Characterization of Surface Oxides on Carbon Nanotubes and their Influence on Environmental Properties

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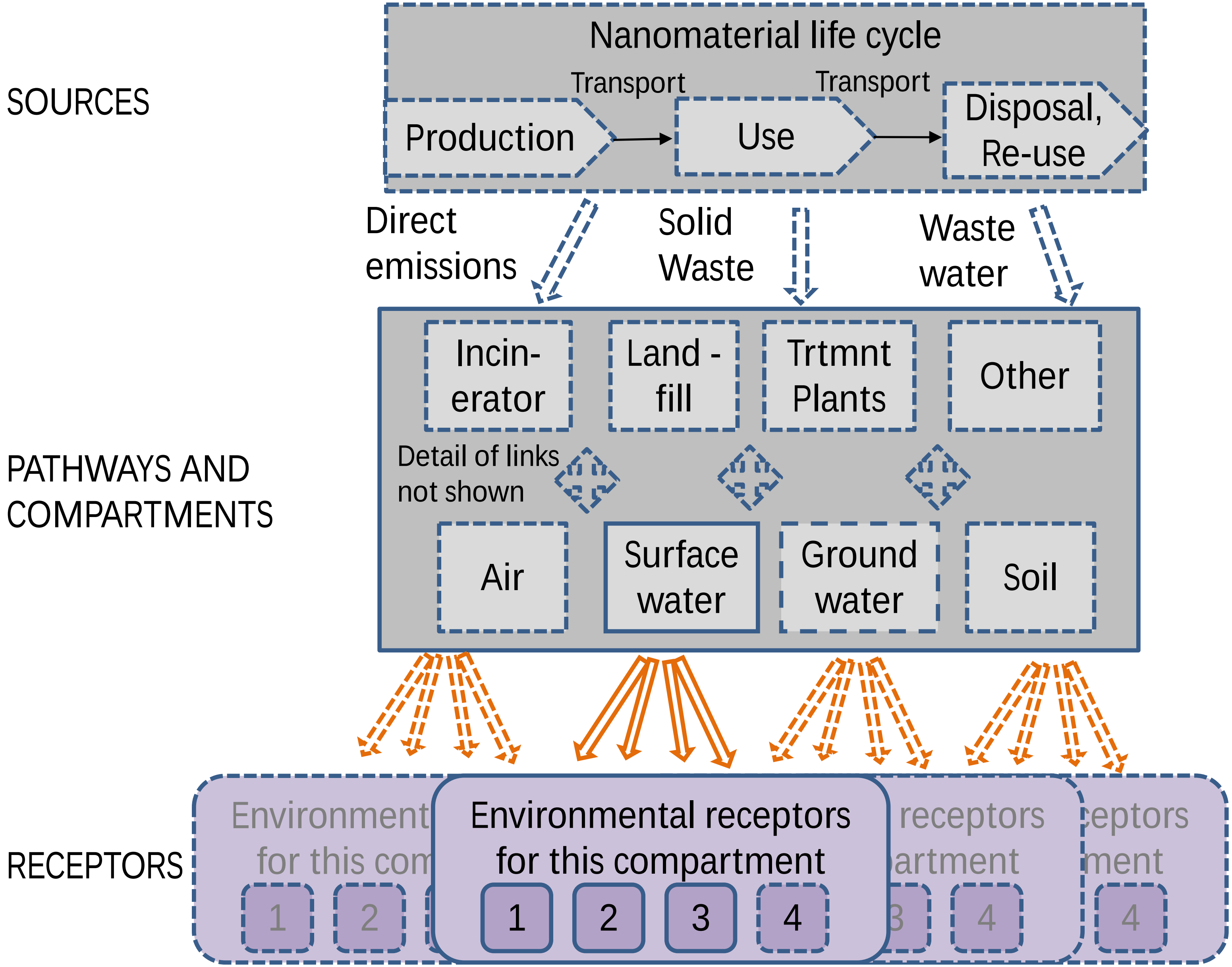
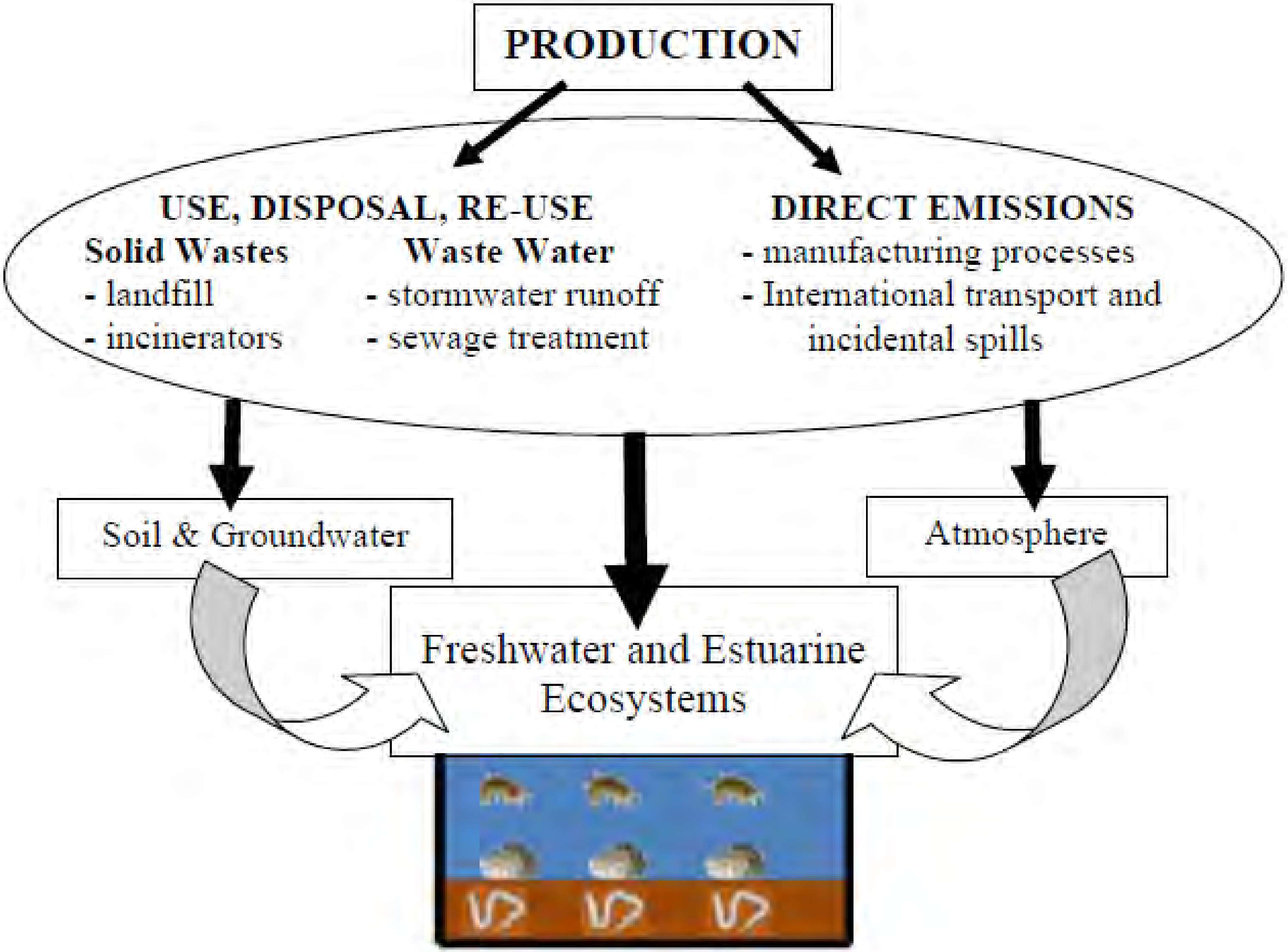
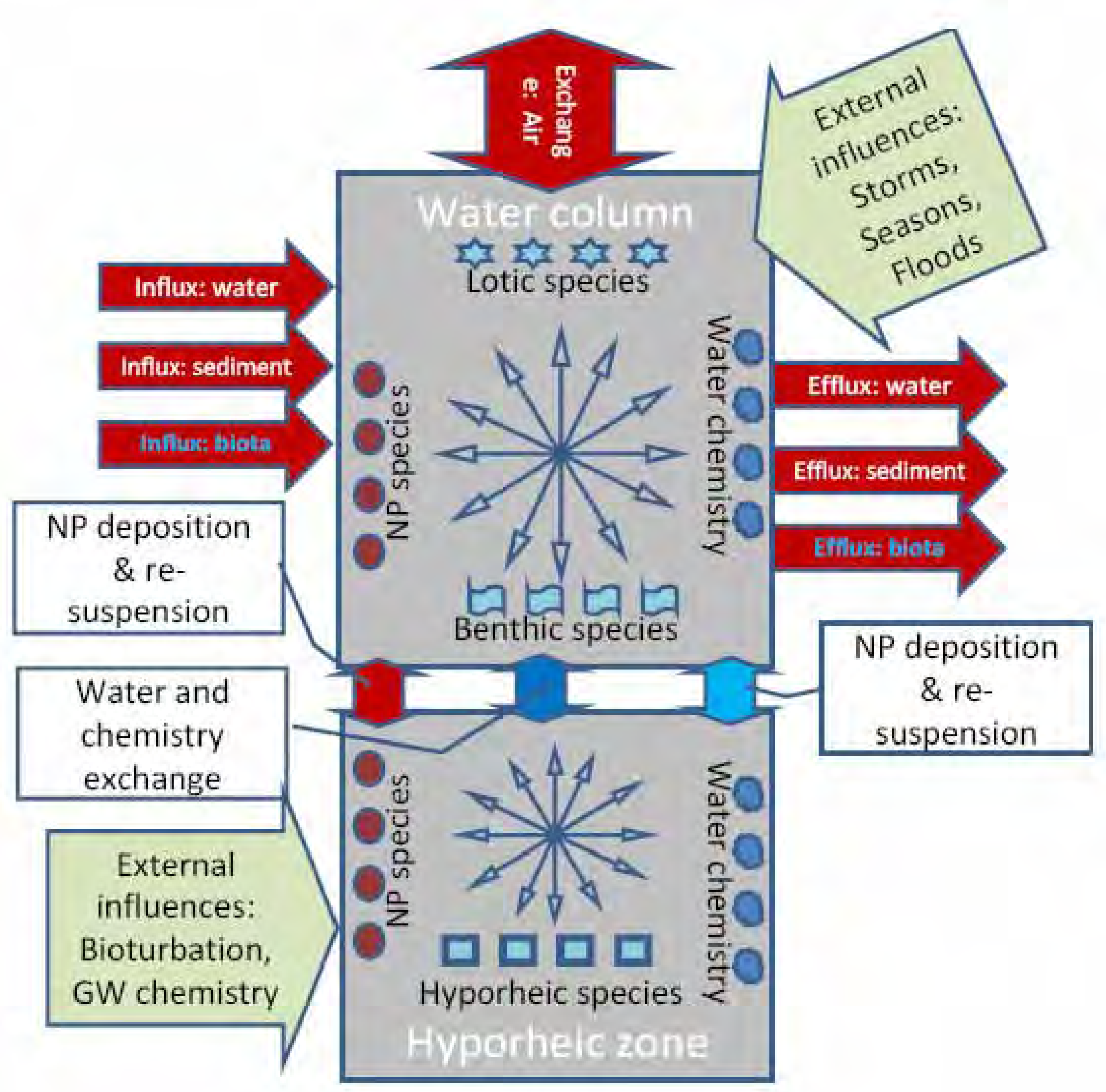

SOURCES
PATHWAYS AND COMPARTMENTS
RECEPTORS
Nanomaterial life cycle
Transport
Transport
Production
Use
Disposal, Re-use
Direct emissions
Solid Waste
Waste water
Incin-erator
Land - fill
Trtmnt Plants
Other
Detail of links not shown
Air
Surface water
Ground water
Soil
Environmental receptors for this compartment
1
2
3
4



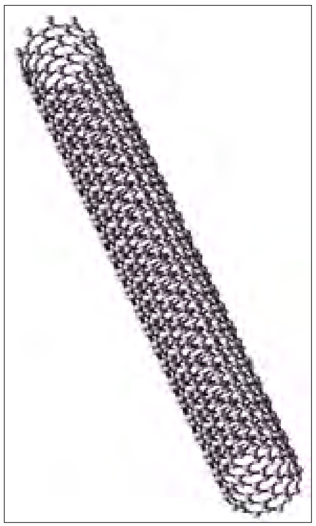
Courtesy Prof. Amy Ringwood, Univ. S. Carolina



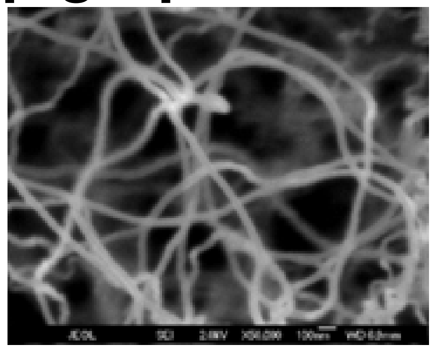
Exchange: Air
Water column
Lotic species
Influx: water
Influx: sediment
Influx: biota
External influences: Storms, Seasons, Floods
Efflux: water
Efflux: sediment
Efflux: biota
NP species
Water chemistry
NP deposition & re-suspension
Benthic species
Water and chemistry exchange
NP deposition & re-suspension
NP species
Water chemistry
External influences: Bioturbation, GW chemistry
Hyporheic species
Hyporheic zone

What are Carbon Nanotubes?

Rolled up graphene sheets

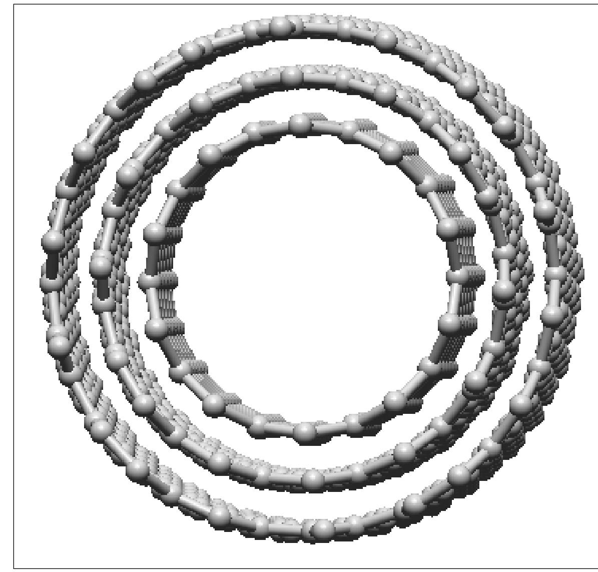


Single Walled Carbon Nanotube (SWCNT)



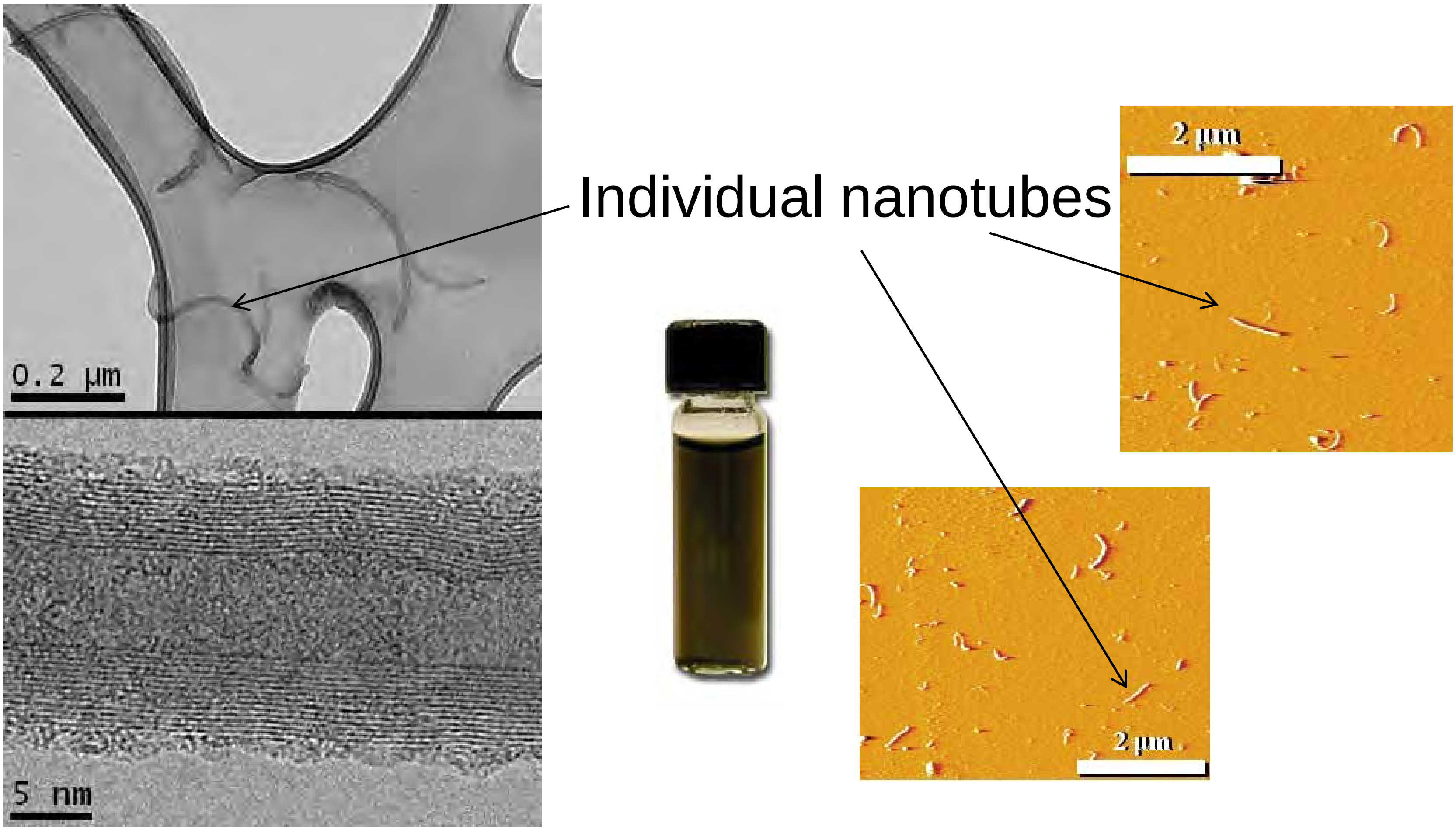
Materials Properties

- **Mechanical Strength**
- **Electrical Conductivity**
- **High Aspect Ratio**

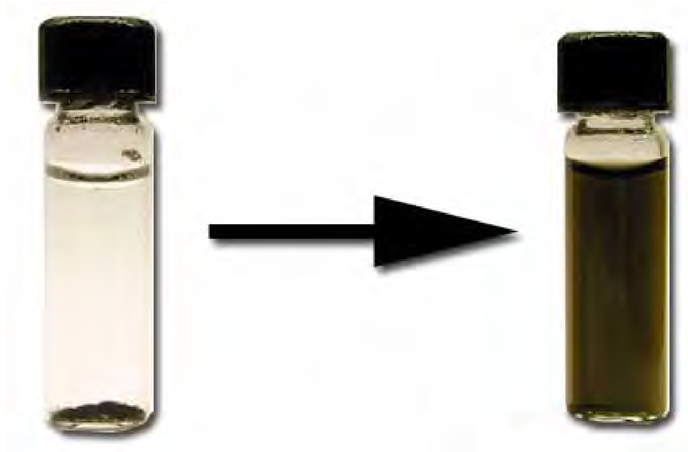


Multi Walled Carbon Nanotubes (MWCNT)

Oxidized MWCNTs in Colloidal Suspension

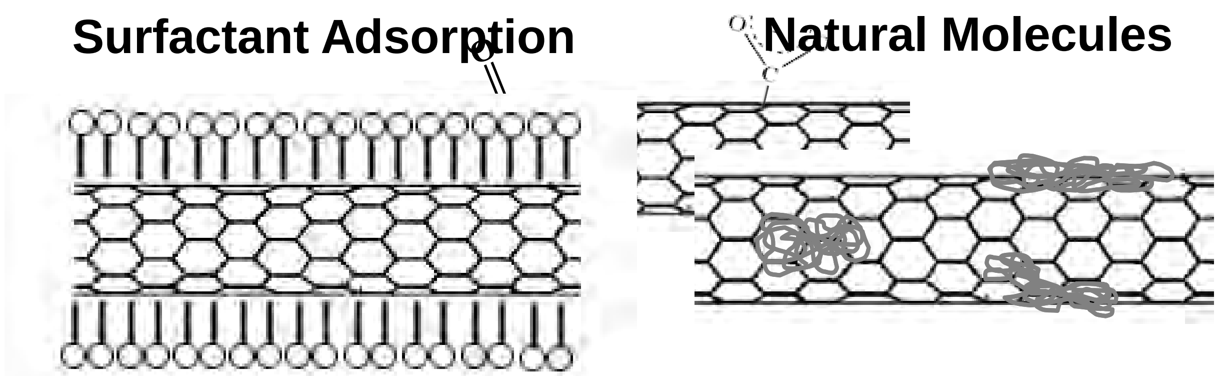


Stabilizing CNTs in Solution

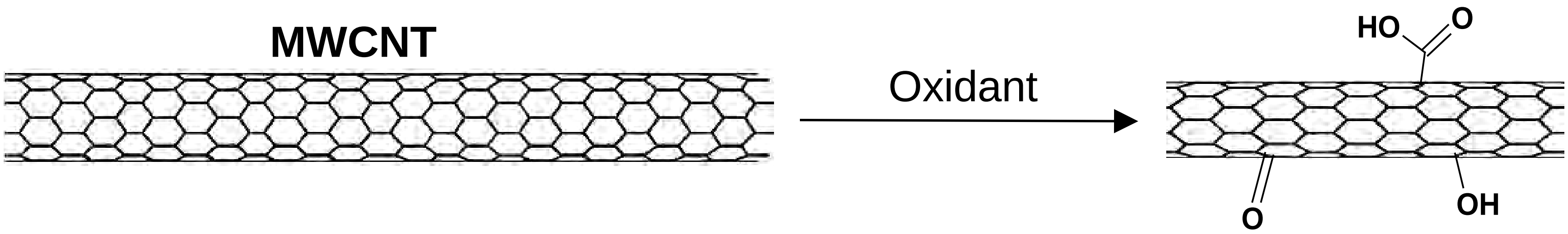


Surface Oxidation

Surfactant Adsorption **Natural Molecules**



Surface Oxidation



Oxidative Routes

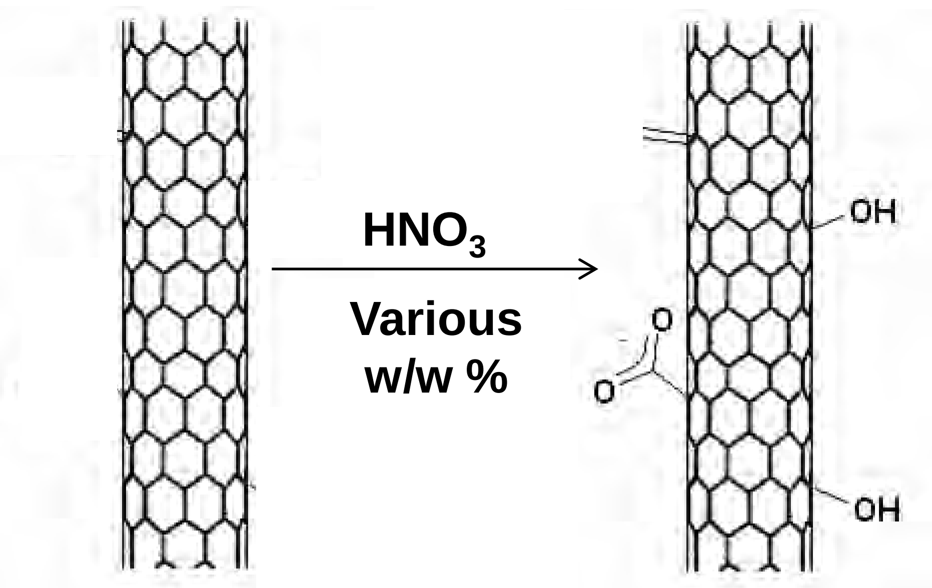
- **Purification**
- **Functionalization**
- **Environmental Transformation**

Oxidants

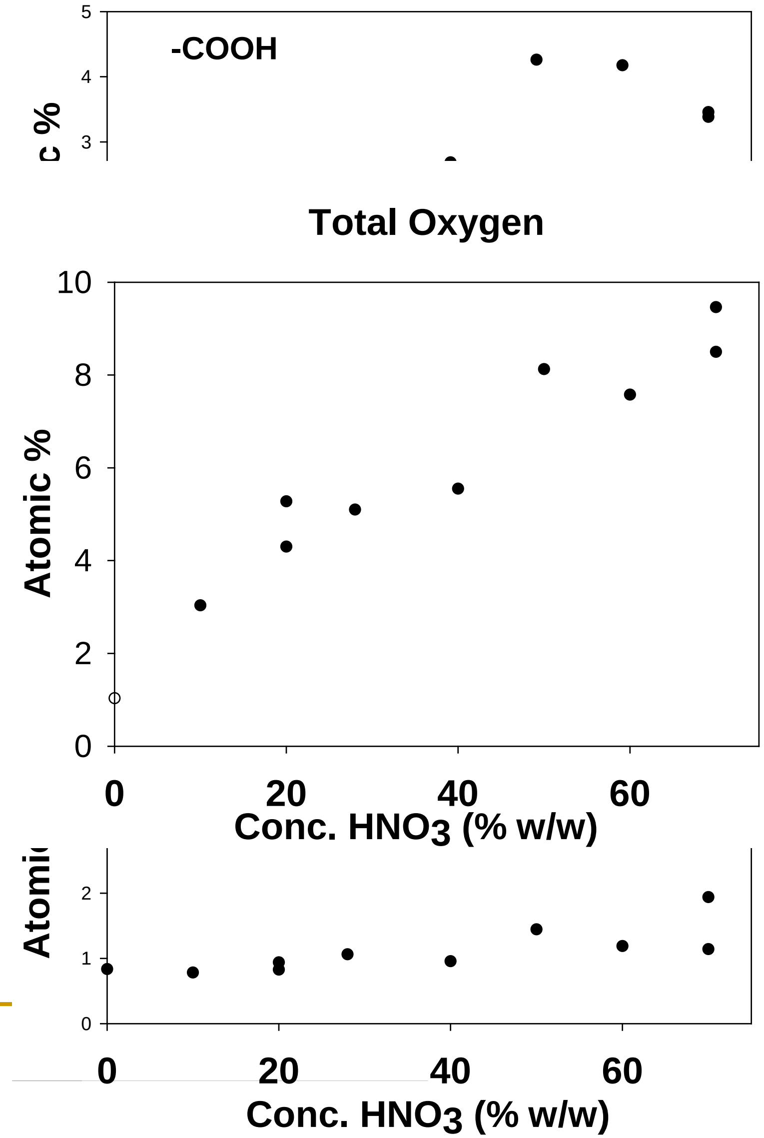
- **$KMnO_4$**
- **H_2O_2**
- **HNO_3**
- **O_3**

Prevalent Oxidative Method

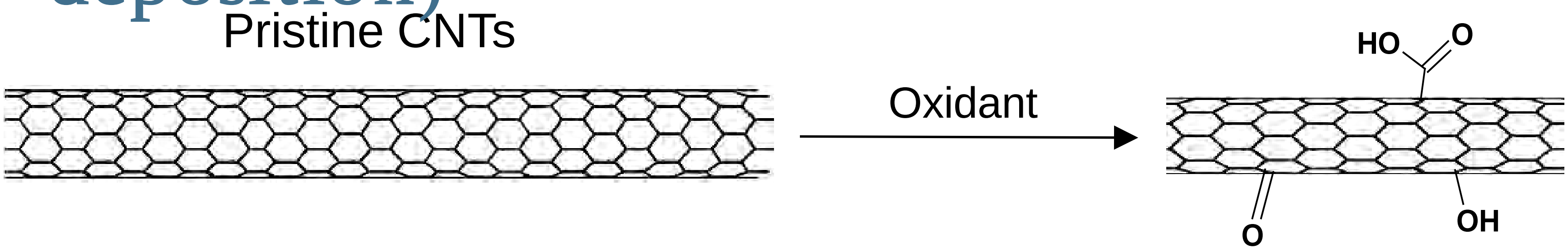
Influence of Oxidizing Conditions

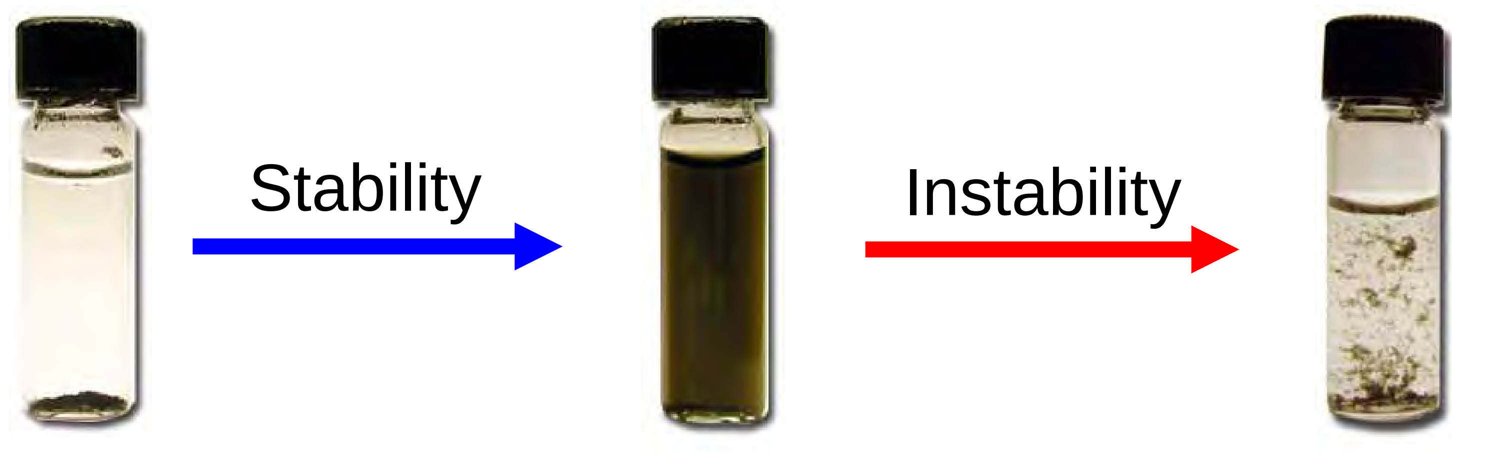


Functional Groups



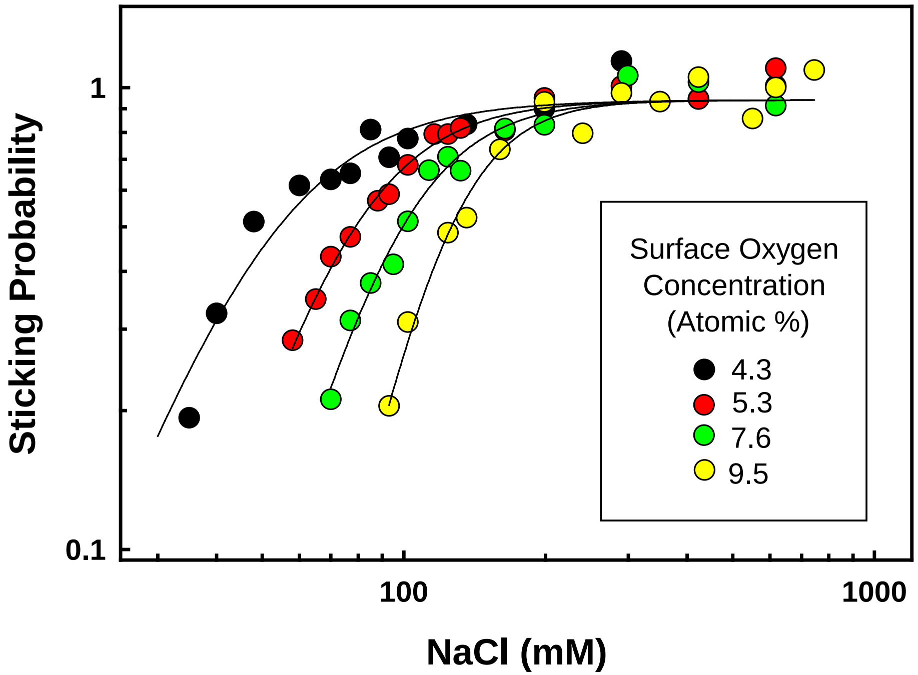
Research Motivation/Objectives (aquatic stability: aggregation, deposition)





Pristine CNTs   Oxidized CNTs   Aggregating CNTs

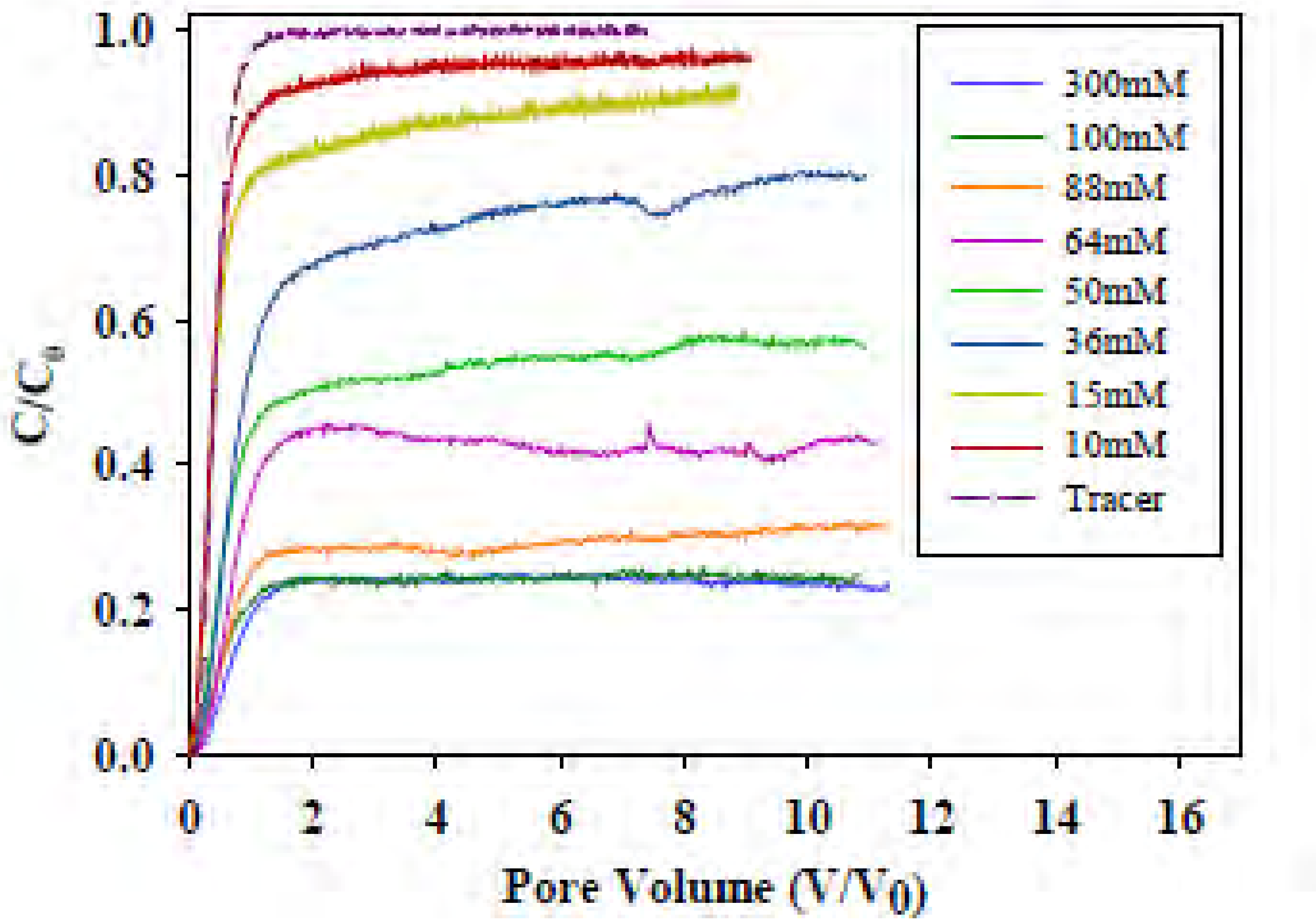
Stability and The CCC



Stability profiles for several oxidized MWCNTs

$$\textbf{Sticking Probability} = \frac{1}{1 + ([CCC]/[NaCl])^{b}}$$

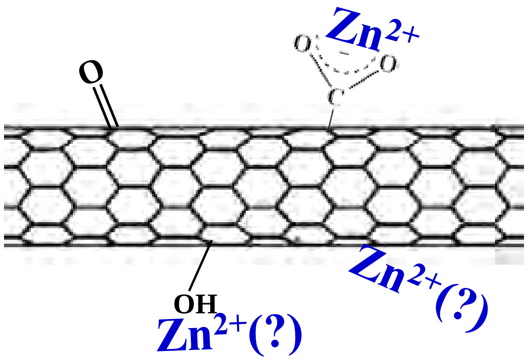
O-MWCNT Transport as Function of NaCl Concentration (pH 7.0; oxidized with 30% HNO_3)



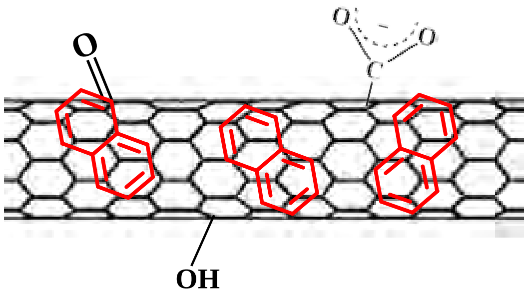
Research Motivation/Objectives (sorption)

- Surface Oxidation is expected to increase sorption of polar or charged contaminants.
- Better understanding is needed of the relationships between surface oxidation and metal sorption isotherms.

Metals (e.g. Zinc)



Nonpolar organic compounds (e.g. Naphthalene)



1. Determine the effects of surface oxidation on Zn(II) sorption by MWCNTs under controlled water quality conditions.

2. Relate changes in sorption to measured changes in the surface functional group distribution.

Naphthalene sorption with MWCNTs

(Cho et al., *ES&T*, 2008)

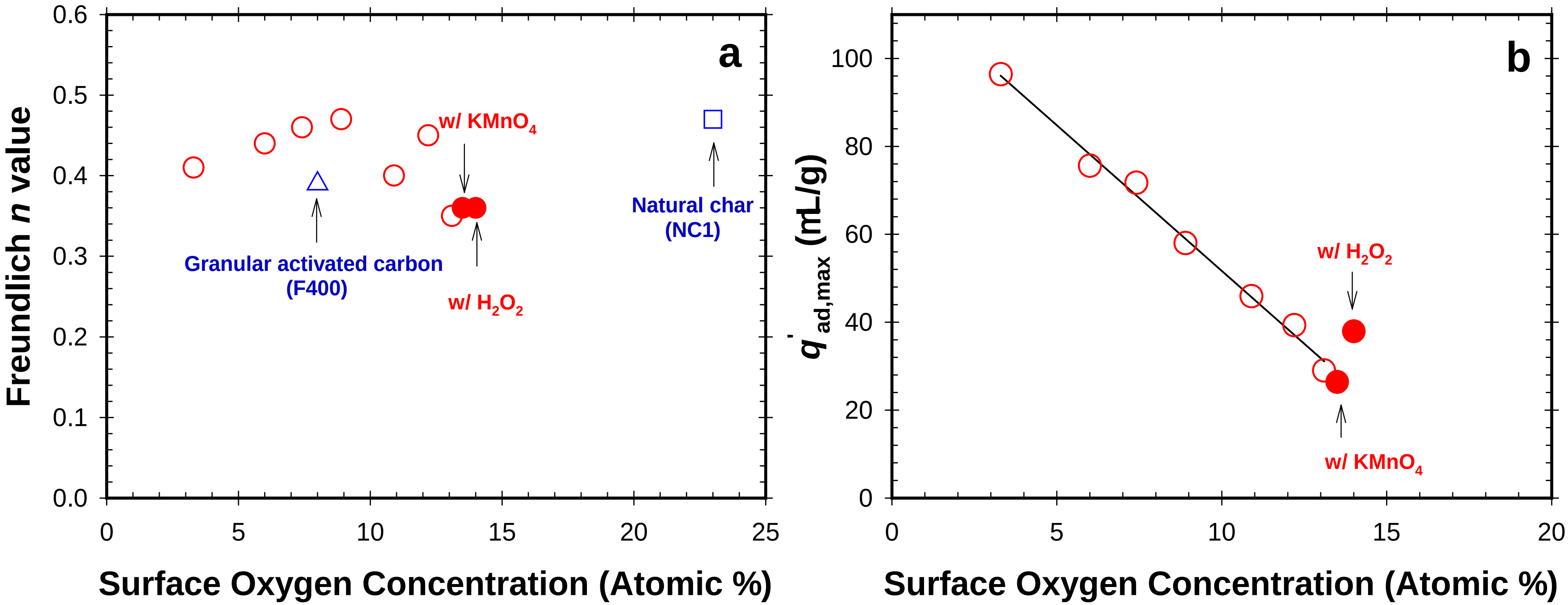


Figure 4. (a) Freundlich *n*-values for naphthalene adsorption plotted against surface oxygen concentration for MWCNTs, natural char (NC1), and granular activated carbon (F400). (b) Maximum adsorption capacity ($q'_{ad,max}$) for naphthalene from the Polanyi-based Dubinin-Astikov adsorption model plotted against surface oxygen concentration.

Langmuir Two-Site Model:

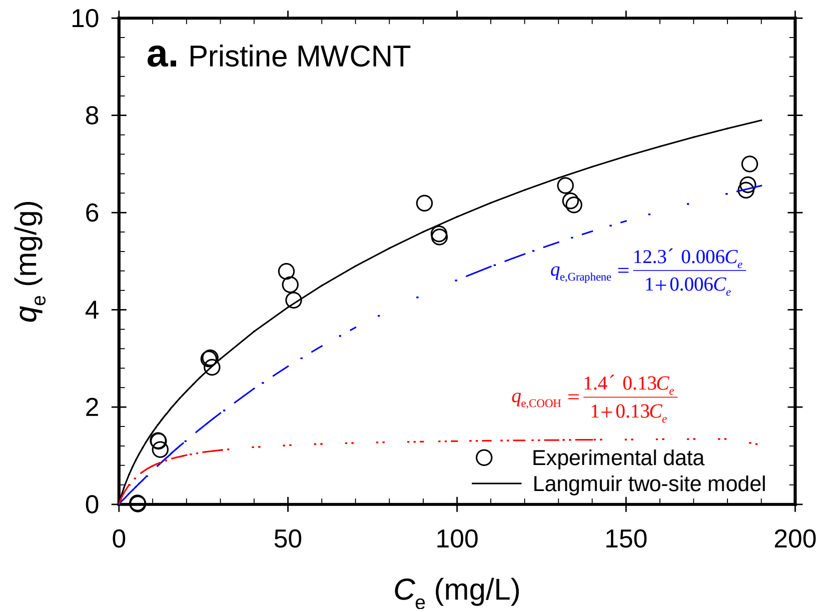
Common $K_{L,G}$, $K_{L,C}$, a, and b:

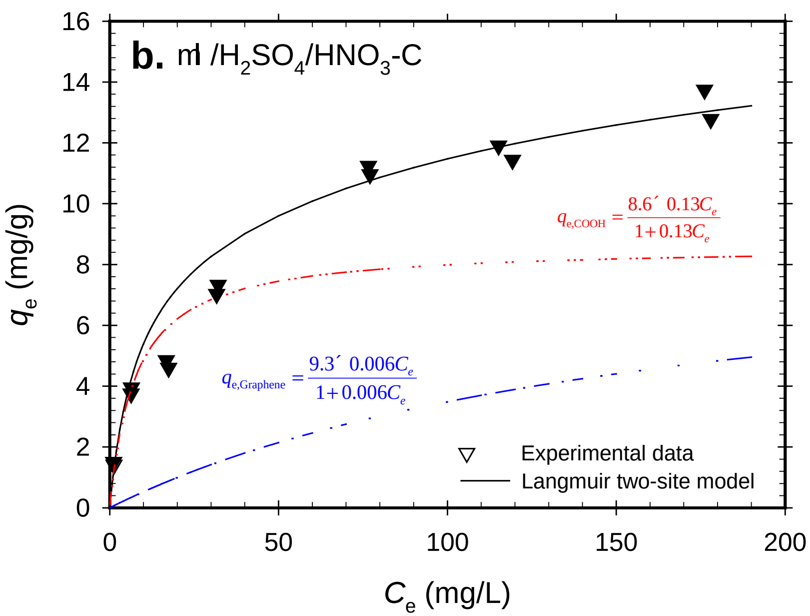
$$q_{e,180} = a[\%C_{Graphene}] + b[\%C_{COOH}]$$

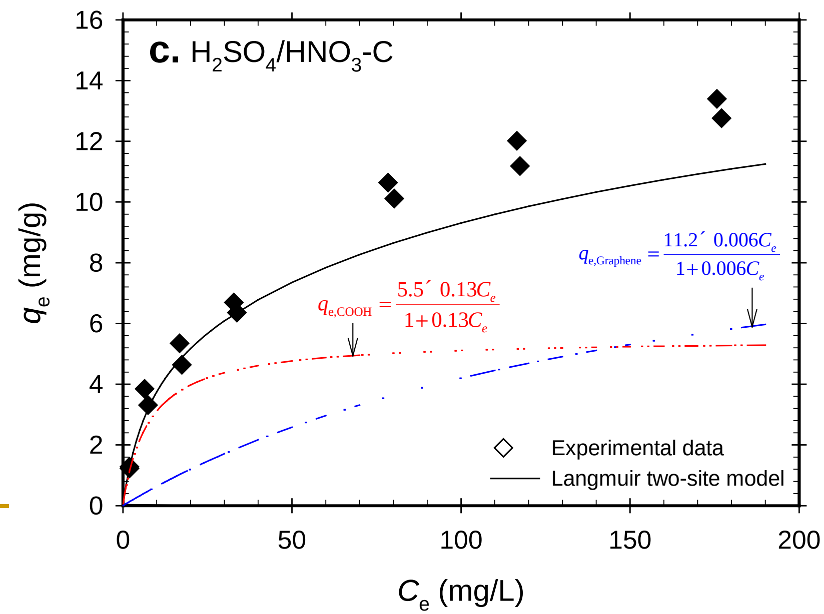
$$q_e = \frac{q_{max,G}K_{L,G}C_e}{1+K_{L,G}C_e} + \frac{q_{max,C}K_{L,C}C_e}{1+K_{L,C}C_e}$$

$$if\ C_e = \infty, \quad \boldsymbol{a} = \frac{q_{max,G}}{[\%C_{Graphene}]}, \ \boldsymbol{b} = \frac{q_{max,COOH}}{[\%C_{COOH}]}$$

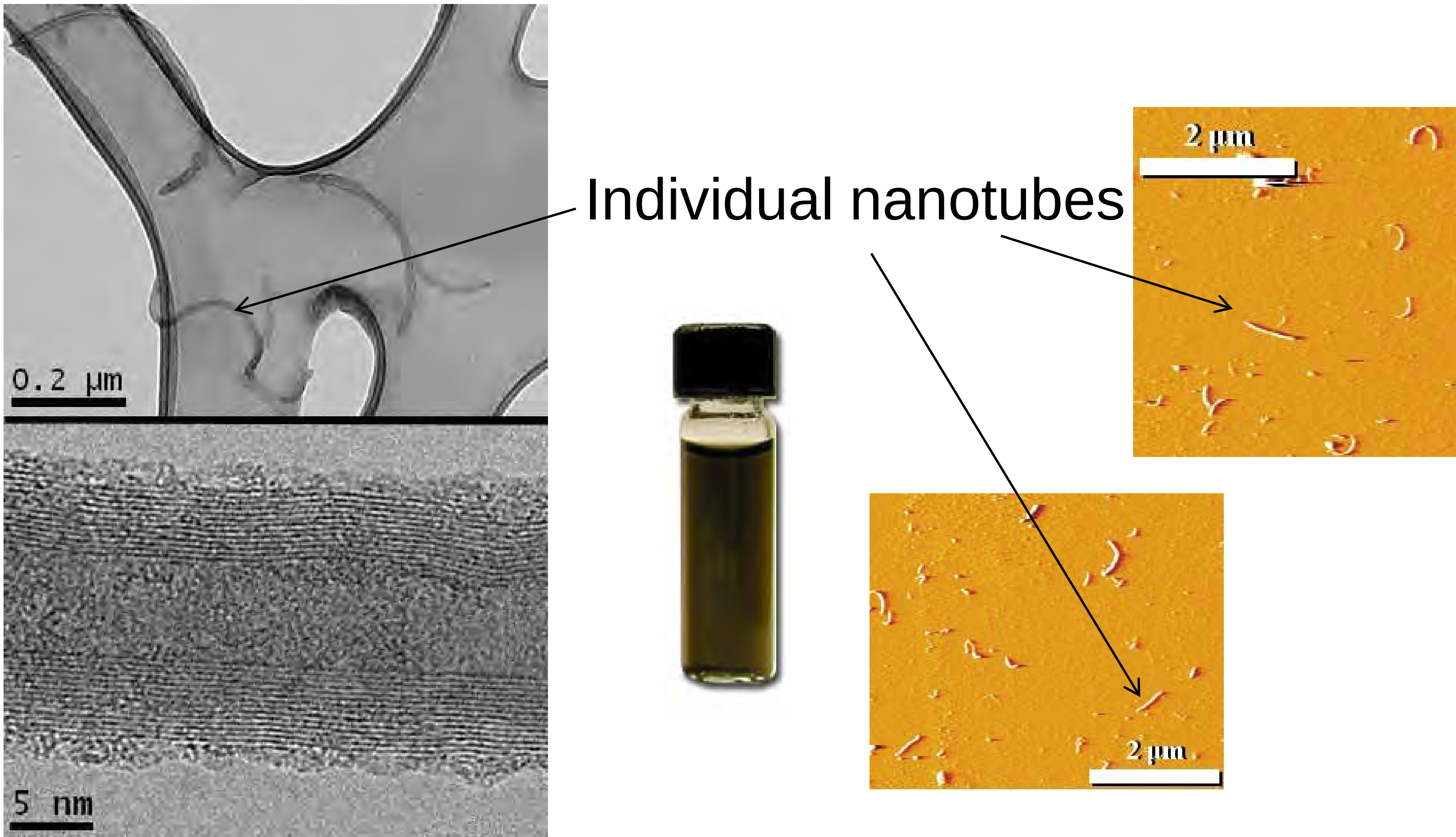
$K_{L,G} = 0.006$, $K_{L,C} = 0.13$, $a = 0.13$, $b = 0.94$







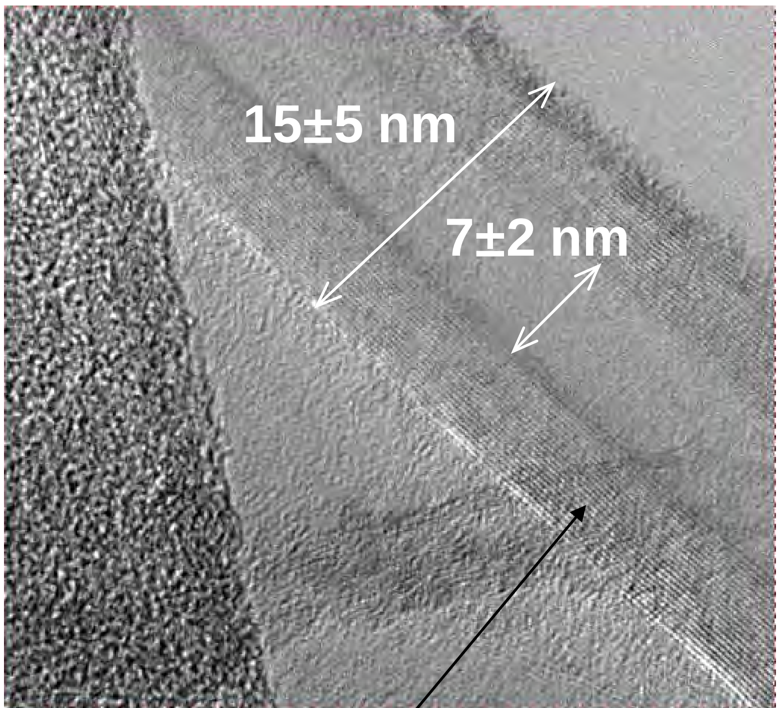
Oxidized MWCNTs in Colloidal Suspension

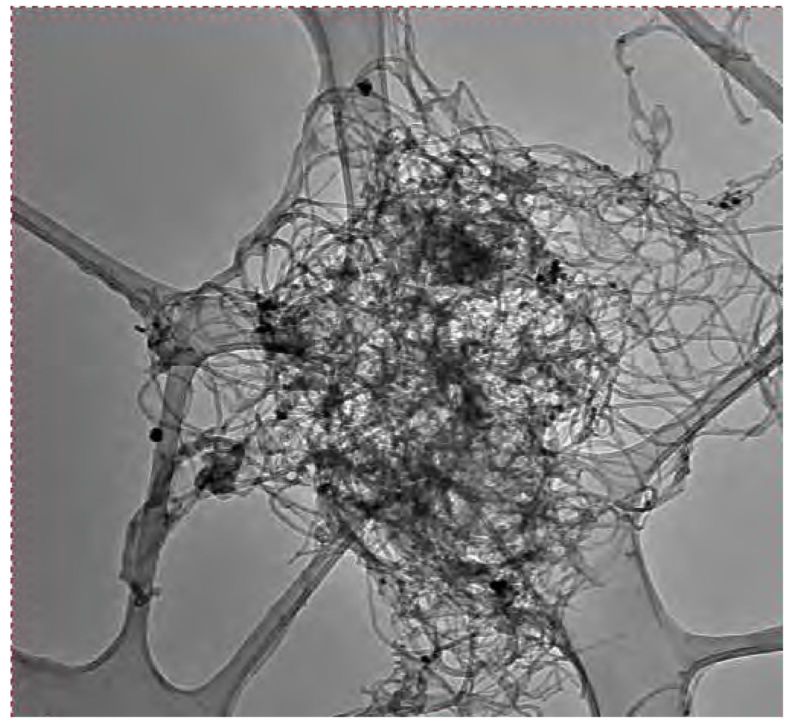


Thank You

Preparing & Characterizing Oxidized CNTs

TEM images of MWCNTs used in our study

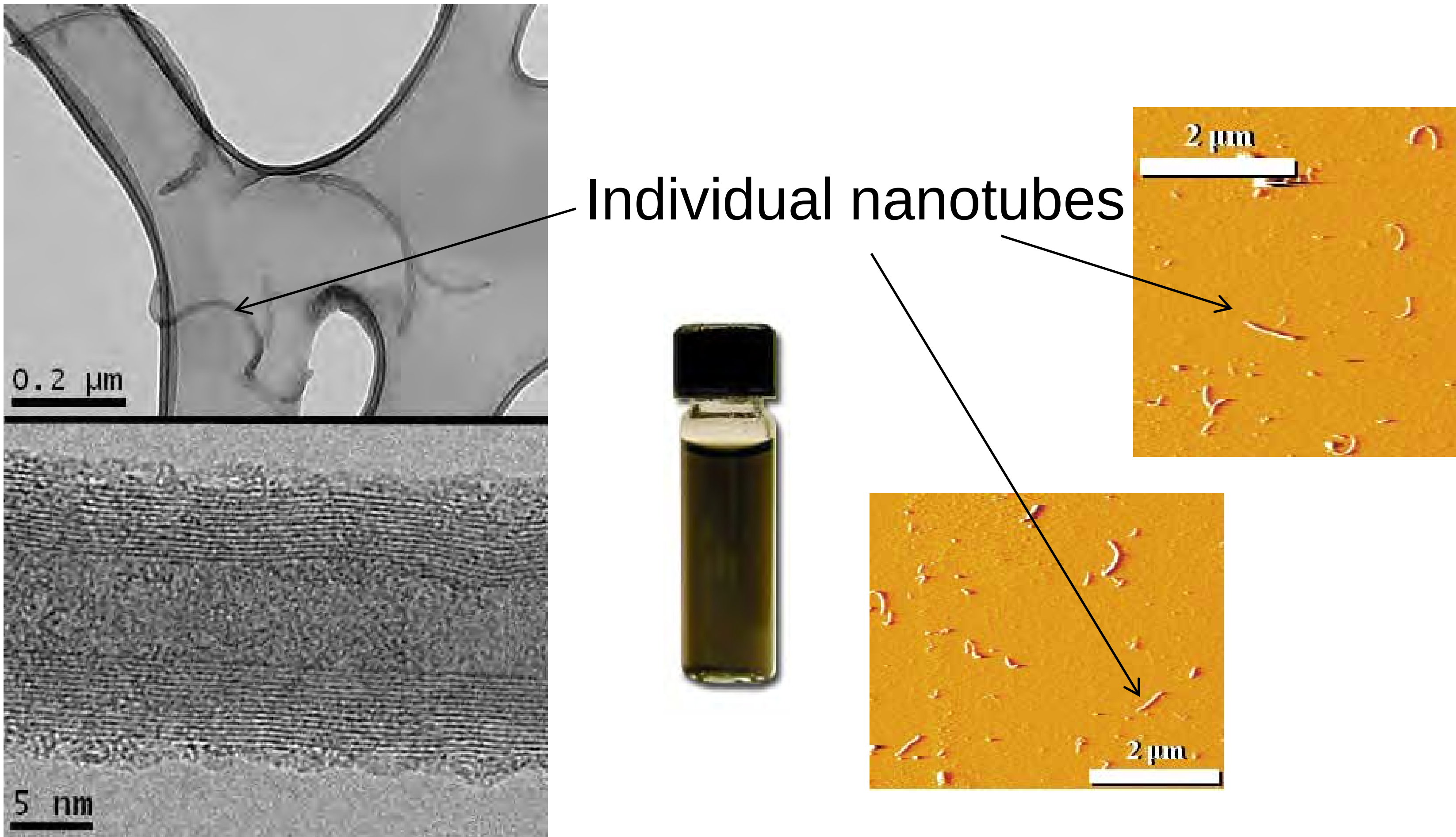




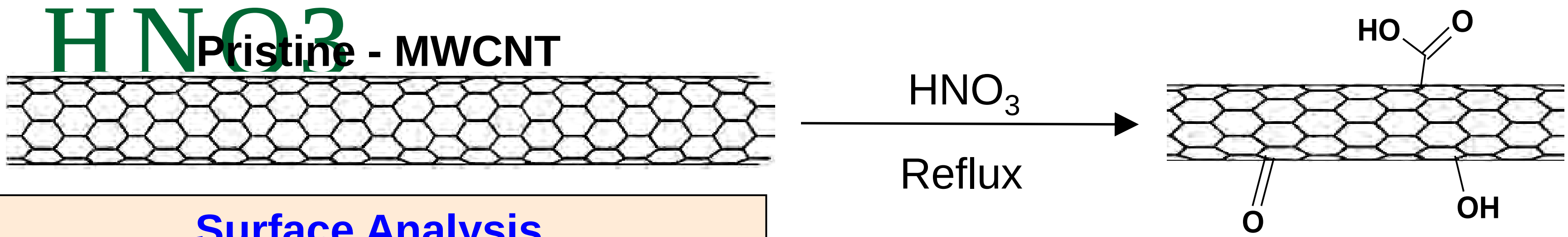
Multiwall CNTs

CNT aggregates

Oxidized MWCNTs in Colloidal Suspension



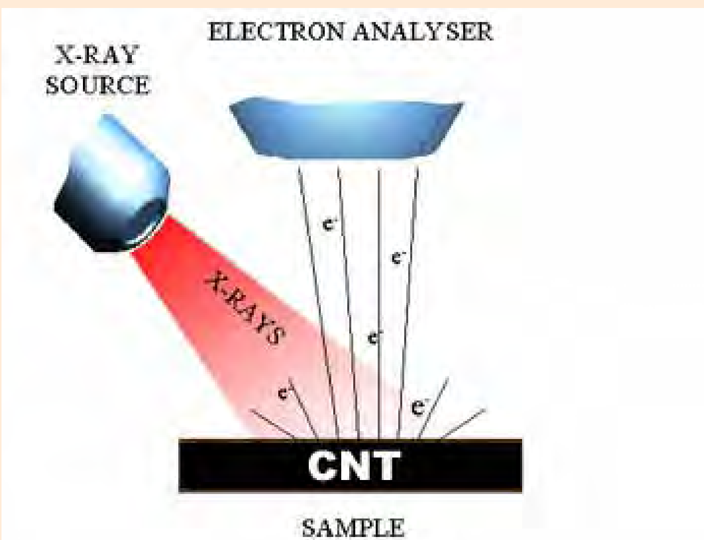
Controlled Oxidation with HNO3



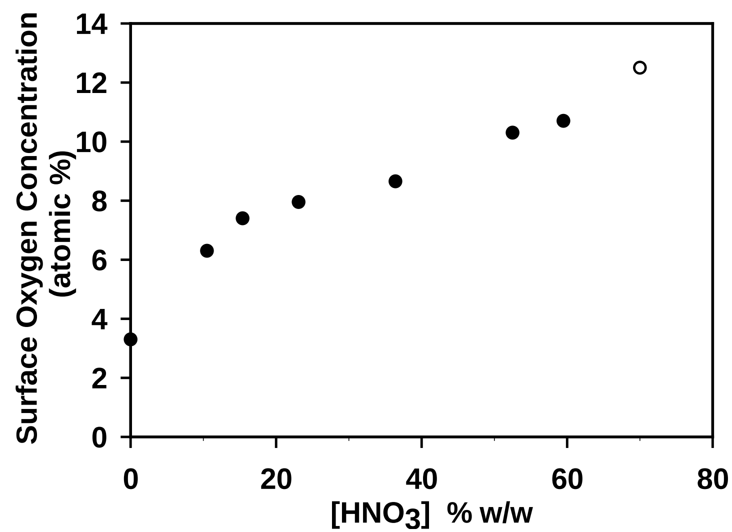
Surface Oxides

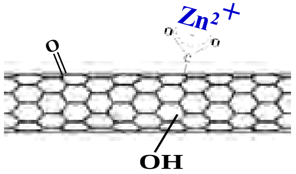
Surface Analysis

X-ray photoelectron Spectroscopy



Determine Surface Oxygen Concentration

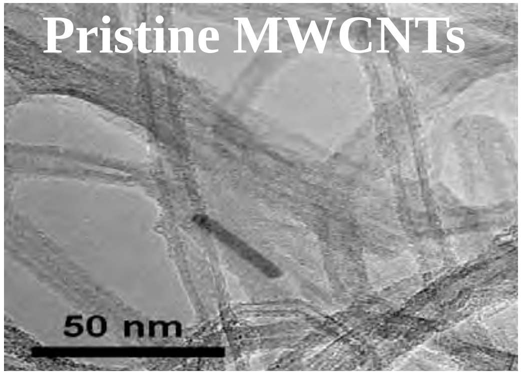




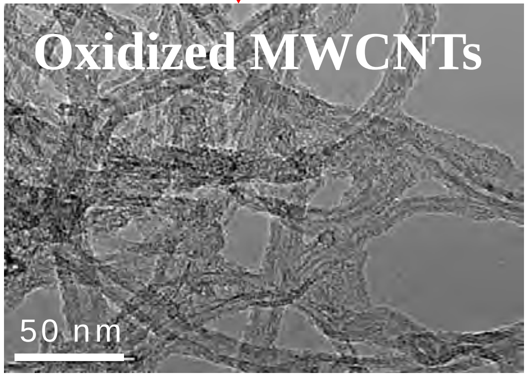
Physical Characterization:

CNTs Before and After Oxidation with HNO_3:

Transmission **E**lectron **M**icroscopy



MWCNTs remain structurally intact



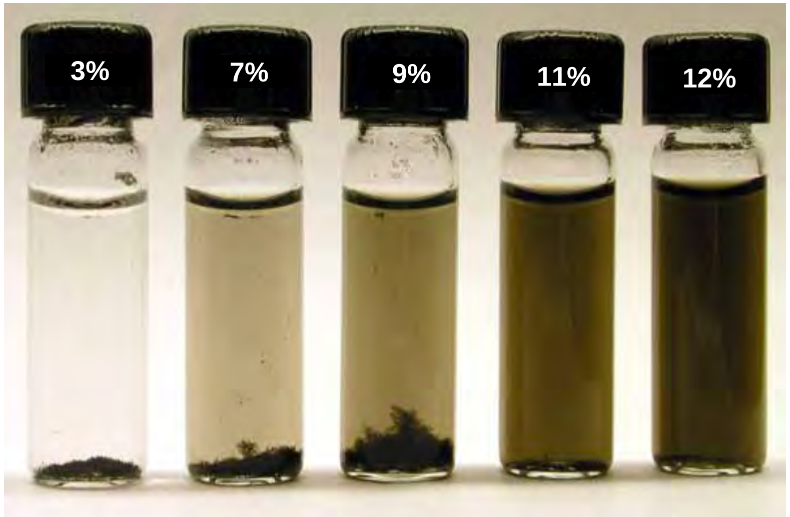
BET-Surface Area

Sorbent	Treatment	Surface oxygen (%)	BET-SA (m^2/g)
NC1	-	23.0	46.0 0.2
GAC	-	8.0	1,004.0 1.0
Pristine MWCNT	-	**2.1**	**270.2 0.4**
O-MWCNT	**HNO_3 (35%)**	**5.9**	**270.3 0.6**
″	**HNO_3 (53%)**	**6.9**	**283.3 0.8**
″	**HNO_3 (70%)**	**9.5**	**255.4 0.5**
″	**HNO_3 (70%)_F[a]**	**4.3**	**261.2 0.4**
″	H_2SO_4/HNO_3-C[b]	6.1	210.4 0.3
″	H_2SO_4/HNO_3	10.6	199.8 0.7
″	ml /H_2SO_4/HNO_3-C[b]	10.8	254.9 0.8

[a] F means that the MWCNTs were treated in the furnace at 400 °C.

[b] C represents commercial samples

Initial Observations of Stability

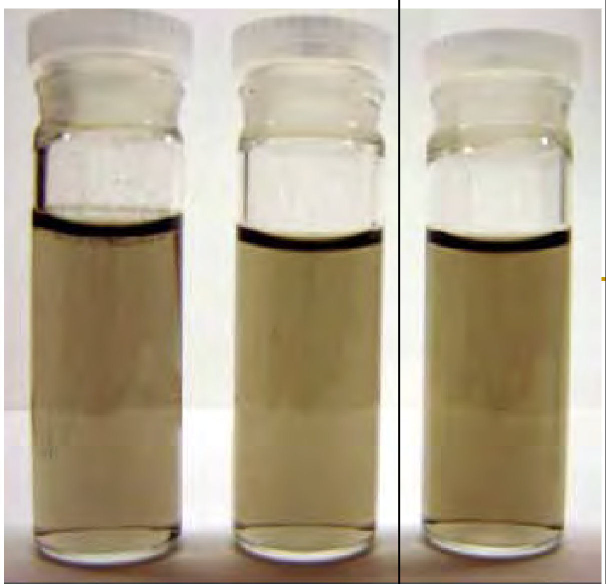


Increasing Aquatic Stability

Colloids

But sometimes oxidation is not a perfect metric

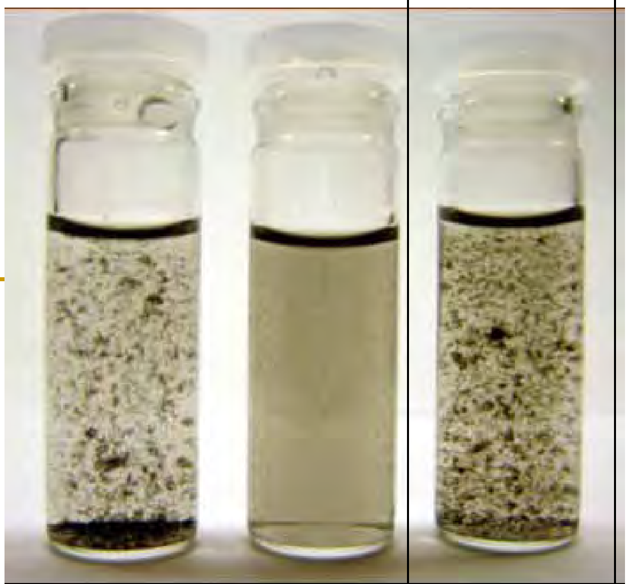
t_0



4 % | 8 % | 9 %

0.07M NaCl

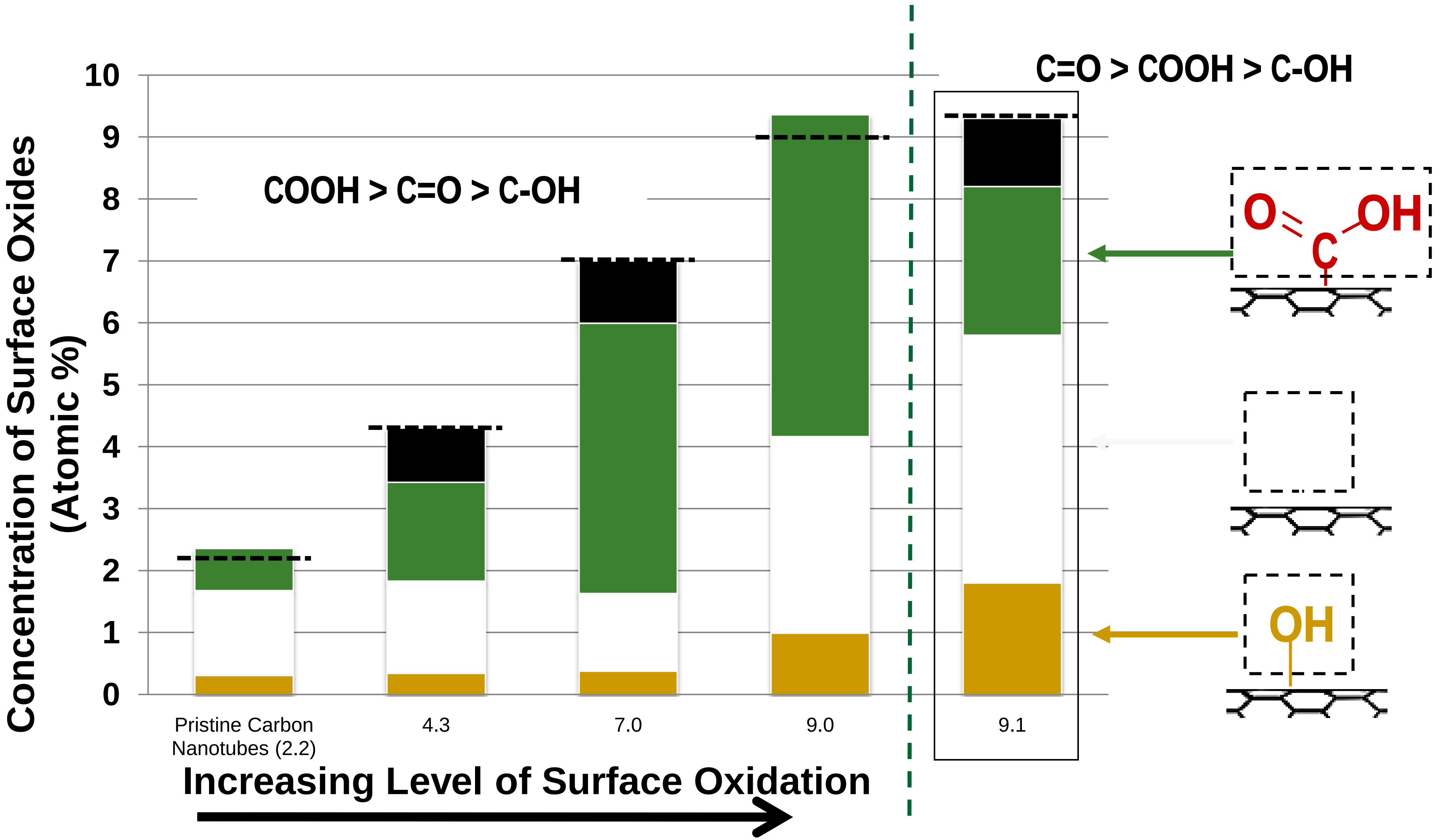
t_{120}



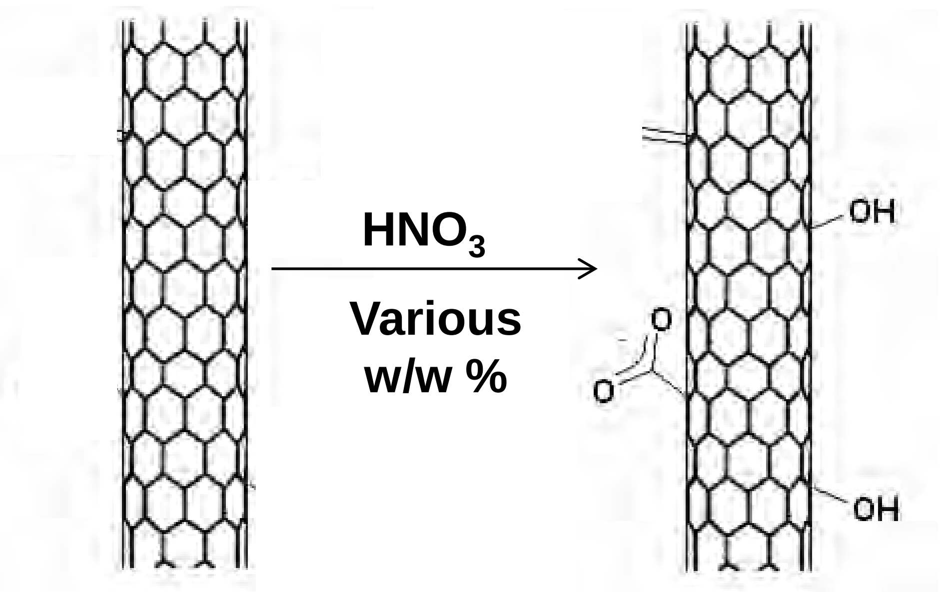
4 % | 8 % | 9 %

Increasing Surface Oxidation

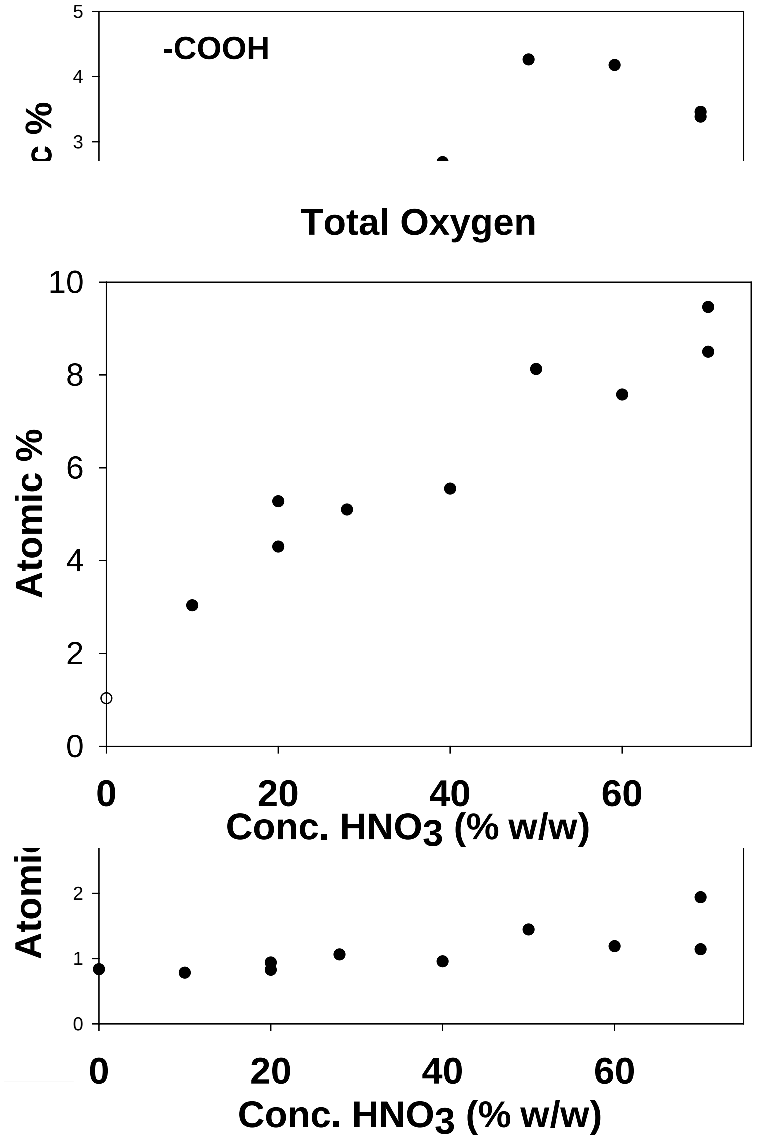
Distribution of Hydroxyl, Carbonyl and Carboxylic Acid Groups on CNTs



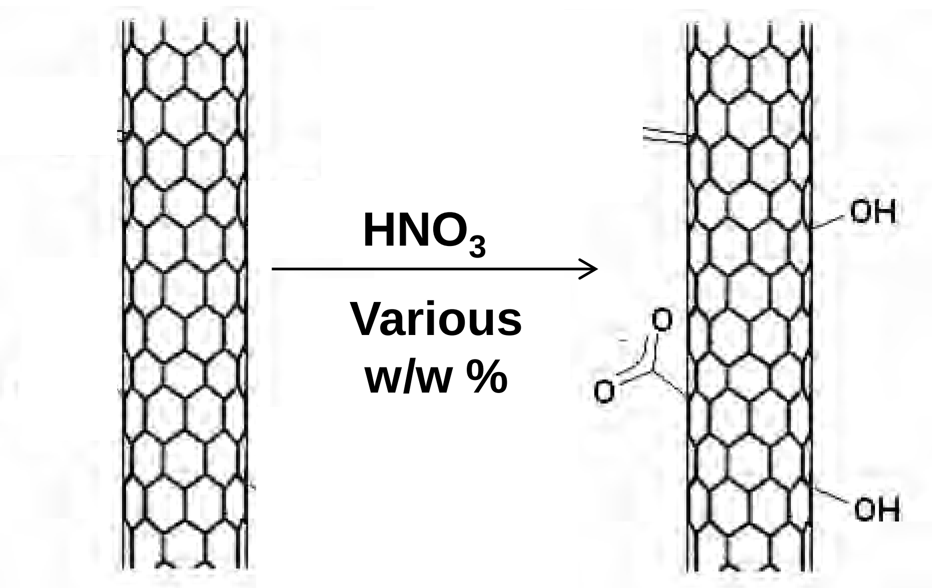
Influence of Oxidizing Conditions



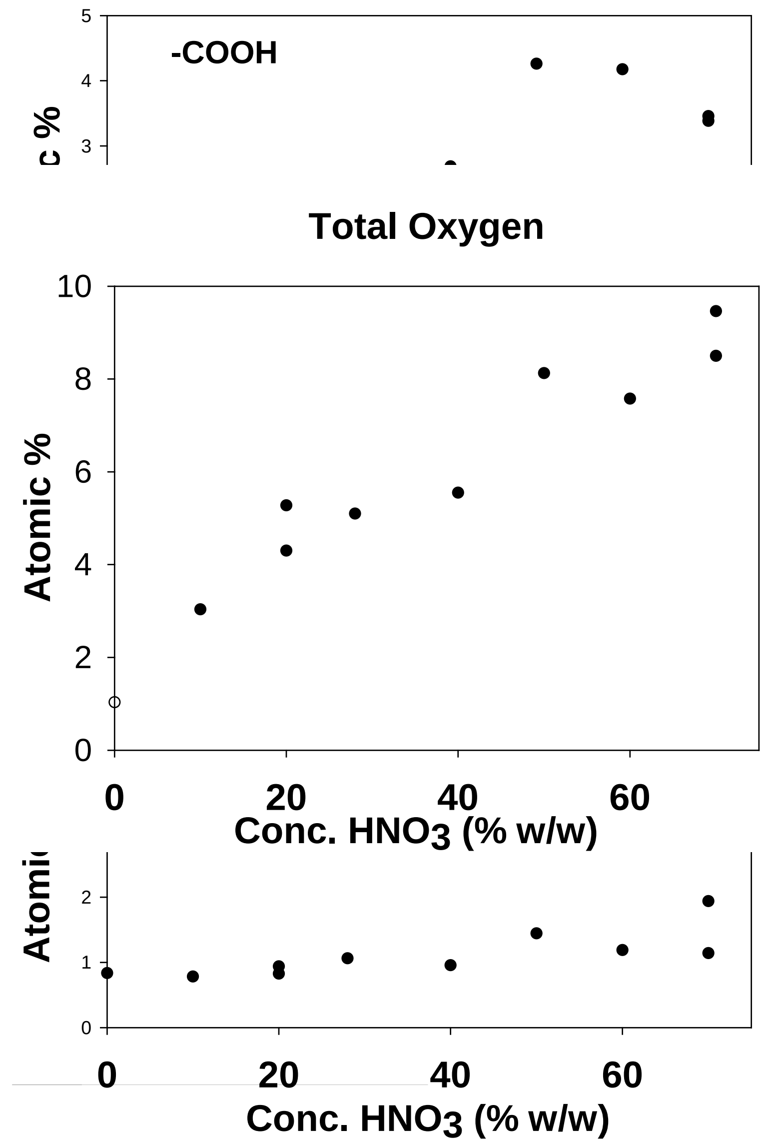
Functional Groups



Influence of Oxidizing Conditions

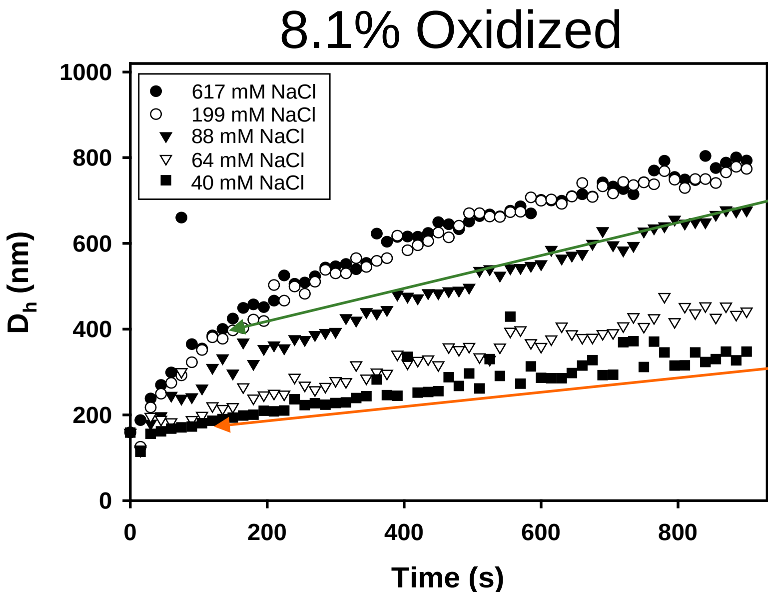


Functional Groups



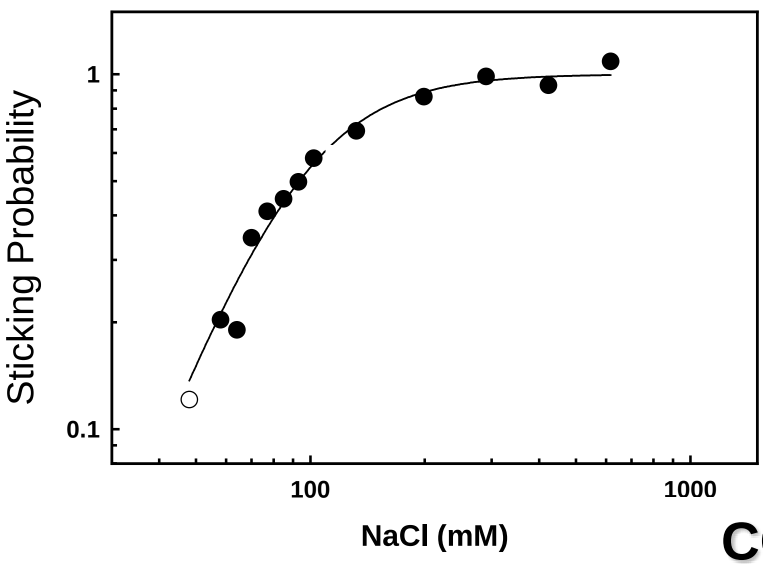
Influence of Surface Oxidation and Water Chemistry on Homogeneous Aggregation

Kinetics with Dynamic Light Scattering



$$\frac{dD_h}{dTime} = k_{agg,fast}N_o$$

$$\frac{dD_h}{dTime} = k_{agg}N_o$$

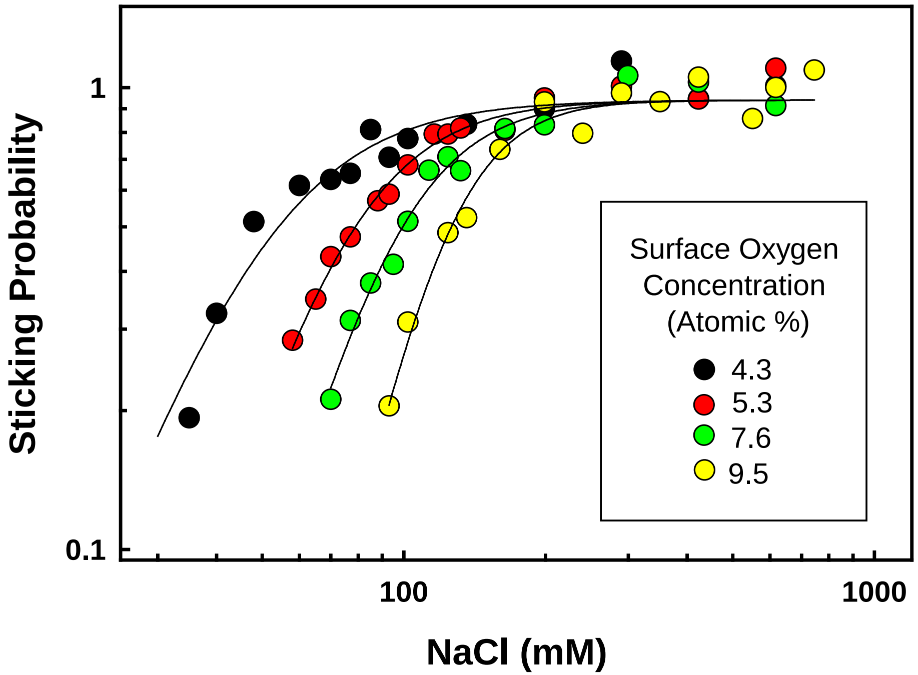


$$\text{Sticking Probability} = \frac{\frac{dD_h}{dTime} \sim k_{agg}N_o}{\frac{dD_h}{dTime} \sim k_{agg,fast}N_o}$$

$$\text{Sticking Probability} = \frac{1}{1+([CCC]/[NaCl])^b}$$

CCC provides a mathematical metric for colloidal stability

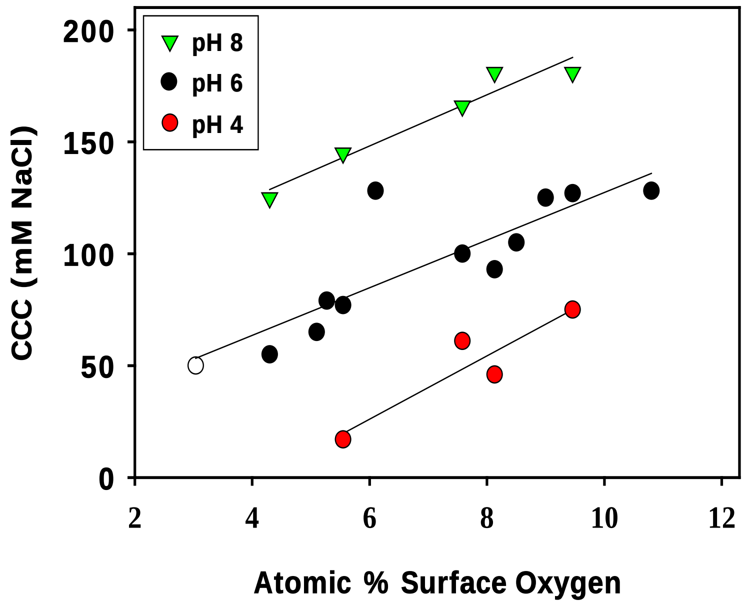
Stability and The CCC

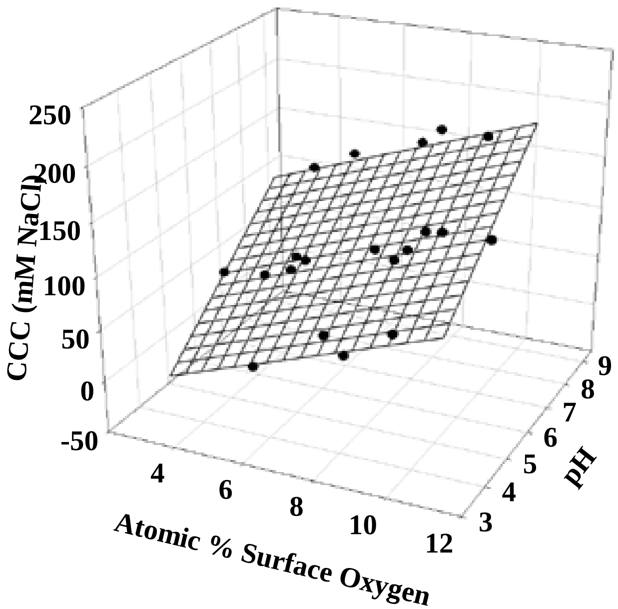


Stability profiles for several oxidized MWCNTs

$$\textbf{Sticking Probability} = \frac{1}{1 + ([CCC]/[NaCl])^b}$$

Surface Oxidation, the CCC and pH



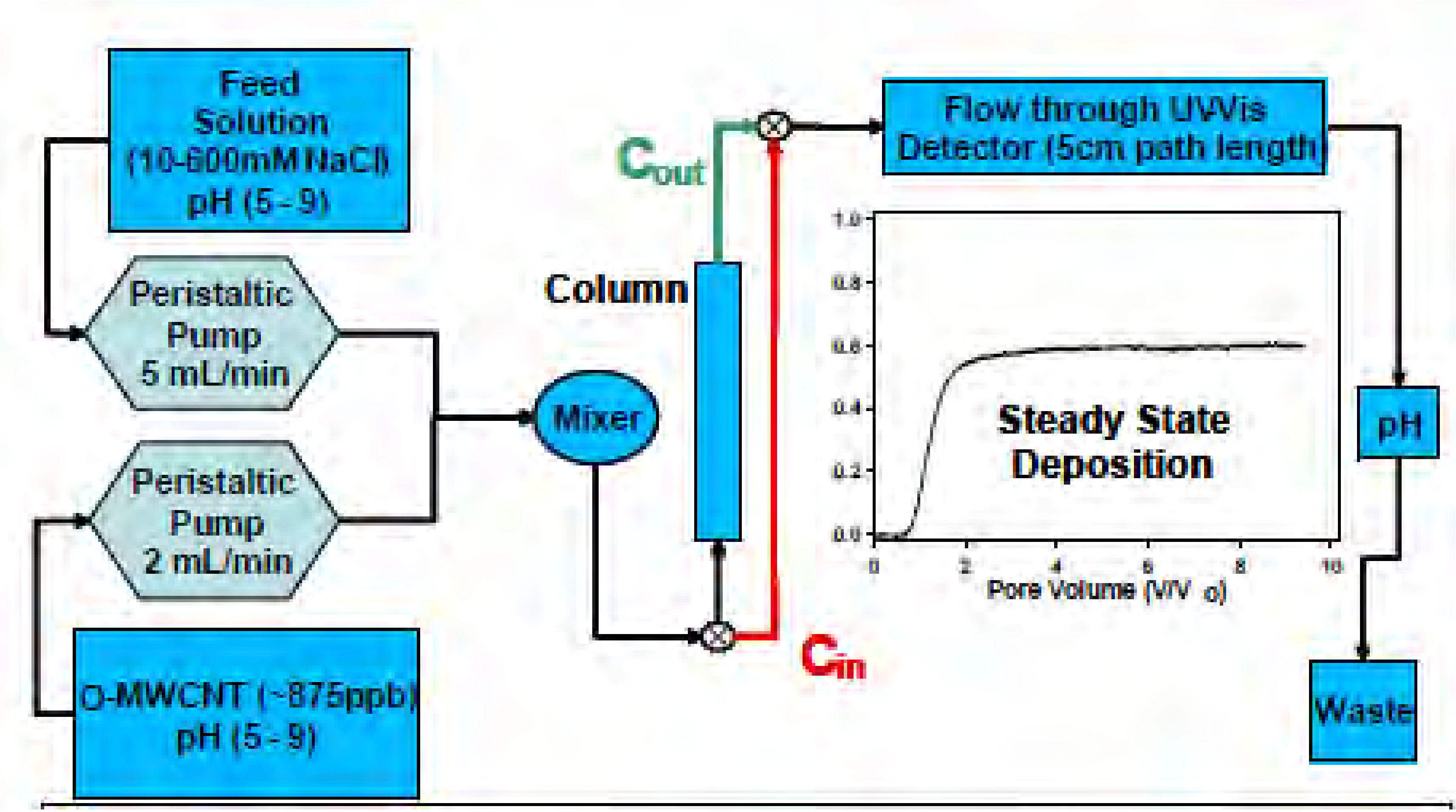


Total oxidation provides a good metric for colloidal stability

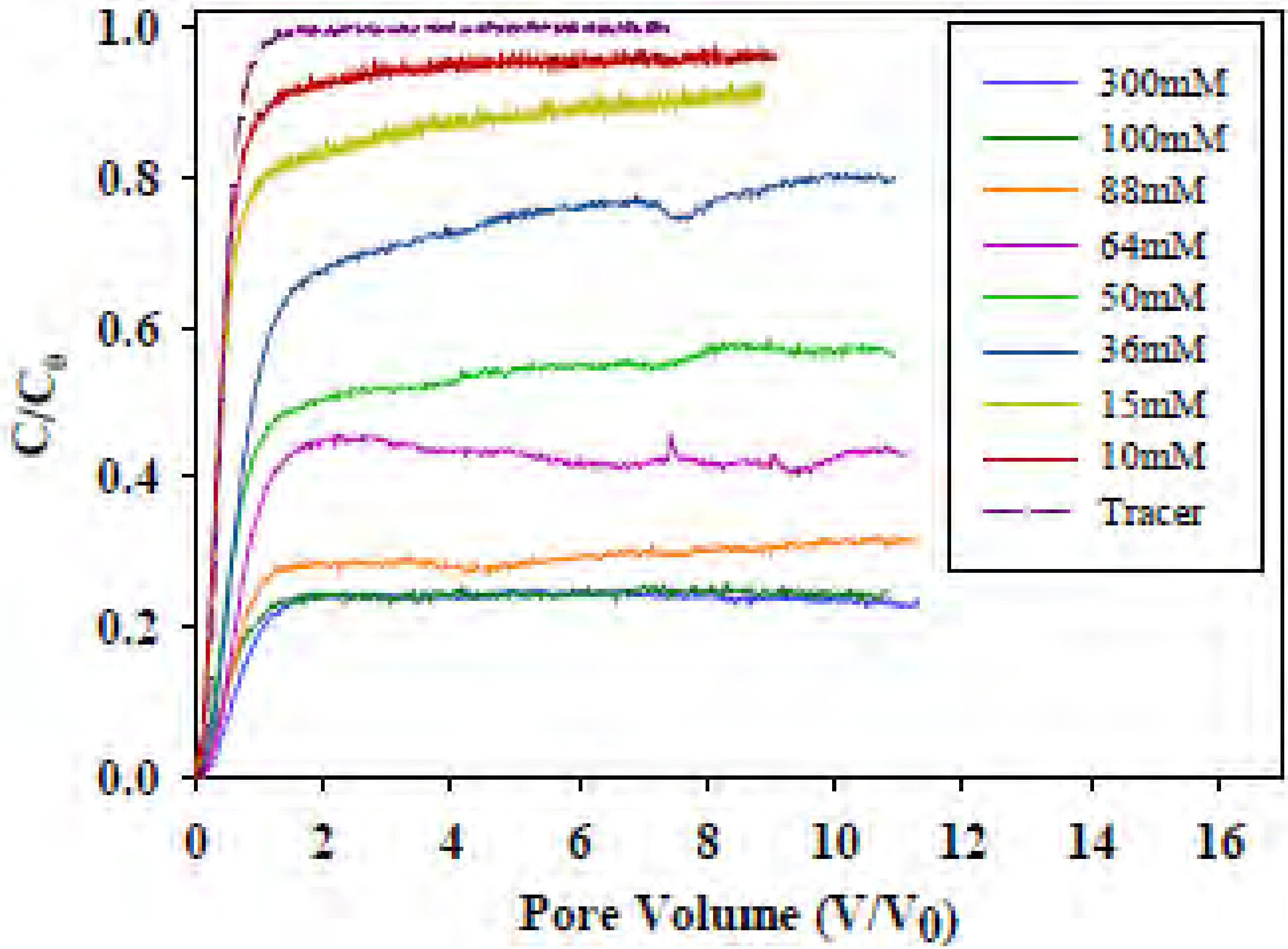
Measurements of materials properties can be used to predict colloidal properties

Influence of Surface Oxidation and Water Chemistry on Deposition

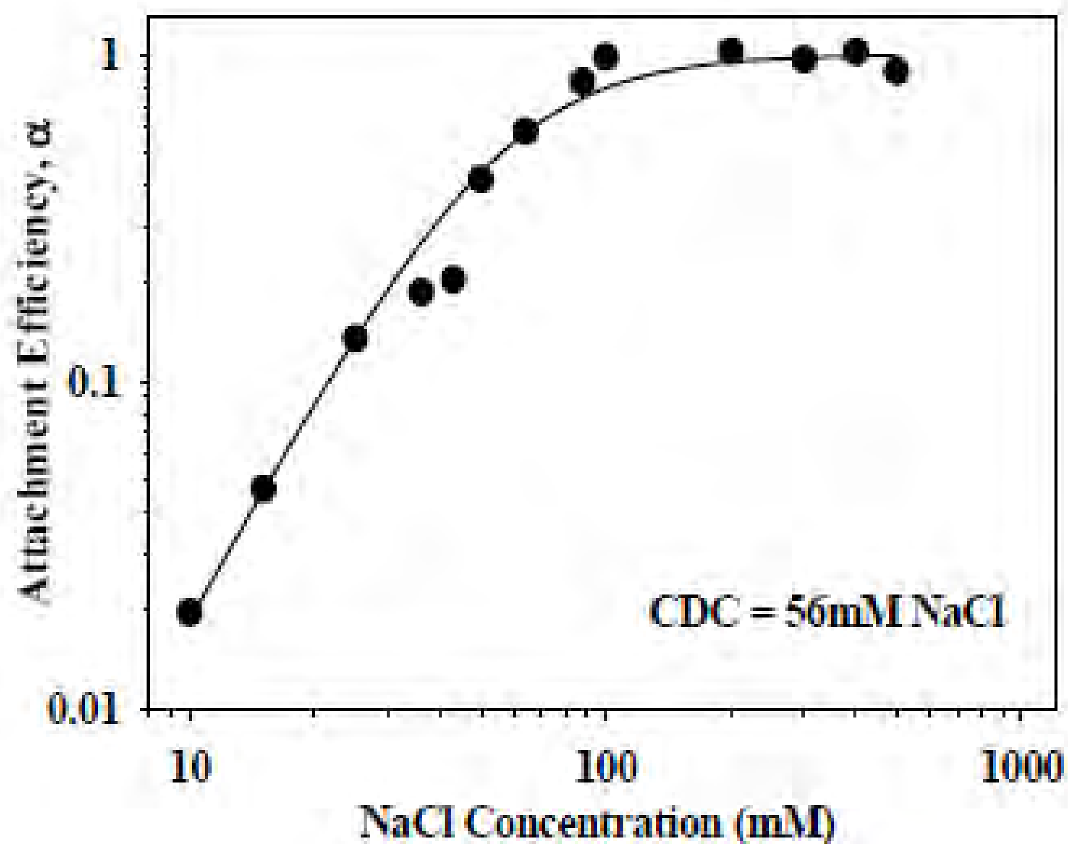
Studying Deposition in Porous M



O-MWCNT Transport as Function of NaCl Concentration (pH 7.0; oxidized with 30% HNO_3)



O-MWCNT "Sticking Probability" as Function of NaCl (pH 7.0; oxidized with 30% HNO_3)



Influence of Surface Oxidation and Water Chemistry on Sorption Properties with Respect to HOCs and Metals

Naphthalene sorption with MWCNTs
(Cho et al., *ES&T*, 2008)

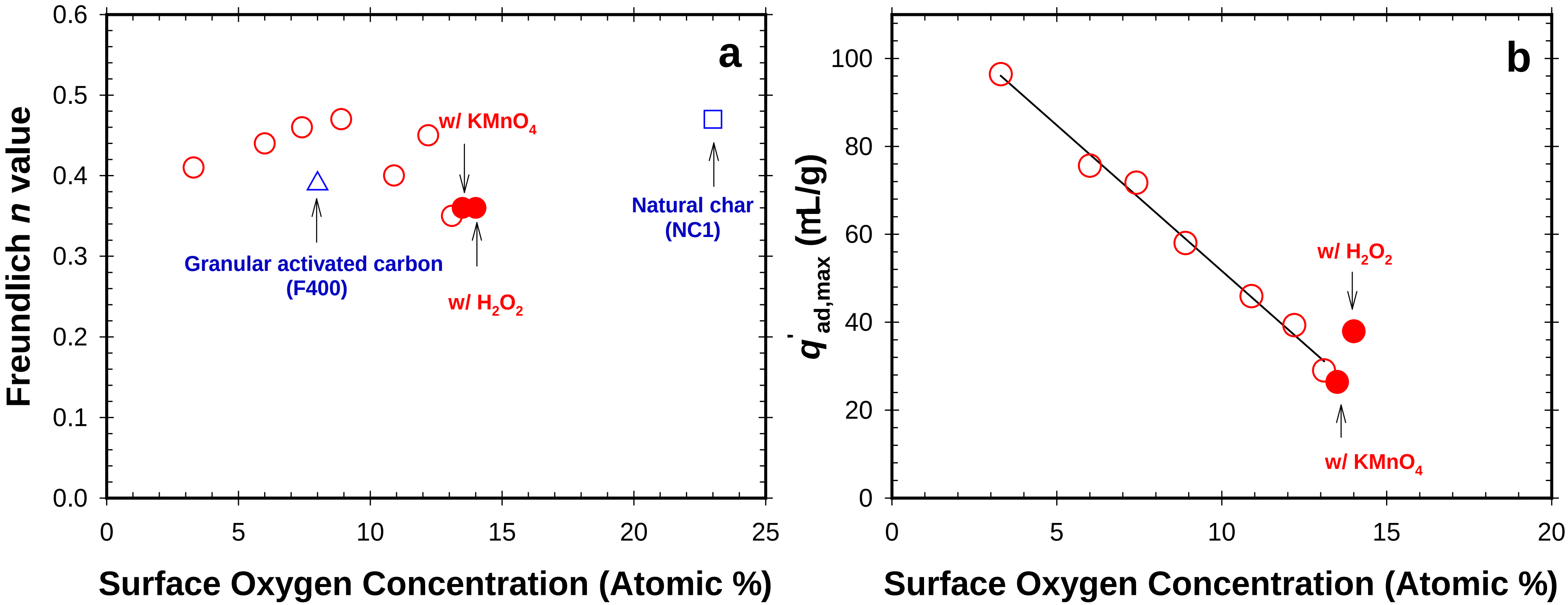
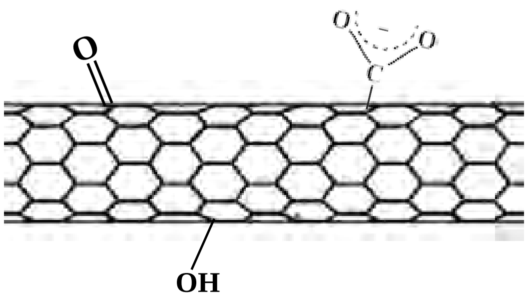


Figure 4. (a) Freundlich *n*-values for naphthalene adsorption plotted against surface oxygen concentration for MWCNTs, natural char (NC1), and granular activated carbon (F400). (b) Maximum adsorption capacity ($q'_{ad,max}$) for naphthalene from the Polanyi-based Dubinin-Astikov adsorption model plotted against surface oxygen concentration.

Sorption of Inorganic Contaminants (Metal Cations)

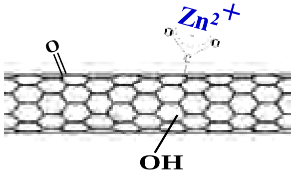


$\xrightarrow{M^{2+}_{(aq)}}$?

$M^{2+}_{(aq)}$ e.g.: Cd^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}

Comparison of Zn(II) Sorption:

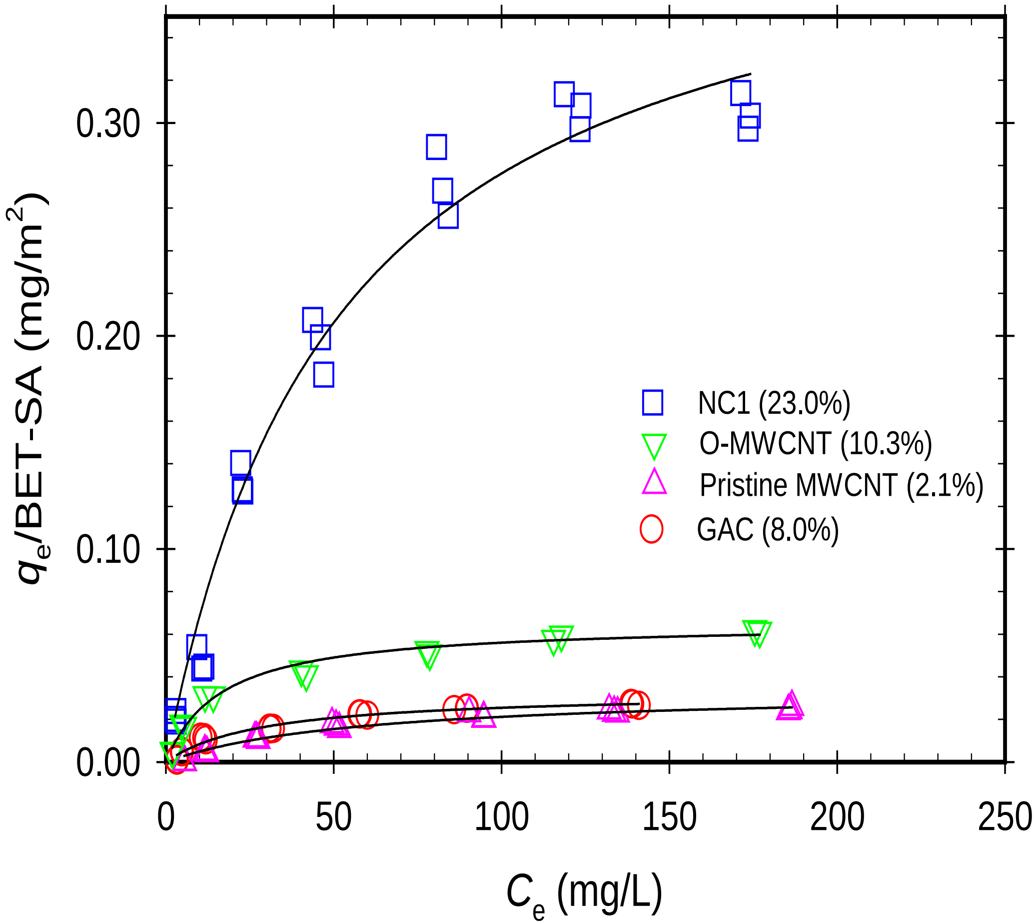
Carbonaceous Materials



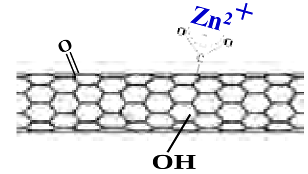
$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

q_{max} (mg/g)	SA	Oxid.
GAC (33.1)	High	Mod.
NC1 (20.5)	Low	High
O-MWCNT (17.6)	Mod.	Mod.
MWCNT (9.1)	Mod.	Low

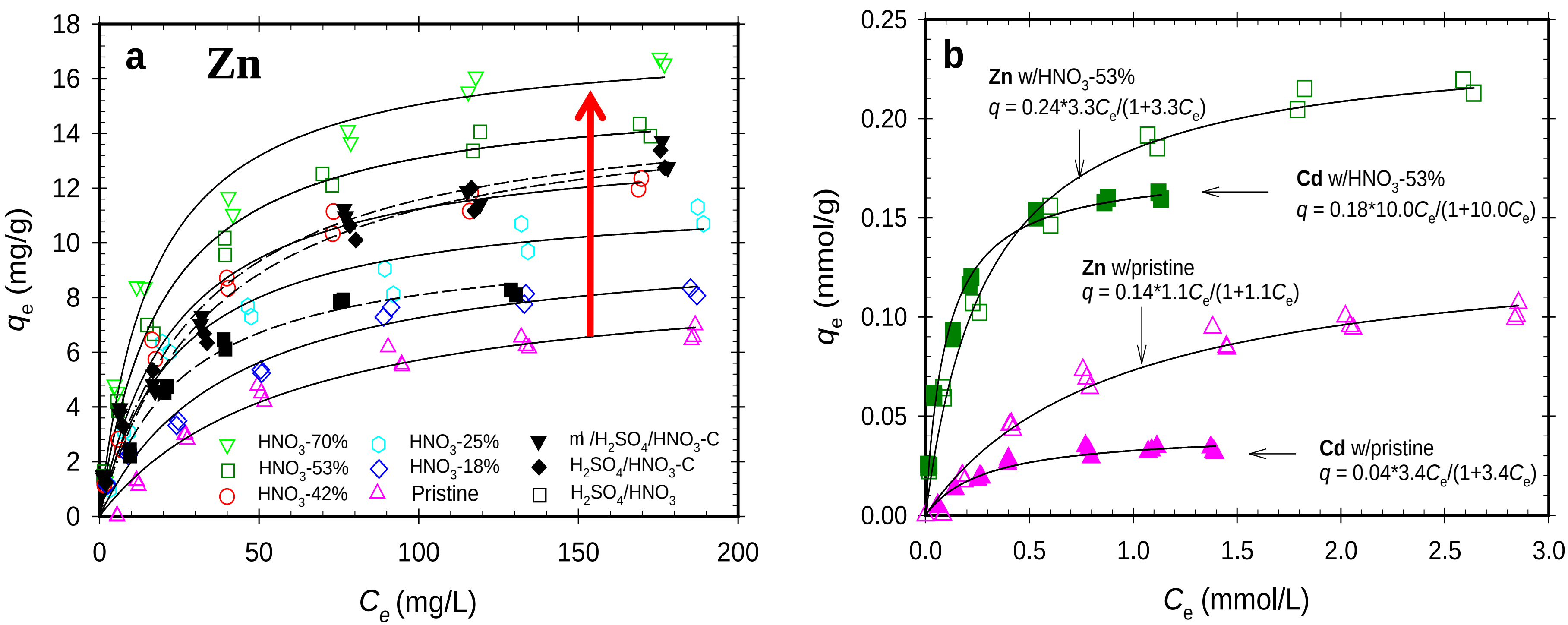
q_{max} /SA (mg/m²)	SA	Oxid.
NC1 (0.42)	Low	High
O-MWCNT (0.065)	Mod.	Mod.
MWCNT (0.034)	Mod.	Low
GAC (0.033)	High	Mod.



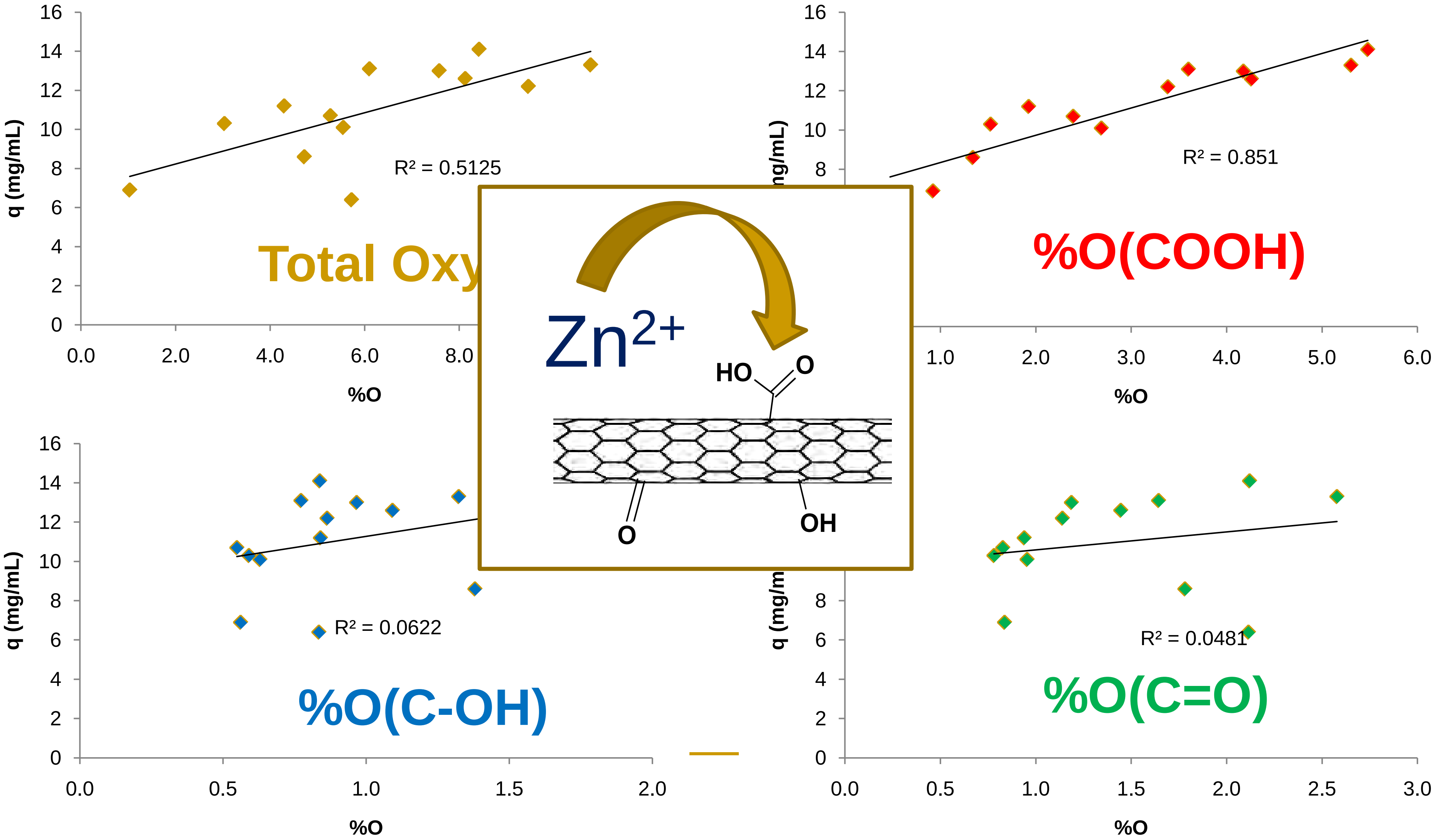
Effect of Surface Oxidation:



Zn(II) and Cd(II) sorption isotherms



Correlation of $q_{e,180}$ with Selected Surface Functional Groups:



Langmuir Two-Site Model:

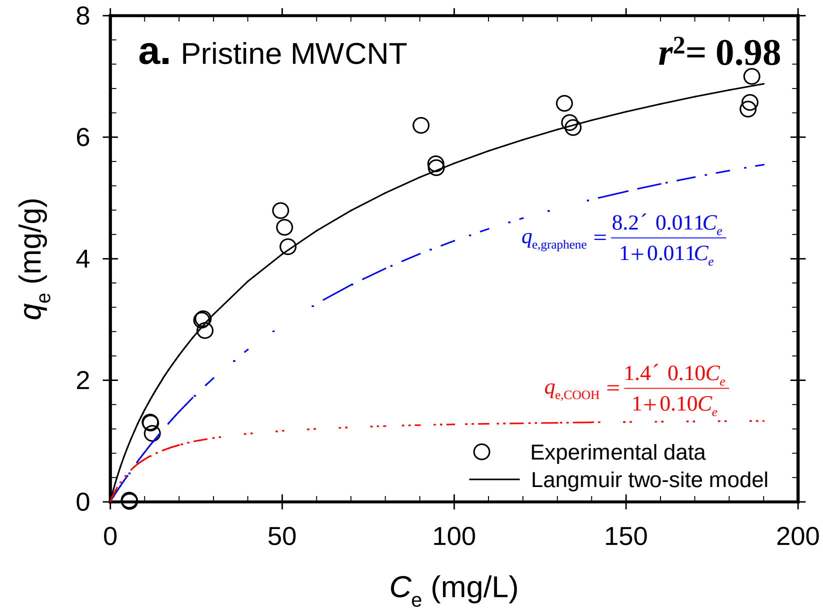
Individual fits

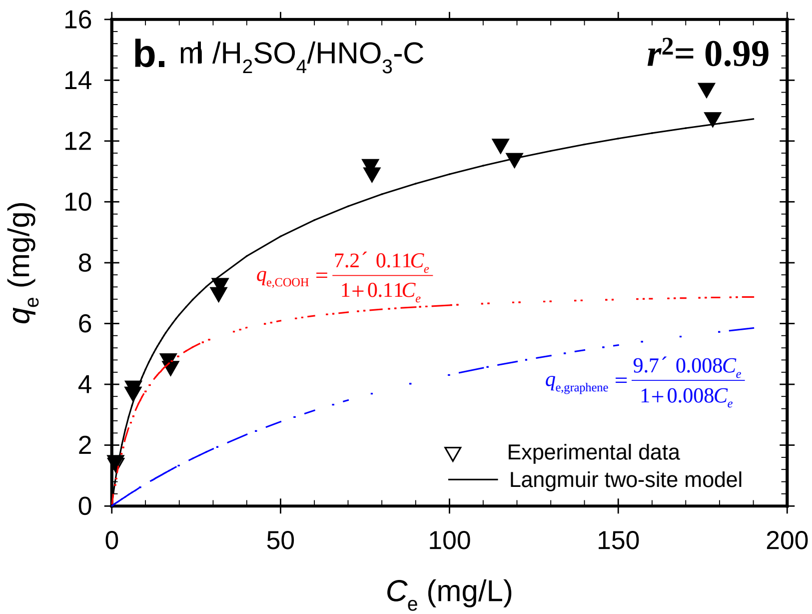
$$q_e = q_{e,Graphene} + q_{e,COOH}$$

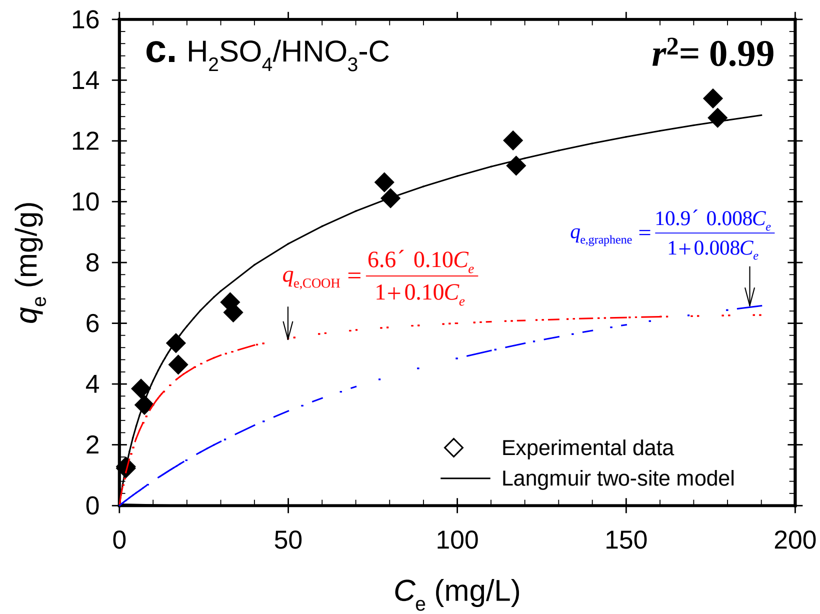
$$= \frac{q_{max,G} K_{L,G} C_e}{1 + K_{L,G} C_e} + \frac{q_{max,C} K_{L,C} C_e}{1 + K_{L,C} C_e}$$

$K_{L,G} = 0.008 \sim 0.010$

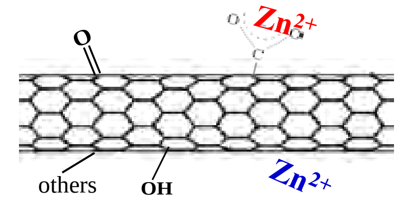
$K_{L,C} = 0.10 \sim 0.11$





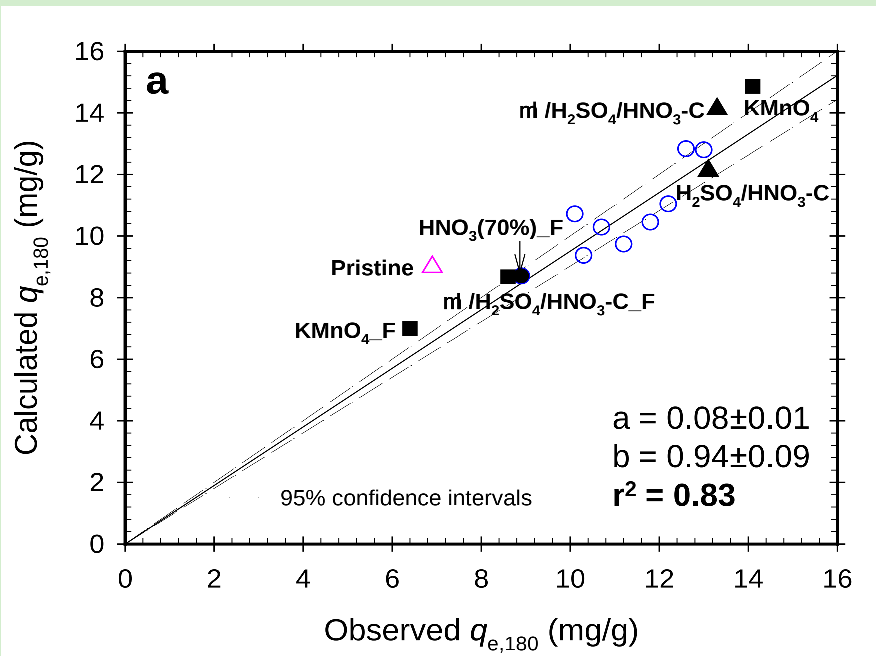


Correlation of $q_{e,180}$ with Multiple Surface Functional Groups:



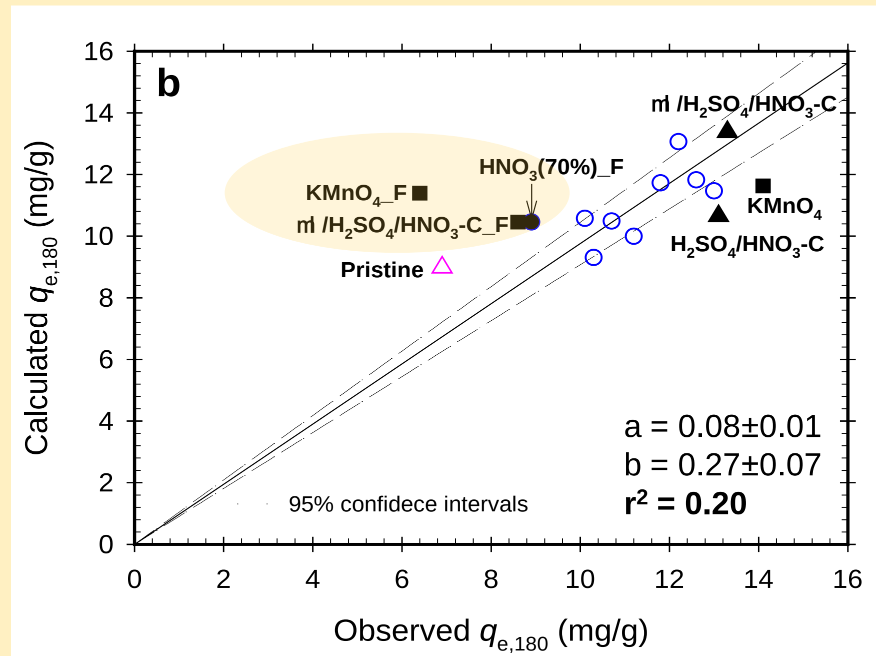
Multiple-linear regression analysis

$$q_{e,180} = 0.08[\%C_{Graphene}] + 0.94[\%C_{COOH}]$$



F value= 1.04

$$q_{e,180} = 0.08[\%C_{Graphene}] + 0.27[\%C_{OT}]$$



F value= 4.45

Modeling of Cd(II) Sorption:

Two-Site Langmuir isotherm model (in single-solute system):

$$q_e = q_{e,Graphene} + q_{e,COOH} = \frac{q_{\max,\mathrm{G}} K_{\mathrm{L,G}} C_e}{1 + K_{\mathrm{L,G}} C_e} + \frac{q_{\max,\mathrm{C}} K_{\mathrm{L,C}} C_e}{1 + K_{\mathrm{L,C}} C_e}$$

q_e : adsorbed concentration at equilibrium (mmol/g)

C_e : aqueous concentration at equilibrium (mmol/L)

$K_{L,G}$, $K_{L,C}$: adsorption affinities (L/mmol) for graphenic and carboxyl group sites

$q_{max,G}$, $q_{max,C}$: maximum adsorption capacity (mmol/g) for graphenic and carboxyl group sites

Langmuir Two-Site Model:

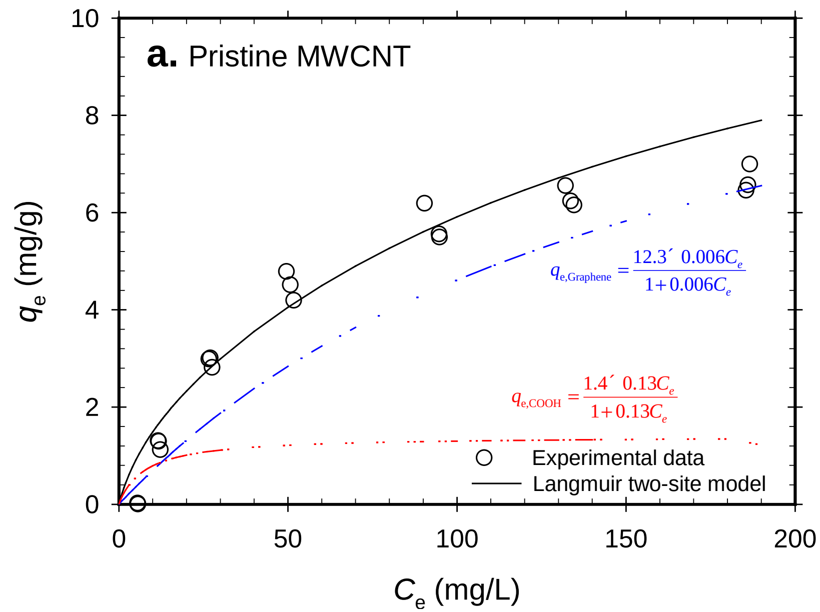
Common $K_{L,G}$, $K_{L,C}$, a, and b:

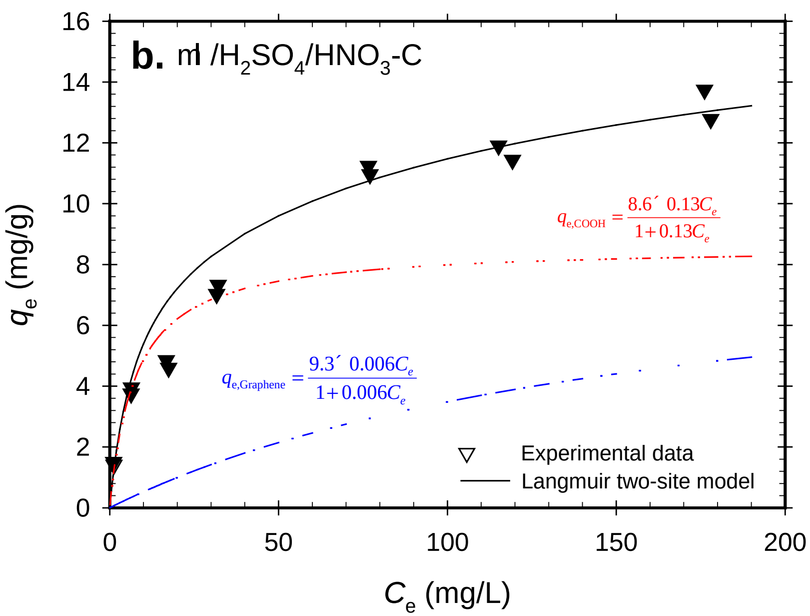
$$q_{e,180} = a[\%C_{Graphene}] + b[\%C_{COOH}]$$

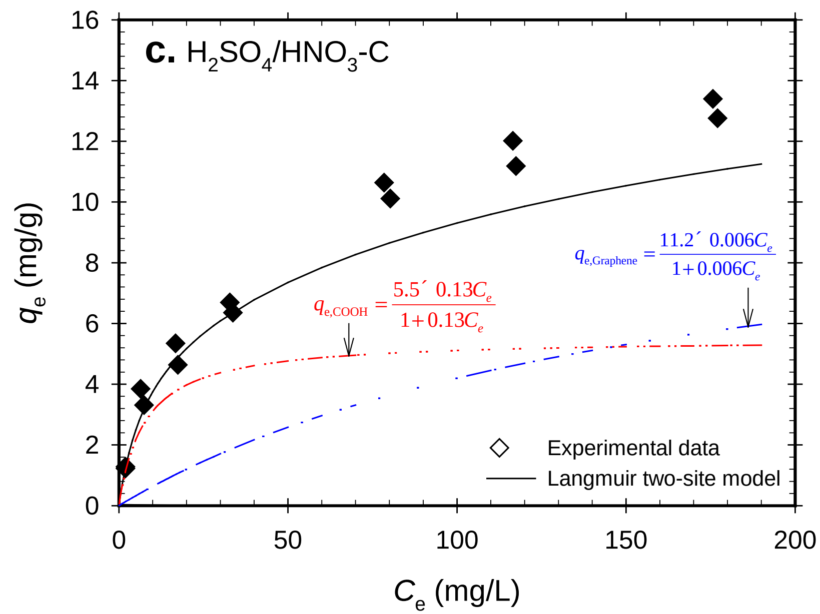
$$q_e = \frac{q_{max,G} K_{L,G} C_e}{1 + K_{L,G} C_e} + \frac{q_{max,C} K_{L,C} C_e}{1 + K_{L,C} C_e}$$

$$if\ C_e = ¥, \quad \boldsymbol{a} = \frac{q_{max,G}}{[\%C_{Graphene}]}, \ \boldsymbol{b} = \frac{q_{max,COOH}}{[\%C_{COOH}]}$$

$\mathbf{K_{L,G} = 0.006, K_{L,C} = 0.13, \ \mathit{a} = 0.13, \mathit{b} = 0.94}$







Modeling of competitive sorption of Cd(II):

Competitive Two-Site Langmuir isotherm model (in binary-solute system):

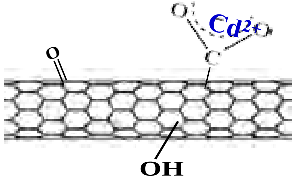
$$q_e = \frac{q_{\max,\mathrm{G}} K_{\mathrm{L,G}} C_{e,Cd}}{1 + K_{\mathrm{L,G,Cd}} C_{e,Cd} + \boxed{K_{\mathrm{L,G,Co\text{-}sorbate}} C_{e,Co\text{-}sorbate}}} + \frac{q_{\max,\mathrm{C}} K_{\mathrm{L,C,Cd}} C_{e,Cd}}{1 + K_{\mathrm{L,C,Cd}} C_{e,Cd} + \boxed{K_{\mathrm{L,C,Co\text{-}sorbate}} C_{e,Co\text{-}sorbate}}}$$

Parameters for Langmuir isotherm equation for observed Cd(II) with co-sorbate sorption data

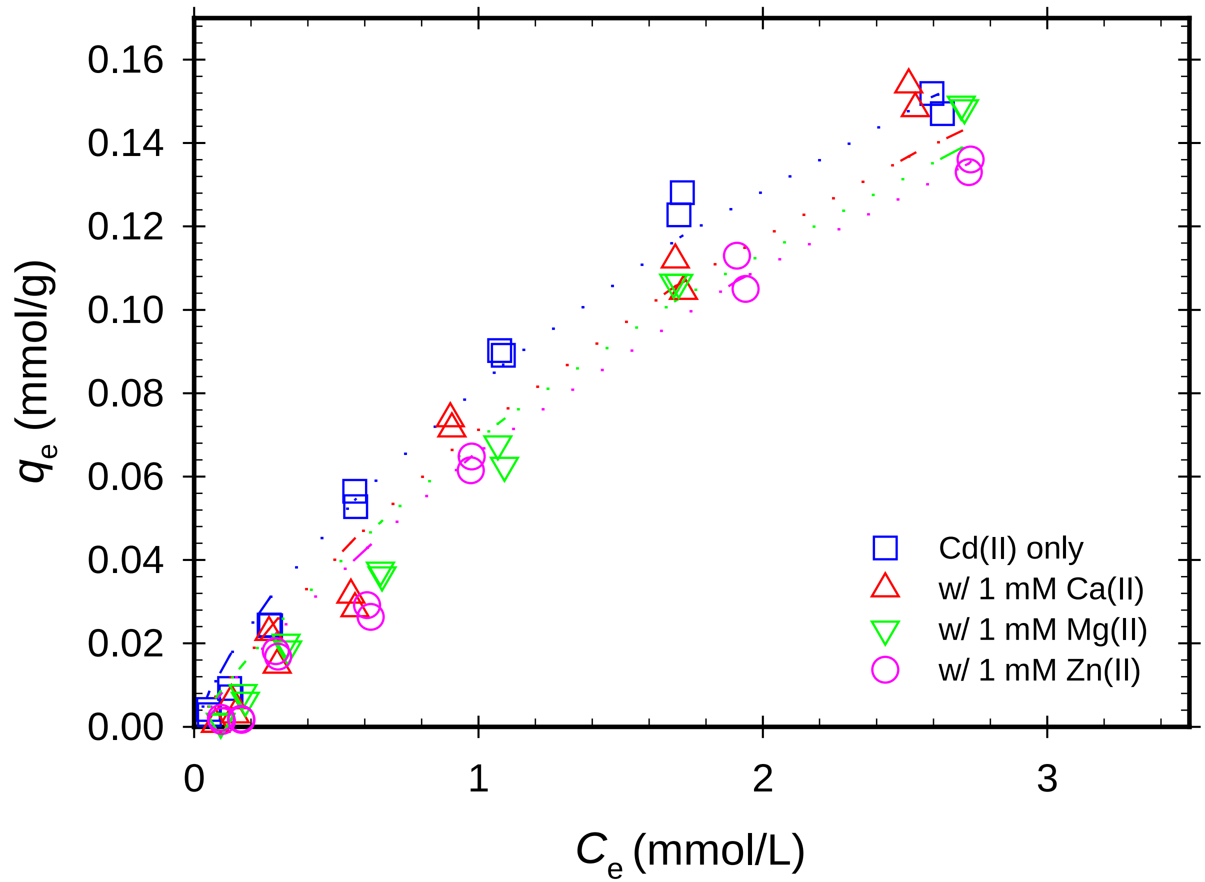
Sorbent	Surface Oxygen (%)	N	$q_{max,G}$ (mmol/g)	$q_{max,C}$ (mmol/g)	Cd $K_{L,G}$ (L/mmol)	Cd $K_{L,C}$ (L/mmol)	Zn $K_{L,G}$ (L/mmol)	Zn $K_{L,C}$ (L/mmol)	Ca $K_{L,G}$ (L/mmol)	Ca $K_{L,C}$ (L/mmol)	Mg $K_{L,G}$ (L/mmol)	Mg $K_{L,C}$ (L/mmol)	1/nå $(q_{mea}-q_{mod})^2$	r^2
Pristine MWCNT	2.1	56	0.36	0.016										0.98
O-MWCNT (H_2SO_4/HNO_3)	12.3	54	0.076	0.67										0.99
O-MWCNT (70%-HNO_3)	5.4	24	0.28	0.49	**0.23**	**5.61**	**0.20**	**6.87**	**0.10**	**3.37**	**0.18**	**4.06**	0.00011	0.99
Activated Carbon (F400)	8.0	28	0.24	0.22					-	-	-	-		0.99
Natural Char (NC1)	23.0	28	0.33	0.15					-	-	-	-		0.99

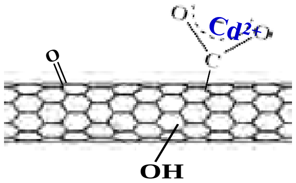
Sorption affinity for carboxyl group site ($K_{L,C}$): Zn > Cd > Mg > Ca

Competitive sorption of Cd(II):



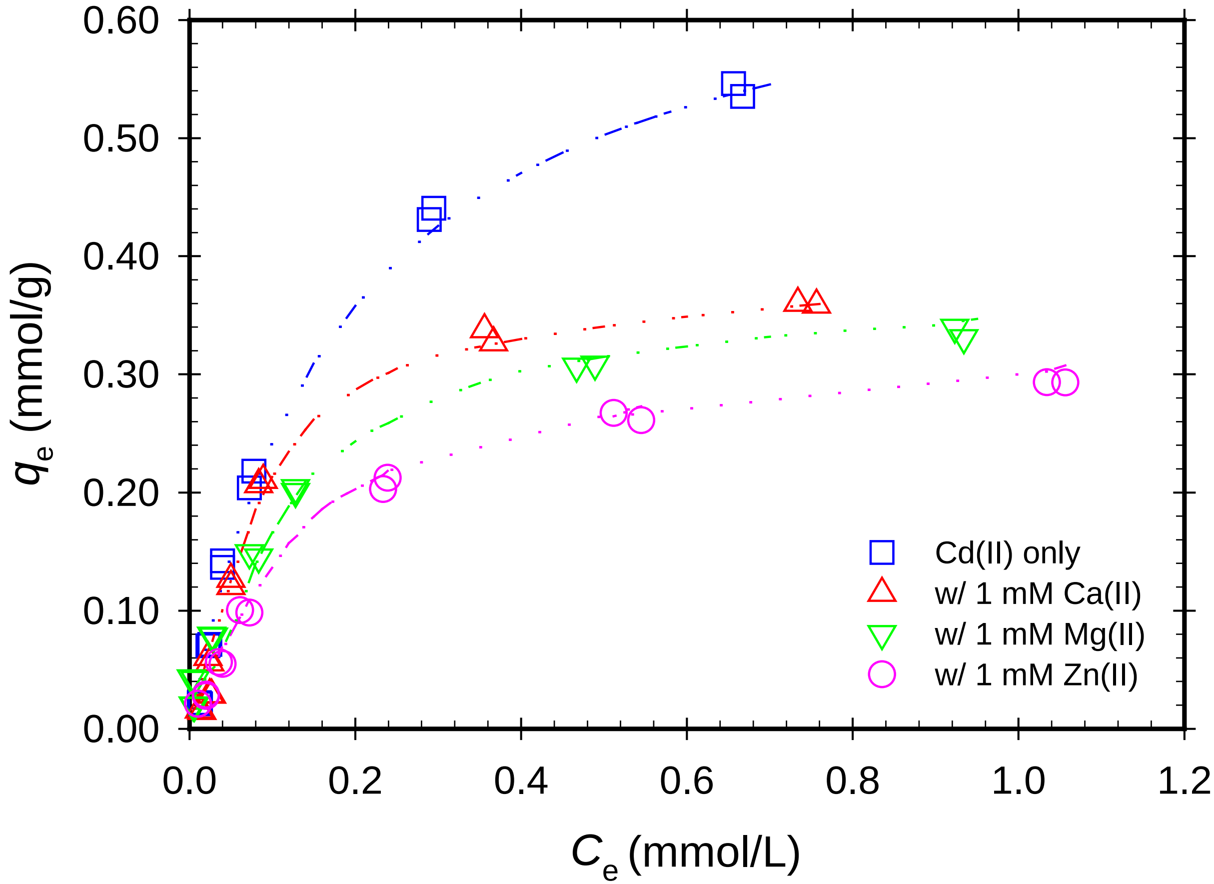
Pristine MWCNTs





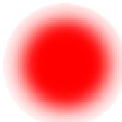
Competitive sorption of Cd(II):

Oxidized MWCNTs (H_2SO_4/HNO_3)



Thank You

Why are Colloids “stable/unstable” - (DLVO)



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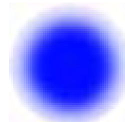

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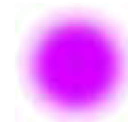
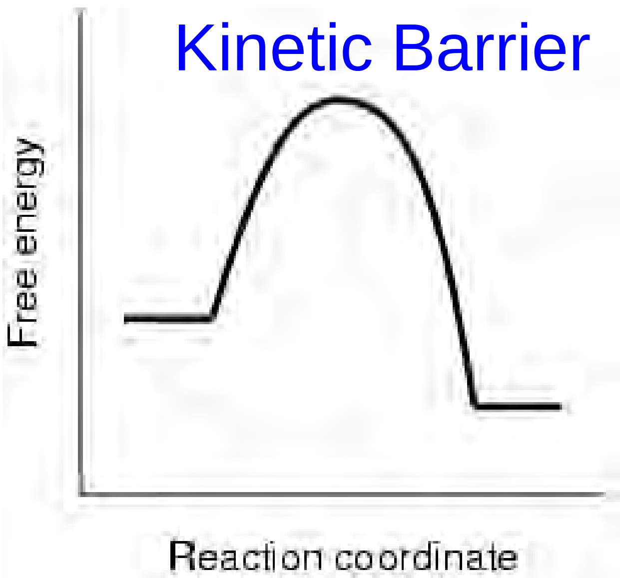
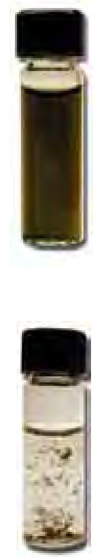
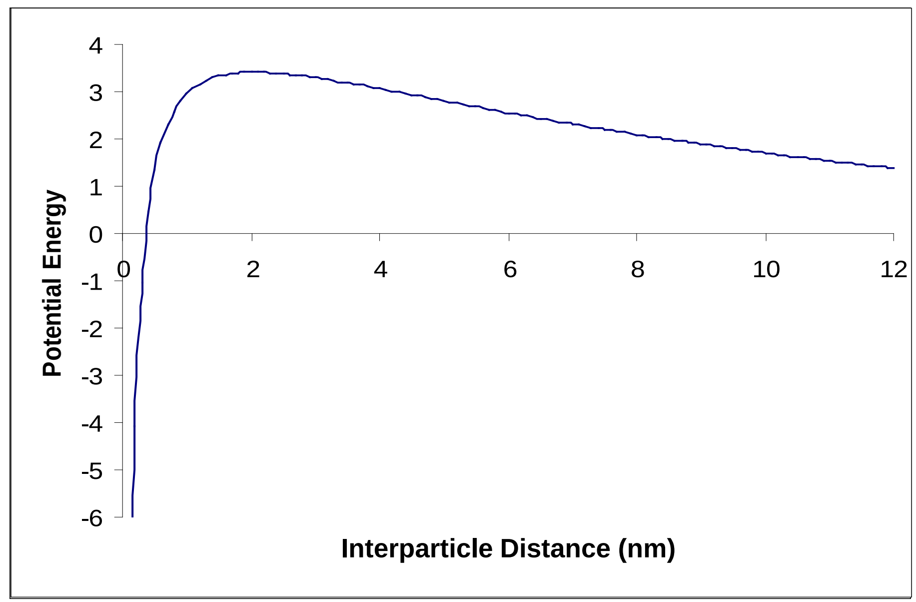


$Attractive_E$ $Repulsive_E$ $Total_E$

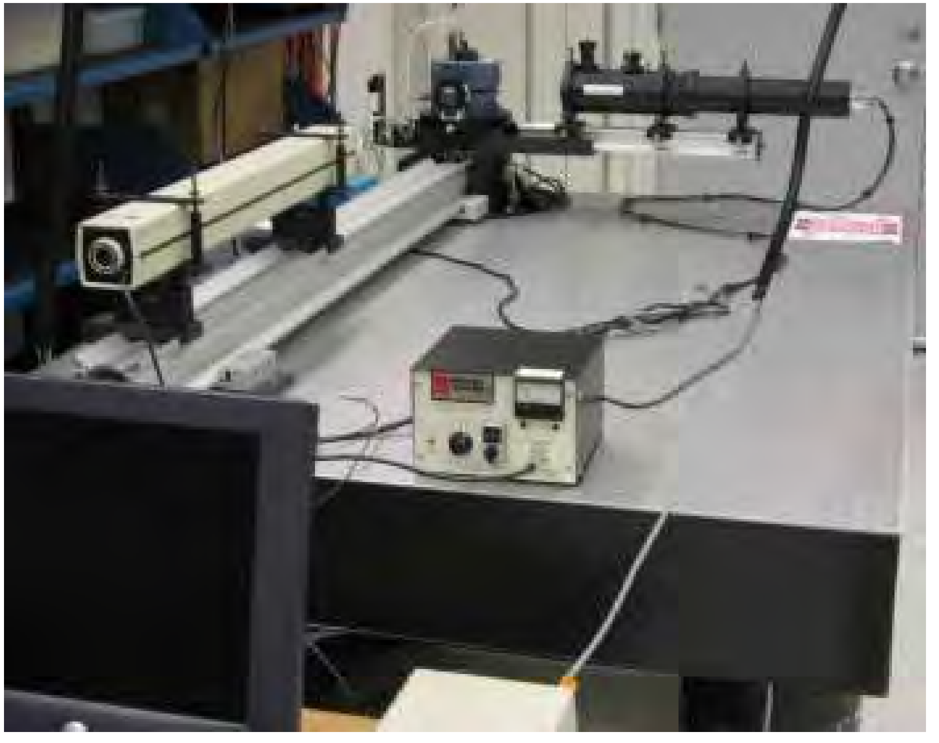






.001 M

Determining Particle Stability with Dynamic Light Scattering

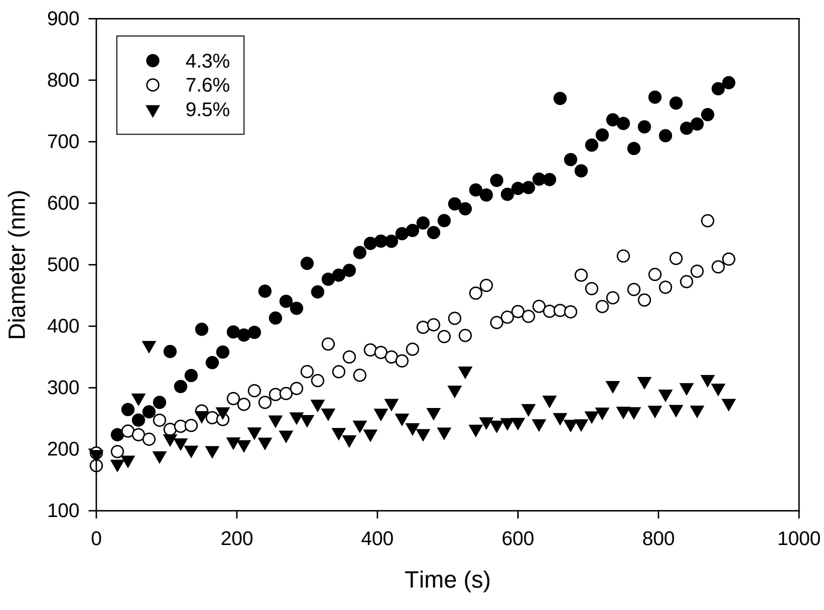


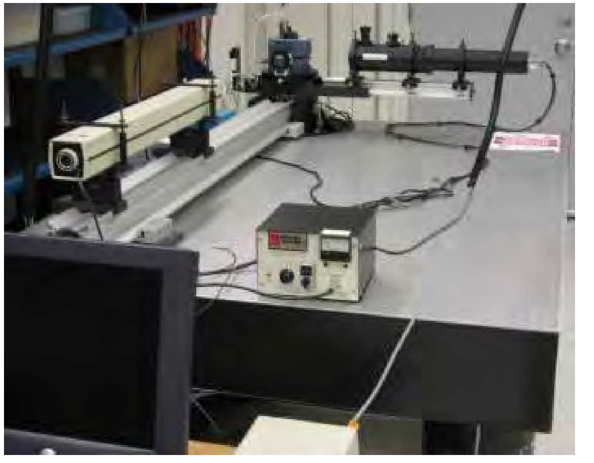
- As particles aggregate their scattering properties change
- DLS allows us to measure the rate of change

in the scattering properties ® aggregation rate

Kinetics with Dynamic Light Scattering

Time resolved particle size analysis

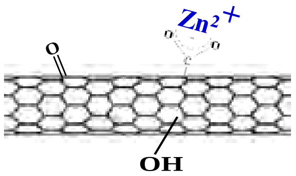




- pH = 6
- 64 mM NaCl
- 7.5 mg CNT/L

Comparison of Zn(II) Sorption:

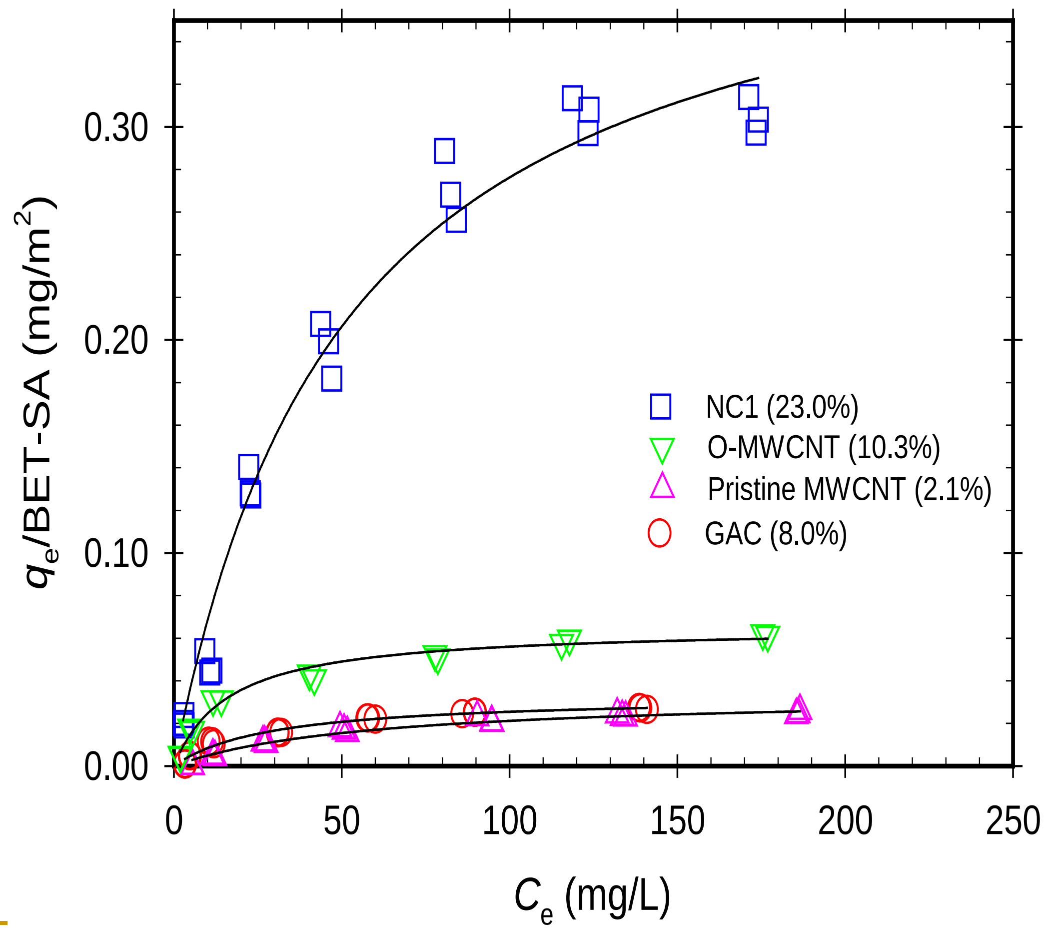
Carbonaceous Materials



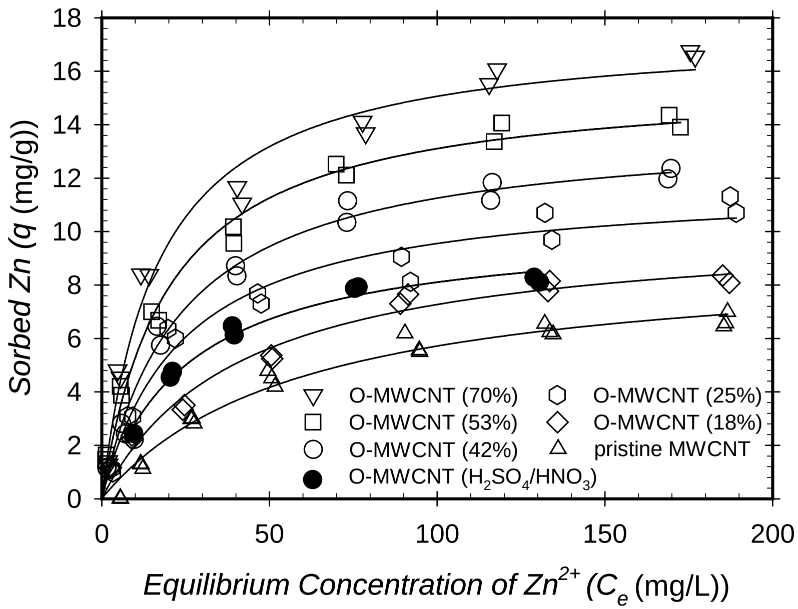
$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

q_{max} (mg/g)	SA	Oxid.
GAC (33.1)	High	Mod.
NC1 (20.5)	Low	High
O-MWCNT (17.6)	Mod.	Mod.
MWCNT (9.1)	Mod	Low

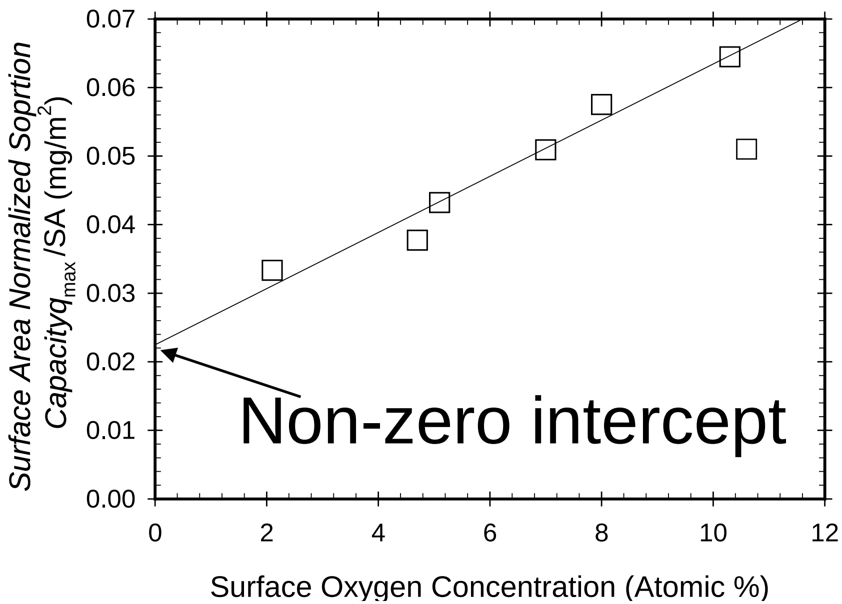
q_{max} /SA (mg/m²)	SA	Oxid.
NC1 (0.42)	Low	High
O-MWCNT (0.065)	Mod.	Mod.
MWCNT (0.034)	Mod.	Low
GAC (0.033)	High	Mod.



Sorption of Zn^{2+} onto MWCNTs

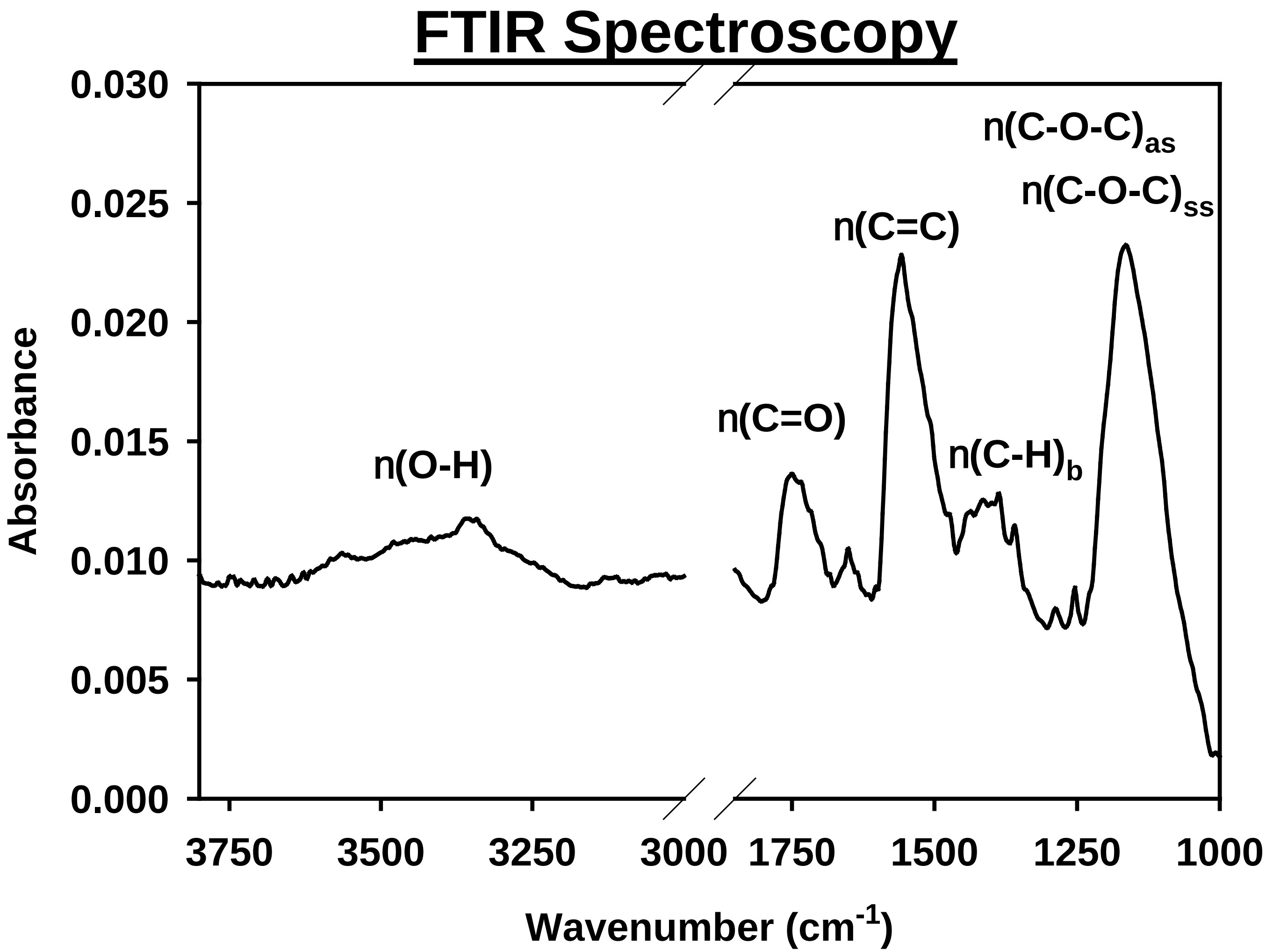


Adsorption of Zn^{2+} onto MWCNTs



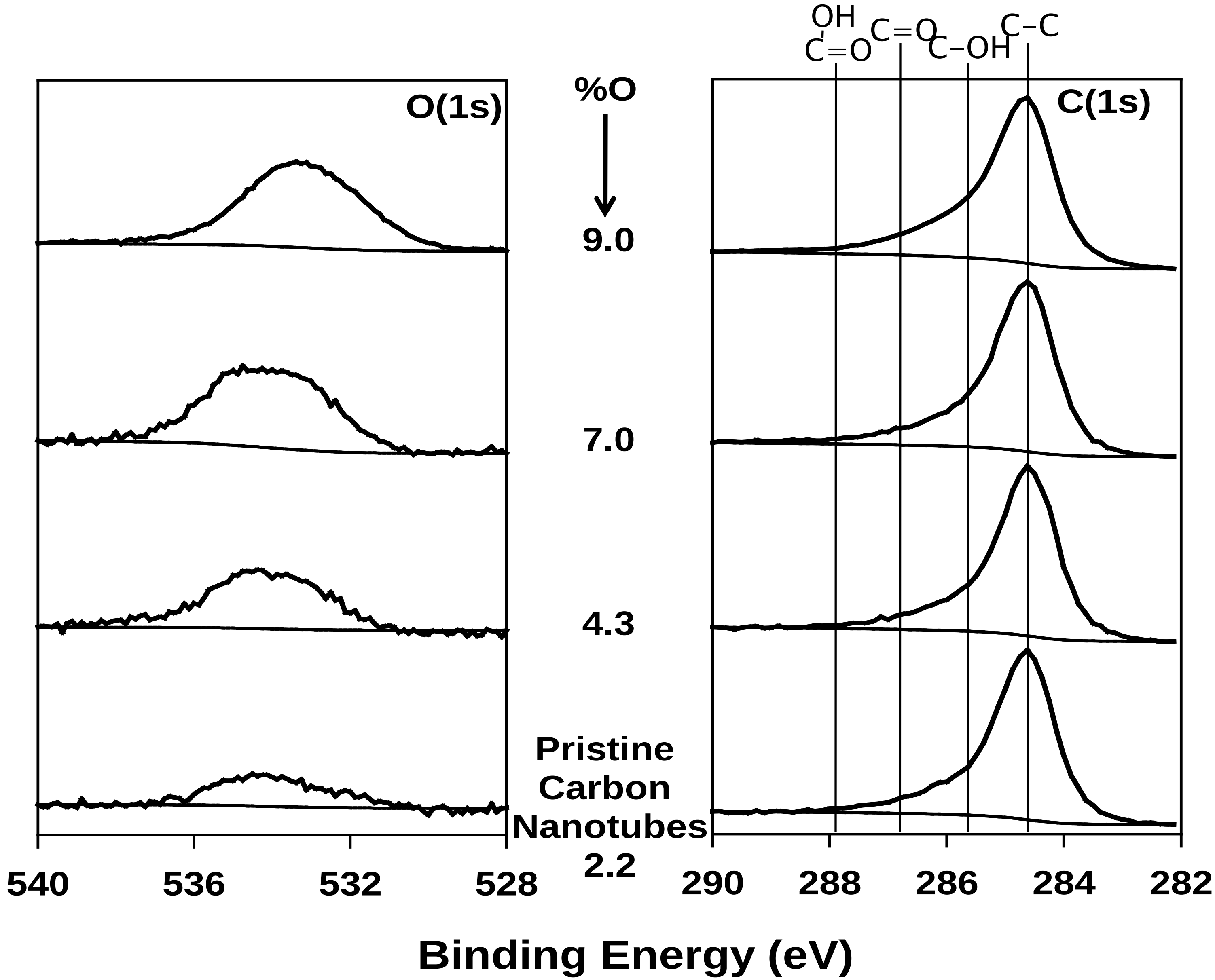
Graphene sheets can adsorb metals

Characterization of Oxides on CNTs



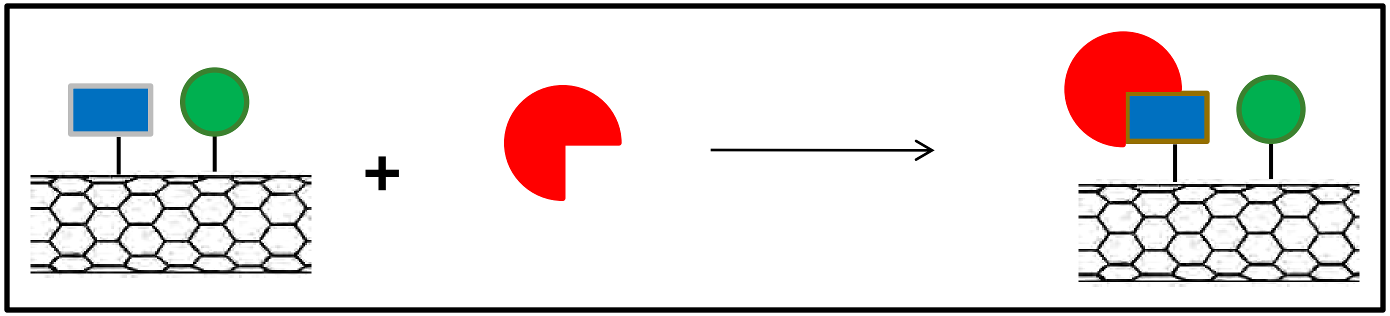
FTIR identifies oxygen functional groups but provides no quantification

XPS of Pristine & Oxidized CNTs



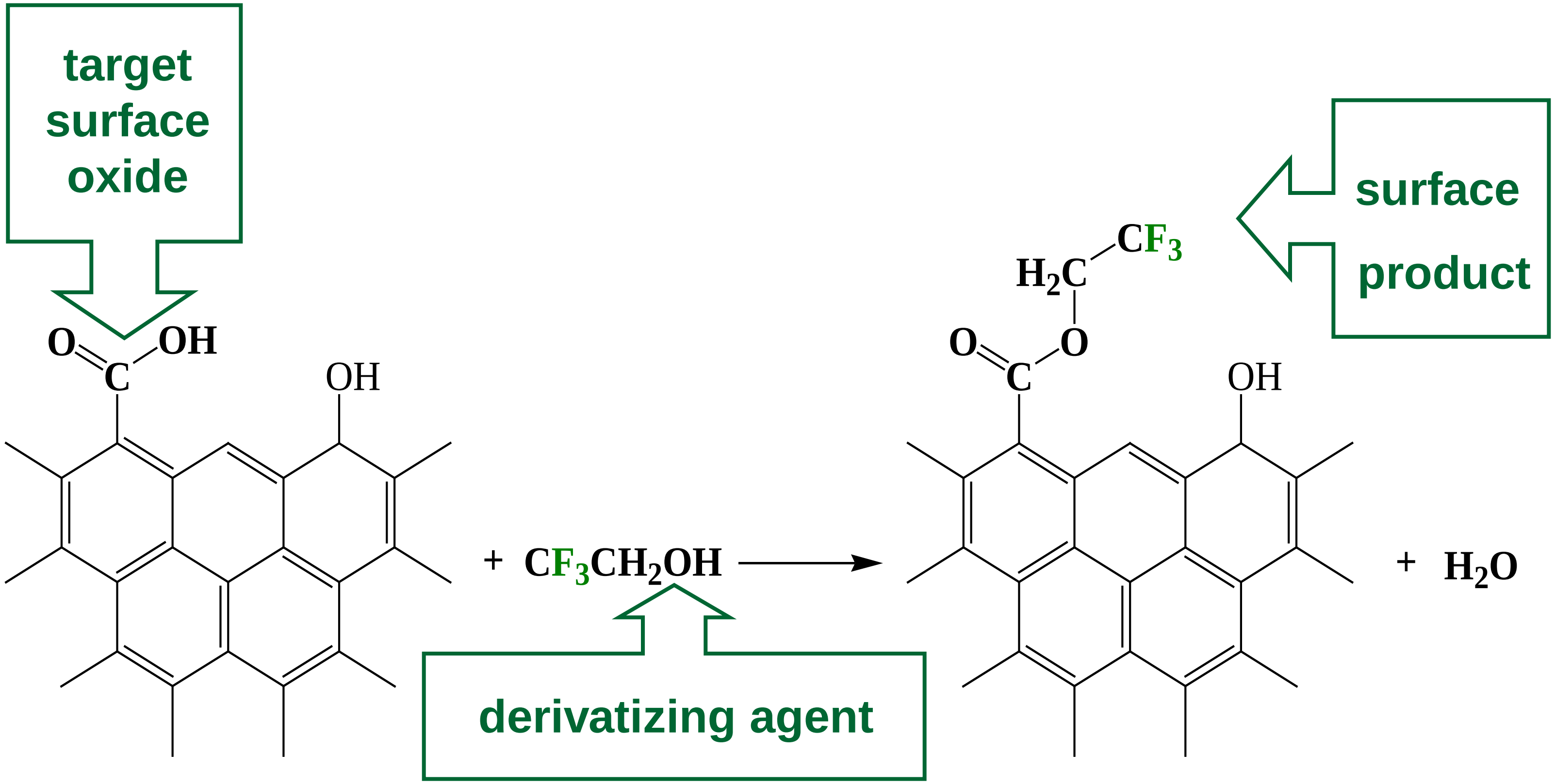
What is Chemical Derivatization?

- Reagent selectively reacts with specific functional groups
- Reagent contains a CF_3 tag.
- Vapor phase chemical process
- Label chemical quantified by XPS

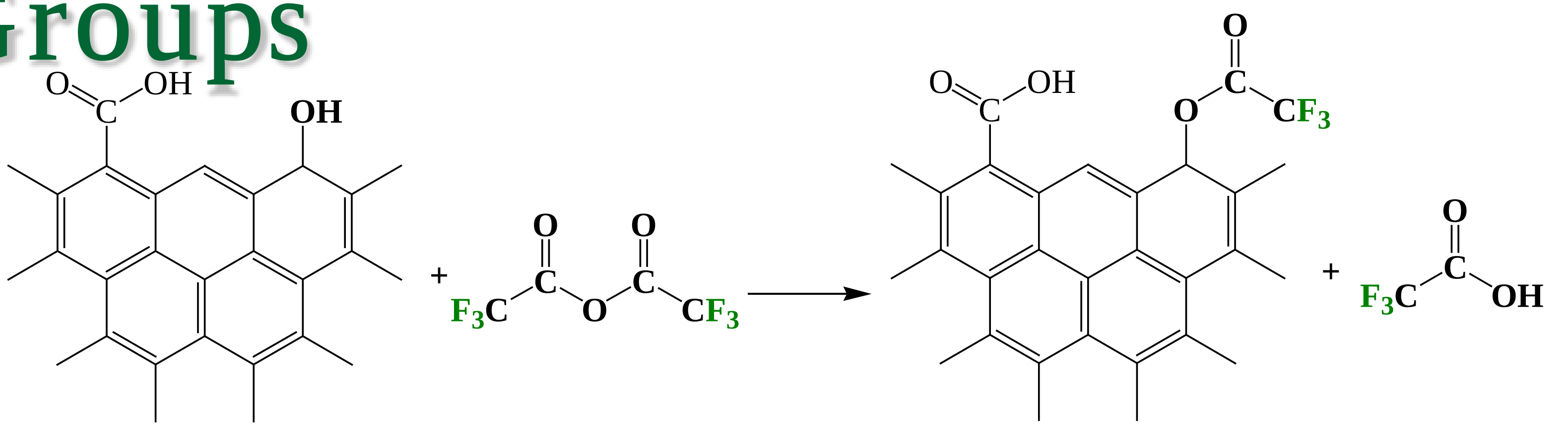


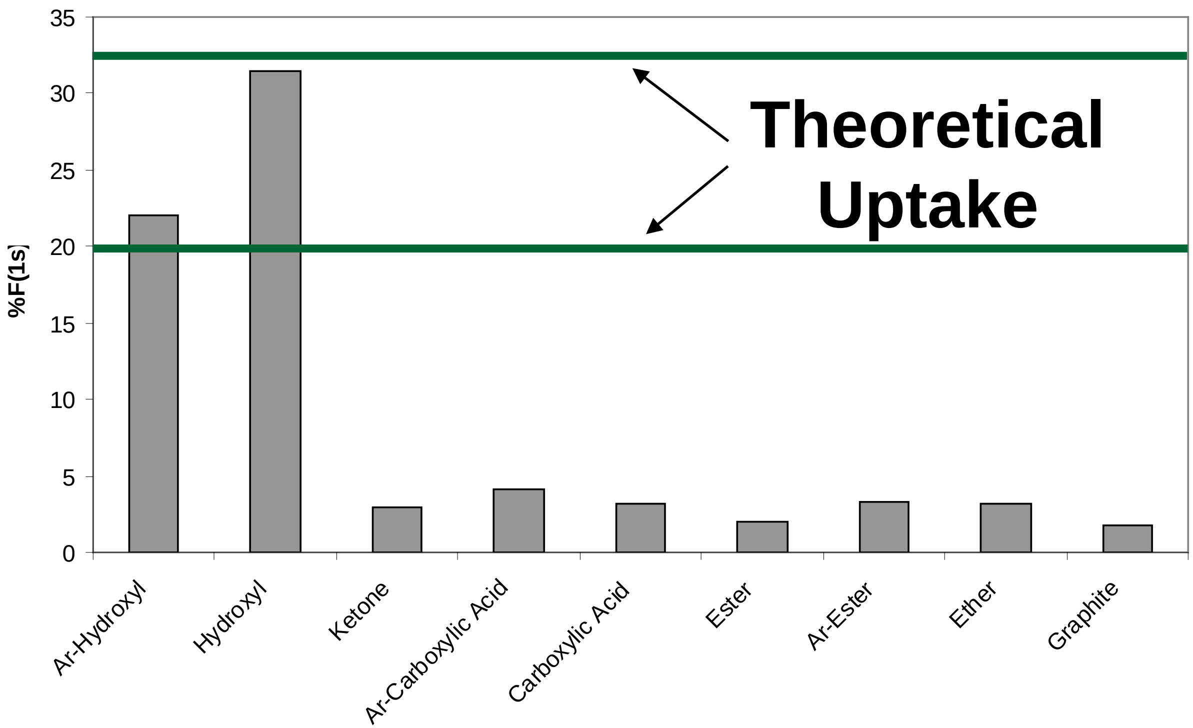
Chemical Derivatization XPS

- Technique exploiting a reaction that selectively targets one surface functionality with a **derivatizing agent**, containing an easily detectable chemical **tag (fluorine)**

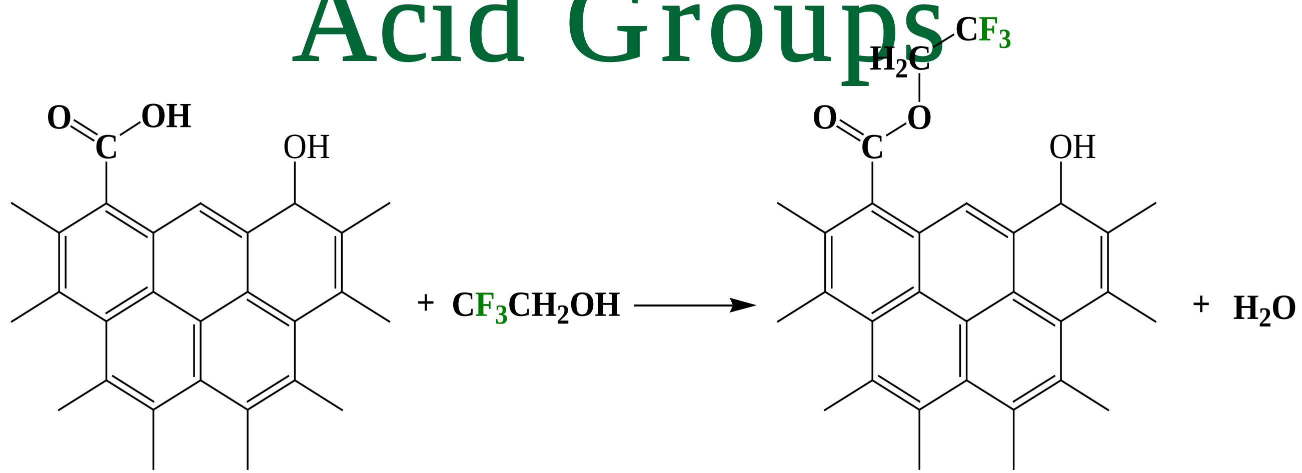


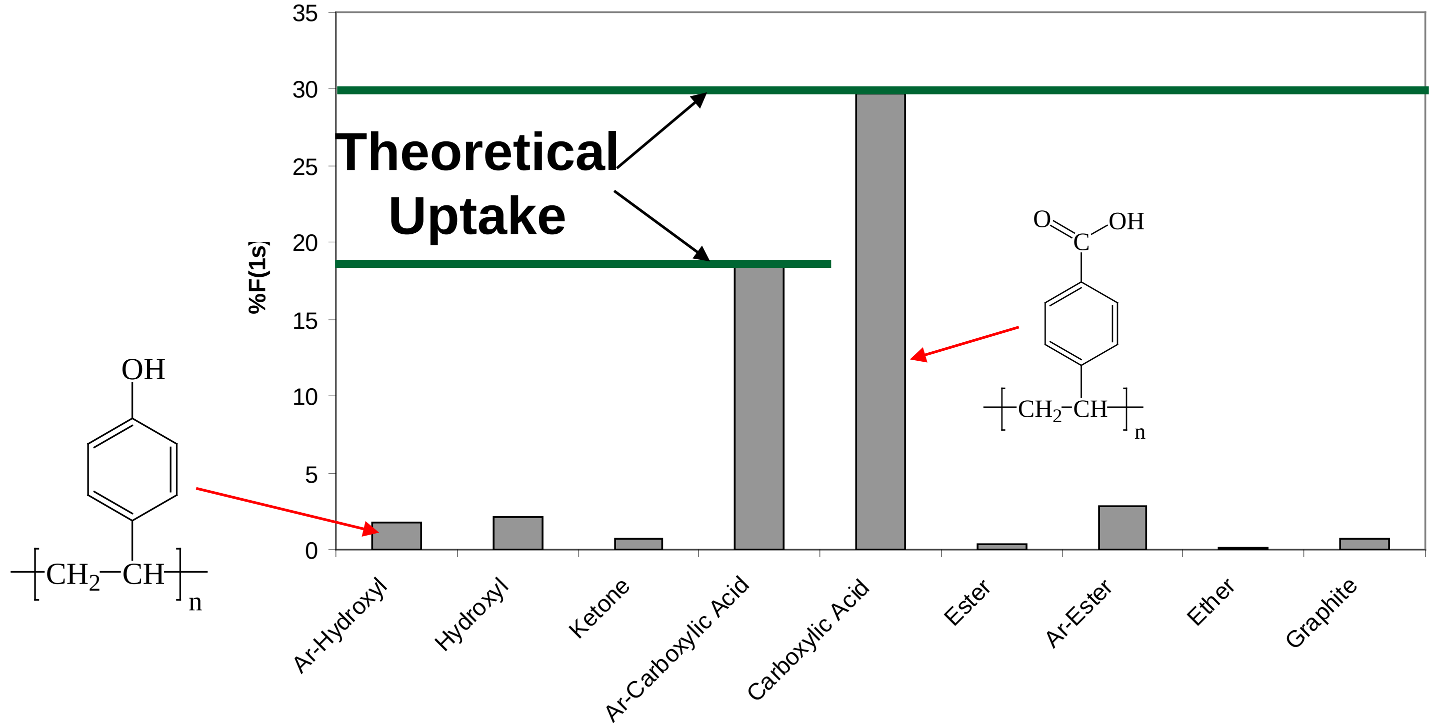
Derivatization of Hydroxyl Groups



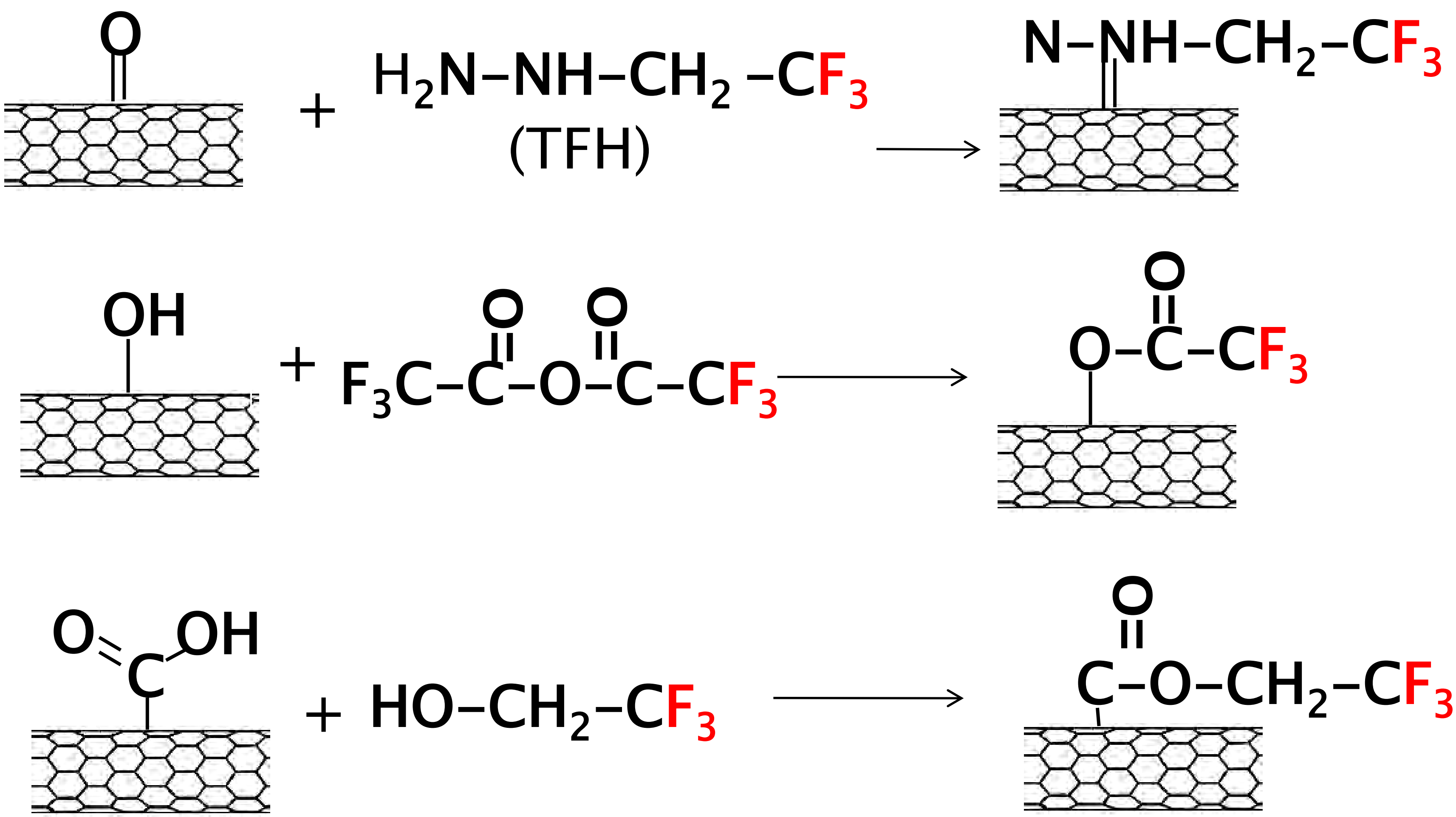


Derivatization of Carboxylic Acid Groups





Labeling Reaction Schemes



Chemistry of Materials **2006**, *18,* 169. *Carbon* **2007**, *45, 47.*