

Environmental Impacts and Controls Associated with Work Involving Nanomaterials

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BROOKHAVEN
NATIONAL LABORATORY

a passion for discovery

 Office of
Science
U.S. DEPARTMENT OF ENERGY



Agenda

Part I:

- *Relevance and Applicability to Environmental Management*

Part II:

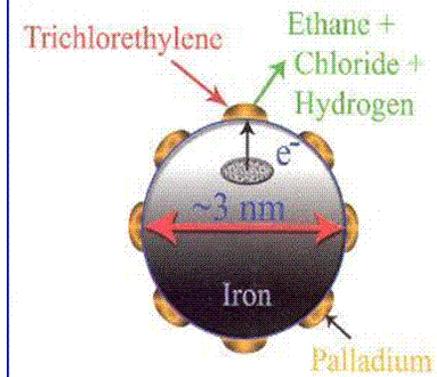
- *Risk Management & ISM*
- *Available Controls*

Part I:
Relevance and Applicability to
Environmental Management

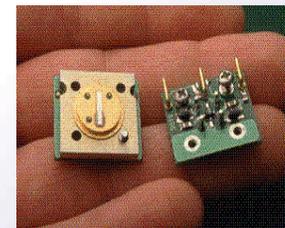
Lots of Positive Applications....

EPA Research – Remediation:

- Iron nanoparticles - soil and ground water remediation.
- Other research to remediate chlorinated solvents, lead, fuel, metals, etc...
 - Office of Solid Waste and Emergency Response (OSWER)



“Dog on a chip”



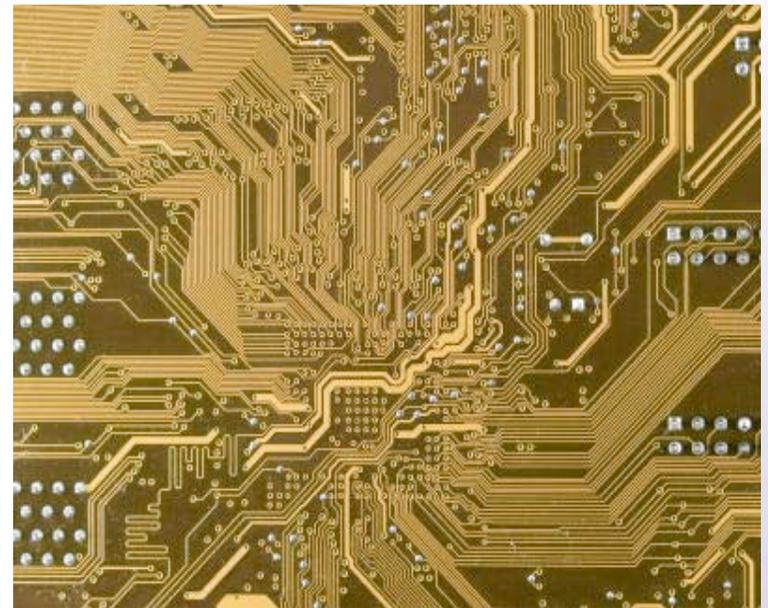
- Nano-sized sensors - improved detection and tracking of contaminants.
- Small sized, wide range, highly sensitive

Nanotechnology and Office of Solid Waste and Emergency Response (OSWER) Symposium, Oak Ridge Center for Advanced Studies, Nanotechnology Applications in Environmental Health: Big Plans for Little Particles, 5-31-07

Applications...

EPA's Office of Pollution Prevention and Toxics (OPPT)

- Pollution Prevention Act (PPA) of 1990.
 - 2007 Pollution Prevention Conference
<http://www.epa.gov/oppt/nano/agenda.htm>
 - Life cycle analysis
 - Green chemistry
 - Improved batteries and the all-electric car
 - Bottoms-up manufacturing



Products on the Market



- 610 products already on the market (disclaimer: based on manufacturer claims, not verified)

- Cosmetics
- Shampoos
- Sunscreens
- Drugs/Supplements
- Wound Dressing
- Tennis Rackets & Balls
- Cleaners
- Filtration
- Toys
- Food
- Tableware
- Batteries
- Paints...



Source: Project on Emerging Nanotechnologies (<http://www.nanotechproject.org/inventories/consumer/>)

Products on the Market

- 610 products already on the market (disclaimer: based on manufacturer claims, not verified)
 - Cosmetics
 - Shampoos



Disposal:

Where will the nano go???

- Toys
- Food
- Tableware
- Batteries
- Paints...



Source: Project on Emerging Nanotechnologies (<http://www.nanotechproject.org/inventories/consumer/>)

Questions Regarding Oversight



- **Public Concern: How well is the safety of new product formulations being evaluated?**
- **What effect can they have on the environment?**



New washing machine uses silver ions to destroy odors in clothes...

EPA – Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)



Colloidal silver washing machine causes waste water concerns...

- EPA acts under FIFRA.
 - Nanosilver is a pesticide
 - Not a nanotech ruling
 - Ruling has nothing to do with the size of the silver particle.
 - Issues 1st enforcement action: [EPA Fines Southern California Technology Company \\$208,000 for "Nano Coating" Pesticide Claims on Computer Peripherals](http://www.epa.gov/agriculture/lfraenf.html#socialnano)
<http://epa.gov/agriculture/lfraenf.html#socialnano>



Who's Concerned? Some examples...

Sierra Club

Green Peace

Natural Resources Defense Council

Environmental Defense Fund

ETC Group

Rachel Carson Council Inc.

Beyond Pesticides

Breast Cancer Fund

Center For Environmental Health

Clean Production Action

Environmental Health Fund

Ecology Center

Environmental Research Foundation

Science and Environmental Health Network

Science Corps

Accion Ecologica (Ecuador)

Agricultural Missions (U.S.)

African Centre for Biosafety

American Federation of Labor and Congress of Industrial Organizations (U.S.)

Bakery, Confectionery, Tobacco Workers and Grain Millers International Union

Beyond Pesticides (U.S.)

Biological Farmers of Australia

Canadian Environmental Law Association

Center for Biological Diversity (U.S.)

Center for Community Action and Environmental Justice (U.S.)

Center for Food Safety (U.S.)

Center for Environmental Health (U.S.)

Center for Genetics and Society (U.S.)

Center for the Study of Responsive Law (U.S.)

Clean Production Action (Canada)

Ecological Club Eremurus (Russia)

EcoNexus (United Kingdom)

Edmonds Institute (U.S.)

Essential Action (U.S.)

Forum for Biotechnology and Food Security (India)

Friends of the Earth Australia

Friends of the Earth Europe

Friends of the Earth United States

GeneEthics (Australia)

Health and Environment Alliance (Belgium)

India Institute for Critical Action-Centre in Movement

Institute for Agriculture and Trade Policy (U.S.)

Institute for Sustainable Development (Ethiopia)

International Center for Technology Assessment (U.S.)

International Society of Doctors for the Environment (Austria)

International Trade Union Confederation

International Union of Food, Agricultural, Hotel, Restaurant, Catering, Tobacco and Allied Workers' Associations

Loka Institute (U.S.)

National Toxics Network (Australia)

Public Employees for Environmental Responsibility (U.S.)

Science and Environmental Health Network (U.S.)

Silicon Valley Toxics Coalition (U.S.)

Tebtebba Foundation - Indigenous Peoples' International Centre for Policy Research and Education (Philippines)

The Soils Association (United Kingdom)

Third World Network (China)

United Steelworkers (U.S.)

Vivagora (France)

Sources: http://www.icta.org/press/release.cfm?news_id=26, SFGate.com, Nanotech material toxicity debated, More oversight being urged by environmentalists, 9-12-2005 (article archive)

Concern for DOE Labs

Why manage nano? – Protect yourself, Protect your work

Unknown
potential for
ecological
harm

+

Materials
already
entering the
environment

+

Vocal
public &
activists

=

- Future regulations and legal liabilities
- Potential loss of markets
- Potential loss of funding
- *It might be dangerous*



Michel Gangne/Agence France-Presse
— Getty Images

Part II:
Risk Management & ISM
Available Controls

Risk Management Approach

BNL – R&D, small user of nano

25 – 35 experiments, about 15 use free particulate

Atoms – micrograms / experiment

20 – 25 grams this year total



Precautionary approach - because the environmental, safety and health implications of nanomaterials are not well understood.

- Implement very conservative controls.
- Prevent release to the environment by containing the nanomaterials.

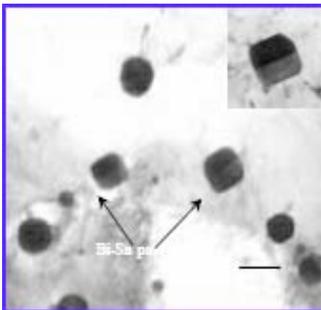
Apply the Graded Approach as much as possible based on what we do know.

Risk Identification - Hierarchy

LOWER RISK

HIGHER RISK

Solid materials with imbedded nanoparticles.



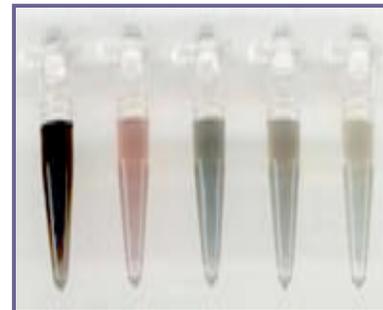
- Nanomaterials don't break free.
- Very low potential for contamination.

Solid nanomaterials with nanostructures fixed to the materials surface



- Nanomaterials can be dissolved into solution.

Nanoparticles suspended in liquids



- Capable of going down a drain.
- May evaporate.
- Contact contamination.

Dry, dispersible engineered nanoparticles, agglomerates, or aggregates



- Mobile/airborne.
- Highest contamination potential.

LOWER CONTROLS

HIGHER CONTROLS

Risk Management through Work Planning & Control

- ISM - Review all work
 - **Define Scope**
 - Identify work with nanomaterials
 - **Identify Risks**
 - Air Emissions
 - Sink discharge
 - Spills
 - Transportation
 - Waste management
 - **Develop & Implement Controls**
 - based on the NSRC “Working with Nanomaterials ES&H” document.
 - **Conduct Work within Controls**
 - **Collect Feedback & Make Improvements**



*Emission Controls – Section 3.3.2
Filter or otherwise “clean” exhaust
air.*

Air Emissions

Control of airborne engineered nanomaterials

High-Efficiency Particulate Air Filters (HEPA)
are the best available control technology.



**Bench-top HEPA-
filtered enclosure**

HEPA filtered hoods



- Typical HEPA filter rating is 99.99% efficient for particle dia = $0.3\mu\text{m}$ (300nm)
- Tests are being performed by entities such as NIOSH, 3M and Rice University show they are effective for smaller particles.



Evaluate the potential for worker exposure to nanomaterials and their escape into the environment before removing, remodeling, servicing, maintaining, or repairing laboratory equipment and exhaust systems.

Air Emissions, cont...



Glove Box



Glove Bag

Bubbler



Approach Doc, Sec 3.3.2: If it is not practicable to handle dispersible nanoparticles in such a containment system, conduct and document the results of a hazards analysis before using alternative hazard controls.

Air Emissions, cont...

Consider alternatives:

Chemical Vapor Deposition Unit (CVD)
(tube furnace for growing nanotubes)



- Comes with burner/scrubber for flammable gasses
- Operates @ 1560 – 1740 °F
- It will likely destroy nanotubes in exhaust, though it's not a manufacturer claim.

Carbon nanotubes will burn ~ 600-700 °C (1100 – 1290 °F)

Source: *Nanotubes in a Flash--Ignition and Reconstruction*, Science, 26 April 2002

Combustion products cleaned in scrubber
Water will be collected and analyzed.

Waste Management Controls

Waste Management

No engineered nanomaterials in the trash.



Or down the drain...



Waste Management

What's a nanomaterial waste?

- Nanomaterials themselves
- Things that contain nanomaterials
- Things contaminated with nanomaterials



0.05 μm blue colloidal silica polishing compound

-been around for a long time!

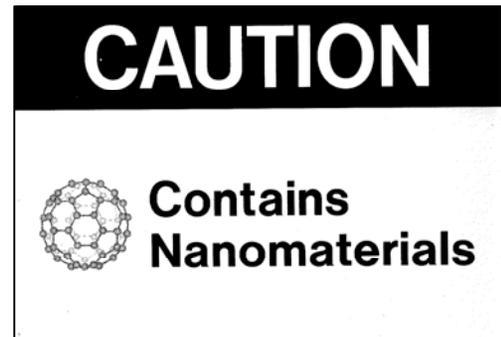


Approach Doc, Sec 3.3.2: The guidance does not apply to nanomaterials embedded in a solid matrix that cannot reasonably be expected to break free or leach out when they contact air or water.

Waste Management, cont...

- Management of solid & liquid waste containing engineered nanomaterials:
 - Accumulate waste in controlled area,
 - Double containers, sealed,
 - Wet-down or encapsulate dispersible material,
 - Label to identify the presence of engineered nanomaterials.
 - Manage the waste through the Waste Management group.

- Classification of waste containing engineered nanomaterials:
 - May be hazardous per EPA Definition: Corrosive, Ignitable, Toxic or Reactive
 - TCLP – will mass really remain a viable method to determine toxicity?
 - May be nonhazardous in that it does not meet the EPA definition of hazardous.



Waste Management, cont...



- **Section 6.3:** “Send otherwise non-hazardous nanomaterial-bearing waste to an RCRA-permitted treatment, storage and disposal facility (TSD). Direct the TSD as to the selected treatment method best suited to controlling hazards associated with the waste.”

- The intent was to encourage Waste Management (RCRA) professionals to think about what treatment technologies best limited potential nano-related hazards.
- Options to consider:
 - Landfill (hazardous waste)
 - Encapsulate and landfill
 - Incineration
 - Others?

Waste Management, cont...

- All waste from BNL that contains engineered nanomaterials goes to a EPA permitted hazardous waste incinerator
 - Incinerated ~ 1090 °C (2000 °F)
 - Air emissions are scrubbed
 - All ash disposed in a hazardous waste landfill
 - Double-lined to prevent leaching.

*Controls For:
Housekeeping
Spills
Transportation*

Housekeeping & Spills

Housekeeping

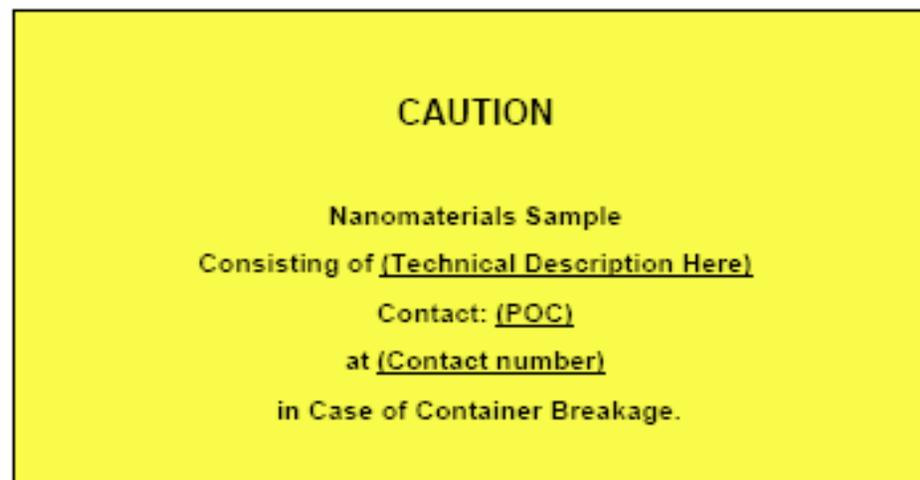
- Wet-wiping and HEPA vacuuming of surfaces.
- Collection of cleaning materials as nano waste.

Spills

- Liquid or solid, procedure similar
 - Move people away & contact qualified responder.
 - Have Emergency Response people been trained?
 - Place barriers that will minimize air currents across the spill surface
 - Sticky pad at exit
 - Wet-wipe or dedicated HEPA Vacuum
 - Treat all material generated during spill clean-up as nano waste.

Transportation

- Descriptions of the materials (MSDS or other information)
- Notifications to receiver of incoming shipment
- Recommend using hazmat shipper, but not required.
- Packaging:
 - Inner container - double sealed
 - Outer container - contain shock-absorbing material that can absorb any leak/spill.



Other Issues to Consider:

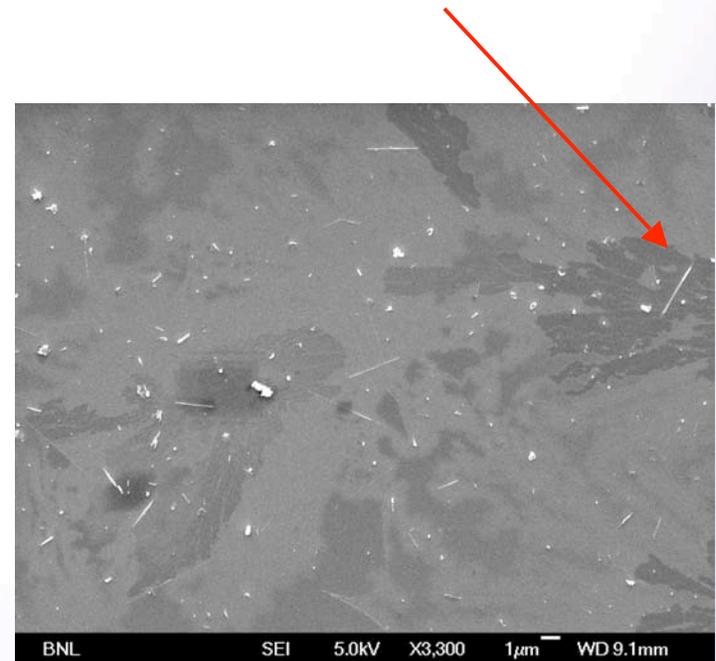
- How can we ensure the exterior of waste packages are clean?
- Are your non-scientific staff, like Waste Management and maintenance personnel, implementing the Approach Document?
 - WM folks may open waste packages
- Medical nanowaste and sharps
- Radioactive nanowaste management
- Management of commercial products
 - Paints?
 - Cleaners?
 - Any variety of things with silver ions (bandaids to tabletops to clothing)?

Summary

- Nano is here and the public is waking up to it.
- Best way to avoid controversy about the impact to the environment is to keep it from getting into the environment in the first place – hence the controls in the approach document.
- Make sure more than just the nano-scientists are aware – look at support staff as well.
- Consider the implications regarding products being brought in to the Lab.
- Exploit the positive side of the field – look at implementing green chemistry techniques! Water treatment! Clean up! Assign an “e” person to cook up possibilities!

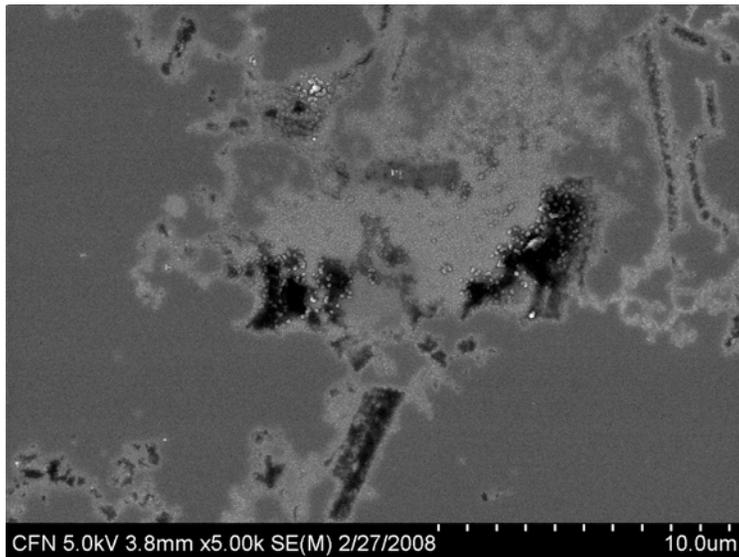
SEM of water drops

- Method:
 - two samples: CVD scrubber water; one tap water
 - drop of water onto silicon piece. Air dry.
 - SEM imaging at 5kV in Hitachi 6800
 - checked multiple areas on CVD sample.
- Water leaves trail of “debris” where it dries, making it easy to find where the contents of the water have been deposited on the substrate
- Carbon nanotubes (CNT's) are usually easy to find – appear as high-contrast strings or needles on the substrate
- Results: both samples looked identical in the SEM
 - No CNT's could be seen.

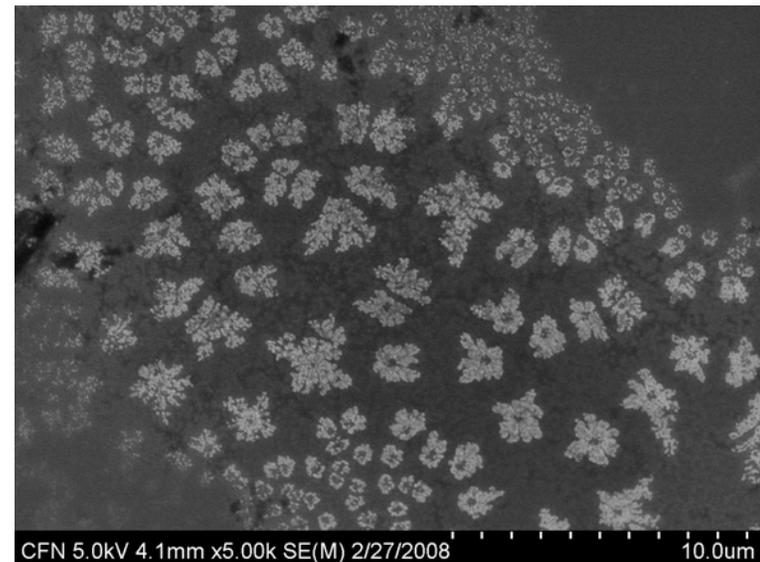


This is not a verified methodology, and no claims are made as to its accuracy.

Results



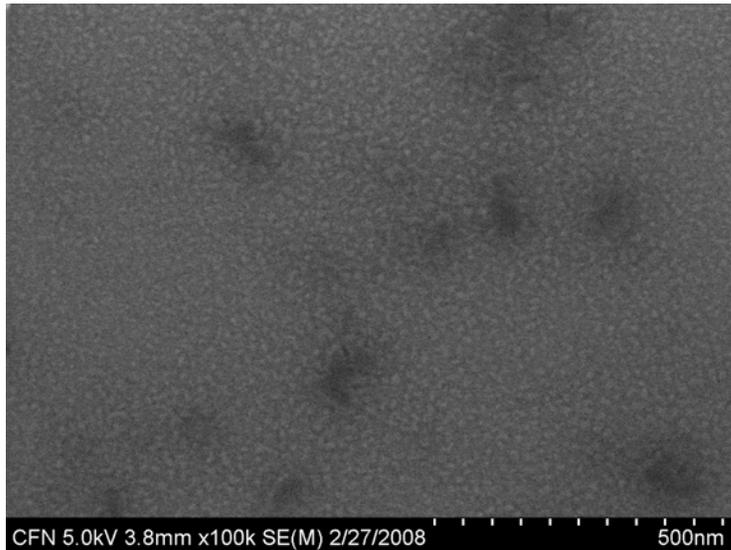
CVD water



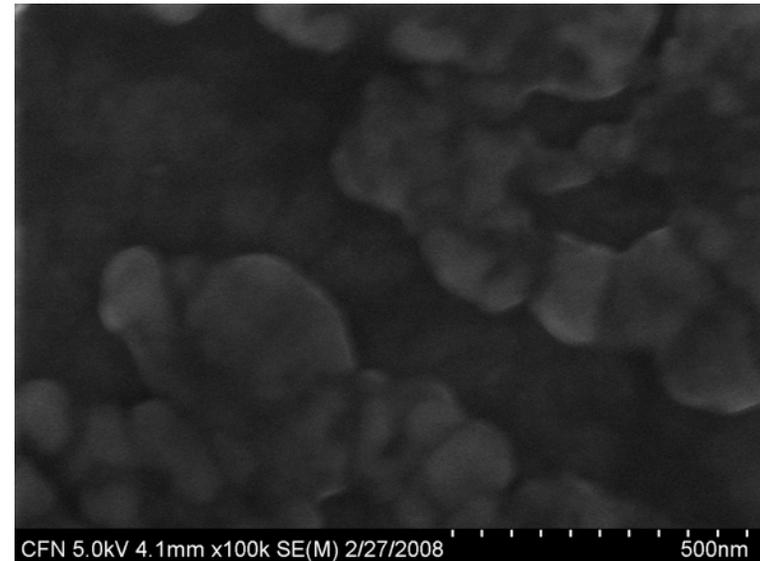
Tap water

This is not a verified methodology, and no claims are made as to its accuracy.

Results



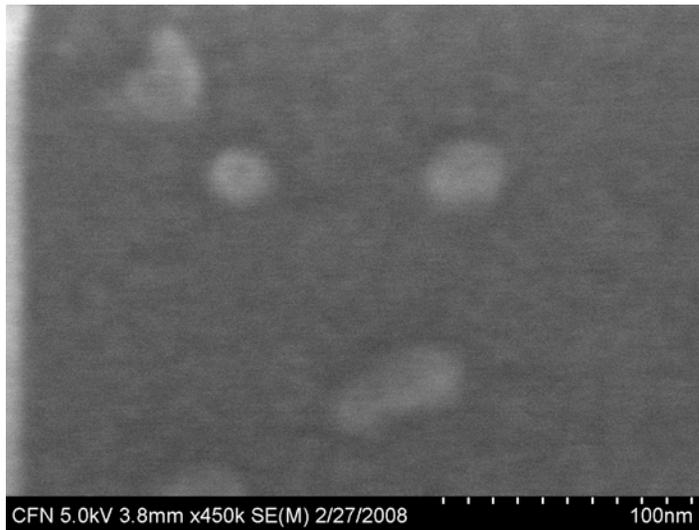
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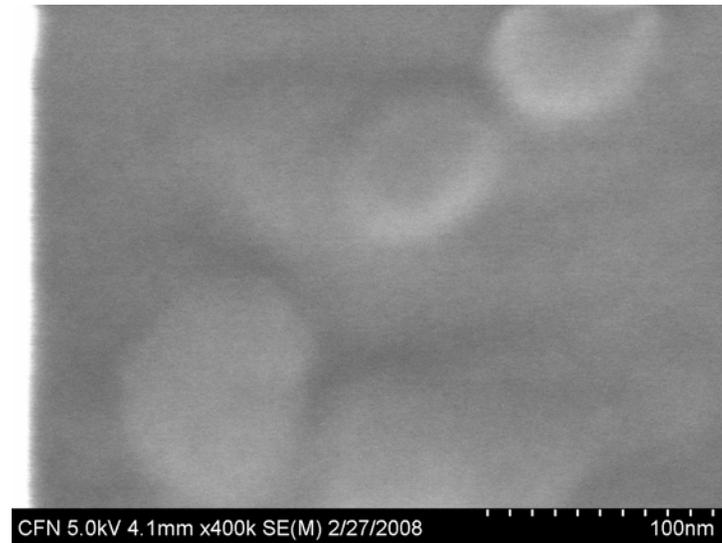
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Results



CVD water



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