Fate and Transport of Multiwalled Carbon Nanotubes in Aquatic Systems

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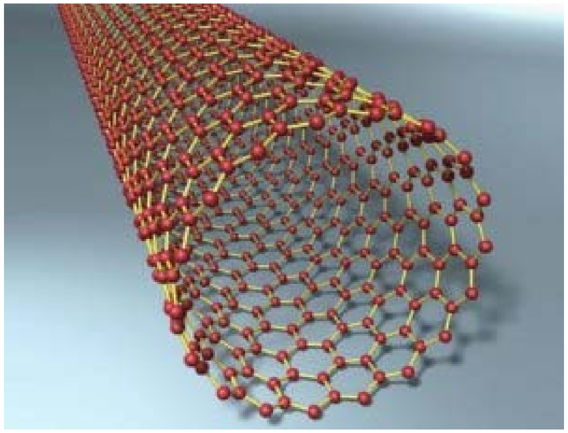
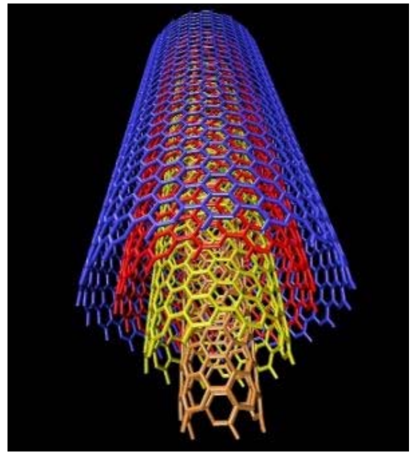
Overview

- Background on carbon nanotubes (CNTs)
- Objective
- Preparation and characterization of multiwalled carbon nanotubes (MWNTs)
- Aggregation kinetics of MWNTs
- Kinetics and reversibility of MWNT deposition on silica surfaces
- Conclusions

Carbon Nanotubes



mrbarlow.wordpress.com



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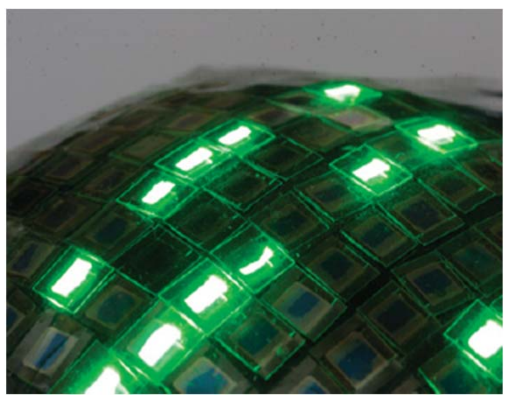
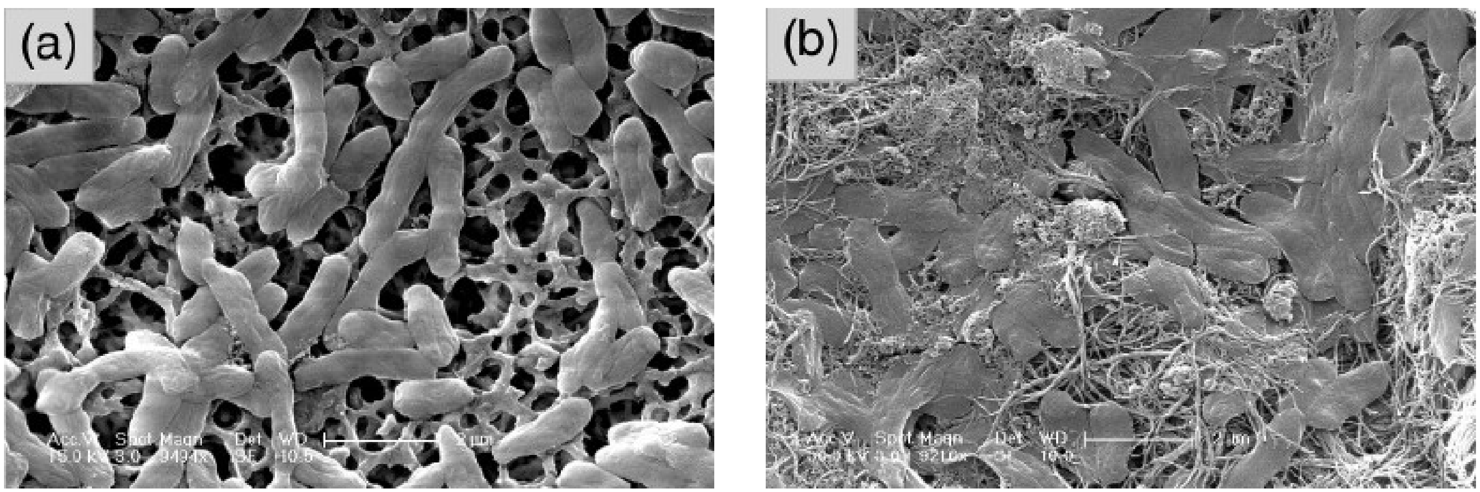


Sekitani et al., *Nature Materials*, **2009**, 494-499

- Mechanical properties: high strength; light weight
- Electronic properties: semiconducting or metallic

Toxicity of Carbon Nanotubes

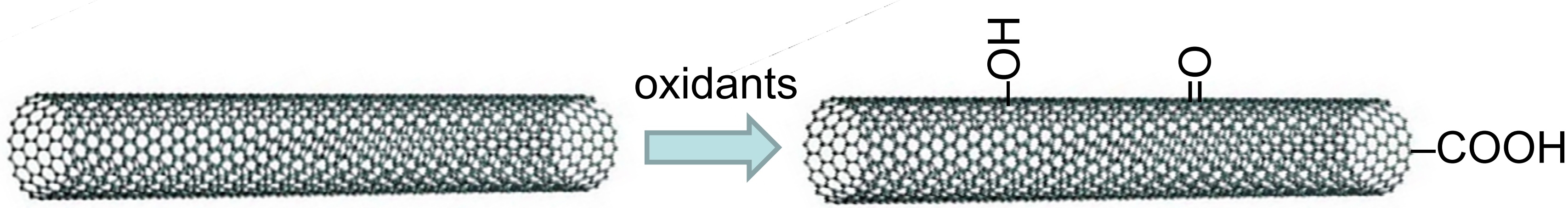
- Cause pulmonary inflammation and fibrosis in lungs of mice
- Damage bacterial membrane and inhibit bacterial growth



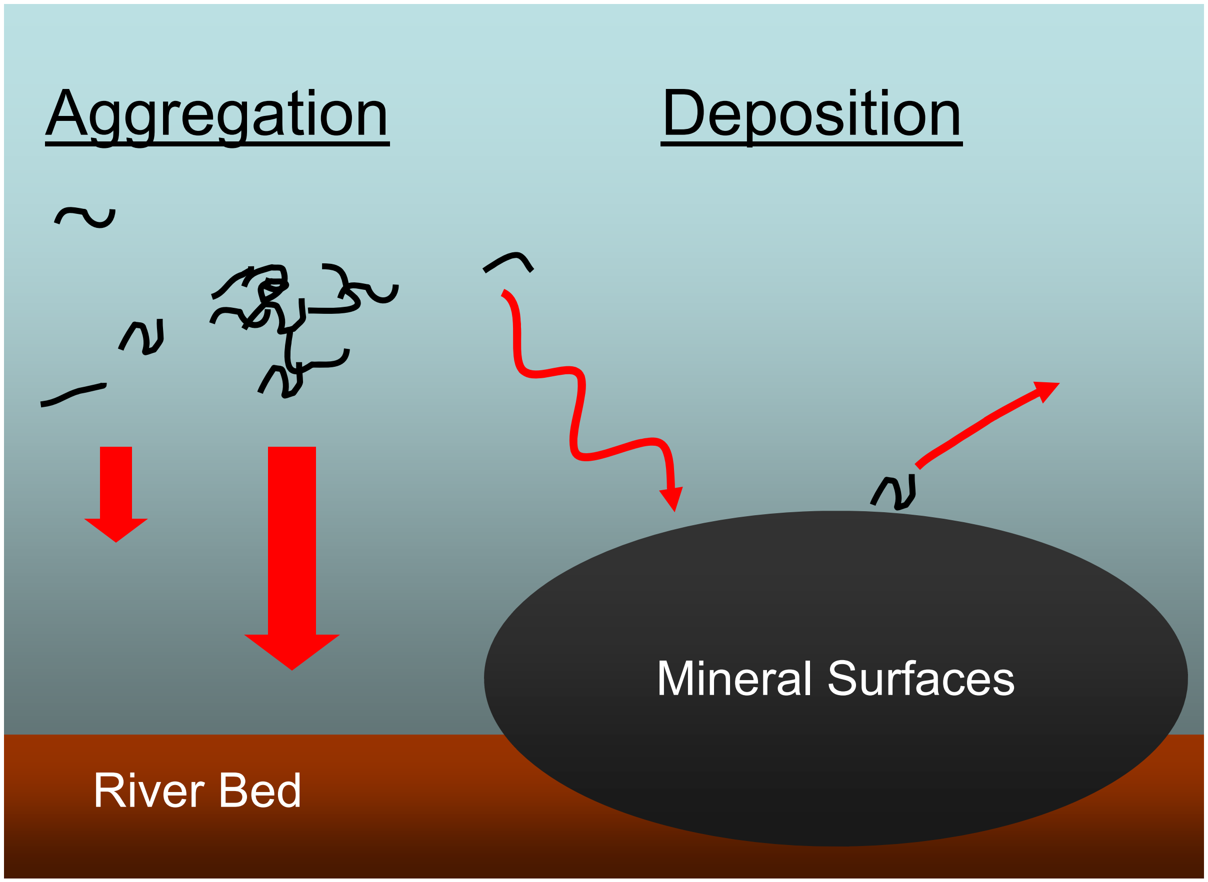
Kang et al., *Langmuir* **2007**, 23, 8670-8673

Release of Carbon Nanotubes into the Environment

- Potential Routes of Release
  - Consumer products that contain CNTs as they undergo wear and tear
  - Factories producing CNTs and CNT-based products
  - CNT-based products disposed in waste disposal facilities, e.g., incinerators and landfills
- Surface of CNTs can be oxidized in natural and engineered aquatic systems

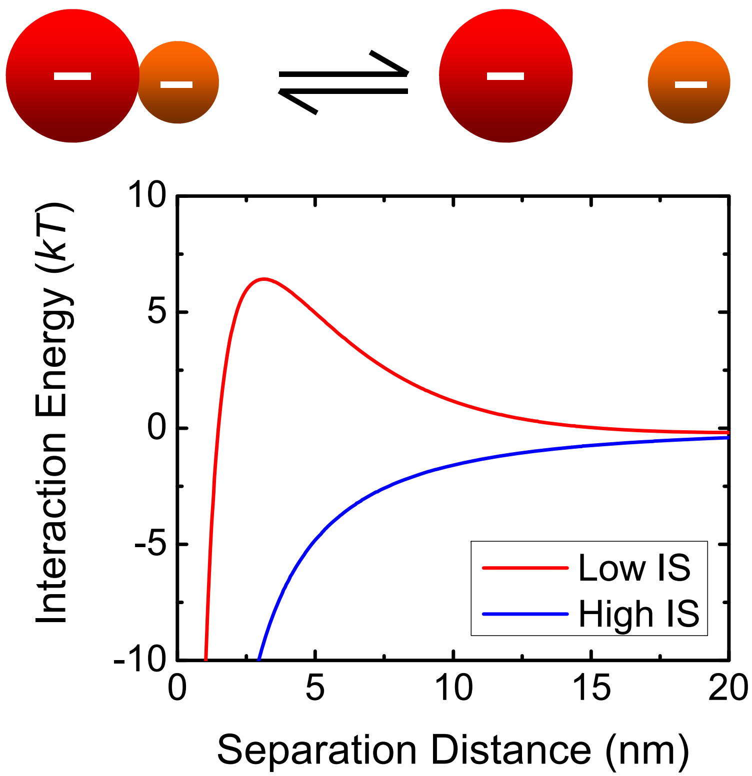


Aggregation and Deposition Behavior Controls Fate and Transport of CNTs



- Aggregation and deposition can be conceptualized as a two-stage process: transport and attachment

Attachment Depends on Surface and Solution Chemistries



- *Derjaguin–Landau–Verwey–Overbeek (DLVO) Theory*:

  Total energy of interaction = van der Waals attraction + electrostatic interaction
- Particle shape and size, material, surface properties, solution chemistry

Objective

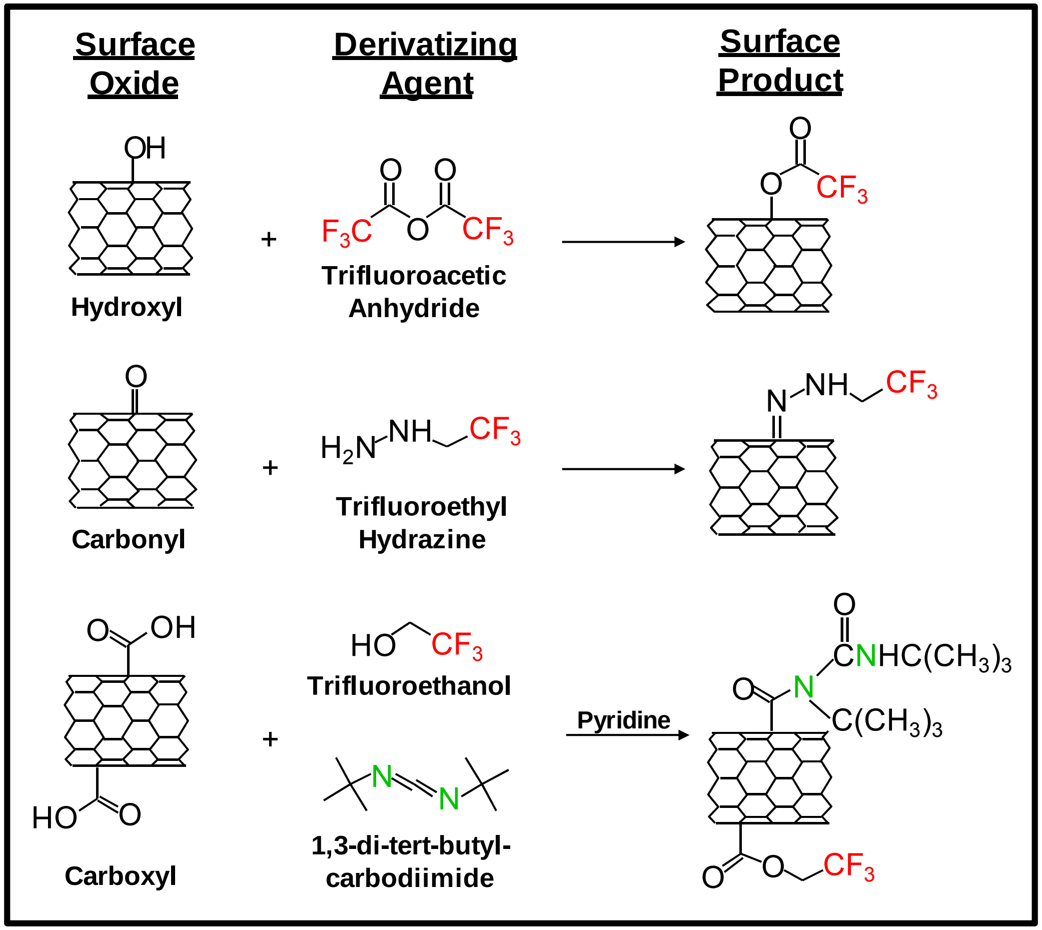
To investigate the influence of surface oxidation and solution chemistry on the aggregation and deposition of MWNTs in aqueous solutions

Preparation of Two MWNTs with Different Degrees of Surface Oxidation

- MWNTs purchased from NanoLab (8 to 10 walls) were used as starting material
- Expose MWNTs to a 3:1 mixture of 98% H_2SO_4 and 69% HNO_3 or a 4-time diluted acid mixture at 70^{o}C for 8 hours
- Repeated cycles of dilution with DI water, centrifugation, and decantation of the supernatant
- The highly and lowly oxidized MWNTs (HO-MWNTs and LO-MWNTs) were dried overnight at 100^{o}C and then pulverized in a ball-mill

Surface Characterization of MWNTs

- The distribution of carboxyl (COOH), hydroxyl (C-OH), and carbonyl (C=O) groups was quantified by X-ray photoelectron spectroscopy (XPS) in conjunction with vapor phase chemical derivatization



Chen et al., *Environmental Chemistry* **2010**, 7, 10-27

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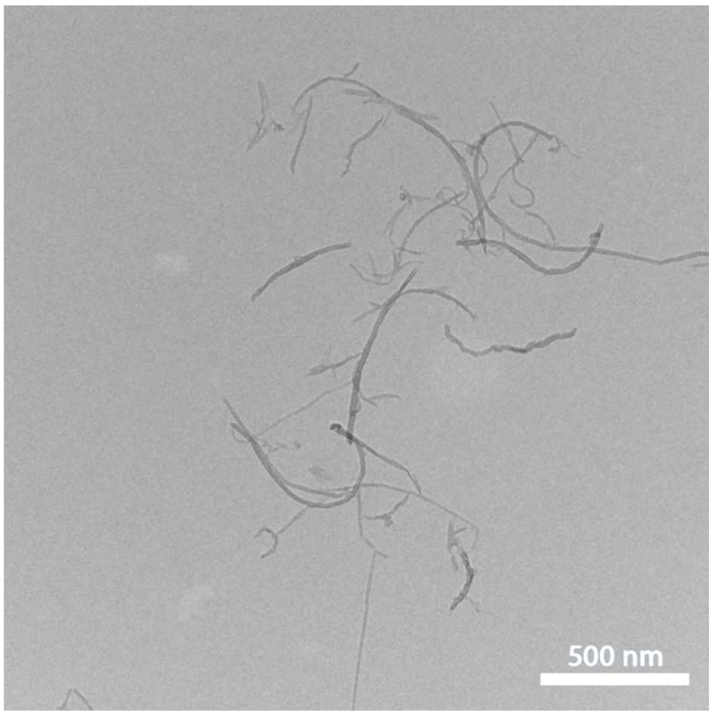
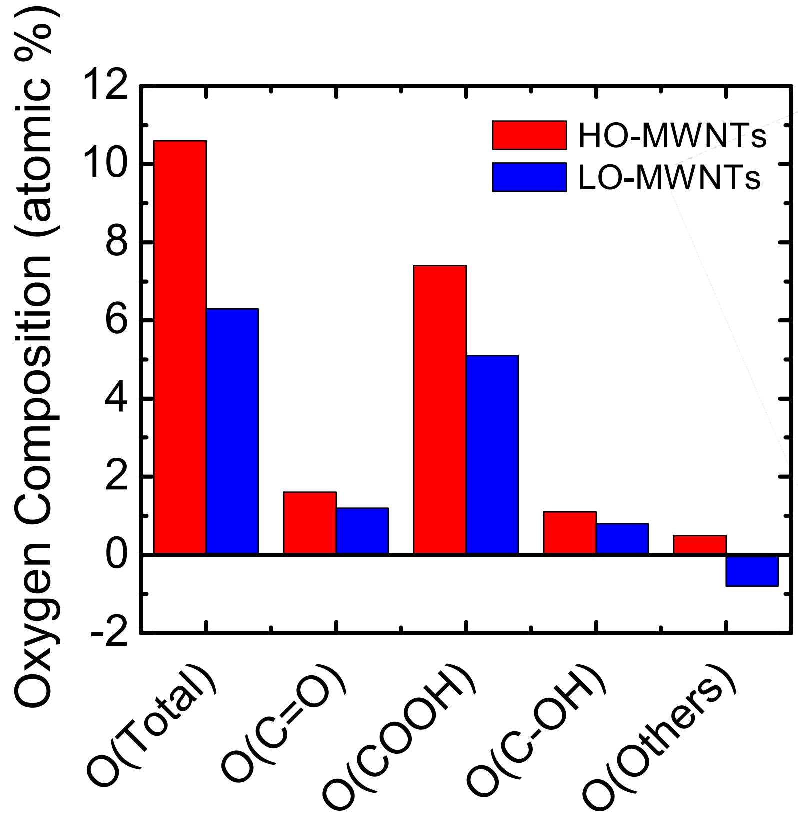
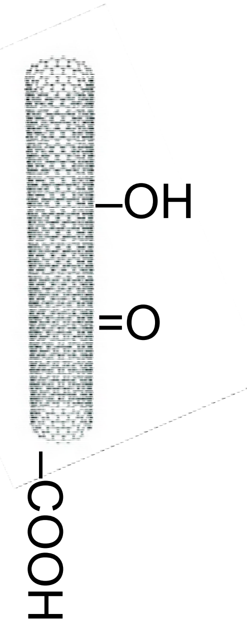
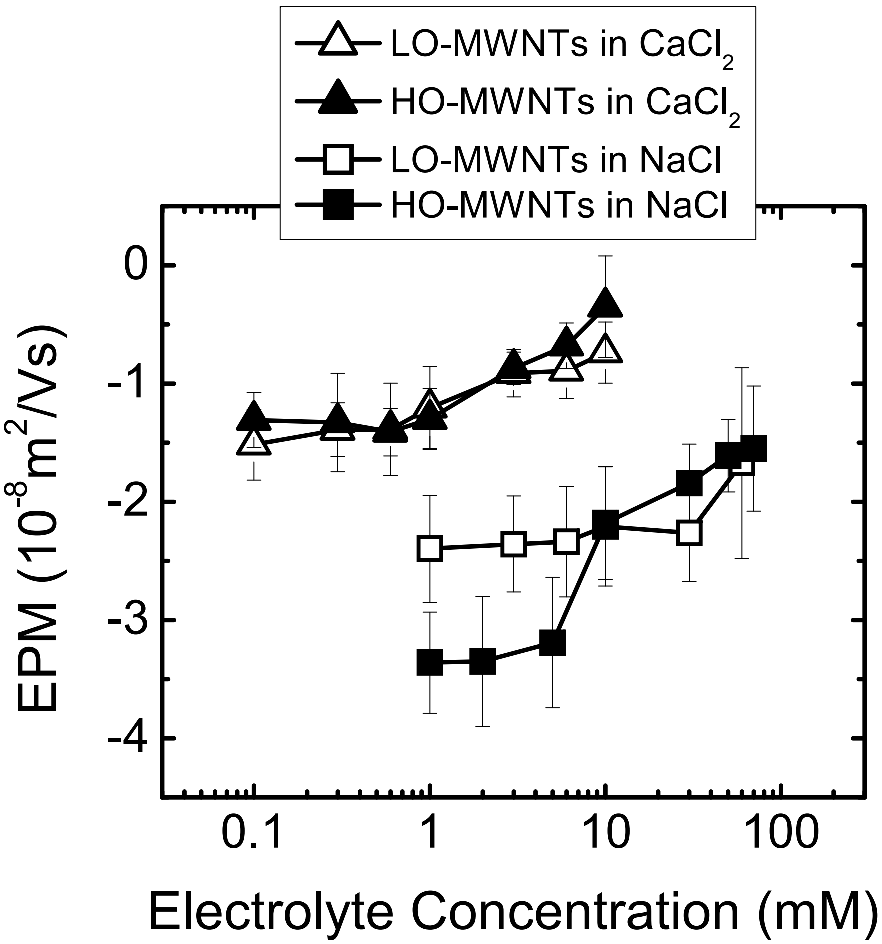






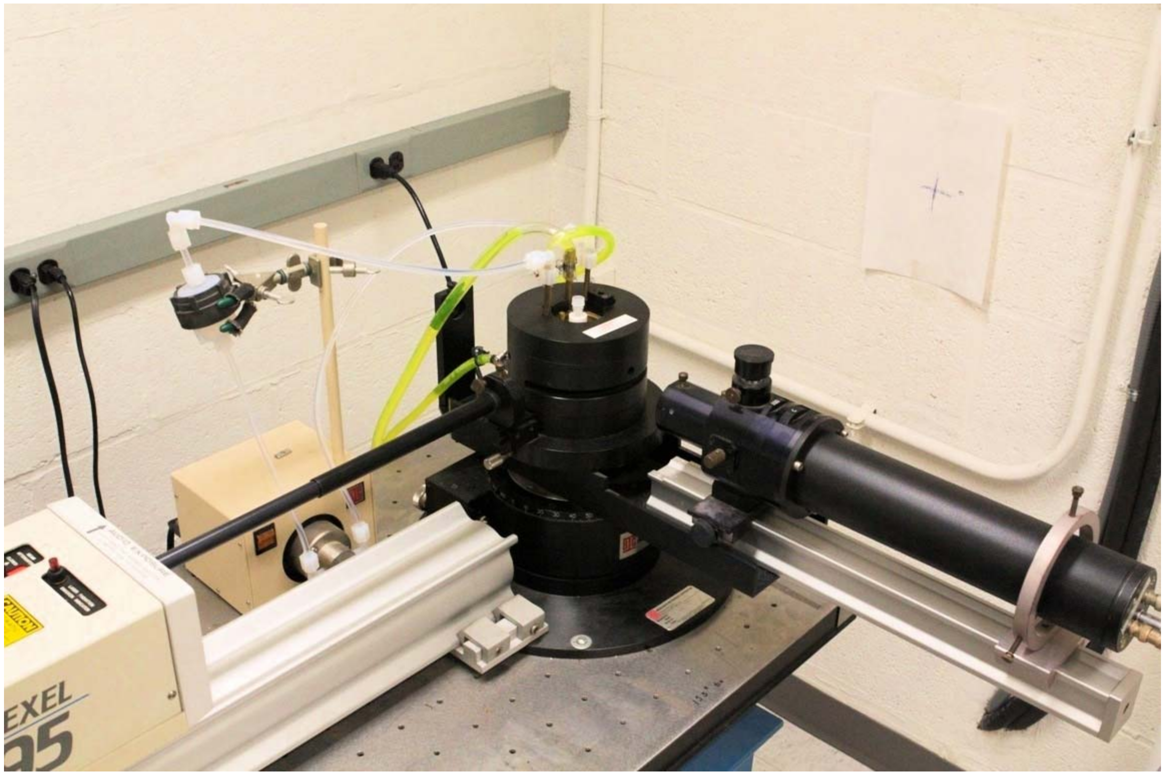
Oxygen-Containing Functional Groups

Electrokinetic Properties of MWNTs in NaCl and $CaCl_2$ Solutions



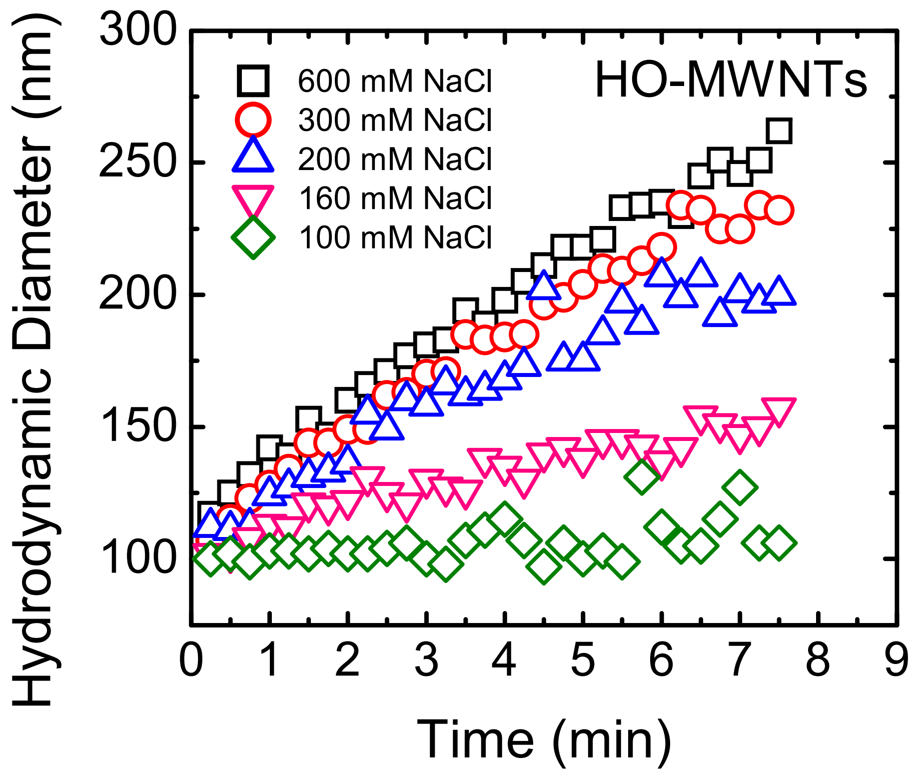
- Electrophoretic mobility (EPM)
- Brookhaven ZetaPALS
- pH 7.1 – carboxyl groups are deprotonated

Time-Resolved Dynamic Light Scattering



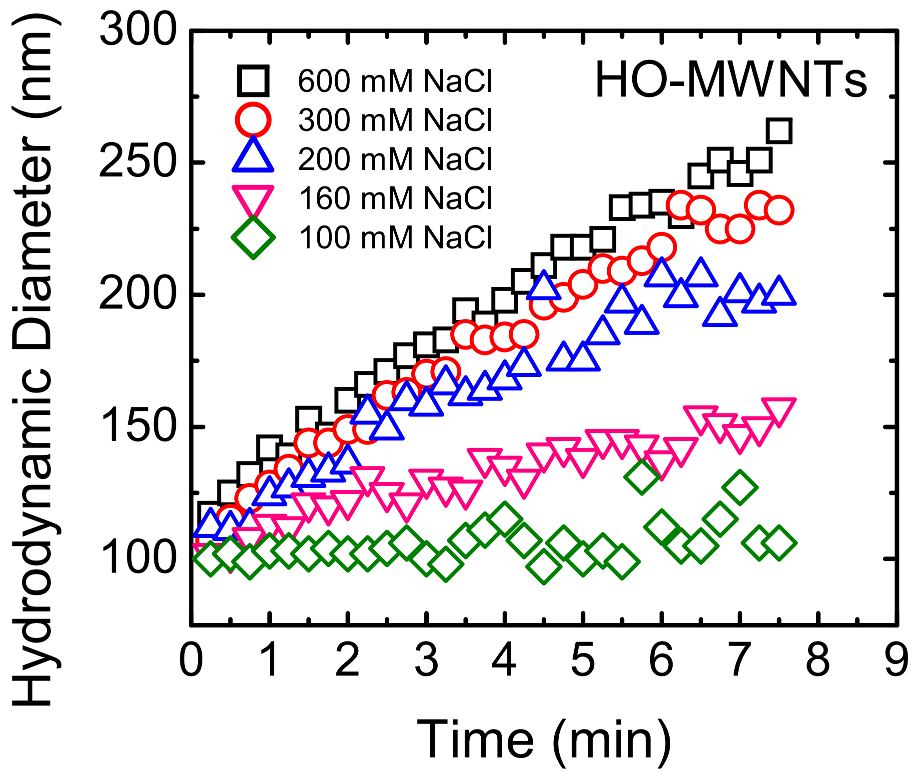
- Brookhaven BI-200SM goniometer
- Lexel 95 argon laser
- Wavelength 488 nm
- Scattering angle 90°

Determining Aggregation Kinetics using Time-Resolved Dynamic Light Scattering



- Particle concentration = 0.1 mg/L
- pH = 7.1

Determining Aggregation Kinetics using Time-Resolved Dynamic Light Scattering



Initial aggregation kinetics:

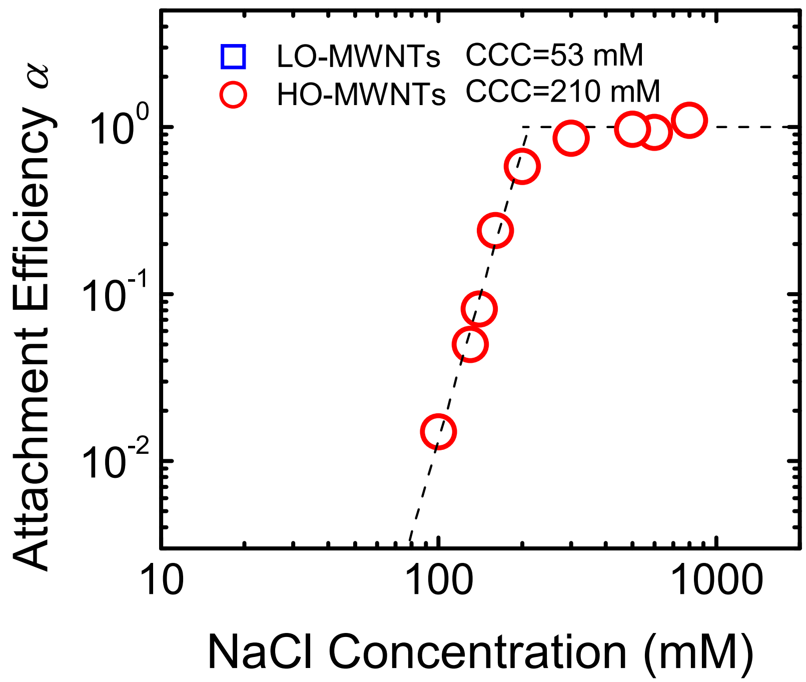
$$k = \left(\frac{dD_h(t)}{dt} \right)_{t \to 0}$$

Attachment efficiency:

$$\alpha = \frac{k}{k_{fast}}$$

- Particle concentration = 0.1 mg/L
- pH = 7.1

Influence of Surface Oxidation on Colloidal Stability of MWNTs



- Na^+ screens the surface charge of MWNTs, and results in an increase in aggregation kinetics

Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

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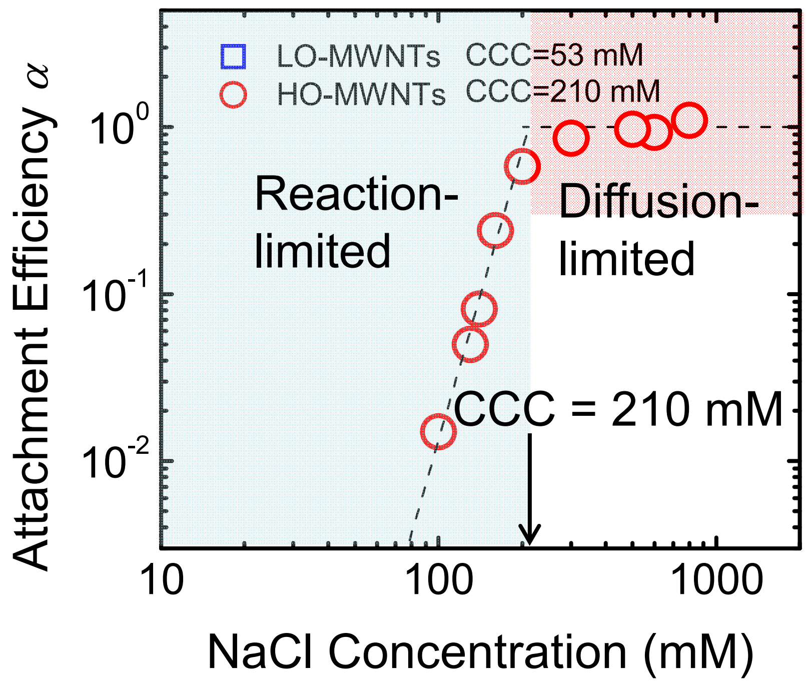

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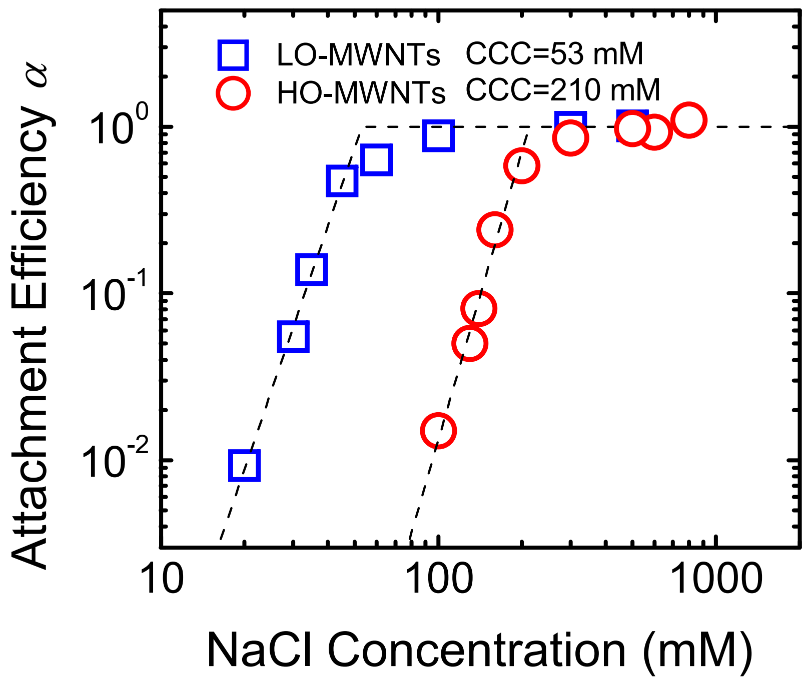

- A lower NaCl concentration is required to destabilize the less negatively charged LO-MWNTs

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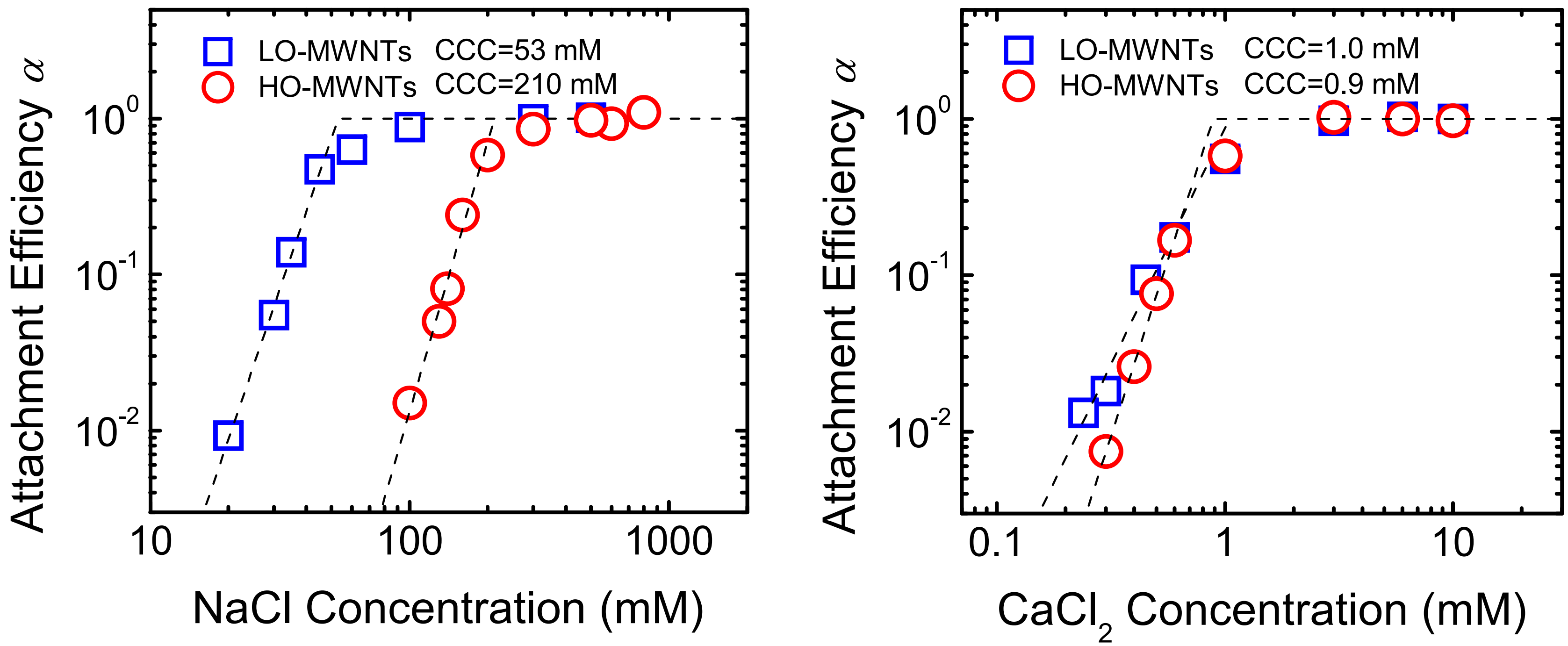
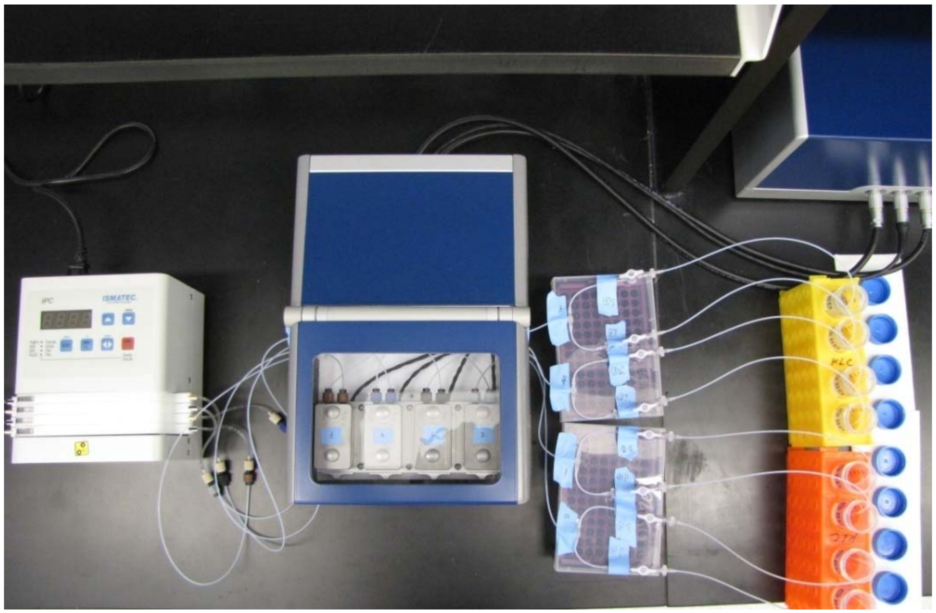
Influence of Surface Oxidation on Colloidal Stability of MWNTs

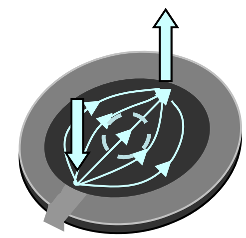


- Ca^{2+} binds to carboxyl groups, effectively neutralizing the surface charge of MWNTs

 Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)



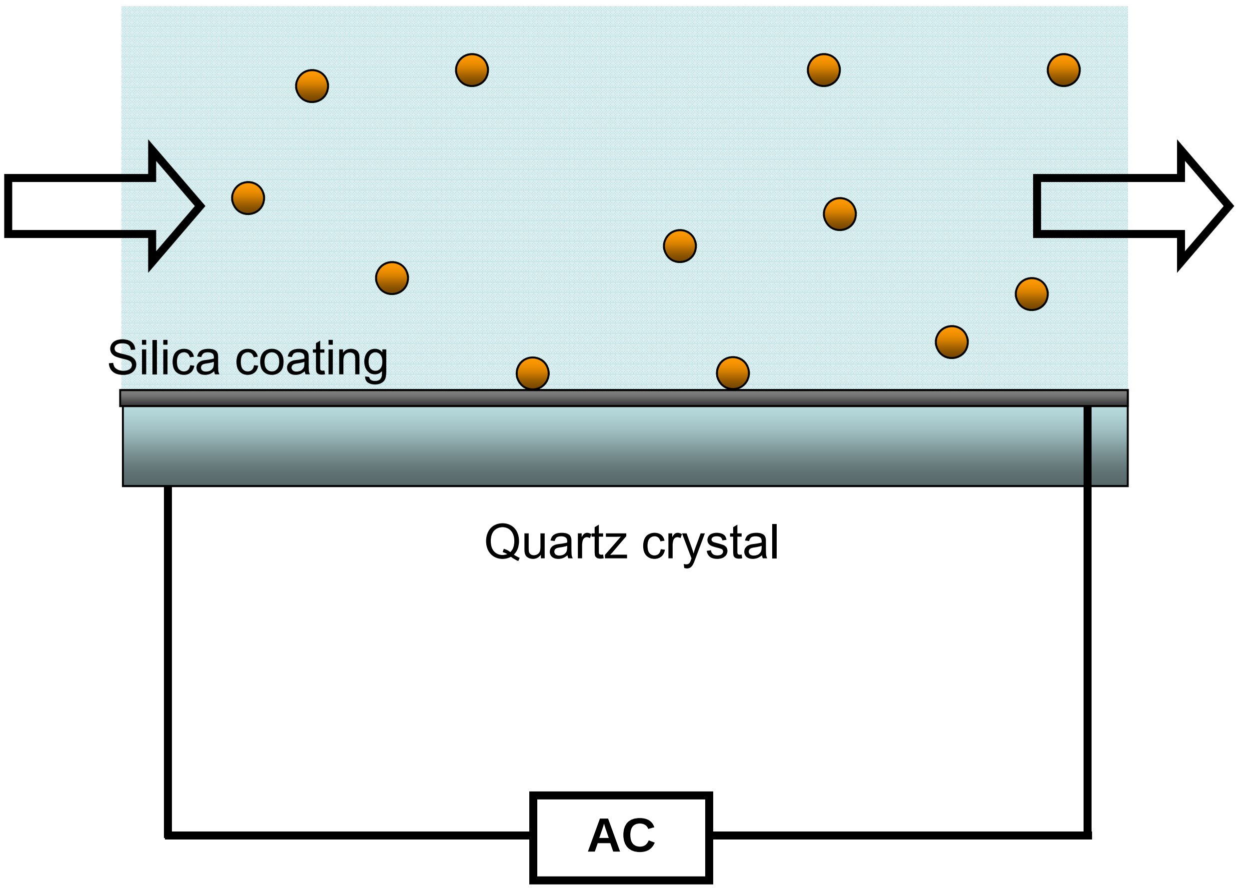


- Laminar flow at 0.6 mL/min
- [MWNT] = 0.5–1.2 mg/L
- T = 25^{o}C, pH = 7.1

From Q-Sense

Principle of QCM-D: Frequency

Flow Cell:



Sauerbrey relationship:

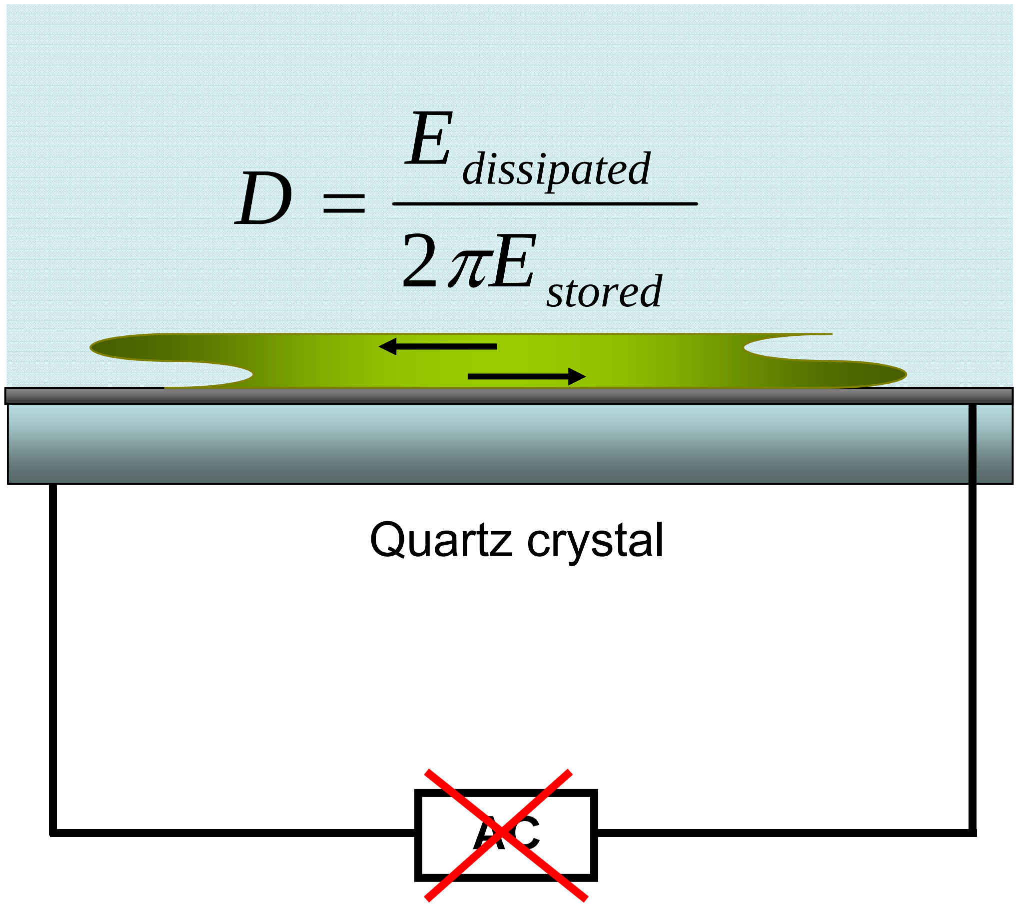
$$\Delta m = -C\Delta f_{(n)}$$

where C = 17.7 ng/(Hz.cm^2)

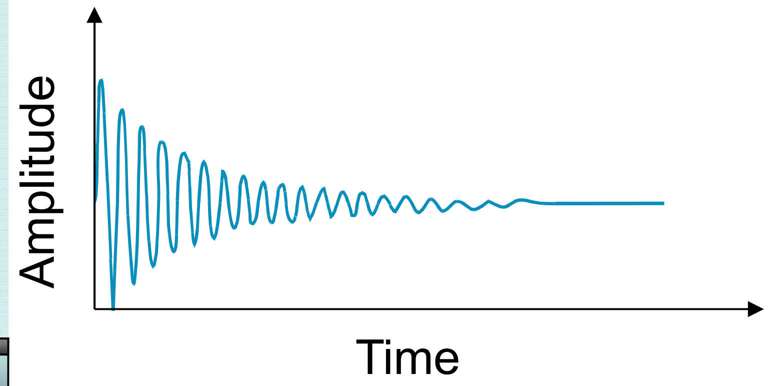
- Deposited mass is proportional to frequency shift with C as the constant of proportionality

Principle of QCM-D: Dissipation

Flow Cell:



$$D = \frac{E_{dissipated}}{2\pi E_{stored}}$$



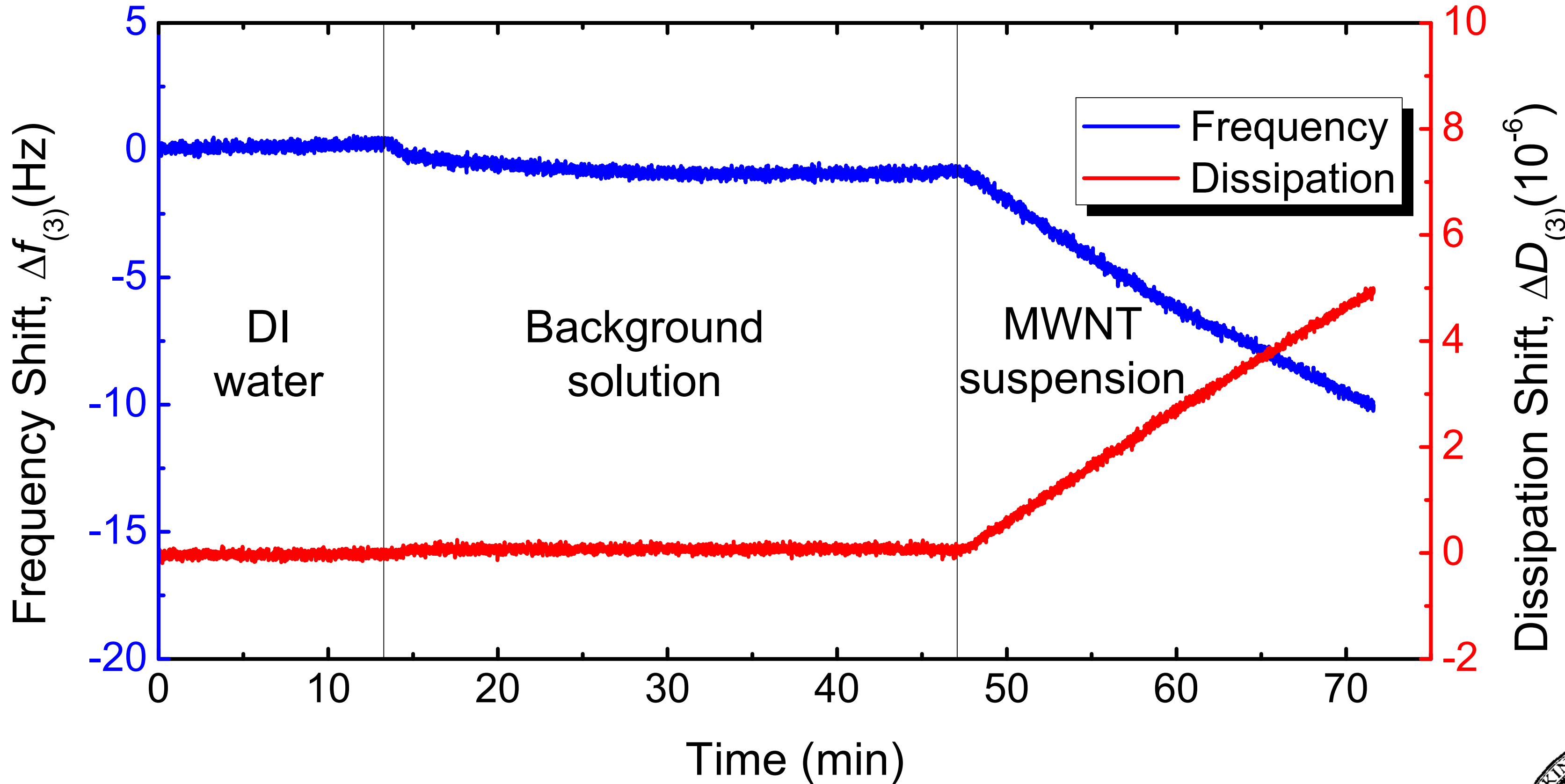
$$A(t)=A_0 \cdot \exp(-t/\tau)\cdot \sin(2\pi f t+\phi)$$

$$D=1/\pi f \tau$$

- Oscillatory motion in attached film results in energy dissipation
- *D* is related to viscoelastic properties of film

From Q-Sense

Deposition of MWNTs on Silica Surfaces



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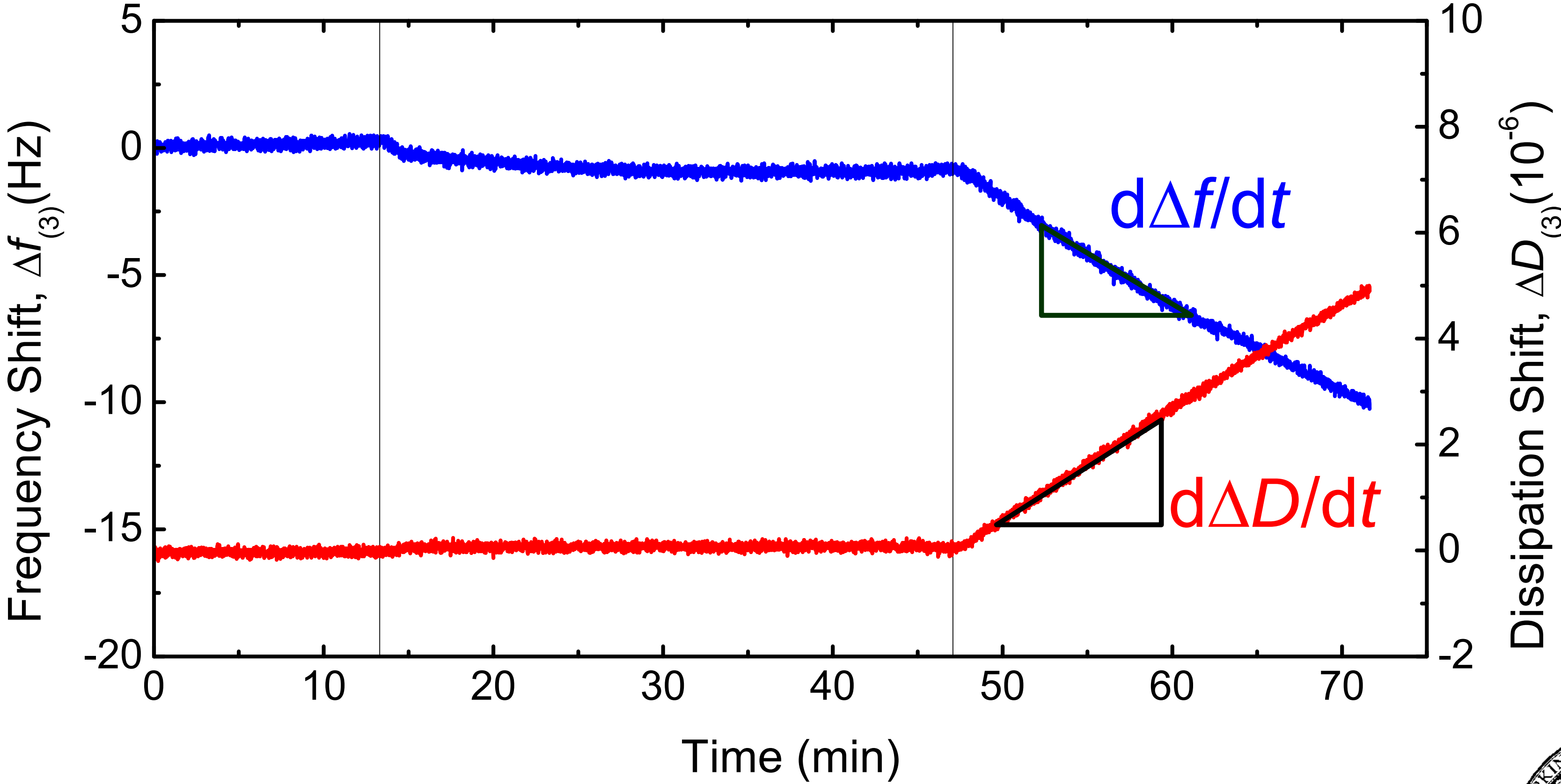
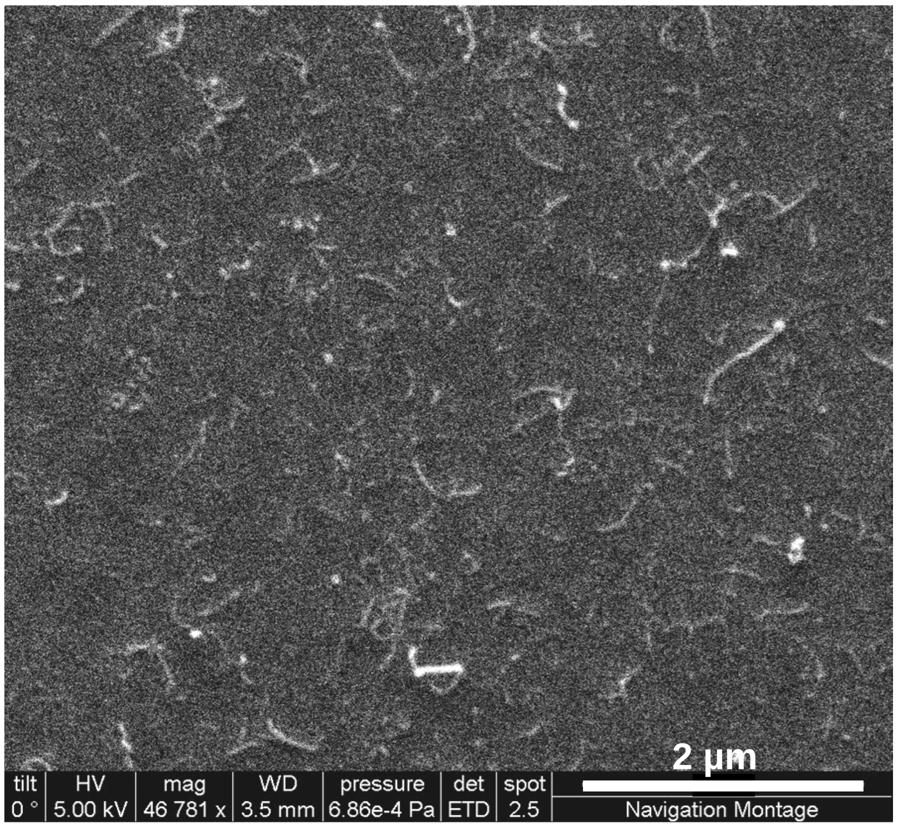
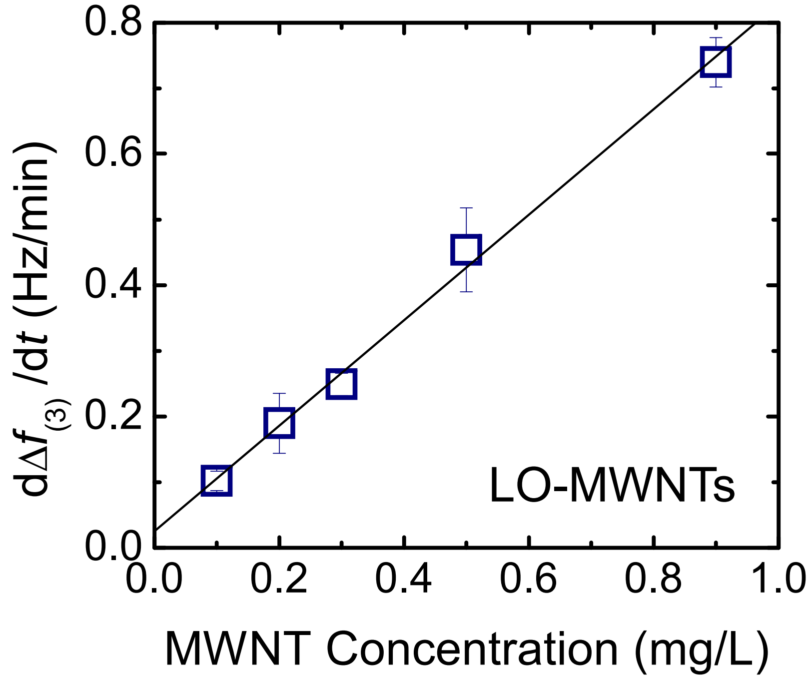


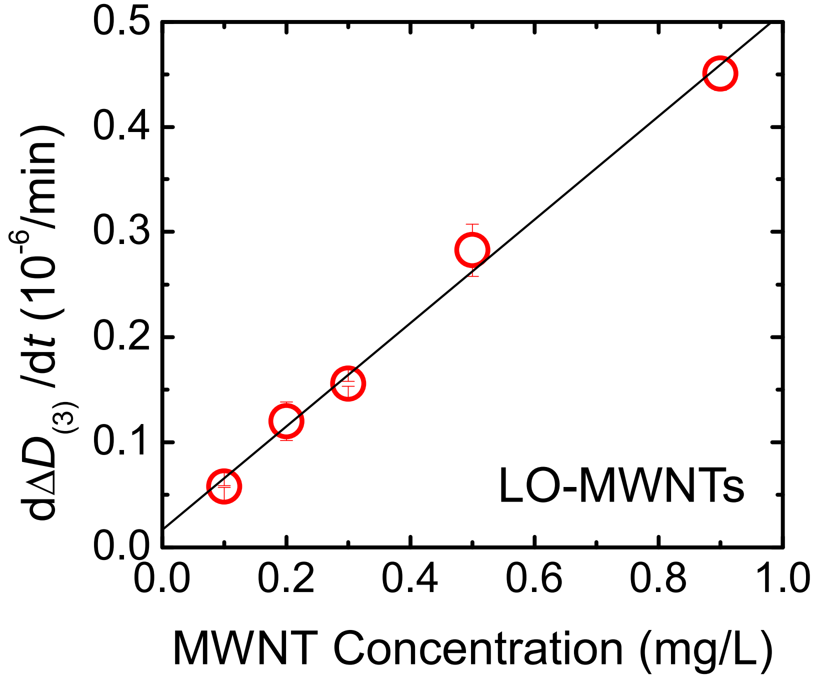
Scanning Electron Microscopy (SEM) Imaging of MWNTs



- HO-MWNTs deposited on poly-L-lysine (PLL)-coated silica surface at 1.5 mM $CaCl_2$
- Corresponds to $\Delta f_{(3)}$ of –36 Hz and $\Delta D_{(3)}$ of 1.7×10^{-5}

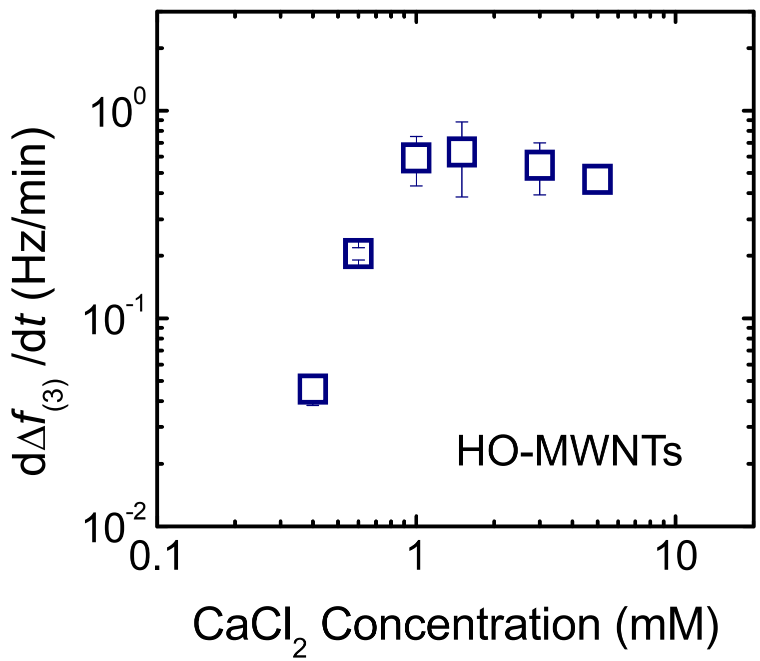
Rates of Frequency and Dissipation Shift are Proportional to Deposition Rate

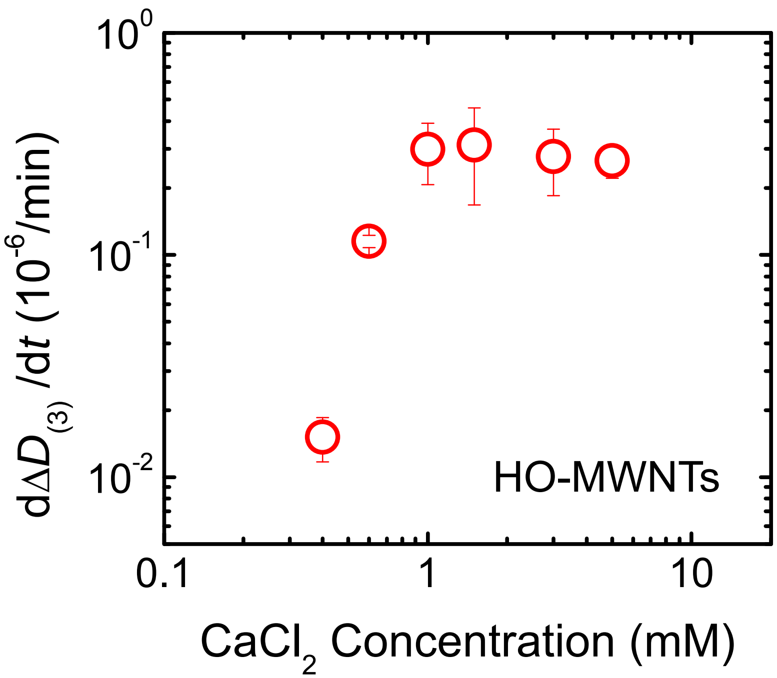


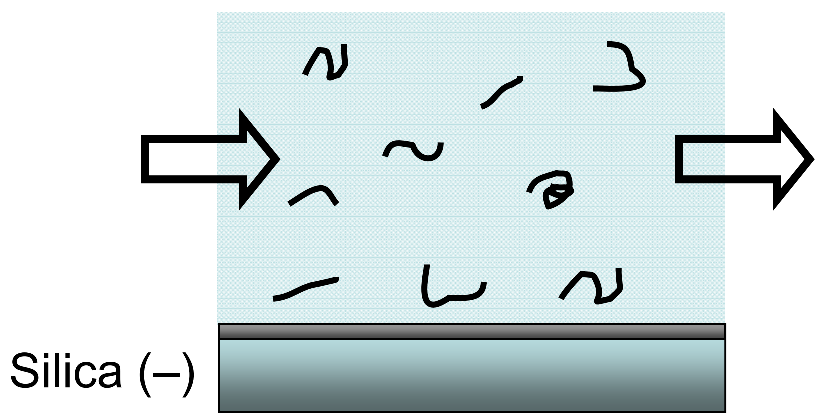


Deposition on PLL-modified surfaces at 1 mM NaCl and pH 7.1

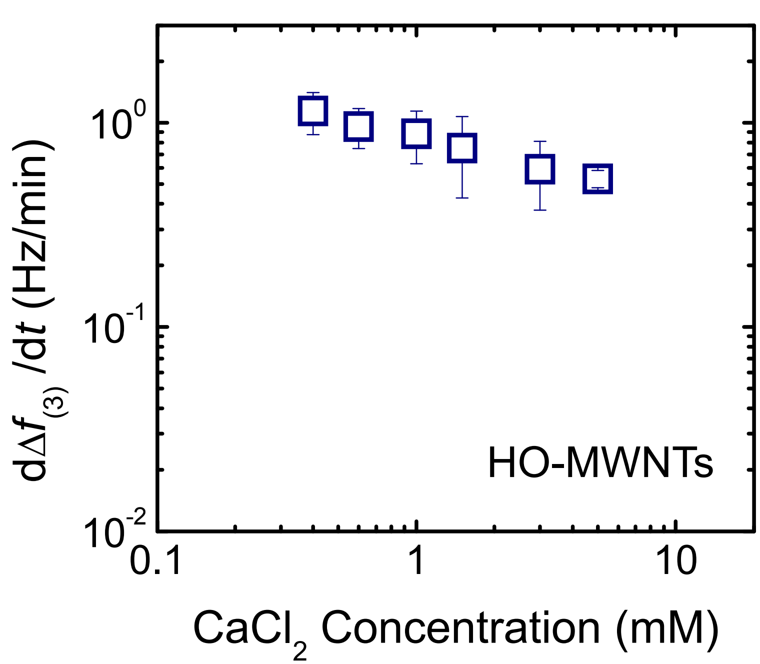
Deposition Rates on Silica Surfaces

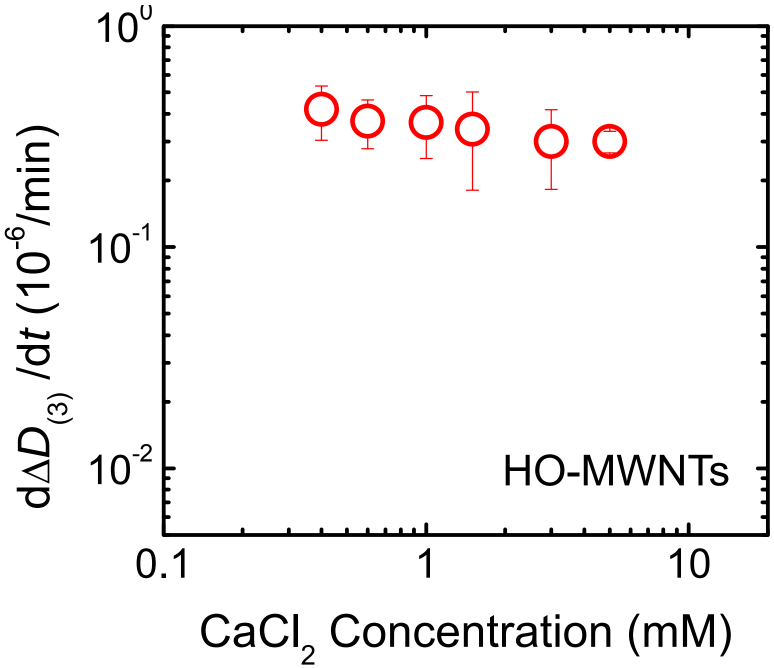


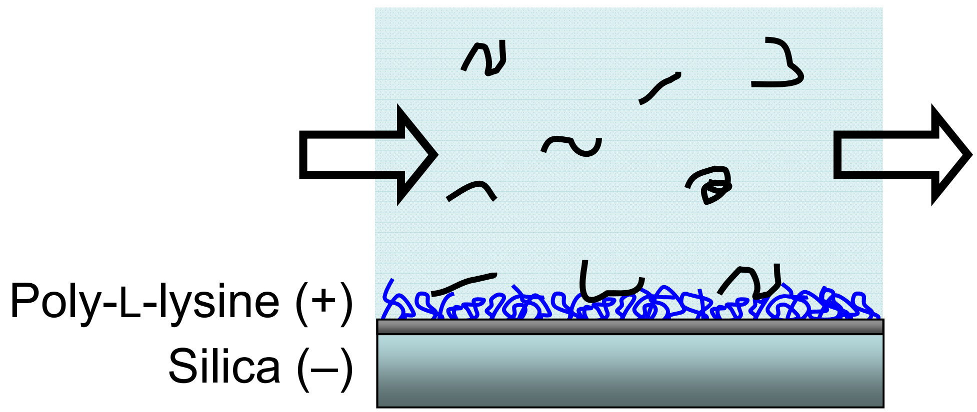




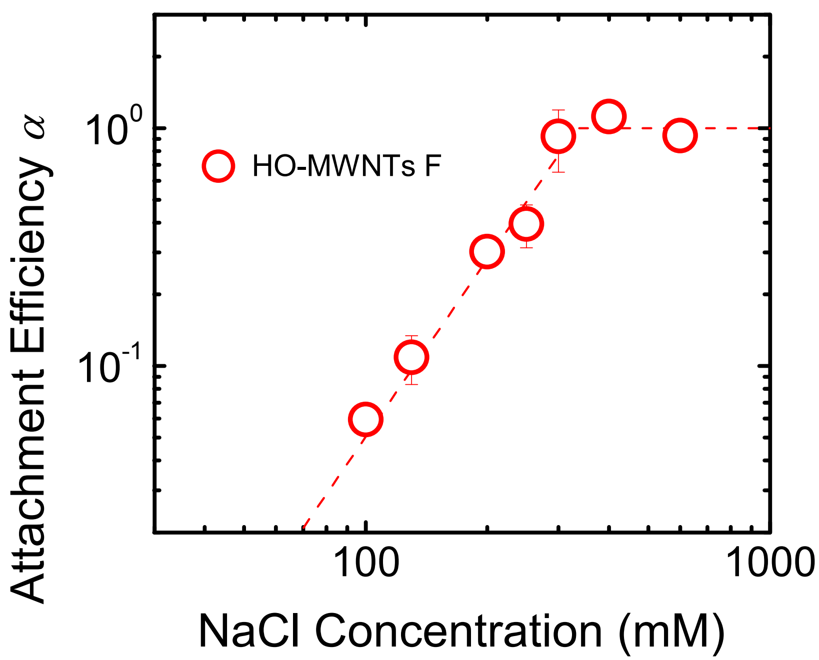
Favorable (Transport-Limited) Deposition Rates







Attachment Efficiency α and Critical Deposition Concentration (CDC)



Attachment Efficiency:

$$\alpha = \frac{d\Delta f / dt}{\left(d\Delta f / dt\right)_{fav}}$$

Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

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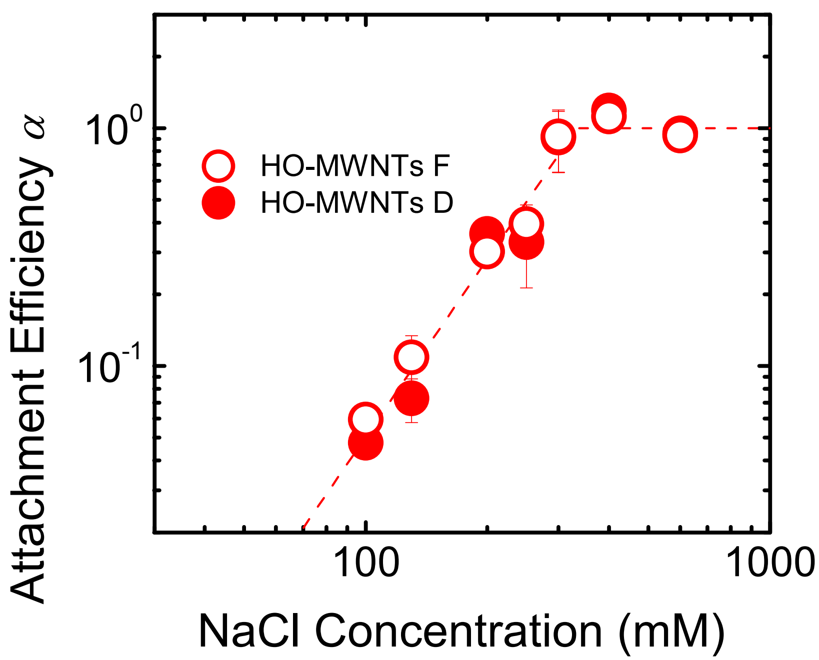

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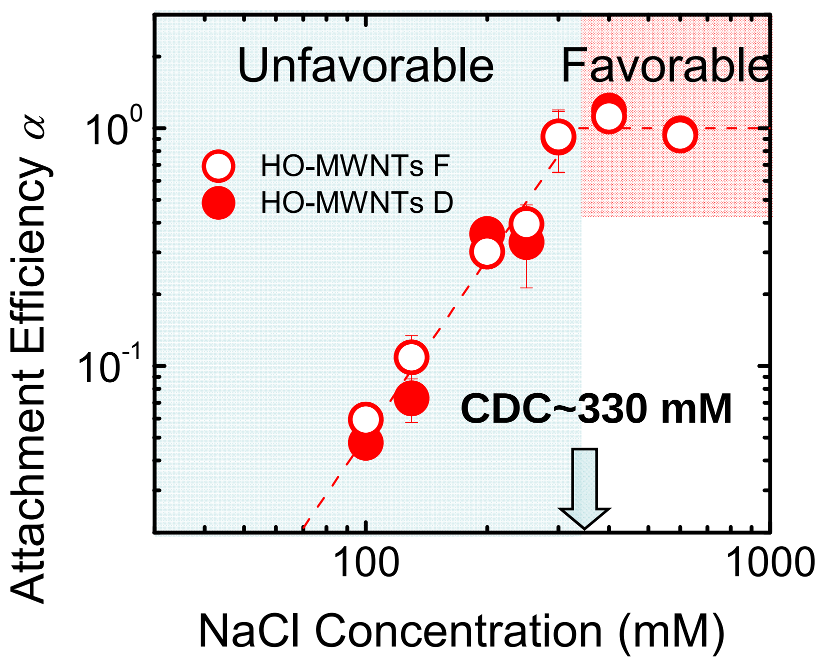

Attachment Efficiency:

$$\alpha = \frac{d\Delta f / dt}{\left(d\Delta f / dt\right)_{fav}}$$

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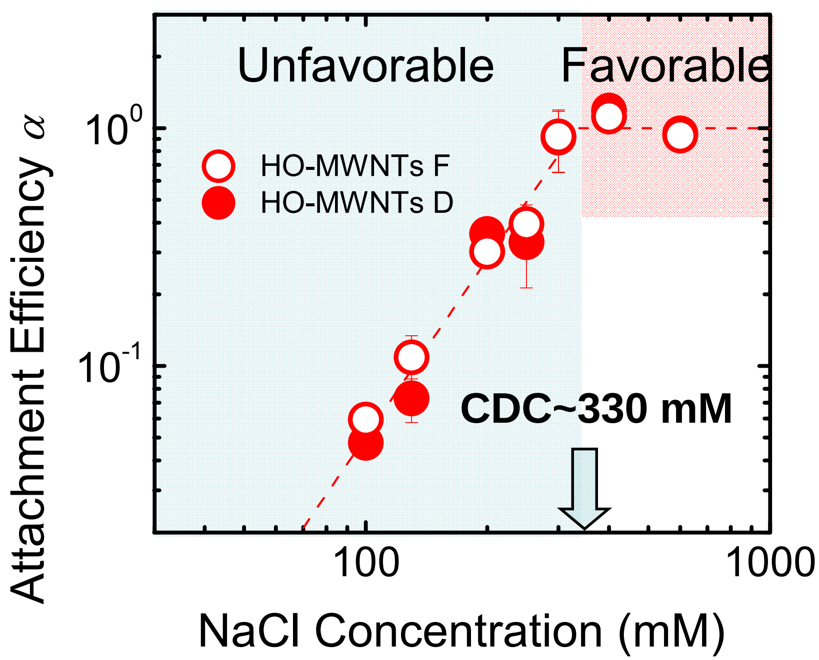
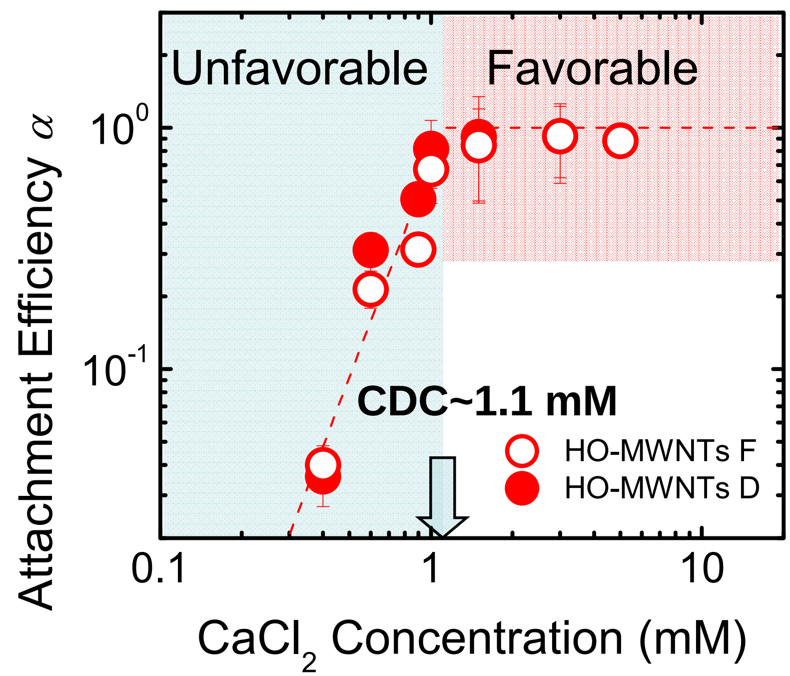
- Qualitative agreement with classical DLVO deposition behavior

Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

Attachment Efficiency α and Critical Deposition Concentration (CDC)

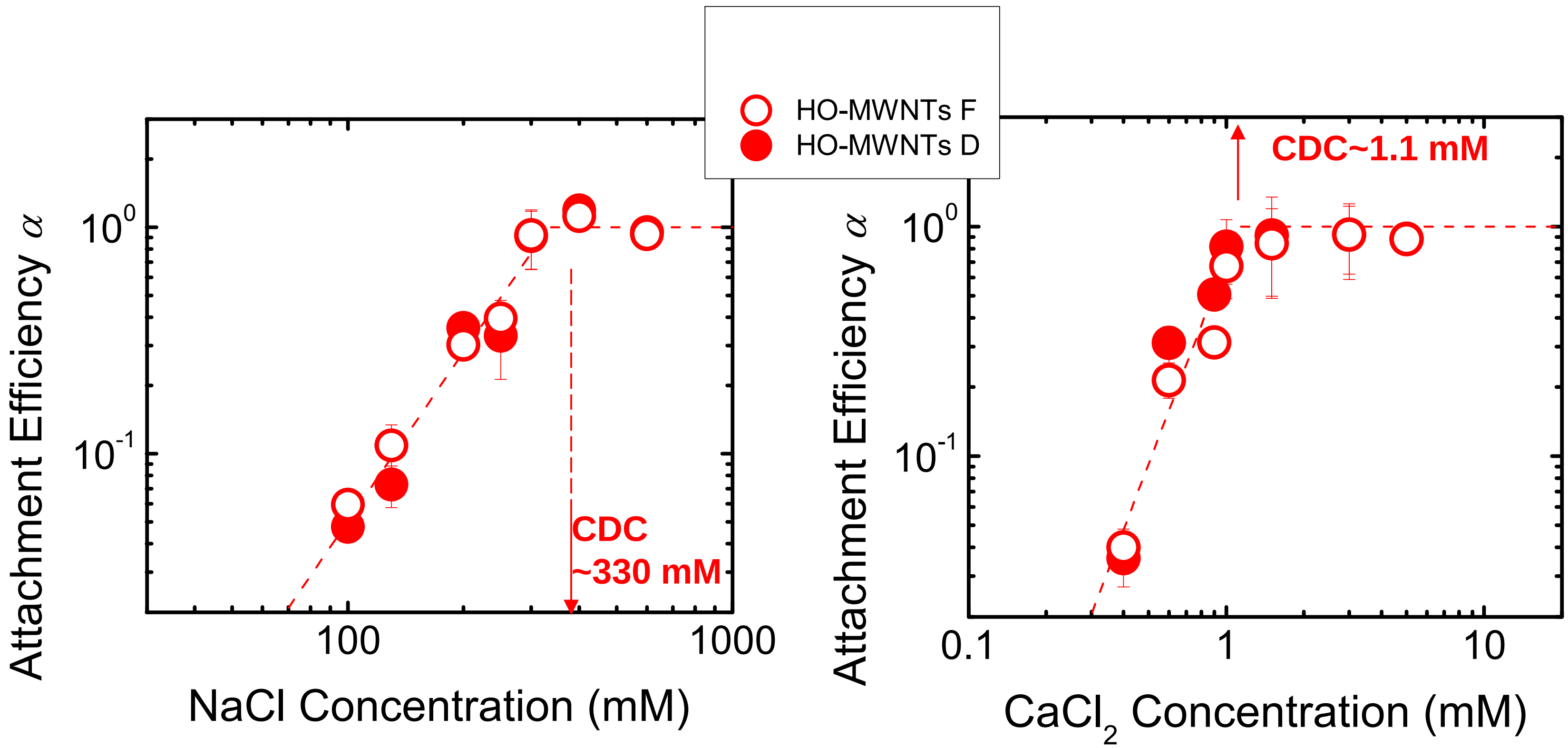




- The CDC in NaCl is much higher than the CDC in $CaCl_2$

Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

Influence of Surface Oxidation on Deposition Kinetics of MWNTs



CDC	NaCl	$CaCl_2$
HO-MWNTs	330 mM	1.1 mM

Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

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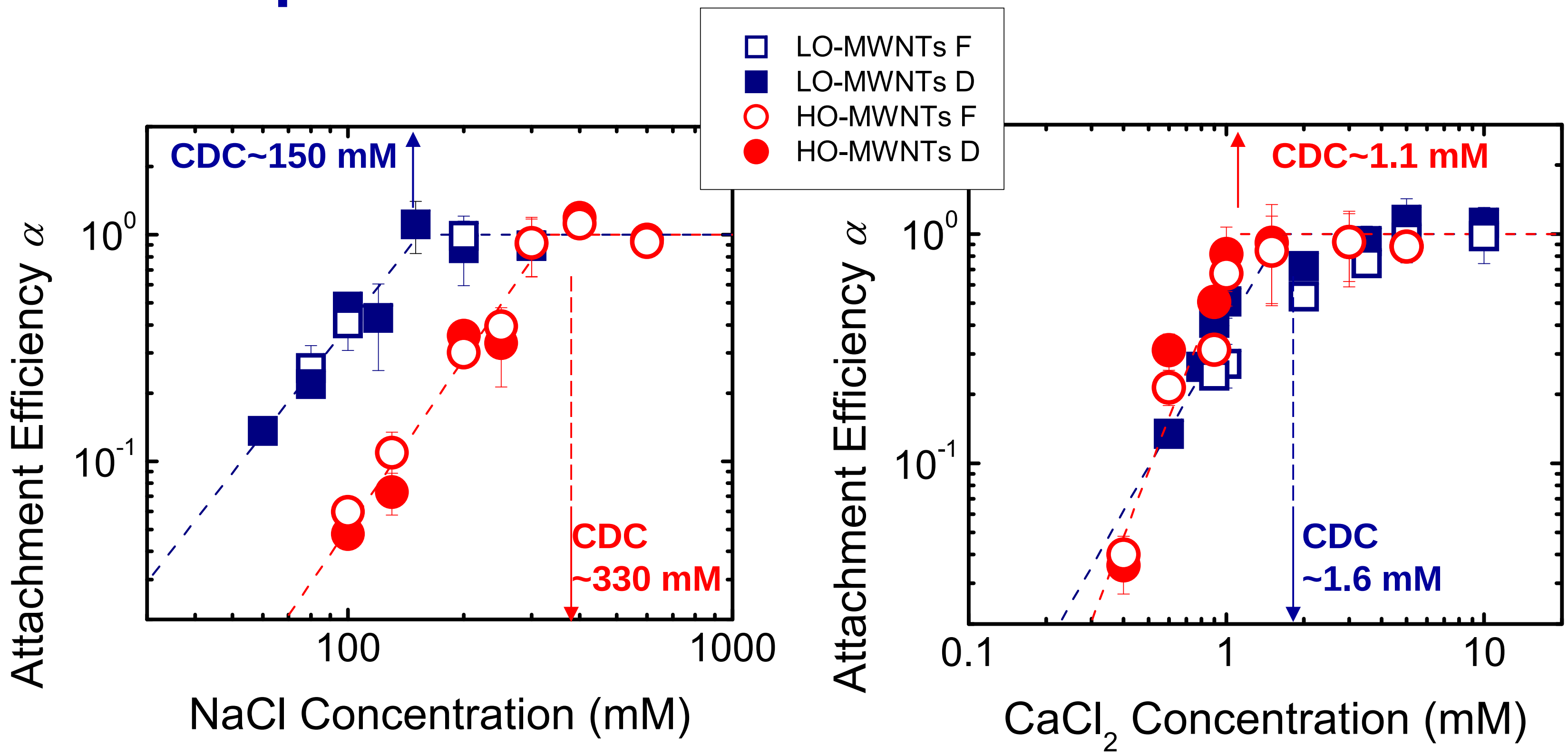
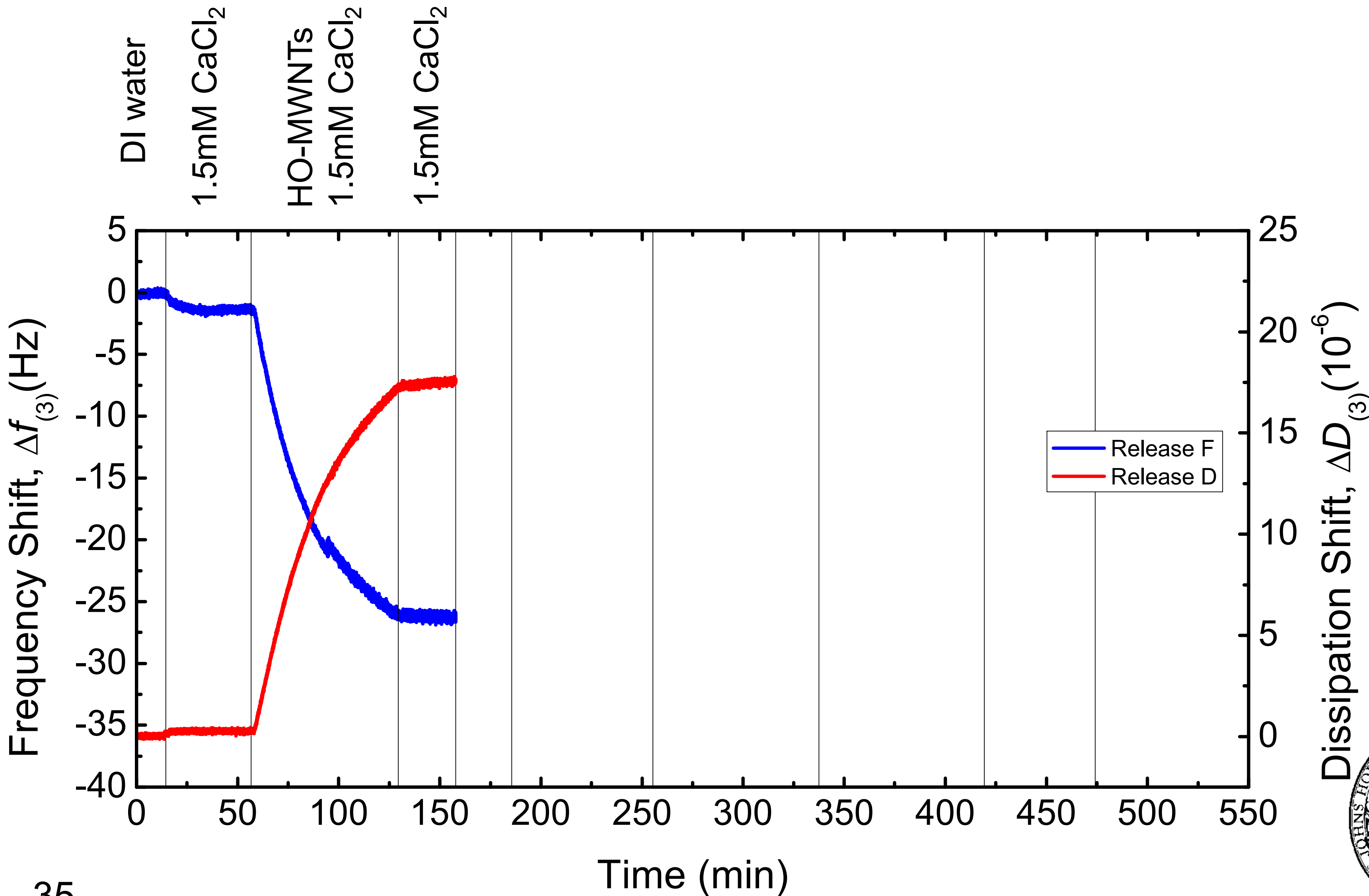


CDC	NaCl	$CaCl_2$
LO-MWNTs	150 mM	1.6 mM
HO-MWNTs	330 mM	1.1 mM

Yi and Chen, *Langmuir* **2011**, 27, 3588–3599.

Release of MWNTs from Silica Surfaces



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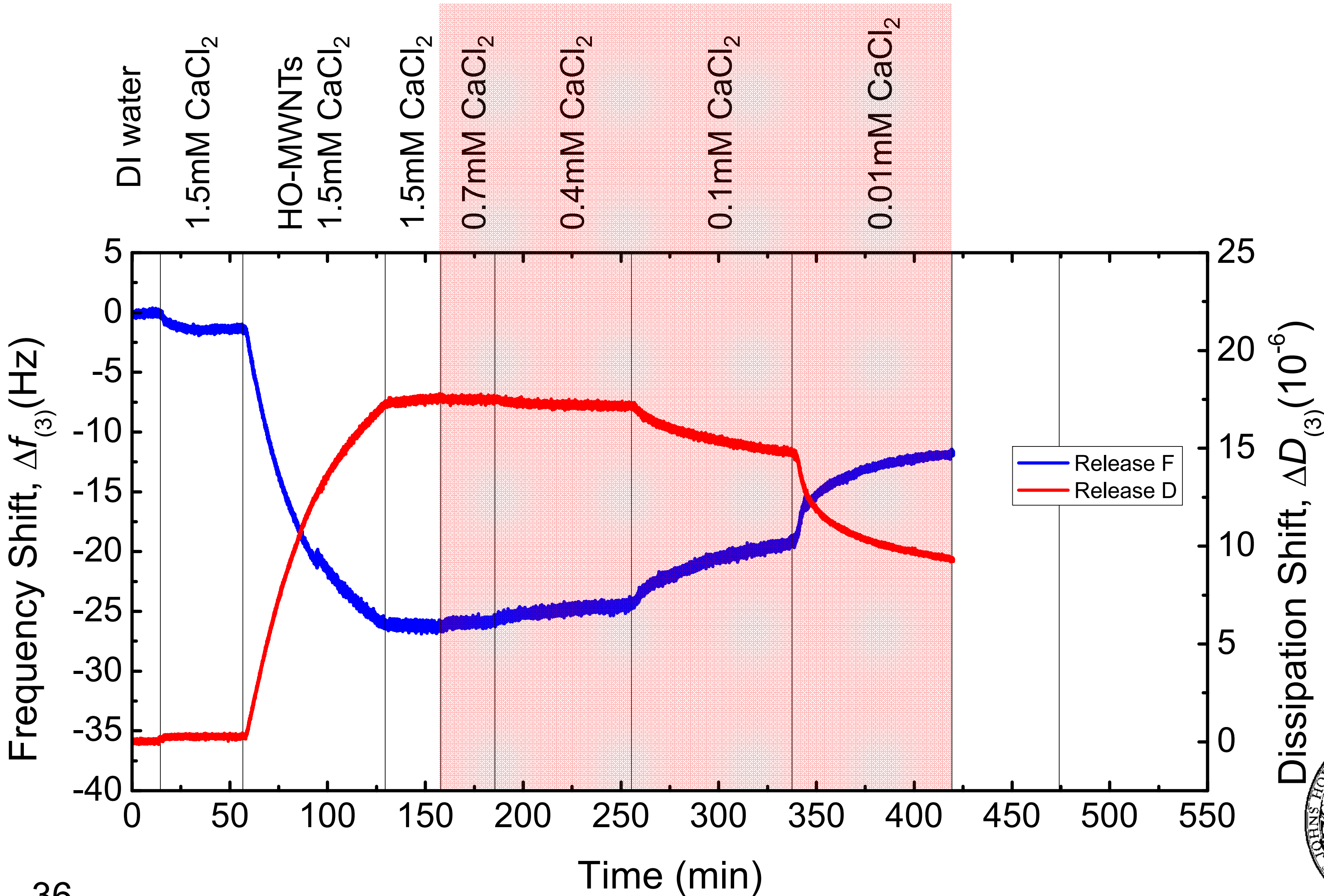

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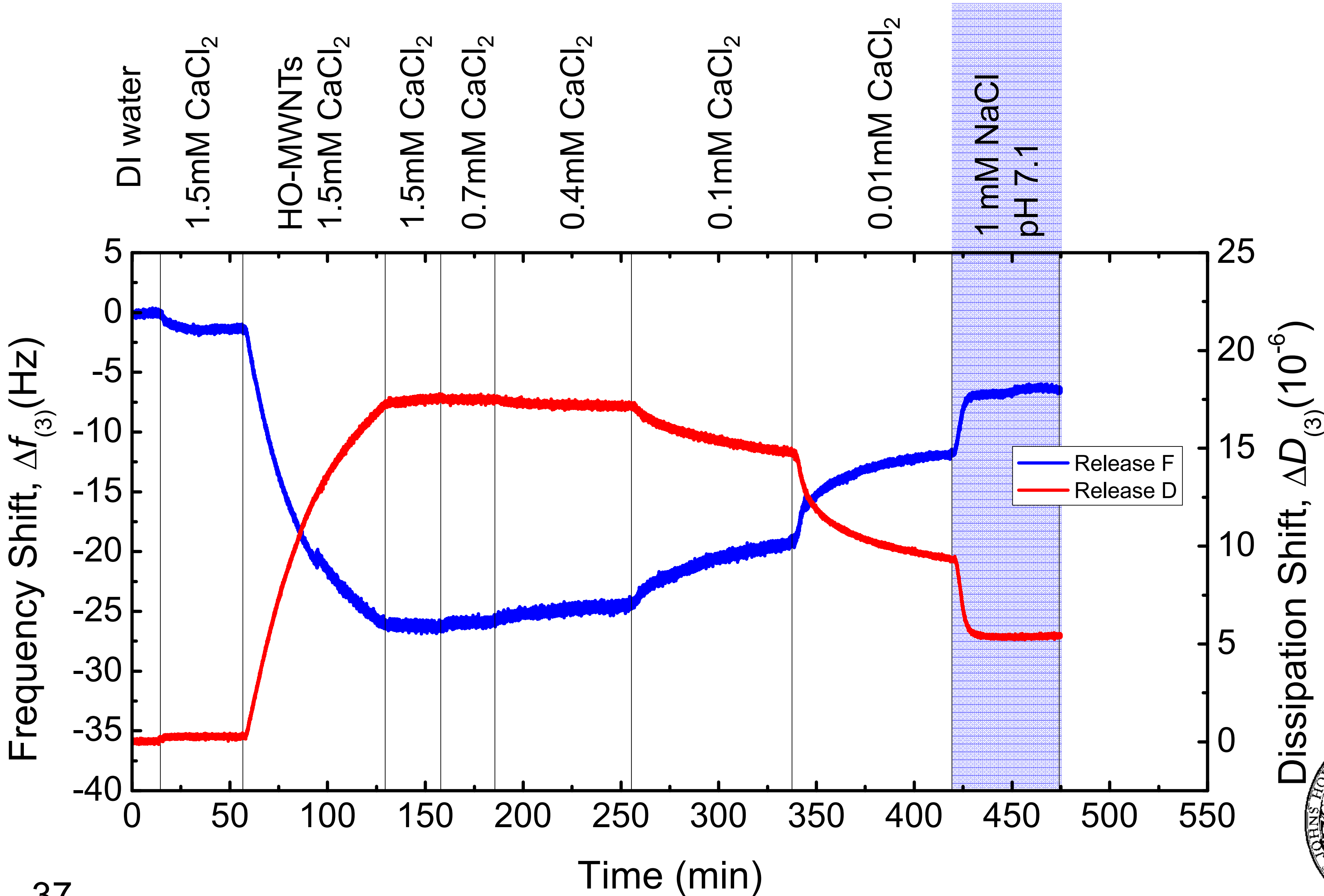

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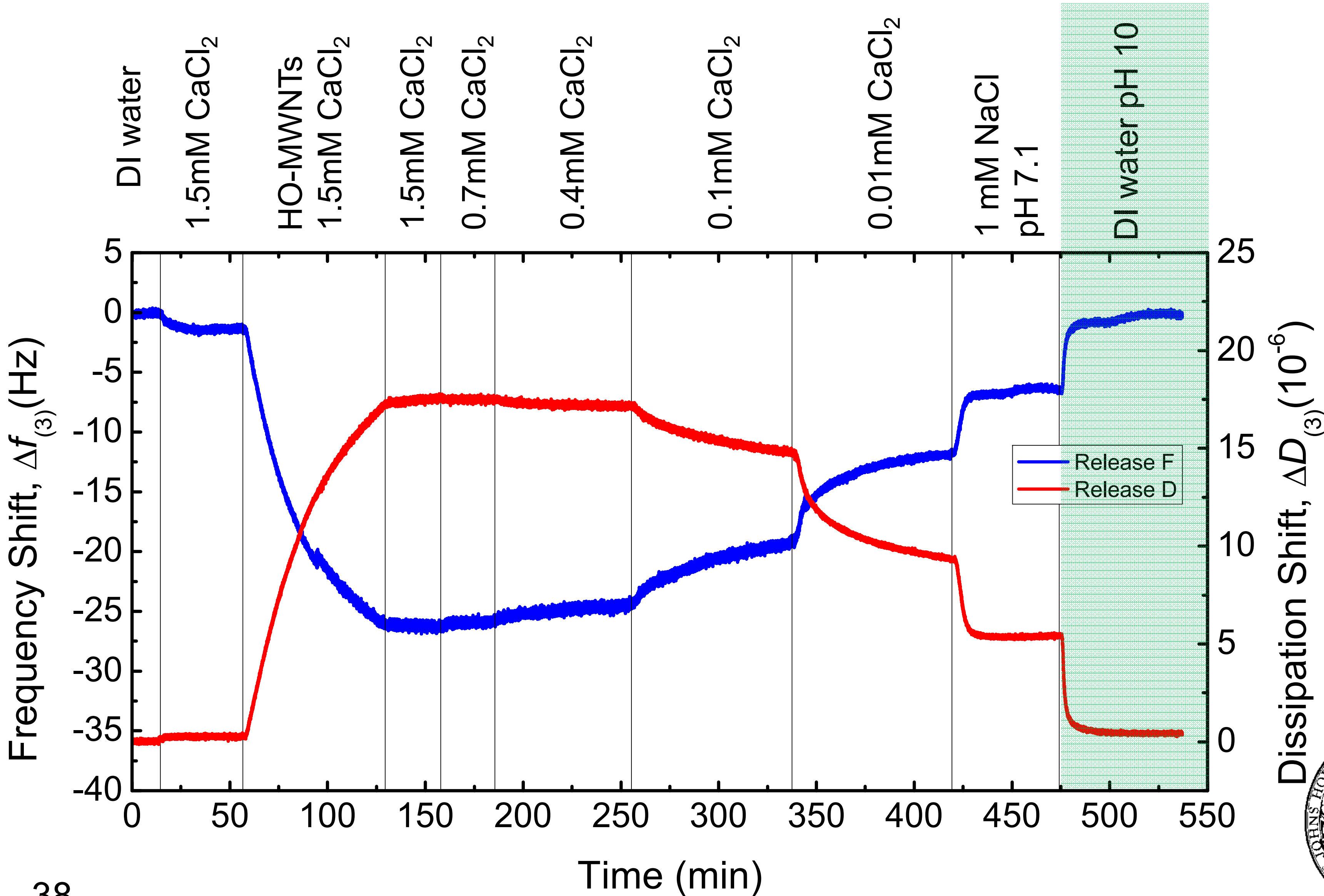
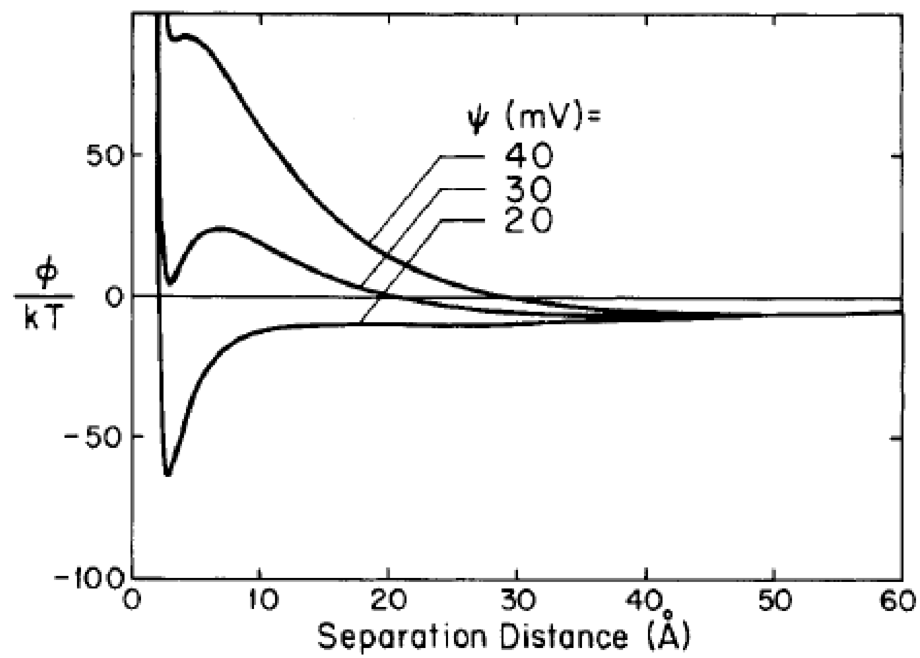


Release of MWNTs from Silica Surfaces

- Degree of release increases when:
  - $CaCl_2$ Concentration ↓
  - $CaCl_2$ ⇨ NaCl
  - pH of solution ↑
- Increase in surface potential of both MWNTs and silica surface may lead to decrease in the depth of primary energy minimum



Ruckenstein and Prieve, *AIChE Journal*, **1976**, 276-283

Conclusions

- Classic aggregation and deposition behavior with favorable and unfavorable regimes is observed for MWNTs
- HO-MWNTs are more stable to aggregation and deposition than LO-MWNTs in NaCl. However, stabilities of both MWNTs are similar in $CaCl_2$.
- Deposited MWNTs are released from silica surfaces during a change in solution chemistry that leads to an increase in the magnitude of their surface potential

Acknowledgements

- Ph.D. student Peng Yi
- Dr. Howard Fairbrother's group (Dept. of Chemistry)
- Oak Ridge Associated Universities

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