Release of Multiwalled Carbon Nanotubes from Silica Surfaces

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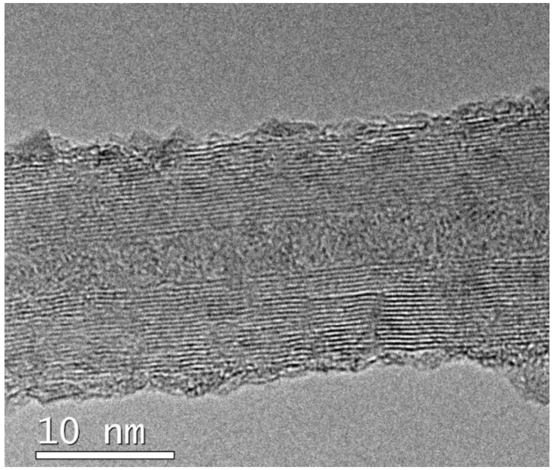
Overview

- Background
- Objective
- Quartz crystal microbalance with dissipation monitoring (QCM-D) and Voigt modeling
- Release degree and kinetics of deposited multiwalled carbon nanotubes (MWNTs) from silica surfaces
- Conclusions

Carbon Nanotubes (CNTs)



http://itech.dickinson.edu

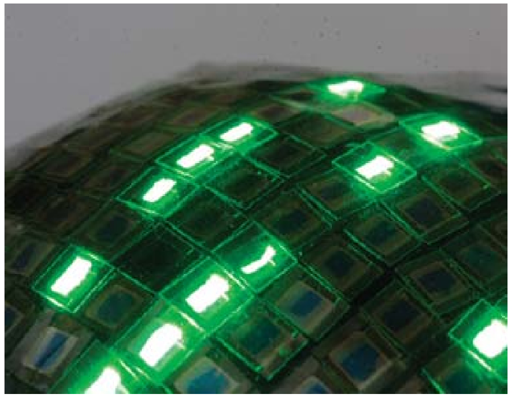
Single-walled nanotubes (SWNTs)

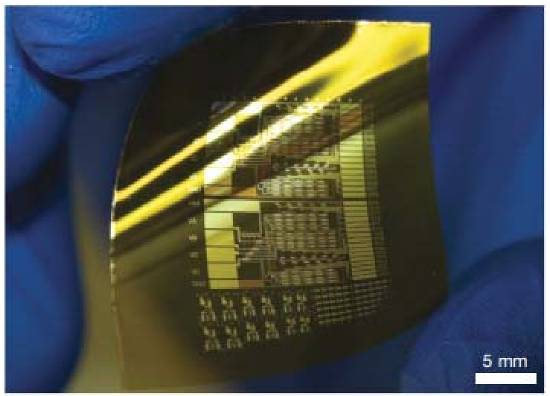
Multiwalled nanotubes (MWNTs)

Application of Carbon Nanotubes (CNTs)

www.bayerus.com

- Mechanical properties: high strength; light weight





- Electronic properties: semiconducting or metallic

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

Cao et al., *Nature*, **2008**, 495–500

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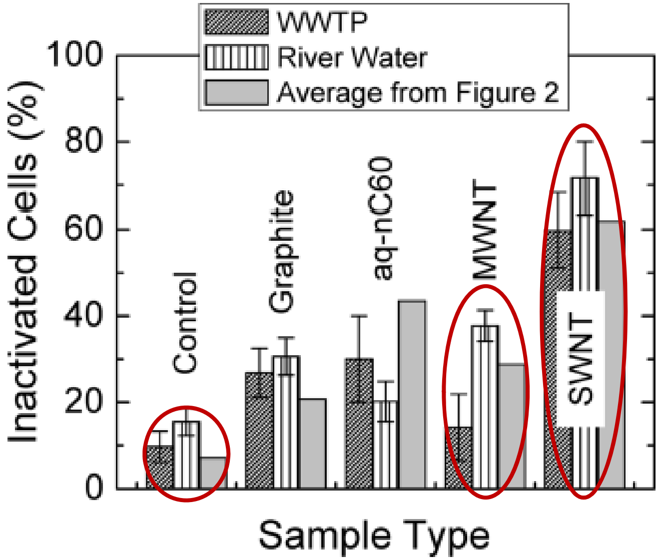
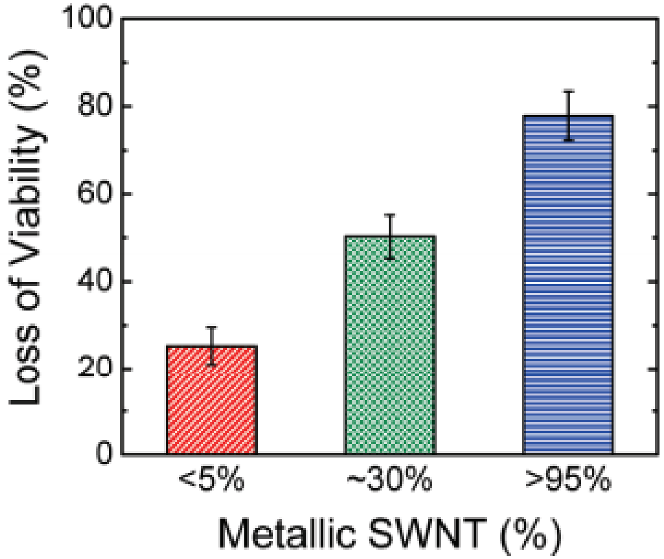
Toxicity of Carbon Nanotubes

- Cause embryotoxicity in mice
- Inactivate microorganisms



Kang et al., *ES&T,* **2009**, 2648-2653



Vecitis et al., *ACS Nano,* **2010**, 5471-5479

- Penetrate human keratinocytes and lymphocytes

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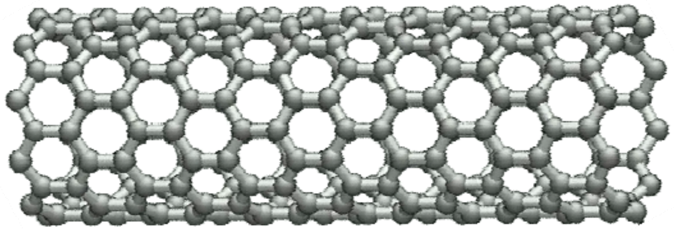
Fate and Transport of CNTs

- Oxidation of CNTs during transport in natural and engineered aquatic systems



Fate and Transport of CNTs

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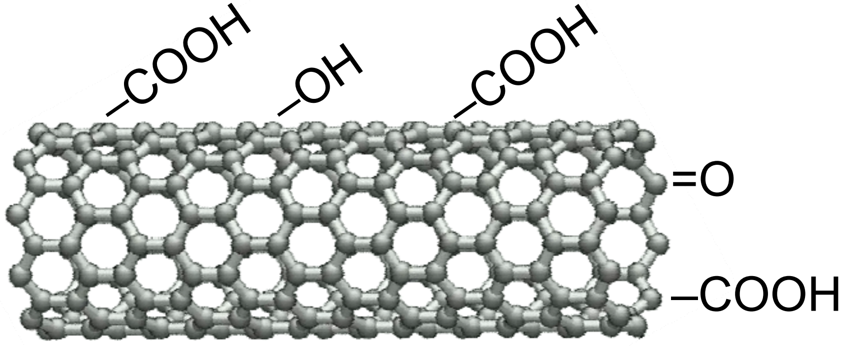

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Fate and Transport of CNTs

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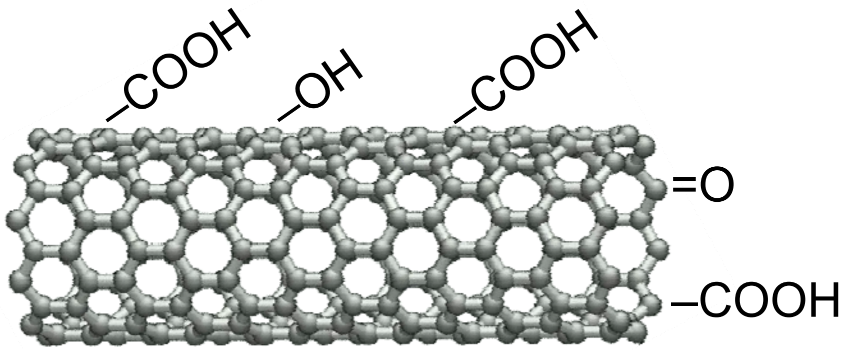
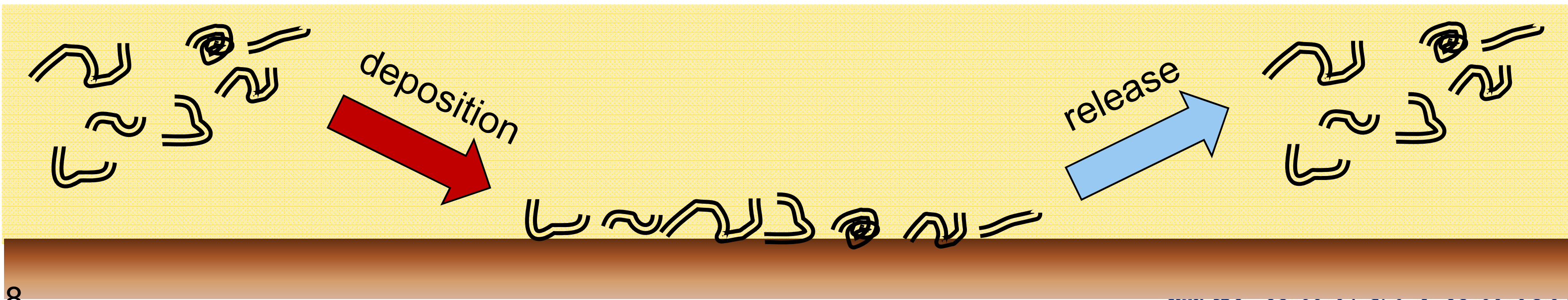


- Deposition and remobilization of CNTs on naturally occurring surfaces, e.g., silica surfaces

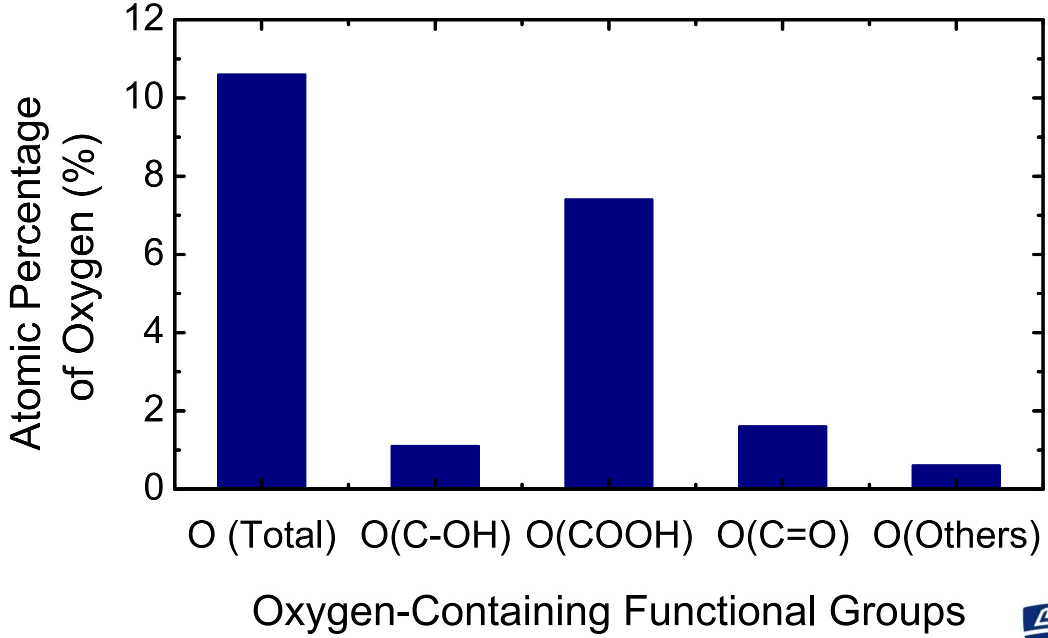


Objective

To investigate the influence of solution chemistry on the degree and kinetics of MWNT release from silica surfaces

Oxidization and Characterization of MWNTs

- Expose pristine MWNTs to a 3:1 acid mixture of 98% H_2SO_4 and 69% HNO_3
- The distribution of oxygen-containing functional groups was quantified by XPS in conjunction with vapor phase chemical derivatization



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

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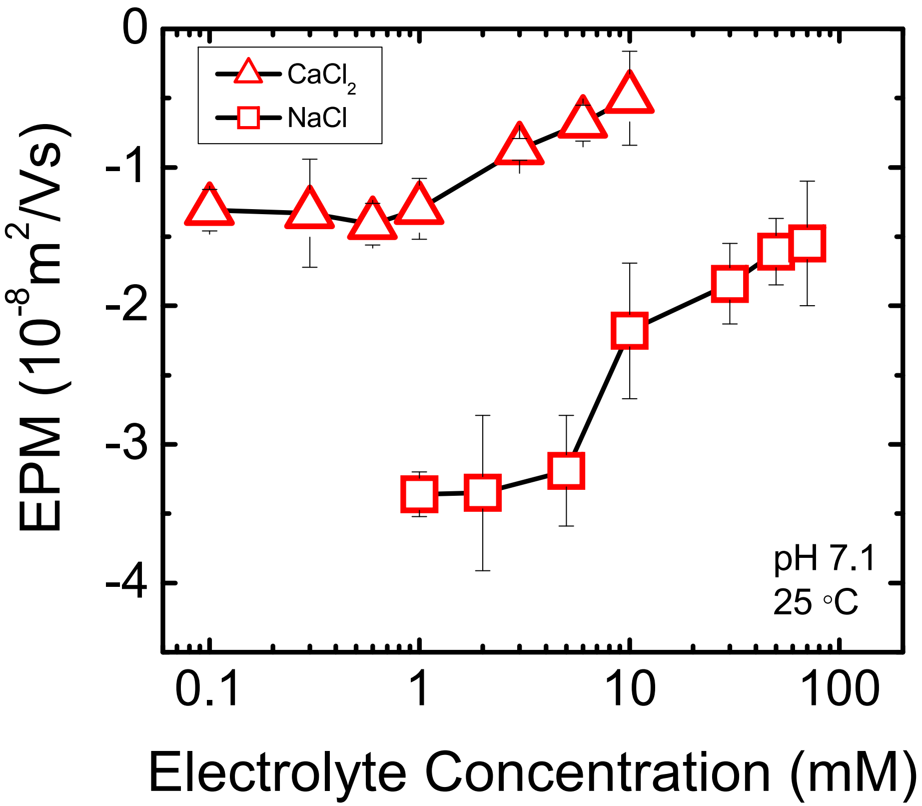
Electrophoretic Mobilities (EPMs) of MWNTs in NaCl and $CaCl_2$ Solutions



- Brookhaven ZetaPALS
- The predominant functional groups on MWNTs are carboxyl groups
- At pH 7.1, most carboxyl groups are expected to be deprotonated

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

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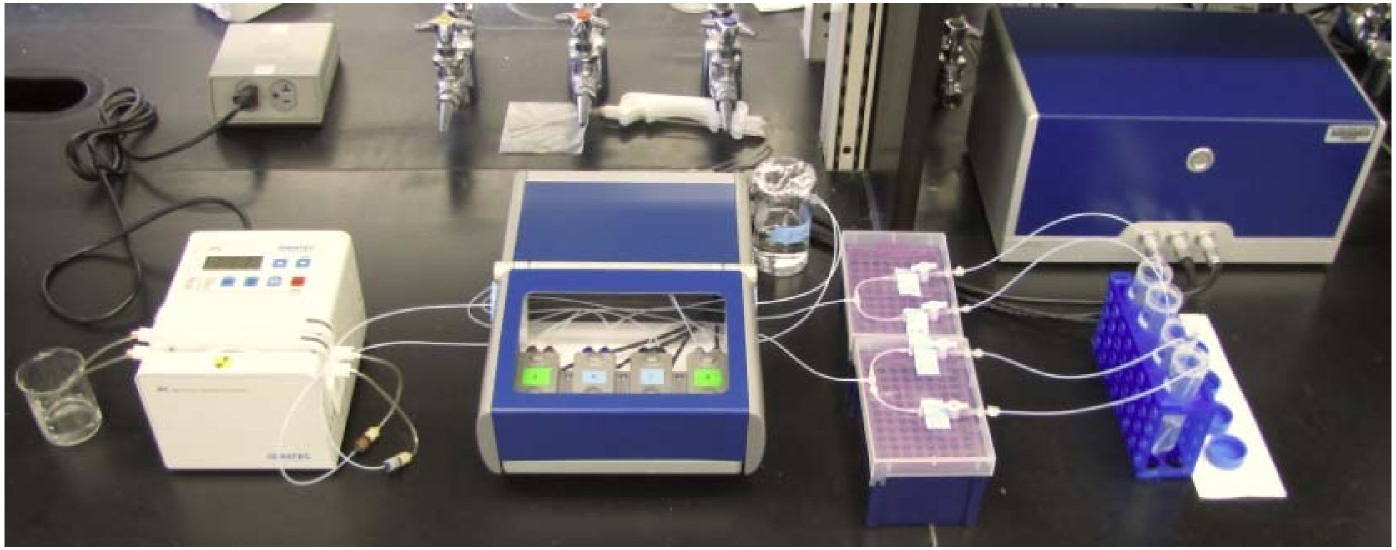
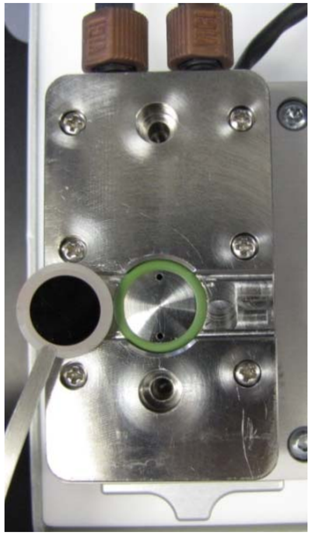
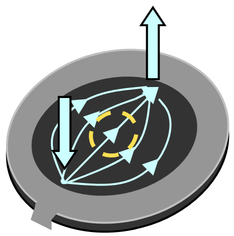
Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)







- Laminar flow at 0.6 mL/min
- [MWNT] = ca. 0.5 mg/L
- T = 25 ºC, pH = 7.1
- Frequency (*f*) and Dissipation (*D*)

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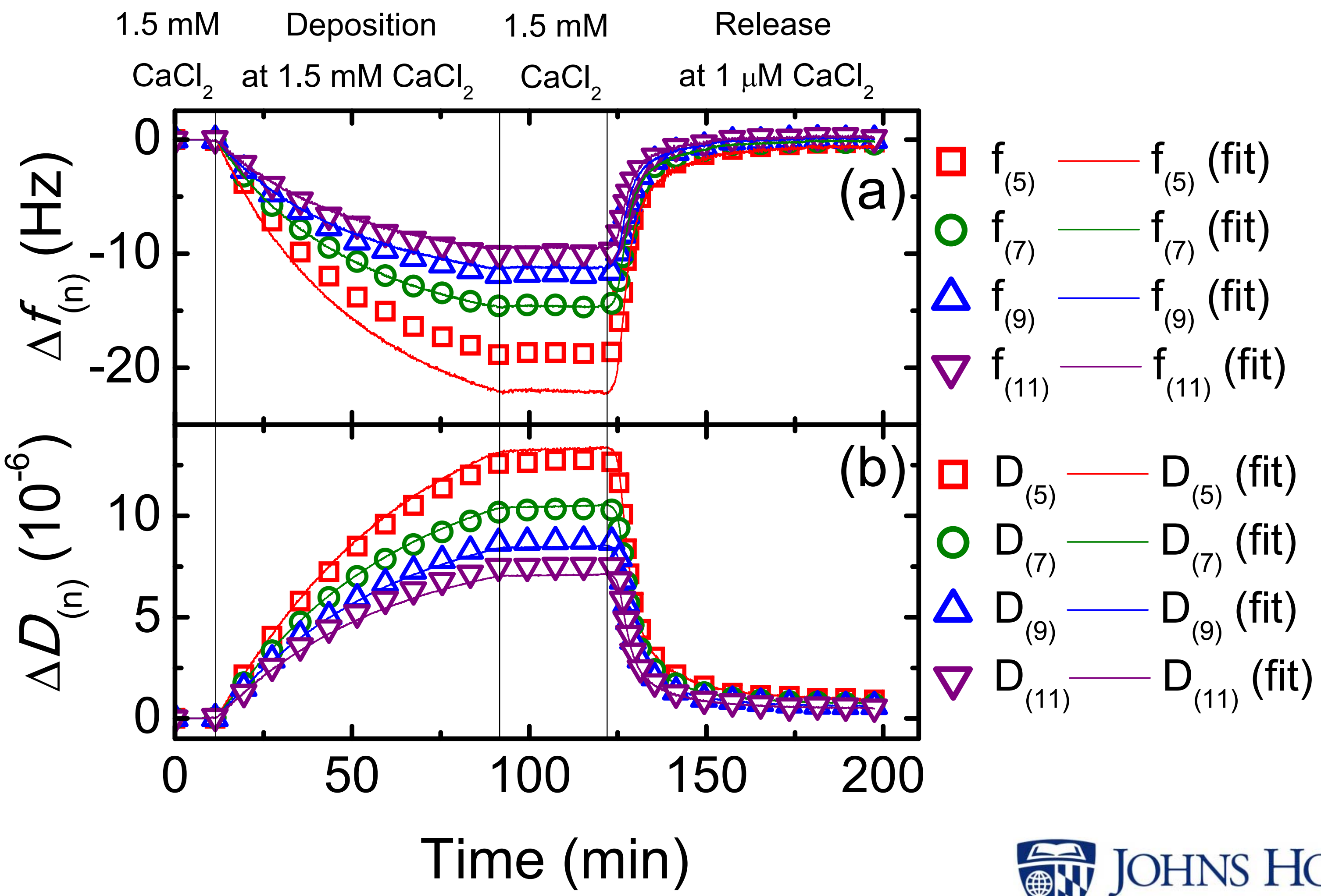
Quantifying the Surface Mass Concentration of Deposited MWNTs using Voigt Model

- Voigt model is commonly used for viscoelastic layers
- Δf and ΔD are functions of surface mass concentration (m), shear modulus (μ), and viscosity (η) of CNT layer
- Δf and ΔD (5^{th}, 7^{th}, 9^{th}, and 11^{th}) were fitted with Voigt model using m, μ, and η as fitting parameters
- Thus, the surface mass concentration of MWNTs can be quantified throughout the deposition and release experiment

Quantifying the Surface Concentration of Deposited MWNTs using Voigt Model



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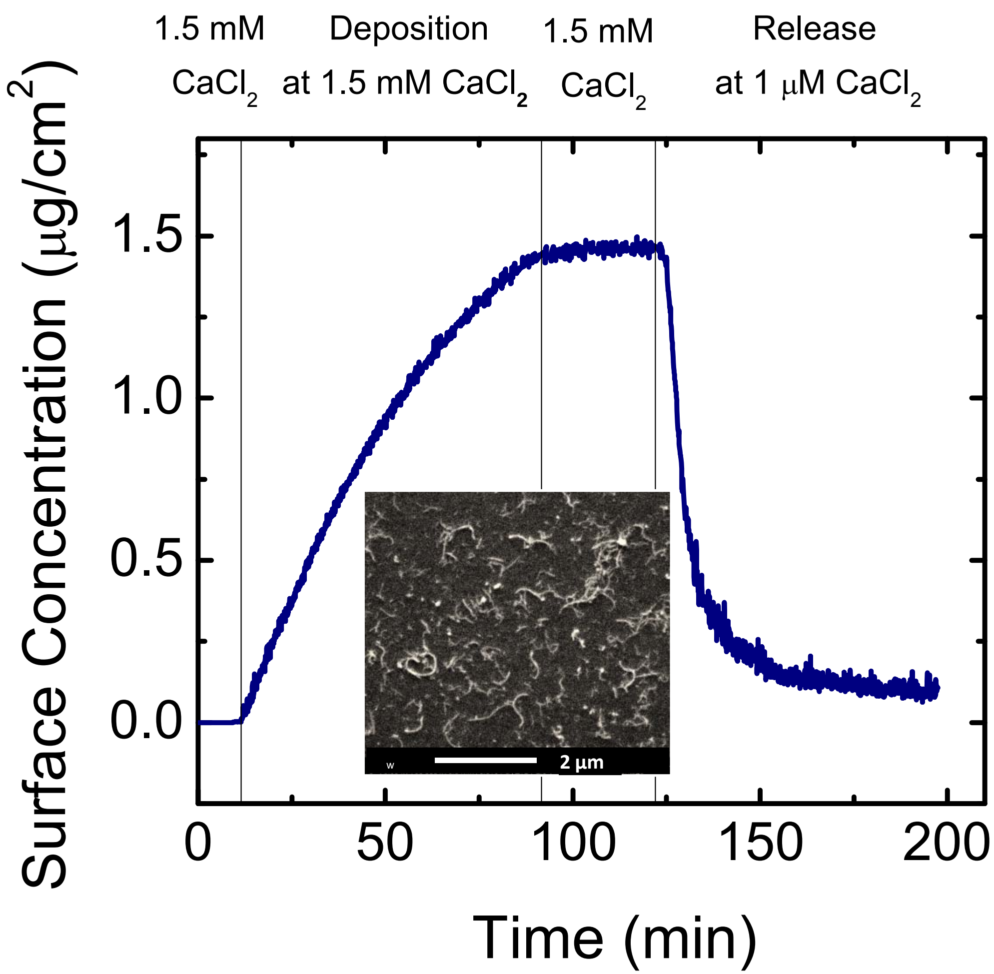
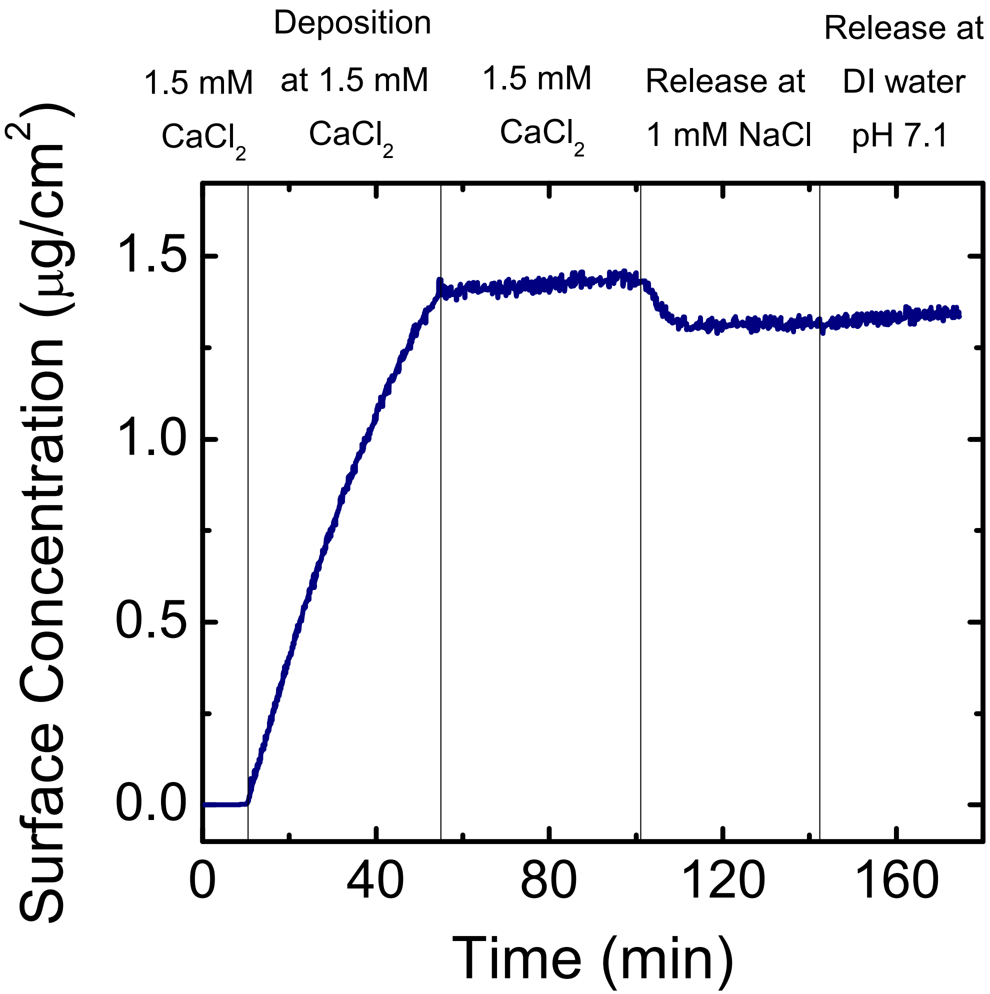
Release of MWNTs from Silica Surfaces after Deposition in $CaCl_2$



- The surface concentration of deposited MWNTs was quantified by Voigt modeling
- 93% of deposited MWNTs were released at 1 μM $CaCl_2$

Release of MWNTs were mainly through Detachment from Silica Surfaces



- The silica surface was first modified with positively charged poly-L-lysine (PLL)
- Only 4% of MWNTs deposited on PLL were released at DI water

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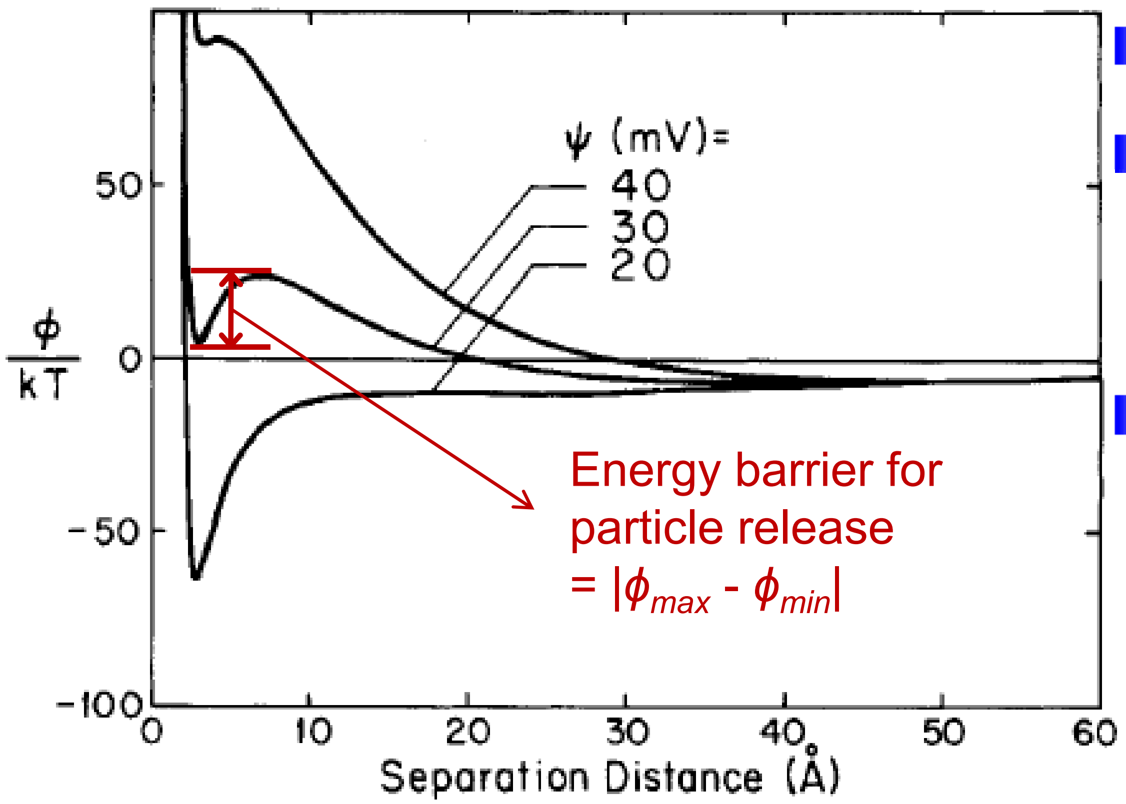
Particle Release from Primary Minimum when Surface Potentials Increased



- $\phi_{tot} = \phi_{edl} + \phi_{vdw} + \phi_{Born}$
- $|\phi_{max} - \phi_{min}|$ is reduced as surface potential (ψ) increases
- The ψ of both MWNTs and silica surfaces were enhanced when 1.5 mM $CaCl_2$ was replaced by 1 µM $CaCl_2$

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

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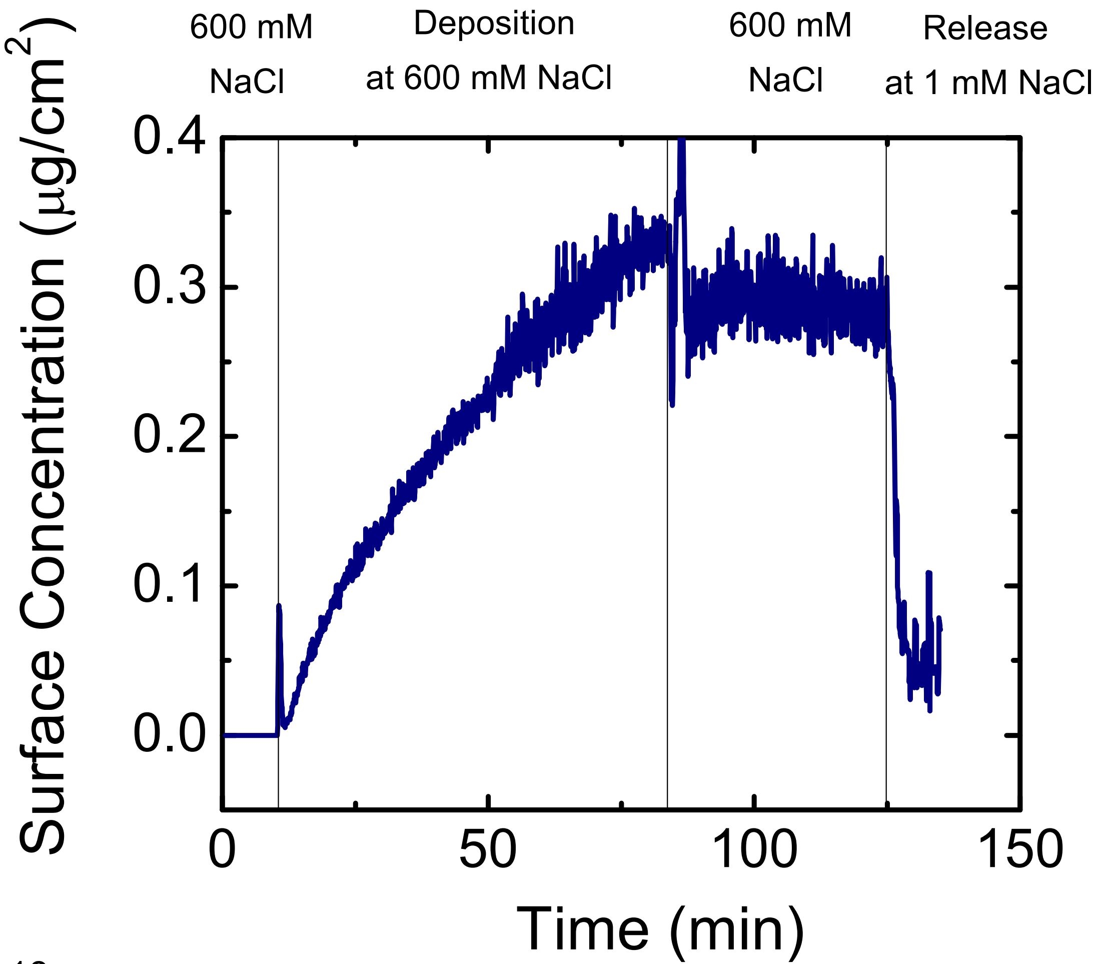
Release of MWNTs from Silica Surfaces after Deposition in NaCl



- 91% of deposited MWNTs were released at 1 mM NaCl

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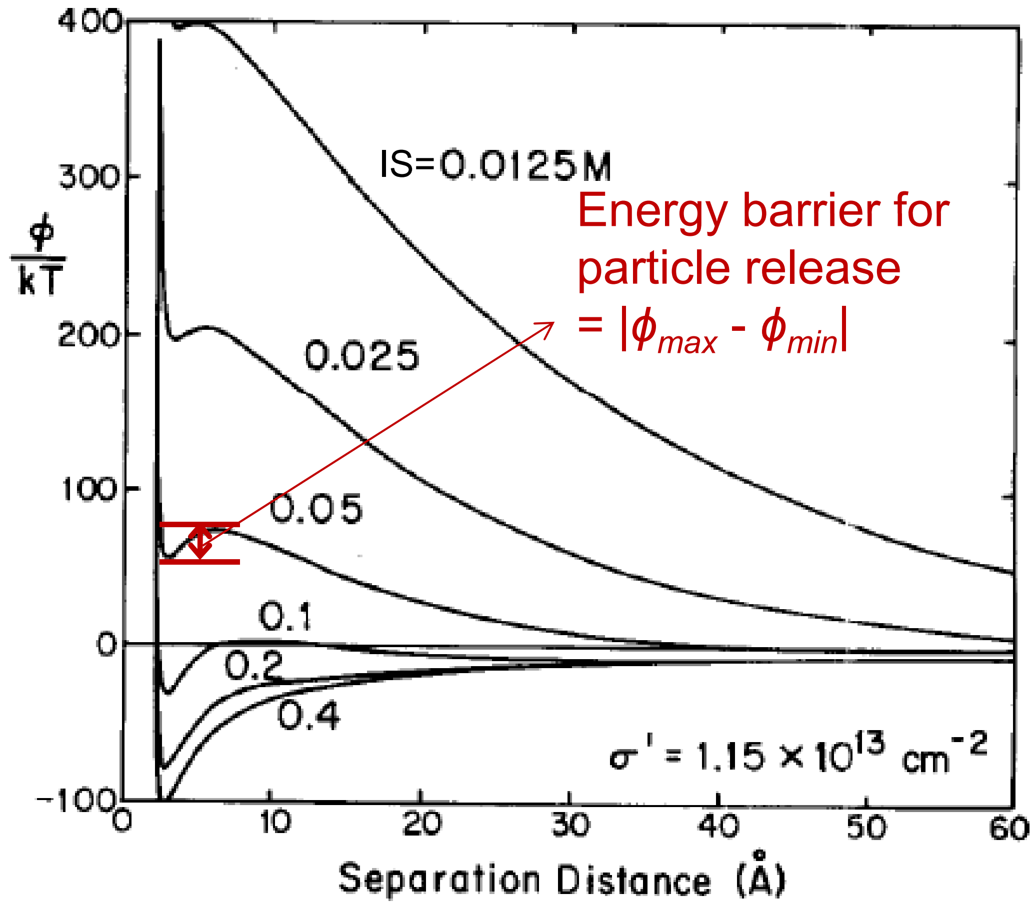
Particle Release from Primary Minimum when Ionic Strength Decreased



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

- $|\phi_{max} - \phi_{min}|$ is reduced as ionic strength (IS) decreases when constant charge assumption is made
- Constant charge assumption is appropriate for both MWNTs and silica surfaces

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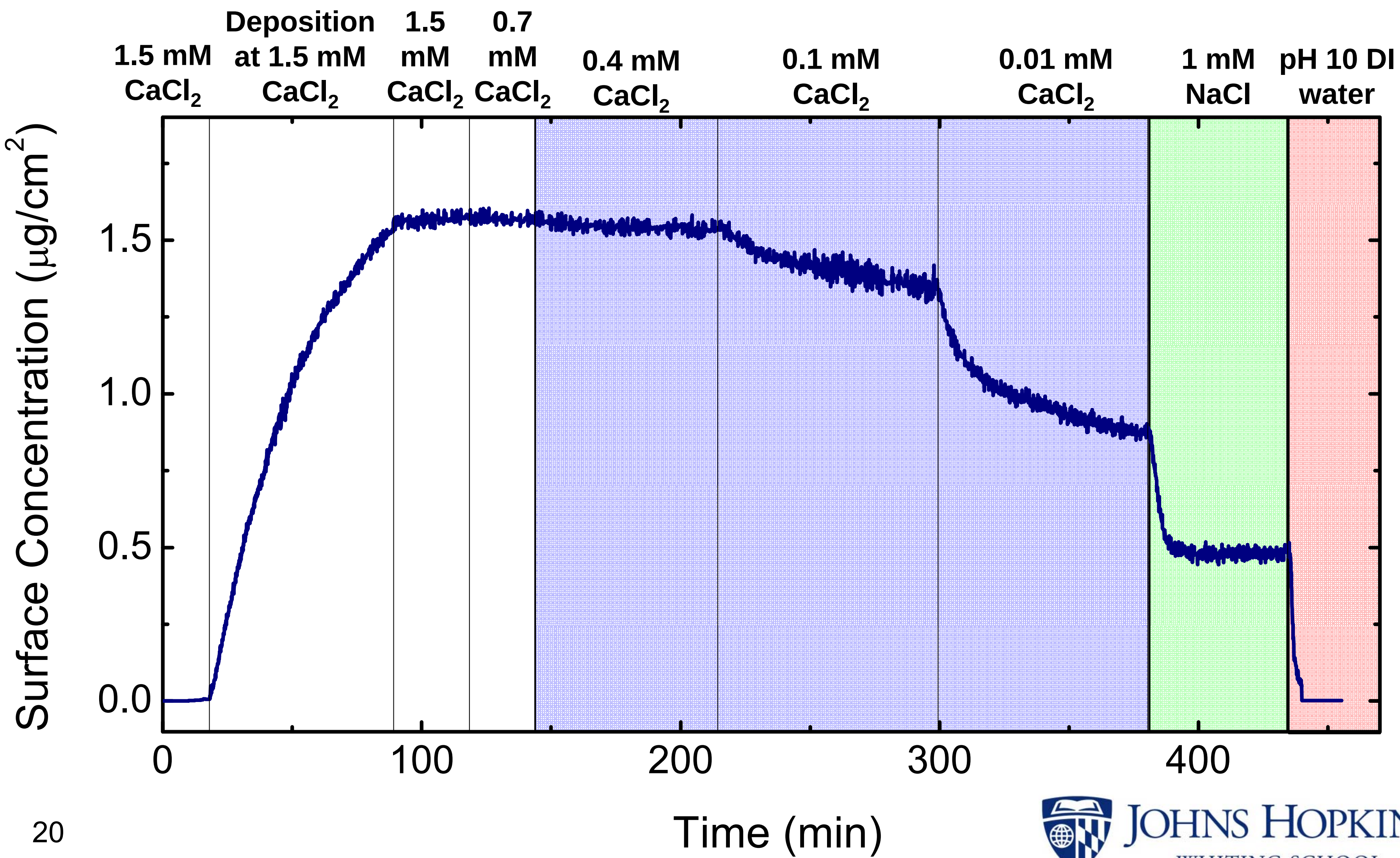
Sequential Release of MWNTs from Silica Surfaces in $CaCl_2$



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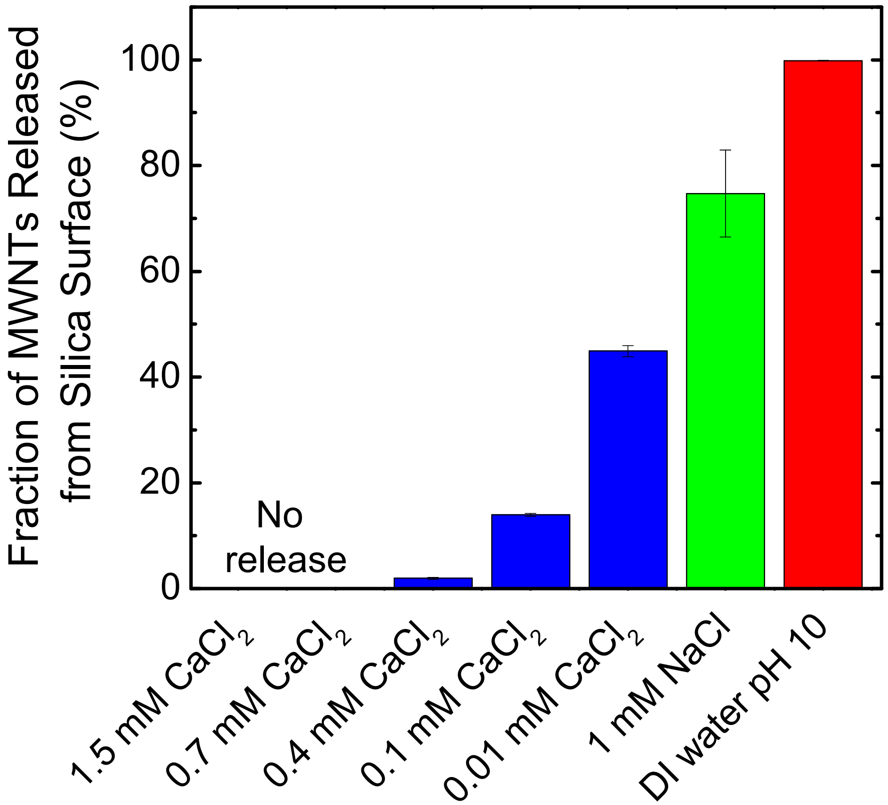
Sequential Release of MWNTs from Silica Surfaces in $CaCl_2$



- Surface charges of MWNTs and silica were enhanced when:
  - $CaCl_2$ Concentration ↓
  - $CaCl_2$ ⇨ NaCl
  - pH of solution ↑
- The stepwise release behavior may be due to the surface charge heterogeneity of MWNTs

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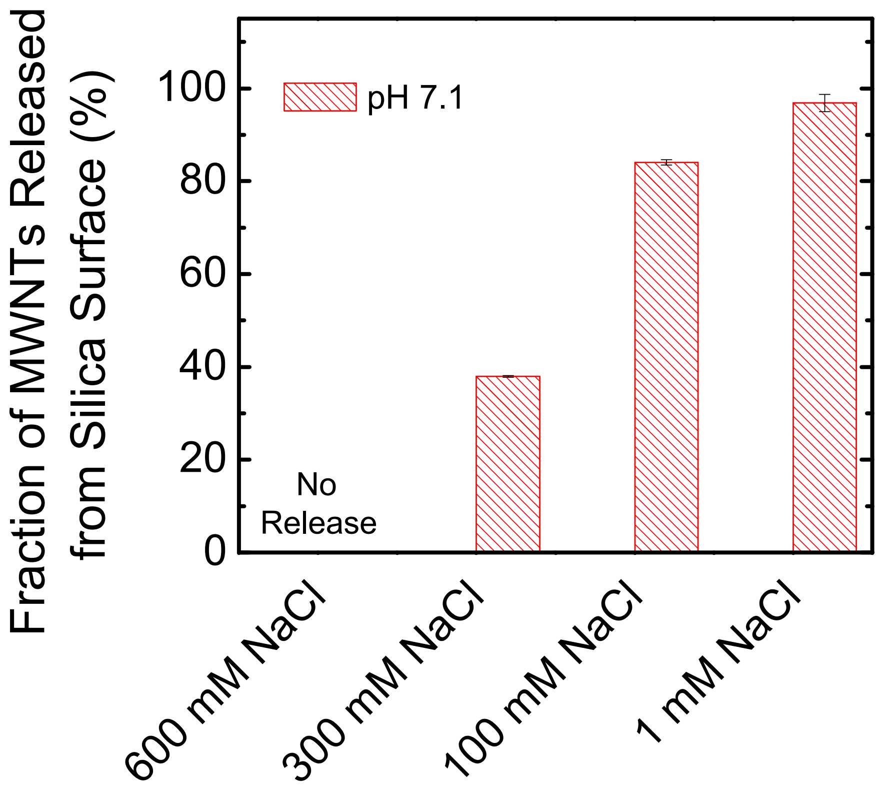
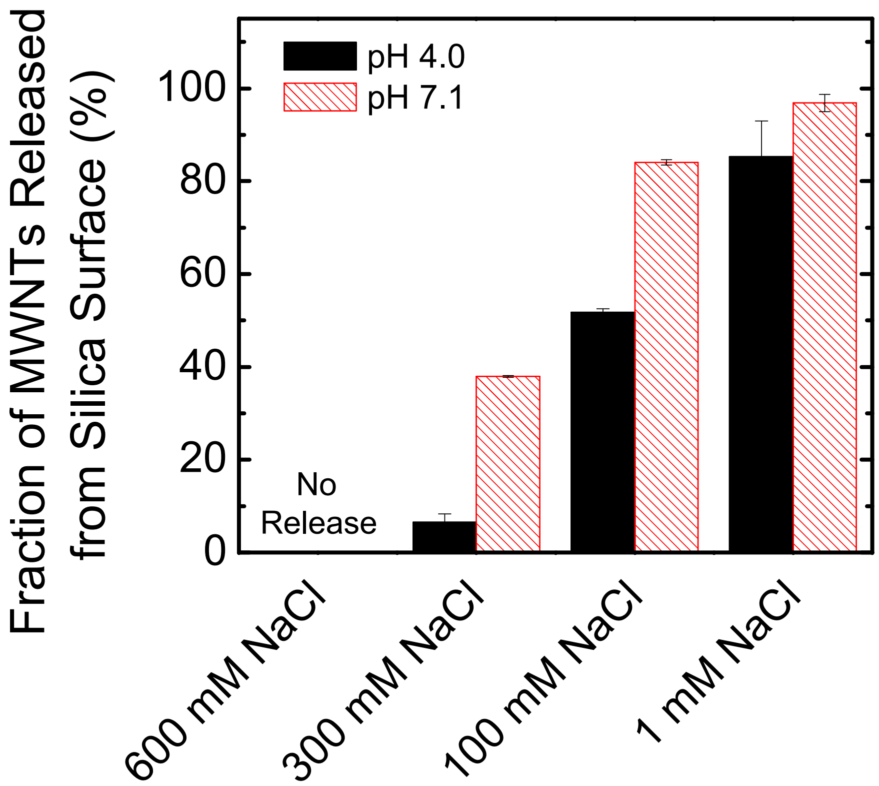
Sequential Release of MWNTs from Silica Surfaces in NaCl



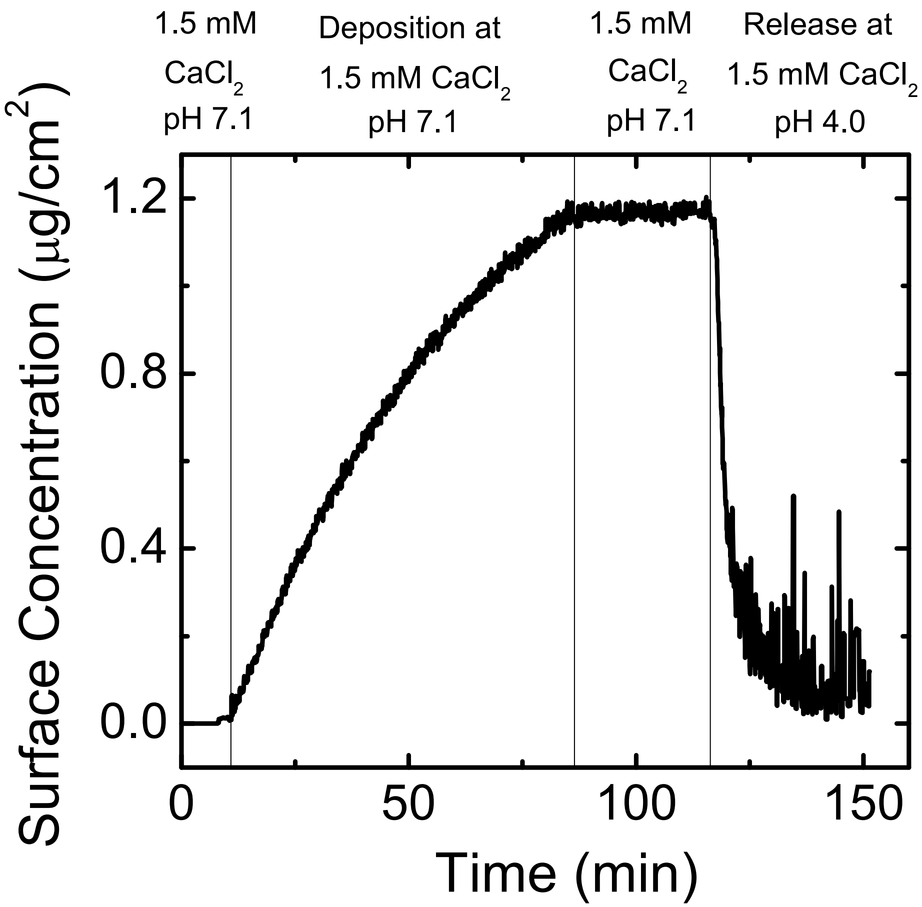
- The stepwise release behavior may be due to the surface charge heterogeneity of MWNTs
- MWNTs with higher surface charge densities were released at relatively higher NaCl concentrations while MWNTs with less surface charge densities require a further reduction of NaCl concentration to be released

Influence of pH on the Degree of MWNT Release in NaCl



- Fewer carboxyl groups on MWNTs and silanol groups on silica surfaces were deprotonated at pH 4.0
- Lower surface potentials at pH 4.0 resulted in lower degree of release compared to pH 7.1

Influence of pH on the Degree of MWNT Release in $CaCl_2$



- 90% of deposited MWNTs were released when pH decreased from 7.0 to 4.0 in 1.5 mM $CaCl_2$

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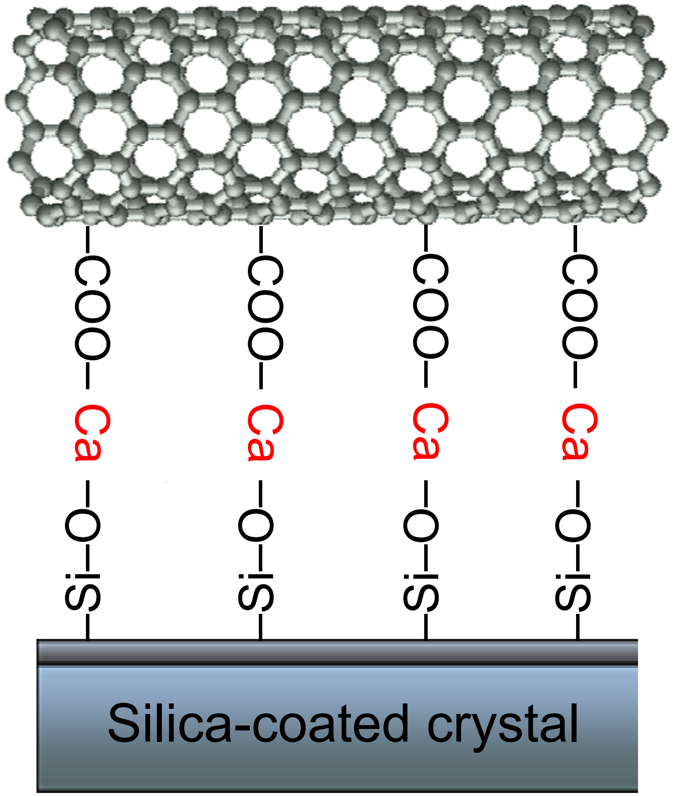
Influence of pH on the Degree of MWNT Release in $CaCl_2$



- Calcium cations have been reported to bridge deprotonated carboxyl groups on organic matter and ionized OH groups ($–O^–$) on mineral surfaces through complex formation

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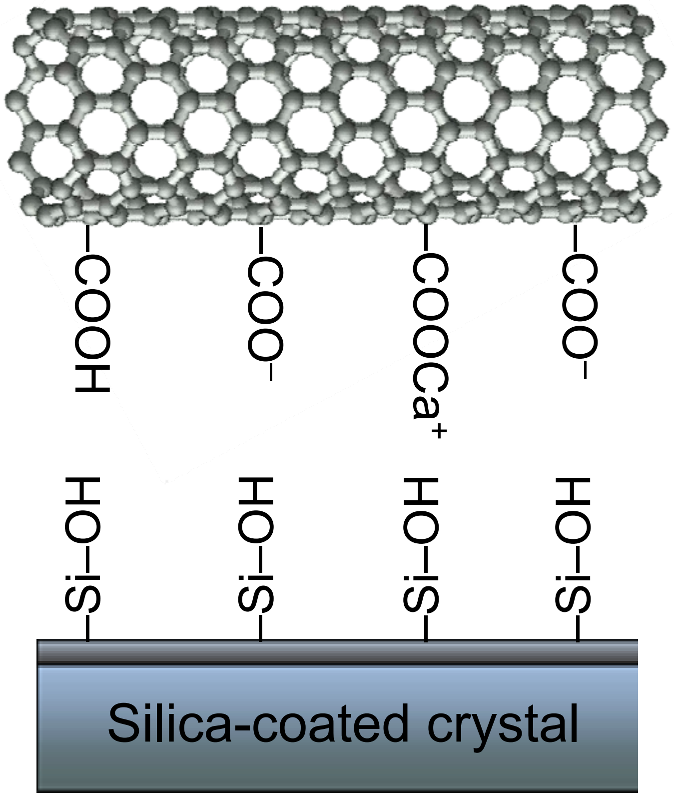
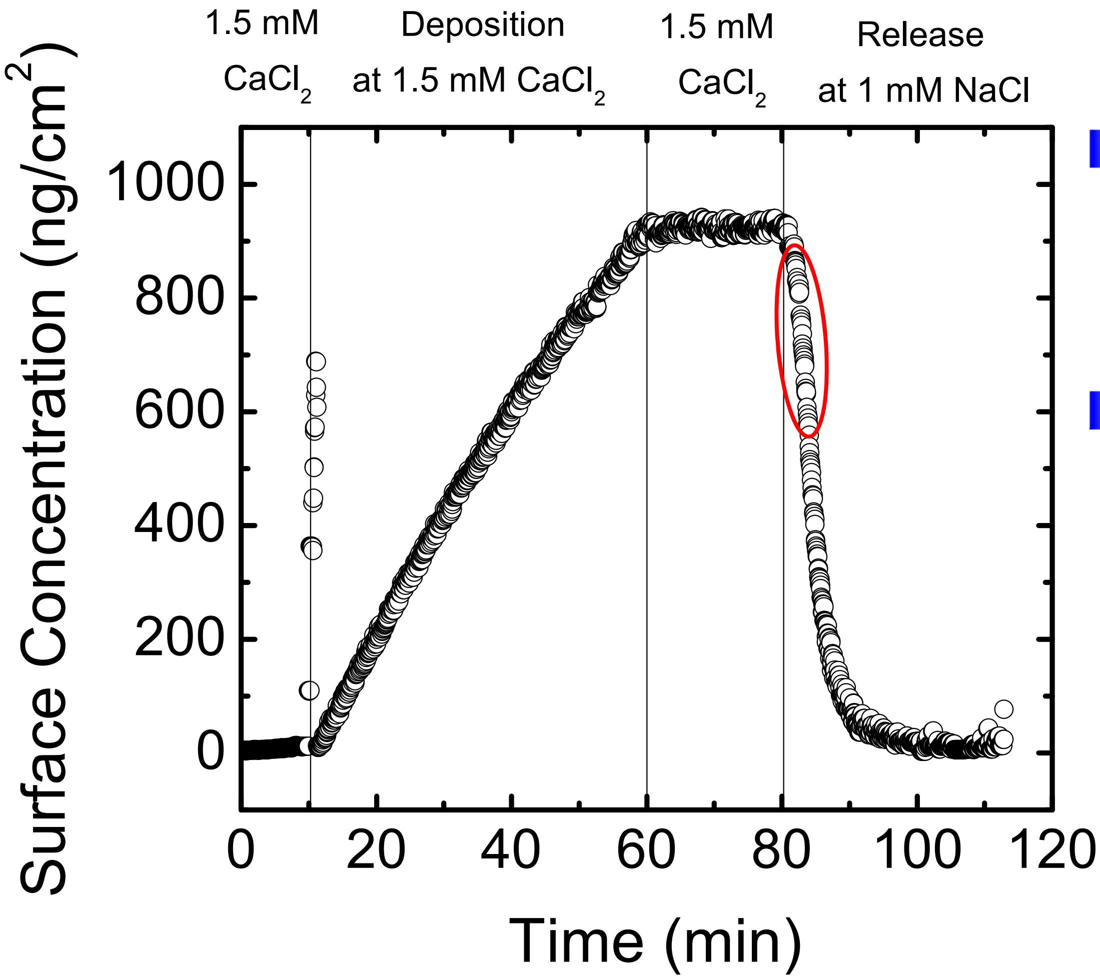
Influence of pH on the Degree of MWNT Release in $CaCl_2$



- The elimination of Ca^{2+} bridging between MWNTs and silica surfaces at pH 4.0 may have resulted in the release of deposited MWNTs

Initial Rates of MWNT Release from Silica Surfaces



- Initial rate of MWNT release is 193 ng/(cm^2·min)
- 99.2% of deposited MWNTs were eventually released

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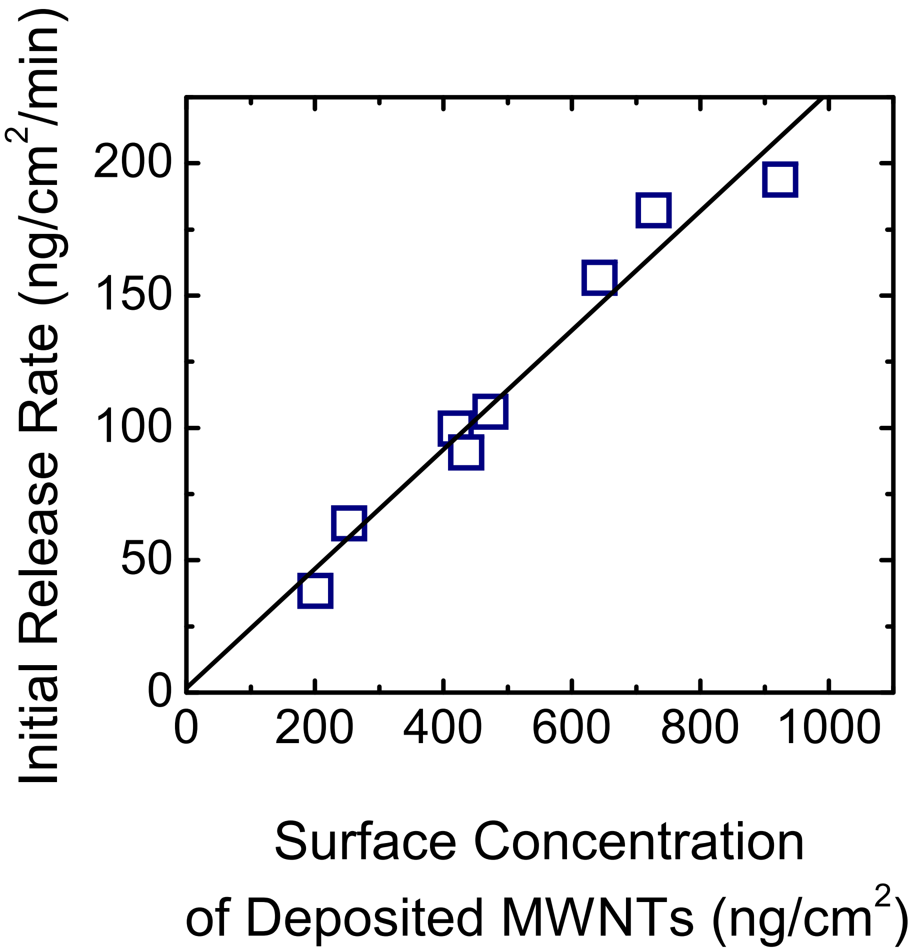
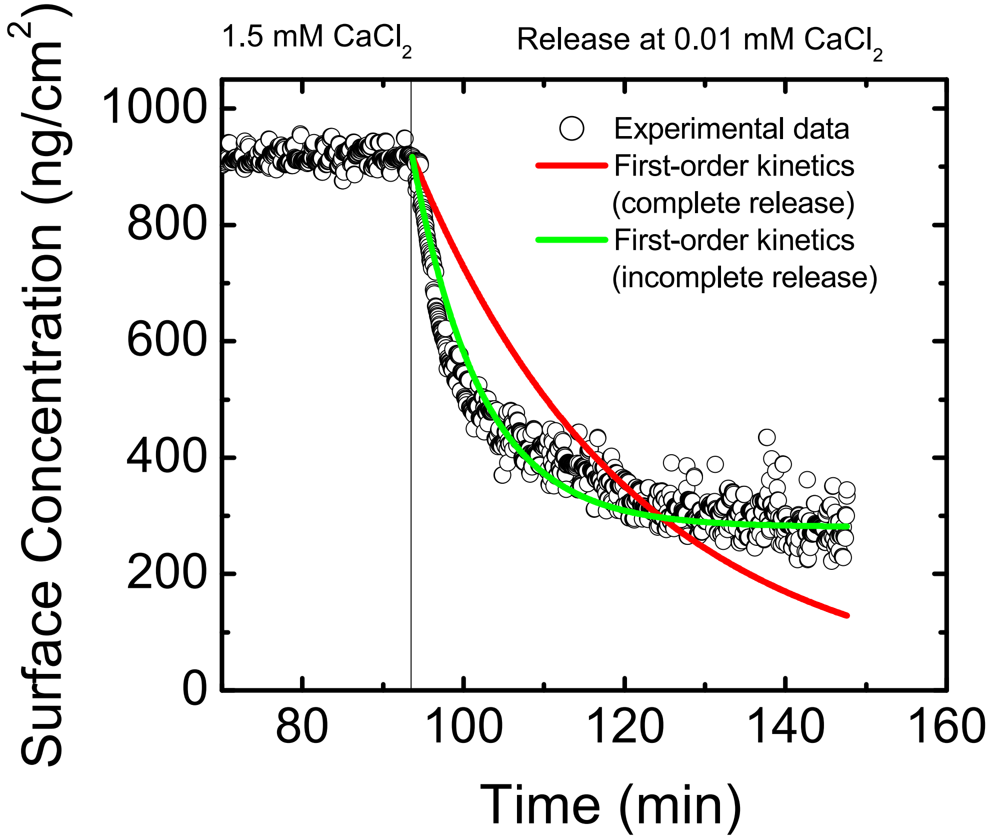
Release Kinetics under Complete Release Conditions



- MWNTs were first deposited on silica surfaces at 1.5 mM $CaCl_2$ until the target surface concentration was reached
- The deposited MWNTs were then released at 1 mM NaCl
- $\left(\frac{dm}{dt}\right)_t = -k' m_t$ or $m_t = m_0 e^{-k't}$

Release Kinetics under Partial Release Conditions



- $m_t = m_0 e^{-k't}$ (red line) does not fit the experimental data well
- Two fractions of MWNTs were present — highly-charged MWNTs that can be released and lowly-charged MWNTs that cannot be released
- $\left(\frac{dm}{dt}\right)_t = -k\ (m_t - m_{stable})$ or $m_t = (m_0 - m_{stable})e^{-kt} + m_{stable}$ (green line) fits the data well

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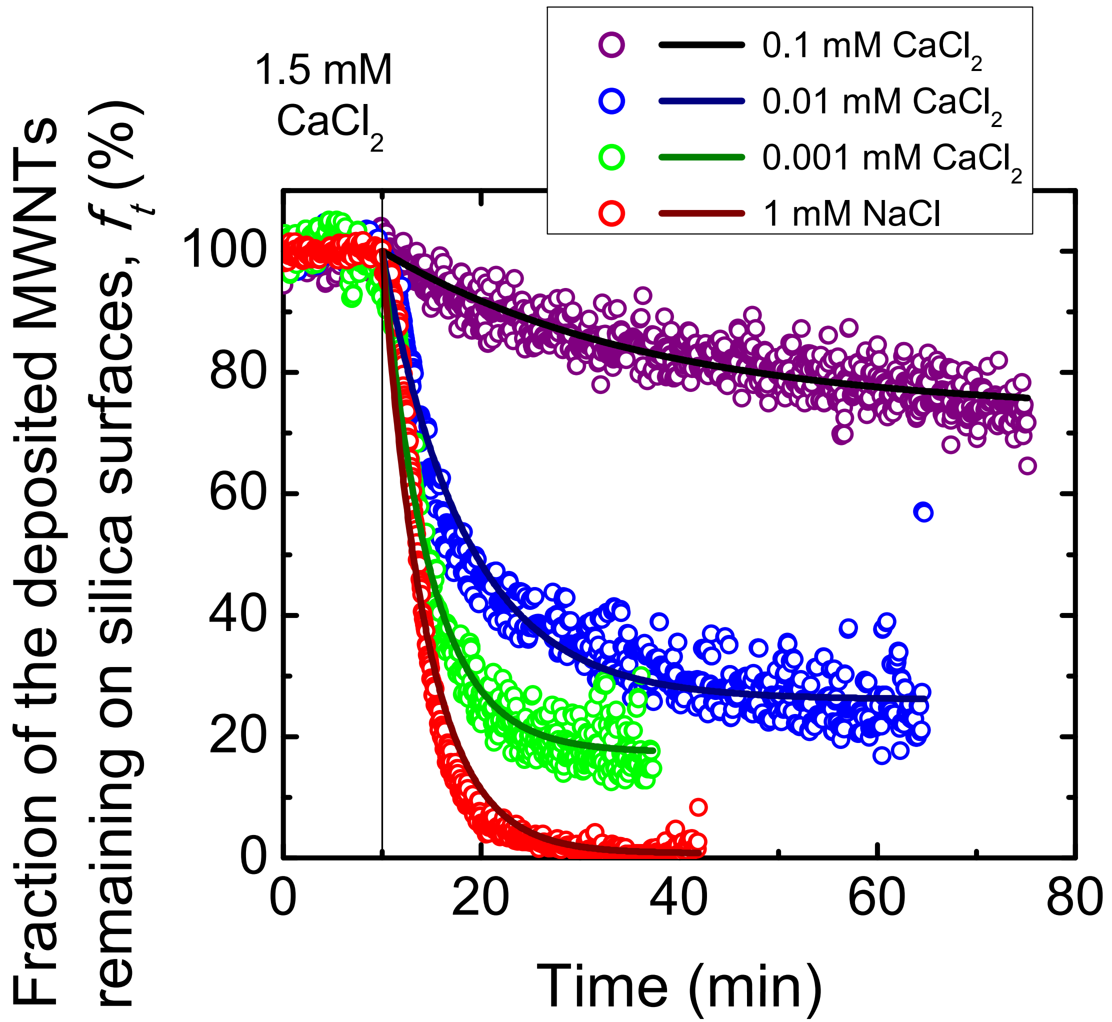
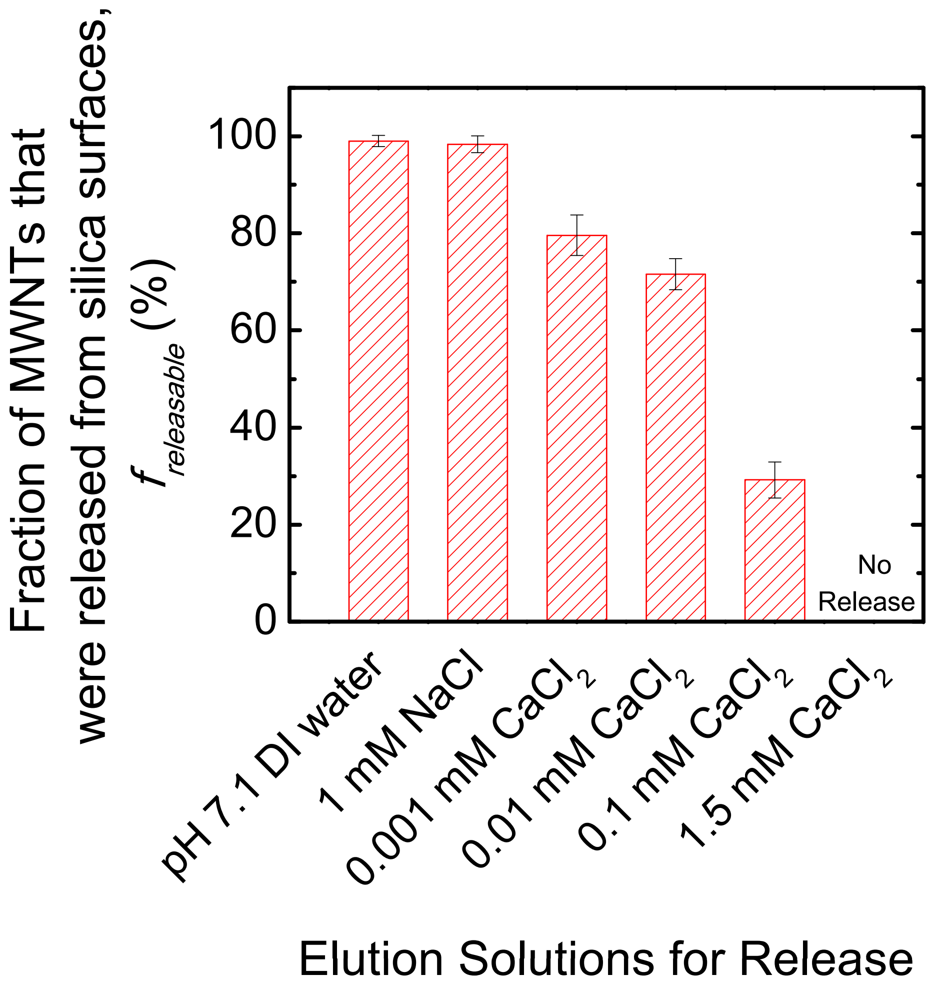
Influence of Solution Chemistry on the Release Kinetics of MWNTs



- Release rate coefficient k
- Fraction of deposited MWNTs that can be released $f_{releasable} = (m_0 - m_{stable})/m_0$

- $$f_t = f_{releasable} e^{-kt} + (1 - f_{releasable})$$

Influence of Solution Chemistry on the Fraction of Releasable MWNTs, $f_{releasable}$



- The incomplete release in $CaCl_2$ is due to the heterogeneity in surface charge density of the MWNTs
- $f_{releasable}$ increased when the surface charges of MWNTs and silica surfaces were enhanced at decreased $CaCl_2$ concentrations

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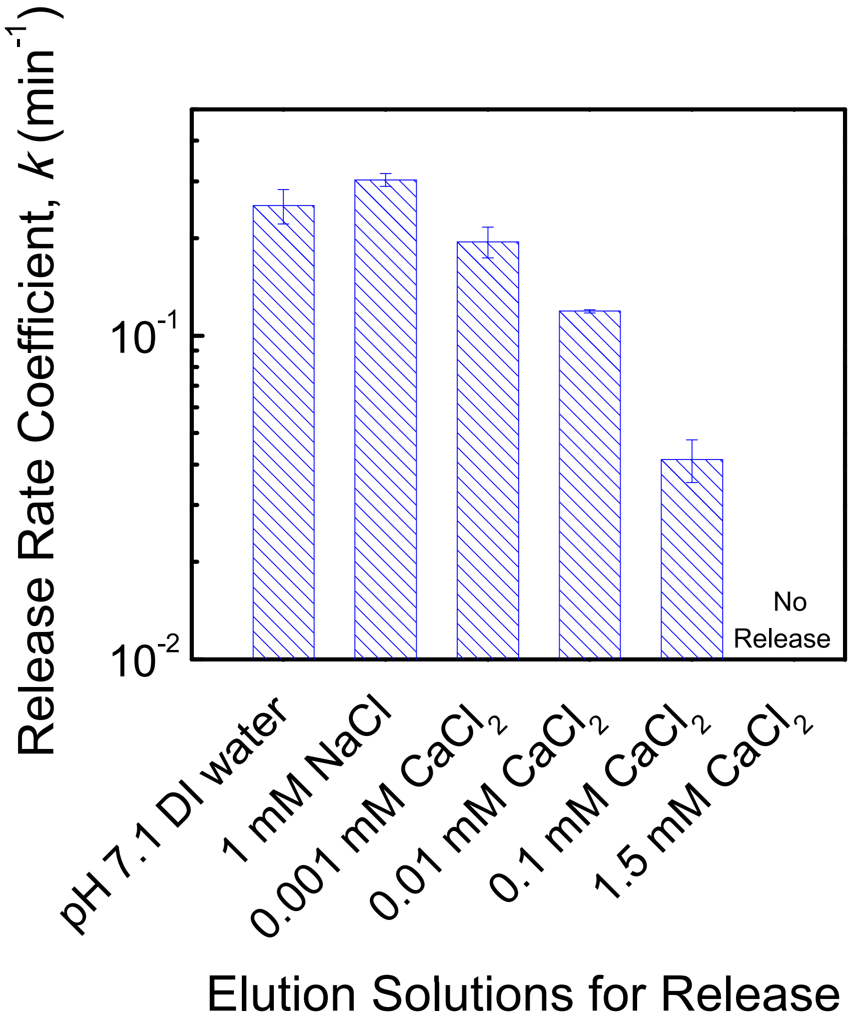
Influence of Solution Chemistry on the Release Rate Coefficient, *k*



- $k \propto \exp\left(-\frac{\phi_{max} - \phi_{min}}{k_B T}\right)$

based on Ruckenstein and Prieve theory

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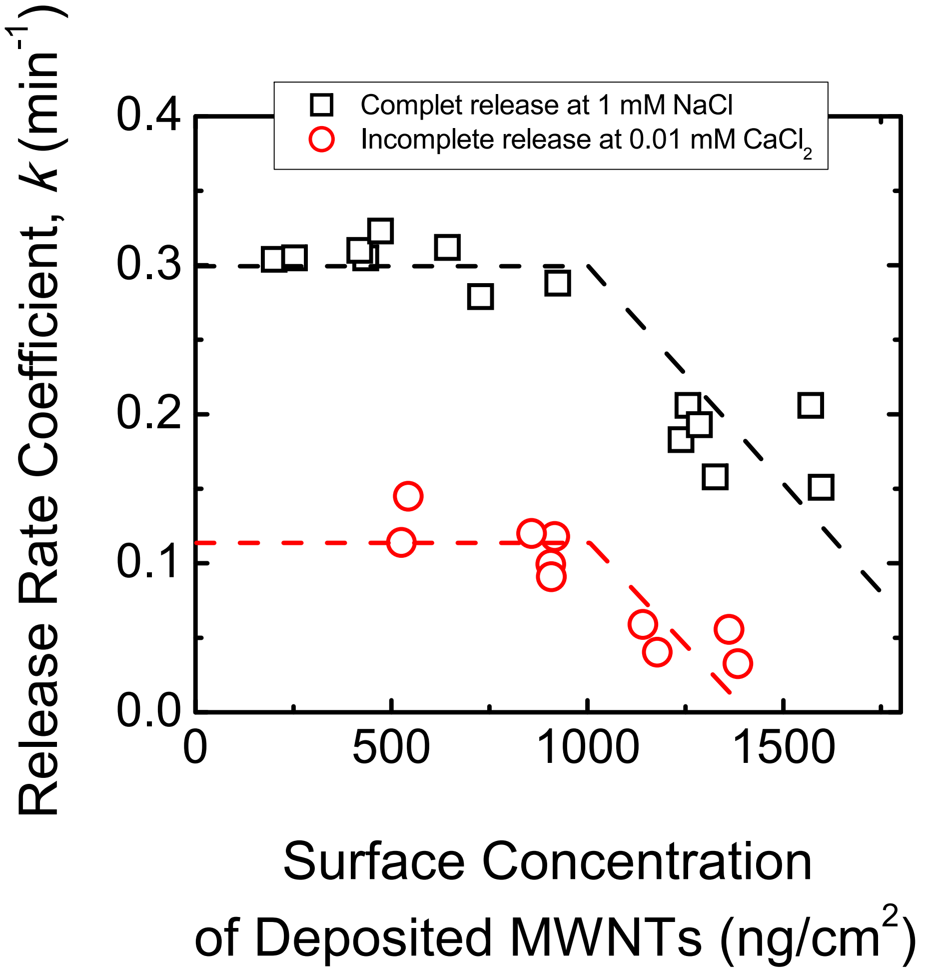
Influence of MWNT Surface Coverage on the Release Rate Coefficient



- *k* decreased when surface coverage was higher than 1000 ng/cm²
- The formation of MWNT surface-bound aggregates at higher than 1000 ng/cm² resulted in lower diffusion coefficients for MWNTs release

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Conclusions

- The deposited MWNTs were released from primary minimum at lower electrolyte concentrations. This release behavior is consistent with Ruckenstein and Prieve theory
- The stepwise release at decreasing $CaCl_2$ and NaCl concentrations may be due to the heterogeneity of MWNT surface charge density
- Decreasing pH has different effects on the degree of MWNT release in the presence of NaCl and $CaCl_2$

Conclusions

- The release kinetics of MWNTs can be described by a two-fraction first-order release model
- Both the fraction of releasable MWNTs and the release rate coefficient increased with decreasing electrolyte concentrations due to lower energy barrier for MWNT release
- Increasing the surface coverage of MWNTs may retard the release kinetics of MWNTs, probably due to the formation of surface-bound aggregates and the resultant decreased diffusion rate coefficient

Acknowledgements

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