Rates and Mechanisms of Heteroaggregation Between Carbon Nanotubes and Hematite Nanoparticles in Aquatic Environments

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Overview

- Background
- Objective
- Preparation and characterization of carbon nanotubes (CNTs) and hematite nanoparticles (HemNPs)
- Heteroaggregation rates of CNTs and HemNPs
- Cryogenic TEM imaging
- Influence of humic acid on the heteroaggregation behavior
- Conclusions

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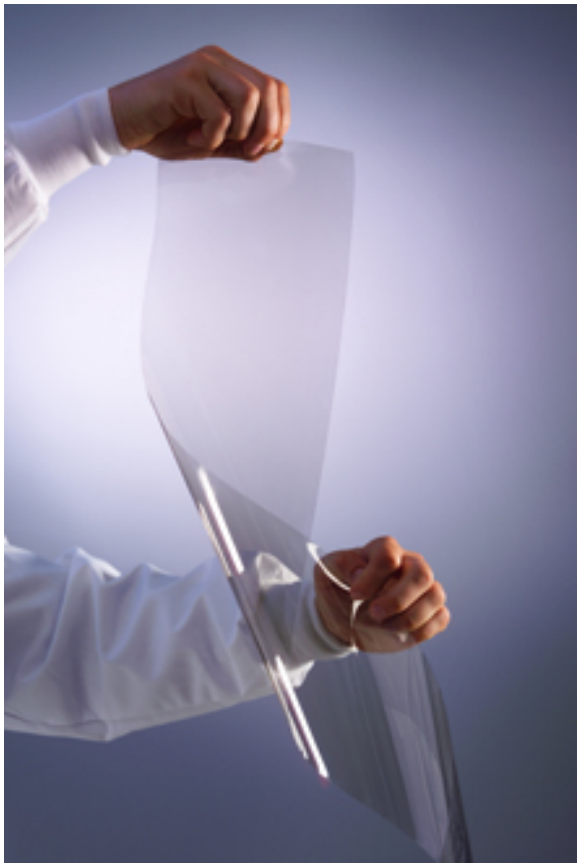
Application of CNTs

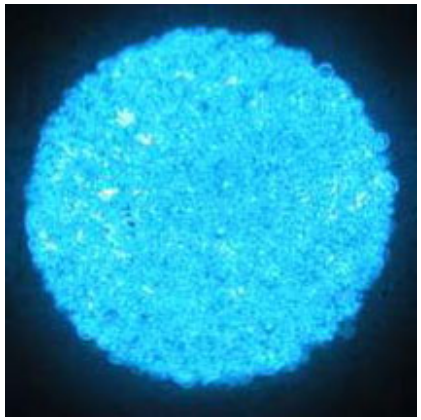
CNTs are widely used in consumer products, as well as research and industrial applications

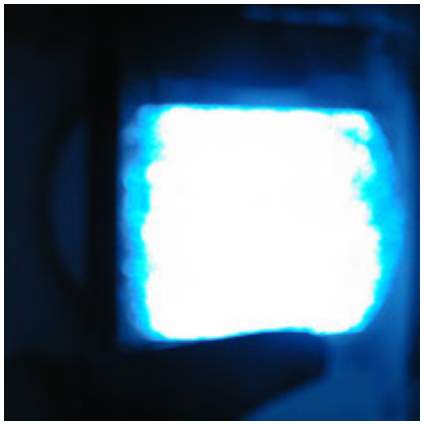


http://www.technologyreview.com/business/22009

http://eagle.fi - Eaglepower 2

http://nanotechweb.org/cws/article/tech/22597





http://www.xintek.com/products/cathodes/diode.htm

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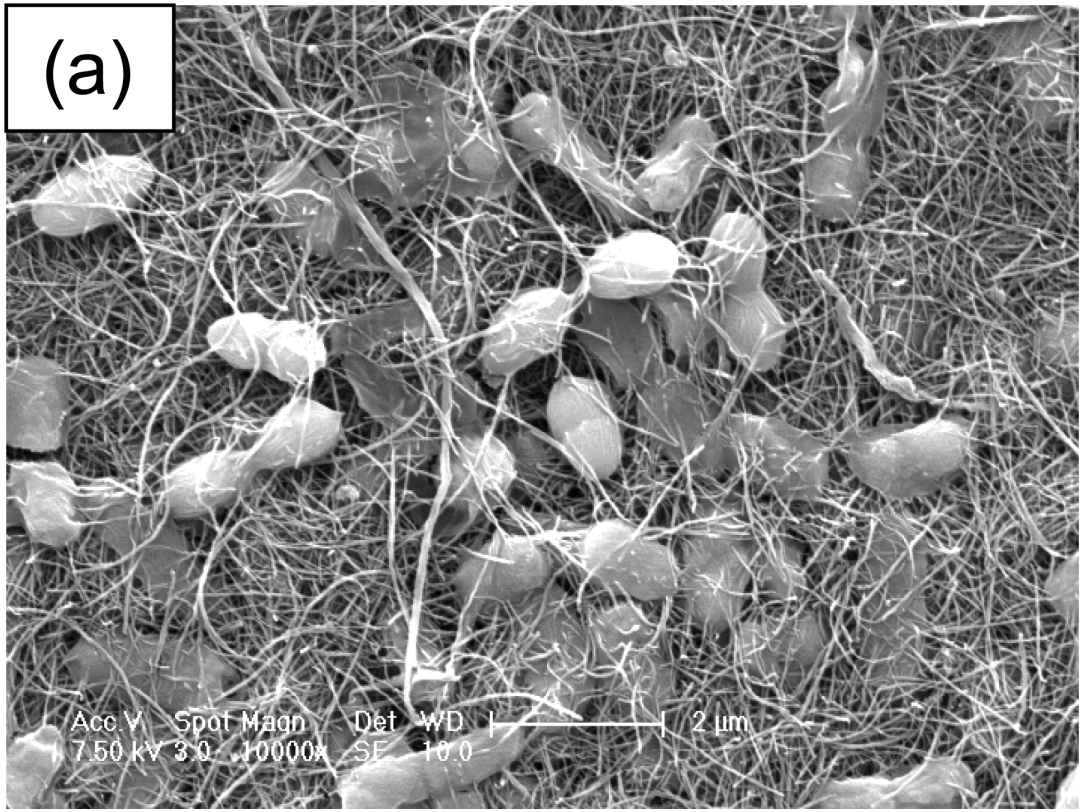
Toxicity of CNTs

CNTs exhibit toxic effects on bacteria and mammalian cells



Kang et al., *ES&T*, 42 (2008), 7528-7534

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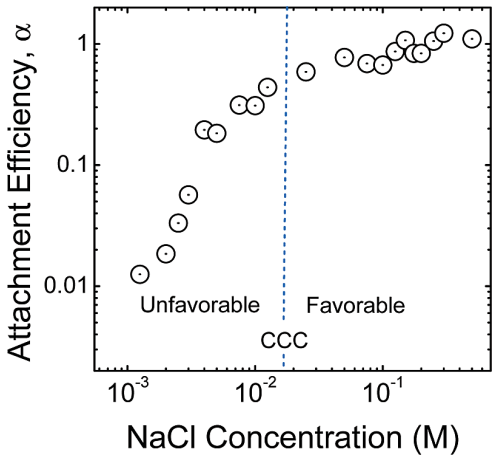
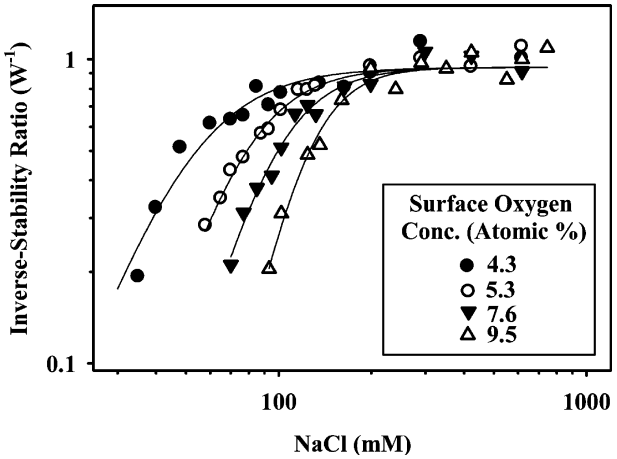
Fate and Transport of CNTs in Aquatic Systems

- Aggregation is important in controlling the environmental fate, transport, and toxicity of CNTs
- Once released into aquatic systems, CNTs can undergo both homoaggregation and heteroaggregation.
- Homoaggregation is the aggregation between the same type of particles. Several studies on homoaggregation of CNTs have been conducted



Saleh et al., *ES&T*, 42 (2008), 7963 – 7969



Smith et al., *Langmuir*, 25 (2009), 9767 – 9776

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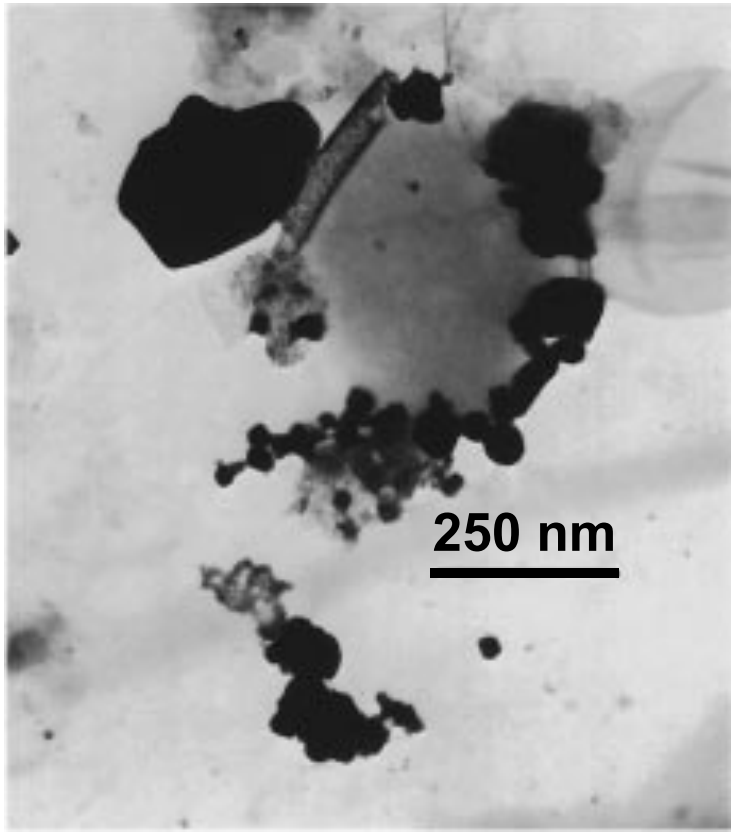
Fate and Transport of CNTs in Aquatic Systems

- Heteroaggregation is the aggregation between different types of particles in a mixed particulate system
- This process occurs in both engineered and natural aquatic systems since they contain a wide variety of naturally occurring colloids such as hematite and microorganisms



Buffle et al., *ES&T*, 32 (1998), 2887-2899

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Fate and Transport of CNTs in Aquatic Systems

- Since the concentration of naturally occurring colloids is expected to be much higher than that of CNTs, heteroaggregation between CNTs and natural occurring colloids is likely to be more important than CNT homoaggregation in determining the environmental fate and transport of these nanotubes
- To date, the heteroaggregation between CNTs and naturally occurring colloids has not been investigated

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Objective

To investigate the heteroaggregation behavior of oxidized CNTs and HemNPs in the absence and presence of humic acid

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Preparation of Colloidal Particles

- **CNTs**
  - Pristine multiwalled CNTs were purchased from NanoLab, Inc.
  - Oxidization of CNTs: refluxing pristine CNTs in a mixture of 98% H_2SO_4 and 69% HNO_3 (3:1 volume ratio) at 70 °C for 8 hours
- **HemNPs**
  - Synthesized by the forced hydrolysis of $FeCl_3$, as described by Matijević and Scheiner, *J. Colloid Interface Sci.* 63 (1978), 509-524

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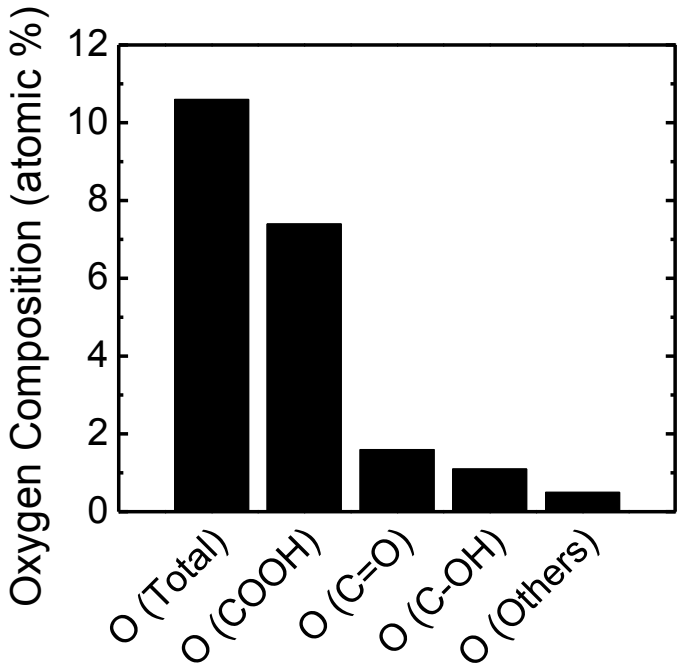
Characterization of CNTs

- **Hydrodynamic diameter = 110 nm**
- **EPM = –2.09×10^{-8} m^2/Vs (pH 5.2, 0.1 mM NaCl)**
- **TOC = 1.39 mg/L (combustion catalytic oxidation)**



Yi and Chen, *Langmuir*, 27 (2011), 3588 - 3599

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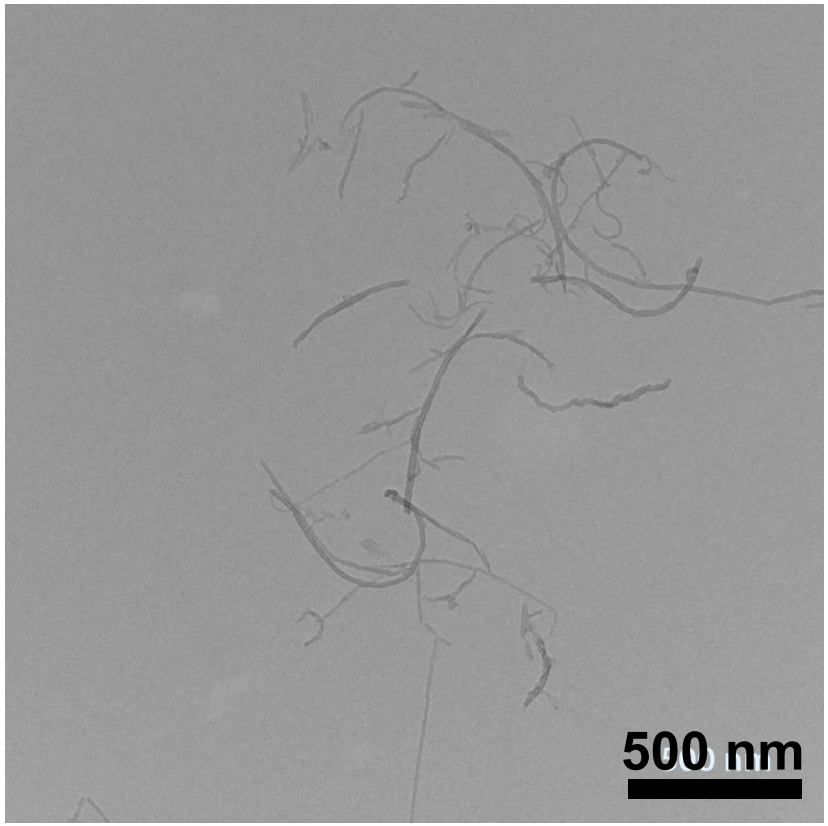
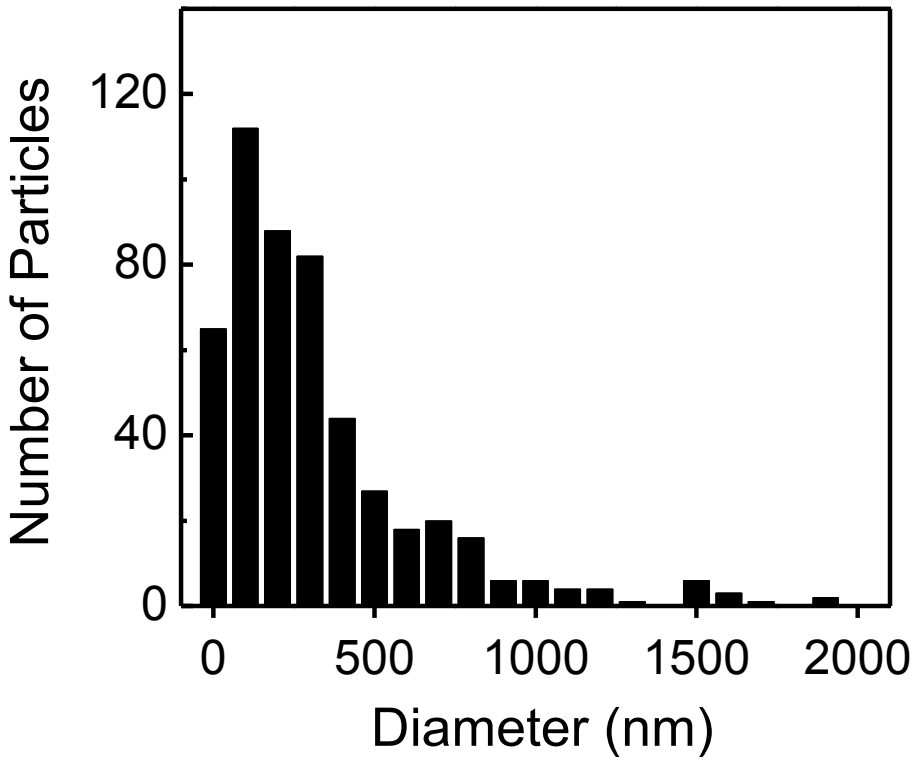
Characterization of CNTs





- **Average length = 376 nm**
- **Standard deviation = 327 nm**

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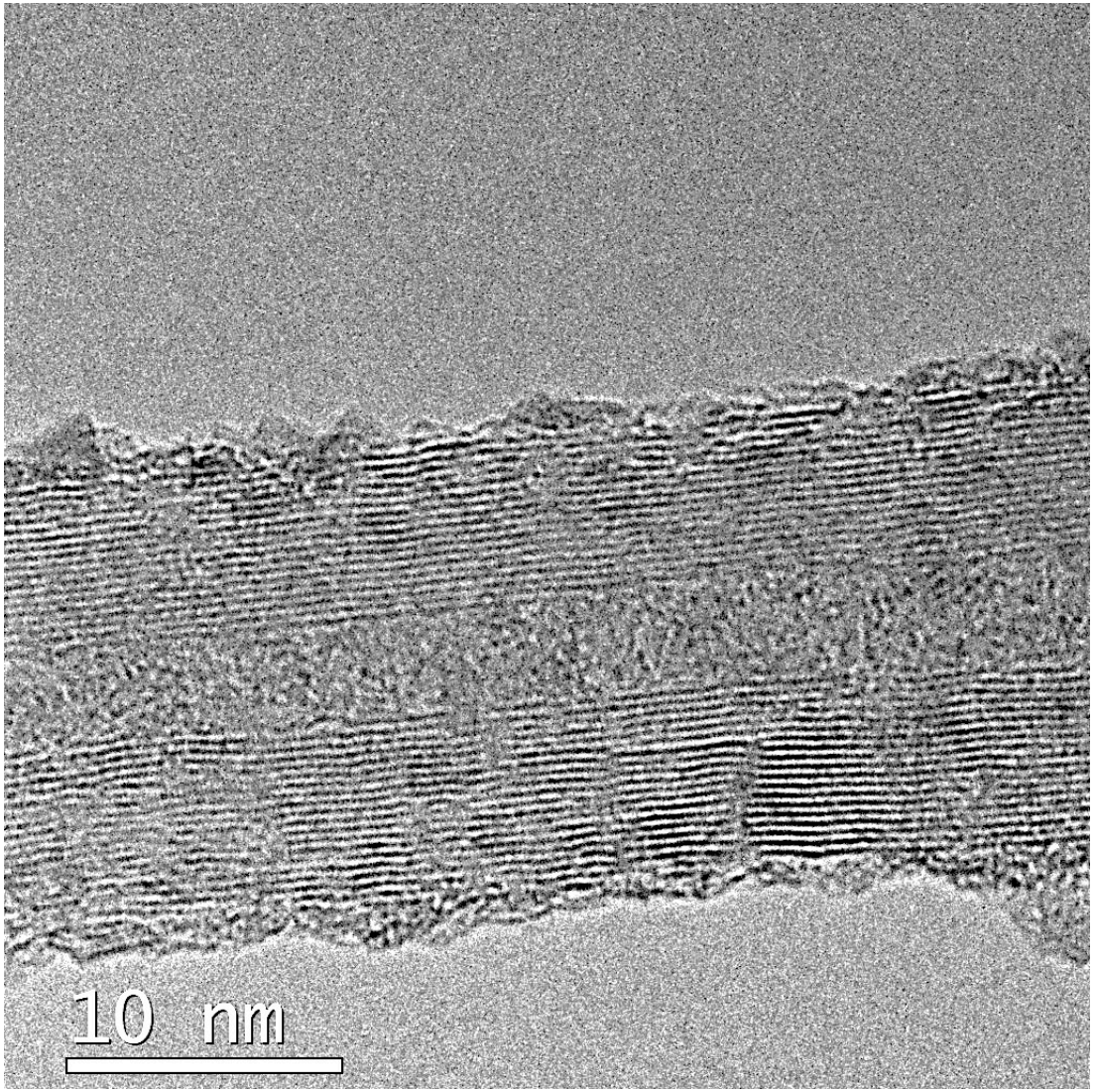
Characterization of CNTs



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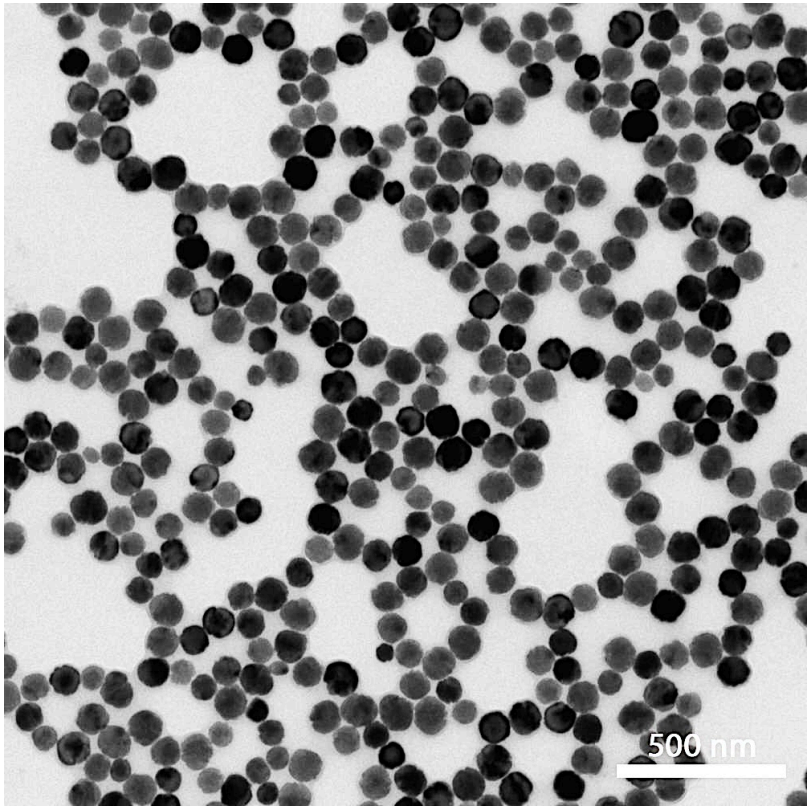
Characterization of HemNPs

- Hydrodynamic diameter = 81 nm
- EPM = $+1.79\times10^{-8}$ m^2/Vs (pH 5.2, 0.1 mM NaCl)
- Concentration = 4.4 g/L (gravimetric analysis)



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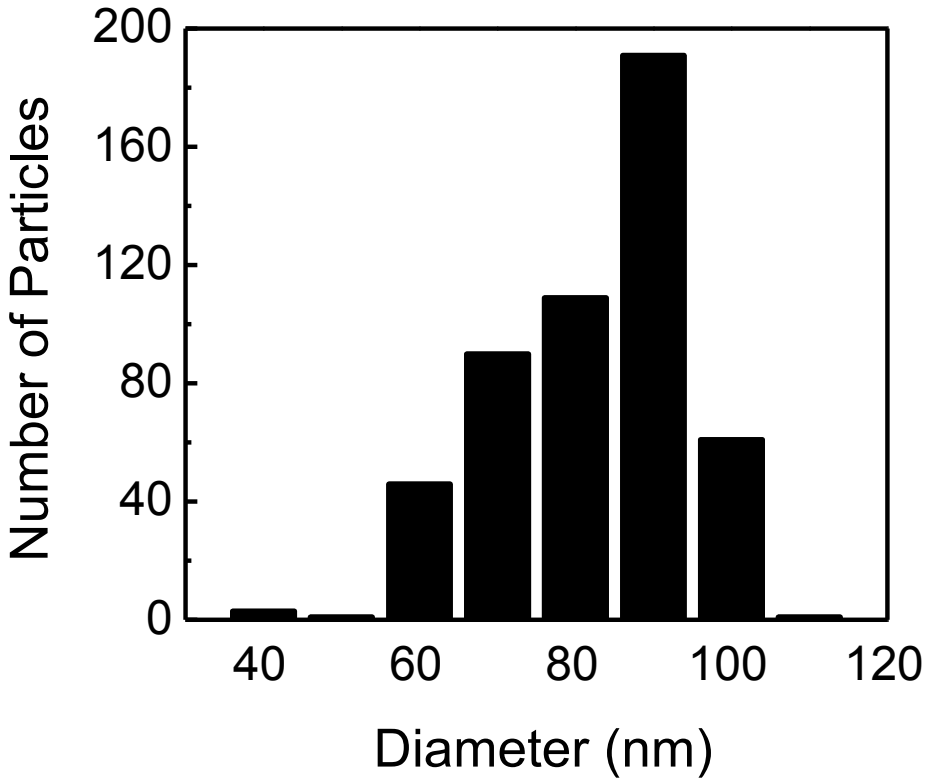
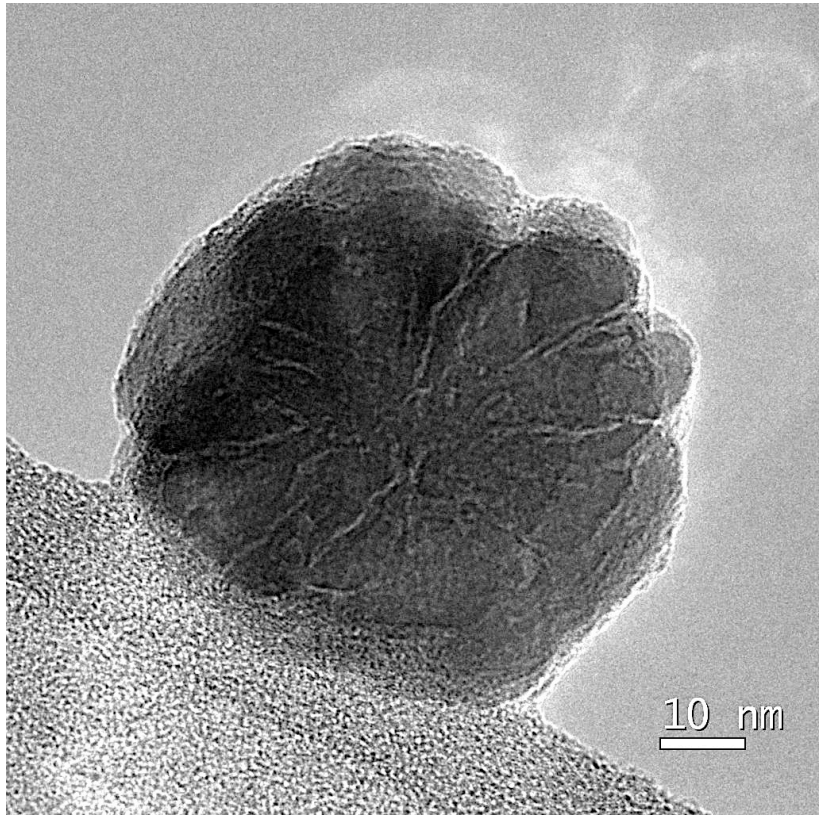
Characterization of HemNPs





- **Average diameter = 87 nm**
- **Standard deviation = 12 nm**

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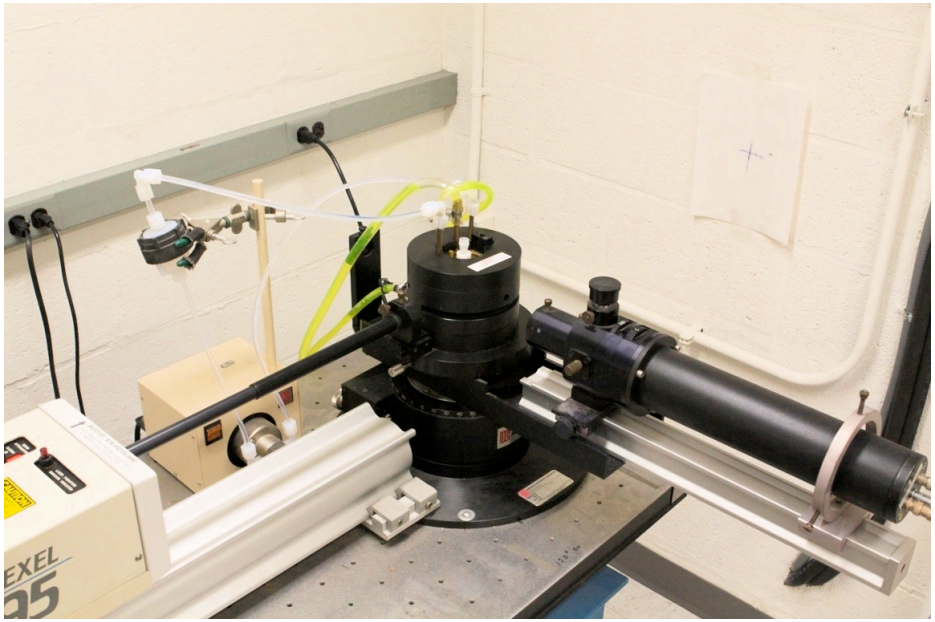
Dynamic Light Scattering (DLS)

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



- **Experimental conditions**
  - 0.1 mM NaCl and pH 5.2 (unadjusted pH)
  - 0.44 mg/L HemNPs and 1–28 µg/L TOC CNTs
  - 0–500 µg/L TOC humic acid

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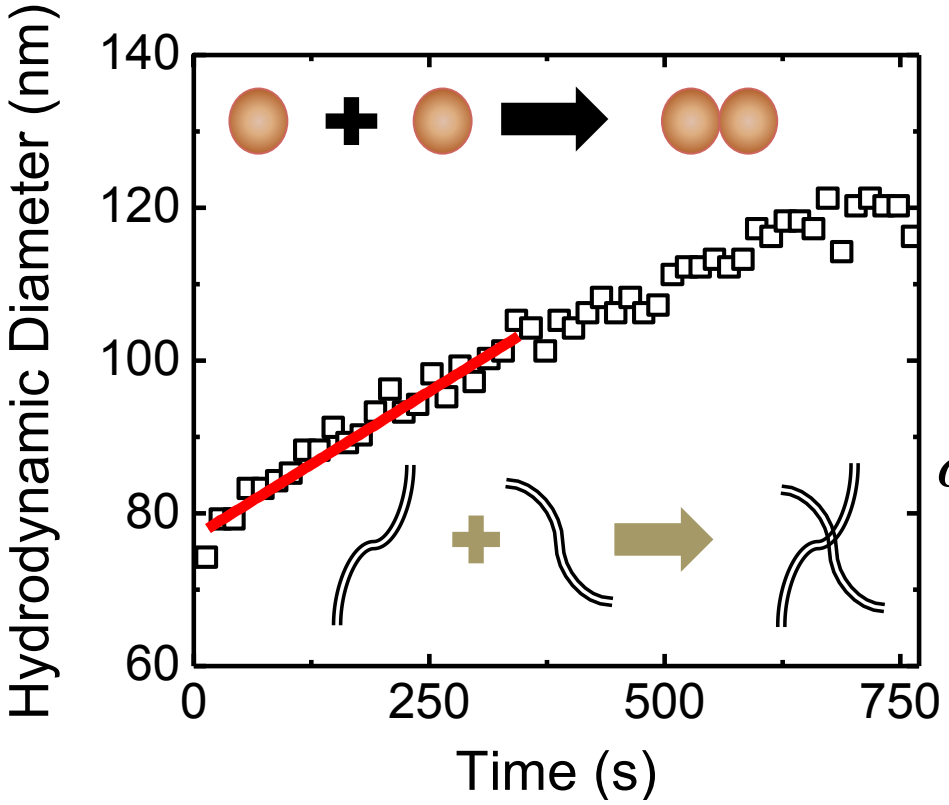
Quantifying Homoaggregation Kinetics

Attachment efficiency, α

The probability of an irreversible attachment resulting from the collision of two colloidal particles



$$\left(\frac{da_h(t)}{dt}\right)_{t\to 0} \propto kN_0$$

$$\alpha = \frac{k}{k_{fast}} = \frac{\frac{1}{N_0}\left(\frac{da_h(t)}{dt}\right)_{t\to 0}}{\left(\frac{1}{N_0}\right)_{fast}\left(\frac{da_h(t)}{dt}\right)_{t\to 0,fast}}$$

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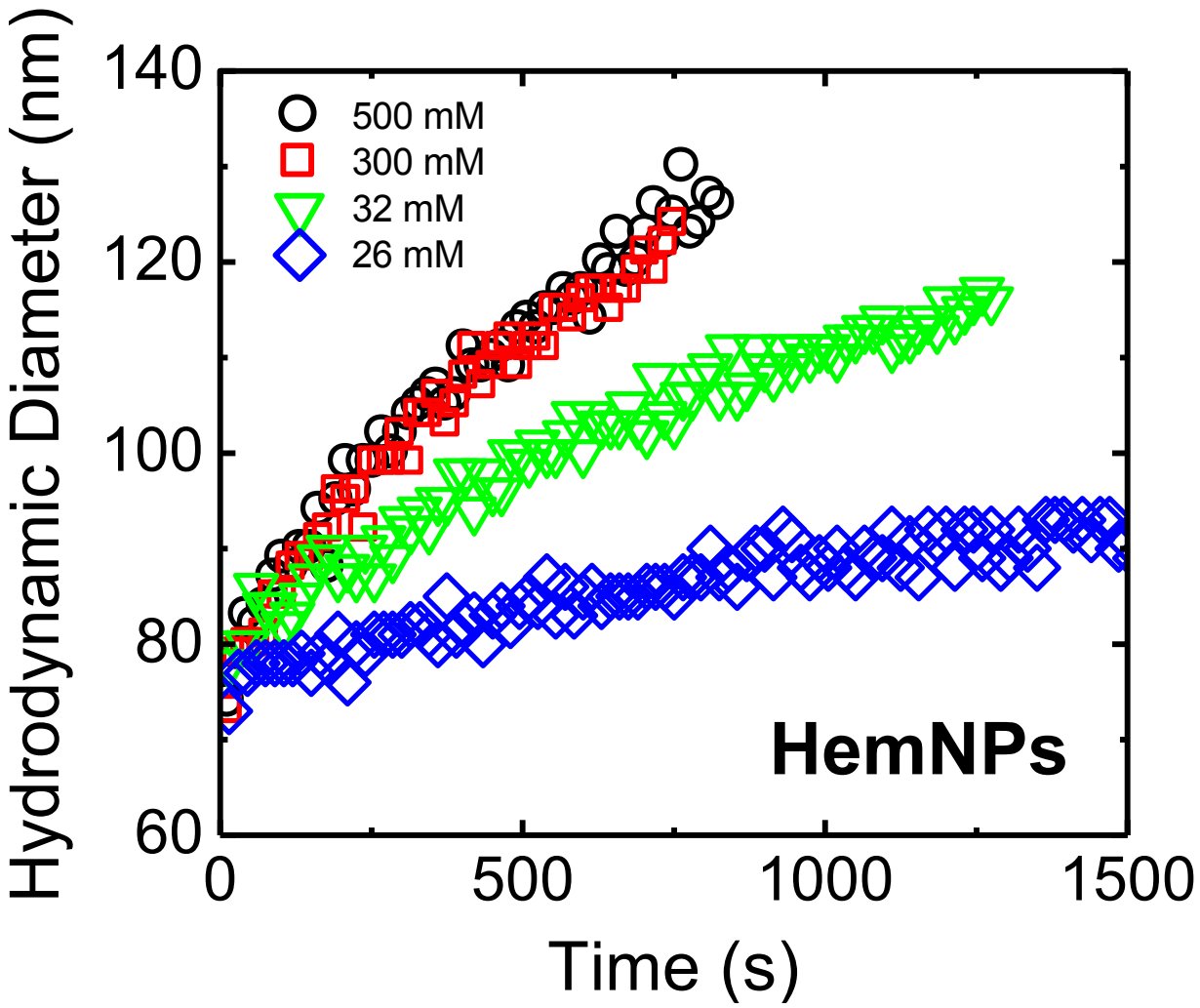
Homoaggregation Kinetics of HemNPs and CNTs



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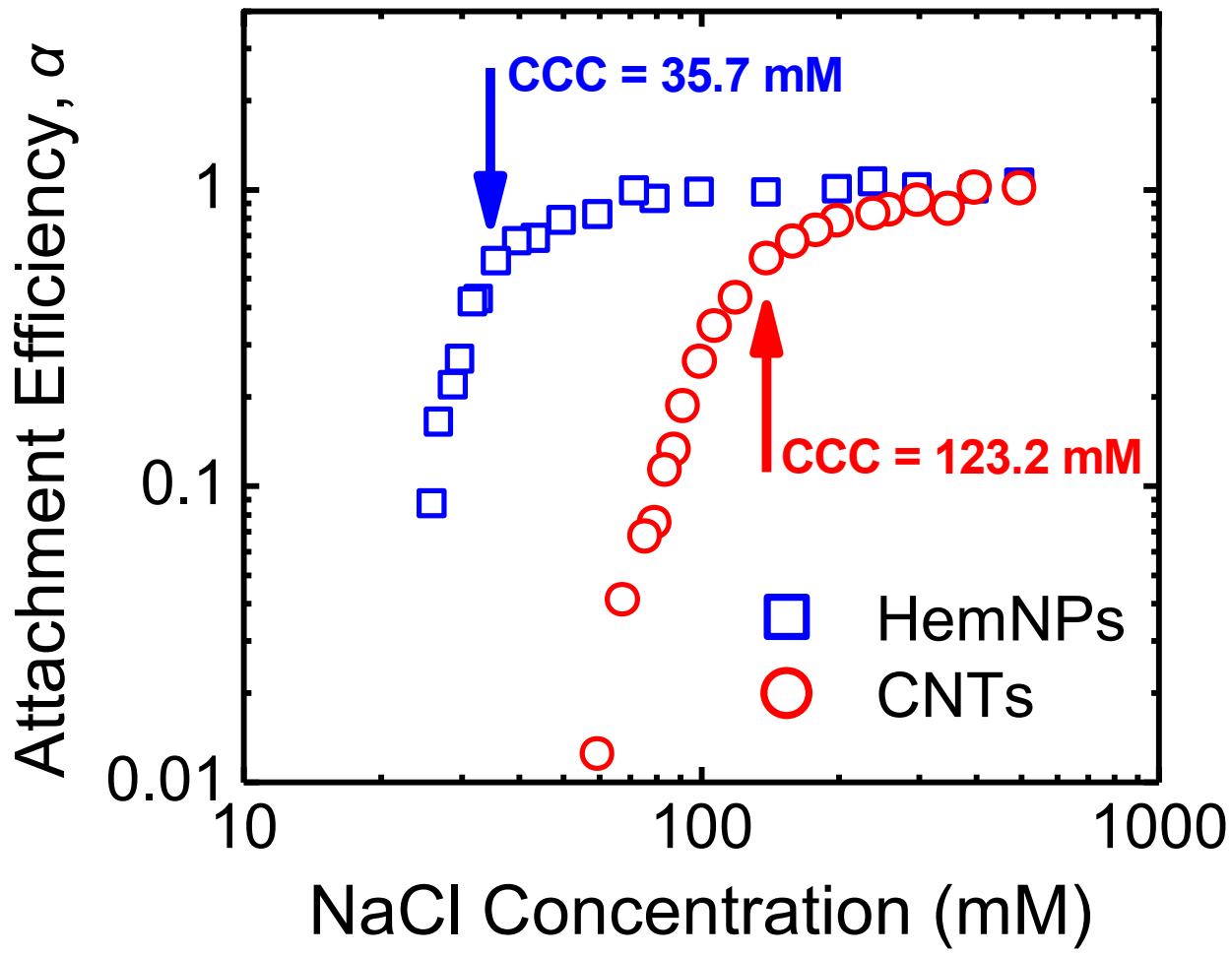
Homoaggregation Kinetics of HemNPs and CNTs



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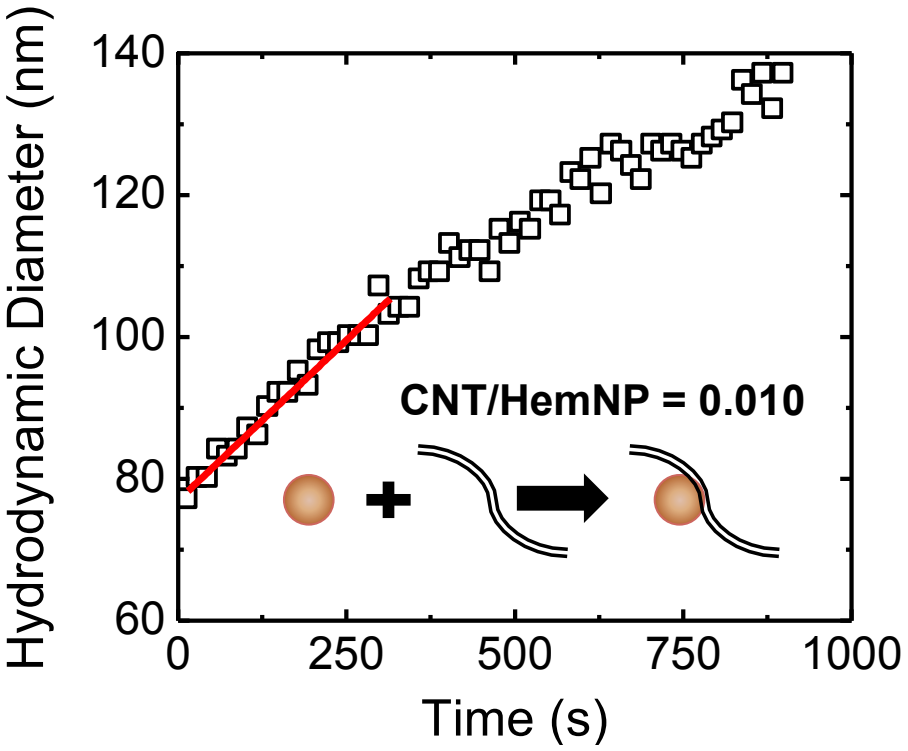
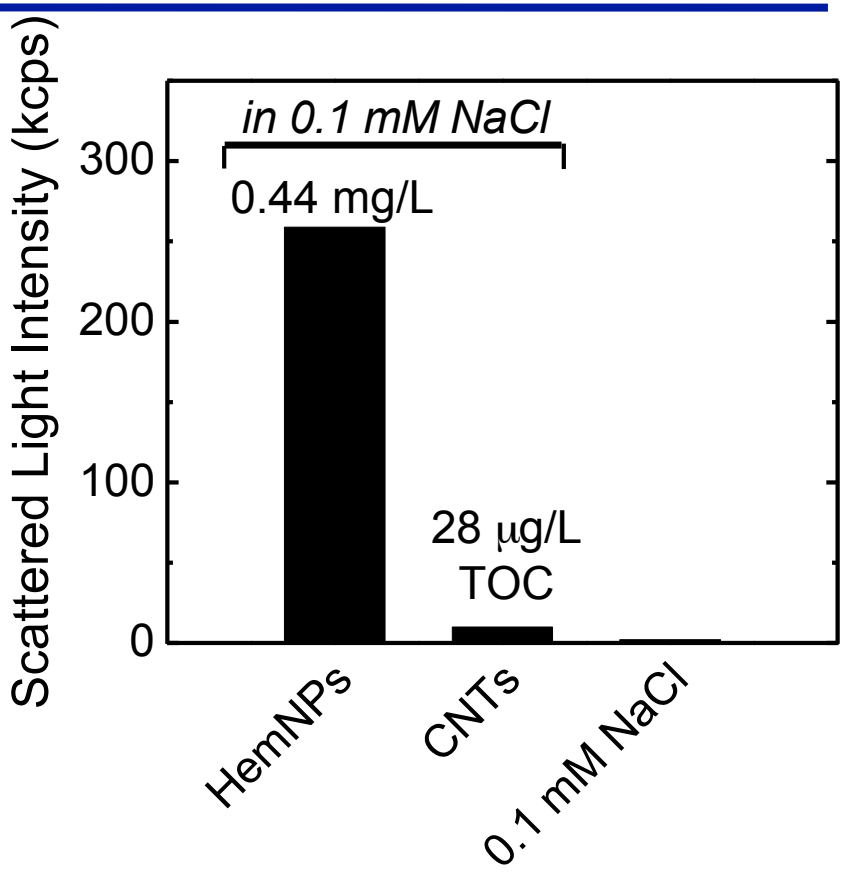
Measuring Heteroaggregation Rates





Heteroaggregation rate

$$\left(\frac{da_h(t)}{dt}\right)_{t\to 0} = 0.0905 \text{ nm/s}$$

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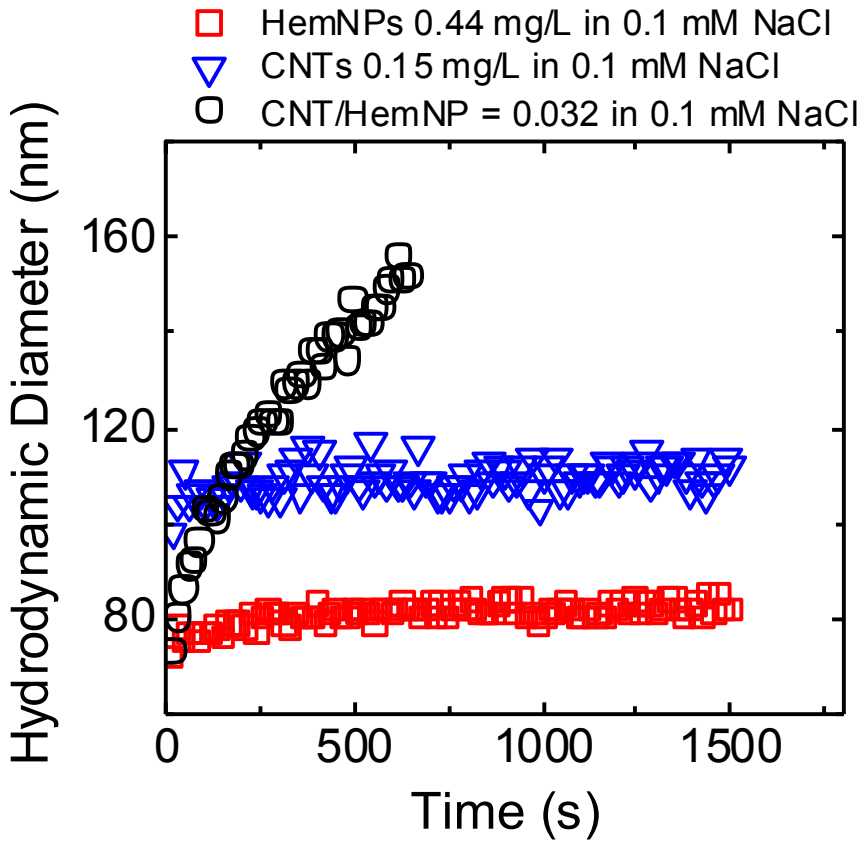
Heteroaggregation Rates at Different CNT/HemNP Ratios



- **At 0.1 mM NaCl, homoaggregation is negligible and heteroaggregation occurs exclusively**

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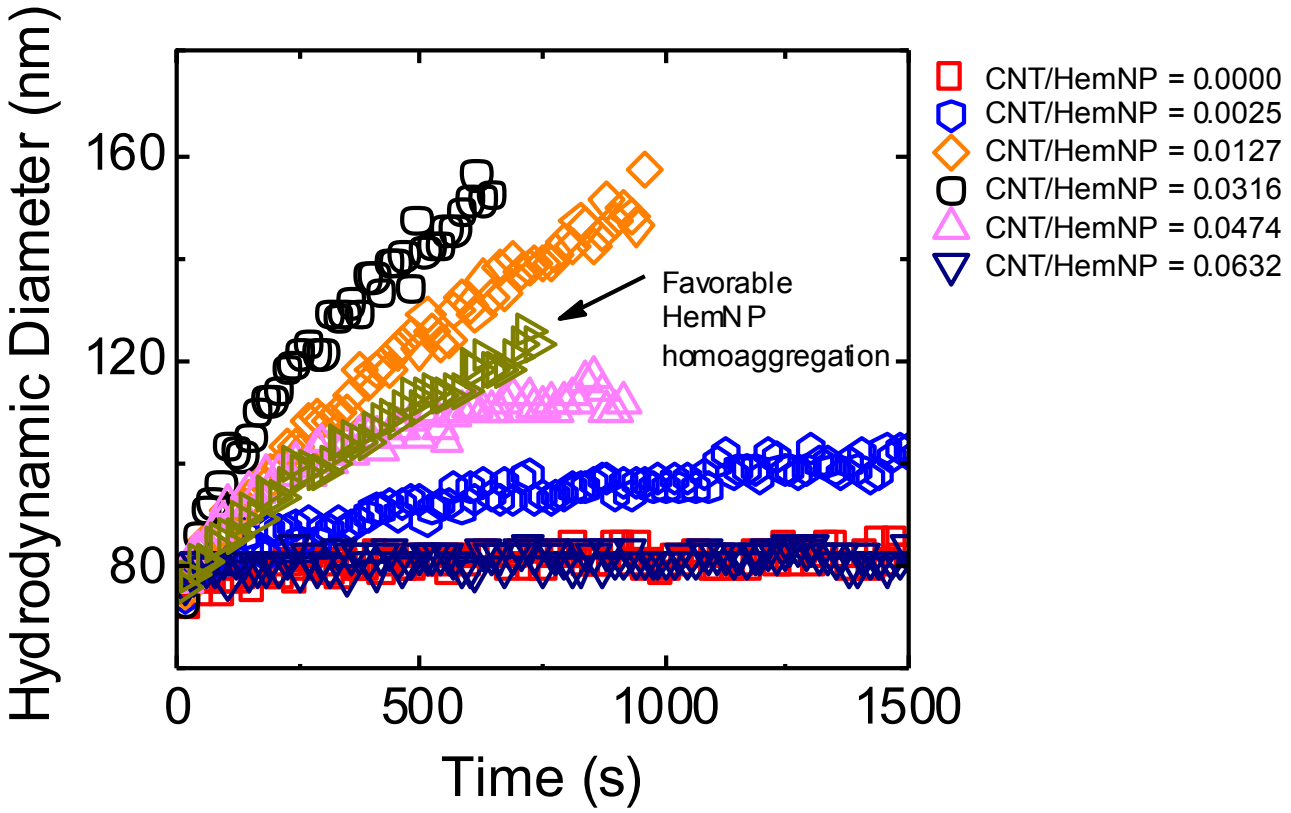
Heteroaggregation Rates at Different CNT/HemNP Ratios



- **HemNP concentration was fixed at 0.44 mg/L**
- **CNT concentrations were from 1 to 28 µg/L TOC**

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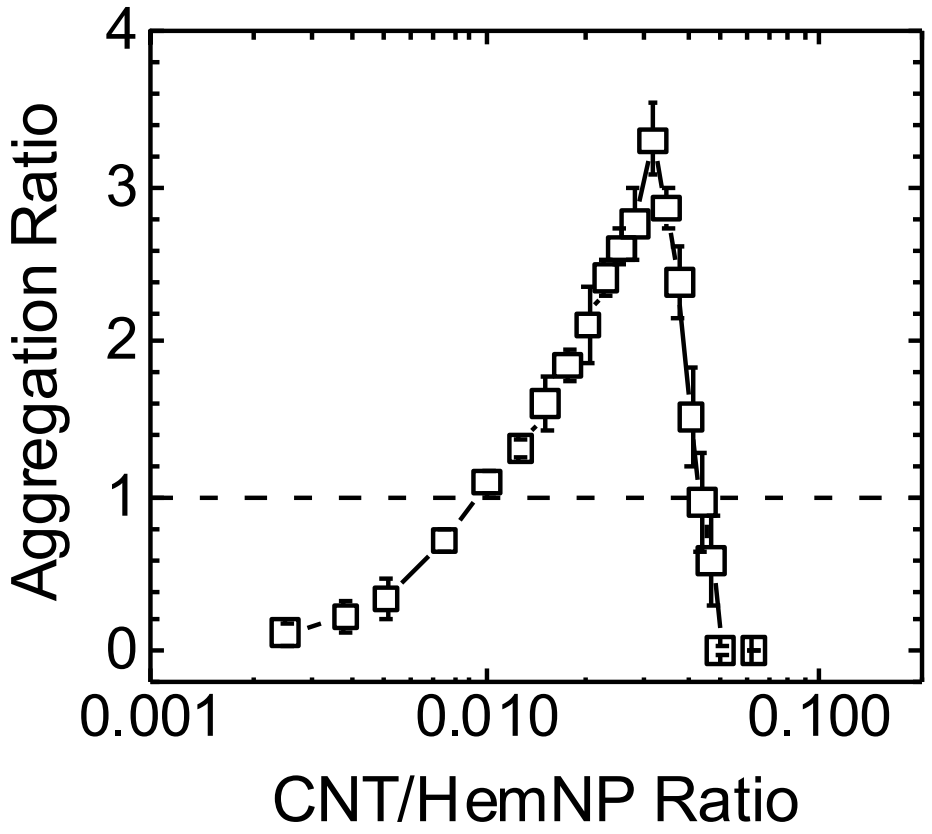
Heteroaggregation Rates at Different CNT/HemNP Ratios



$$\text{Aggregation ratio} = \frac{\text{Rate of CNT-HemNP heteroaggregation}}{\text{Rate of HemNP homoaggregation}}$$

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Cryogenic Transmission Microscopy (cryo-TEM)

- **Specimen preparation for standard TEM imaging**
  - Deformation of aggregate structure
  - Promotion of unintended agglomeration between neighboring aggregates
- **These effects can be minimized by the employment of cryo-TEM**
- **Main procedures for cryo-TEM**
  - Specimen vitrification
  - Transferring the vitrified specimen into the TEM
  - Cryo-TEM imaging

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Cryogenic Transmission Microscopy (cryo-TEM)

- **Specimen vitrification**
  - A copper TEM grid, which was coated with lacey carbon, was ionized for 30 s
  - The specimen was blotted with filter paper at 22 °C and 90 % relative humidity to leave a thin film of suspension (ca. 200 – 300 nm) on the grid
  - The specimen was rapidly plunged in liquid ethane which was conductively cooled by liquid nitrogen
  - Blotting and vitrification are done automatically by a **Vitrobot** (FEI, OR).

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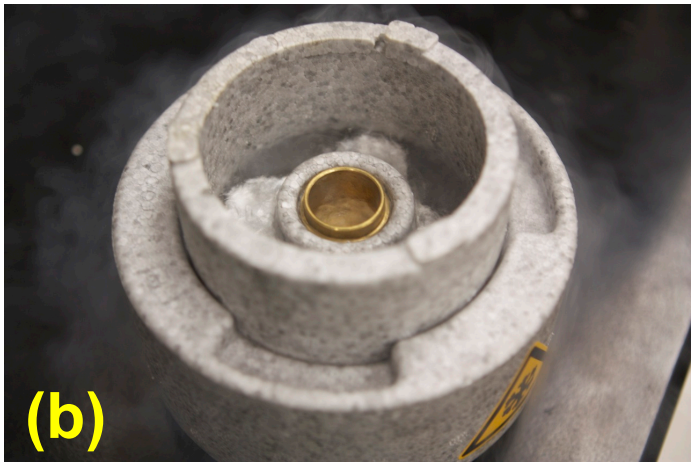
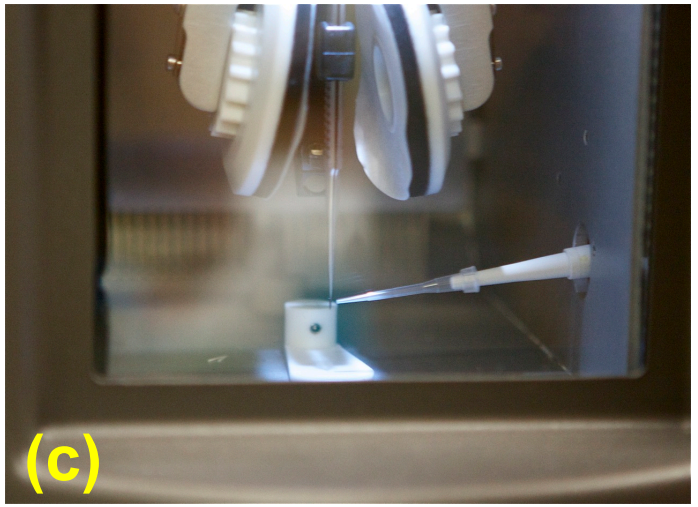
Cryogenic Transmission Microscopy (cryo-TEM)

- **Specimen vitrification**





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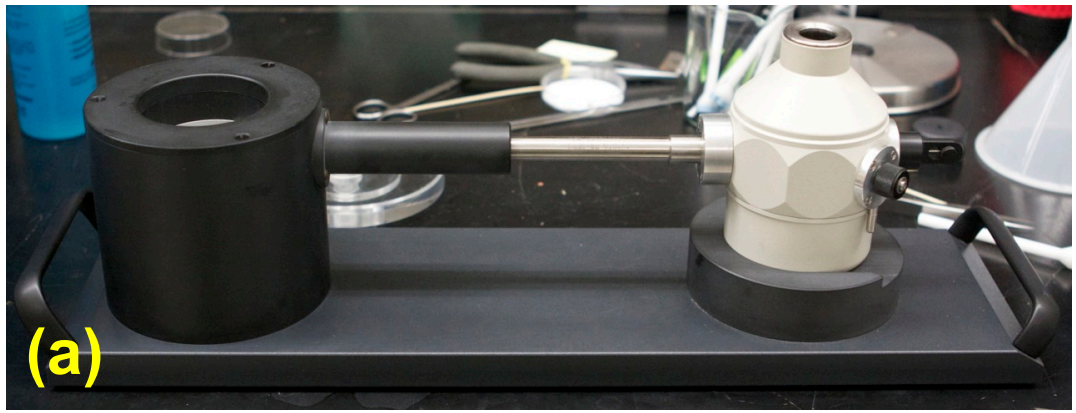
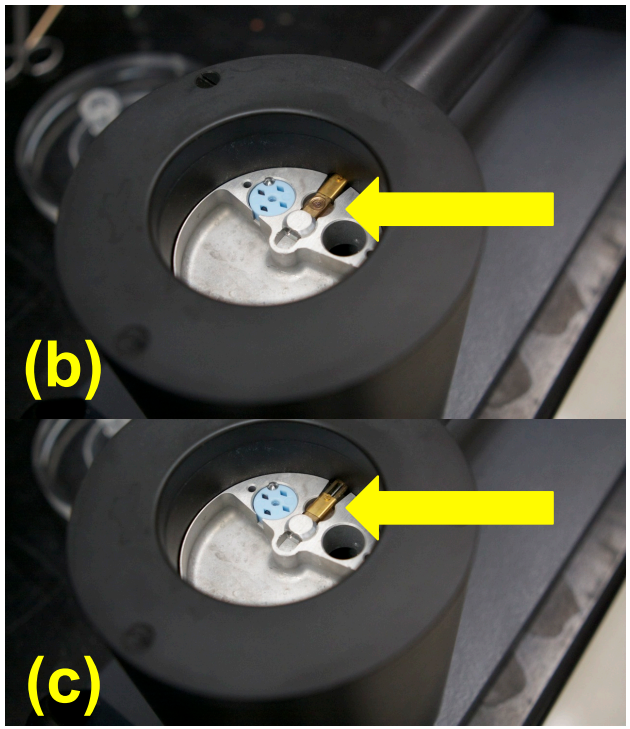
Cryogenic Transmission Microscopy (cryo-TEM)

- **Transferring the vitrified specimen into the TEM**





Liquid nitrogen cryo transfer holder and workstation (Model 626, Gatan, CA)

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Cryogenic Transmission Microscopy (cryo-TEM)

- **Cryo-TEM imaging**
  - Technai 12 TWIN (FEI) operated at 100 kV
  - Eagle 2k CCD camera

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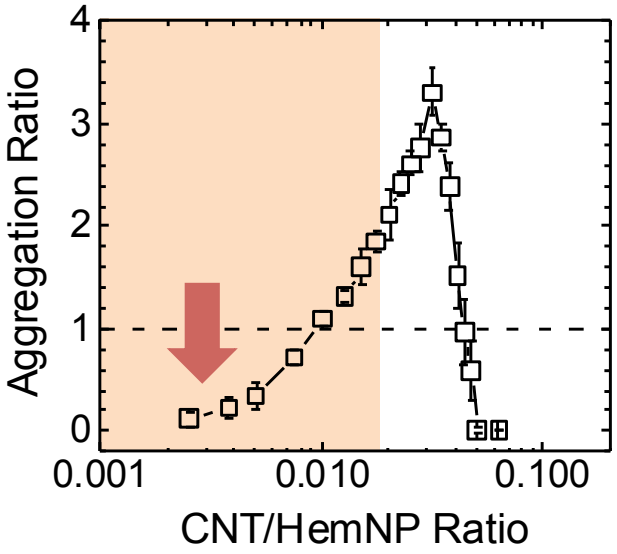
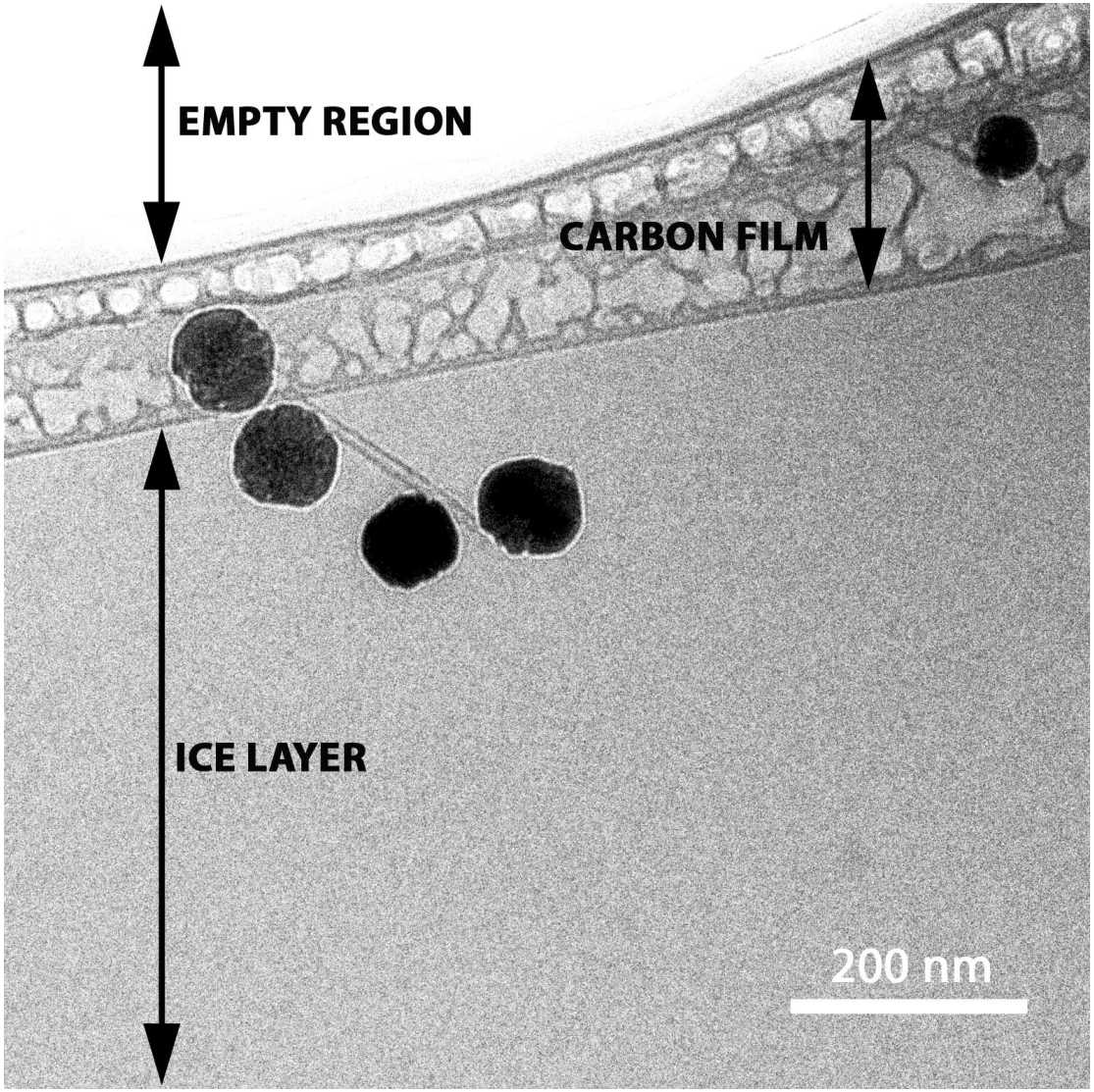
Cryo-TEM Images at Different CNT/HemNP Ratios

CNT/HemNP = 0.003





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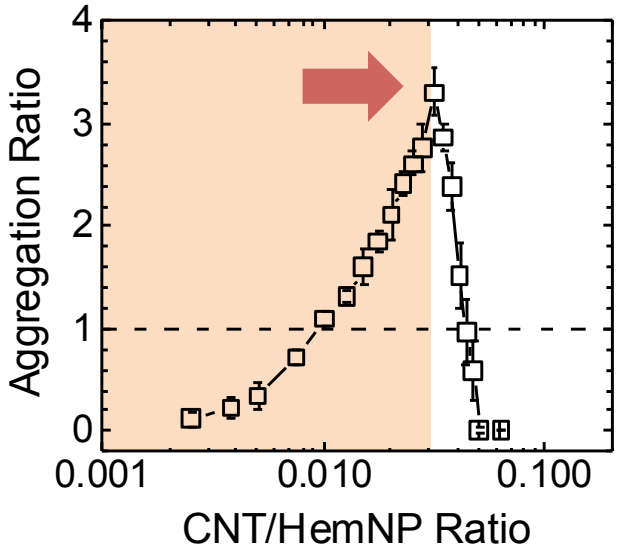
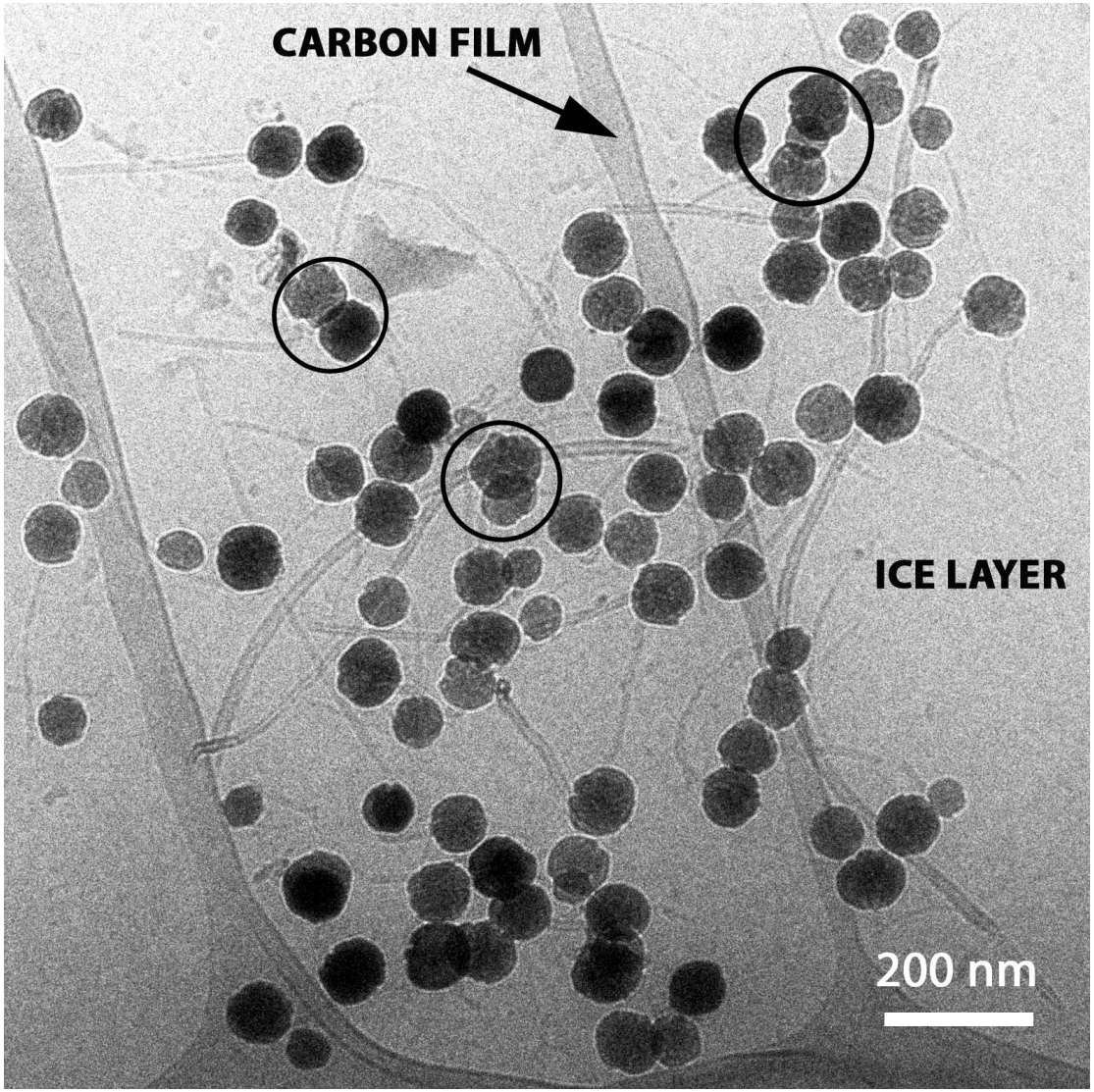
Cryo-TEM Images at Different CNT/HemNP Ratios

CNT/HemNP = 0.032





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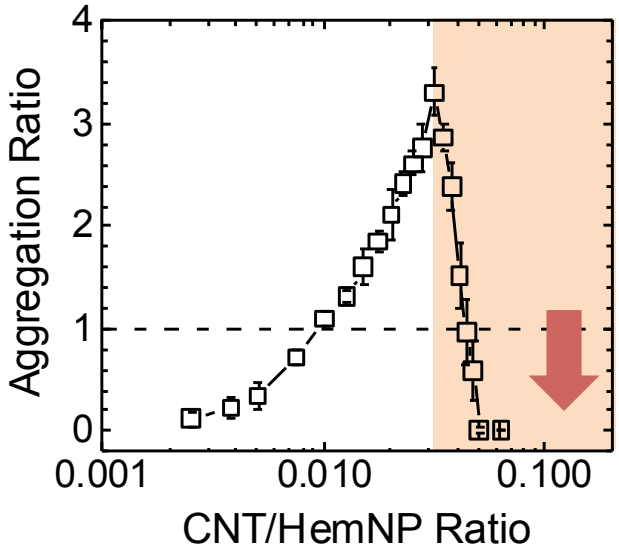
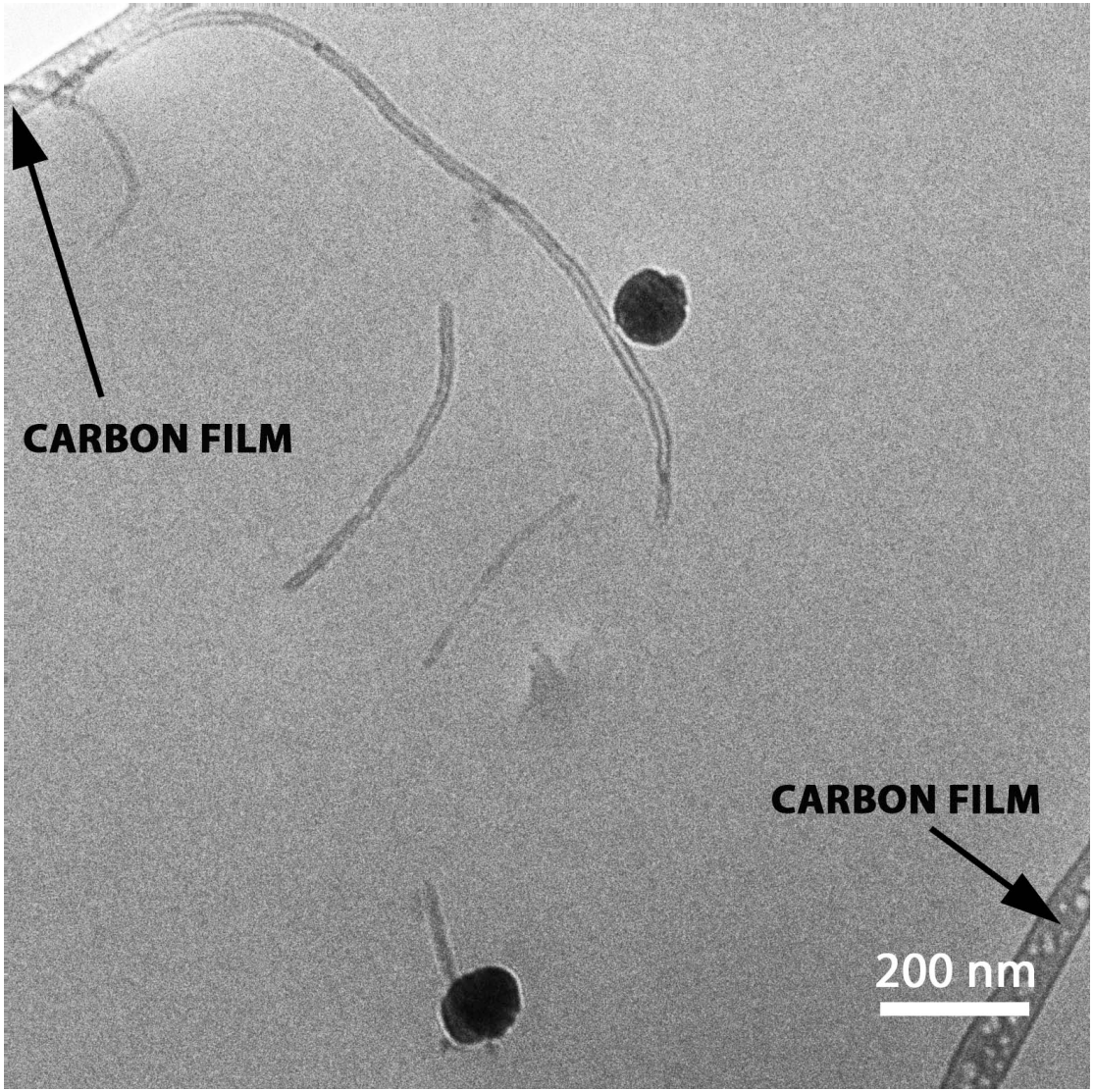
Cryo-TEM Images at Different CNT/HemNP Ratios

CNT/HemNP = 0.126





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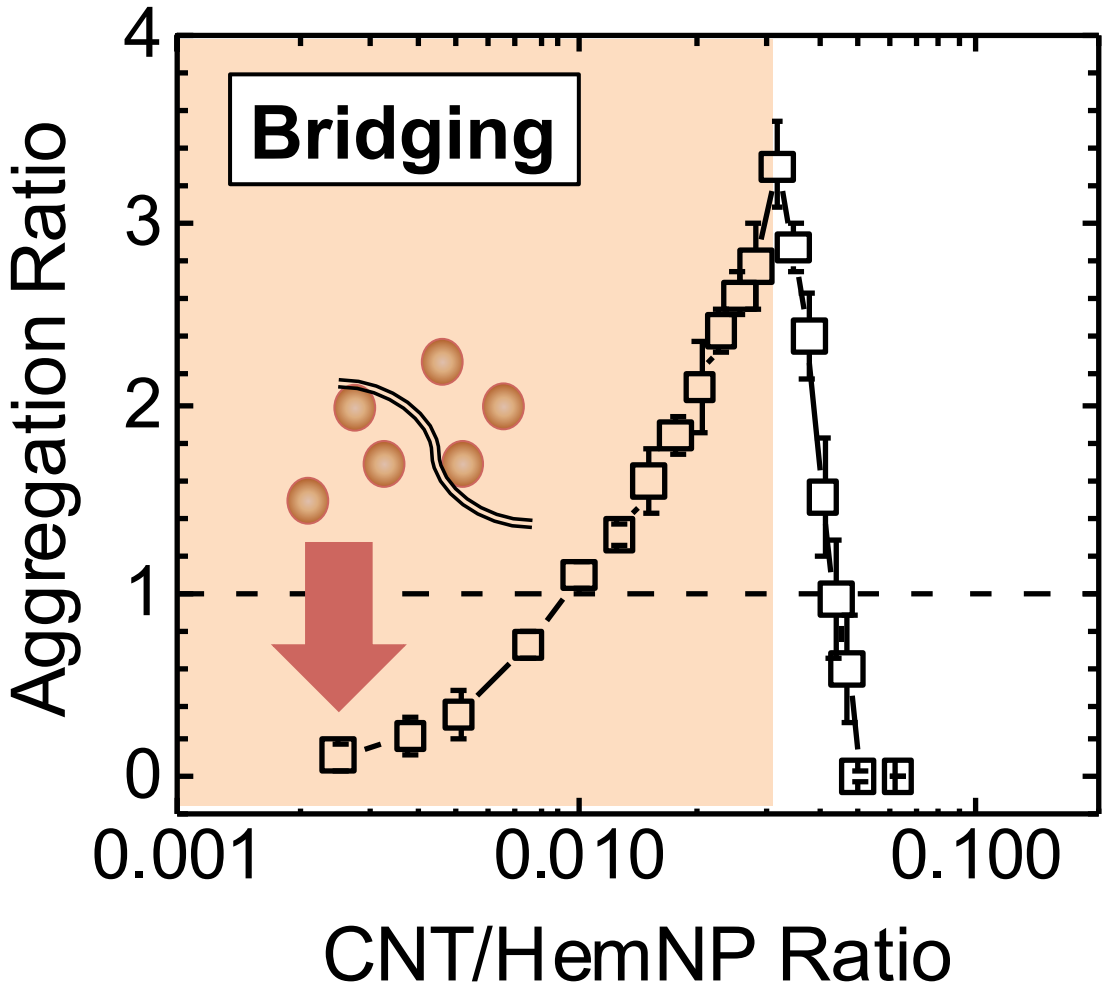
Mechanisms at Different CNT/HemNP Ratios



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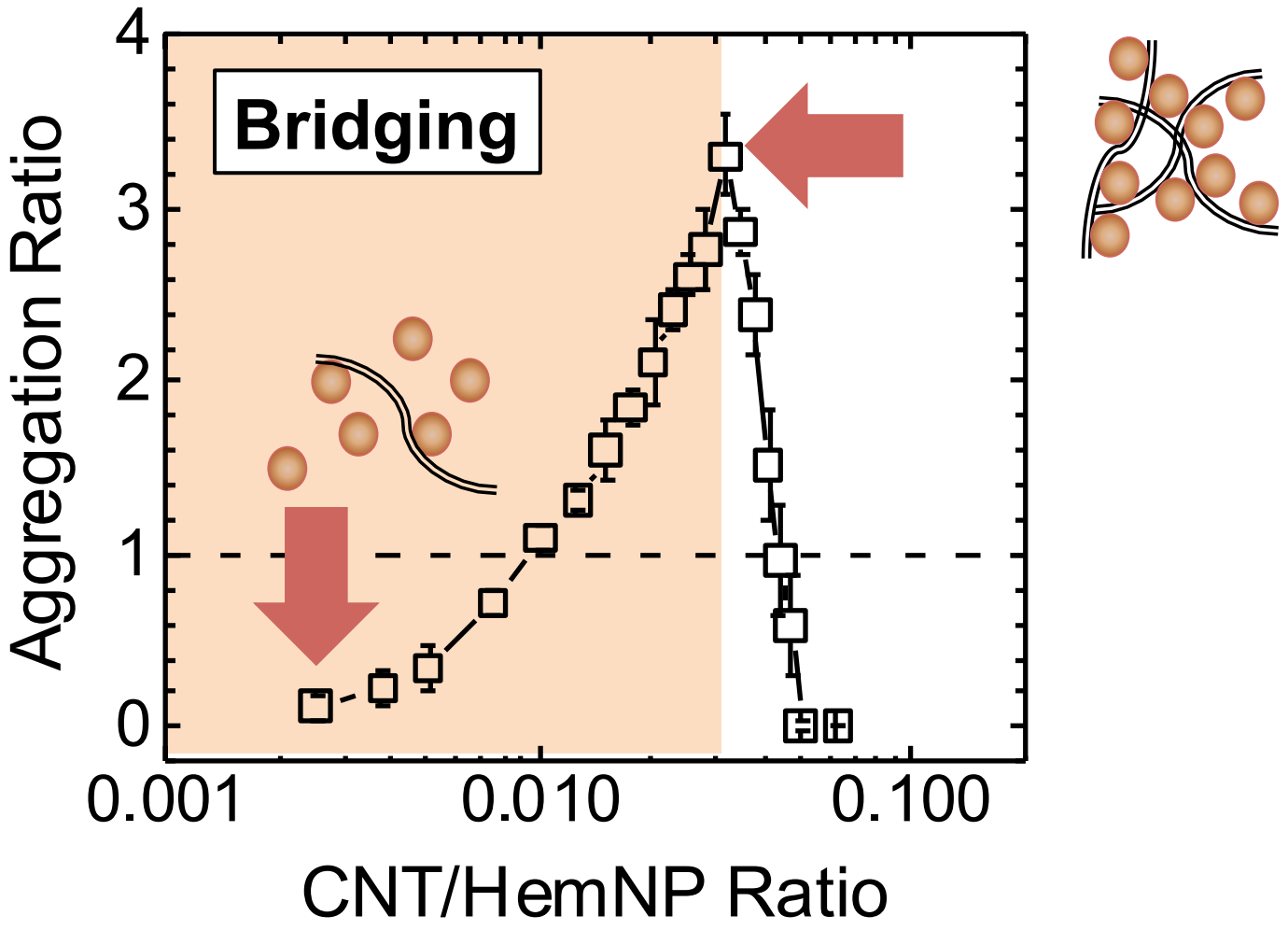
Mechanisms at Different CNT/HemNP Ratios



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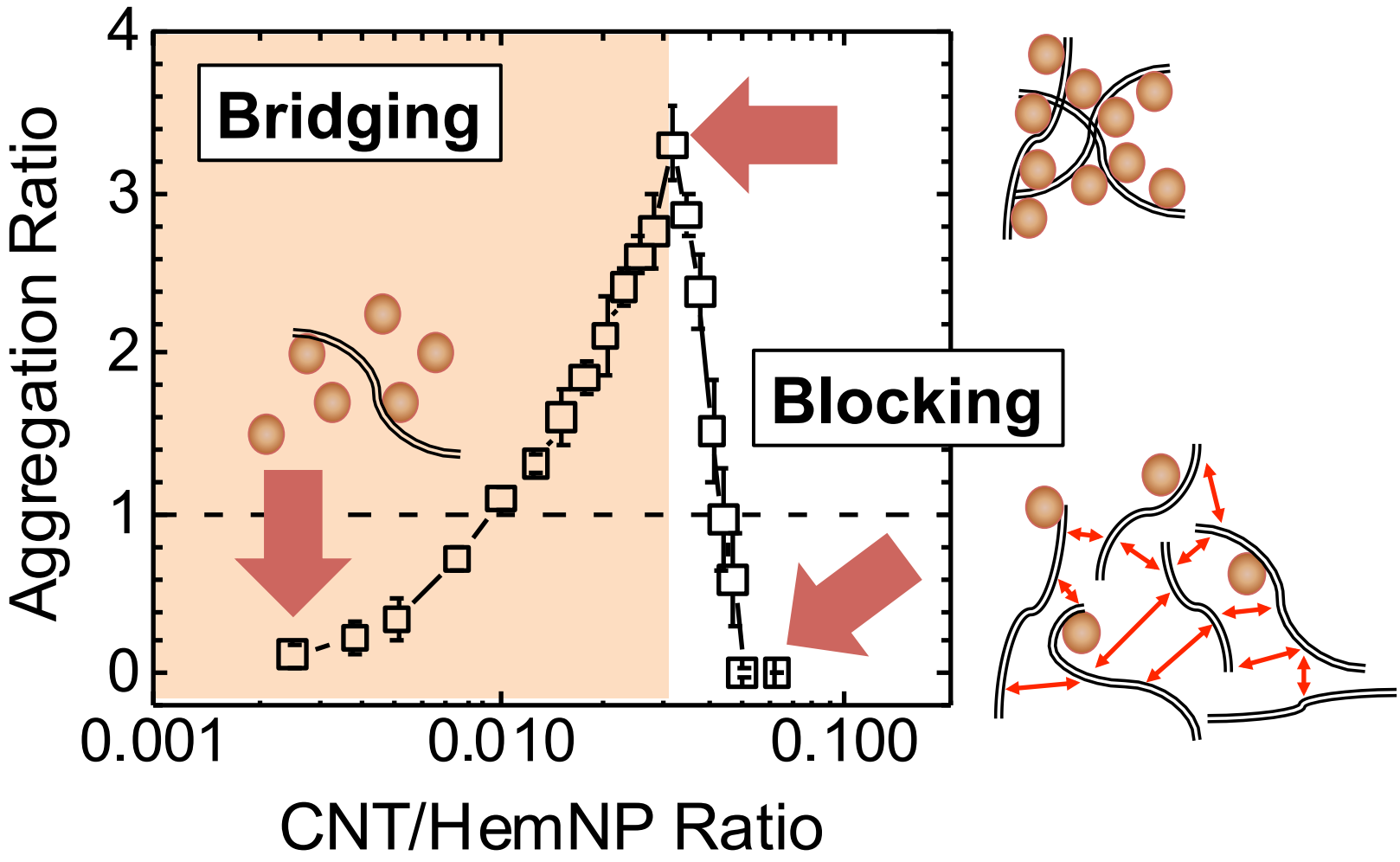
Mechanisms at Different CNT/HemNP Ratios



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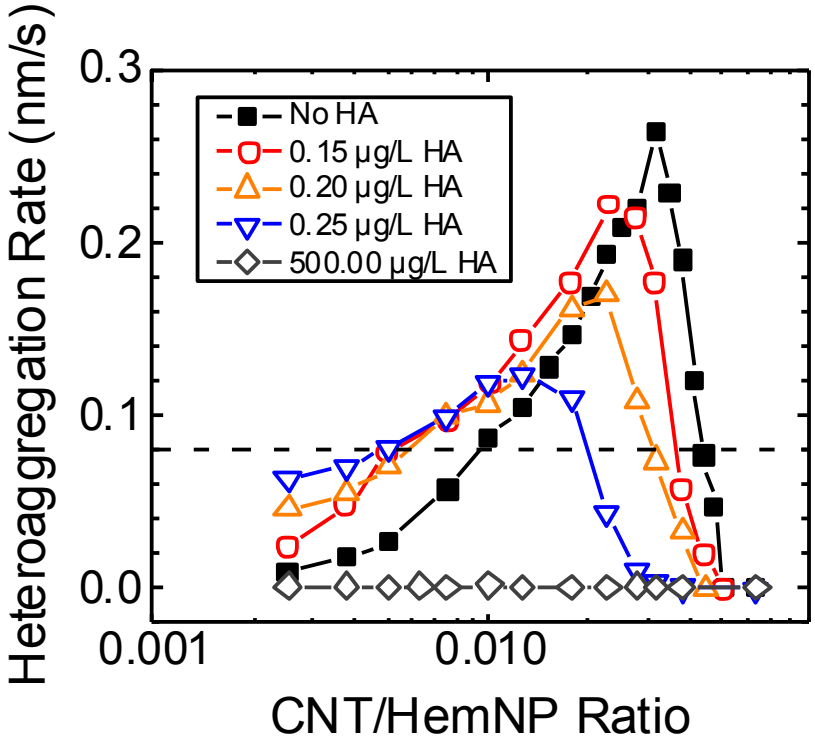
Heteroaggregation in the Presence of Humic Acid



- At different humic acid concentrations, the trends in the variation of heteroaggregation rate with CNT/HemNP ratio are similar to that in the absence of humic acid
- Maximum heteroaggregation rate decreases as humic acid concentration increases

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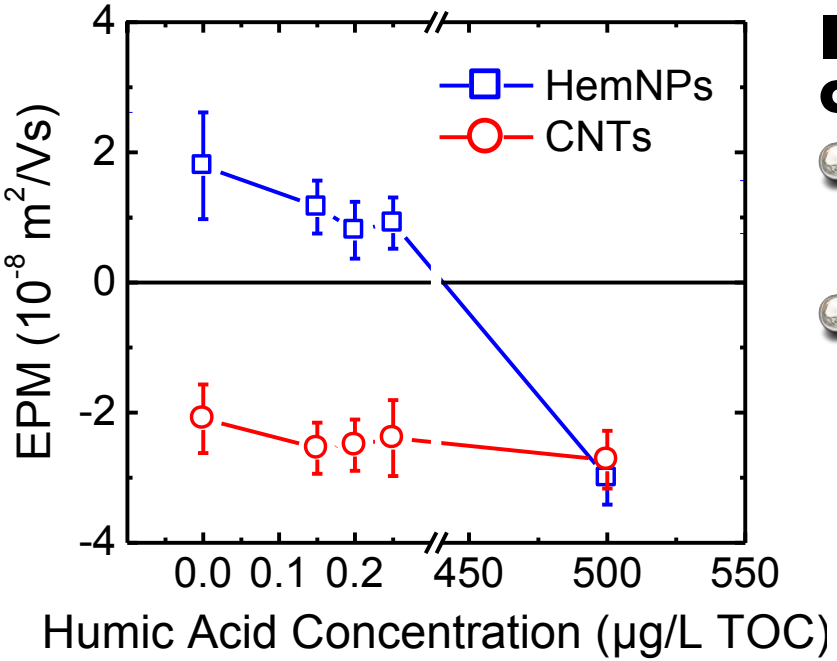
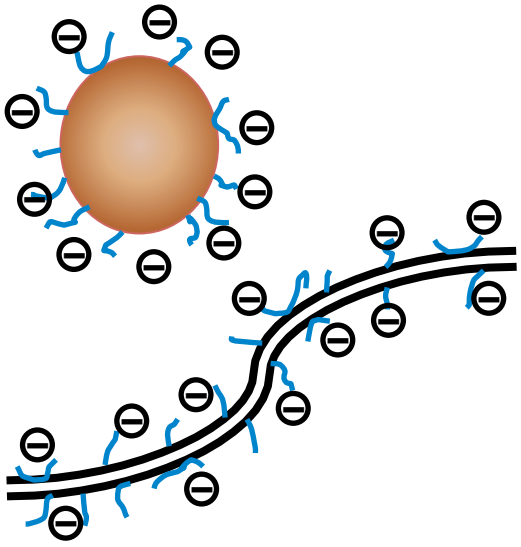
Heteroaggregation in the Presence of Humic Acid



Increase in humic acid concentrations

- Had no significant effect on the surface charge of CNTs
- Reduced the positive charge of HemNPs



Decrease in heteroaggregation rates in the presence of humic acid

- Decrease in electrostatic attraction
- Presence of electrosteric repulsion

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Conclusions

- The growth rates of heteroaggregates are dependent on CNT/HemNP ratios
- Bridging and blocking are speculated to occur at low and high CNT/HemNP ratios, respectively
- The increase in humic acid concentration results in a decrease in heteroaggregation rates due to charge neutralization (or reversal) of HemNPs and electrosteric repulsion

The results of this study have been published on *EST*, 46 (2012), 5912 - 5920

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