FINAL REPORT

Detection of Engineered Nanomaterials: Semi-Conductor Facilities and Consumer Devices

(Task Number: 425.040)

PIs:

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- **Manuel Montano,** PhD (graduated), Chemistry**, CSM**
- **Kyle Doudrick,** PhD (graduated), Sch. of Sustainable Eng. & The Built Environment, **ASU**
- **Takayuki Nosaka,** PhD candidate, Student Materials Science and Engineering **(ASU)**
- **Charles Corredor,** PhD candidate, Mechanical Engineering **(Univ. Washington)**

Undergraduate Students: --

Other Researchers (Post-doc):

- **Drs. Yu Yang, Sungyung Lee, Robert Reed** (School of Sustainable Engineering & The Built Environment, ASU)

Objectives

- **Goal:**
  - **To develop analytical methods for detecting and quantifying trace quantities nanomaterials relevant to the semiconductor industry in waste and recycled water, in lab air, and leached from packaged semiconductors**
- **Objectives:**
  - **Develop analytical methods for NM size distribution and quantification**
  - **Develop capability to monitor NMs used in semiconducting manufacturing in air and water**
  - **Assess NM release or leaching from electronic devices**

ESH Metrics and Impact

1. **Provides analytical methods and SOPs using commercially available instruments for EHS monitoring of NMs in air and water**

1. **Aid in ESH workplace exposure monitoring and assessment of remedial actions to reduce exposures, and in monitoring NMs after they leave fabrication facilities**

1. **Aids in documenting nanomaterial fate over their life cycle**

1. **Organized research and industry consortium which procured well-defined CMP solutions for characterization, toxicity and fate testing**

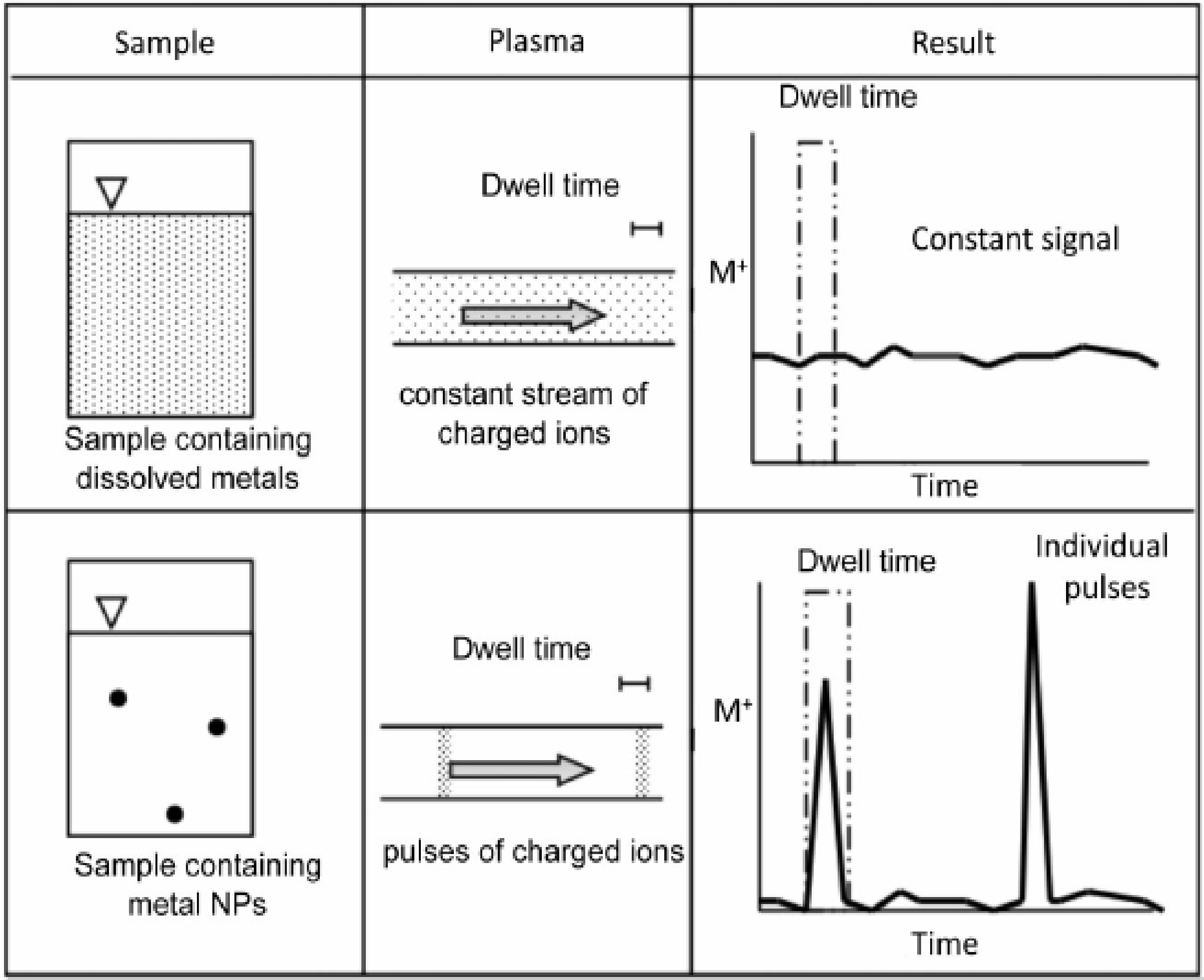
Selected Nanomaterials

- As identified in the International Technology Roadmap for Semiconductors (ITRS):
  - CMP: silica, alumina, cerium oxide
  - Carbon nanotubes (MWCNT) in self-assembly or advanced packaging processes (alone and embedded in polymer matrices)
  - Explored detection of nanographene plateletes because of their electronic properties

Detection & Size Characterization of **Metallic** NPs

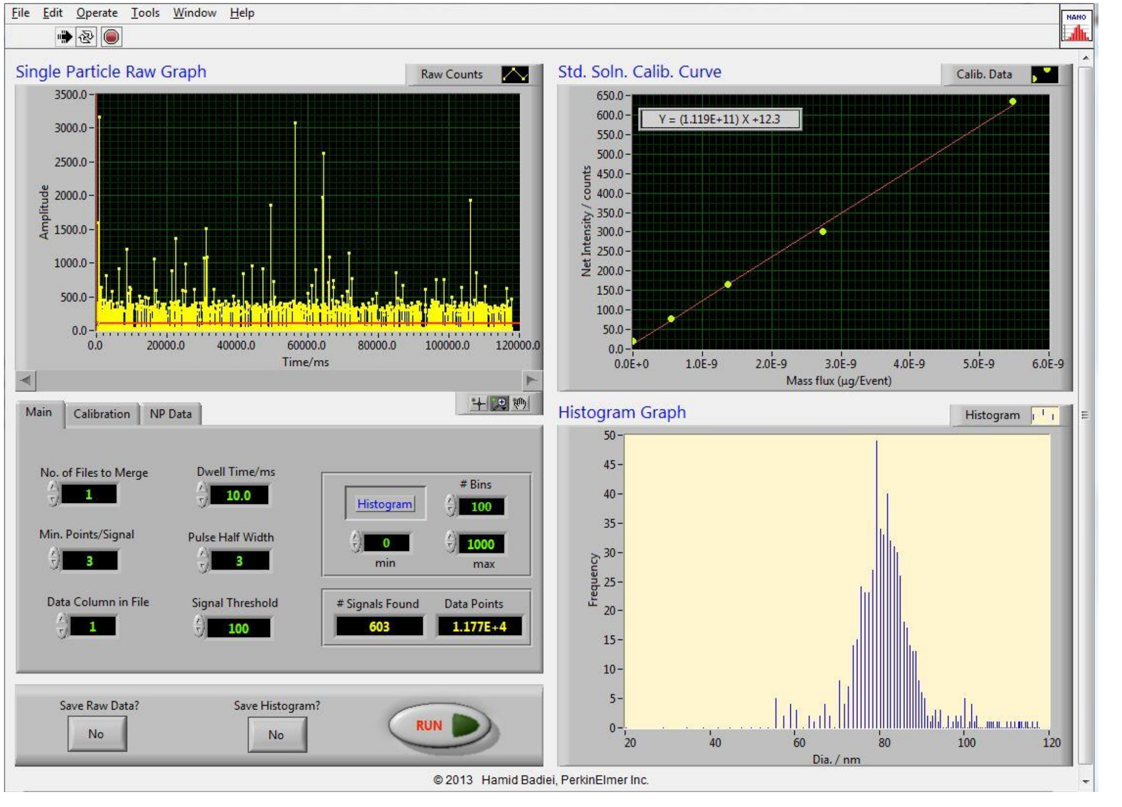
- S. Lee, X. Bi, R. Reed, J. Ranville, P. Herckes and P. Westerhoff. **Nanoparticle size detection limits by single particle ICP-MS for 40 elements**, *Environmental Science and Technology*, **48**, 10291–10300, 2014.
- X. Bi, S. Lee, J.F. Ranville, P. Sattigeri, A. Spanias, P. Herckes and P. Westerhoff, **Quantitative resolution of nanoparticle sizes using single particle inductively coupled plasma mass spectrometry with the K-means clustering algorithm**, *Journal of Analytical Atomic Spectrometry*, **29**,1630 – 1639, 2014
- Many other papers enabled by these methods
- Participated in 20+ lab world-wide intra-lab validation study on spICP-MS

spICP-MS Methodology



Single Particle ICP-MS

- Assisted <u>Perkin-Elmer</u> bringing soft-ware and new instrumentation to market
- Showed applicability for CeO_2 & Al_2O_3



Developed new K-means data-processing algorithms for spICP-MS

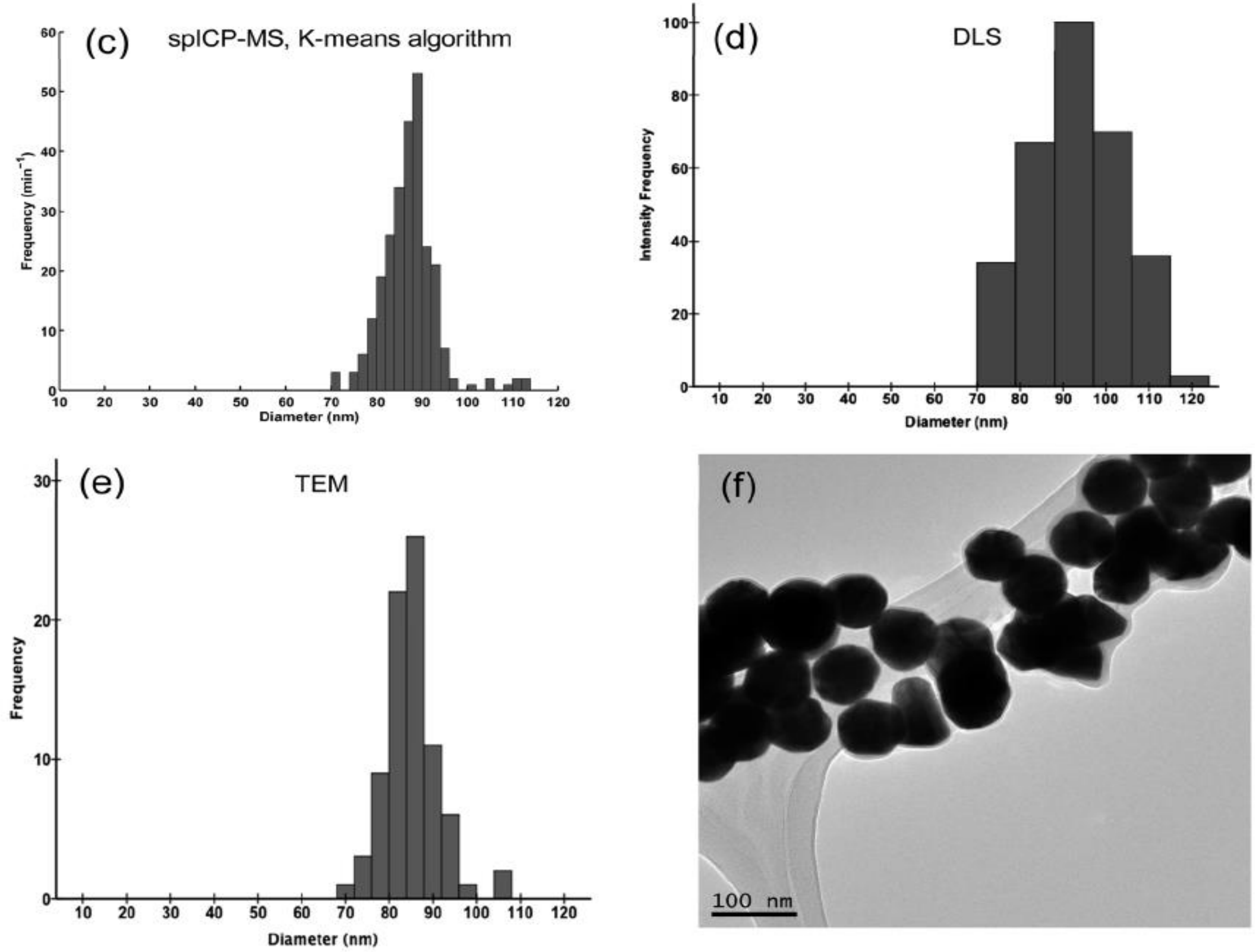
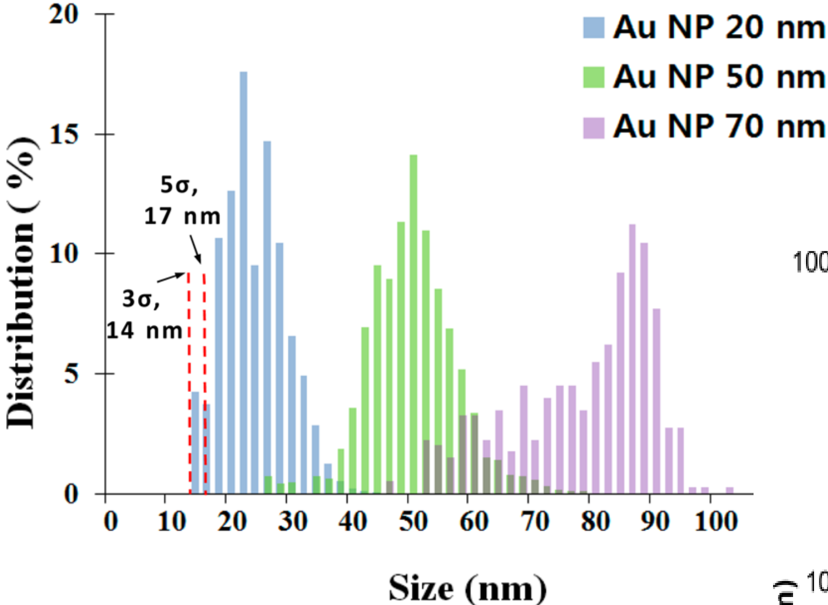
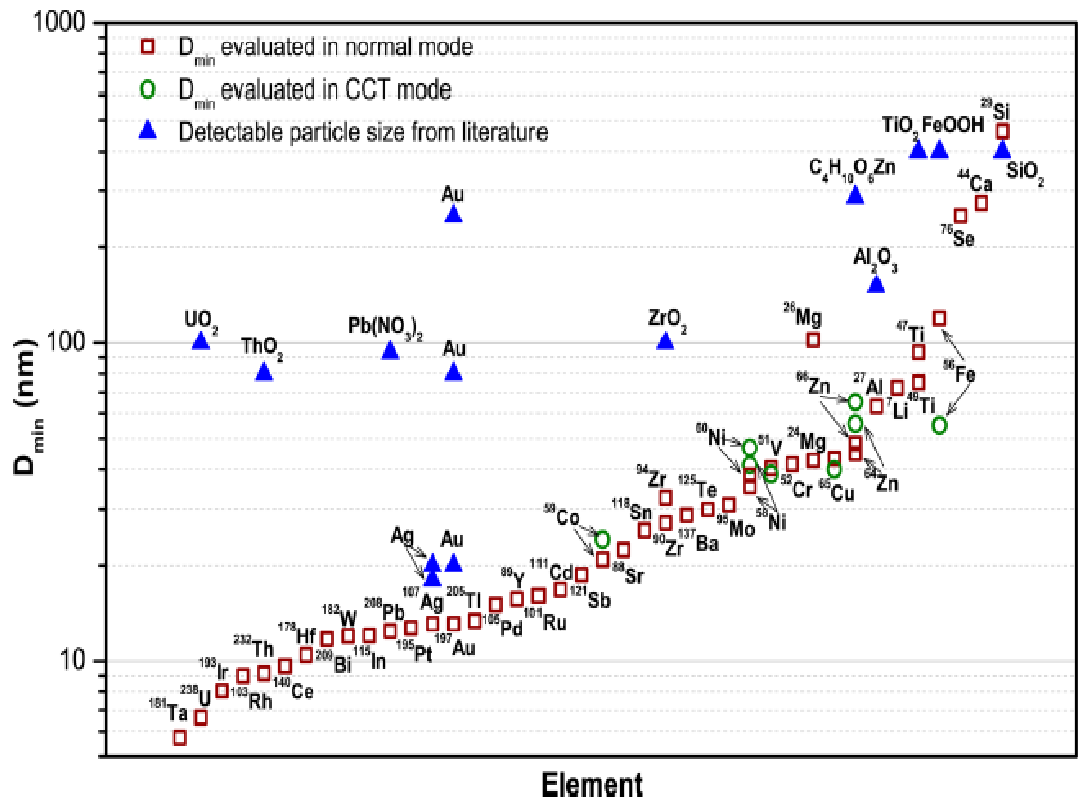


Fig. 2 (a–e) Particle size distribution histograms of BBI 80 nm AuNPs determined by different methods: (a) spICP-MS with 4σ threshold signal processing, (b) spICP-MS with 5σ threshold signal processing, (c) spICP-MS with K-means algorithm signal processing, (d) DLS, and (e) TEM based on counting >100 particles. (f) TEM image of AuNPs.

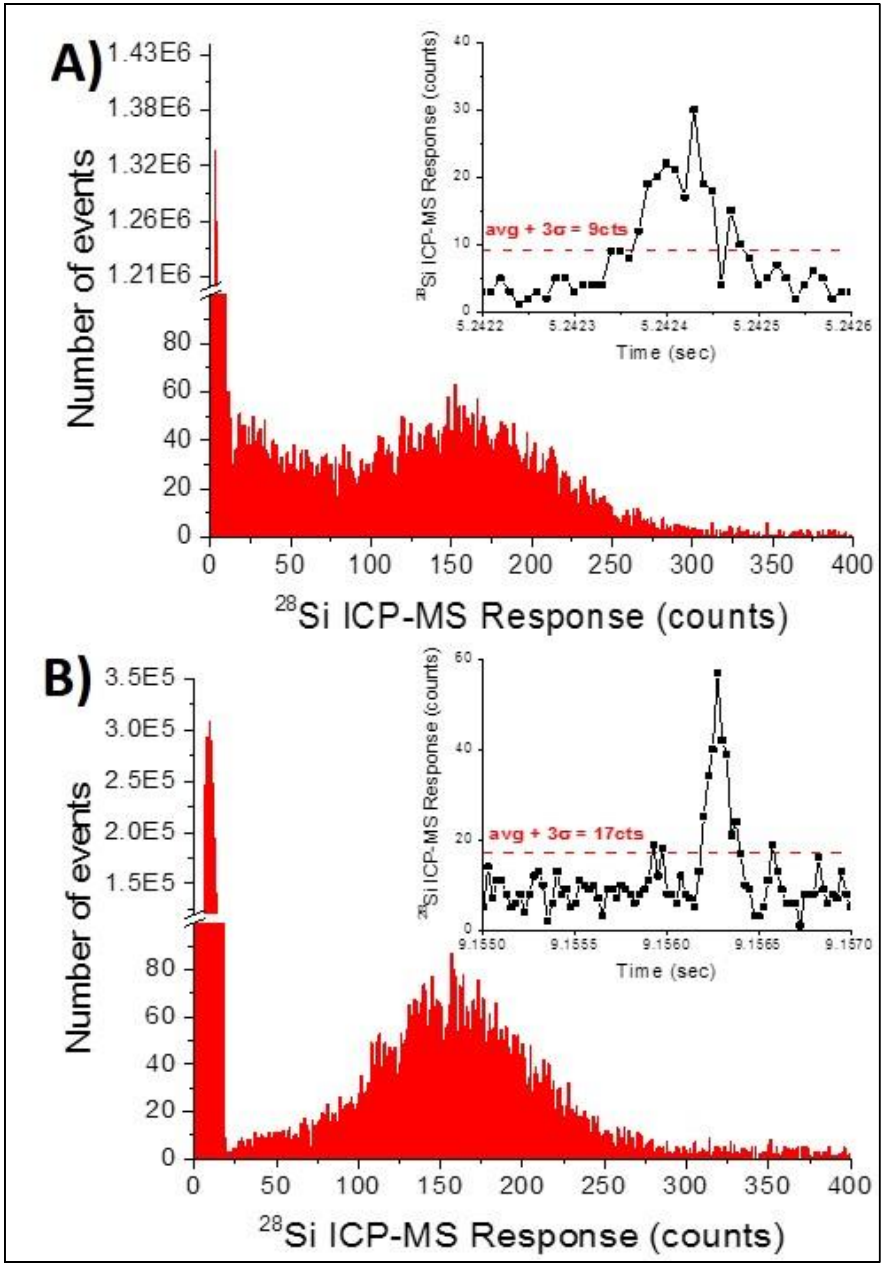
Determined Minimum Detection Sizes for Metallic NPs





$$D_{min} = \left(\frac{6 \times 3\sigma_{DI}}{R \times f_a \times \rho \times \pi} \right)^{1/3}$$

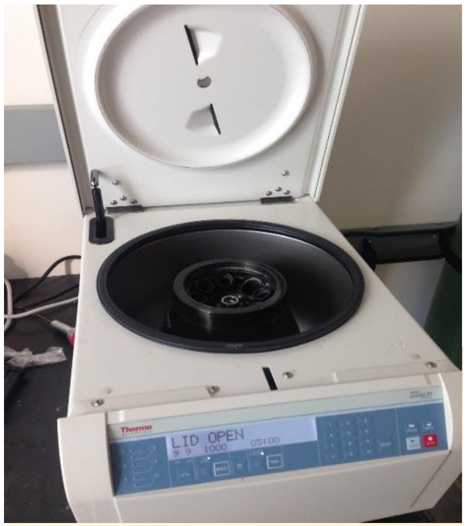
SRC Engineering Research Center for



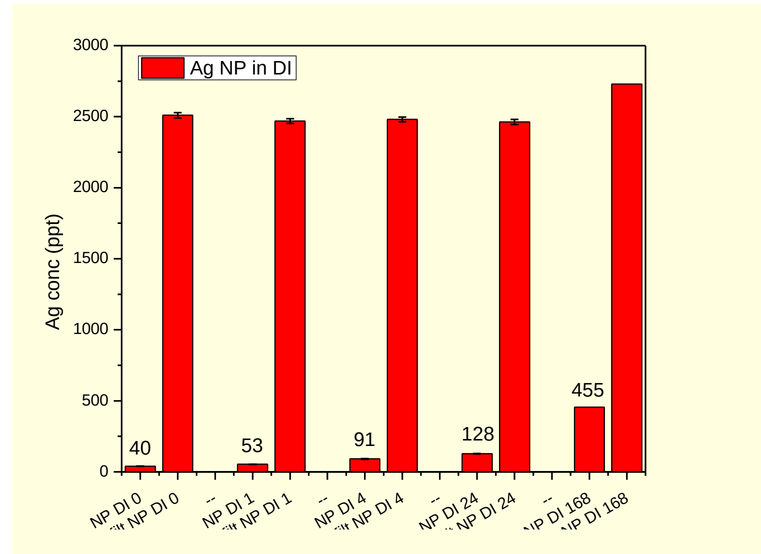
Advanced Analytical Method

- New *FAST SCAN* mode
  - Montano et al., Improvements in the detection and characterization of engineered nanoparticles using spICP-MS with microsecond dwell times, Environ Sci. Nano (2014)
- Reduced size resolution by ~ 4 to 5x for SiO_2
  - Montano et al., Methods for improving the detection and characterization of silica nanoparticles by spICP-MS, JAAS (under review)

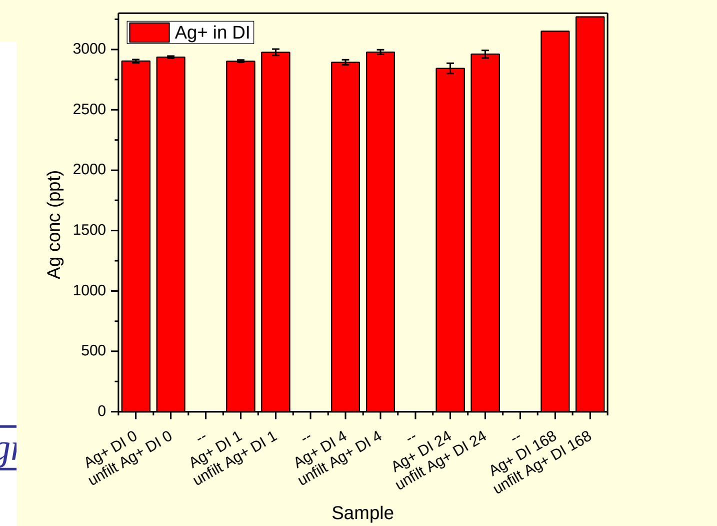
Sample Pretreatment Separating Ionic from NP



NPs in Ultrapure water



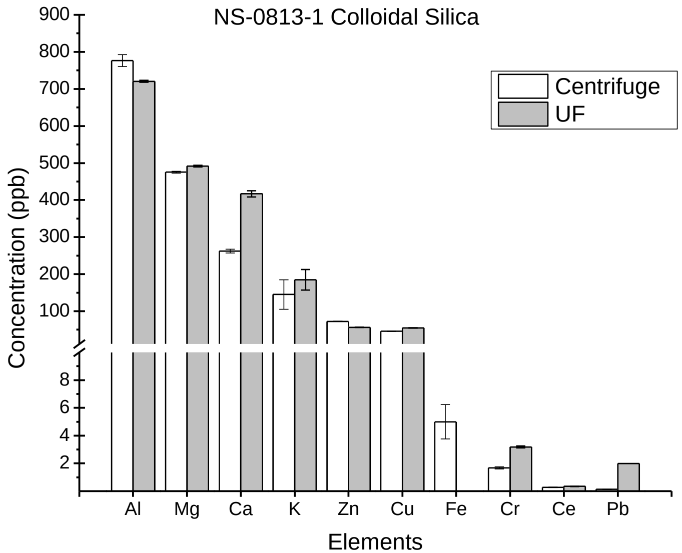
Ag-ions in Ultrapure water

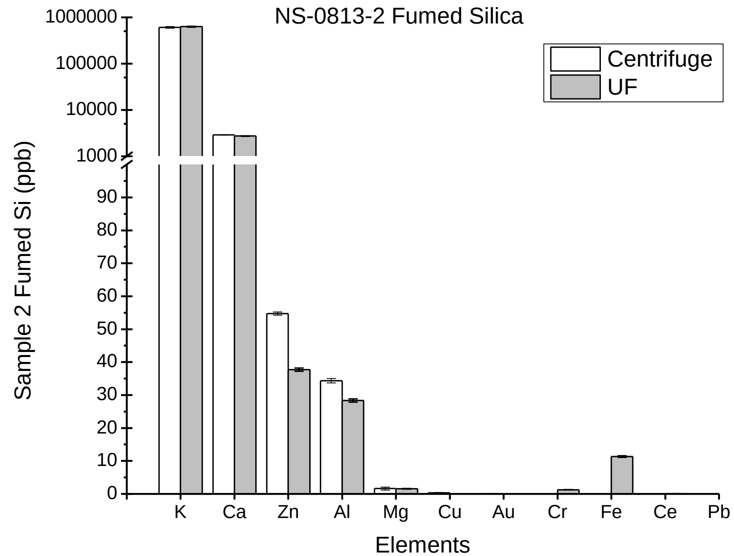


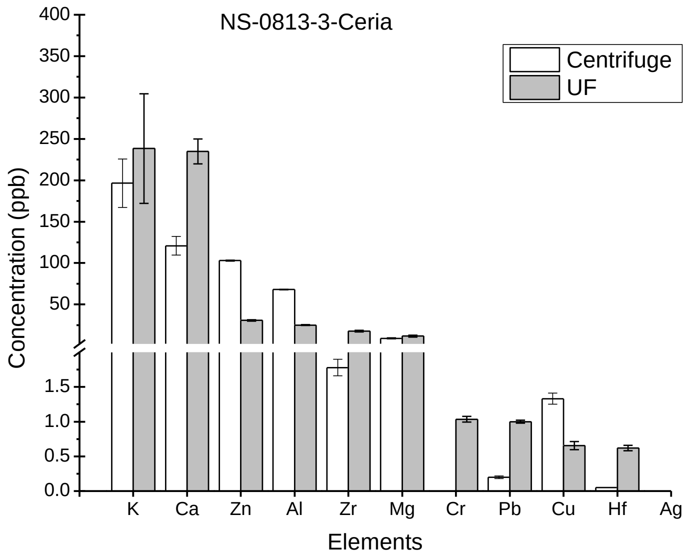
What is in the CMP Slurry other than NPs?

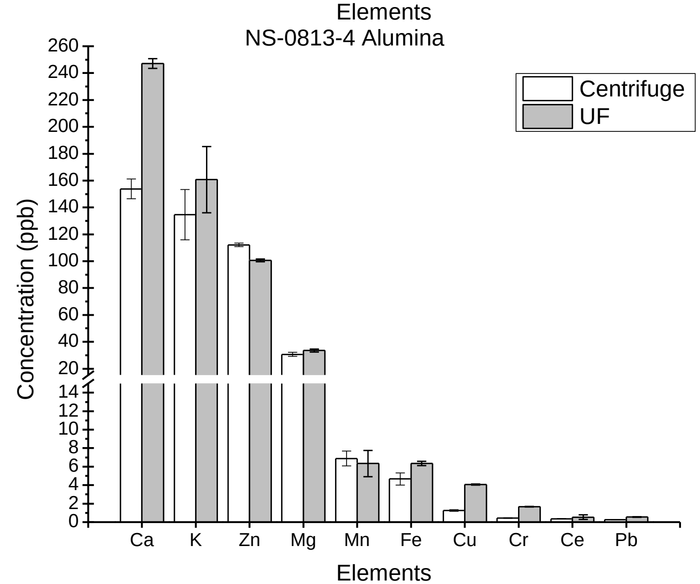
- Removed NPs by:
  - High speed centrifugation (UT-Dallas)
  - Centrifugal Ultrafiltration at lower speed

Concentrations of dissolved elements in CMP slurries. “Centrifuge” corresponds to samples from UTD. “UF” corresponds to samples treated with centrifugal ultrafiltration (30K Da).



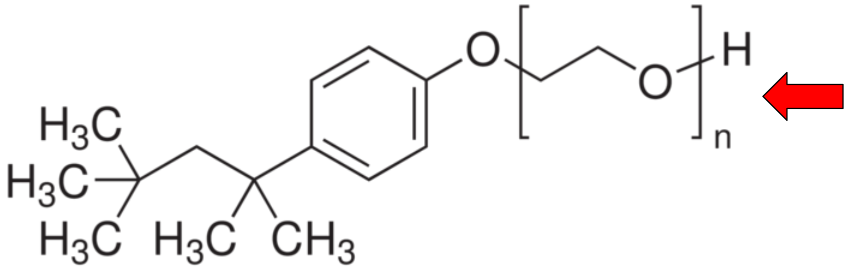






Cloud Point Extraction (CPE)

- A surfactant – Trition 114 can be used for CPE *(Liu., et al., Chemical Communication, 2009).*

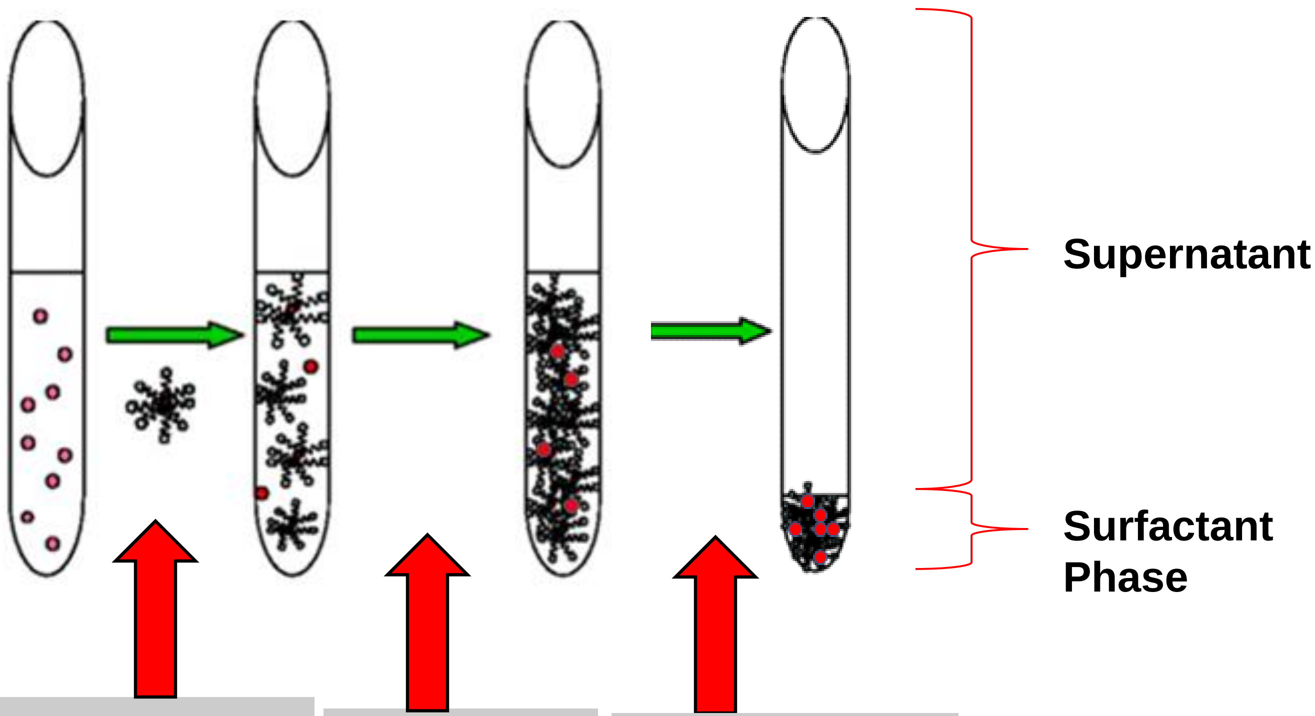


Surfactant : Triton 114

- When the temperature increases above the temperature - cloud point (CPT), the micelles become dehydrated and aggregates, forming cloudy phase.
- Cooling down and centrifuge→ phase separation
- Nanoparticles move from water phase to surfactant phase

Chao et al., Analytical Chemistry, 2011

Cloud-point Extraction Process



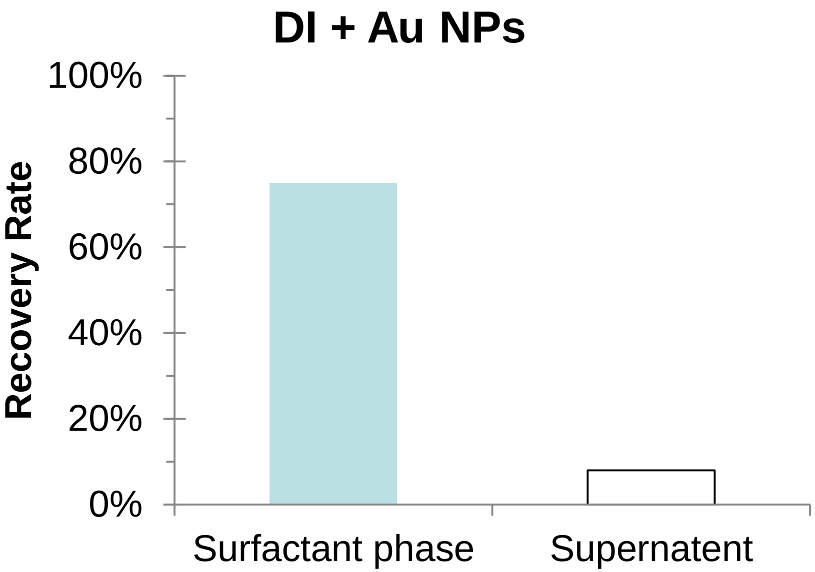
Step 1.
Adding surfactant (Triton 114) to get a final concentration of 5% (W/V)

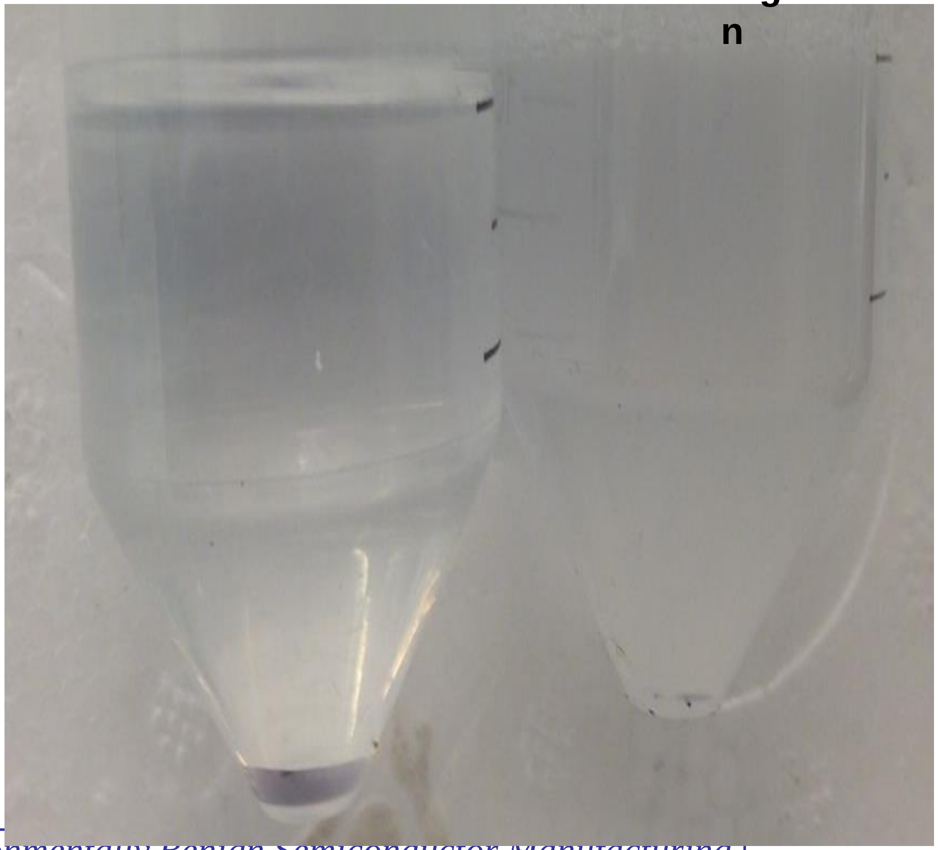
Step2.
Water bath at 40 °C for 30 minutes

Step 3.
Cooling down, and centrifuge

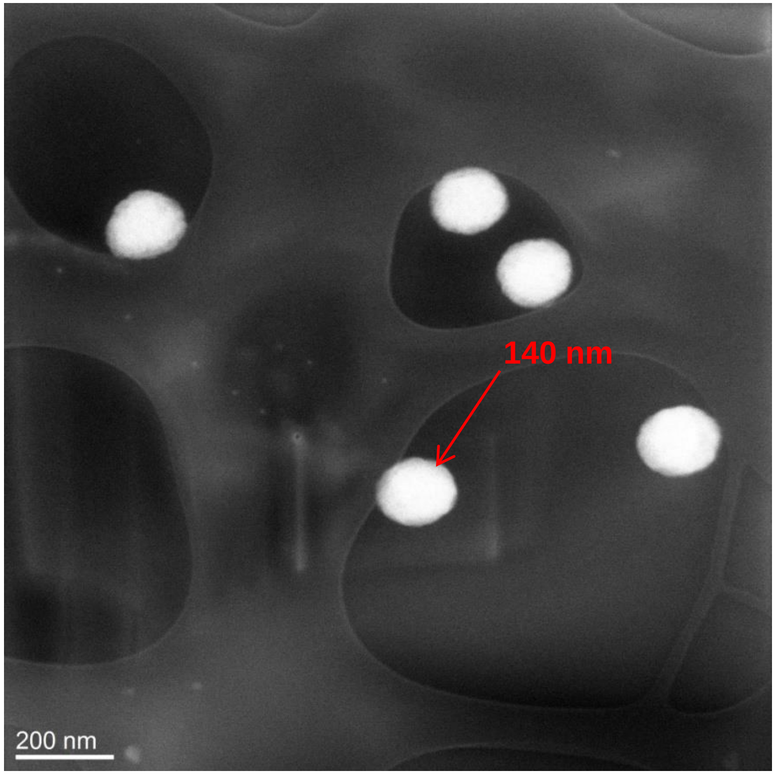
(Ojeda.,et.al., Microchimica Acta, 2012)

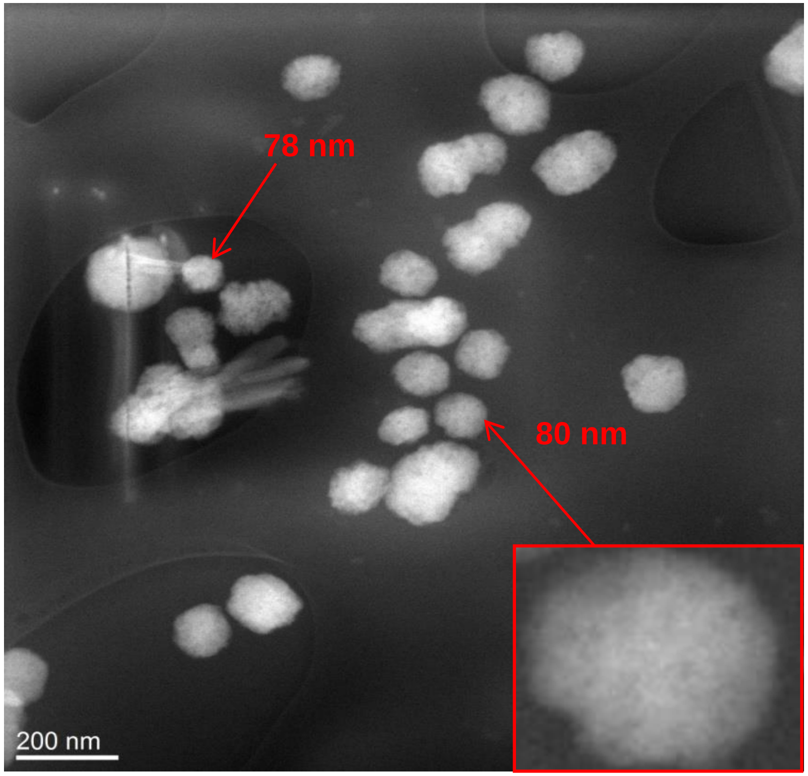
Example of CPE: Recovery Rate of Au Nanoparticles from Nanopure water





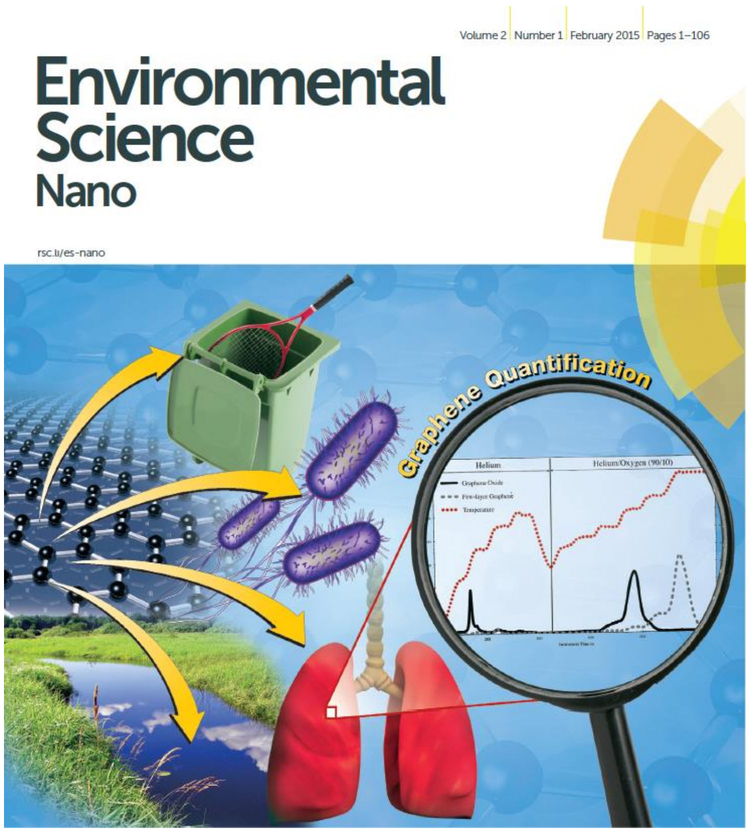
Nanoparticles from Arizona Wastewater Treatment Plants
(Spherical SiO_2 NPs – polishing agents?)



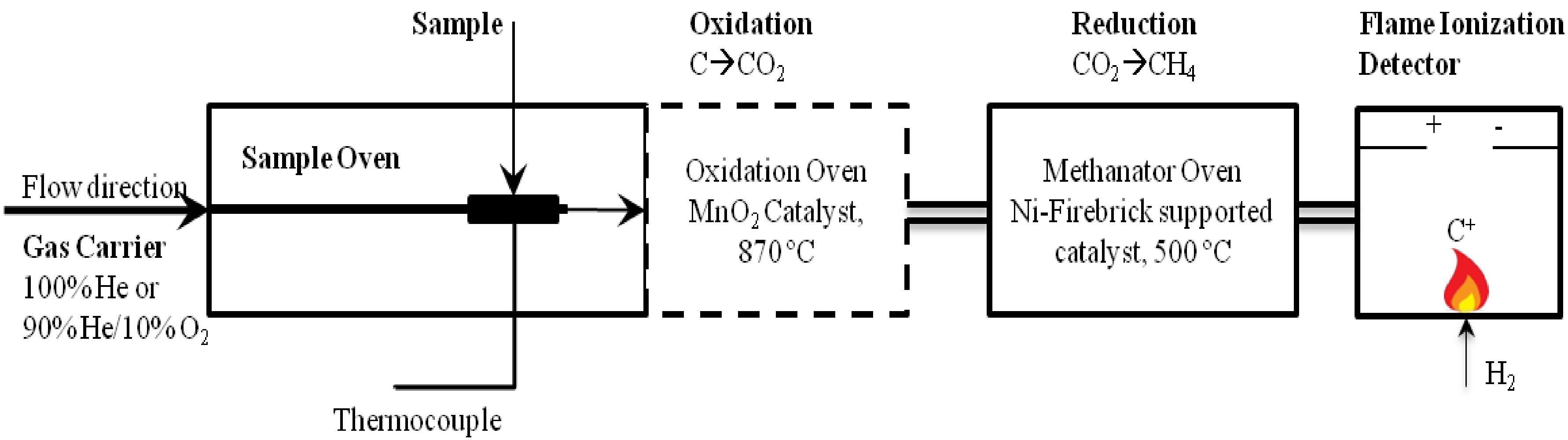


Carbonaceous NM Detection

- Plata, D., Ferguson, L., Westerhoff, P. “**Express it in numbers: efforts to quantify carbon nanotubes in environmental matrices advance**”, A Viewpoint in *Environmental Science and Technology* 46: 12243-12245 (2012).
- Doudrick, K., Herckes, P., Westerhoff, P. “**Detection of Carbon Nanotubes in Environmental Matrices Using Programmed Thermal Analysis**”, *Environmental Science and Technology* 46: 12246-12253 (2012)
- Doudrick, K., Corson, N., Oberdorster, G., Elder, A.C., Herckes, P., Halden, R.U., Westerhoff, P. “**Extraction and Quantification of Carbon Nanotubes in Biological Matrices with Application to Rat Lung Tissue**”, *ACS Nano*, 7:10: 8849-8856 DOI: 10.1021/nn403302s (2013)
- Doudrick, K., Nosaka, T., Herckes, P., Westerhoff, P. “**Quantification of Graphene and Graphene Oxide in Complex Organic Matrices**”, *Environmental Science: Nano* 2:1:60-67(2015)



Thermal Analysis of CNTs, FLG, GO



Sunset Laboratories Lab OC-EC Aerosol Analyzer

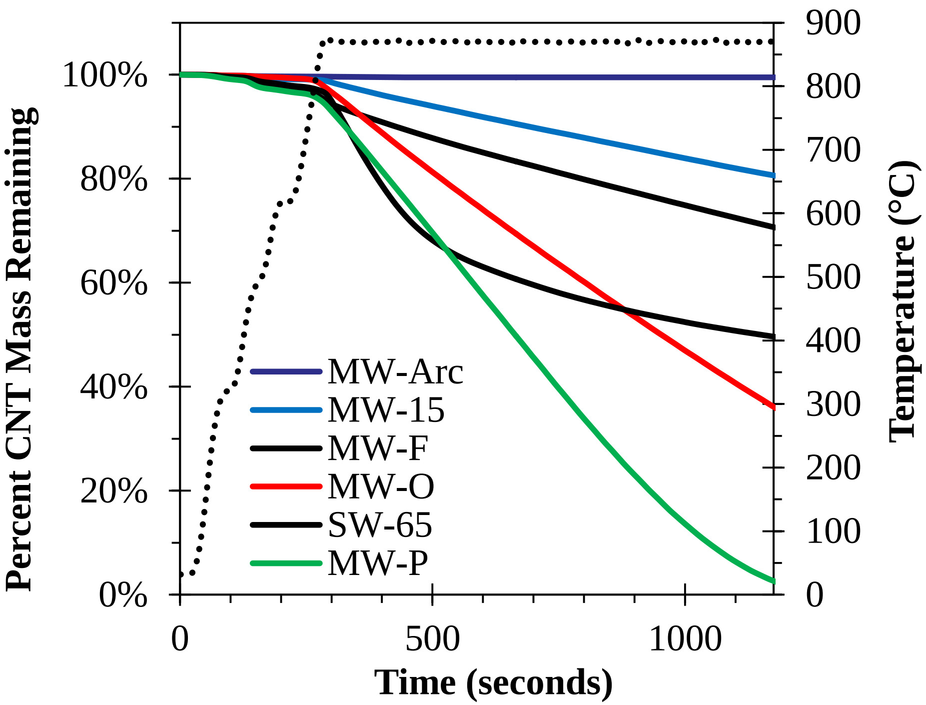
Not All CNTs are Equivalent – So we examined 15 different CNTs

Table 1. Properties of CNTs Used in This Study

CNT ID	CNT type	state	purity[a]	metal content[b]	outer diameter (nm)	inner diameter (nm)	length (μm)
MW-O	MWCNT	raw	>95%	<6%	20–30	5–10	10–30
MW-P	MWCNT	purified	>98%	<2%	20–30	5–10	10–30
MW-F	MWCNT	functionlized	>99.9%	<0.01%	20–30	5–10	10–30
MW-15	MWCNT	raw	>95%	<5%	7–15	3–16	0.5–200
MW-20	MWCNT	raw	>95%	<5%	10–20	5–10	0.5–200
MW-30	MWCNT	raw	>95%	<5%	10–30	5–10	0.5–500
MW-100	MWCNT	raw	>95%	<5%	60–100	5–10	0.5–500
MW-OH	MWCNT	functionalized	>95%	<1.5%	8–15	3–5	10–50
MW-COOH	MWCNT	fucntionalized	>95%	<1.5%	8–15	3–5	10–50
MW15G[c]	MWCNT	annealed	>97%	<1%	7–15	3–6	0.5–100
MW-Mitsui	MWCNT	raw	>98%	<1%	20–70	NA	NA
MW-arc	MWCNT[d]	raw	<50%	0%	5–10[e]	NA	NA
SW	SWCNT	raw	<50%	<10%	1.1	NA	0.5–100
SW-65	SWCNT	purified	<75%	<10%	0.8	NA	0.45–2

[a]CNT content reported by manufacturer. MW-P and MW-F calculated assuming no amorphous carbon remaining. [b]Metal content reported by manufacturer except for MW-F and MW-P determined using energy-dispersive X-ray spectroscopy and MW-15G using thermogravimetric analysis. [c]MW-15 annealed at ~2000 °C in UHP He. [d]Synthesized using arc method; all others are CVD. [e]Obtained from TEM images; all others reported by manufacturer.

Thermal Properties of CNTs

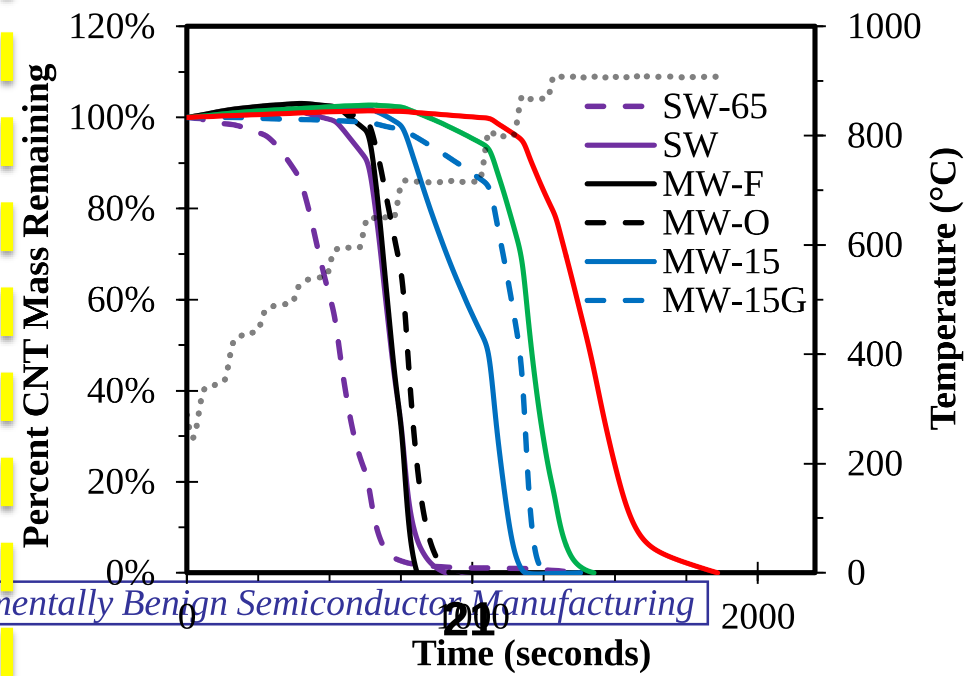


Inert conditions (100% He)

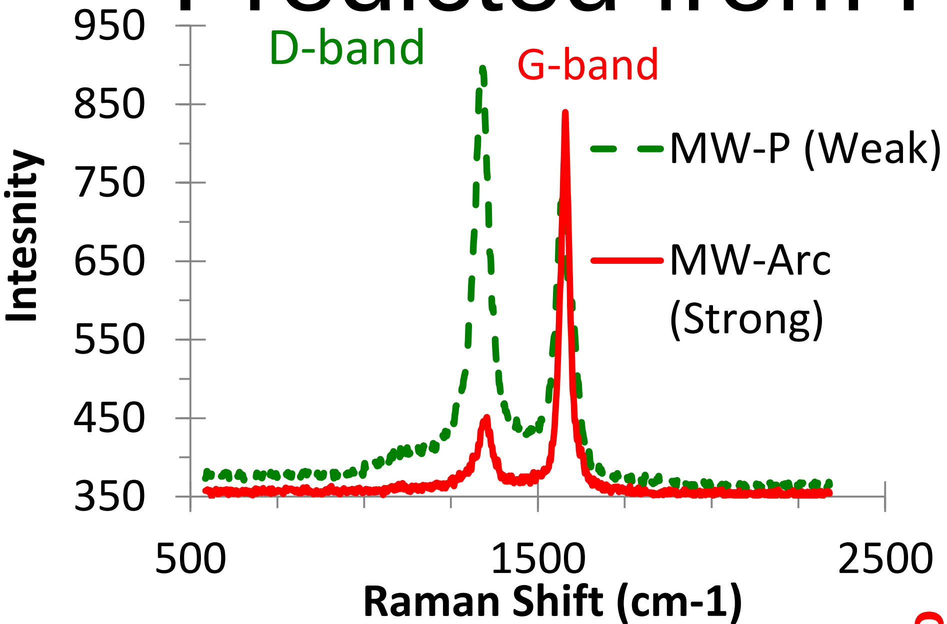
Conclusion: Surface oxygen groups allow some CNTs to burn in inert gas environment

Oxidizing conditions (90% He/ 10% O_2)

Conclusion: Not all CNTs "burn" at the same temperature

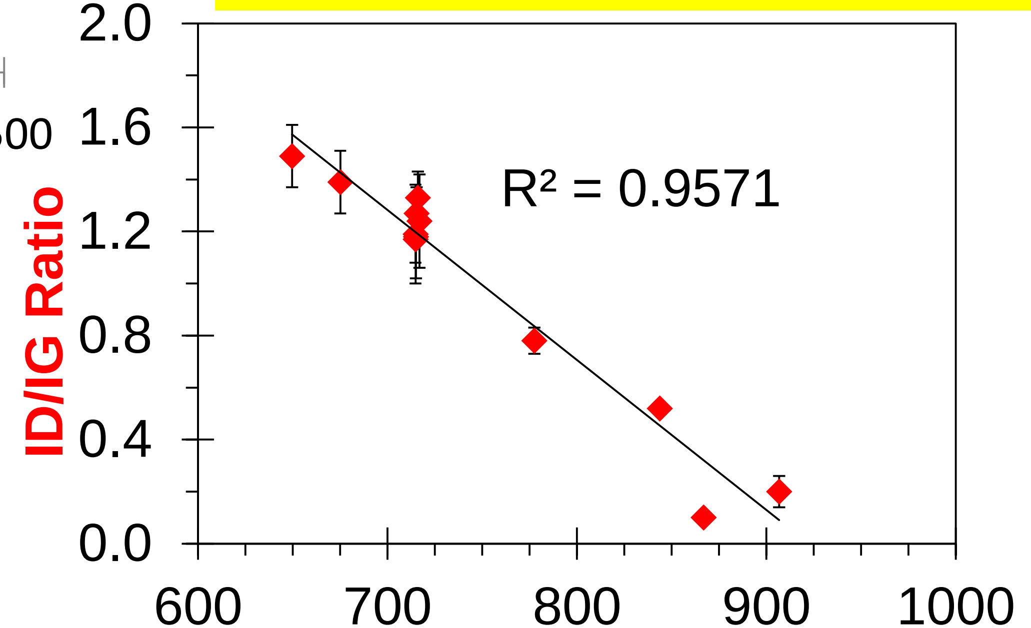


Oxidation "Capability" Can be Predicted from Raman Spectra



Raman spectra of two CNTs

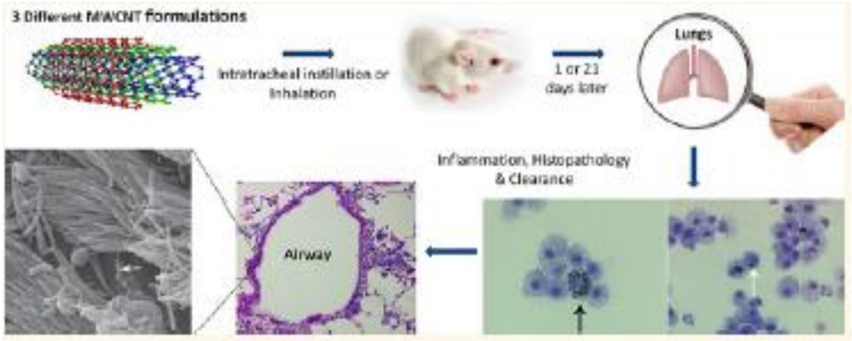
Correlation between oxidation temperature at 50% mass loss and the I_D/I_G ratio



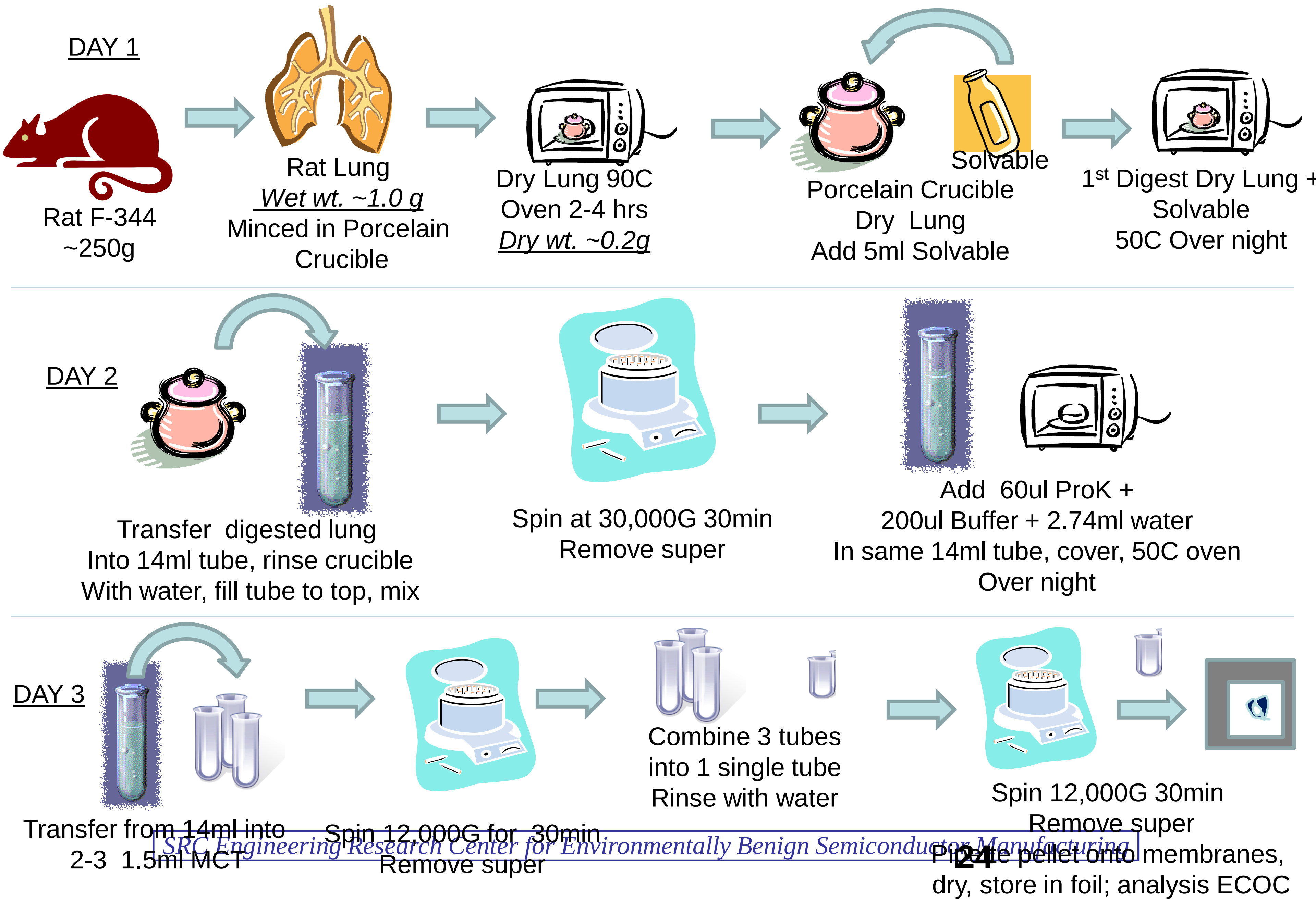
Oxidation Temperature at 50% Mass Loss (°C)

New Carbonaceous NM Detection method ENABLES toxicity work

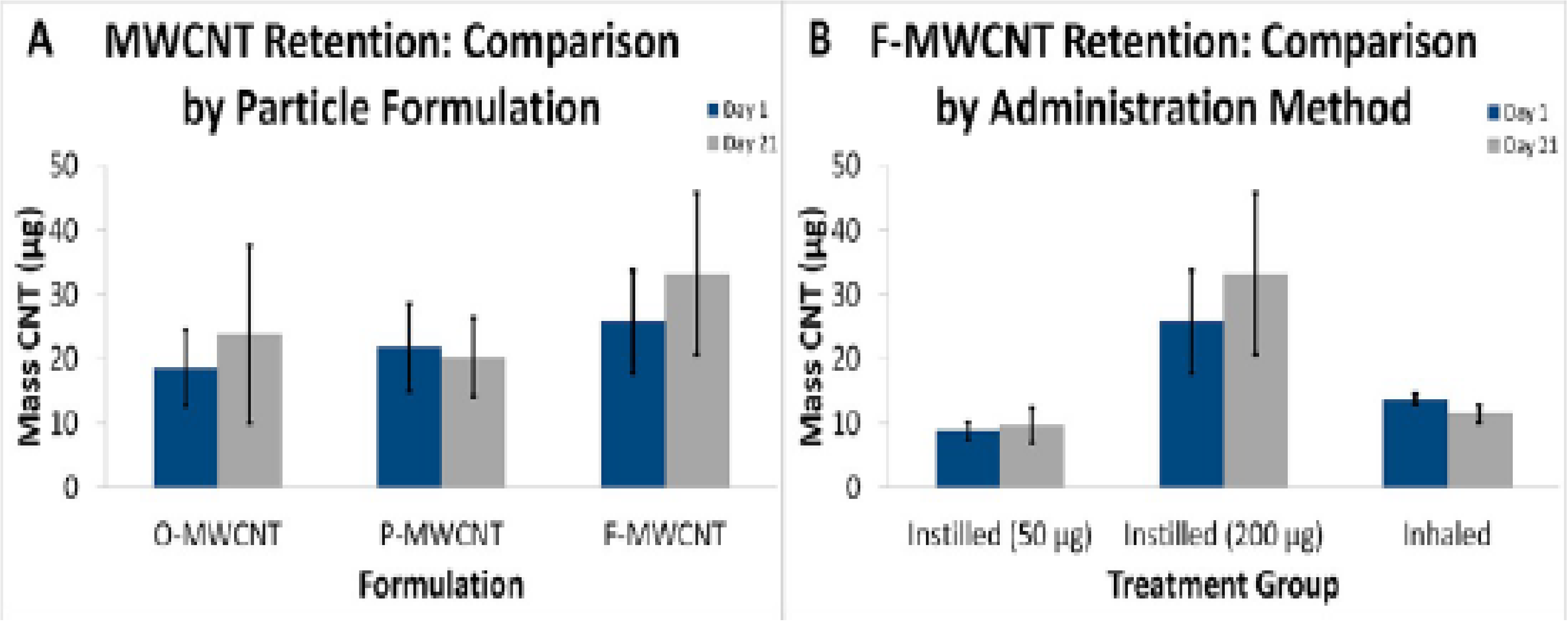
- K. Doudrick, N. Corson, G. Oberdörster, A. Eder, P. Herckes, R. Halden and P. Westerhoff, **Extraction of carbon nanotubes from complex organic matrices with application to rat lung tissue**, *ACS Nano*, **7**, 8849-8856, 2013
- Silva, R., Doudrick, K., Franzi, L., TeeSy, C., Anderson, D., Wu, Z., Mitra, S., Vu, V., Dutrow, G., Evans, J., Westerhoff, P., Van Winkle, L., Raabe, O., Pinkerton, K. “ **Instillation versus Inhalation of Multi-Walled Carbon Nanotubes: Exposure-Related Health Effects, Clearance, and the Role of Particle Characteristics**", *ACS Nano*, 8:9:8911-8931(2014).



Optimized CNT Extraction from Rat Lungs



Method enabled dosimetry measurements & clearance rates



Air Sampling

- Goal: To quantify the presence of CNTs in the presence of background air particulates
- Quartz fiber filters were loading into the personal air exposure monitor (Leland Legacy ® Pump (SKC Inc.)).
- Two air samples were obtained representing
  - an indoor facility (e.g., manufacturing lab)
  - Outdoors in Arizona .
- Air monitor run for 24 hours 10 L/min.
- Each sample location was collected in duplicate.
- Filters then spiked with CNT
- Samples analyzed for organic carbon and CNT by PTA

Recovery of CNTs on air filter samples

(Conclusion: Excellent CNT recoveries indicates viability to monitor CNTs in workplace air)

"Strong" MWCNT

Indoor air

Spiked CNT / ug	TOT data / ug
1	1.00±0.15
5	4.35±0.32
10	9.59±0.58

Outdoor air

Spiked CNT / ug	TOT data / ug
1	0.80±0.17
5	4.48±0.36
10	10.06±0.63

"Weak" MWCNT

Indoor air

Spiked CNT / ug	TOT data / ug
1	0.73±0.14
5	4.82±0.34
10	10.29±0.62

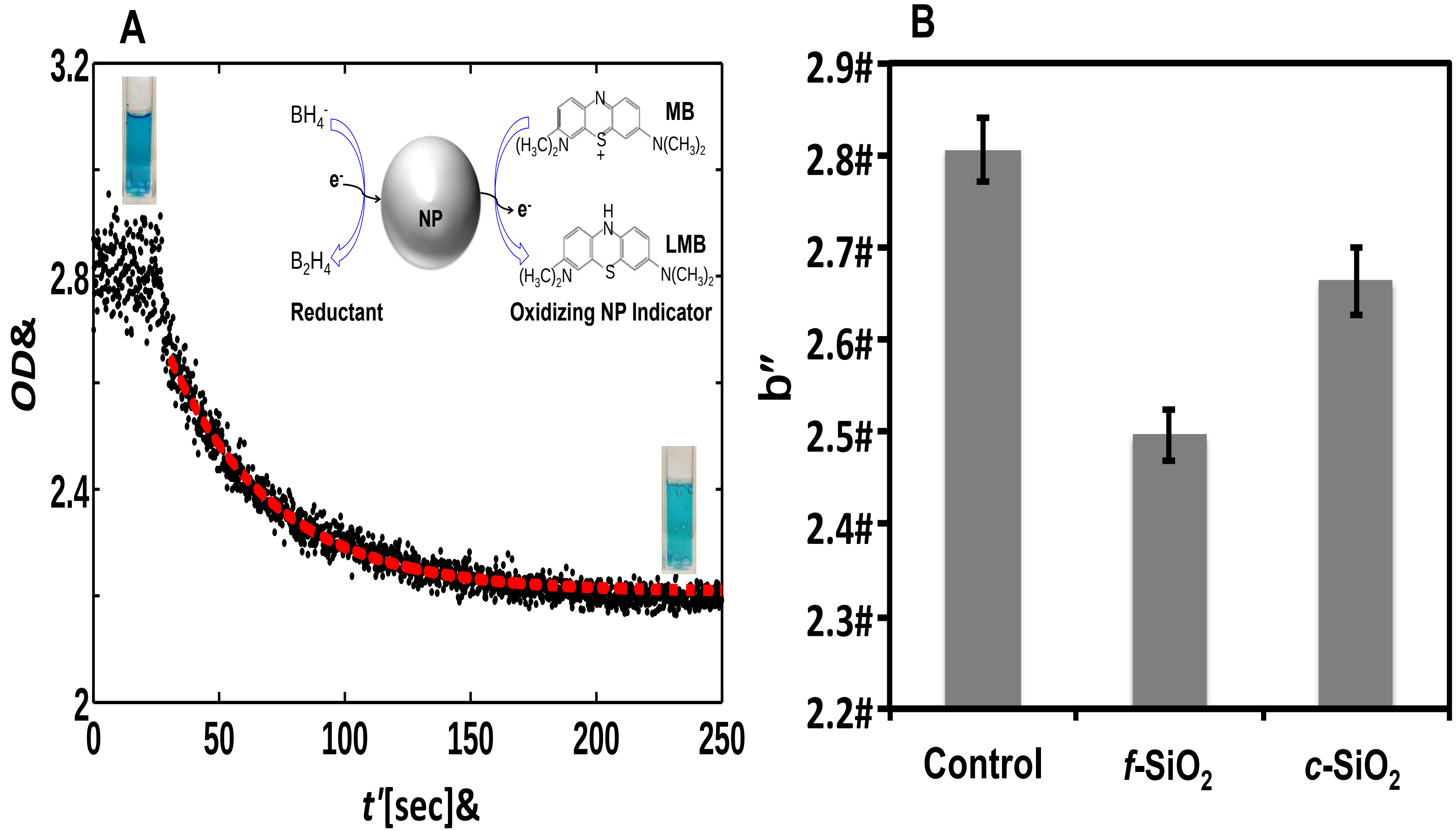
Outdoor air

Spiked CNT / ug	TOT data / ug
1	1.71±0.22
5	4.71±0.37
10	9.70±0.62

Reactivity Tests

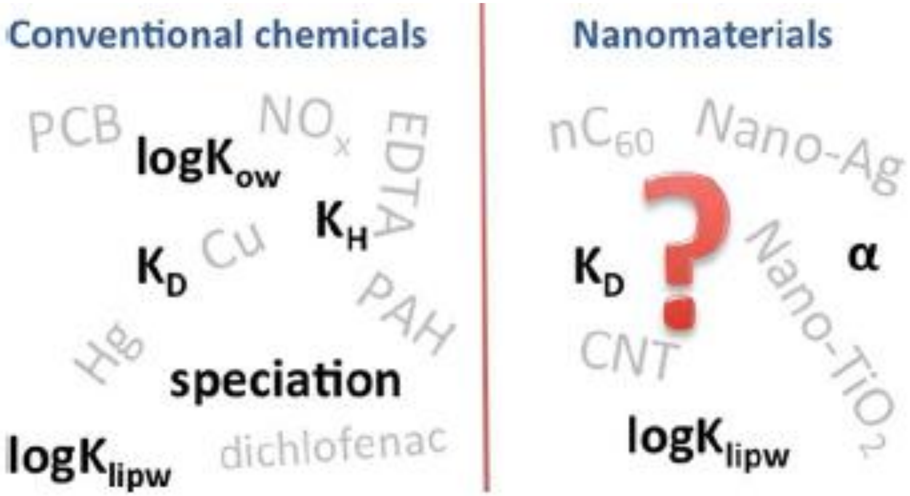
- Negoda, A., Liu, Y., Hou, W.C., Corredor, C., Moghadam, B.Y., Musolff, C., Li, L., Walker, W., Westerhoff, P. Mason, A.J., Duxbury, P., Posner, J.D., Worden, R.M. "**Engineered Nanomaterial Interactions with Bilayer Lipid Membranes: A Screening Platform to Assess Nanoparticle Toxicity**" *Int. J. Biomedical Nanoscience and Nanotechnology*, 3:1/2:52- 83(2013)
- Corredor, C., Hou, W-C, Klein, S.A., Moghadam, B.Y., Goryll, M. Doudrick, K., Westerhoff, P., Posner, J.D. "**Disruption of Model Cell Membranes by Carbon Nanotubes**", *Carbon*, 60:67-75 (2013)
- Corredor, C., Borysiak, M., Wolfer, J., Westerhoff, P., Posner, J. "**Colorimetric Detection of Catalytic Reactivity of Nanoparticles in Complex Matrices**", *Environmental Science & Technology* (in-press)

Surface Reactivity



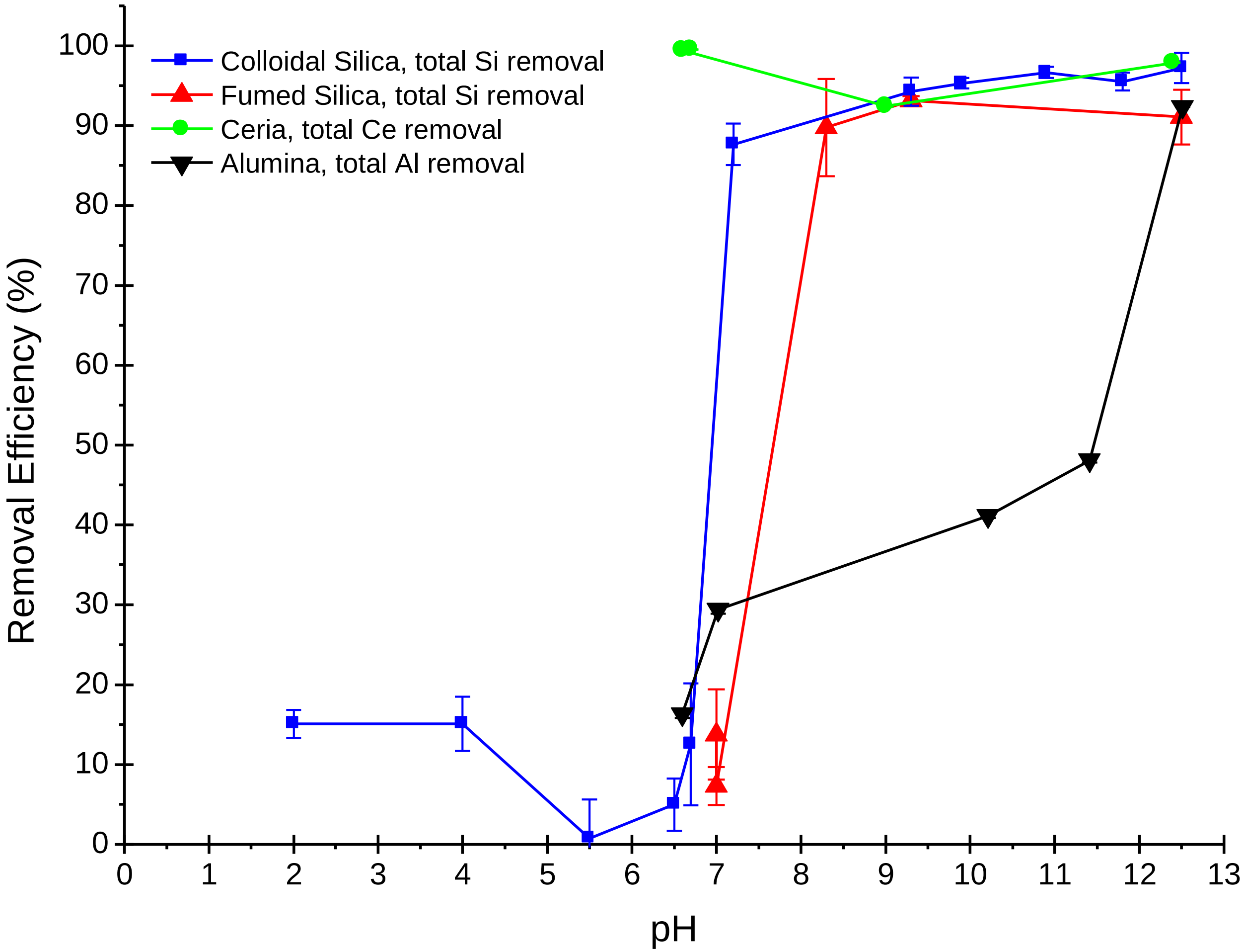
NM Fate Studies

- Westerhoff, P. and Nowack, B. "**Searching for Global Descriptors of Engineered Nanomaterial Fate and Transport in the Environment**", *Accounts of Chemical Research* , 46:3:844-853 **DOI:** 10.1021/ar300030n (2013)



- Bi, X, Reed, R., Westerhoff, P. **Chapter 8- Control of nanoparticles used in chemical mechanical polishing/planarization slurries during on-site industrial and municipal biological wastewater treatment**, in Characterization of Nanomaterials in Complex Environmental and Biological Media (Eds. Baalousha, M. and Lead, J.), ISBN: 9780080999487, (expected June 2015)

Removal efficiencies of Si, Ce and Al for four types of nanoparticles in CMP slurries under different pH conditions. Ca dosage was 1.9 mM in all cases.



Consortium Activities

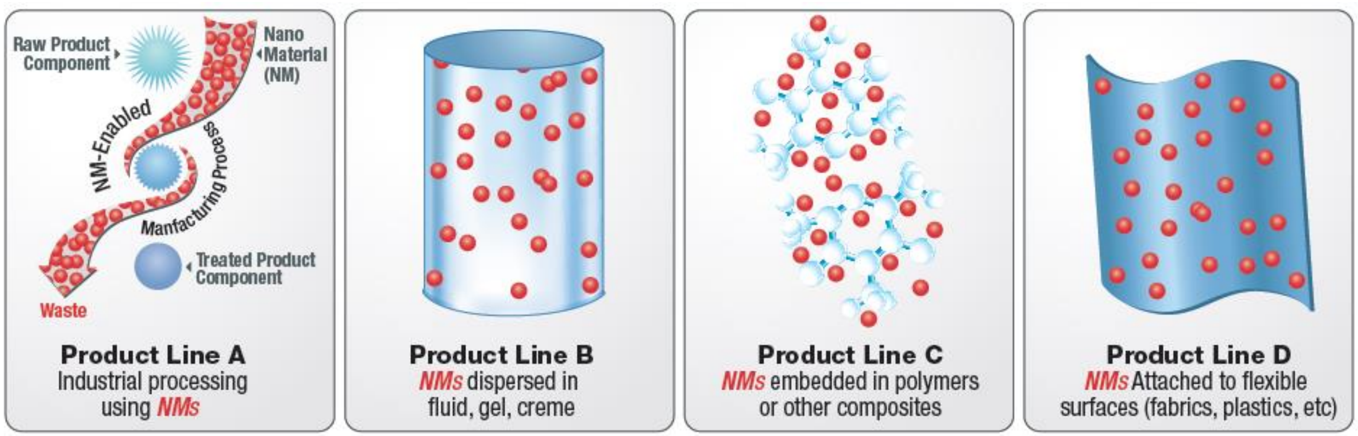
- Helped organize CMP Consortium slurry design, procurement and characterization
- Journal paper submitted to Environ. Sci. Nano

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]

SRC Project Motivated Other Funding

- NSF – “Nanoprospecting” ($300k, 2013-2016)
- EPA – Life Cycle of Nanomaterials Network ($5M, 2014-2018)



Final Report Findings

- Sensitive monitoring techniques are available for all relevant Semiconductor Relevant nanomaterials in complex matrices
- Techniques can be applied to air, water, soil, tissue matrices to assess exposures & fate of nanomaterials
- Next steps: Understand interaction of nanomaterials in complex matrices with III/V ions