SNNI — SAFER NANOMATERIALS AND NANOMANUFACTURING INITIATIVE | ONAMI — OREGON NANOSCIENCE AND MICROTECHNOLOGIES INSTITUTE

Toward Greener Production of Nanomaterials: Lessons from Functionalized Nanoparticle Synthesis

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Green nanoscience

Greener:
- Synthesis
- Purification
- Fabrication of structures

Nanotechnology promises exciting breakthroughs for a thriving, sustainable future

A clean, sustainable world for all future generations

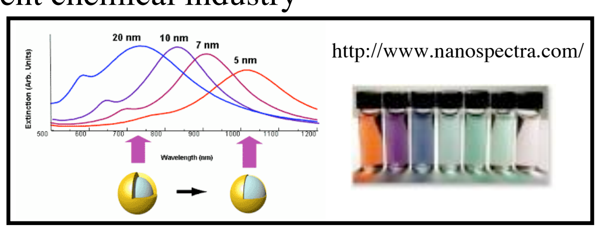
Abundant clean energy from the sun

Drinkable water for everyone around the world

Rapid, point-of-care medical diagnostics and treatment

Phototherapeutics - A cure for cancer by 2020?

Cleaner, more efficient chemical industry



Possible health and environmental effects of new materials and products?

Applies to all materials…nano or otherwise!

Do the properties contribute to:

- Toxicity?
- Ecotoxicity?
- Persistence?
- Transport?
- Bioavailability?
- Bioaccumulation?

***Design* for performance and safety**

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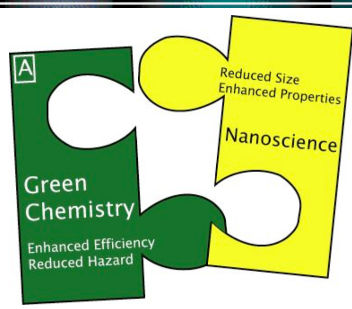
Applying green chemistry to nanomaterials and nanomanufacturing



Higher performance
Cheaper
More convenient
Greener

Green chemistry applied to nanoscience:

- **Design** nanomaterials that provide new properties and performance, but do not pose harm to human health or the environment
- **Manufacture** complex nanomaterials efficiently, without using hazardous substances
- **Assemble/interface** nanomaterials using bottom-up approaches and self-assembly to enhance performance and reduce waste

McKenzie and Hutchison "Green nanoscience," *Chemistry Today,* **2004**, 30.

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Need for greener approaches in the *production* of nanoscale products

The 1.7 Kilogram Microchip: Energy and Material Use in the Production of Semiconductor Devices

ERIC D. WILLIAMS,*,† ROBERT U. AYRES,‡ AND MIRIAM HELLER§

United Nations University, 53-67 Jingumae 5-chome, Shibuya-ku, Tokyo, Japan, INSEAD, Boulevard de Constance, Fontainebleau, 77305 Cedex, France, and National Science Foundation, 4201 Wilson Boulevard, Arlington, Virginia 22230

For a 2-g DRAM chip:

Chemical input ~72g
Energy (fossil fuels)
~1,600 - 2,300 g
Water ~ 20,000 g
Gases ~ 500 g

Environ. Sci. Technol. **2002**, *36*, 5504−5510

Bottom-up manufacturing has potential to improve materials efficiency, however…

"Discovery scale" production of nanoparticle building blocks
- Low yields
- Toxic reagents
- Inefficient functionalization
- Wasteful purification

New ideas are needed to transition from discovery to market

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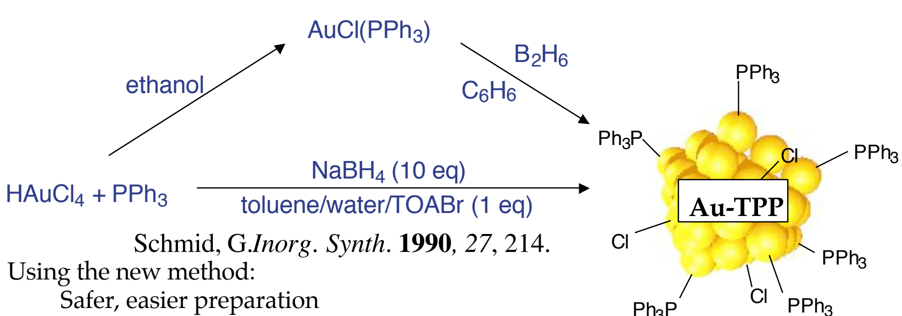
Example 1: A greener synthesis of a key nanoparticle building block



Schmid, G. *Inorg. Synth.* **1990**, *27*, 214.

Narrow dispersity (d = 1.5 +/- 0.4 nm)

Using the new method:
- Safer, easier preparation
- Eliminates >600 cu. ft. of diborane/pound of NPs and 1,100 pounds of benzene /pound of NPs
- Rapid synthesis of gram quantities
- Cheaper (~ $500/g vs. "$300,000/g")

Weare, Reed, Warner, Hutchison *J. Am. Chem. Soc.* **2000**, *122*, 12890.
Hutchison, et al. *Inorg. Syn.* **2004**, *34*, 228.

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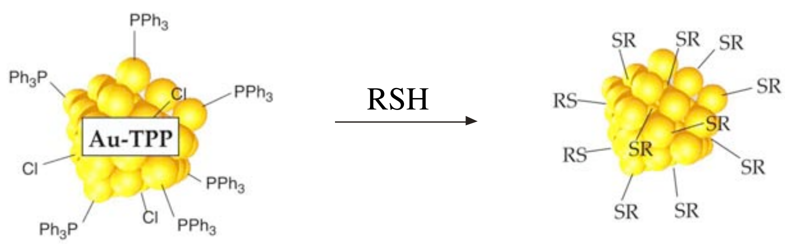
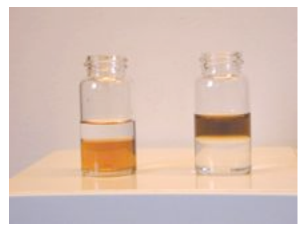
Functionalized nanoparticles prepared by *efficient* ligand exchange reactions



d_{CORE} = 0.8 or 1.5 nm



Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 12384

Woehrle, G. H.; Warner, M.G.; Hutchison, J.E. *J. Phys. Chem. B* **2002**, *106*, 9979

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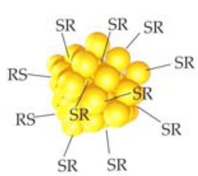
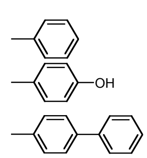
A diverse family of functionalized nanoparticles has been prepared for 1.5-nm (and 0.8-nm) core sizes



R =

Organic

- $-(CH_2)_{17}CH_3$
- $-(CH_2)_{15}CH_3$
- $-(CH_2)_{11}CH_3$
- $-(CH_2)_9CH_3$
- $-(CH_2)_8CH_3$
- $-(CH_2)_7CH_3$
- $-(CH_2)_5CH_3$
- $-(CH_2)_2CH_3$
- $-(CH_2)_2Si(OMe)_3$



Aqueous

- $-(CH_2)_2SO_3^-Na^+$
- $-(CH_2)_3SO_3^-Na^+$
- $-(CH_2)_2N^+HMe_2Cl^-$
- $-(CH_2)_2N^+Me_3Cl^-$
- $-(CH_2)_2O(CH_2)_2N^+Me_3{}^-OTs$
- $-(CH_2)_2O(CH_2)_2O(CH_2)_2N^+Me_3{}^-OTs$
- $-(CH_2)_2O(CH_2)_2O(CH_2)_2N^+Et_3{}^-OTs$

- $-CH_2COO^-Na^+$
- $-(CH_2)_2COOH$
- $-(CH_2)_{11}COOH$
- $-(CH_2)_2OH$
- $-(CH_2)_2PO(OH)_2$
- $-[(CH_2)_2O]_2(CH_2)_2OH$
- $-(CH_2)_2O(CH_2)_2OH$
- $-[(CH_2)_2O]_2CH_2COOH$
- -(CH2)2COGlyGlyOH
- $-(CH_2)_2CONH(CH_2)_{14}CH_3$

Solubility   Interparticle spacing   Functionality

J. Am. Chem. Soc. **2005**, *127*, 2172 and *Inorg. Chem.* **2005**, *44*, 6149

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Progress and challenges in nanoparticle production

At "discovery" scale we can:

- Control core size and dispersity
- Adjust core and ligand shell composition/functionality
- Use efficient syntheses and ligand exchange methods to produce milligram to gram quantities

Substantial challenges exist regarding:

- Purification
  - Obtaining pure material
  - Reducing solvent use
- Larger scale production

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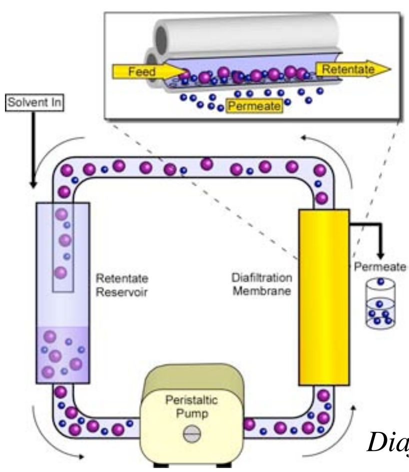
Example 2: Greener purification of functionalized nanoparticles



Nanomaterials purification

Traditional:
- 15L solvent per gram NP
- 3 days work

Diafiltration:
- No organic solvent
  - (eliminates > 10,000 pounds/pound NPs)
- 15 minutes work

*Diafiltration reduces solvent consumption and provides **cleaner, well-defined building blocks***

Sweeney, Woehrle, Hutchison
J. Am. Chem. Soc. ***2006****, 128*, 3190.

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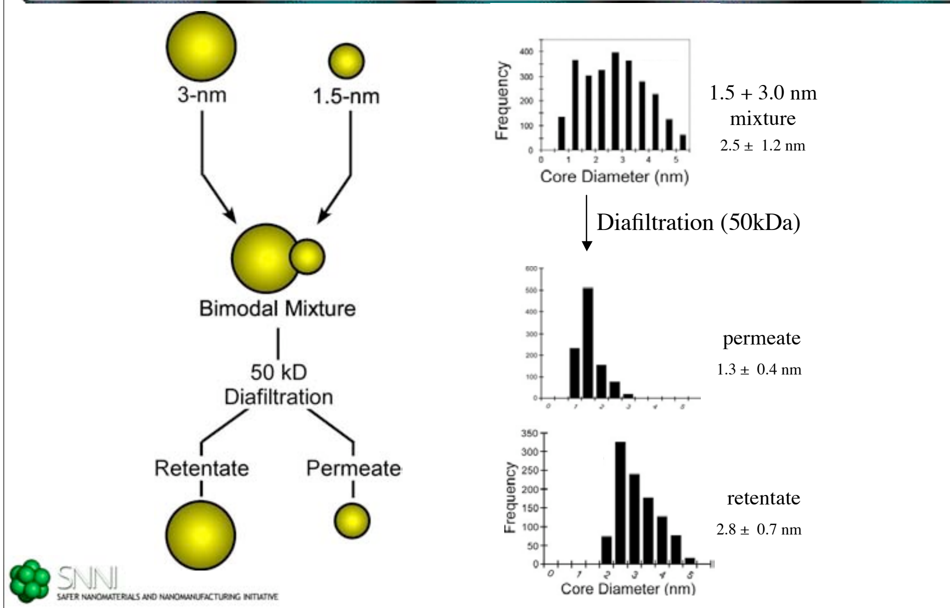
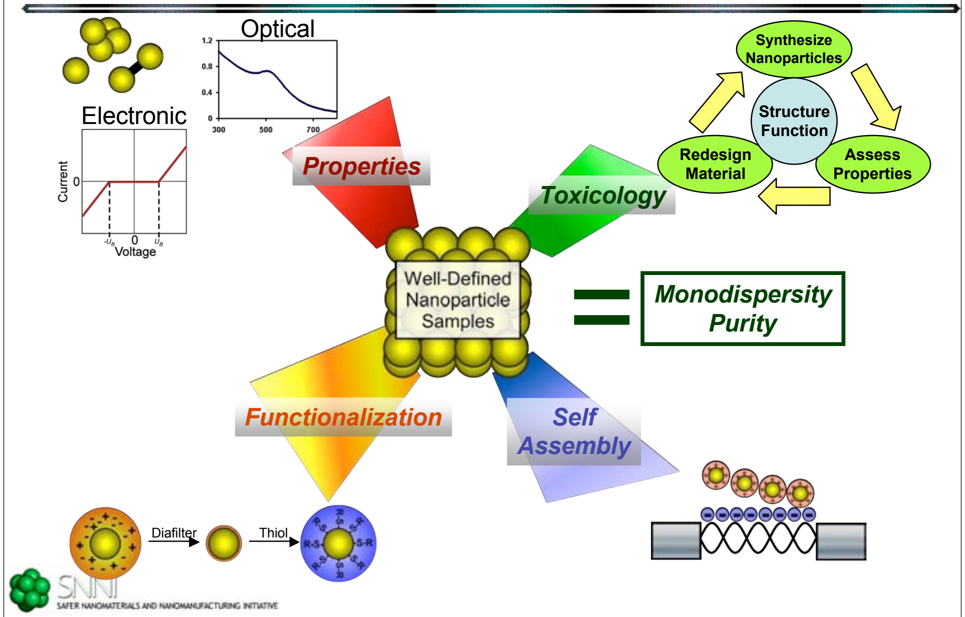
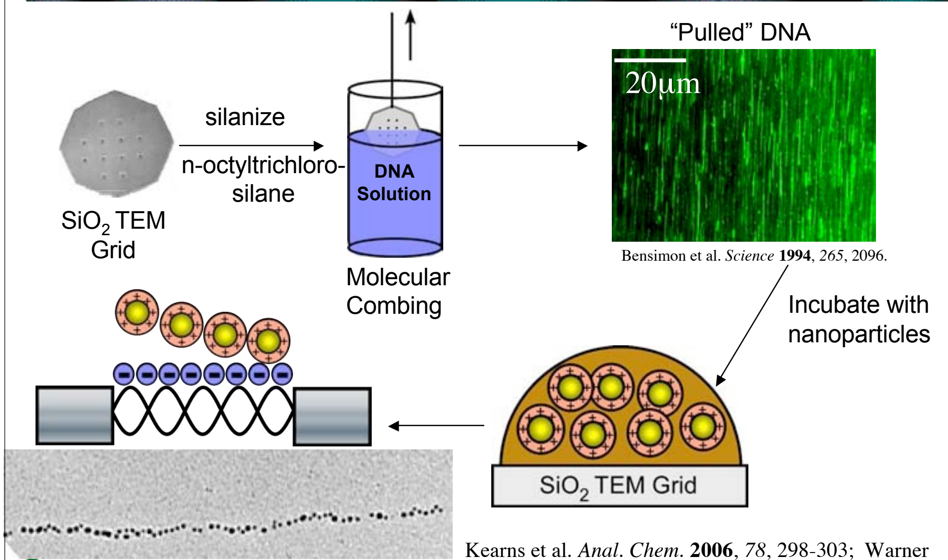
Nanoparticle size selection using diafiltration



Where has purity influenced performance?

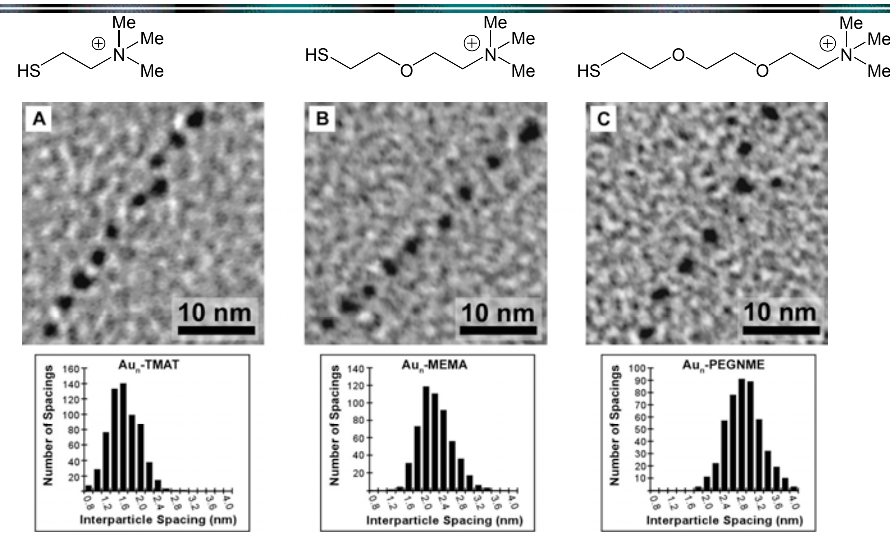


Example 3: Biomolecular Nanolithography



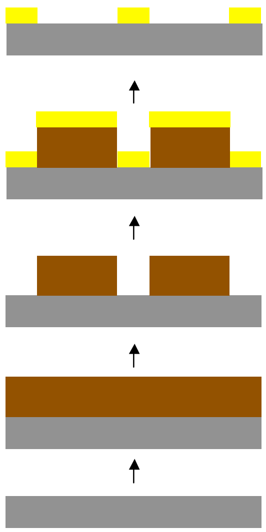
Kearns et al. *Anal. Chem.* **2006**, *78*, 298-303; Warner et al. *Nature Mater.*, **2003**, *2*, 272-277.

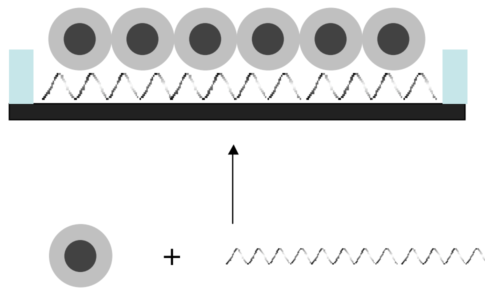
Controlling interparticle spacing along the DNA scaffold



Woehrle, Warner, Hutchison, *Langmuir*. **2004,** *20*, 5982

Assembling from the bottom up offers green chemistry advantages





Eliminates processing steps

Incorporates more raw materials in product

Reduces water and solvent use

Provides access to smaller structures

Greener - Higher performance - Cheaper - More convenient

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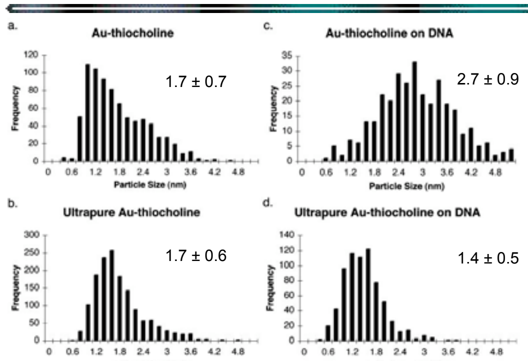
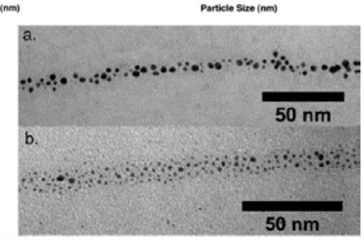
Nanoparticle purity has a strong influence on self- assembly chemistry





"Ultrapure" nanoparticles retain original core size.

Important for retaining desirable electronic properties.

Kearns, G.J.; Foster, E.W.; Hutchison J. E. *Anal. Chem.* **2006**, *78*, 298-303.

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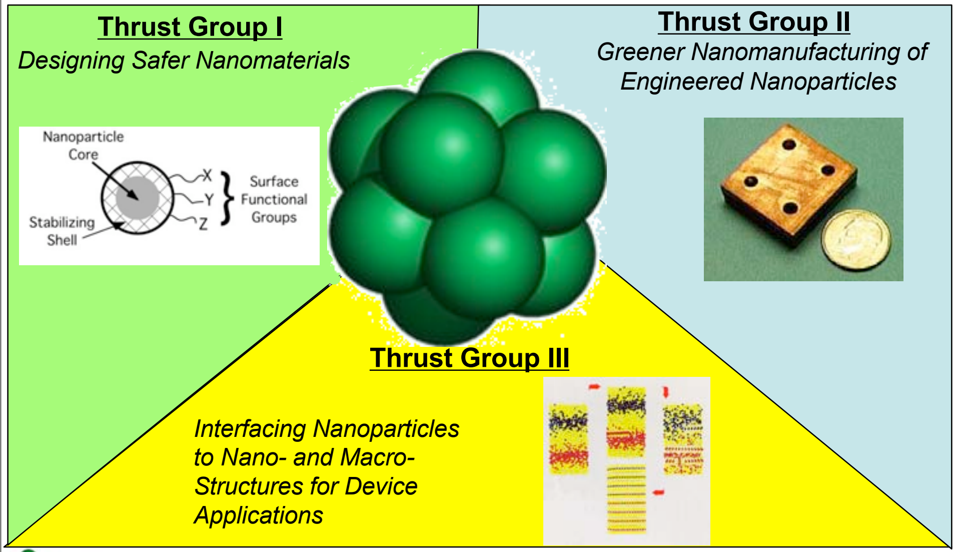
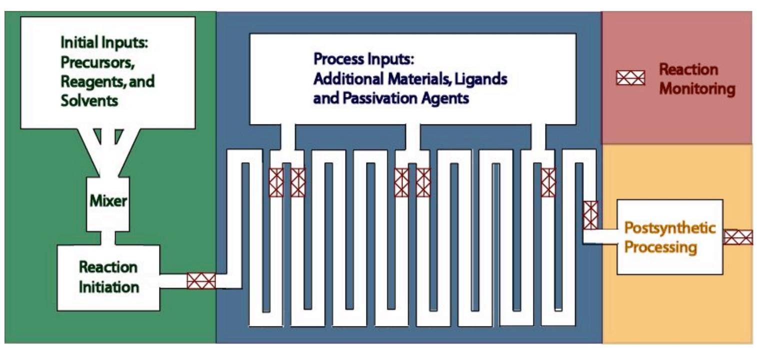
ONAMI SNNI Research Thrust Groups

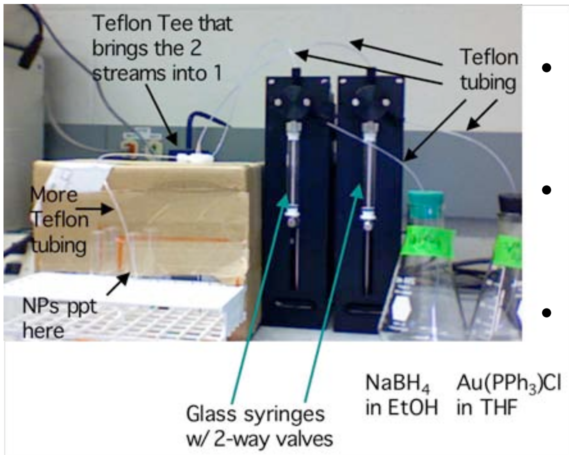


Nanoparticle production in integrated microreactor systems



- Rapid mixing
- Precise process control
- In situ monitoring
- Facile scale-up
- Reduced waste
- Improved yields
- New precursors and approaches
- Point-of-use production

Microcapillary system for continuous production of NPs



- Continuous flow system for $Au_{11}(PPh_3)_8Cl_3$ synthesis
- At least 10-fold increase in production rate (g/hour)
- At least five-fold decrease in solvent waste

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Lessons for greener production of nanoparticles

- Green chemistry applies readily to nanosynthesis
  - Identifying alternative reagents and solvents to reduce hazard
  - Eliminating or reducing solvent use through nanofiltration techniques
  - Harnessing self-assembly methods that enhance material efficiency
- Examples highlight how greener approaches can lead to enhanced performance and lower cost
- Nanoparticle purity impacts a wide range of material properties
- Green nanoscience provides opportunities to:
  - Bring new, beneficial technologies to society
  - Protect the human health and the environment
  - Reduce barriers to commercialization
  - Spur innovation

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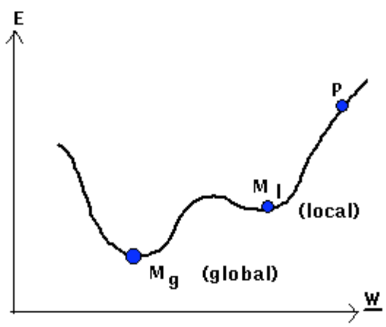
Green chemistry - A *driver* for innovation?



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