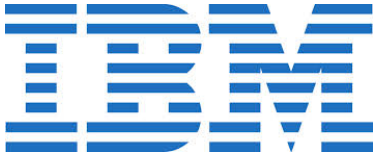
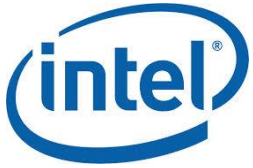
Summary of Interactions on Nano-Materials Projects

- University contributors




- Industrial collaborators





Objectives

- **Goal:**
  - **Work as a research consortium to solve a common set of questions regarding NPs used in CMP slurries**
- **Objectives:**
  - **Phase I**
    - **Procure "realistic" CMP slurries with representative NPs**
    - **Characterize physical properties & Toxicity of NPs**
  - **Phase II – Assess contribution of NPs relative to other additives in more complex CMP fluids & NPs in post-polishing fluids**
  - **Phase III – Work to characterize NPs in full-scale fabrication facilities using toxicity and analytical tools developed in Phases I/II**

Journal Paper Submitted!!

Environmental Science: Nano

Physical, Chemical, and *In Vitro* Toxicological Characterization of Nanoparticles in Chemical Mechanical Planarization Suspensions Used in the Semiconductor Industry: Towards Environmental Health and Safety Assessments

David Speed [1], Paul Westerhoff [2*], Reyes Sierra-Alvarez [3], Rockford Draper [4], Paul Pantano [4], Shyam Aravamudhan [5], Kai Loon Chen [6], Kiril Hristovski [2], Pierre Herckes [2], Xiangyu Bi [2], Yu Yang [2], Chao Zeng [3], Lila Otero-Gonzalez [3], Carole Mikoryak [4], Blake A. Wilson [4], Karshak Kosaraju [5], Mubin Tarannum [5], Steven Crawford [5], Peng Yi [6,9], Xitong Liu [6], S.V. Babu [7], Mansour Moinpour [8], James Ranville [10], Manuel Montano [10], Charlie Corredor [11], Jonathan Posner [11], and Farhang Shadman [3]

CMP Procurement

- 4 “simple” CMP slurries developed with input from industry experts (Babu), industrial partners, and university researchers

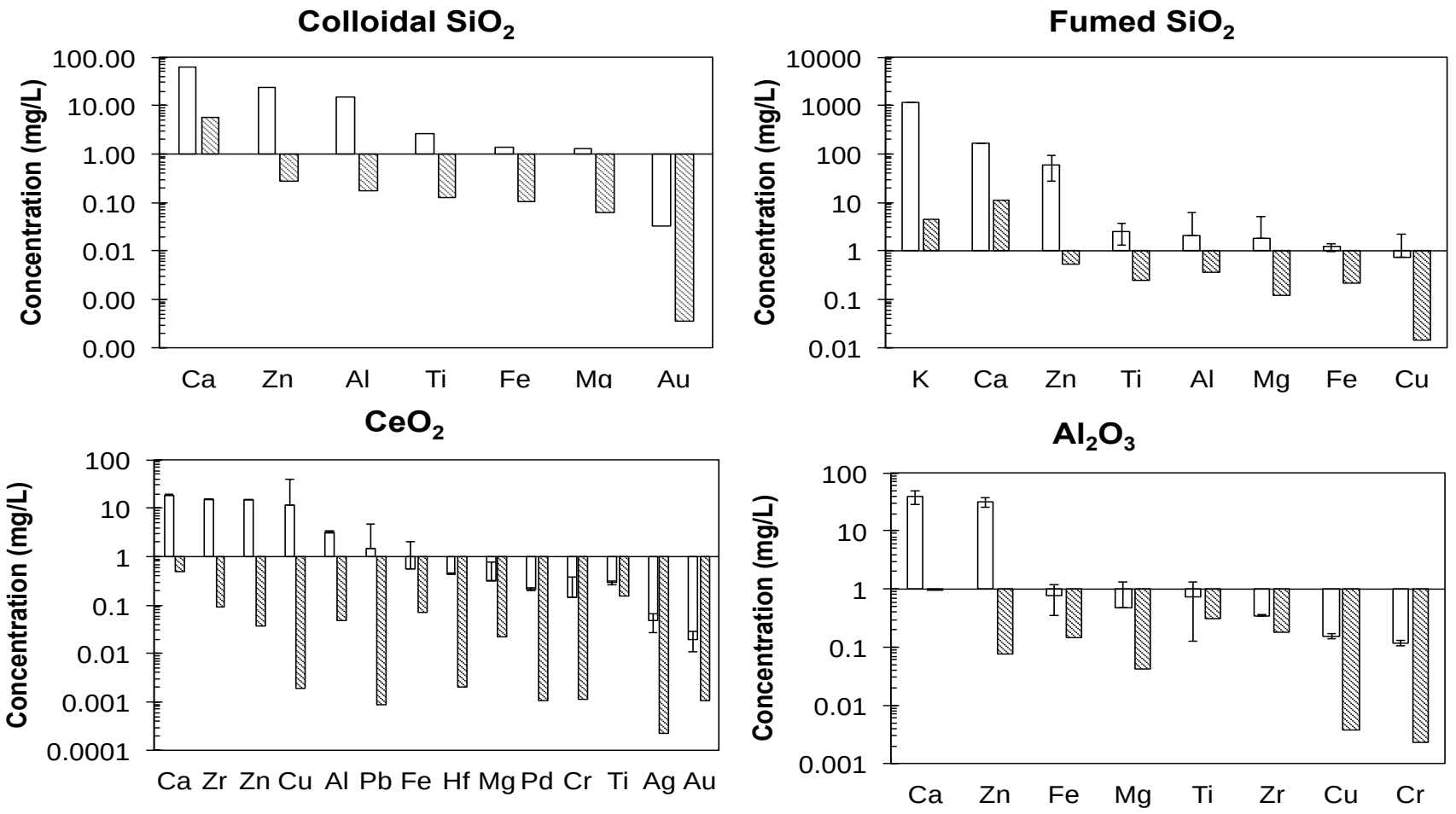
Slurry ID	pH	NP Composition	NP size by SEM (nm)	NP size by DLS (nm)	NP Conc.	Zeta Potential at slurry pH
CMP1	pH 3.3 in acetate	Colloidal SiO_2	37 ± 7	45	27 g Si/L	-21 mV
CMP2	pH 10.6 in KOH	Fumed SiO_2	38 ± 14	184	50 g Si/L	-50 mV
CMP3	pH 4.0	CeO_2	43 ± 16	185	9.6 g Ce/L	43 mV
CMP4	pH 4.2 in nitric acid	Al_2O_3	85± 21	157	29 g Al/L	55 mV

- Samples prepared by Cabot Corp with minimal additives
- Samples shipped to researchers in early November 2013

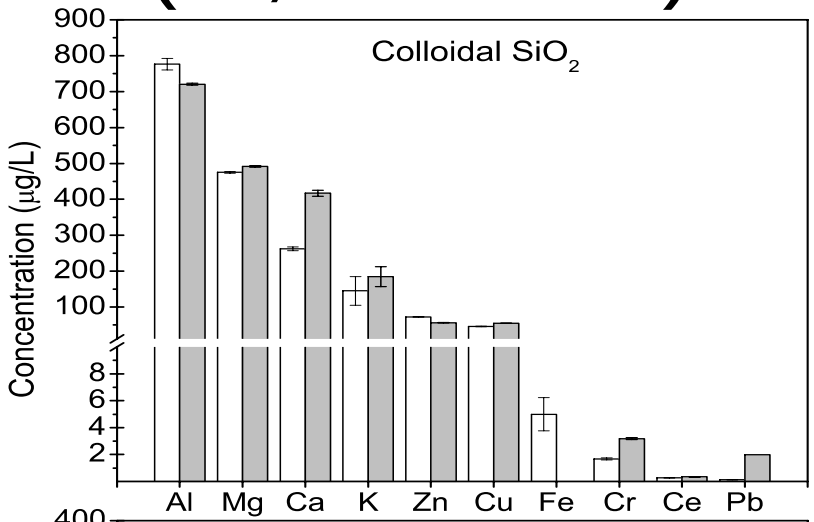
Physical Characterization

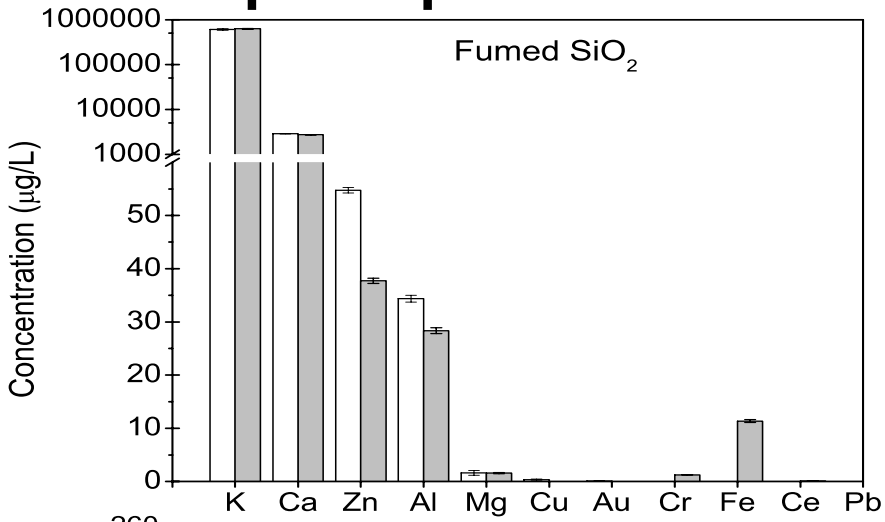
- Wide range of methods applied
- Analyses were cross-validated by at least 2 university partners in most cases
- Methods cross-validation is good (TEM, DLS, sp ICP-MS)
- All primary NPs are < 100 nm; some aggregate in the slurry or at neutral pH
- Elemental composition of slurry & NPs show impurities

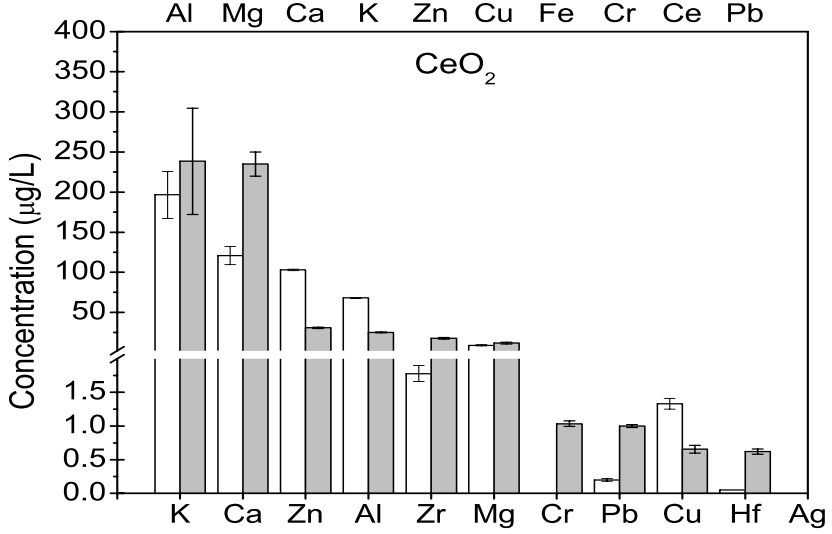
Concentrations of elements other than the primary metal (Si, Ce or Al)

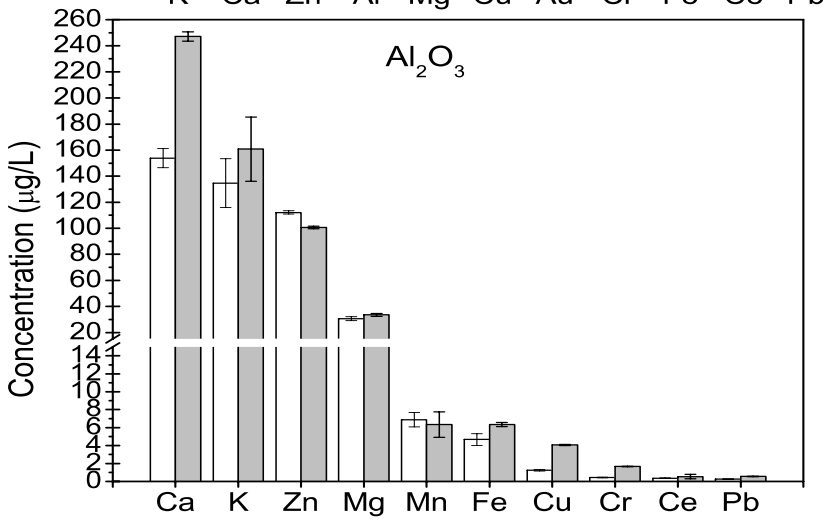


Elements other than the major metals (Si, Ce or Al) in the liquid phase

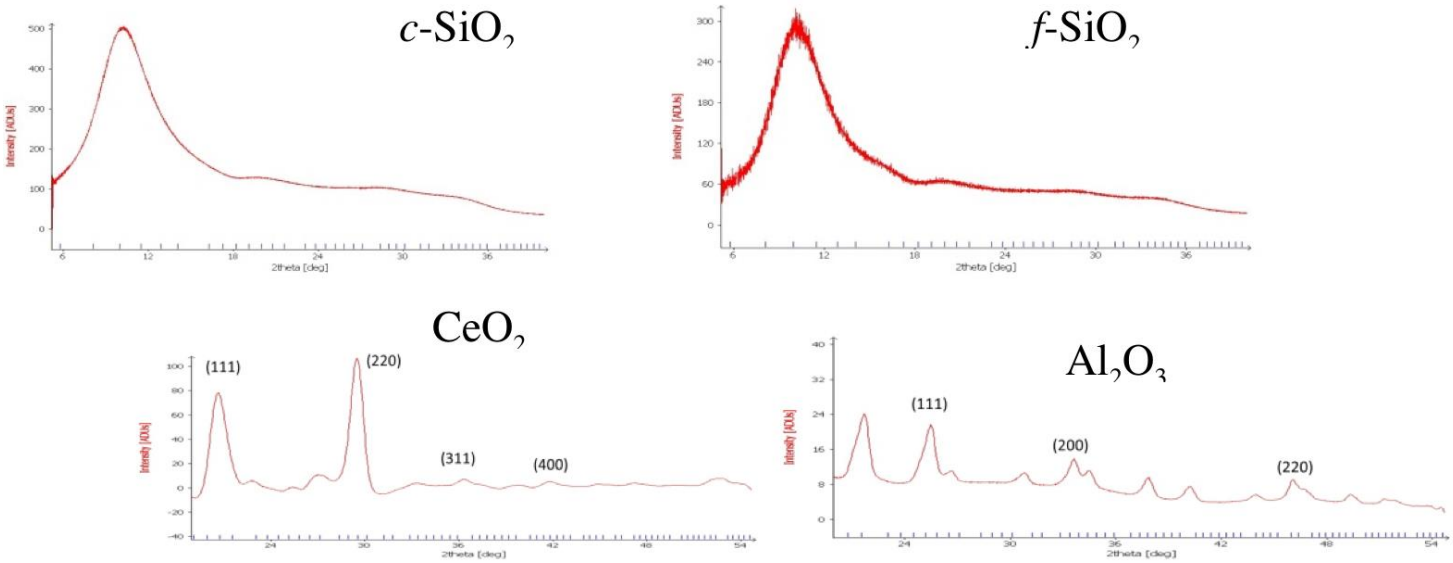




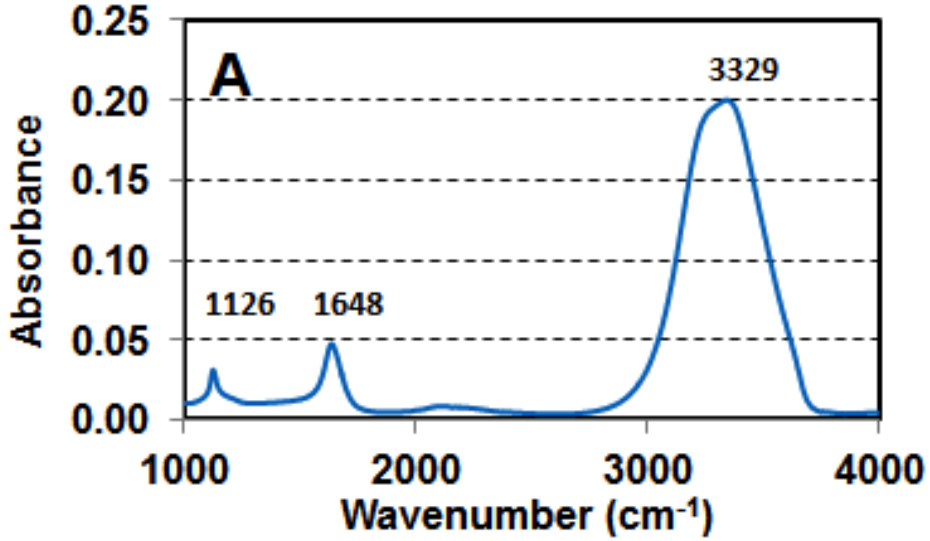


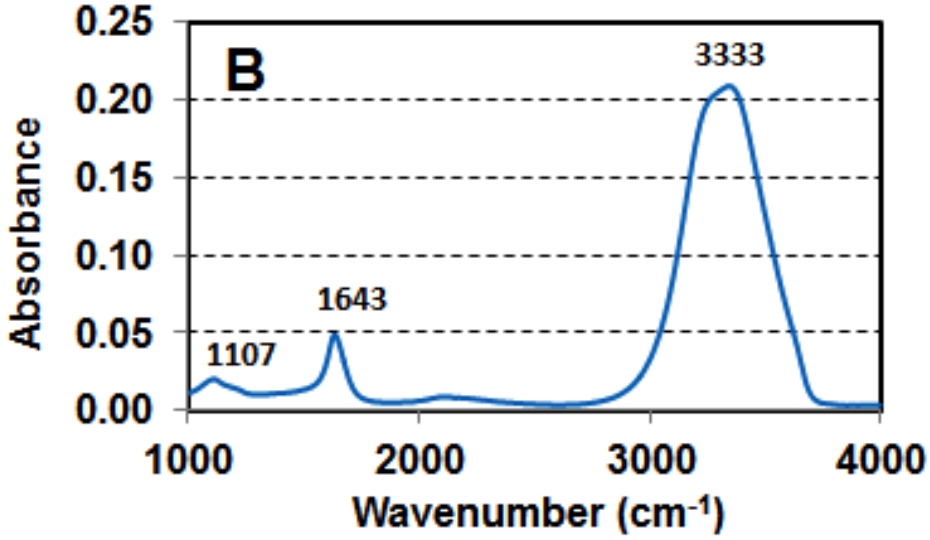


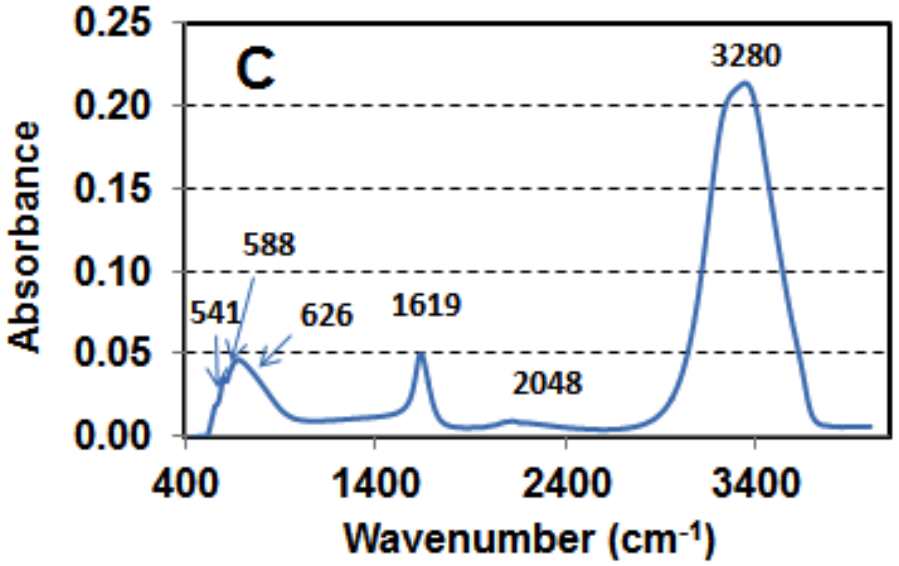
X-ray diffraction after Sample Drying

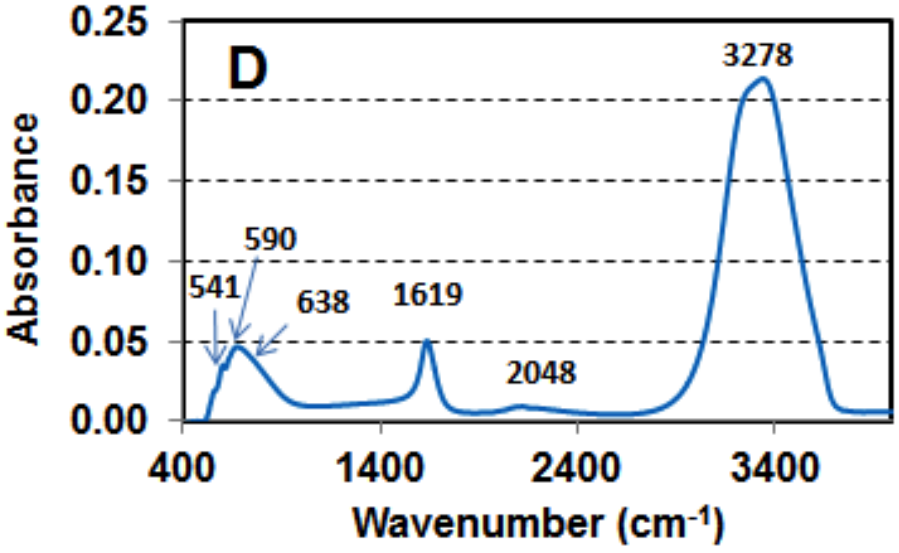


FTIR spectra of *c*-SiO_2 (A), *f*-SiO_2 (B), CeO_2 (C), and Al_2O_3 (D) slurries



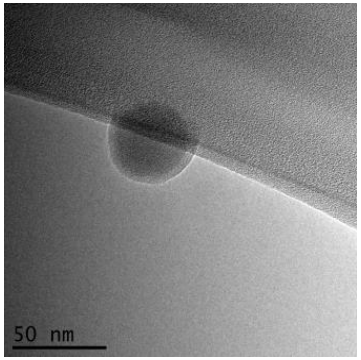




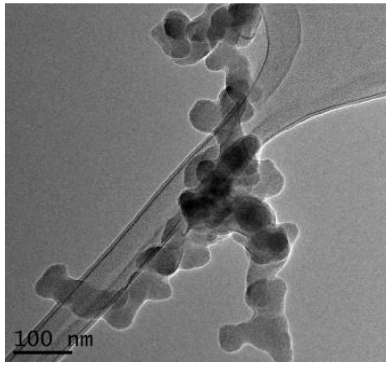


TEM Analysis

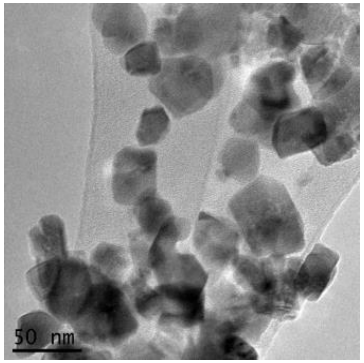
Colloidal SiO_2



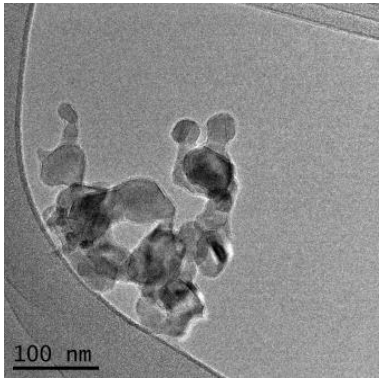
Fumed SiO_2

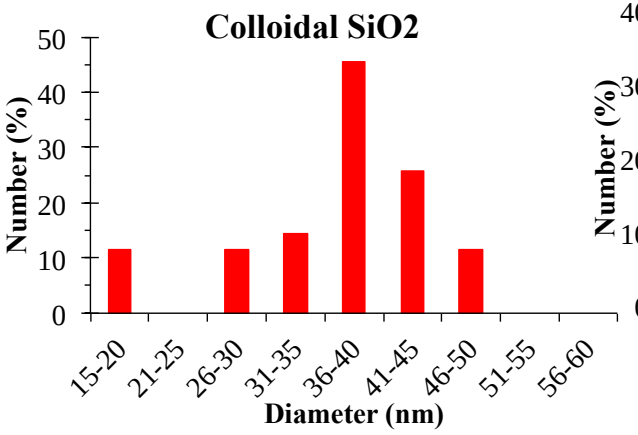


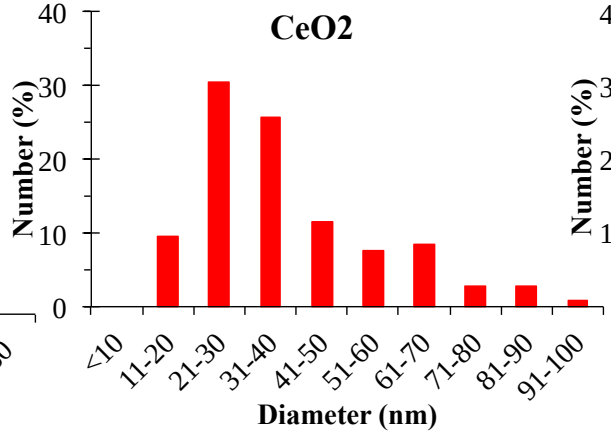
CeO_2

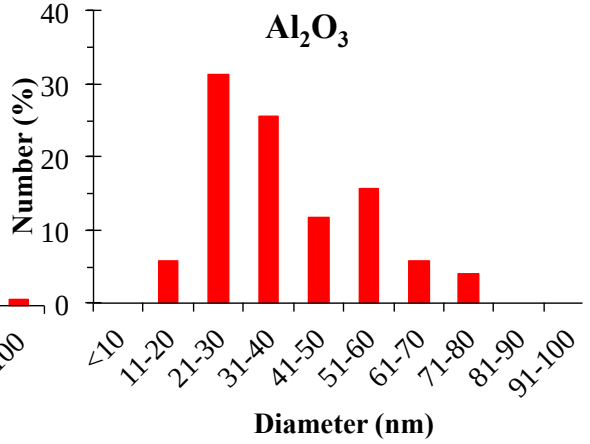


Al_2O_3

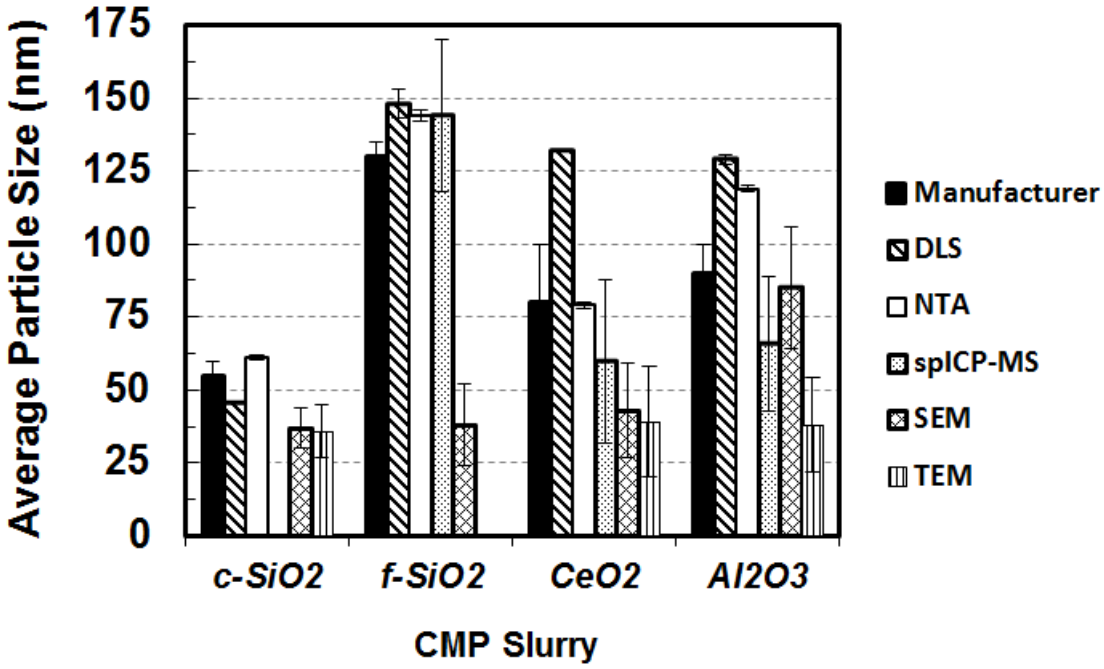


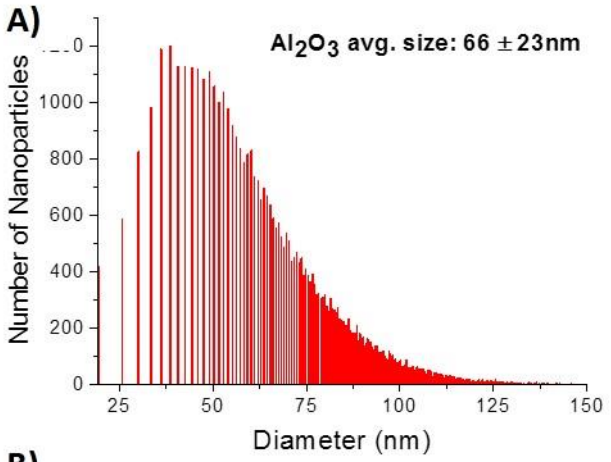


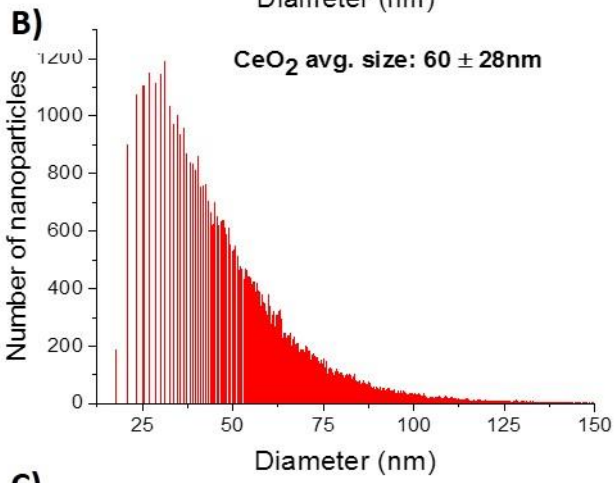


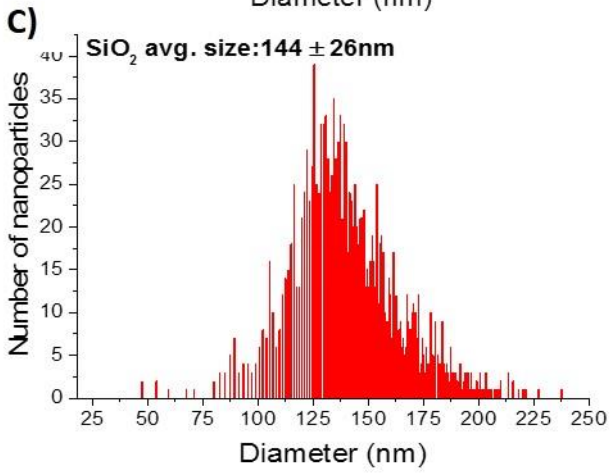


Sizing in Solution

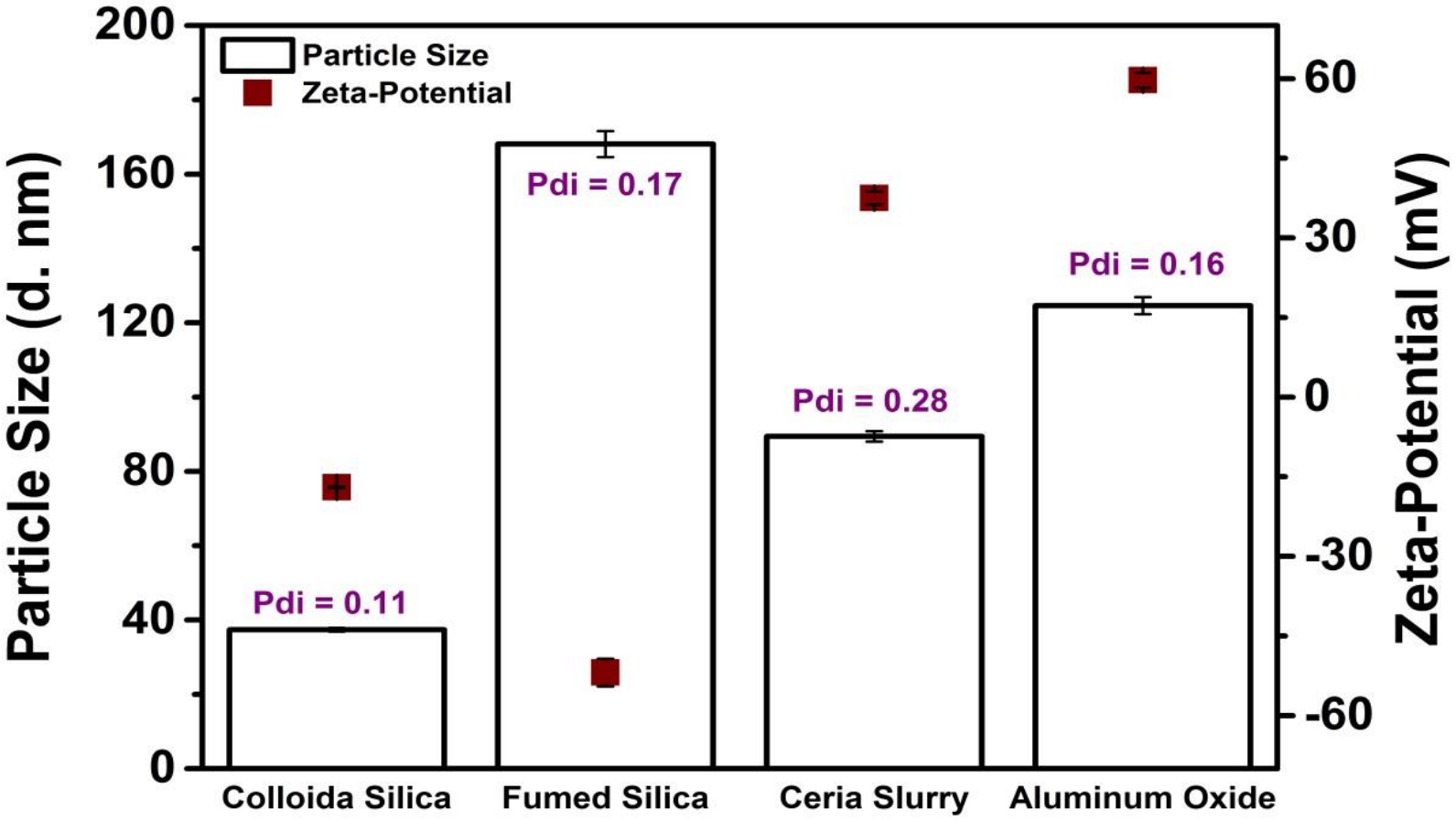




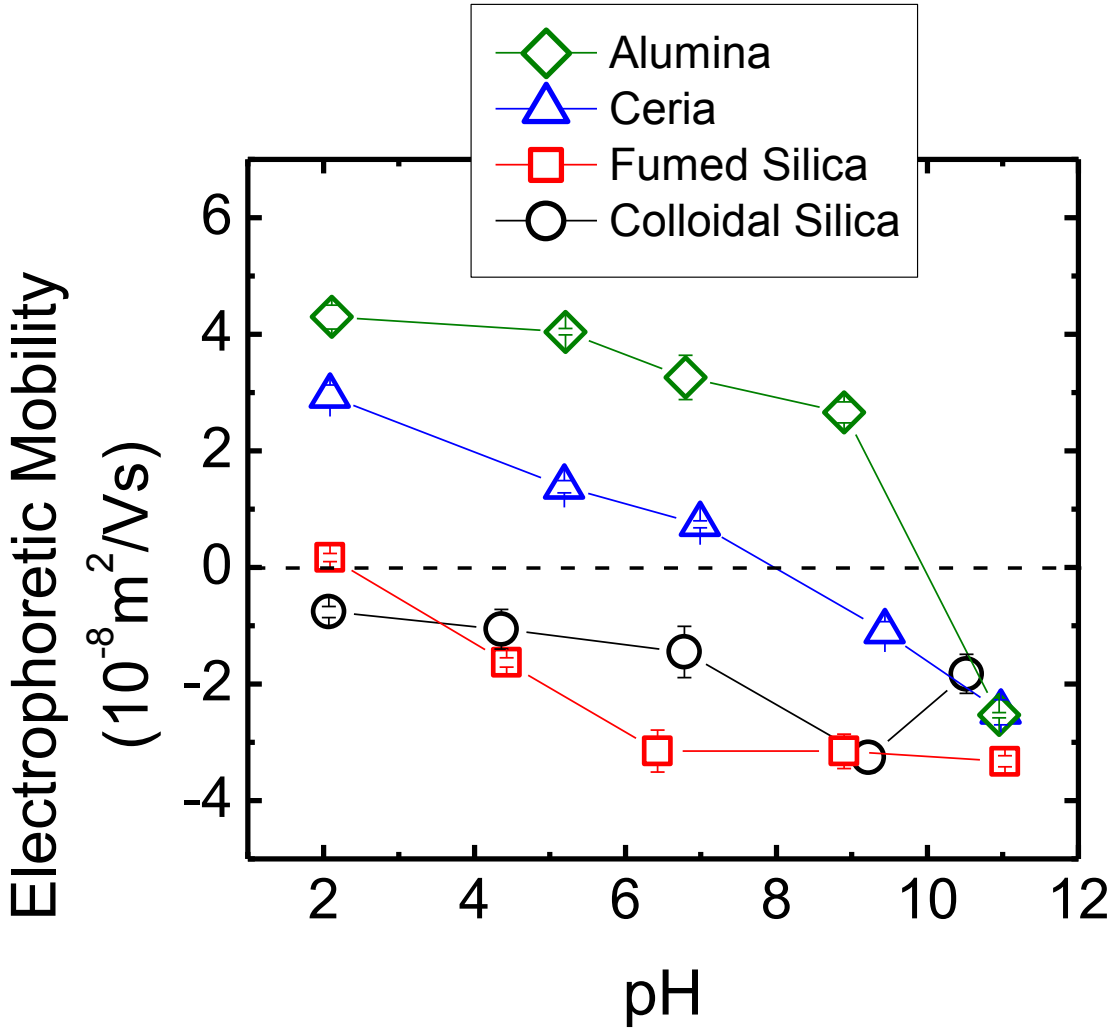




As Received Slurries

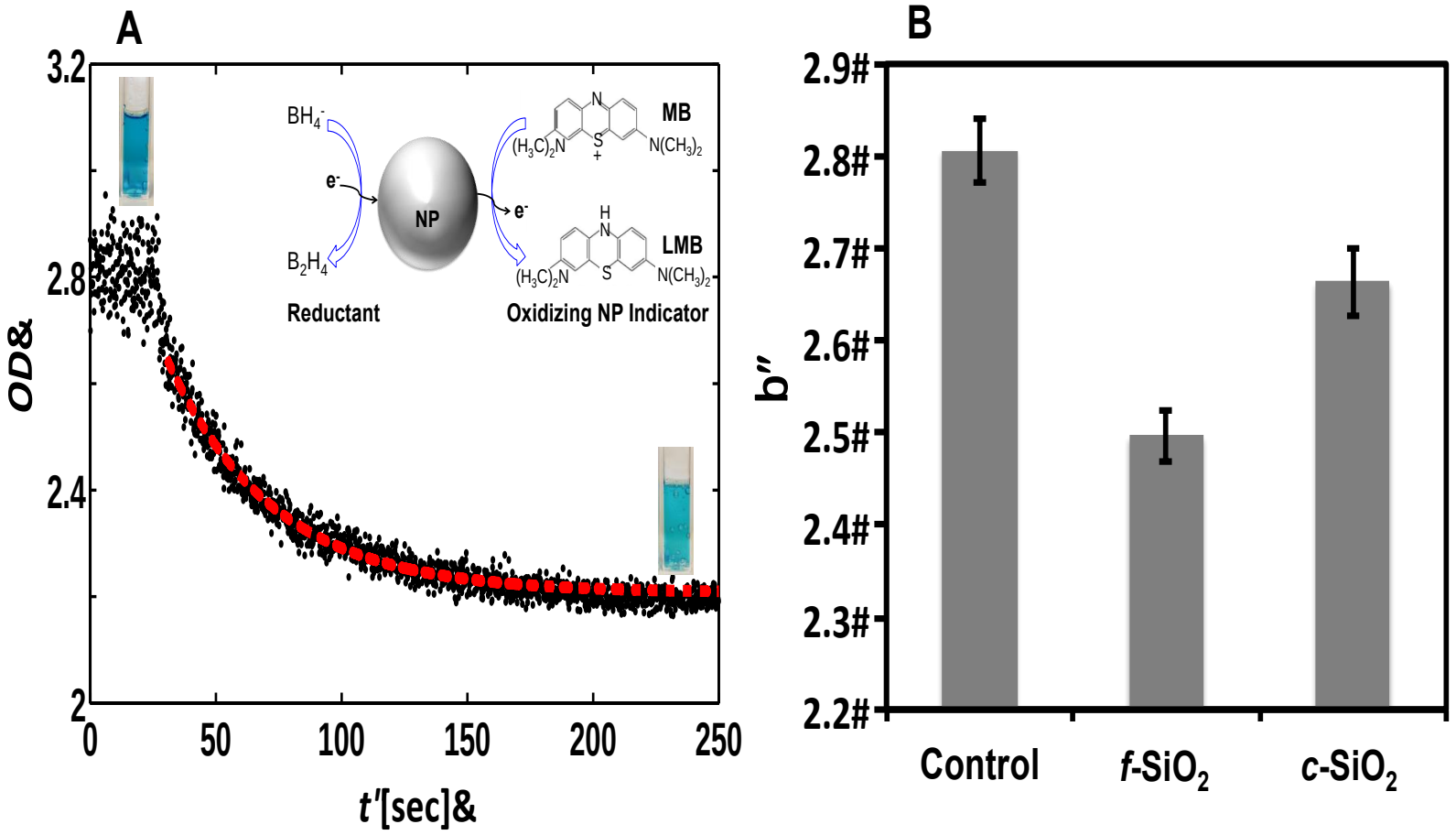


Electrophoretic Mobility



Name	*c*-SiO_2	*f*-SiO_2	CeO_2	Al_2O_3
Manufacturer Reported				
- Material	Colloidal SiO_2	Fumed SiO_2	CeO_2	Al_2O_3
- Composition	3% SiO_2	5% SiO_2	1% CeO_2	3% Al_2O_3
- Additive	< 1% acetic acid	< 1% KOH	none	<1% nitric acid
- pH	2.5 – 4.5	10	3-4	4.5-5.0
- Particle size (nm)	50-60	120-140	60-100	80-100
Primary metal concentration	27 g Si/L	50 g Si/L	9.6 g Ce/L	29 g Al/L
Dissolved organic carbon (DOC; mg/L)	320.5 ± 0.5	4.84 ± 0.03	1.90 ± 0.03	6.77 ± 0.18
Other additives	801.9 ± 1.3 mg/L acetic acid	--	--	134.7 ± 0.8 mg NO_3^-/L BDL* for nitrite
Diameter by SEM (nm)	37 ± 7	38 ± 14	43 ± 16	85± 21
Diameter by TEM (nm)	36 ± 9	ND[#]	39 ± 19	38 ± 16
Mean diameter by DLS (nm) (Polydispersity Index)	46 ± 0.2 (0.08)	148 ± 5.1 (0.11)	132 ± 0.1 (0.16)	129± 1.6 (0.11)
Diameter by NTA (nm)	61± 0.9	144 ± 1.8	79 ± 1.3	119 ± 1.1
Single particle ICP-MS (nm)	ND	144 ± 26	60 ± 28	66± 23
Zeta potential at slurry pH (mV)	-21	-50	43	55

Surface Reactivity



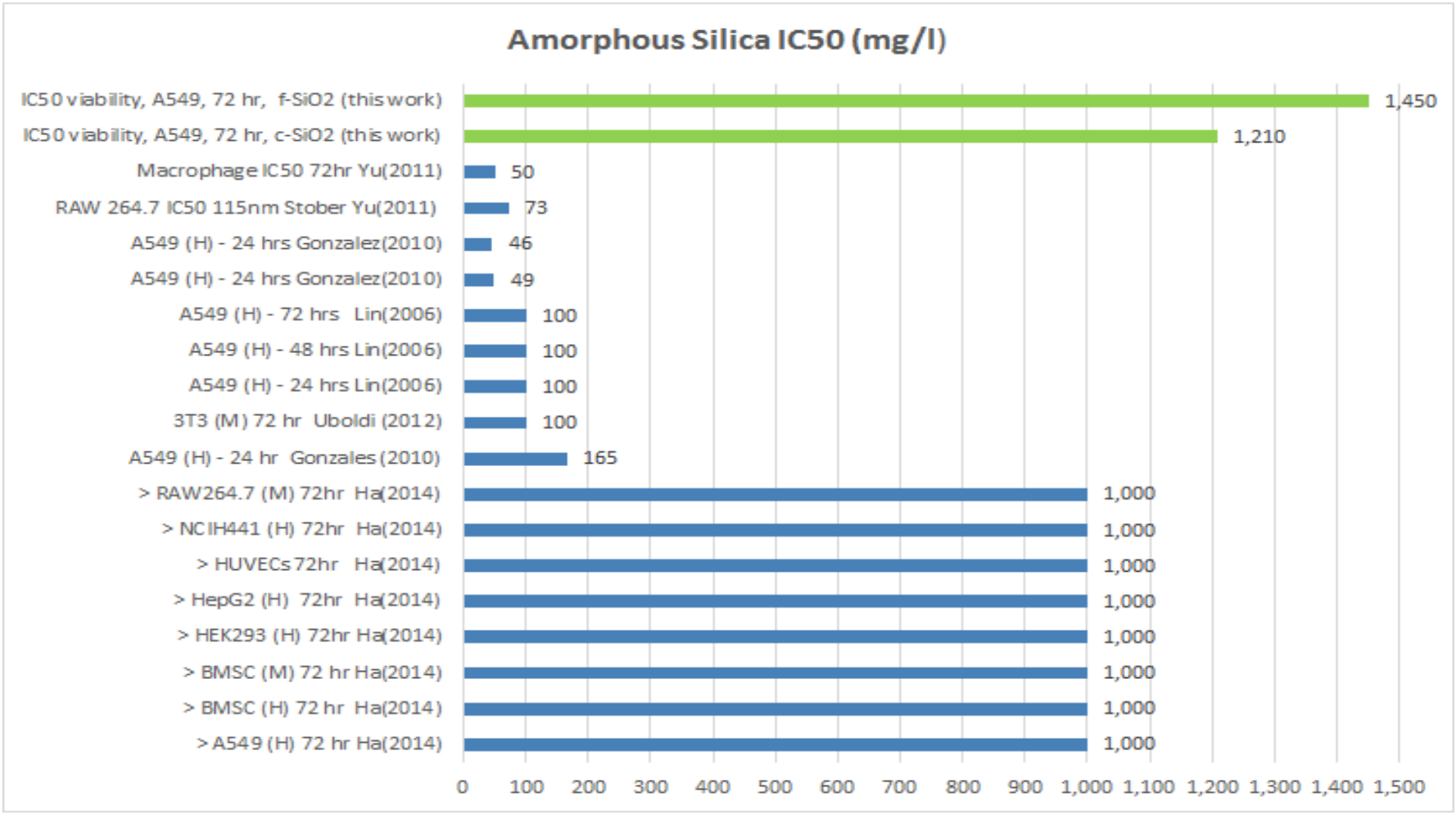
Toxicity Trends

- Toxicity of CMP fluids in physiologically relevant fluids had low toxicity (IC50 > 1 mg/mL)
- No DNA damage up to 0.1 mg/mL of slurry
- Fumed silica slurry more toxic than colloidal silica slurry; consistent with literature
- 2 silica slurries have higher propensity to bind to lipid bilayers than other 2 slurries
- Some additives in slurries (K, Zn) themselves impart toxic responses in some cell lines
- All testing has been *in vitro* ; future work with daphnia or other organisms would be useful
- 3 slurries showed no response in zebrafish embryonic assay (only Al_2O_3 showed some response)

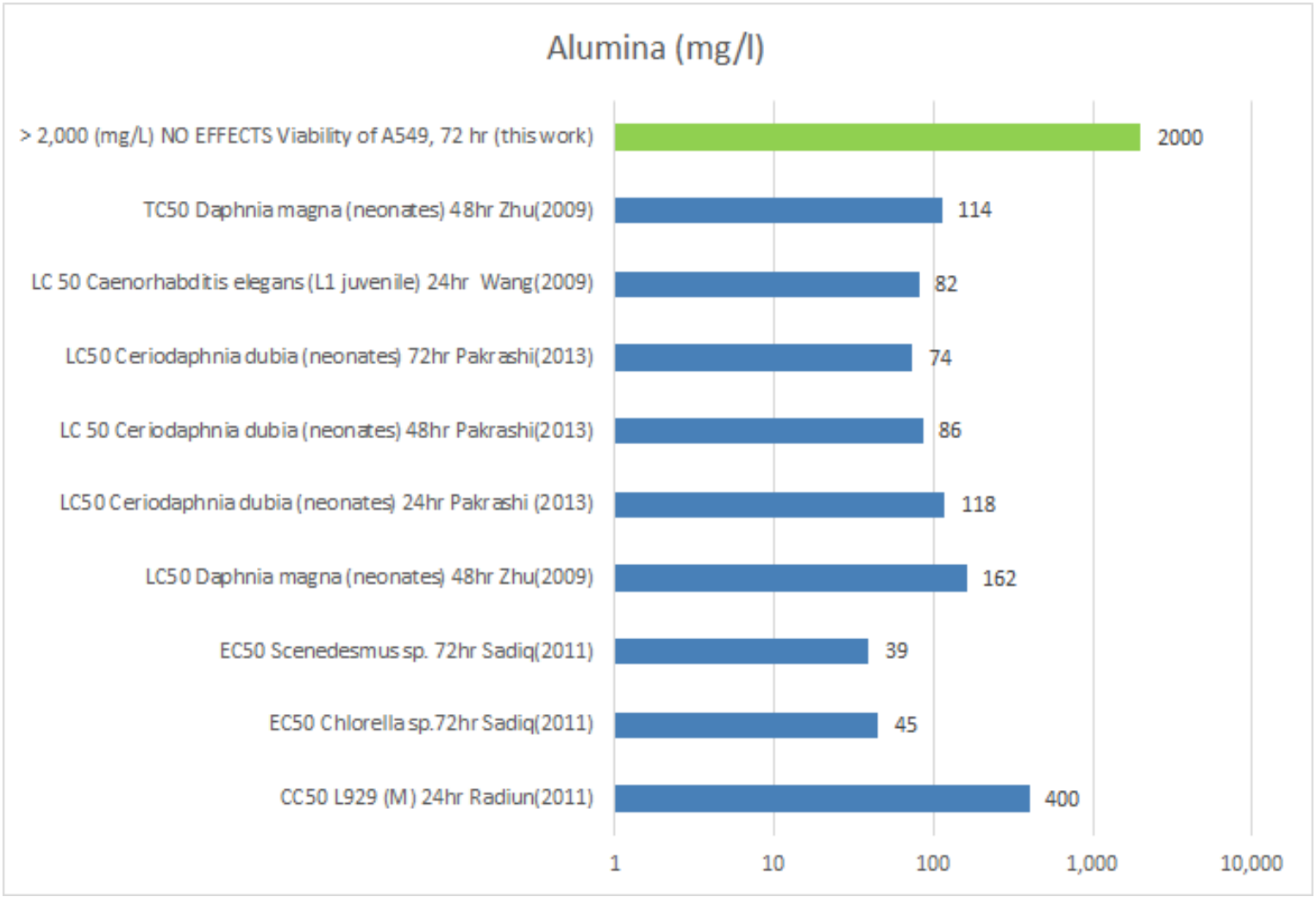
The effects of slurries on the proliferation, viability, or membrane integrity of model organisms

Assay	**IC-50 (mg/mL)**			
	c-SiO_2	*f*-SiO_2	CeO_2	Al_2O_3
Bioluminescence of *A. fischeri*	ND[1]	ND[2]	ND[3]	ND[4]
Proliferation of A549 cells	3.8± 1.3	3.6 ± 0.2	ND[5]	ND[6]
Viability of A549 cells	1.2 ± 0.2	1.5 ± 0.2	ND[7]	ND[8]
Integrity of A549 cells	4.6 ± 0.2	3.1 ± 0.2	ND[7]	ND[8]

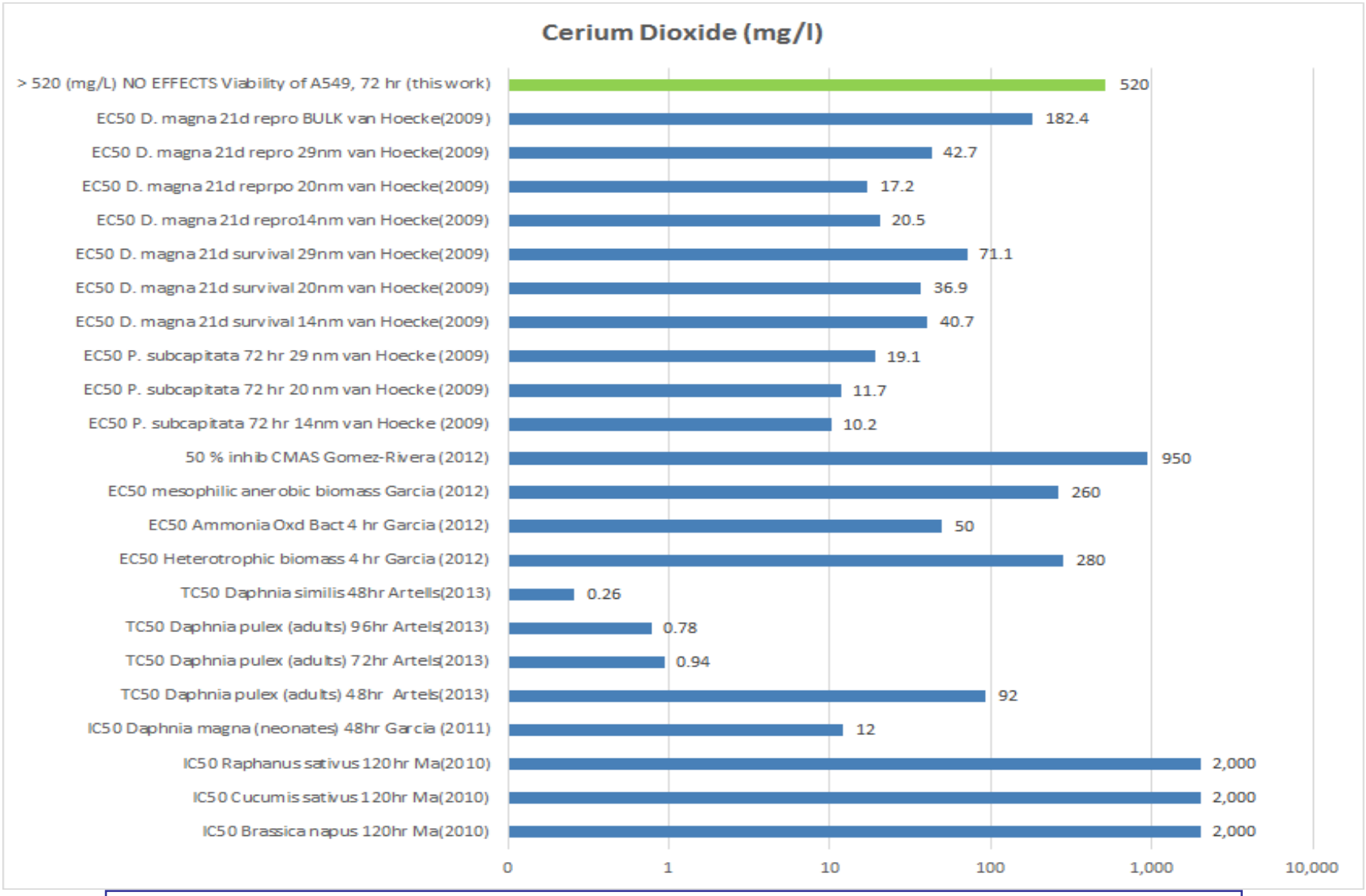
Toxicity Comparisons



Toxicity Comparisons



Toxicity Comparisons

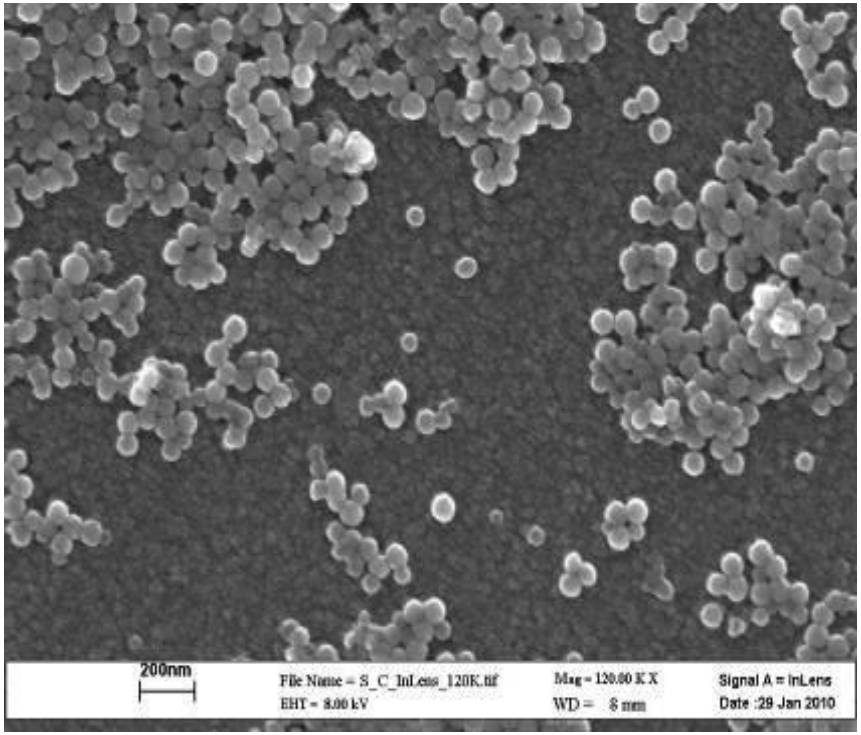


CMP Effluent Concentrations

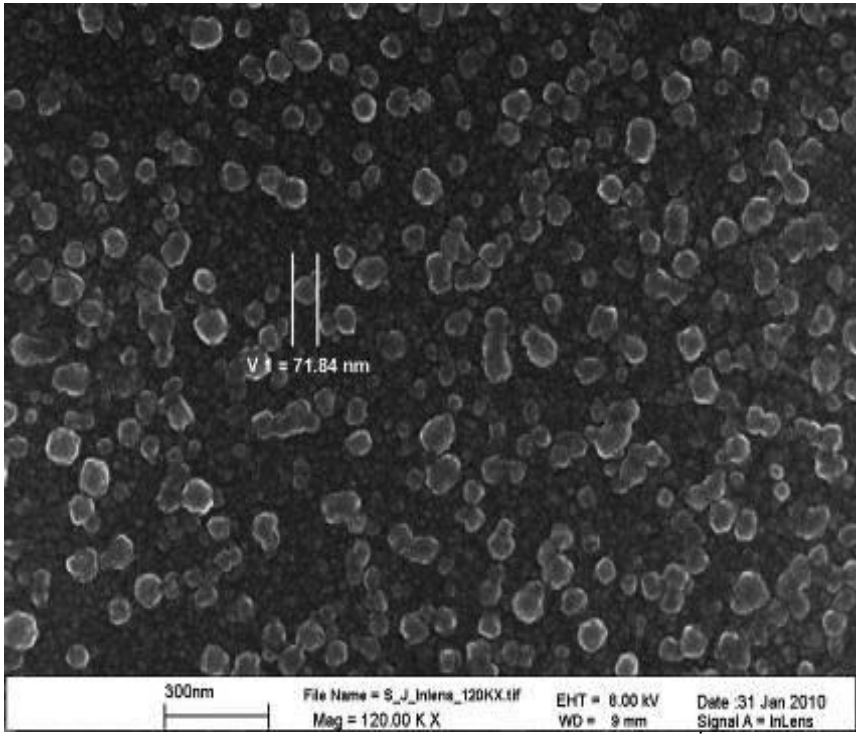
Total [Si] (mg/l)	tot [Al] (mg/l)	Description	Reference
400 - 800	NA	"Oxide" CMP WW effluent from Hsinchu Park (Taiwan)	Den et al (2006)
810 tot; 362 after 0.45 um	NA	CMP WW effluent from Hsinchu Park (Taiwan).	Huang et al (2004)
1580 tot, 398 passing 0.2 um	NA	CMP WW effluent from a 300 mm fab in southern Taiwan.	Kuan and Hu (2009)
467	1.2	DRAM manufacturer in Hsin-chu Science park in Northern Taiwan.	Liu and Lien (2006).
98 - 224	.01 - 11.8	Oxide and metal CMP waste from semiconductor fab in Taiwan	Lo and Lo (2004)
4000	NA	Downstream of ultrafilter at DRAM manufacturer in Hsinchu Park, Taiwan	Tsai et al (2007)
609 as Si	4.8	"Oxide-CMP" WW from wafer fab in southern Taiwan	Yang et al (2003,2004)

TEM of SiO_2 at influent & effluent of a full-scale CMP Wastewater Treatment facility

a) Influent ~ 70 (nm) SiO_2(s)



b) Effluent ~ 70 (nm) SiO_2(s)



Phase II Ideas
(open for discussion)

- Use 4 slurries in pilot CMP polishing lines to characterize (physical and toxicity) what changes during polishing from a ESH perspective
- Look at toxicity of CMP slurries with and without NPs, relative to IC50 of other common CMP additives (corrosion inhibitors, surfactants, oxidants) & how their presence affects stability of NPs themselves in wastestreams
- Look at if these CMP NPs facilitate migration of III/V ions, and associated toxicity, in wastestreams

Final thoughts & discussion

- Thanks to everyone in the consortium for an engaging & collaborative project
- Open discussion about directions for consortium from industry members