Environmentally-benign nanomanufacturing: Merging green chemistry and nanoscience

Green chemistry <----> Nanoscience

Nanoscale products
Production of complex nanomaterials
Greener applications of nanomaterials

Green Chemistry
At the University of Oregon

ONAMI
OREGON NANOSCIENCE AND MICROTECHNOLOGIES INSTITUTE

Nanoscience is expect to provide many benefits to society

Current technologies

Microelectronics

Catalysis

Future technologies - The next industrial revolution

Space Exploration

Environment

Defense

Building Materials

Medicine

Transportation

Electronics

New properties found at the nanoscale will make these innovations possible

Growing concerns about nanotechnology stem from new, unknown properties

Will the **products** of nanotechnology….
…be harmful to human health?
…pose risks to the environment?

Will the **manufacture** of these products generate new hazardous (toxic) wastestreams?

July 2004: *Nanoscience and nanotechnologies: opportunities and uncertainties* (RSC report)

The case is being made that untested nanomaterials are being forced on the public

Lessons from GMOs - public acceptance as a barrier to commercialization

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

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The scale of environmental impacts associated with the manufacture of microchips is characterized through analysis of material and energy inputs into processes in the production chain. The total weight of secondary fossil fuel and chemical inputs to produce and use a single 2-gram 32MB DRAM chip are estimated at 1600 g and 72 g, respectively. Use of water and elemental gases (mainly N_2) in the fabrication stage are 32 000 and 700 g per chip, respectively. The production chain yielding silicon wafers from quartz uses 160 times the energy required for typical silicon, indicating that purification to semiconductor grade materials is energy intensive. Due to its extremely low-entropy, organized structure, the materials intensity of a microchip is orders of magnitude higher than that of "traditional" goods. Future analysis of semiconductor and other low entropy high-tech goods needs to include the use of secondary materials, especially for purification.

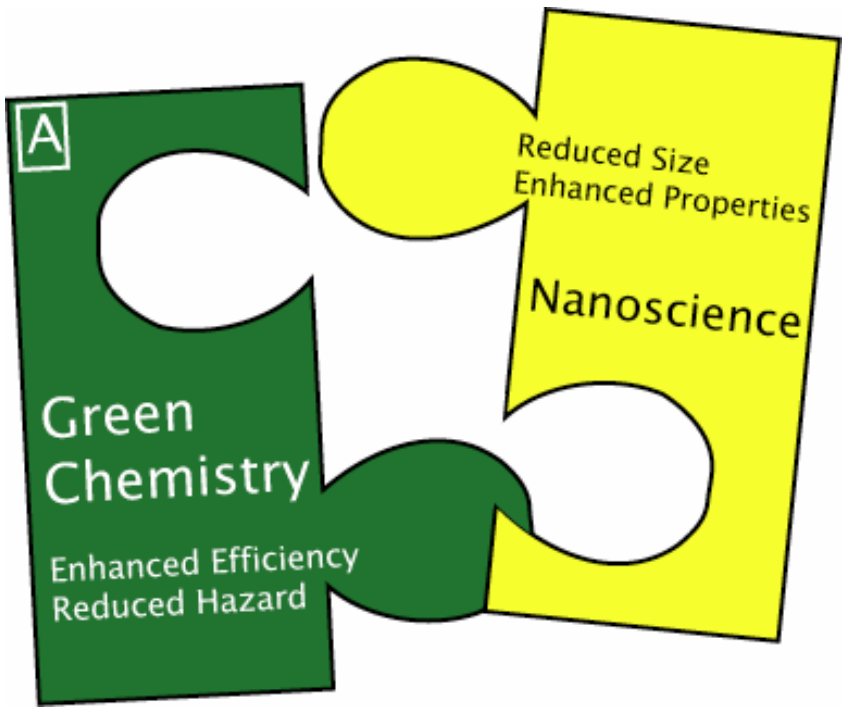
Environ. Sci. Technol. **2002**, *36*, 5504−5510

Selected principles of green chemistry

1. Incorporate all raw materials into products
2. Avoid hazardous reagents
3. Design safer products
4. Minimize solvent use
5. Increase energy efficiency
6. Omit needless steps
7. Use catalytic reagents
8. Design for end-of-life

Reduce hazards - Enhance efficiency

Application of green chemistry to nanoscience



Product

Process

Applications

McKenzie, L.C; Hutchison, J.E. “Green nanoscience,” *Chemistry Today*, **2004**, 30-33.

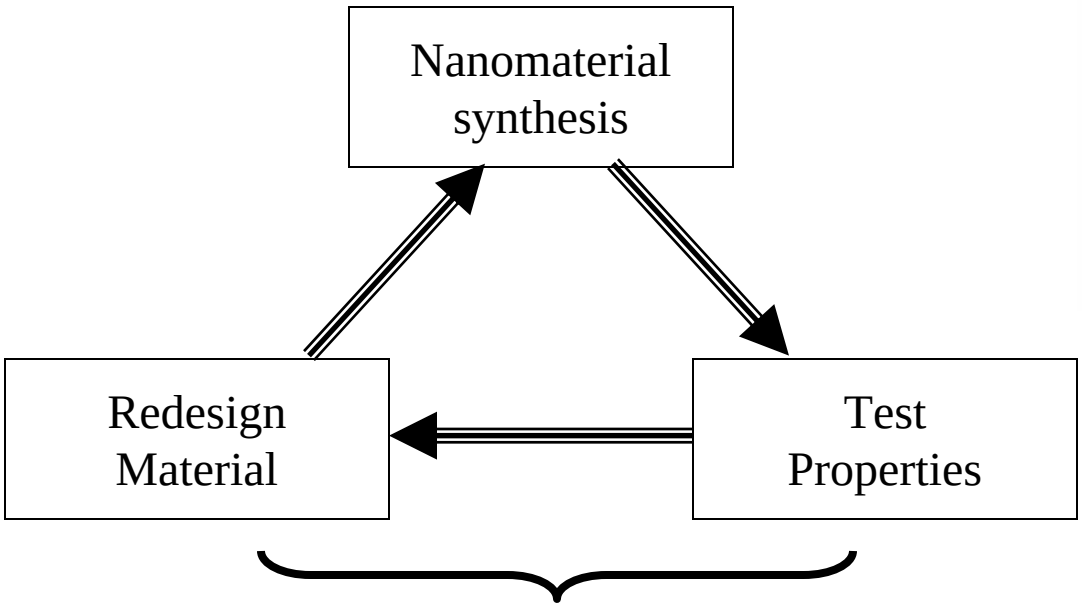
Importance of green chemistry in *product* design for nanotechnology

In order to improve human health and safety and sustainability

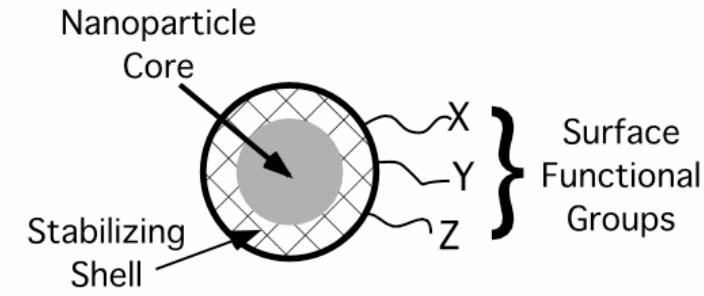
- Need to know health/biological impacts
  - Medical (pharmaceutical agents, devices)
  - Cosmetics (sunscreens, etc)
  - Water purification
- Need to know environmental impacts
  - Nanoparticles for remediation of toxics in the environment
  - Fertilizers and soil stabilizers
  - Distributed nanosensor arrays

Need to learn how to design nanomaterials that have the properties that we desire AND are designed to be safe for the environment and human health

Designing safer nanoparticles



Structure/Property Relationships



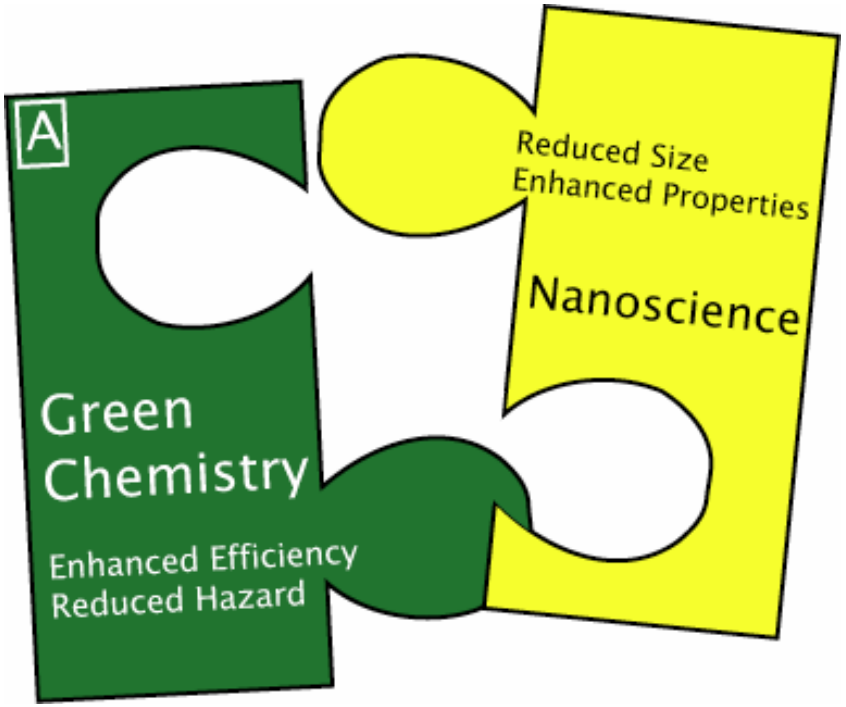
Many groups are now actively investigating the biological impacts of nanoparticles and other nanoscale materials

What about greener processes for manufacturing nanomaterials?

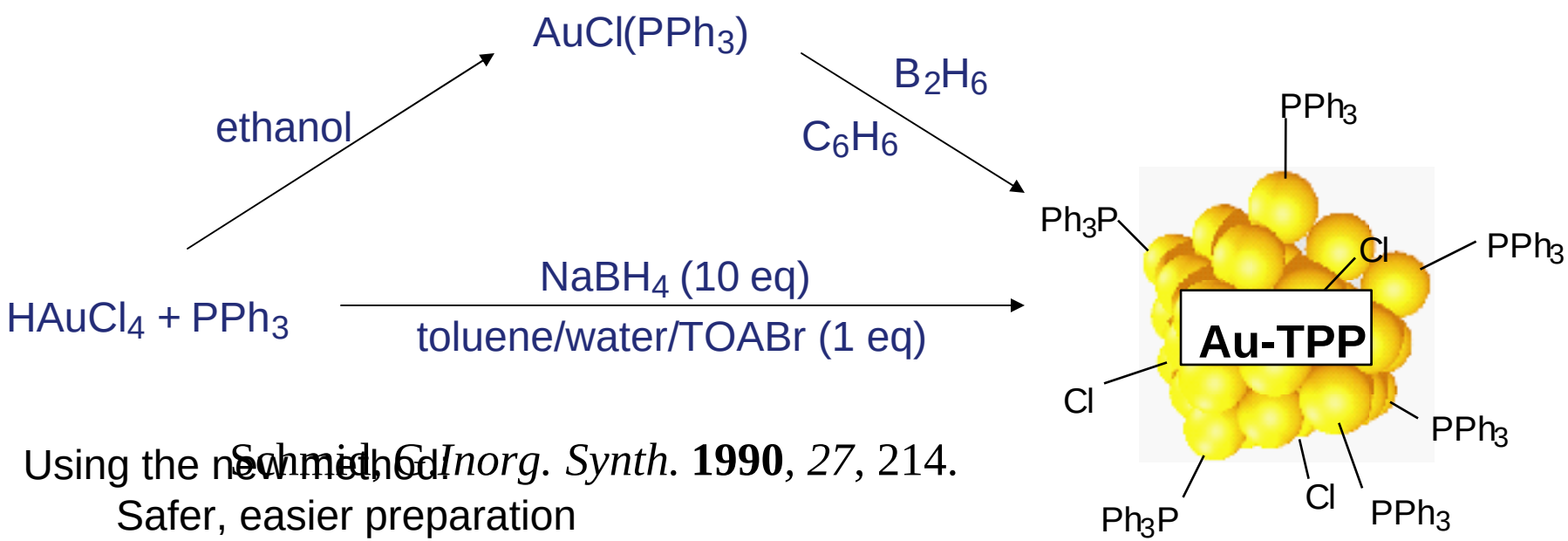
Product

Process

Applications



A greener synthesis of a nanoparticle building block: Triphenylphosphine-stabilized nanoparticles



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

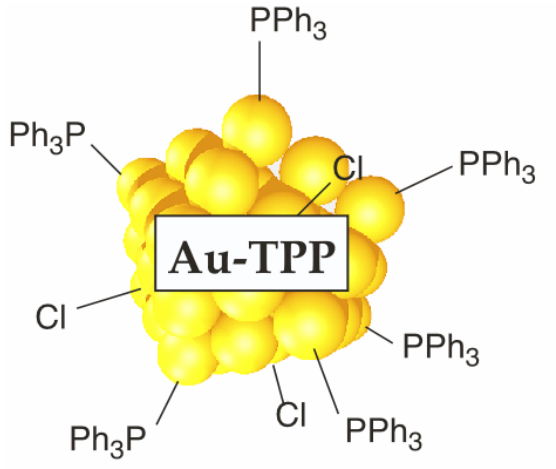
Schmid, G. *Inorg. Synth.* **1990**, *27*, 214.

Using the new method:

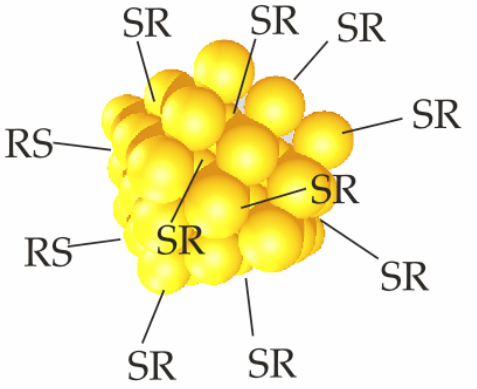
- Safer, easier preparation
- Rapid synthesis of gram quantities
- Faster, more effective purification
- Cheaper (~ $500/g vs. "$300,000/g")

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

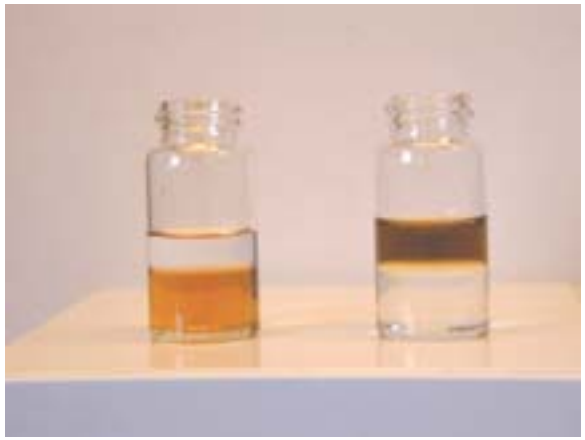
Functionalized nanoparticles prepared by ligand exchange reactions



RSH →



d_{CORE} = 0.8 or 1.5 nm

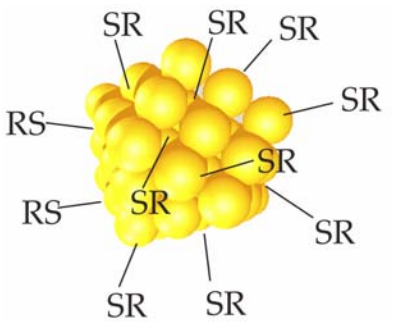


Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 12384

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

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

R =



$-(CH_2)_{17}CH_3$

$-(CH_2)_{15}CH_3$

$-(CH_2)_{11}CH_3$

$-(CH_2)_9CH_3$

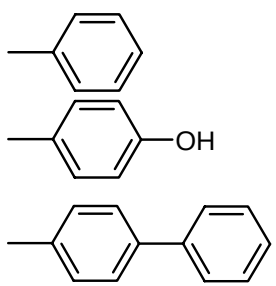
$-(CH_2)_8CH_3$

$-(CH_2)_7CH_3$

$-(CH_2)_5CH_3$

$-(CH_2)_2CH_3$

$-(CH_2)_2Si(OMe)_3$



$-(CH_2)_2SO_3^-Na^+$

$-(CH_2)_3SO_3^-Na^+$

$-(CH_2)_2N^+HMe_2Cl^-$

$-(CH_2)_2N^+Me_3Cl^-$

$-(CH_2)_2O(CH_2)_2N^+Me_3^-OTs$

$-(CH_2)_2O(CH_2)_2O(CH_2)_2N^+Me_3^-OTs$

$-(CH_2)_2O(CH_2)_2O(CH_2)_2N^+Et_3^-OTs$

$-CH_2COO^-Na^+$

$-(CH_2)_2COOH$

$-(CH_2)_{11}COOH$

$-(CH_2)_2OH$

$-(CH_2)_2PO(OH)_2$

$-[(CH_2)_2O]_2(CH_2)_2OH$

$-(CH_2)_2O(CH_2)_2OH$

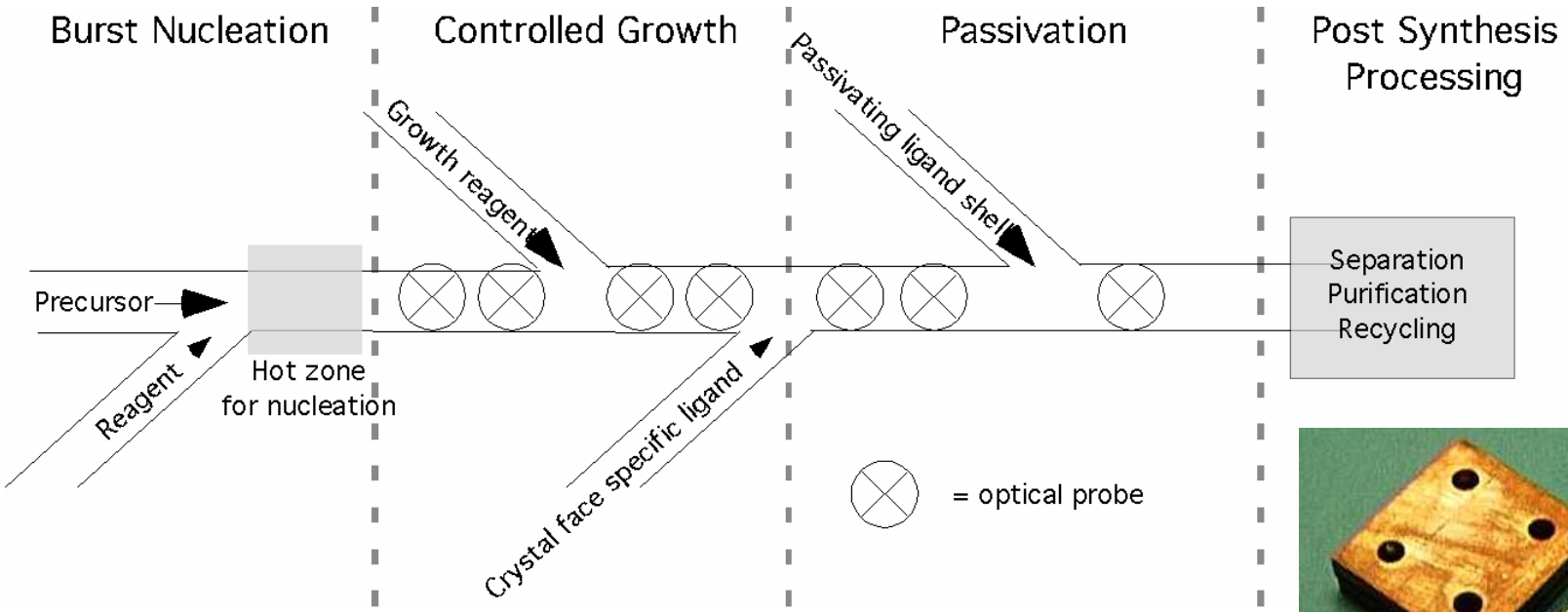
$-[(CH_2)_2O]_2CH_2COOH$

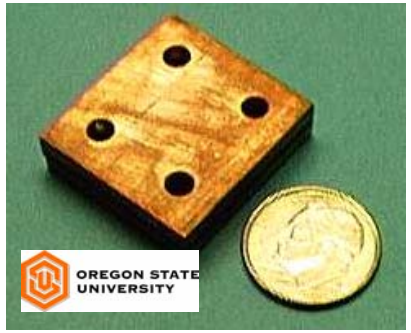
-(CH2)2COGlyGlyOH

$-(CH_2)_2CONH(CH_2)_{14}CH_3$

Solubility Interparticle spacing Functionality

Greener nanomanufacturing in microreactors





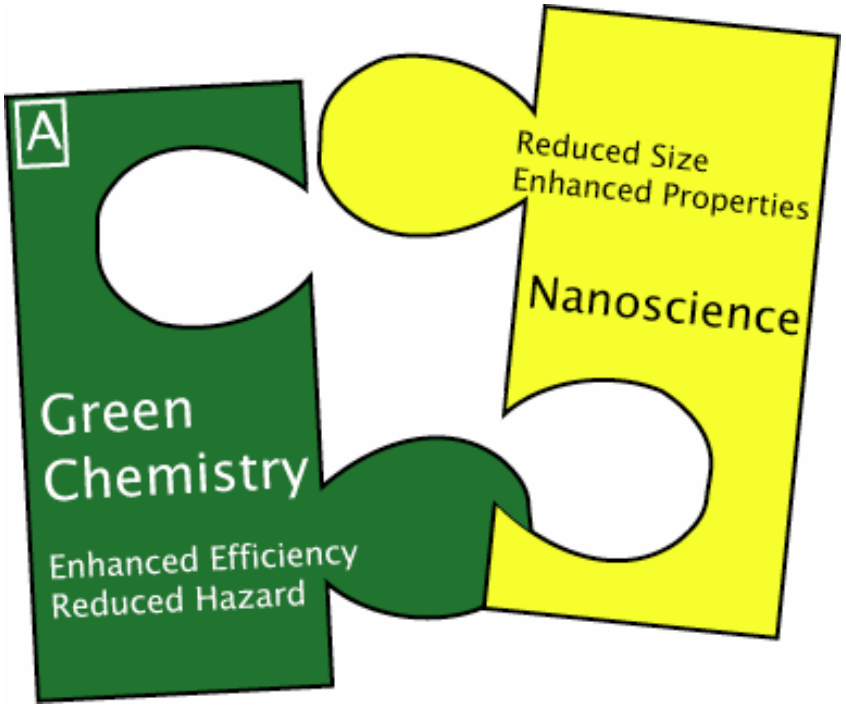
Rapid mixing, temporal separation of reaction steps, enhanced process control, on-board post synthesis processing, rapid, reliable scale-up

Greener processes for manufacturing using the tools of nanoscience

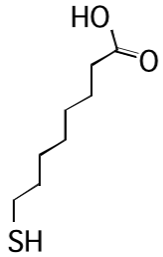
Product

Process

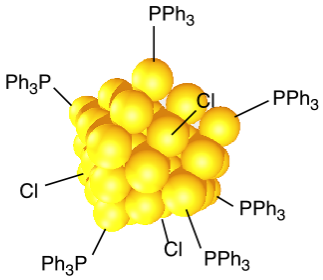
Applications



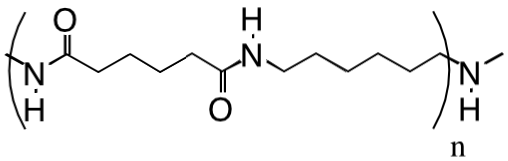
Self-assembly: An important tool in green nanoscience



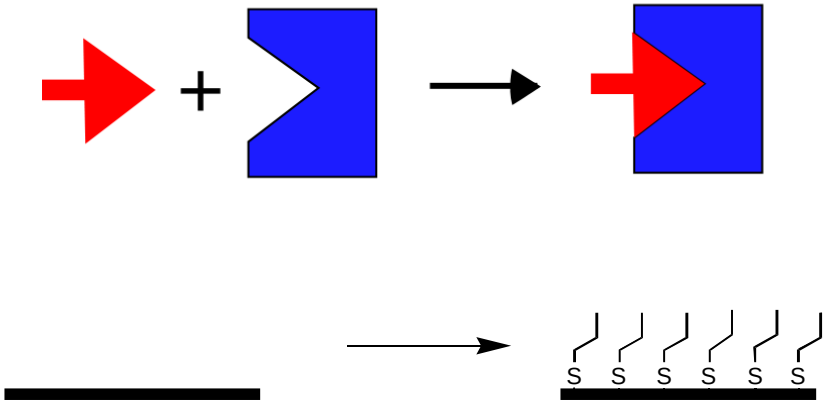
molecule



cluster or nanoparticle



polymer



Alkanethiols on gold

Hot dog slices on water

Nanoscale manufacturing from the top-down and bottom-up

top-down

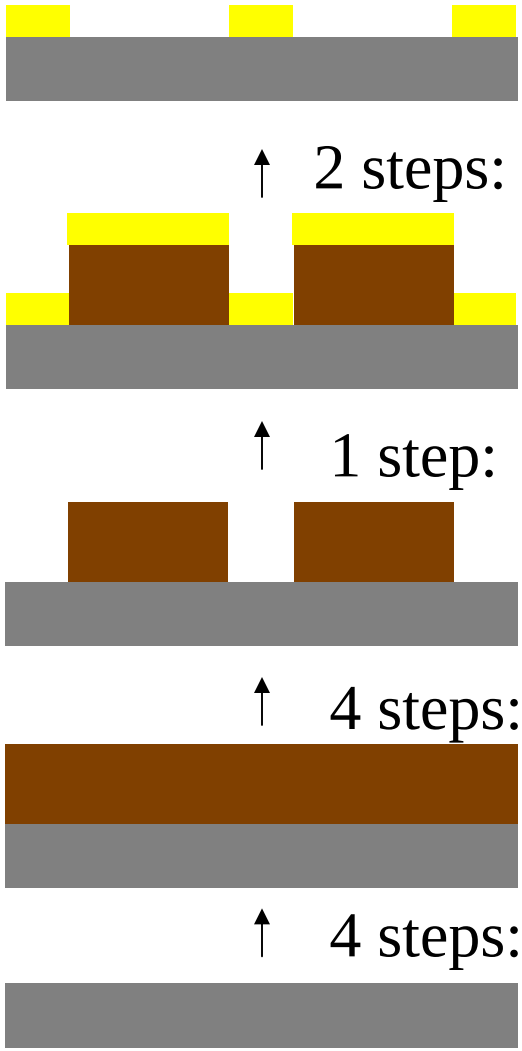
Franklin

bottom-up

The Tick

Bottom-up manufacturing leads to greener processes - “Dematerialization”

Patterning small metal features on a wafer through lithography - a top-down approach



↑ 2 steps: Remove PR w/ solvent, clean

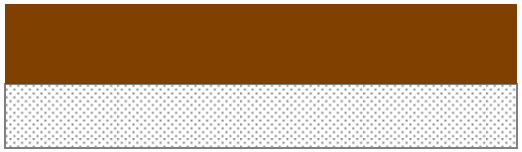
↑ 1 step: Metallize

↑ 4 steps: Soft bake, expose, develop, plasma etch

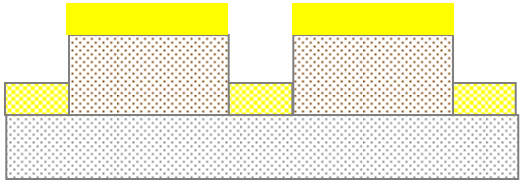
↑ 4 steps: Clean, dehydrate, silanize, apply photoresist

At least 11 steps needed to "protect" wafer surface and deposit metal - material efficiency is low

Wasted materials and processing aids during lithographic patterning of metal features



Photoresist



Metal

Silane

Organic Solvents

Developer (caustic)

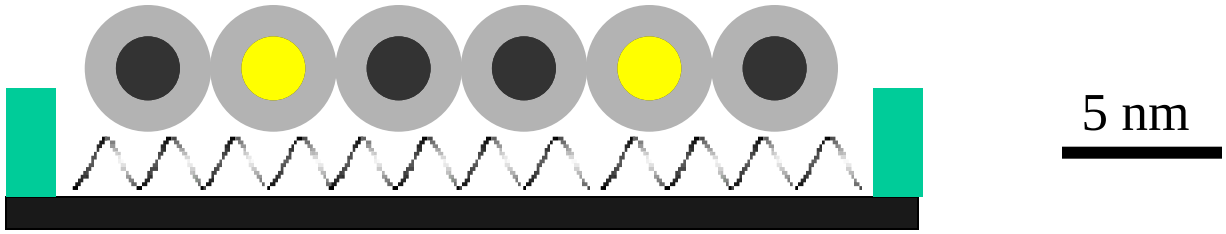
Caustic cleaning agents

High purity gases

Ultrapure water

Energy

Biomolecular nanolithography: Advantages of chemistry-based nanofabrication



Target structures: 2-nm islands with 2-nm separation

Island size - NP dimensions precisely tuned by synthesis

Spacing - Ligand shell controls interparticle spacing

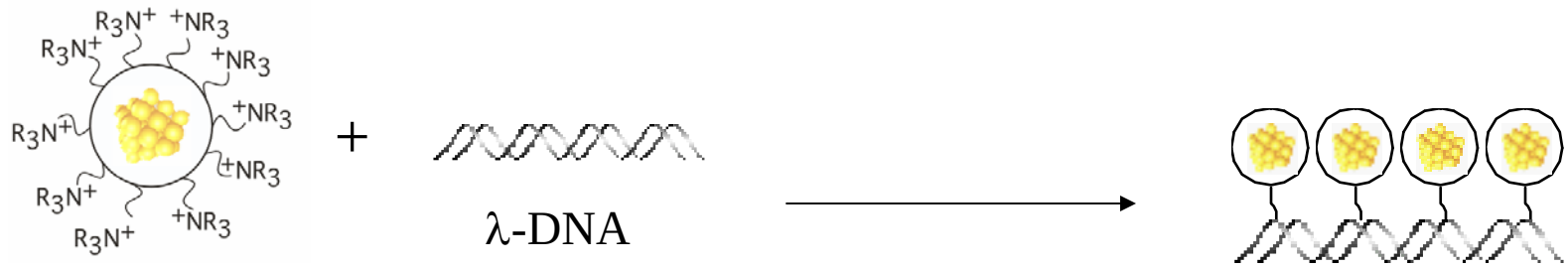
Arrangement - Polymeric scaffold directs arrangement

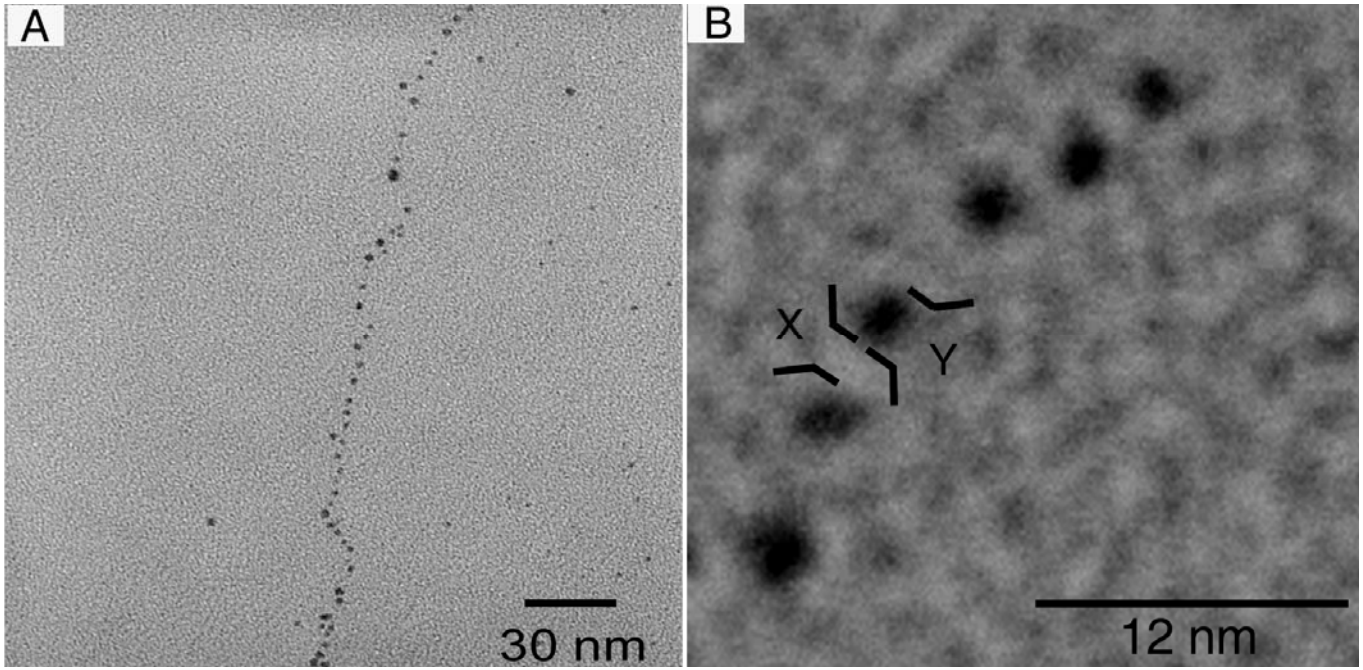
Positioning - Self-assembly positions scaffold on substrates

Composition - Scaffold sequence controls placement of different particles

Additive process reduces number of derivatives

Extended linear chains of closely-spaced particles are accessible using this assembly method

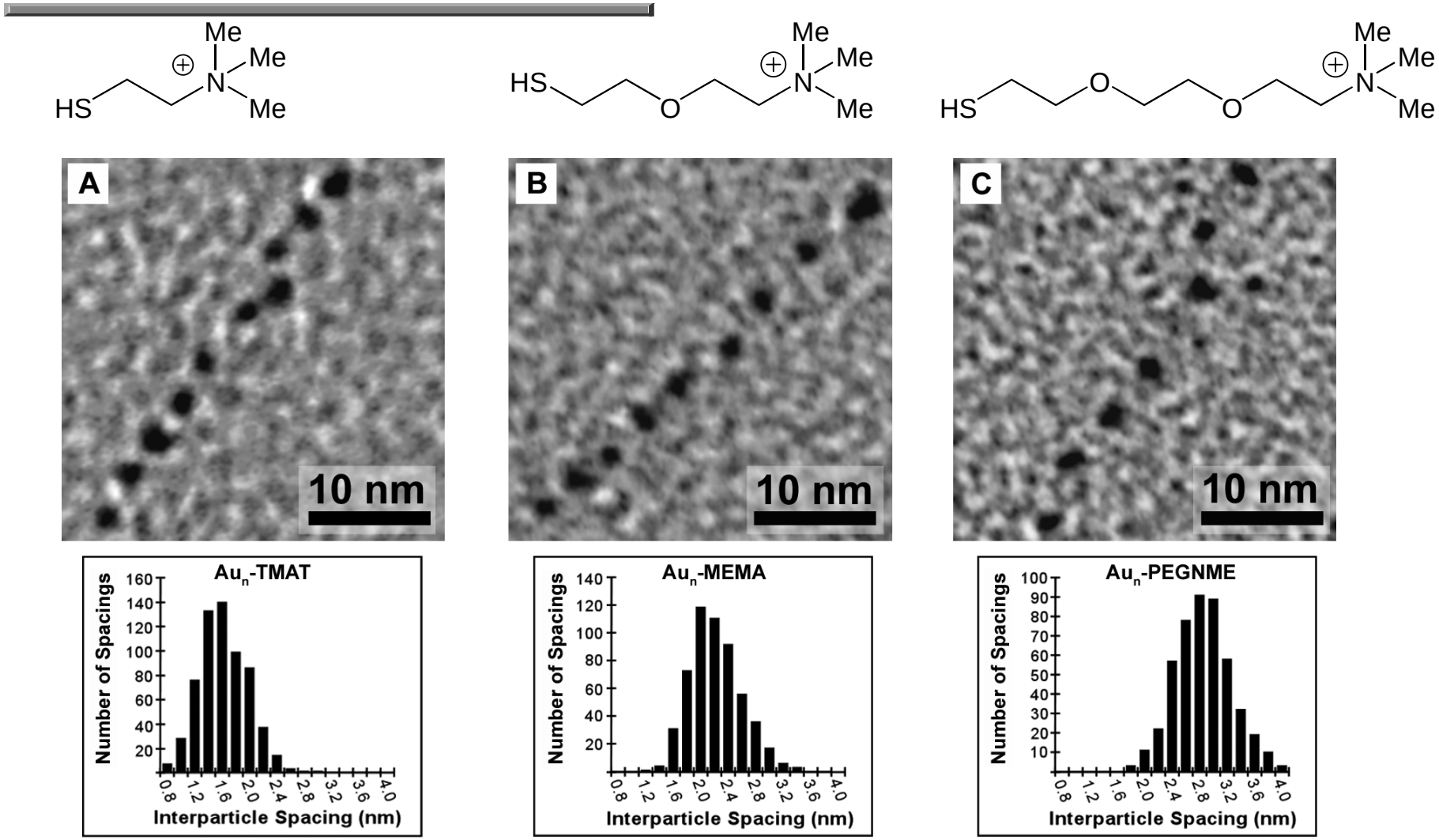




1.9-nm particles separated by 1.5 nm

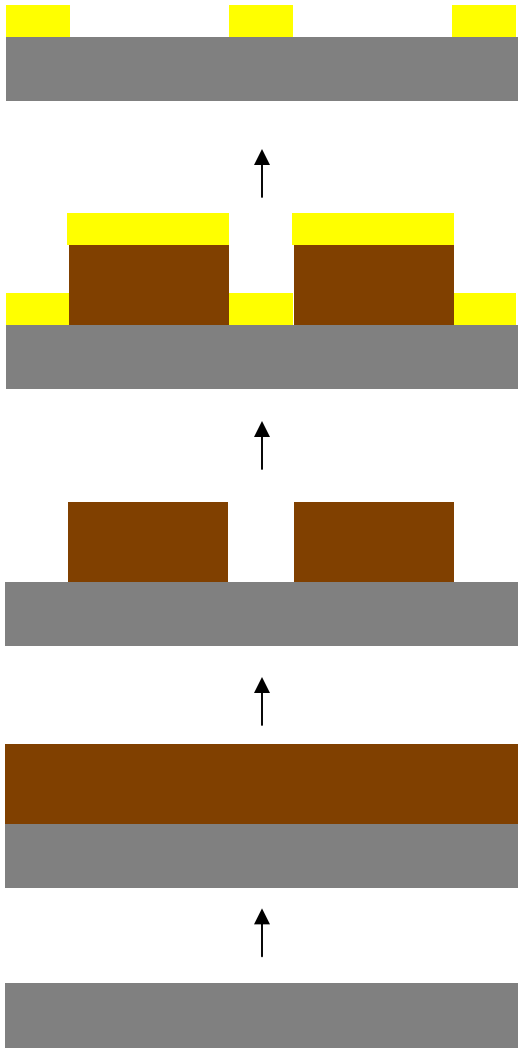
Warner and Hutchison, *Nature Mater*. **2003,** 272-277.

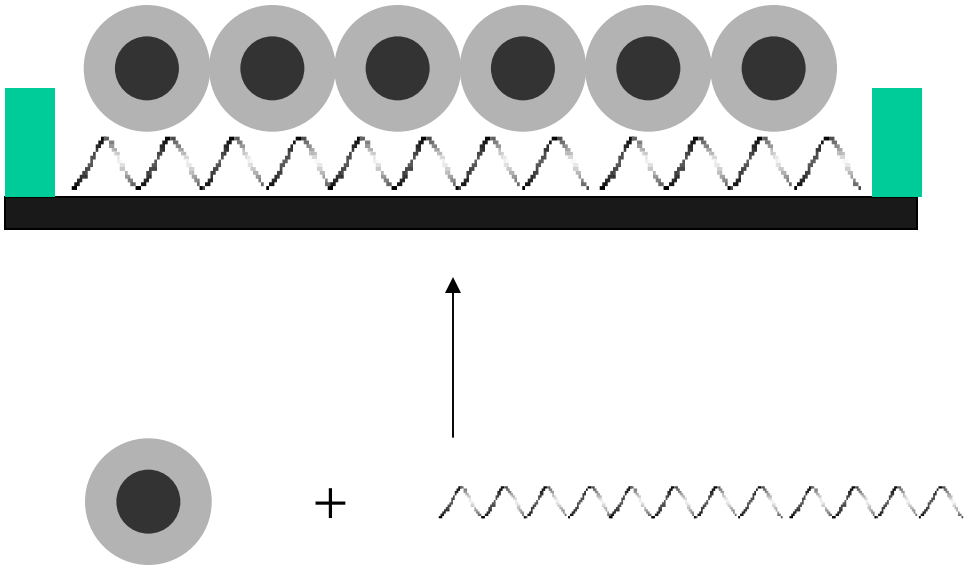
Controlling interparticle spacing along the DNA scaffold



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

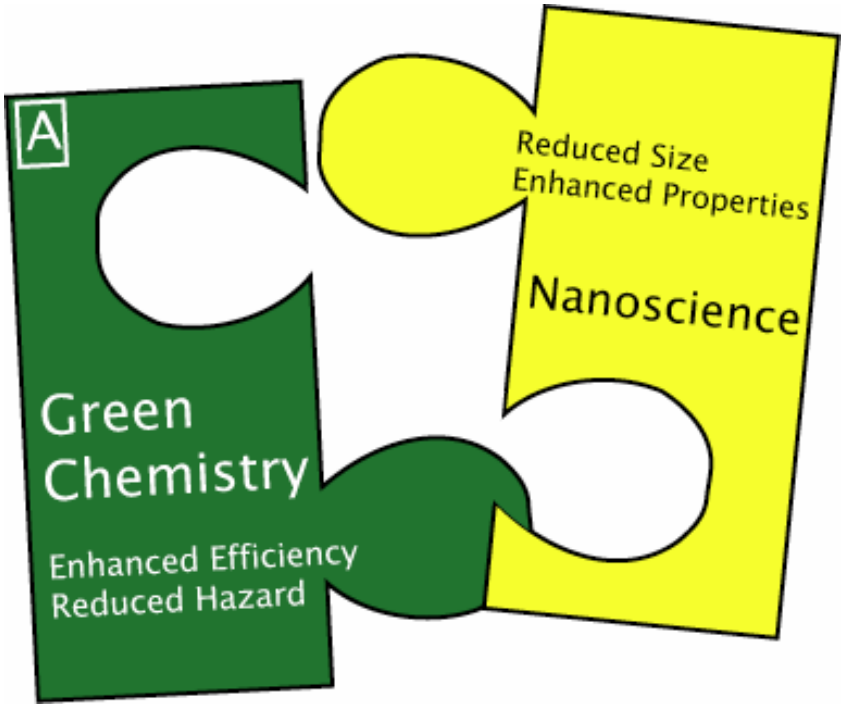
Provides access to smaller structures

Green applications of nanoscience

Product

Process

Applications



Nanoscale properties leading to greener applications

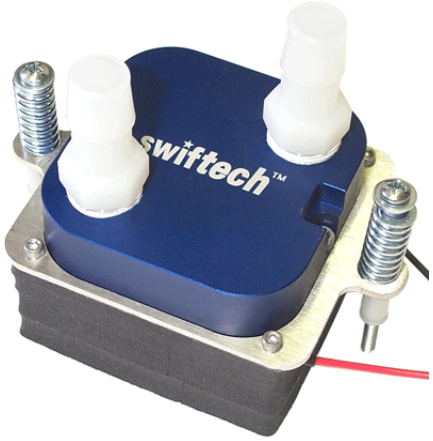
Remediation of chlorinated organic contaminants with iron nanoparticles

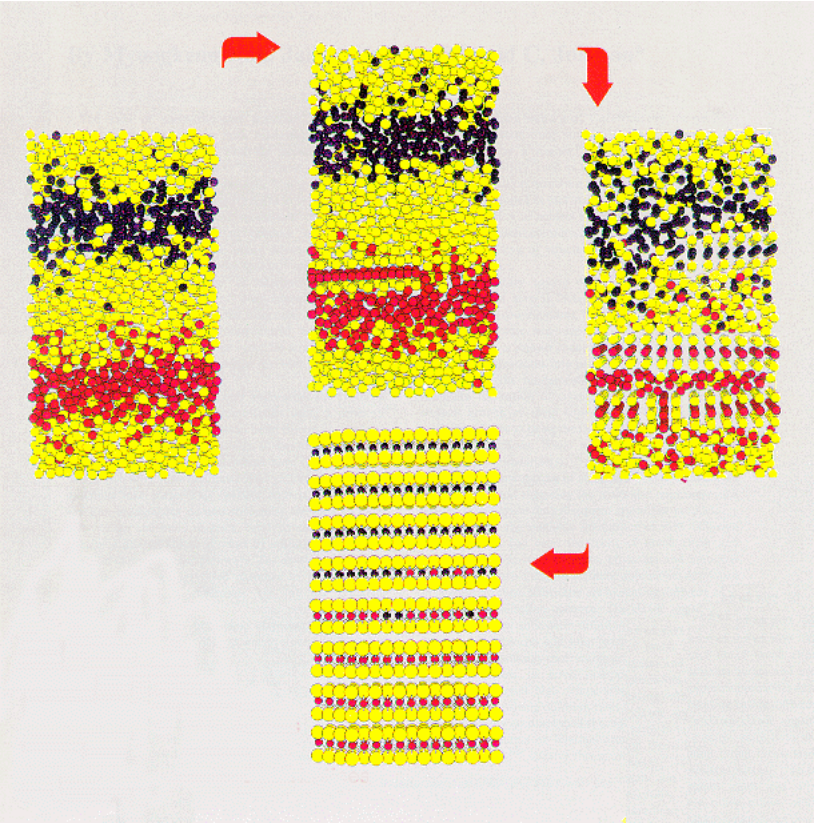
Molecular nano-coatings - using less material to protect surfaces from corrosion or wear

Nanocomposites as ultra-strong, lightweight materials for automobile construction

Thermoelectric coolers - cooling <u>without</u> refrigerants

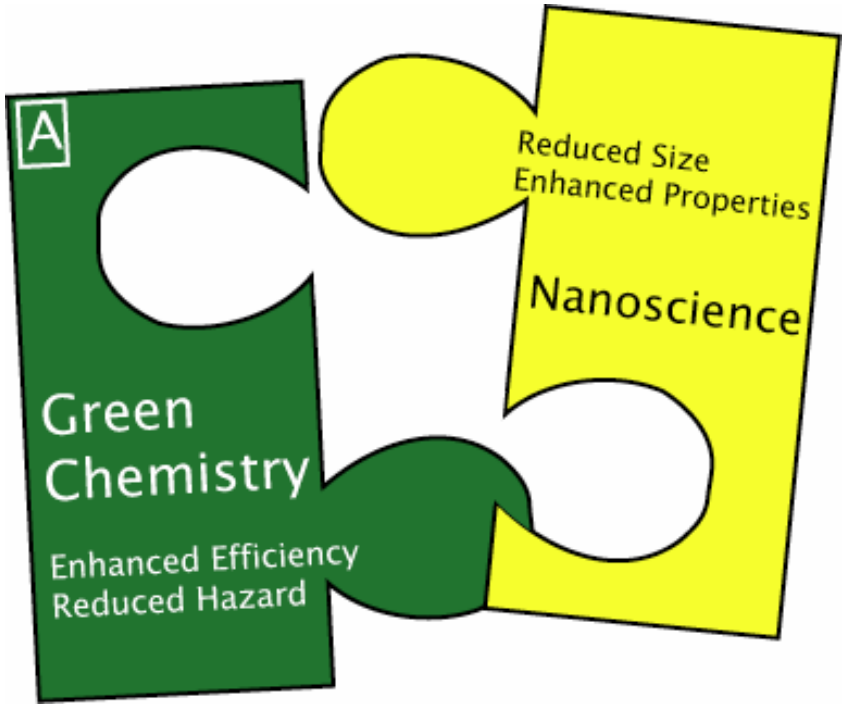
Thermoelectric coolers - performance enabled by nanoscale materials

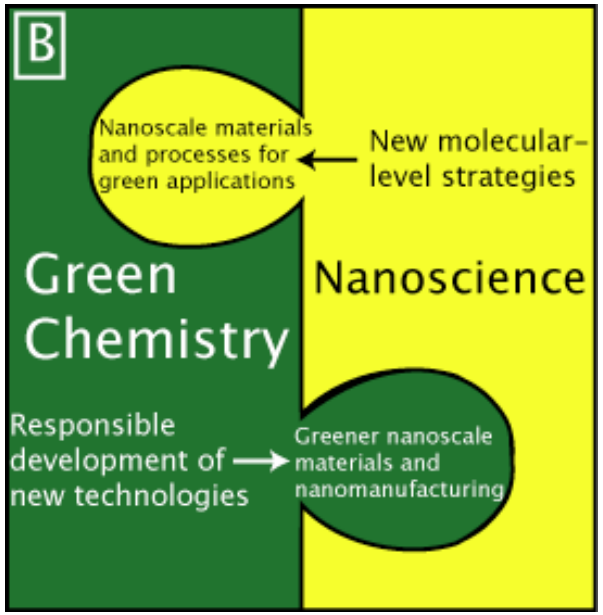




No refrigerants, energy efficient….

Merging green chemistry and nanoscience





McKenzie, L.C; Hutchison, J.E. "Green nanoscience," *Chemistry Today*, **2004**, 30-33.

Summary - Green Nanoscience

Environmental and public health issues should be addressed in the context of developing nanoscience and nanotechnology

Green chemistry will drive the development of higher performance, as well as, environmentally friendlier products and processes

Nanoscience will provide important new technologies that will benefit the environment

The combination of green chemistry and nanoscience offers opportunities for higher performance products that are inherently safer for society and the environment