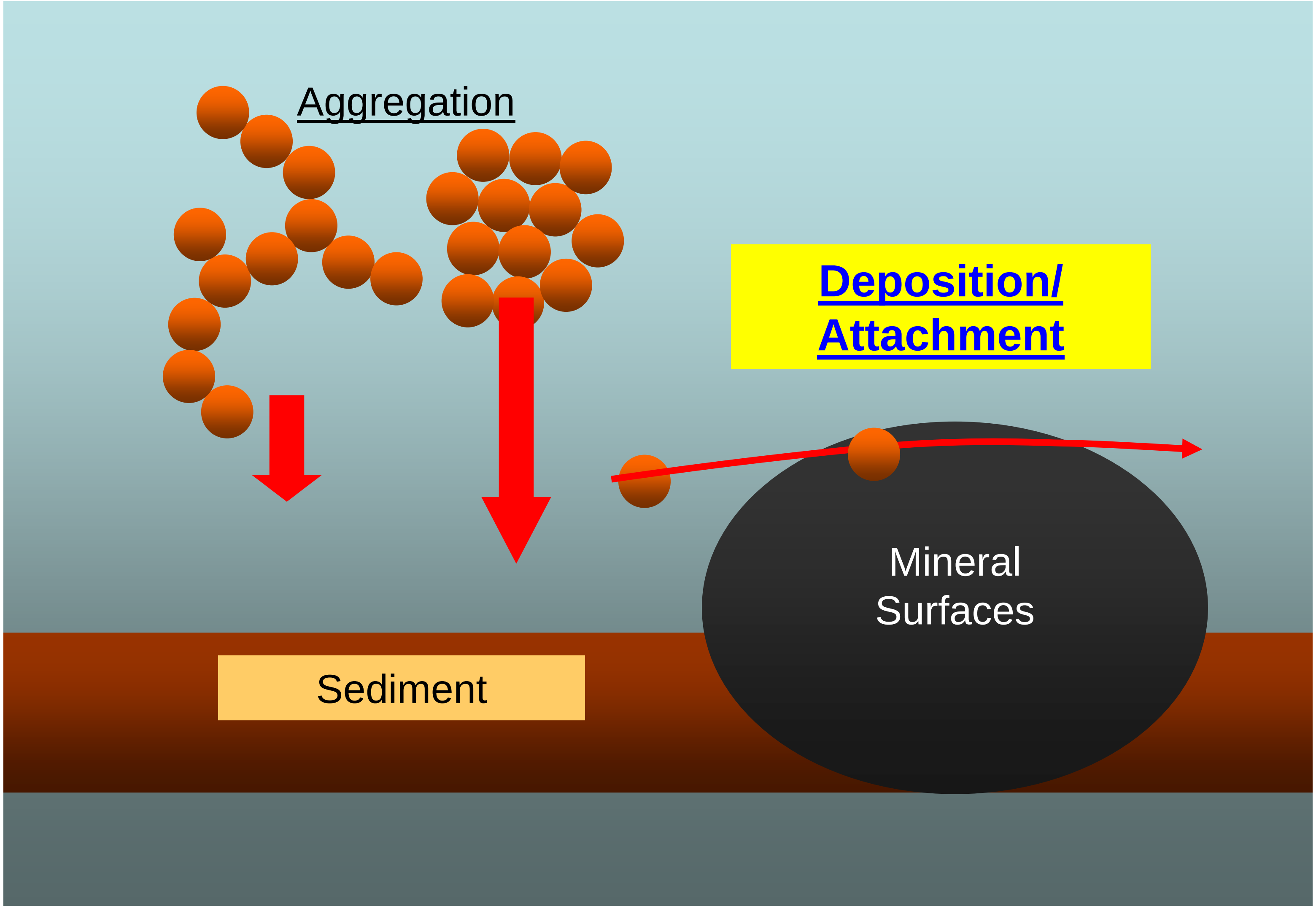




- Classic aggregation behavior with slow and fast regimes

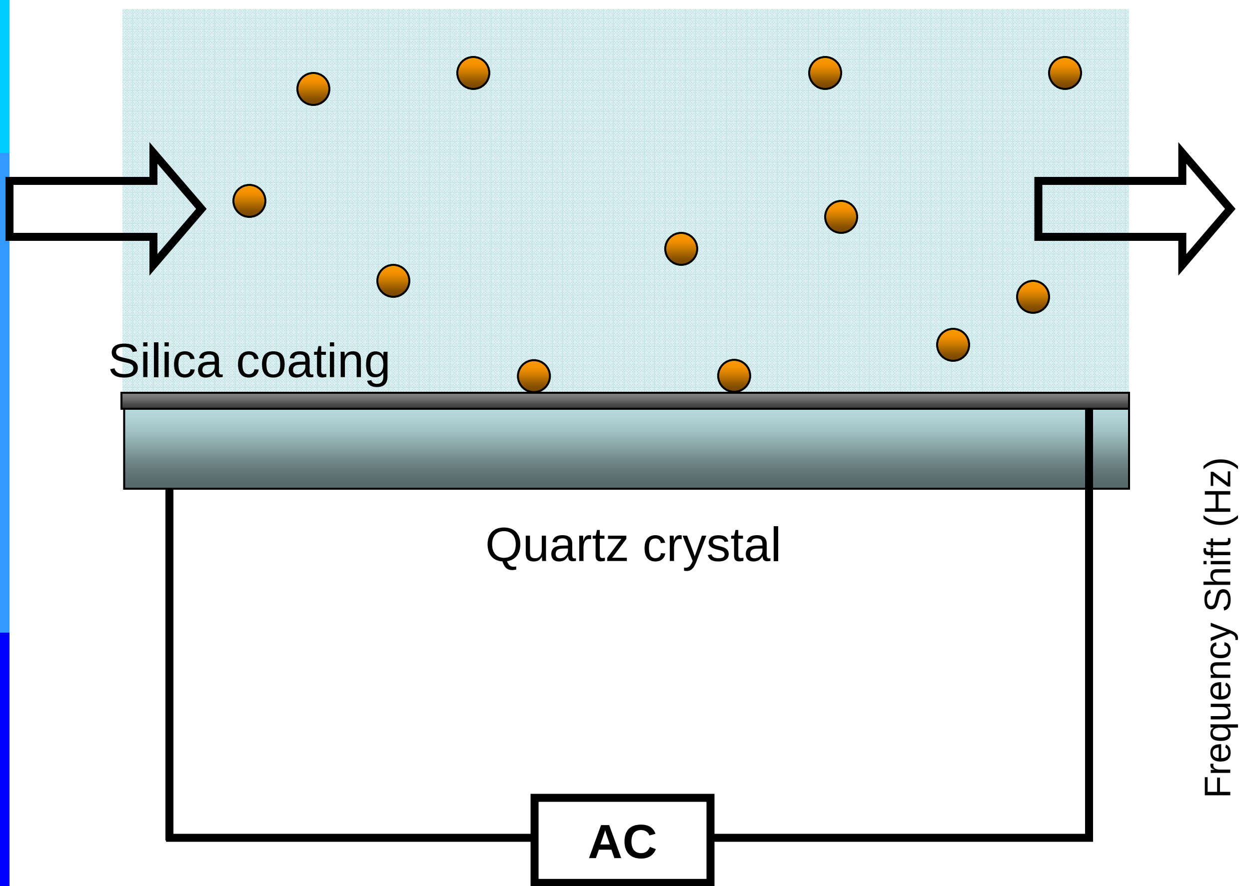
Deposition Kinetics of Fullerene Nanoparticles

Aggregation and Deposition Behavior Determines Fate and Transport



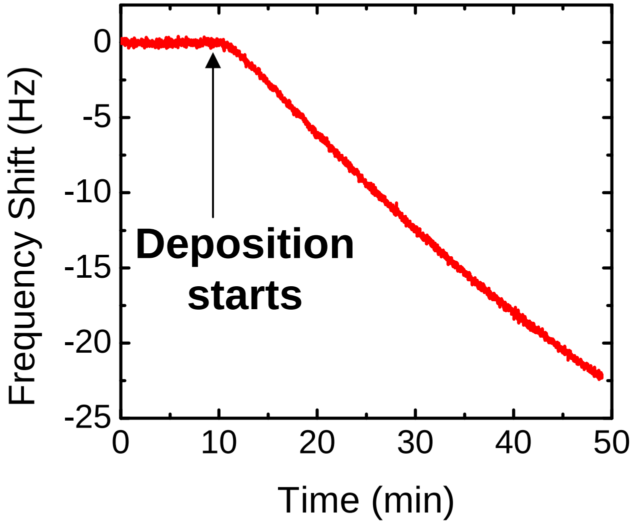
Quartz Crystal Microbalance (QCM)

Flow Cell:

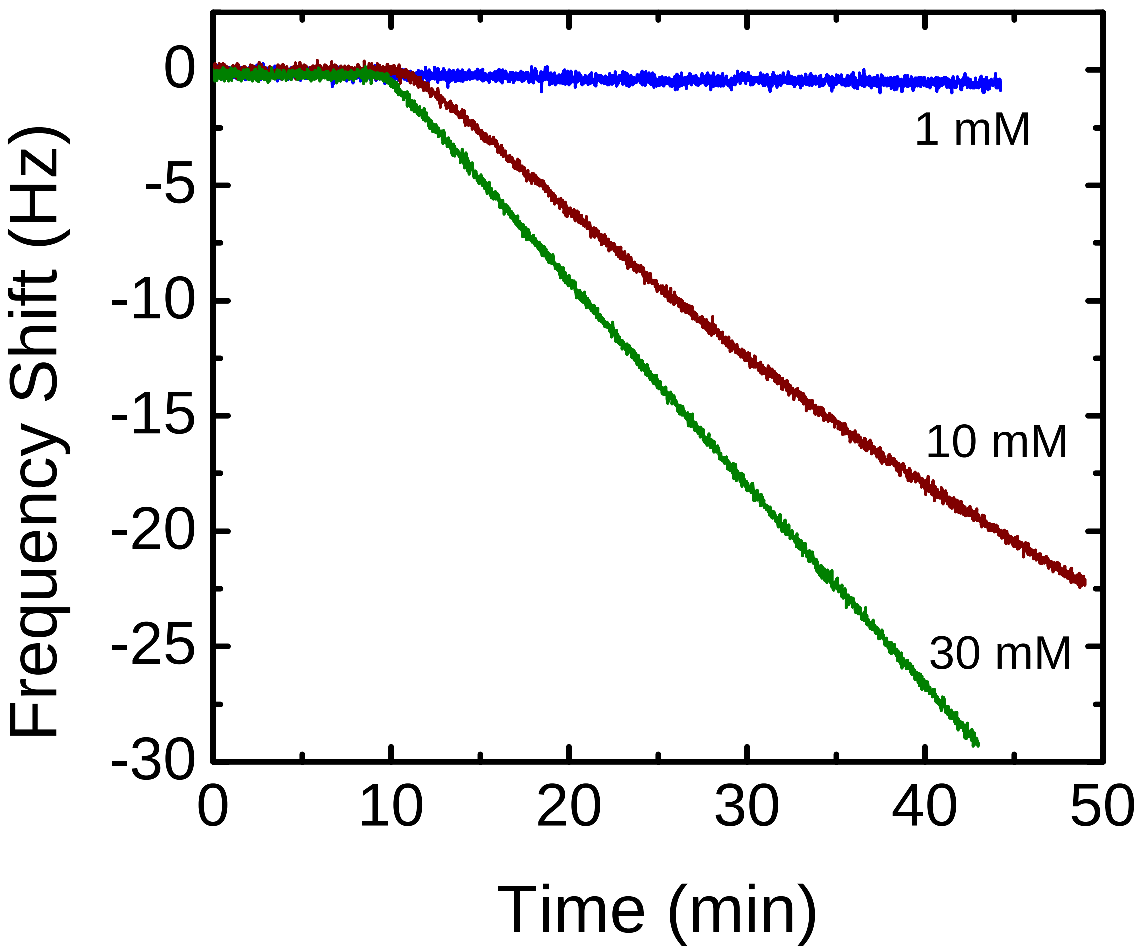


Sauerbrey relationship:

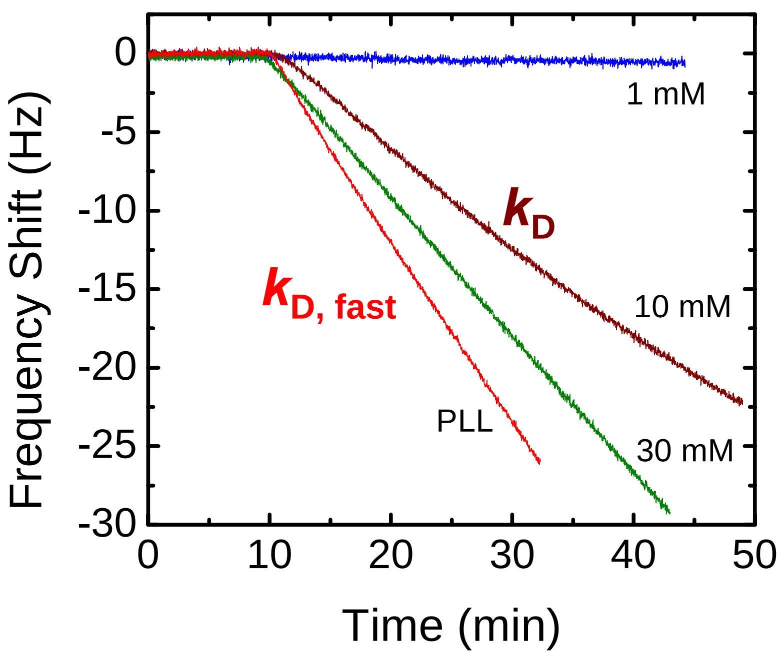
$$\Delta m = -\frac{C \Delta f_n}{n}$$



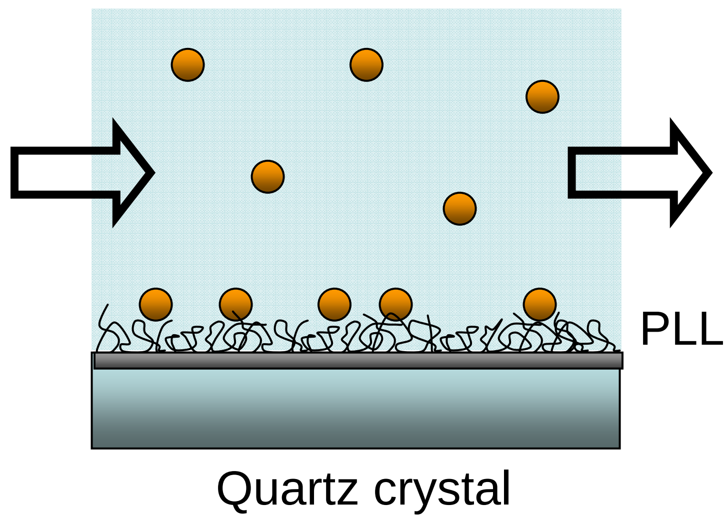
Deposition Kinetics



Attachment Efficiency



Favorable (fast) deposition:

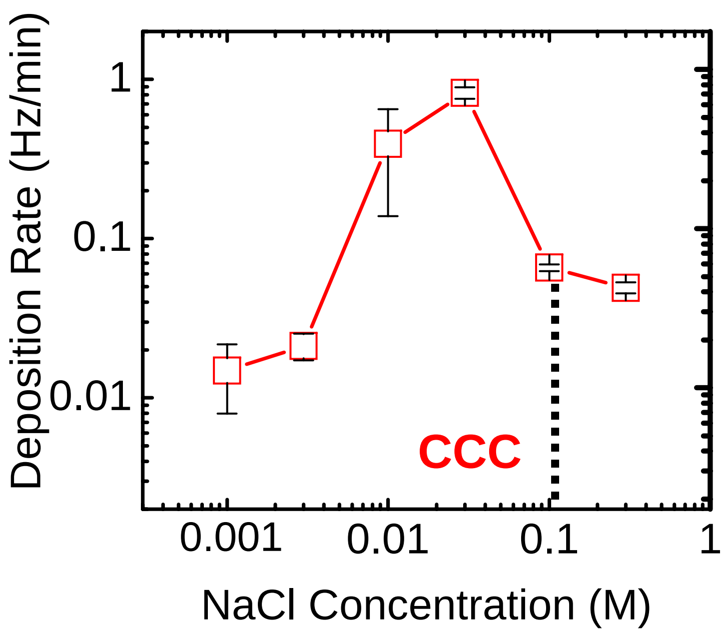


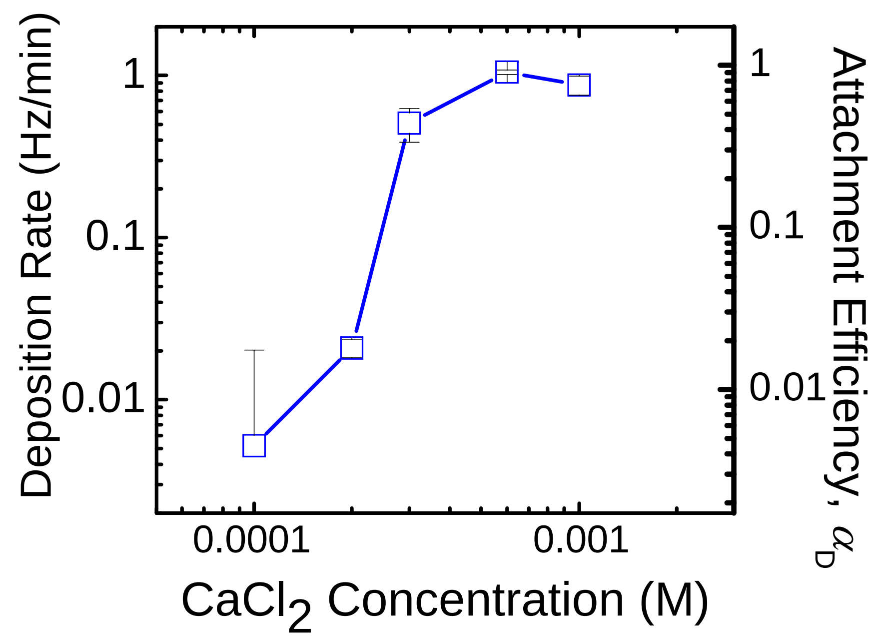
Deposition attachment efficiency:

$$\alpha_D = \frac{k_D}{k_{D,\, fast}}$$

Pre-adsorption of +ve charged poly-L-lysine (PLL) on silica surface

Influence of NaCl and $CaCl_2$ on Deposition Kinetics

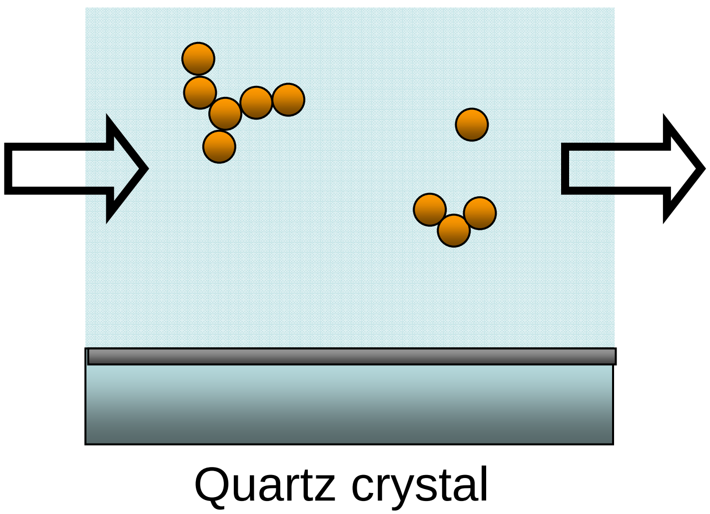


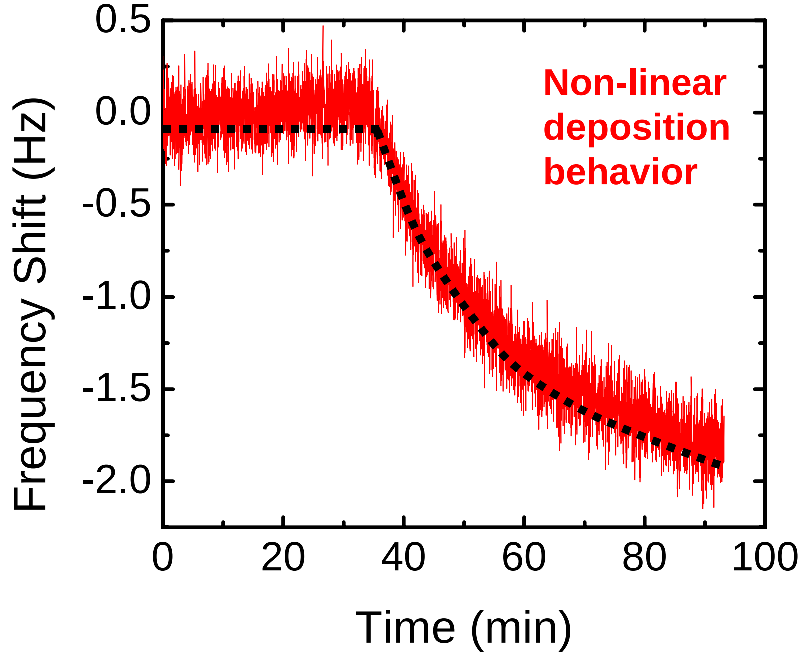


- Below CCC, as electrolyte concentration increases – faster deposition through charge shielding
- Towards CCC and above – significant drop in deposition rate

Simultaneous Deposition and Aggregation at Higher Ionic Strength

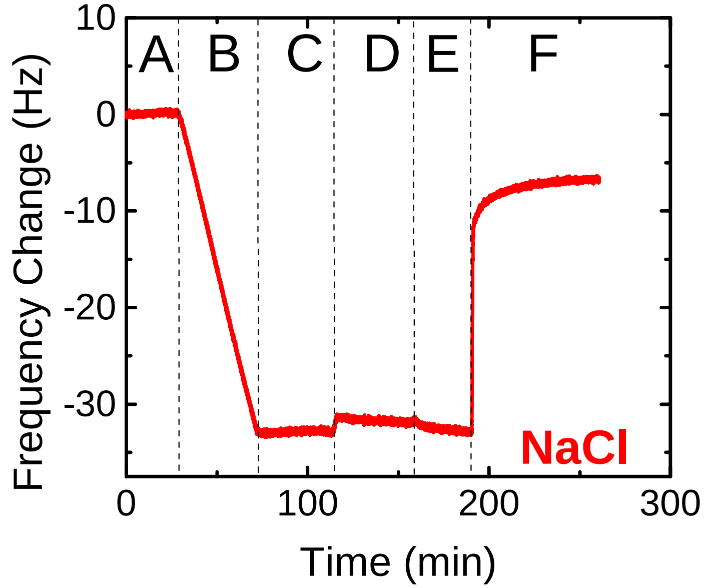
At 100 mM NaCl:

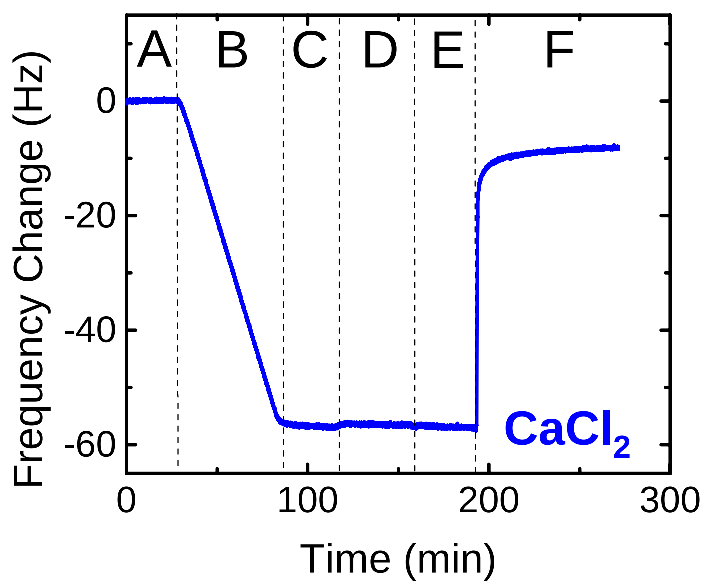




- Aggregate formation – **lower convective-diffusive transport** towards silica surface
- Bigger aggregates formed at later stages – deposition rate decreases even more

Release of Deposited Nanoparticles





A – Baseline (pH 5.7)

B – Deposition at **30 mM NaCl** and **0.6 mM $CaCl_2$ (both α_D ~ 1)**

C – Rinsing with respective electrolytes

D – Rinsing with 1 mM NaCl

E – Rinsing with DI water

F – Rinsing with DI water (pH 12.3)

Release at Stage F – sudden increase in surface potential of C_{60} nanoparticles and silica surface

Concluding Remarks

- Eelectrostatic interactions control the aggregation and deposition behavior of carbon-based nanomaterials (CBNs)
- Humic substances stabilize CBNs by electrosteric repulsion
- Under solution chemistries of natural waters, CBNs are stable and thus expected to be mobile

Acknowledgments

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- NSF BES-0646247