Task Title: Preparation and Characterization of Model CMP Nano-Particles

(Task Number: 426.036)

PIs:

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- **Sara Gallagher**

Other Researchers: ---

Cost Share (other than core ERC funding):

- **UA TRIF program: $10,000**
- **CONACyT doctoral fellowship to JGE**

ESH Metrics and Impact

1. **Reduction in the use or replacement of ESH-problematic materials**

   This project will evaluate the toxicity of four model CMP slurries. This information can assist in selecting materials which are candidates for replacement or use reduction, if any.

2. **Reduction in emission of ESH-problematic material to environment**

   The knowledge gained will be utilized to predict the removal of nanoparticles in CMP waste during municipal wastewater treatment. The project also aims to develop a cost-effective on-site treatment method for the removal CMP NPs prior to indirect discharge into the sewer or direct discharge to surface water.

Overview

1. **Introduction: Need for Model CMP Slurries Supported by Research on the Toxicity of CMP Nanoparticles**
   - ➢ Nanoparticle toxicity influenced by synthesis route
   - ➢ Nanoparticle toxicity affected by particle morphology
   - ➢ Nanoparticle porosity alters cytotoxic response

2. **Model CMP Slurries for Nanoparticle ESH Studies**

3. **Characterization of Model CMP Slurries by SRC CMP Nanoparticle Consortium**

4. **Characterization of Model CMP Slurries at the Univ. of Arizona**
   - ➢ Physico-chemical characterization
   - ➢ Toxicity screening – Microtox assay
   - ➢ Nanoparticle stability in municipal wastewater

Need for Model CMP Slurries Supported by Research on the Toxicity of CMP Nanoparticles

Existing literature shows a considerable variation in the inhibitory impact of engineered nanoparticles (NPs), even in studies using the same target organism and toxicity assay.

This variability is not surprising since the adverse effects of engineered NPs can be affected by factors such as:

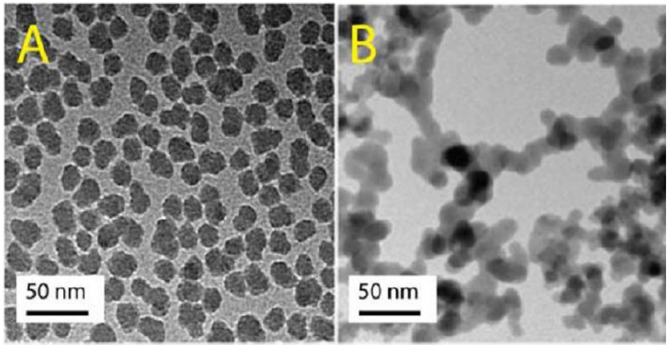
- **Particle size**
- **Particle morphology**
- **NP synthesis method**
- **NP history**
- **Bioassay medium**

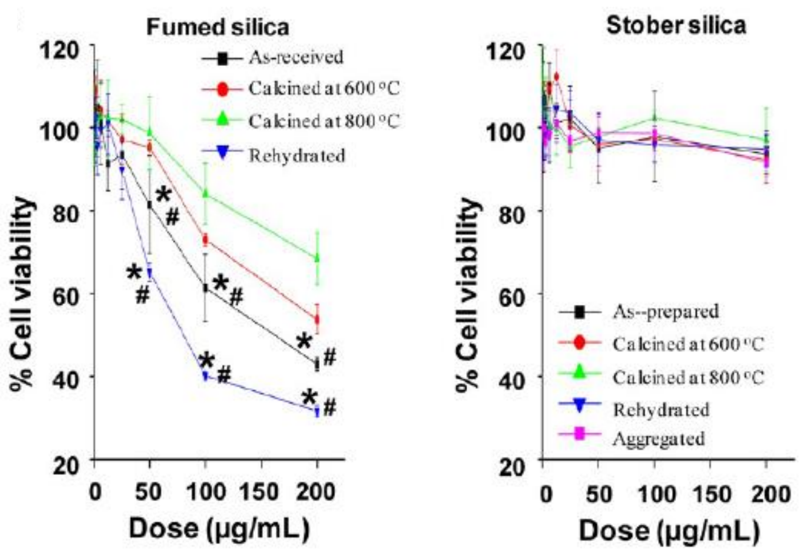
Assessment of the potential toxicity of CMP NPs requires model CMP slurries prepared with the SiO_2, CeO_2 and Al_2O_3 NPs utilized by industry.

Introduction -Toxicity of Colloidal SiO_2 vs Fumed SiO_2

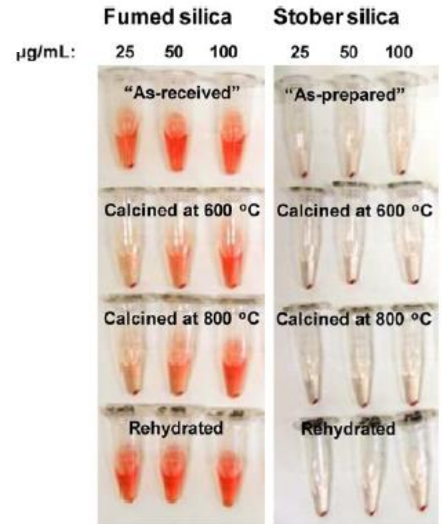
Zhang et al. 2012. J. Am. Chem. Soc. 134:15790−15804

Stöber colloidal silica NPs (A) was not toxic. Fumed silica (B) caused cytotoxicity

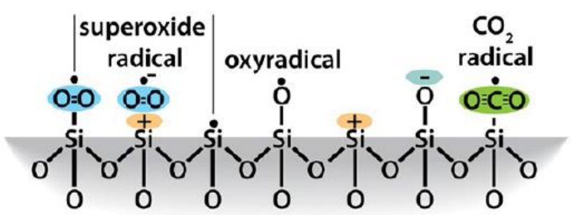




Impact of fumed SiO_2 (A) and colloidal SiO_2 (B) on viability of human bronchial epithelial cells



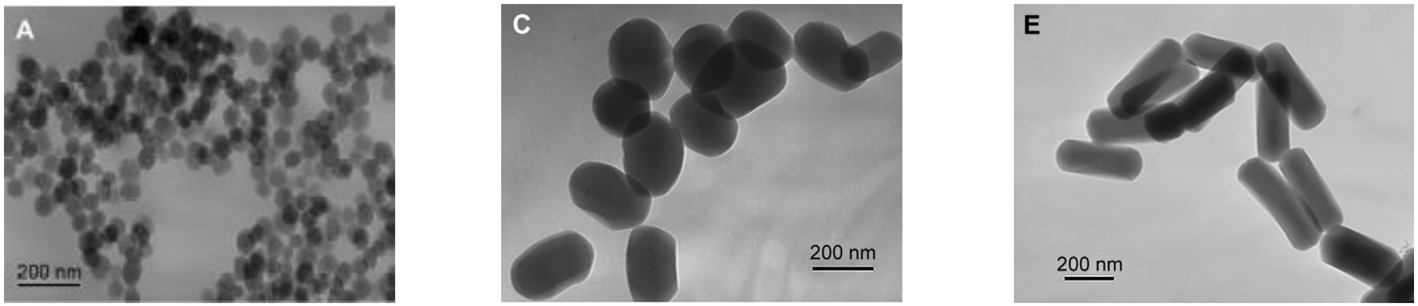
Erythrocyte hemolytic assays



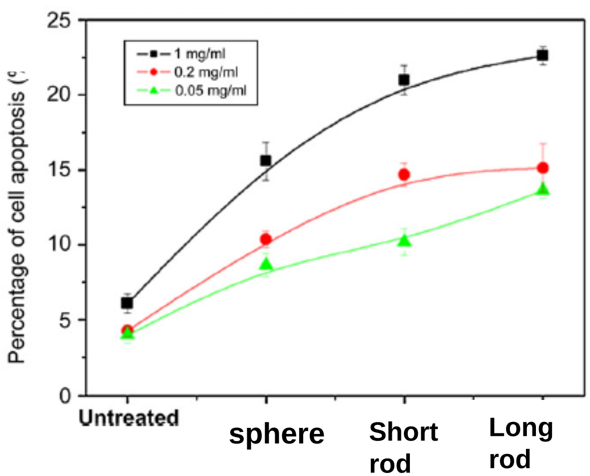
Positive correlation between hydroxyl concn. in fumed silica and its potential to generate reactive oxygen species (ROS) and cause red blood cell hemolysis.

Introduction - Effect of Shape of Mesoporous SiO_2 NPs on Cellular Uptake and Cell Function

Huang et al. 2010. Biomaterials 31:438-448



TEM images of three different shaped mesoporous SiO_2 NPs tested by Huang et al. 2010. The NPs had similar diameter , chemical composition and surface charge.



Effect of NP aspect ratio on early apoptosis of human melanoma cells. Toxicity increased: spheres < short rods < long rods

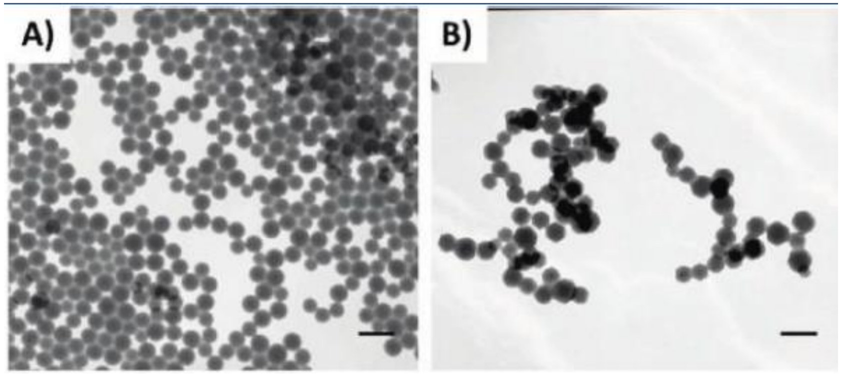
Particles with larger aspect rations were taken up in larger amounts by human melanoma cells and had faster internalization rates.

Particles with larger aspect ratios had a greater impact on different aspects of cellular function including cell proliferation, apoptosis, cytoskeleton formation, adhesion and migration.

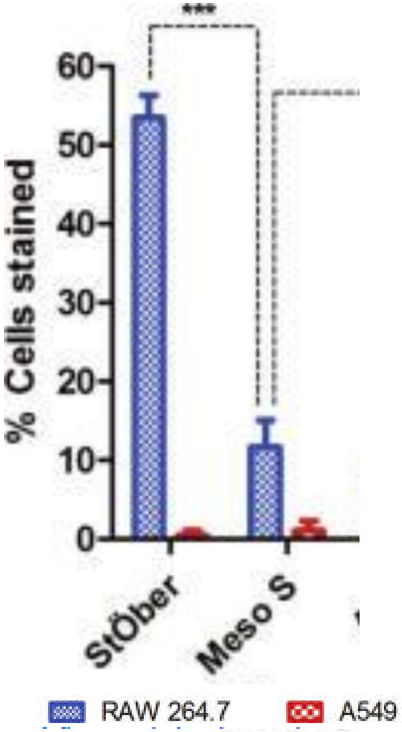
<u>Introduction</u>- Effect of SiO_2 NP Porosity on Cytotoxicity

Yu et al. 2011. ACS Nano, 5(7):5717–5728

The porosity of SiO_2 NPs is believed to affect their cellular toxicity.



TEM images of the Stöber SiO_2 (115 nm diameter) (**A**) and mesoporous SiO_2 (120 nm) (**B**) used by Yu et al. 2011. The surface area of the Stober and mesoporous SiO_2 is **24** and **663** m^2/g, resp.



Percent cells stained (*i.e.*, %cells experiencing plasma membrane damage) in studies with two types of cells, macrophages (blue) and cancer epithelial cells (red). Stober SiO_2 caused more macrophage cell damage than mesoporous SiO_2. None of the silica samples used damaged epithelial cell membranes at the concentrations used.

Model CMP Slurry for Nanoparticle ESH Studies

Background and Motivation:

To select, prepare, and distribute model slurry compound:

- **Uniform and well-defined, known composition, similarity and relevance to slurry used by industry**
- **Distribute to ERC projects and other selected researchers**
- **Signed agreement on usage and distribution of results**

Members of the Advisory Taskforce

- **David Speed (IBM), Chair**
- **S.V. Babu (Clarkson University)**
- **Mansour Moinpour (Intel)**
- **Reed Content (GlobalFoundries)**
- **Tim Yeakley (TI)**
- **Brian Raley (GobalFoundries)**
- **James Powers (Intel)**
- **Michael Trembley (Cabot)**

Samples Prepared By:

- **Cabot Microelectronics Corporation (Contact: Michael Trembley)**

Four Model CMP Slurries were Formulated for Research

Information from Cabot

Slurry Name	Composition (by weight)	pH	Particle Size (d, nm)
Colloidal SiO_2 (NS-0813-1)	**3% silica; < 1% acetic acid**	**2.5-4.5**	**50-60**
Fumed SiO_2 (NS-0813-2)	**5% silica; < 1% KOH**	**10**	**120-140**
CeO_2 (NS-0813-3)	**1% ceria**	**3-4**	**60-100**
Al_2O_3 (NS-0813-4)	**3% alumina, < 1% nitric acid**	**4.5-5.0**	**80-100**

CMP Slurry Characterization by CMP NP Consortium

- **Physico-chemical characterization**
  Size distribution, morphology, zeta potential, BET area, XRD, XPS, chemical analysis.
- **Toxicity studies**
- **Fate and treatment studies**

SRC – CMP Nanoparticle Consortium

Extensive characterization of CMP Slurries & Comparison of different measurement methods

Fragment from a table summarizing testing data

Method:		DLS (Dynamic Light Scattering)												
Data Source	CABOT	ASU [2]	CSM			JHU	NC A&T	UA			UT-D			
Particle Size (d, nm) [1]	**50-60**	45.1 ± 0.1	48.9 ± 0.1	49.0 ± 2.8	48.2 ± 0.6	62	30.1	37.4 ± 0.5	46.0 ± 0.2	56.2 ± 0.7	39.3	47.4	50.6	50.9
Polydispersity Index (PdI)	/	0.072	0.072	0.073	0.1	0.186	0.14	0.11	0.08	0.23	0.126	0.107	0.068	0.167
Refractive Index	/	1.542	1.542	1.542	1.542		1.54	1.47	1.47	1.47	1.47	1.47	1.47	
Dilution Factor	**1**		600 (50ppm)	600 (50ppm)	600 (50ppm)	100	1	1	10	100	1	10	100	1000
Diluent	**I water+ Acetic < 1**	DI water	10mM $NaHCO_3$	DI water	10mM NaCl	DI water	/	/	DI water	DI water	/	DI water	DI water	DI water
pH	**2.5-4.5**		8.4	5.2	4.9			3.3	3.8	4.5				
Particle Size (d, nm)	**120-140**	183.5 ± 2.0	152.7 ± 0.4	162.2 ± 2.8	153.4 ± 0.2	161	135.9	168.1 ± 3.5	147.8 ± 5.1	152.9 ± 3.3	171.5	158	161.1	168.5
Polydispersity Index (PdI)	/	0.109	0.085	0.112	0.109	0.130	0.14	0.17	0.11	0.11	0.173	0.119	0.137	0.128
Refractive Index	**1.460-1.461**	1.542	1.542	1.542	1.542		1.54	1.47	1.47	1.47	1.47	1.47	1.47	1.47
Dilution Factor	**1**		1000 (50ppm)	1000 (50ppm)	1000 (50ppm)	1000	1	1	10	100	1	10	100	1000
Diluent	**DI water+ KOH < 12**	DI water	10mM $NaHCO_3$	DI water	10mM NaCl	DI water	/	/	DI water	DI water	/	DI water	DI water	DI water
pH	**10**		8.5	9.1	7.4	6.12		10.6	10.3	9.8				
Particle Size (d, nm)	**60-100**	184.9 ±2.3	173.8 ± 4.4	144.2 ± 1.4	133.4 ± 7.6	136	98.7	89.4 ± 1.4	132.1 ± 0.1	133.4 ± 2.5	143.7 [3]	145.3	148.7	149.1
Polydispersity Index (PdI)	/	0.17	0.192	0.21	0.162	0.174	0.37	0.28	0.16	0.17	0.219	0.194	0.194	0.238
Refractive Index	/	2.200	2.2	2.2	2.2		2.2	1.8282	1.8282	1.8282	1.8282	1.8282	1.8282	1.8282
Dilution Factor	**1**		200 (50ppm)	200 (50ppm)	200 (50ppm)	1000	1	1	10	100	1	10	100	1000
Diluent	**DI water**	DI water	10mM $NaHCO_3$	DI water	10mM NaCl	DI water	/	/	DI water	DI water	/	DI water	DI water	DI water
pH	**3-4**		8.4	5.4	5.5	5.41		4.0	5.0	6.3				
Particle Size (d, nm)	**80-100**	156.6 ±1.5	1887 ± 90.9	135.0 ± 1.0	135.2 ± 1.6	134	131.6	124.6 ± 2.3	128.1 ± 0.1	129.1 ± 1.6	135.8 [4]	133.4	137.6	142.1 [5]
Polydispersity Index (PdI)	/	0.141	0.323	0.116	0.125	0.102	0.138	0.16	0.11	0.08	0.159	0.138	0.118	0.14
Refractive Index	/	1.765	1.765	1.765	1.765		1.75	1.76	1.76	1.76	1.76	1.76	1.76	1.76
Dilution Factor	**1**		600 (50ppm)	600 (50ppm)	600 (50ppm)	1000	1	1	10	100	1	10	100	1000
Diluent	**I water+ HNO3 < 12**	DI water	10mM $NaHCO_3$	DI water	10mM NaCl	DI water	/	/	DI water	DI water	/	DI water	DI water	DI water
pH	**4.5-5.0**		8.3	5.6	5.3	5.31		4.2	4.4	4.9				

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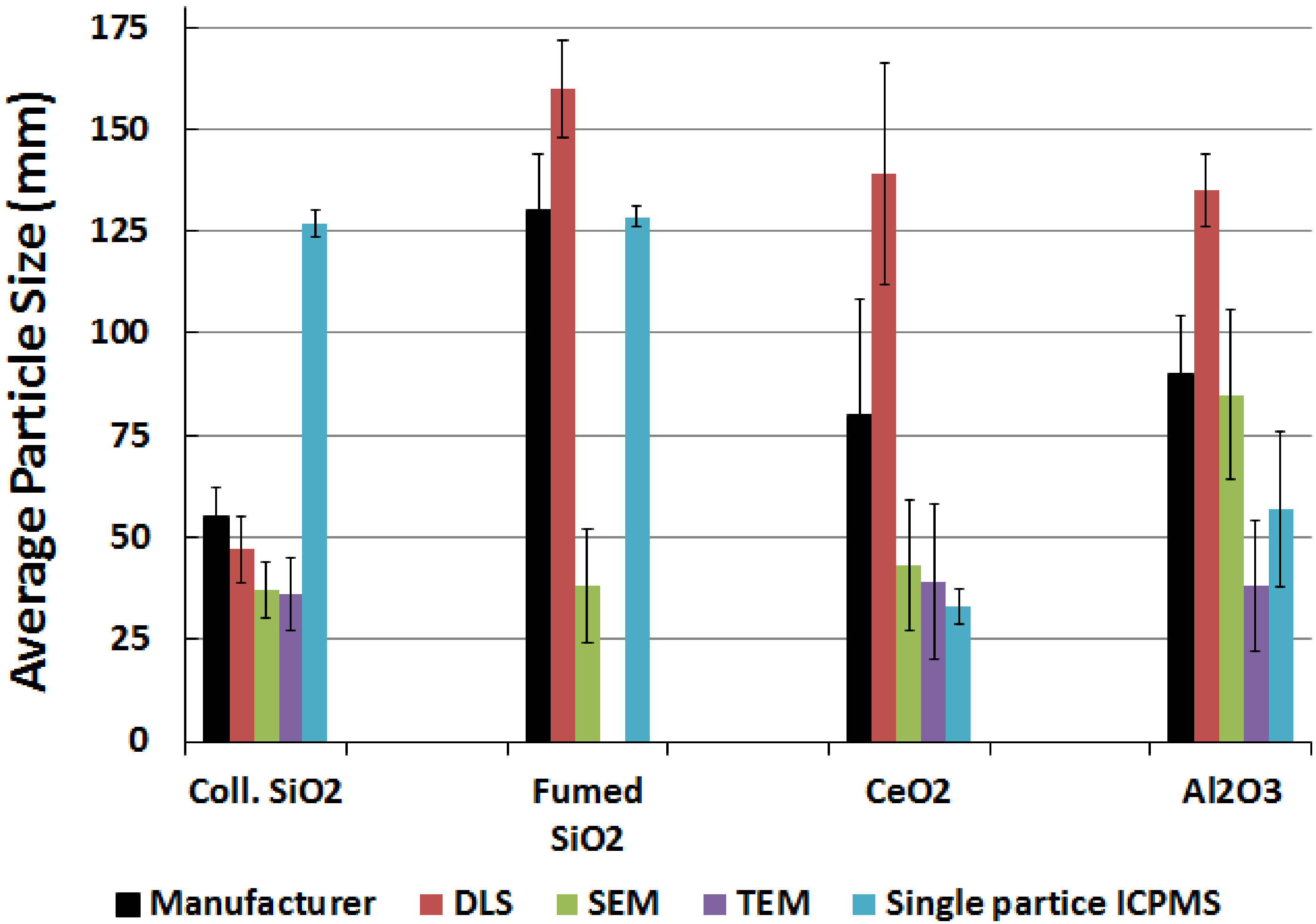
Comparison of Different Methods for NP Size Analysis



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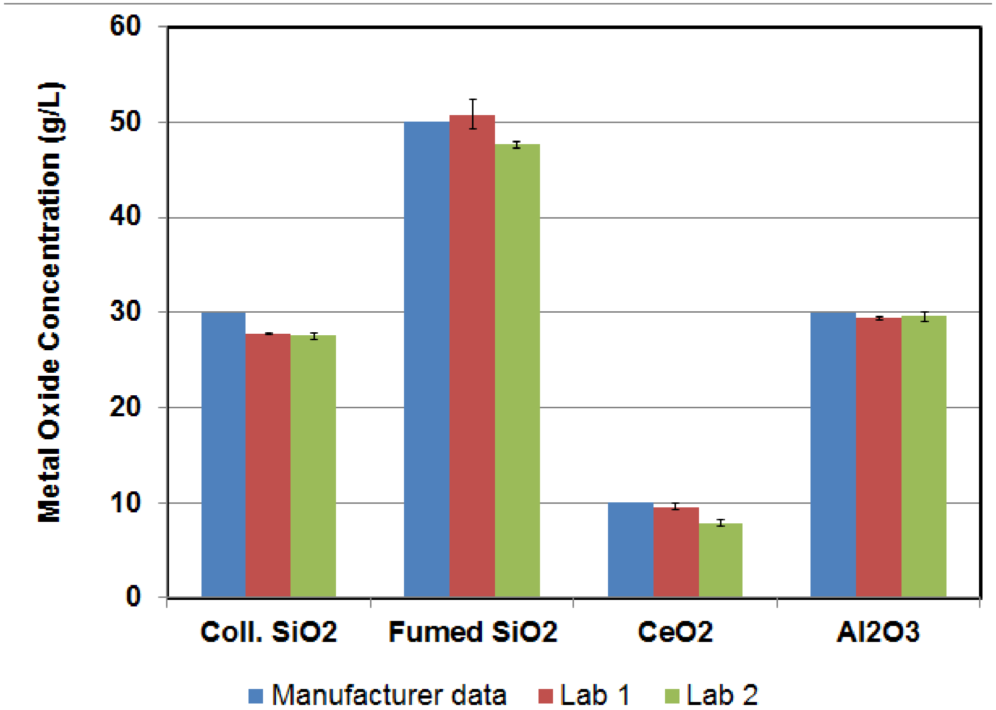
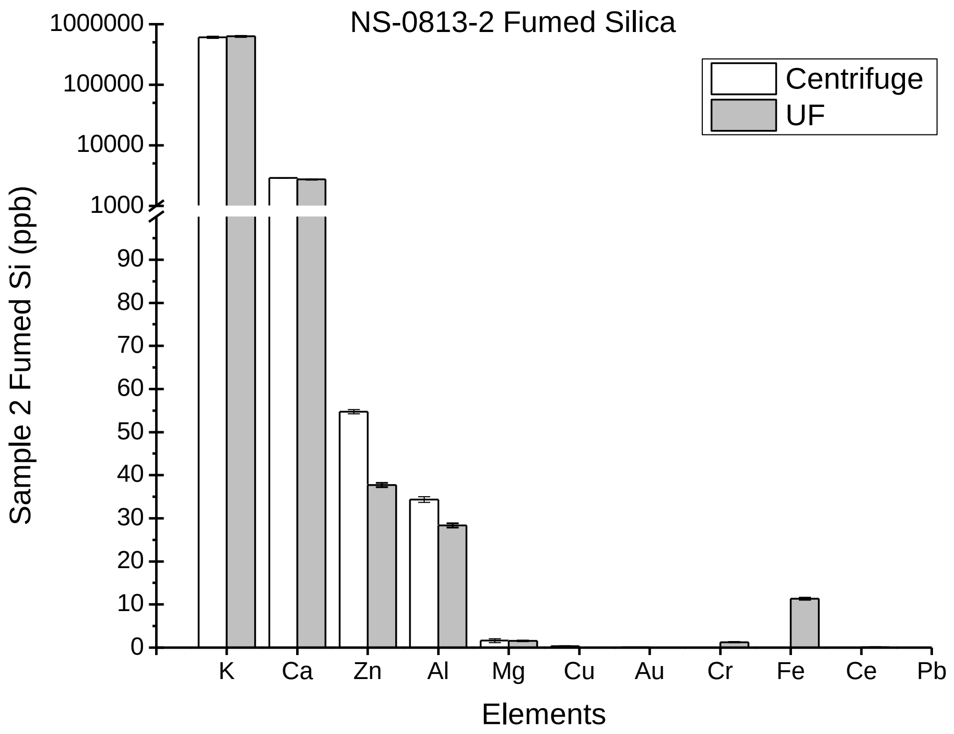
Comparison of Different Methods for NP Digestion



Lab 1 (ASU) - SiO_2: 10 mL samples digested in 24% tetramethylammonium hydroxide (4 mL)
CeO_2: 5 mL sample digested in 50% HF (2 mL) + 70% HNO (8 mL)
Al_2O_3: 5 mL sample digested in 50% HF (2 mL) + 70% HNO_3 (6 mL) + 35% HCl (35%)

Lab 2 (UA)- SiO_2**:** 1 mL samples digested in 1% HF (10 mL)
CeO_2: 1 mL sample digested in 70% HNO_3 (8 mL) + 30% H_2O_2 (2 mL)
Al_2O_3: 1 mL sample digested in 3.65% HCl (10 mL)

Analysis of Dissolved Metals in CMP Slurries and Comparison of Different Methods for NP Removal



Concentrations of dissolved elements in fumed SiO_2 slurry. "Centrifuge" corresponds to samples from UTD. "UF" corresponds to samples treated with centrifugal ultrafiltration (30K Da) at ASU.

Characterization of Model CMP Slurry at U. of Arizona

- ***Physico-chemical characterization***
- ***Toxicity screening – bacterium A. vibrio***
- ***NP Stability in municipal wastewater***

Material and Methods

Particle Size Distribution (PSD):

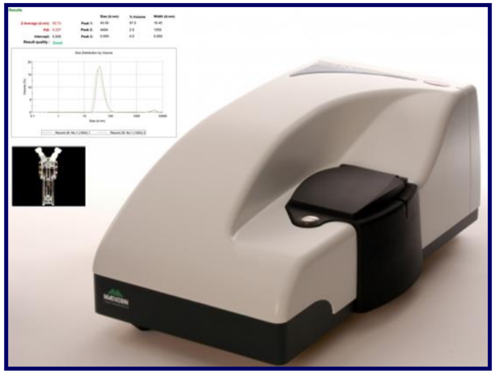
Measured by dynamic light scattering (DLS) using a Malvern ZetaSizer Nano ZS instrument (ZEN3600), with 633 nm laser and 173° scattering angle.

Zeta Potential:

Measured using a Malvern ZetaSizer Nano ZS instrument (ZEN3600).

Chemical analysis:

A microwave assisted digestion system(CEM MARS Xpress) was used for acid digestions. The concentration of Si, Ce and Al was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) at a wavelength of 228.802, 238.578 and 196.026 nm, respectively.

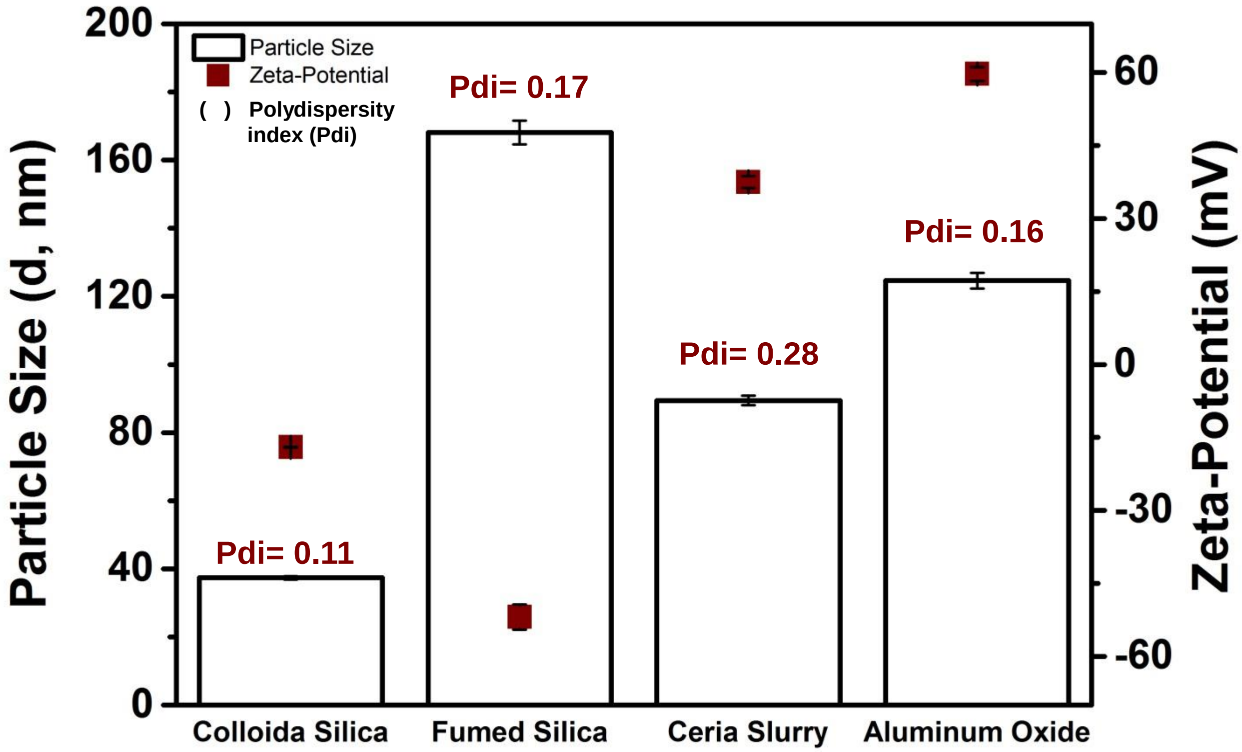


Chemical Characterization

Slurry Code	Category	Reported Data	Determined Data
Acidic Colloidal Silica (NS-0813-1)	SiO_2 conc. (g/L)	30.0	**27.5 ± 0.4**
	pH	2.5-4.5	3.3
	Additives:		
	Acetic Acid (g/L)	< 1%	0.8 ± 0.0
Alkaline Fumed Silica (NS-0813-2)	SiO_2 conc. (g/L)	50.0	**47.6 ± 0.4**
	pH	10.0	10.6
	Additives:		
	KOH (g/L)	< 1%	1.1 ± 0.0
Ceria Slurry (NS-0813-3)	CeO_2 conc. (g/L)	10.0	**7.9 ± 0.3**
	pH	3-4	4.0
	Additives:	/	/
Aluminum Oxide (NS-0813-4)	Al_2O_3 conc. (g/L)	30.0	**29.6 ± 0.5**
	pH	4.5-5.0	4.2
	Additives:		
	HNO_3 (g/L)	< 1%	0.1 ± 0.0

The chemical characterization results obtained are in good agreement with the data reported by Cabot.

Physical Characterization



The average particle size data determined are in agreement with the data provided by Cabot.

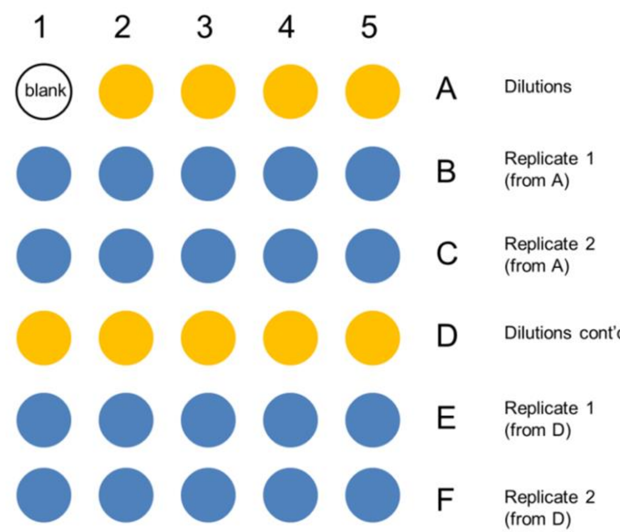
Nano-sized inorganic oxides in the various model CMP slurries are fairly stable under original condition.

Material and Methods

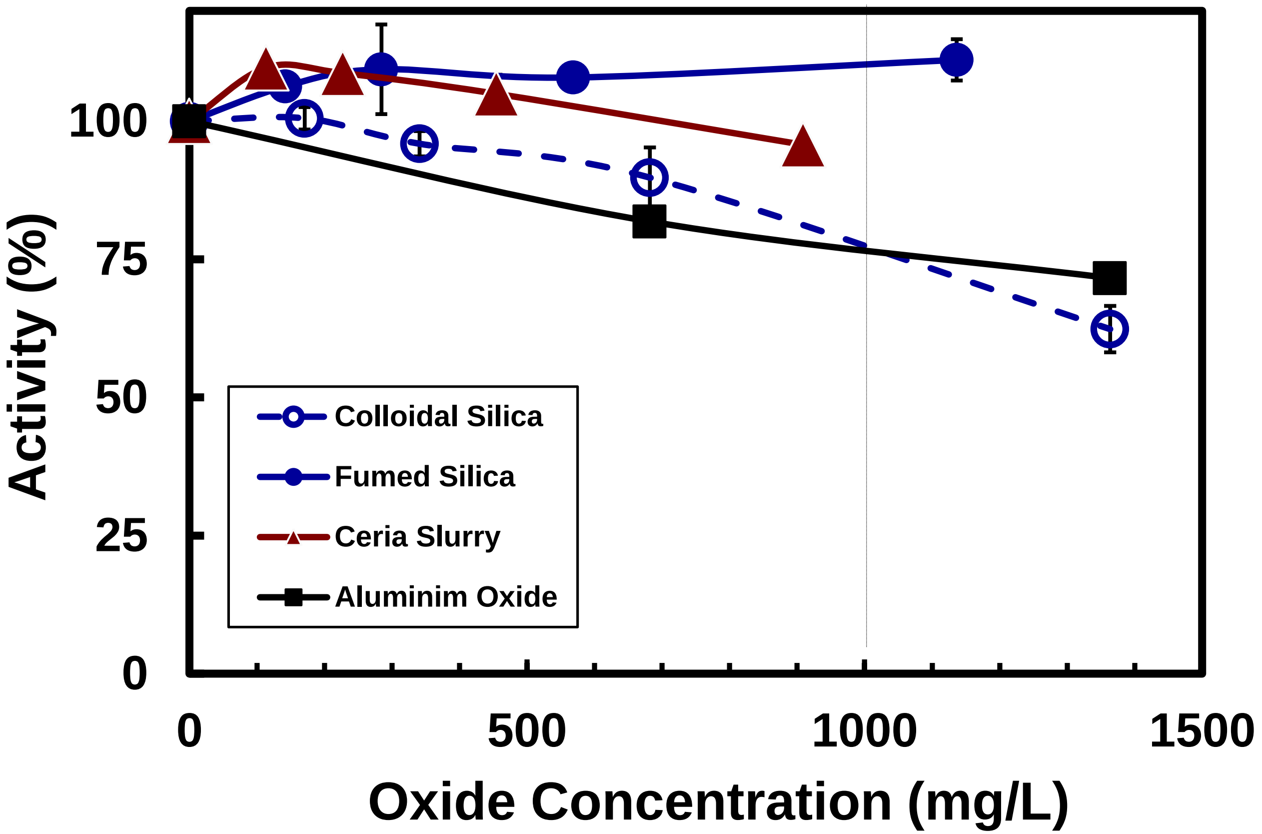
Microtox® Test:

Microtox® is a metabolic inhibition test that uses a bacterium, *Aliivbrio fischeri*, that produces light as by-product of their cellular respiration. Any inhibition of cellular activity (toxicity) results in a decreased rate of luminescence.

In this study, the four model slurries were diluted in DI water to ≈ 3 g oxide/L. NaOH (0.1 M) and HCl (0.1 M) were used to adjust pH to neutral range (6.0~8.0). Light level was tested at 0, 5, 15 and 30 min. 30-min data were used to indicate acute toxicity.

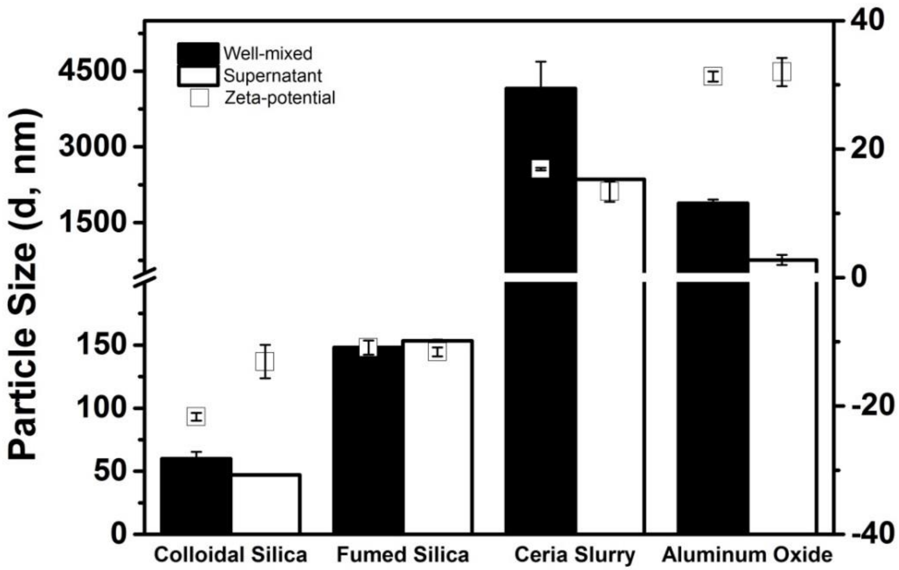


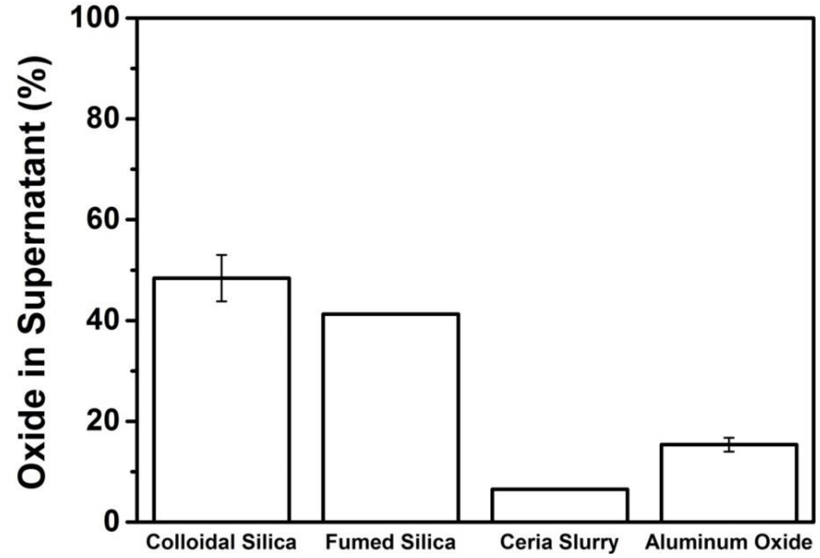
Microtox Test Results



- The various slurries showed low toxicity in the Microtox assay at relatively high concentrations (ca. 1000 mg oxide/L).
- Acidic colloidal silica (NS-0813-1), the most inhibitory sample, only caused 35% inhibition at a concentration of 1500 mg/L.

Stability of CMP Nanoparticles in Microtox Medium





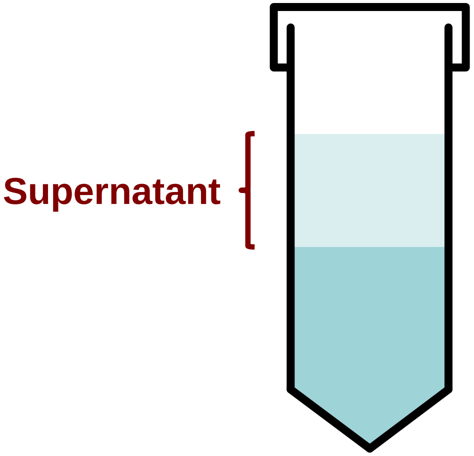
Stability of CMP NPs in Microtox assay medium (250-300 mg oxide/L, 10 g/L NaCl) after 30 min of static incubation

- The stability of the nano-sized in the 4 model slurries decreased significantly in the bioassay medium. Even for the most stable materials (i.e., colloidal- and fumed silica), only 50% of the total Si remained in the supernatant after 30 min of static incubation.
- Ceria and alumina particles aggregated in Microtox medium. This may be due to: 1) the pH value was very close to zero charge point of these NPs; 2) high ionic strength squeezes particle double layers.

Stability of CMP-NPs in wastewater

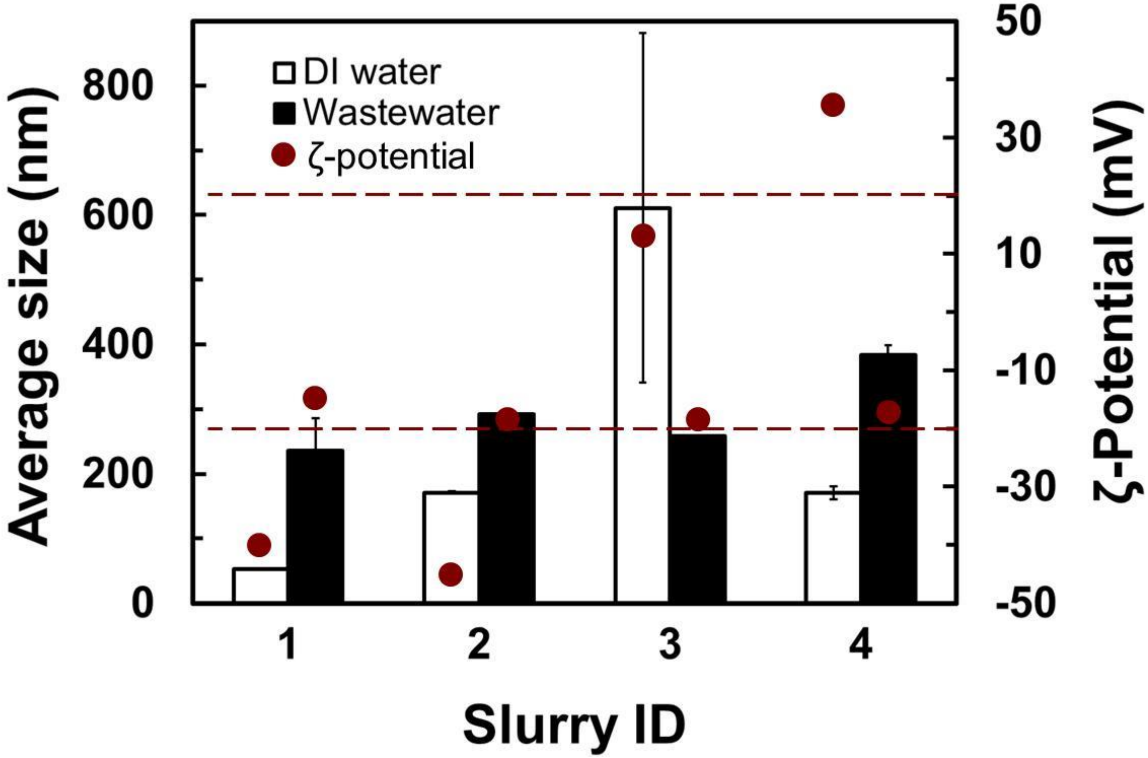
Experimental approach

- CMP slurries were diluted in 0.45-µm filtered primary-treated wastewater & DI water
- Conc. ≈ 20 mg NP L^{-1}
- pH ≈ 8
- Static incubation overnight to allow settling
- Sampling of supernatant & well mixed dispersion
- Analysis of particle size distribution, ζ-potential & NP concentration



Stability of CMP-NPs in wastewater

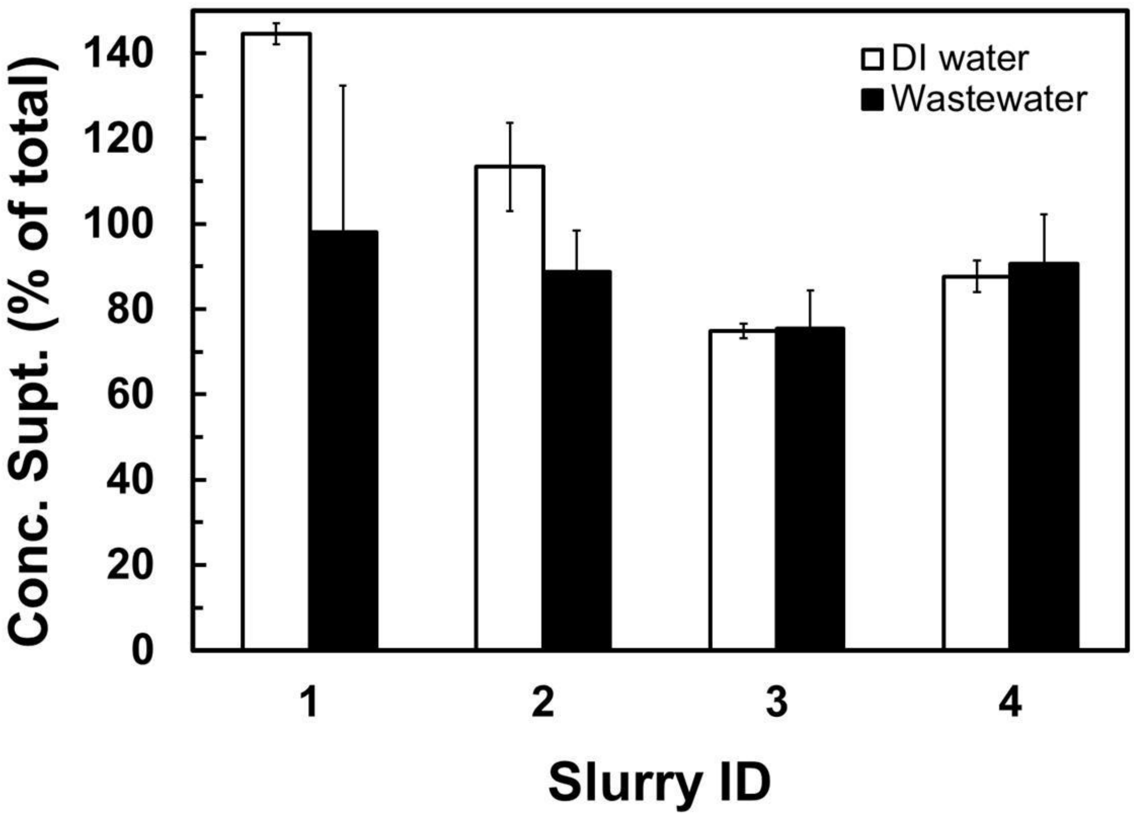
Average particle size and ζ-potential of CMP-NPs in wastewater & DI water



Except for the CeO_2 slurry (#3), dispersion in wastewater led to an increase in aggregation of NPs (larger particle size) and a shift of ζ-potential to values within the instability region (–20/+20 mV).

Stability of CMP-NPs in wastewater

Concentration of CMP-NPs recovered in the supernatant (as % of total)



Aggregation and/or time of incubation was not enough to promote important settling of NPs.

Conclusions

Detailed physico-chemical characterization of the 4 model CMP slurries was accomplished by the ERC Nanoparticle Consortium. There is good agreement in the data obtained by the various research groups. The collaboration also allowed development and comparison of different testing methodologies.

The four model CMP slurries showed low toxicity in the Microtox assay at relatively high concentrations (ca. 1000 mg oxide/L). The most inhibitory sample, acidic colloidal silica, only caused 35% inhibition at a concentration of 1500 mg/L.

Nano-sized inorganic oxides in the various model CMP slurries are fairly stable under original condition. However, NP stability decreased significantly in the Microtox bioassay medium, leading to (partial) NP settling (all slurries) and NP aggregation (only in the case of CeO_2 and Al_2O_3).

When diluted with primarily-treated municipal wastewater, aggregation of CMP NPs and a shift of ζ-potential to values within the instability region (–20/+20 mV) was observed. These results indicate that interactions of the NPs with dissolved organic/inorganic constituents in the wastewater will influence the fate and removal of CMP NPs during conventional wastewater treatment.

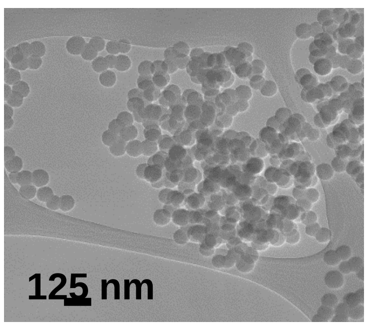
Industrial Interactions and Technology Transfer

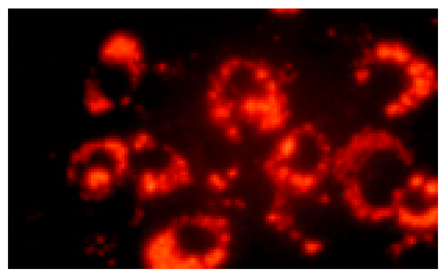
- Cabot Microelectronics
- Reed Content, Global Foundries
- Mansour Moinpour, Intel Corp.
- Chris Lee & Tim Yeakley, Texas Instruments
- Paul Speed, IBM Corp.
- Tim Yeakley, Texas Instruments

Future Plans

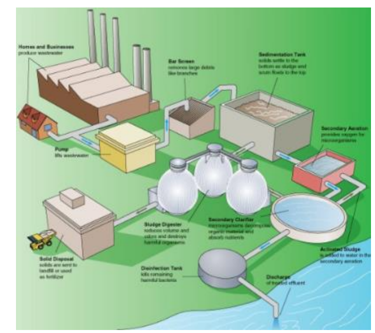
Next Year Plans

- Complete the study of the ecotoxicity of the nanoparticles in the four model CMP slurries.
- Assess the fate of model fluorescent core-shell SiO_2 nanoparticles during conventional wastewater treatment.





Uptake of fluorescent NPs by cells *DOI: 10.1039/B902195G*



Use of fluorescent NPs eliminate interference by background metals (e.g. Si) and facilitate fate and treatment studies with metal oxide NPs .

Future Plans

- Develop on-site treatment method for the abatement of CMP NPs.

Publications, Presentations, and Recognitions/Awards

- **Otero-González L, Field JA, Sierra-Álvarez R**. Inhibition of anaerobic wastewater treatment after long-term exposure to low levels of CuO nanoparticles. *Water Research* [Under review].
- **Gonzalez-Estrella, J., R. Sierra-Alvarez, J.A. Field**. 2013. Toxicity assessment of inorganic nanoparticles to acetoclastic and hydrogenotrophic methanogenic activity in anaerobic granular sludge. *Journal of Hazardous Materials*. 260:278-285.
- **Otero-Gonzalez, L., R. Sierra-Alvarez, S. Boitano, J.A. Field**. 2012. Application and Validation of an Impedance-Based Real Time Cell Analyzer to Measure the Toxicity of Nanoparticles Impacting Human Bronchial Epithelial Cells. *Environmental Science & Technology*. 46:10271-10278.
- **Otero-Gonzalez, L., Field JA, Sierra-Alvarez R. 2014.** Fate and long-term inhibitory impact of ZnO nanoparticles during high-rate anaerobic wastewater treatment. *J. Environmental Management*. 135:110-117.
- **González-Estrella, J., Sierra-Alvarez, R., Field, J. A**. 2012. Toxicity of nanoparticles to anaerobic methanogenic biofilms. SESHA Journal. 5 pp. **[1st Poster Award]**
- **Otero-González, L., Field, J. A., Sierra-Alvarez, R**. 2012. Application of a novel real time impedance-based system for high throughput nanotoxicity assessment. SESHA Journal. 5 pp. **[3rd Poster Award]**
- **Otero-Gonzalez, L., C. Garcia-Saucedo, J.A. Field, R. Sierra-Alvarez.** 2013. Toxicity of TiO_2, ZrO_2, Fe-0, Fe_2O_3, and Mn_2O_3 nanoparticles to the yeast, *Saccharomyces cerevisiae*. *Chemosphere*. 93:1201-1206.