Understanding the Sorption Characteristics of III-V Materials on CMP Nanoparticles and Evaluate their Environmental Impact using a Zebrafish Model

(*Task Number: 425.050*)

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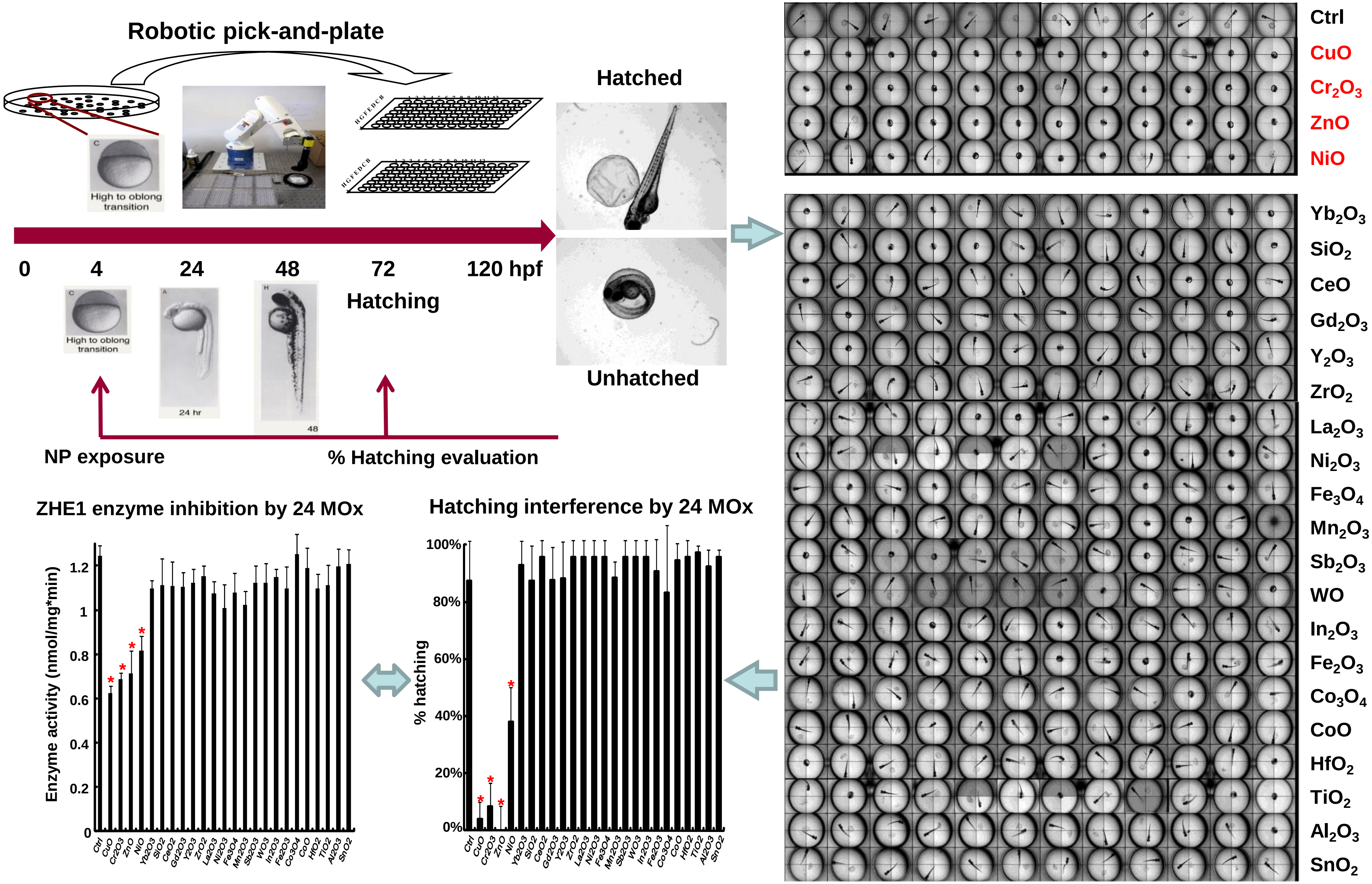
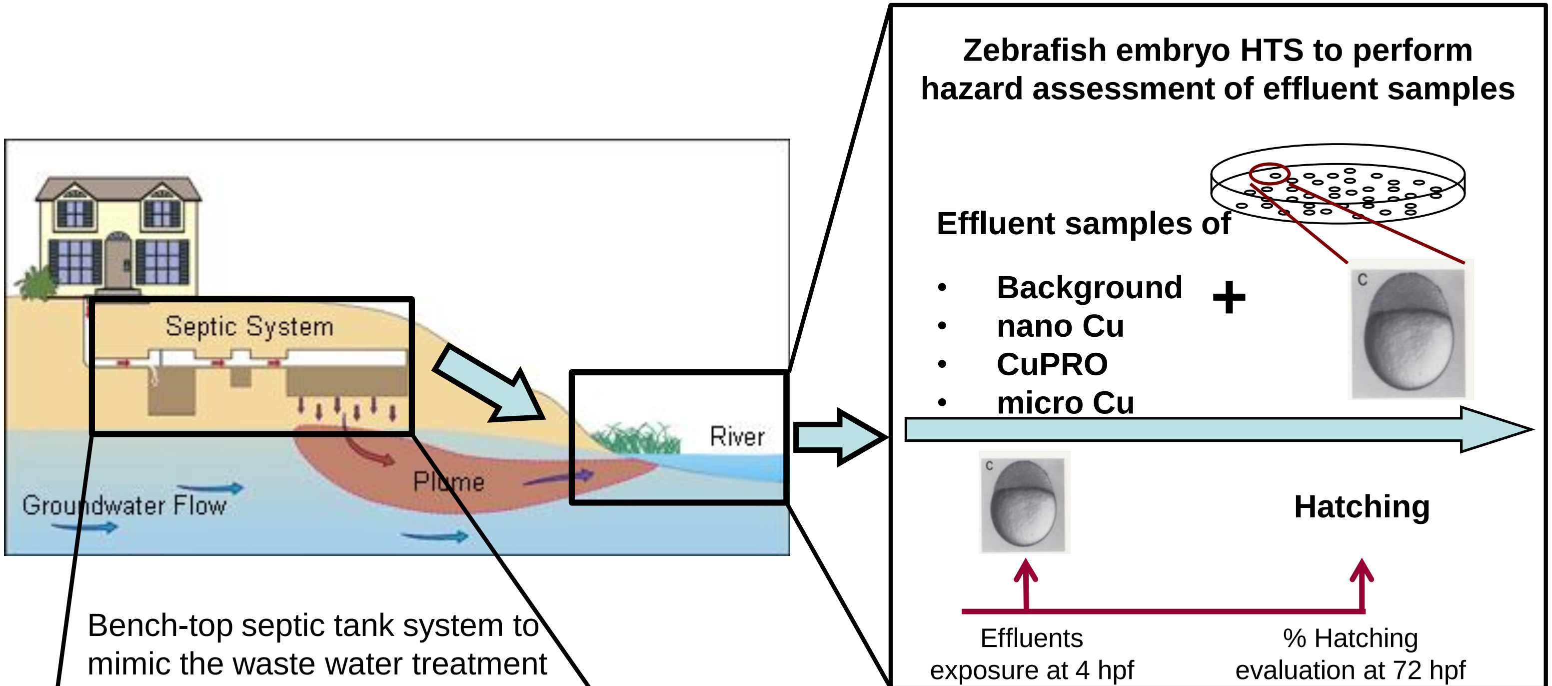
Our Predictive and High Throughput Screening Approach to Study the Hazard Potential of Semiconductor Nanomaterials (24 Metal Oxides)

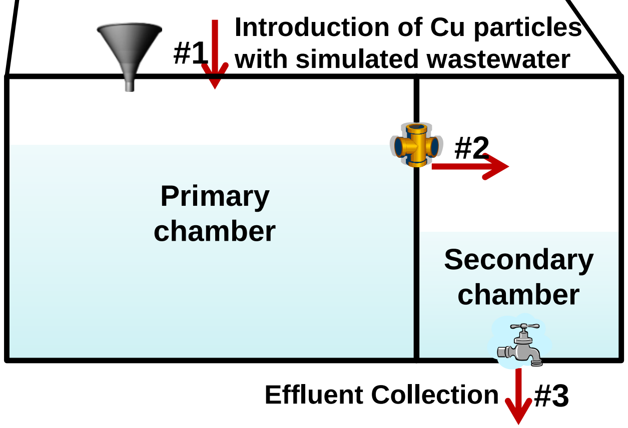


SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Lin et al. ACS Nano, 2011; George et al. ACS Nano, 2011; Lin et al. Small, 2013

Combined Use of Zebrafish and Model Wastewater Treatment to Assess the Environmental Hazard Potential of Nano Cu Materials





Arrow #1: Introduction of Cu particles (i.e. nano Cu, CuPRO and micro Cu) into the primary chamber of septic tank

Arrow # 2: Effluent flow into the secondary chamber of septic tank

Arrow #3: Effluent samples collection from the secondary chamber

Lin et al. ACS Nano, 2015

Objectives

- **Characterize the sorption of III-V metal ions onto the silica nanoparticle surface, by in-house design and synthesis of a library of magnetized silica nanoparticles (MSN);**
- **Use zebrafish as a representative environmental model to assess the hazard potential of sorbed and non-sorbed MSN's as well as the consortium-provided silica nanoparticles;**
- **Implement zebrafish HTS techniques that aims to relate the physiochemical properties of sorbed III-V materials and CMP silica nanoparticles to possible hazard generation by these materials.**

ESH Metrics and Impact

Use the following metrics to give a convincing justification for the ESH significance of this project. Be specific (general statements were criticized in the last review); please be as quantitative as possible.

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

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

3. **Reduction in the use of natural resources (water and energy)**

4. **Reduction in the use of chemicals**

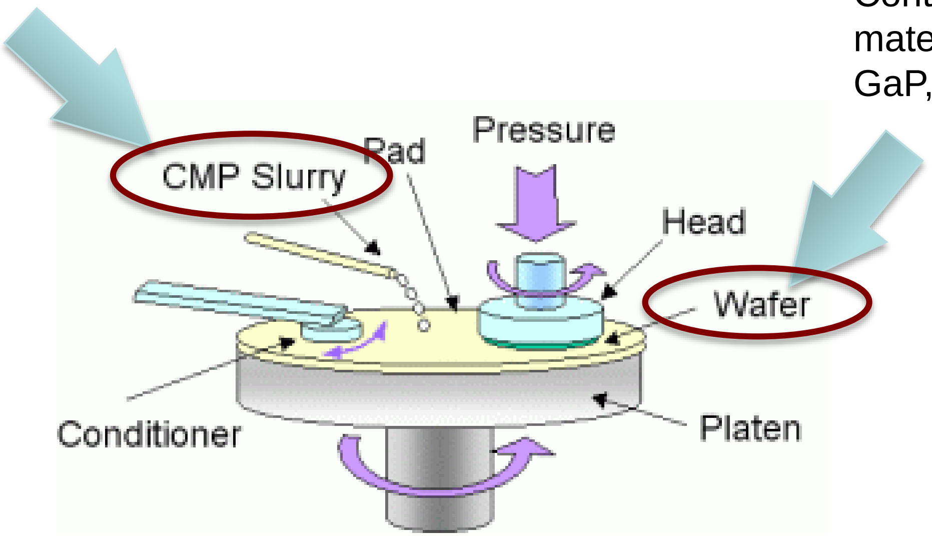
Environmental Concerns:

- The increasing use of III-V materials (Ga, In and As) in wafer production in semiconductor industry
- One particular process involved in wafer production called chemical and mechanical planarization (CMP) uses silica, ceria and alumina nanoparticles to obtain atomic-level smooth wafer surface that generates significant amount of III-V materials containing slurry waste with unknown effect to the environment
- The mixing of III-V species and nanoparticles might alter the hazard profile of each individual chemical and/or nanoparticle

Typical CMP setup

CMP slurry nanoparticles: silica, ceria and alumina

Containing III-V materials such as GaAs, GaP, InAs and InP



The Challenges:

CMP nanoparticles (alumina, ceria and silica) interaction w/ III-V materials

? Limited information on the ecotoxicity of As, Ga, and In species alone?

? Hazard potential of CMP nanoparticles toxicity?

? CMP nanoparticles act as vectors for III-V transport

? The interaction between CMP nanoparticles and III-V materials and the resulted toxicity profile

Potential Toxic Elements

Dissolved chemicals:

- Arsenic
- Indium
- Gallium

- As(III): H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{-2}$, AsO_3^{-3}
- As(V): H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$, AsO_4^{-3}
- In^{+3}, $InOH^{+2}$, $In(OH)_2^+$, $In(OH)_3^o$, $In(OH)_4^-$
- Ga^{+3}, $GaOH^{+2}$, $Ga(OH)_2^+$, $Ga(OH)_3^o$, $Ga(OH)_4^-$

Particulates:

- CMP nanoparticles
- III-V particles (nano- and micron-sized)

The combination of III-V and CMP nanoparticles

Very limited information on III-V materials' environmental toxicity

Chemicals	Models	Toxicity outcomes
$GaCl_3$	Tilapia larvae	96 hr LC50 = 36 mg/L
$Ga_2(SO_4)_3$	Carp	96 hr LC50 = 20 mg/L
$InCl_3$	Tilapia larvae	96 hr LC50 = 37.6 mg/L
$InCl_3$	Zebrafish embryos	96 hr LC50 = 0.1 mM (22 mg/L)
Na_2HAsO_4 (sodium arsenate)	Rainbow trout	Growth retardation above 10 ug/g food intake
$NaAsO_2$ (sodium arsenite)	Fish cell lines (fin and ovary)	LC50 = 80 uM (1 mg/L)
As_2O_3	Zebrafish	96 hr LC50 = 1 mM (400 mg/L)

Method Approach

III-V materials

Ionic solution:

- NaH_2AsO_4
- $GaCl_3$
- $InCl_3$

Supernatant collected from particulate forms of:

- GaP
- GaAs
- InP
- InAs

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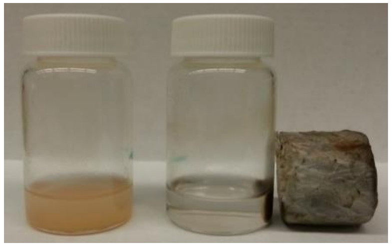
Magnetized silica nanoparticle library (size range 20~500 nm)



Conditions that mimics the CMP processes

Conditions of Sorption:

- Basic, neutral and acidic pH
- Surfactant, i.e. SDS
- Oxidizer, i.e. H_2O_2

Magnetic retrieval

Characterizations of III-V materials sorption:

- ICP-OES for quantification of III-V materials sorption
- XRD analysis to determine the speciation of III-V materials sorbed on model silica surface

Re-dispersed the retrieved silica nanoparticles in zebrafish growth medium

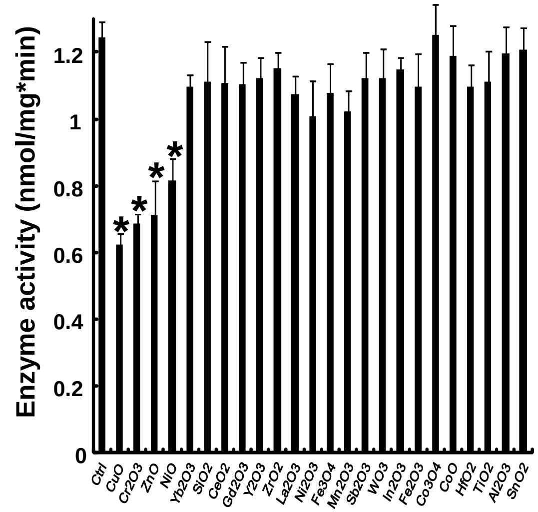
Hazard assessment

- Zebrafish embryo HTS
- ZHE1 enzymatic assay
- Transgenic zebrafish strains for mechanistic investigation (e.g. hsp70:eGFP and ere:eGFP)

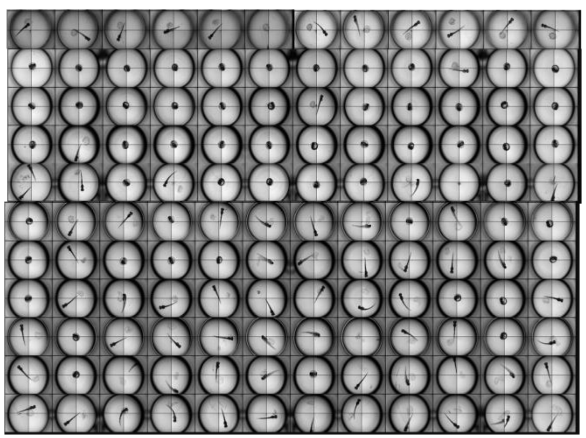
Method Approach (cont'd)

Robotized zebrafish embryo pick-and-placement

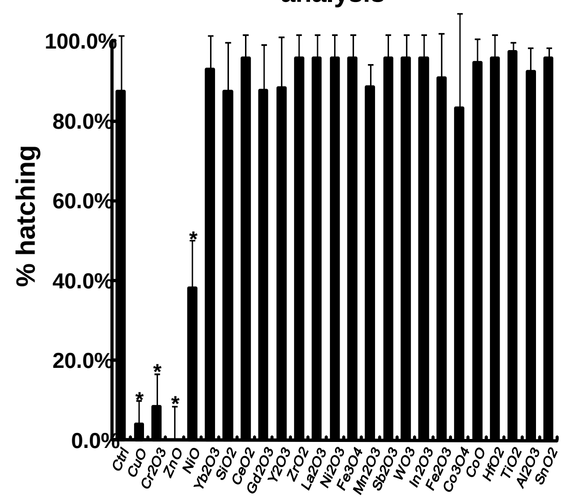
Abiotic ZHE1 enzymatic assay



Automated microscopic imaging



Computer-assisted image analysis



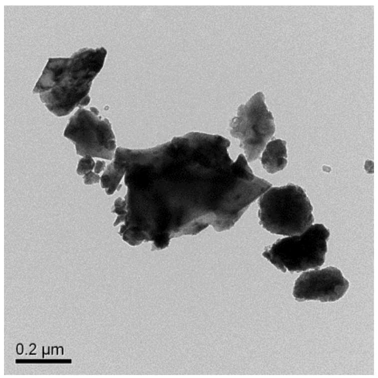
Use of Ionic and Particulate Forms of III-V Materials as Analogues to Study the Sorption Characteristics

Ionic form of III-V materials:

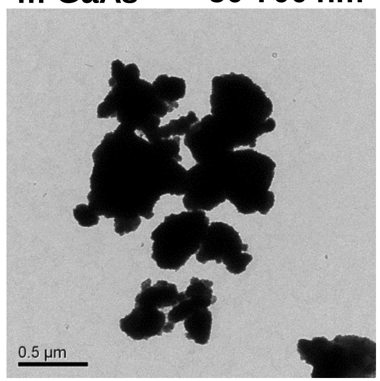
$GaCl_3$, $InCl_3$, $NaHAsO_4$ and $NaAsO_2$

Particulate form of III-V materials:

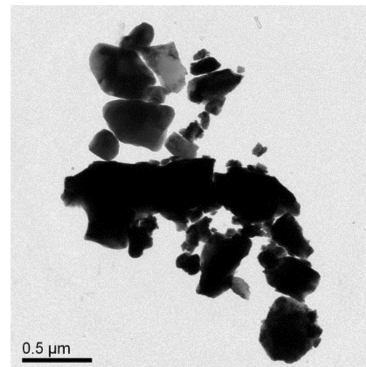
m-GaP 50-3000 nm



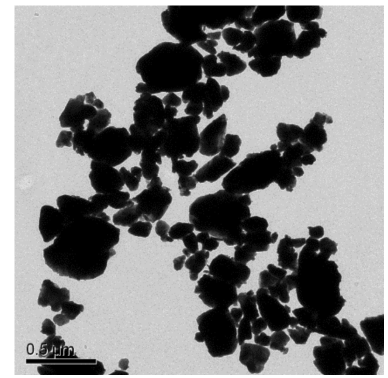
m-GaAs 50-700 nm



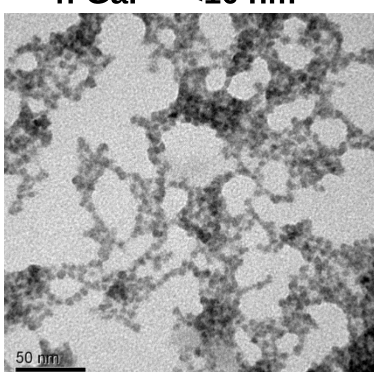
m-InP 80-1100 nm



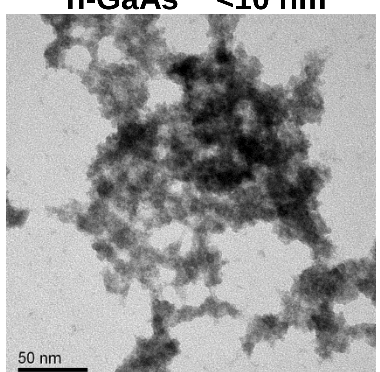
m-InAs 30-650 nm



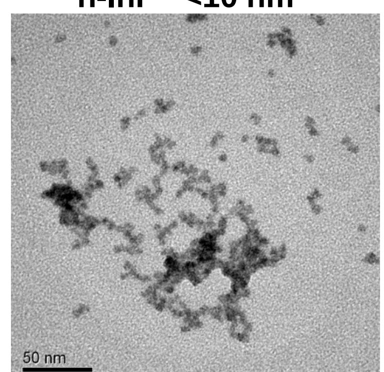
n-GaP <10 nm



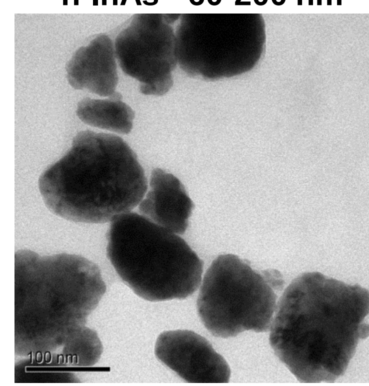
n-GaAs <10 nm



n-InP <10 nm

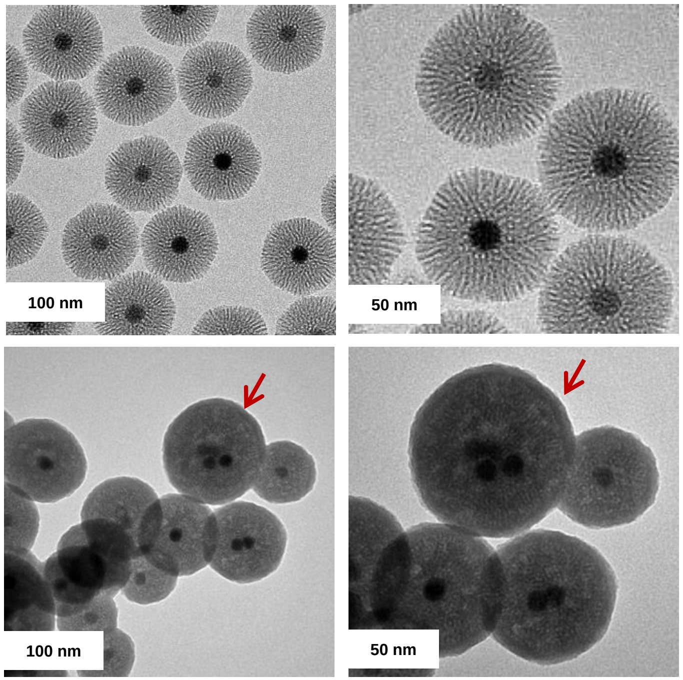


n-InAs 60-200 nm



Highlight of Results (cont'd)

Magnetized silica nanoparticles (MSN)



Representative TEM images of magnetized silica nanoparticles (MSN). Red arrows indicate a layer of solid silica surface coating around MSN.

List of MSN:

- MSN with unmodified surface;
- MSN with positively charged surface (NH_2- modified);
- MSN with negatively charged surface (CH_3PO_2-modified);
- MSN with a layer of solid silica surface;

- Silica nanoparticles without magnetic core for comparison purposes

Industrial Interactions

We envisage:

- To collaborate with the industry partners to establish suitable magnetic silica nanoparticles to study the sorption characteristics of III-V materials;
- To implement zebafish HTS screening to assess the environmental hazard potential of CMP slurries;
- To communicate with the semiconductor industry and to inform our findings on the environmental hazard potential associated with III-V materials;
- To work with the industry partners to help establish necessary EHS guidelines on III-V materials.

Education and Training Opportunities

CEIN offers:

- Student and postdoctoral mentoring and leadership programs;
- Professional development activities to improve skills in the areas of public speaking, professional presentations, and writing;
- Cross campus seminars where researchers present their individual research projects to the broad range of disciplines involved in CEIN’s cross-cutting Nano EHS research

Thank you!!