Transport of Nanoparticles in Porous Media

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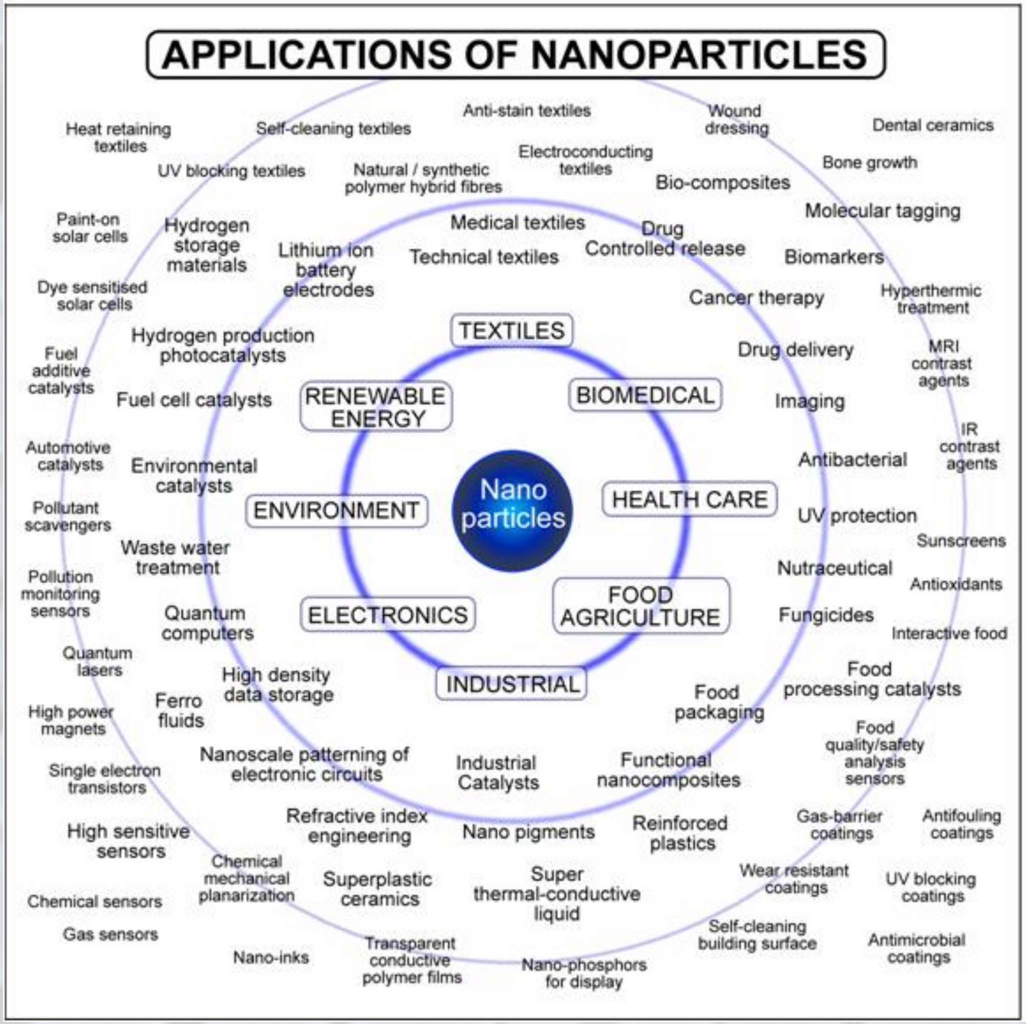
Nanoparticles

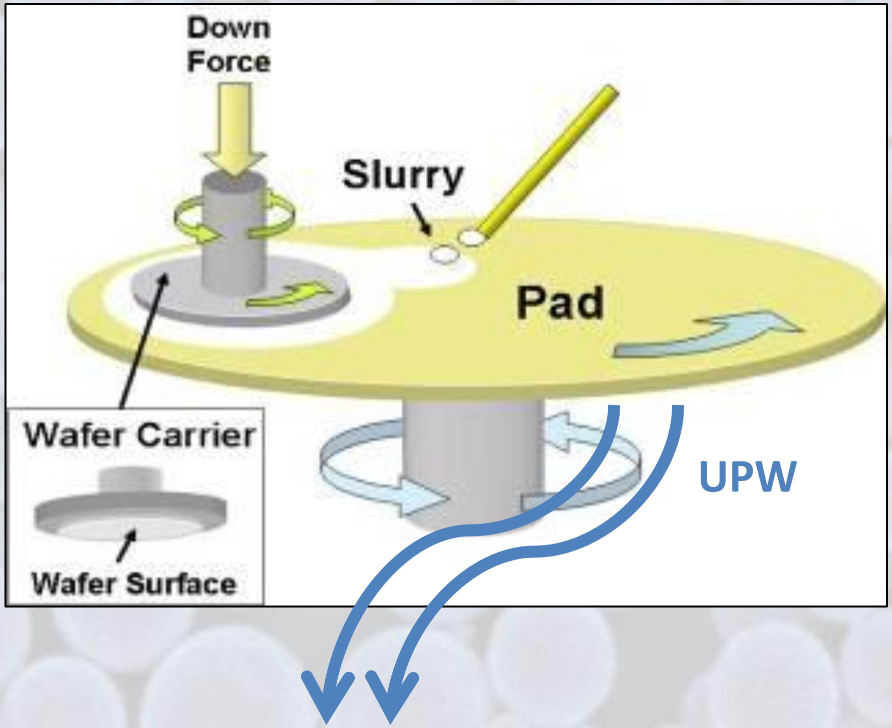
- Unique electronic, optical, thermal and photoactive properties
- Currently found in ~80 consumer products and over 600 raw materials
- Applications in coatings, computers, clothing, cosmetics, sports equipment and medical devices



Semiconductor Manufacturing

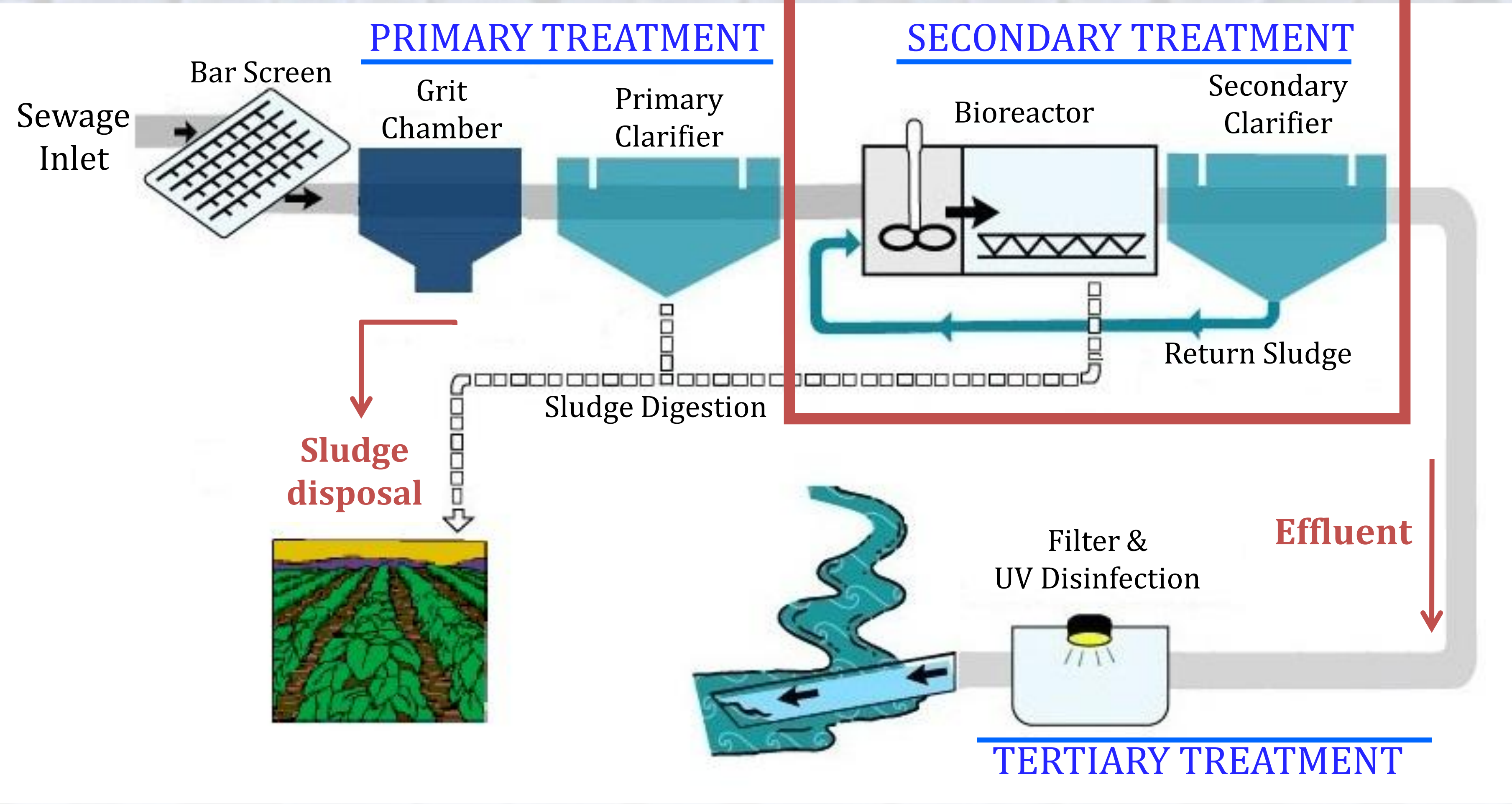
- Nanoparticles utilized in:
  - **CMP**
  - Immersion Lithography
  - CVD

- Common Oxide NPs:
  - Silica
  - Alumina
  - Ceria
  - Titania
  - Zirconia

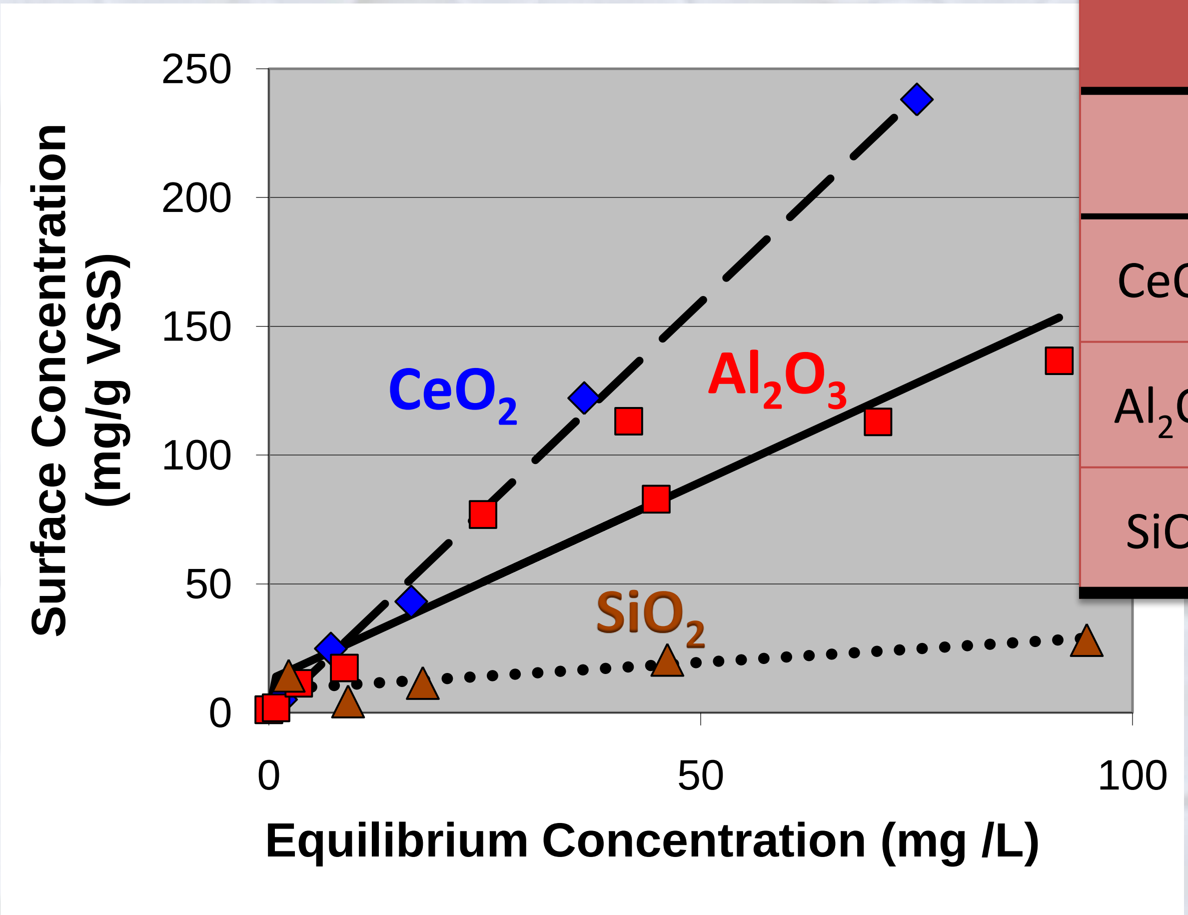


Effluent Nanoparticle Concentration
50 – 500 mg/L

Previous Work



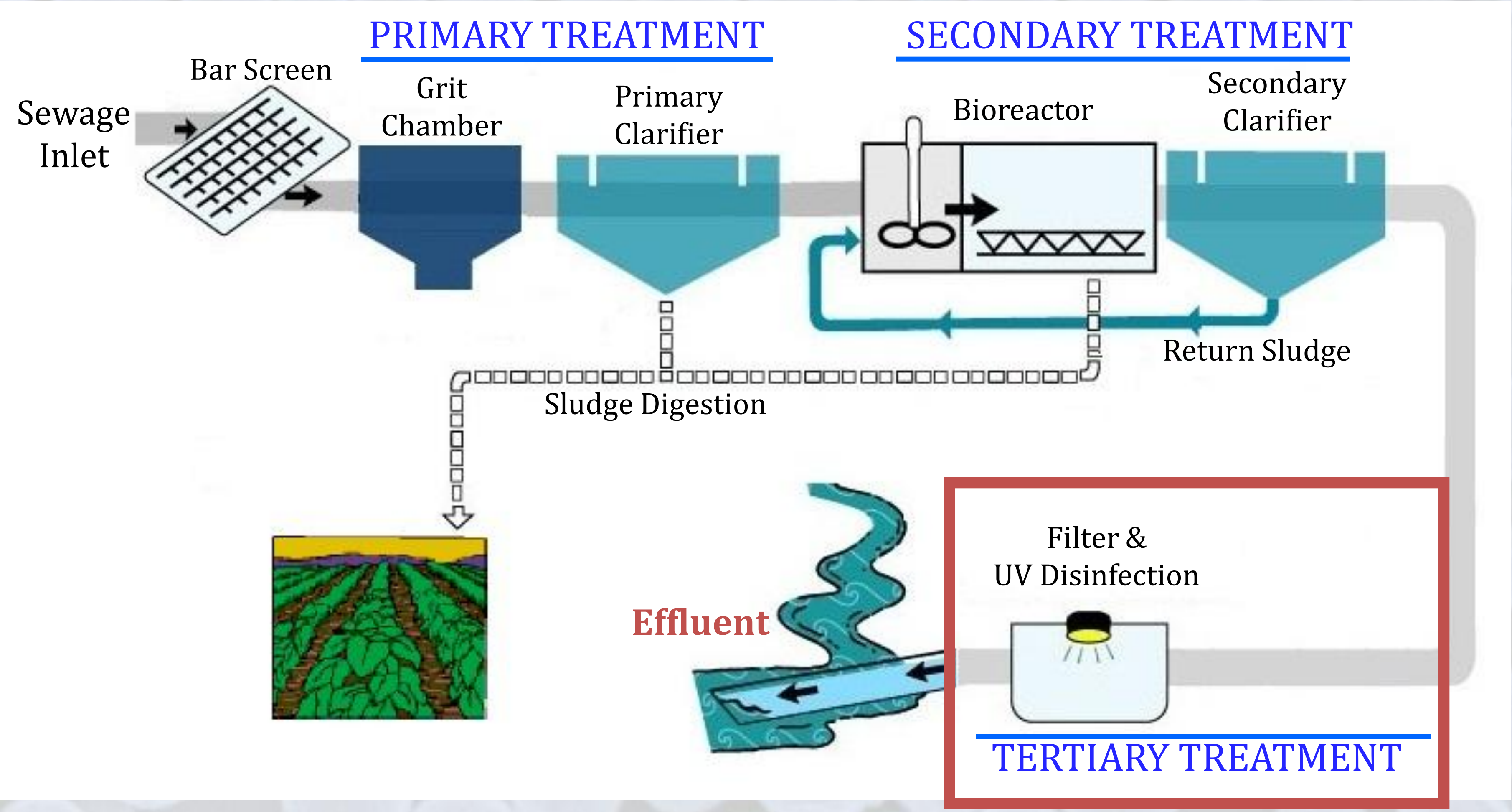
Previous Work



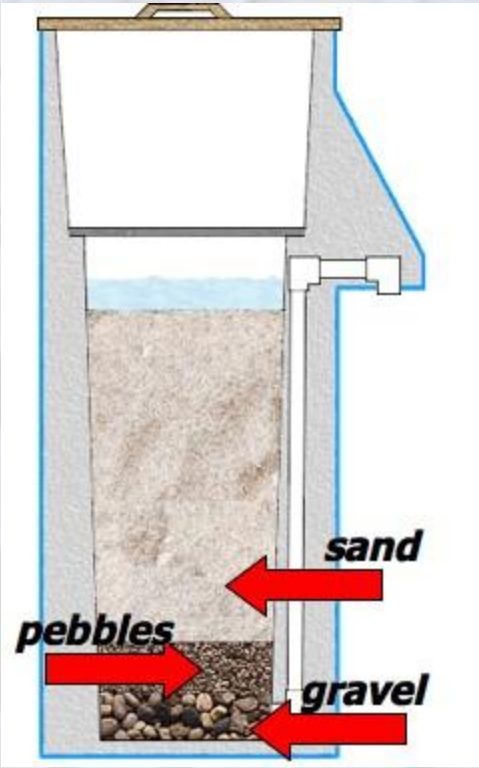
Removal Efficiency

	Settling	*Biosolid*	*Total*
CeO_2	---	50.7%	50.7%
Al_2O_3	29.3%	29.6%	58.9%
SiO_2	---	17.2%	17.2%

Previous Work



Porous Media Filtration

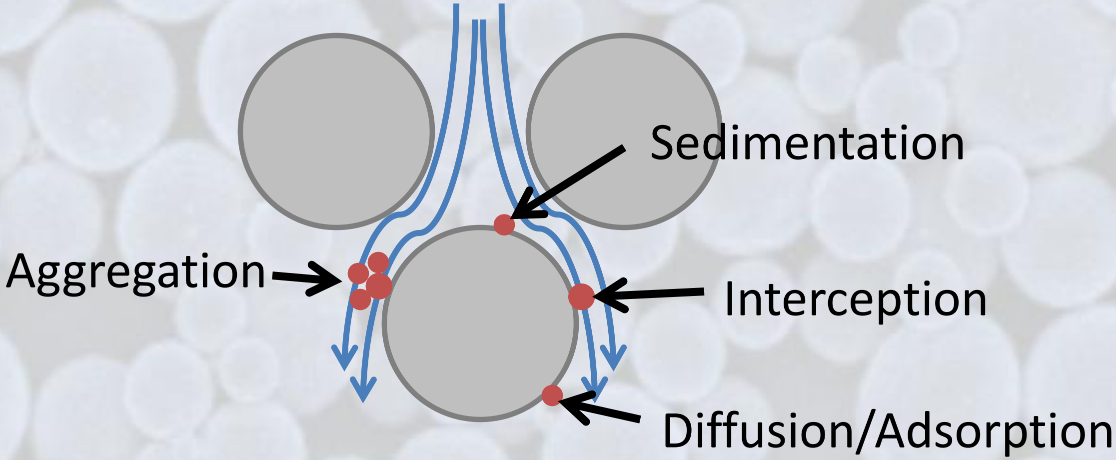


*Blue Energy Group

- One of the oldest water treatment technologies dating to ~2000 B.C.
- Applications in drinking water and wastewater treatment
  - Removal of particulate matter
  - Often used with coagulants
- Also may be used to model transport in the water table

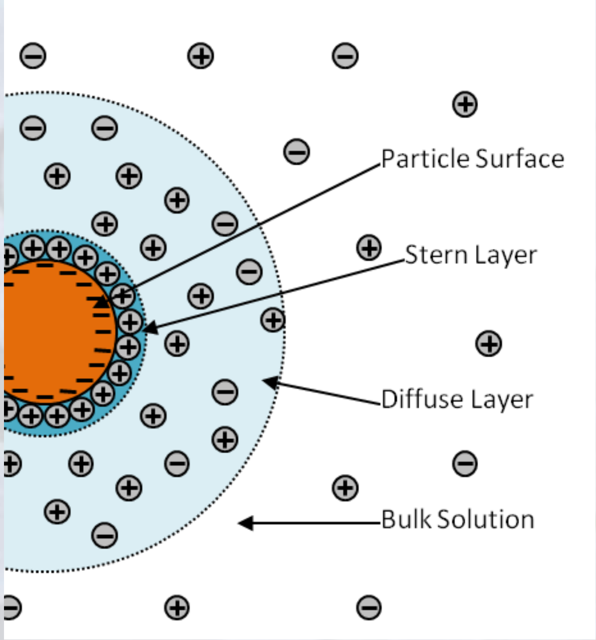
Porous Media Filtration

Removal Mechanisms



Aggregation and Diffusion/Adsorption
are expected to dominate

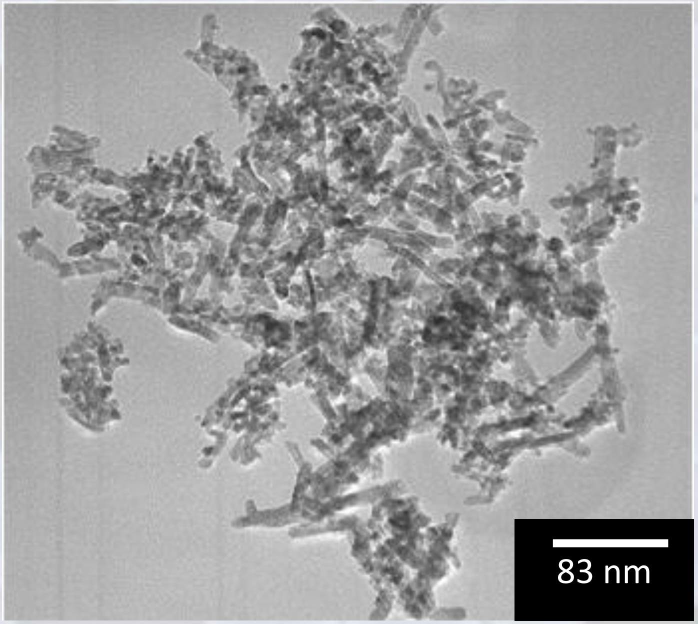
Aggregation Principles

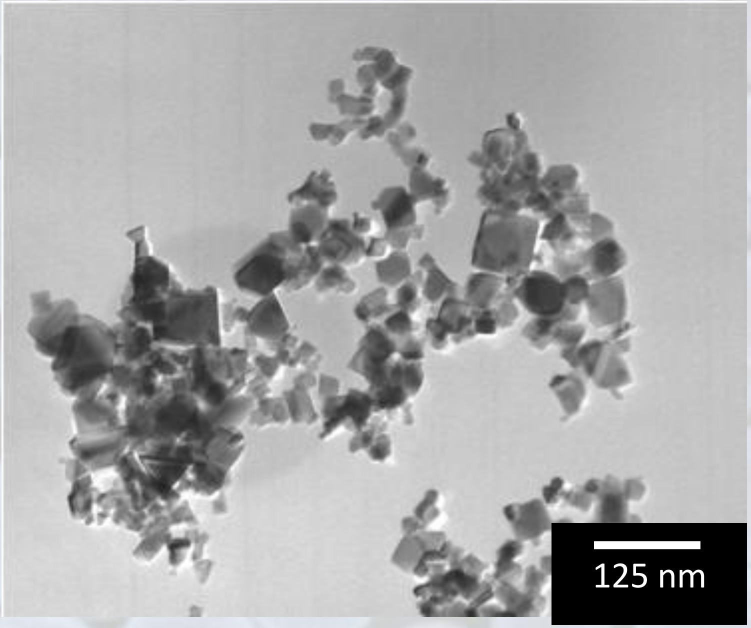


- DLVO Theory Interactions
  - van der Waals
  - Electrical double layer
- Steric Interactions
- Hydration

Nanoparticle Specific Principles

- Heterogenous Collector Surfaces
- Primary Energy Minimum
- Shape Effects





Aggregation Studies

Particle	Size	Concentration	Parameters Studied	Conclusions	Ref
TiO_2	4-6 nm	80 mg/L	4.5 – 16.5mM NaCl 12.8mM CaCl2 pH 4.8 – 8.2	Divalent cations increase aggregation rate	[1]
Fe_2O_3	20nm	10 – 200 mg/L	10-100 mg/L SRHA	HA adsorption contributes to stability	[2]
SiO_2/ Fe_3O_4	56nm	2470 mg/L	2-3 µmol/m^2 Tween 20	Non-ionic Surfactant results in decreased stability	[3]
TiO_2	5 nm	1 mg/L	5 – 100mM NaNO3 0.2 – 5 mg/L FA pH 2 – 8	Aggregation near pH of PZC; FA increased stability	[4]

Adsorption Principles

- Transport governed by Brownian diffusion
- Deposition dependant on:
  - Particle Size
  - Collector Size
  - Solution Chemistry
  - Zeta Potential
  - Hamaker Constant
- Attachment Efficiency

$$\eta = \alpha \eta_o$$

Adsorption Studies

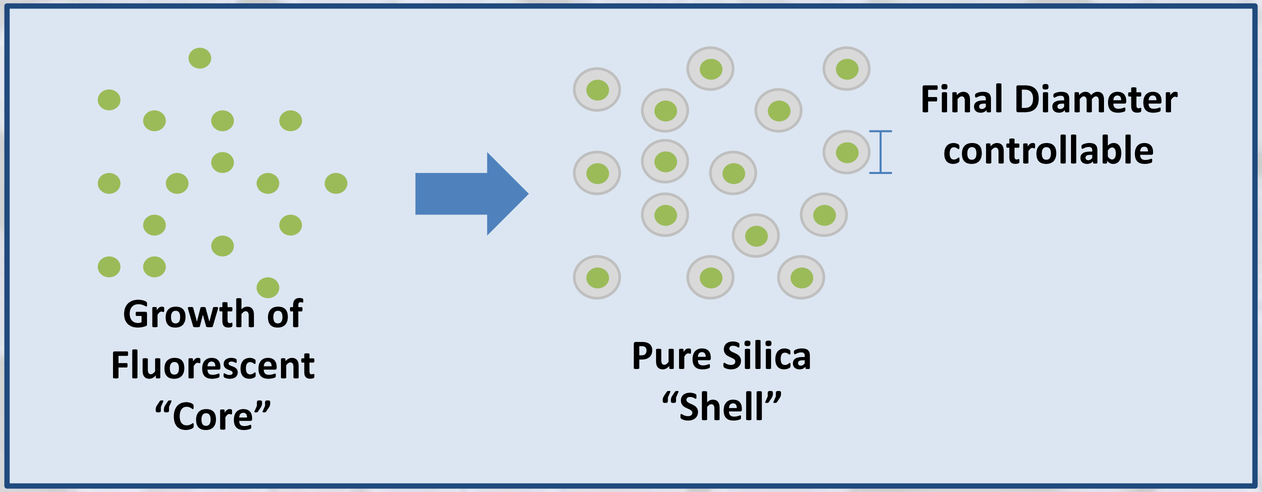
Particle	Size	Conc.	Collector	Parameters	Conclusions	Ref
CuO	372nm (<50 prim.)	9 mg/L	2-D Etched Glass	0.01M NaCl pH 7 0.01 – 0.1% SDS	SDS enhances elution	[5]
SiO_2	57 nm 135 nm	10 mg/L	Glass Beads (355µm)	0.01M NaCl pH 7	Low affinity; Larger particles better retained; no impact due to flow rate change	[6] [7]
TiO_2	<0.1µm	50-100 mg/L	Quartz Sand (200µm)	0.01M NaCl pH 4.5	High particle retention	[8]
TiO_2	32 nm	50 mg/L	Quartz Sand (650µm)	$I = 10^{-3} – 10^{-1}$ M pH 3, 6, 8	Retention increased with increasing ionic strength	[9]
TiO_2 ZnO CuO	<100 nm <100 nm <50 nm	n/a	Glass Beads	0.01-0.1M NaCl pH 7, 12 60mg/L HA	Mobility increases with addition of HA	[10]

Needs in Curent Transport Study

- Highly uniform particle size distribution
  - Ability to compare size effect between nanoparticles
- Real-time aggregation and deposition measurement
- Cohesive model for nanoparticle removal
  - Accounting for aggregation in adsorption
  - Including effect of common contaminants

Nanoparticle Synthesis

- Fluorescent Core/Shell Silica Nanoparticles



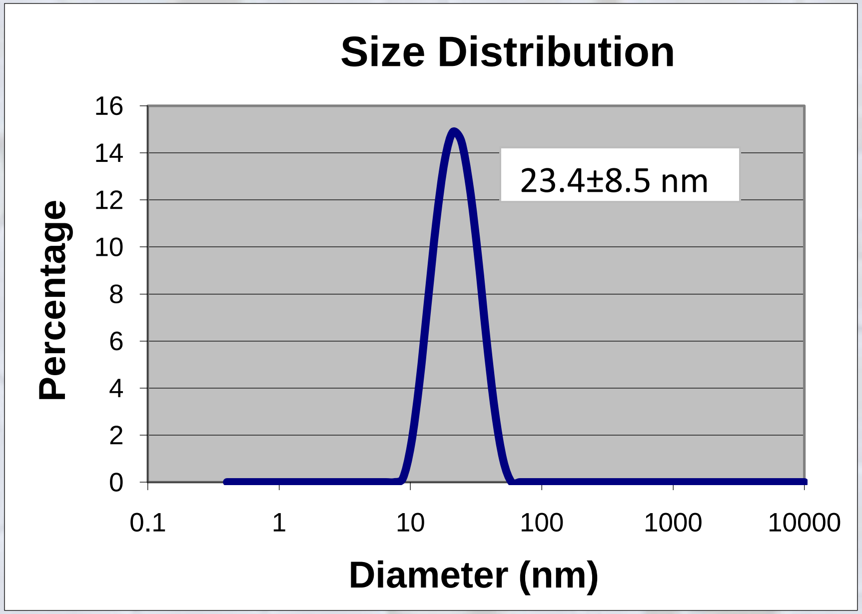
Dye Precursor
APTES and NHS-Fluorescein in Ethanol

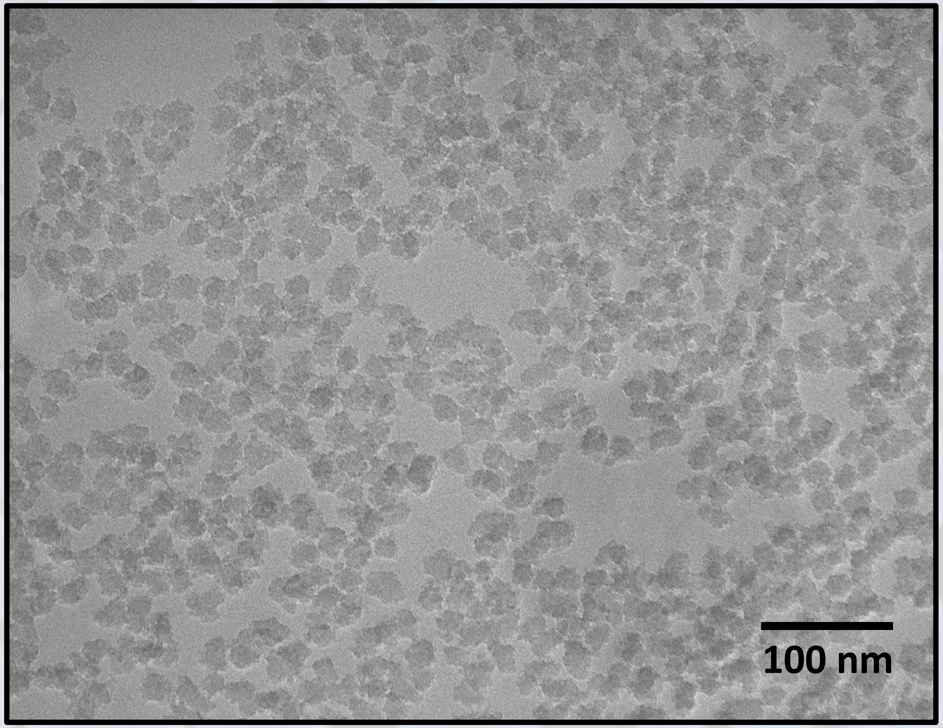
Core
TEOS in ammonia and ethanol solution

Shell
TEOS aliquots added sequentially to desired size

Nanoparticle Synthesis

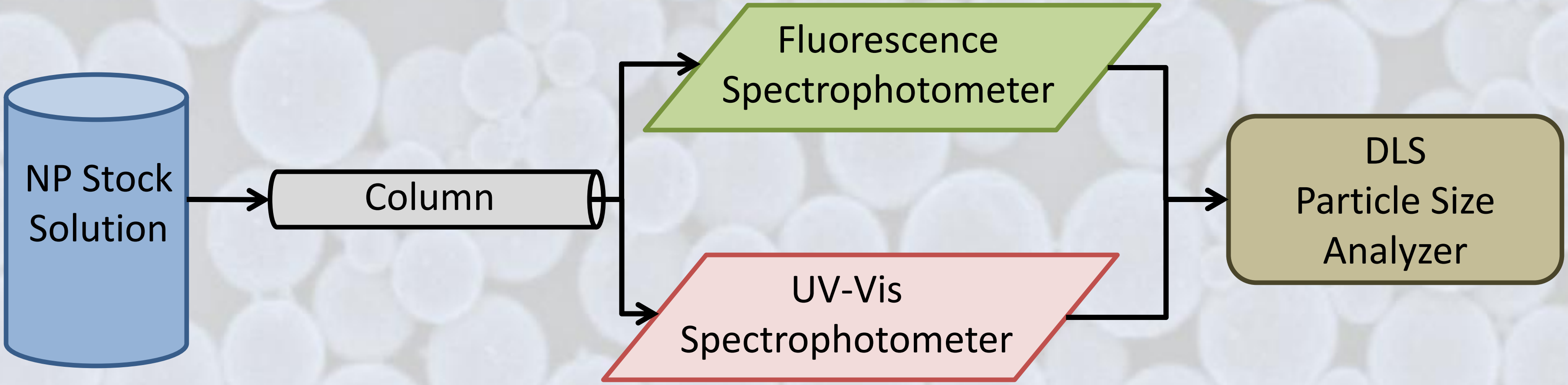
- Fluorescent Core/Shell Silica Nanoparticles





New Experimental Setup

- Measurement of Light Absorption or Fluorescence
- On-line measurement of concentration and particle size



Uptake Model

- Assuming spherical primary particles:

$$\frac{\partial \Gamma}{\partial \tau} = \frac{1}{Pe}\frac{\partial^2 \Gamma}{\partial x^2} - \frac{\partial \Gamma}{\partial x} - \alpha\left[K_a \Gamma(1-\theta) - K_d \theta\right]$$

$$\frac{\partial \theta}{\partial \tau} = K_a \Gamma(1-\theta) - K_d \theta$$

Variables

Γ = relative nanoparticle concentration
Θ = fractional surface coverage
x = dimensionless reactor length
τ = dimensionless time

Fit Parameters

K_a = 1st order adsorption MXC
K_d = 1st order desorption MXC

References

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