Sustainable Nanotechnology Organization

Research | Education | Responsibility

Green Synthesis of Nanomaterials: A Necessity for Sustainability

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National Science Foundation

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National Science Foundation

The National Science Foundation (NSF) is the primary Federal agency supporting research at the frontiers of knowledge, across all fields of science and engineering (S&E) and all levels of S&E education.

NSF Act of 1950 (Public Law 81-507). The NSF Act set forth a mission: *“to promote the progress of science; to advance the national health, prosperity, and welfare; to secure the national defense; and for other purposes.”*

19^{th} Century Chemistry

1803 - John Dalton originates atomic theory, calculating some atomic weights and inventing chemical symbols.

1811- Avogadro proposes his theory of molecules

1818 - Table c … 26 and 1833.

1828 - Birth c … urea.

1856 - New dyes synthesized by William Perkin, Sr. from coal tar. Bessemer's converter revolutionizes iron smelting process. Industries boom as a result of chemical progress.

1858- Friedrich Kekule defines the concept of valence

1867 - Alfred Nobel invents dynamite and nitroglycerine.

1869- The periodic law is put forward by Dmitri Mendeleev

1877 - The synthesis of amyl-benzene encourages production of dyes and pharmaceutical products.

1898 - Discovery of radium by Pierre and Marie Curie.

1900 - Arrhenius introduces the concepts of ions

Unintended results in the 20th Century

Waste

Inefficiency

Hazards

Environmental disaster

Pollution

Disease

Leading to Environmental Laws

Clean Air Act (1970): Sets goals and standards for the quality and purity of air in the United States. By law, it is periodically reviewed. A significant set of amendments in 1990 toughened air quality standards and placed new emphasis on market forces to control air pollution.
Clean Water Act (1972): Establishes and maintains goals and standards for U.S. water quality and purity. It has been amended several times, most prominently in 1987 to increase controls on toxic pollutants, and in 1990, to more effectively address the hazard of oil spills.

Comprehensive Environmental Response, Compensation and Liability Act (1980): Requires the cleanup of sites contaminated with toxic waste. This law is commonly refered to as "Superfund." In 1986 major amendments were made in order to clarify the level of cleanup required and degrees of liability. CERCLA is retroactive, which means it can be used to hold liable those responsible for disposal of hazardous wastes before the law was enacted in 1980.

Emergency Planning and Community Right-to-Know Act (1986): Requires companies to disclose information about toxic chemicals they release into the air and water and dispose of on land.
Endangered Species Act (1973): Is designed to protect and recover endangered and threatened species of fish, wildlife and plants in the United States and beyond. The law works in part by protecting species habitats.

National Environmental Policy Act (1970): Was the first of the modern environmental statutes. NEPA created environmental policies and goals for the country, and established the President's Council on Environmental Quality. Its most important feature is its requirement that federal agencies conduct thorough assessments of the environmental impacts of all major activities undertaken or funded by the federal government. Many states have enacted similar laws governing state activities.

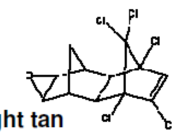
Resource Conservation and Recovery Act (1976): Seeks to prevent the creation of toxic waste dumps by setting standards for the management of hazardous waste. Like CERCLA, this law also includes some provisions for cleanup of existing contaminated sites.

Safe Drinking Water Act (1974): Establishes drinking water standards for tap water safety, and requires rules for groundwater protection from underground injection; amended in 1986 and 1996. The 1996 amendments added a fund to pay for water system upgrades, revised standard: setting requirements, required new standards for common contaminants, and included public "right to know" requirements to inform consumers about their tap water.

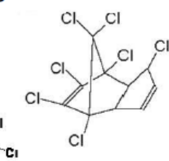
Toxic Substances Control Act (1976): Authorizes the Environmental Protection Agency to regulate the manufacture, distribution, import and processing of certain toxic chemicals.

…And Pollutants

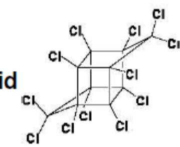
POPs - PESTICIDES



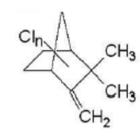
Endrin: White, odourless, crystalline solid (pure); light tan colour with faint chemical odour for technical grade



Heptachlor: White to light tan, waxy solid or crystals with a camphor-like odour



Mirex: White crystalline, odourless solid

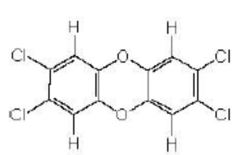


Toxaphene: Yellow, waxy solid w/ chlorine/terpene-like odour

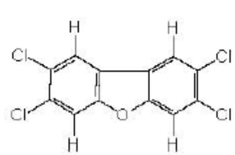
POPs – UNINTENDED BYPRODUCTS

Dibenzodioxins and dibenzofurans

- Byproducts of production of other chemicals
- Detected in incineration of coal, peat, wood, hospital waste, hazardous waste, municipal waste, car emissions
- Of 210 dioxins and furans, 17 are in toxic mixtures



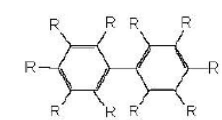
2,3,7,8-TCDD



2,3,7,8-TCDF

UNEP

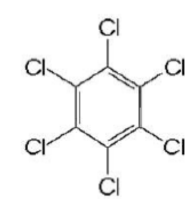
POPs – INDUSTRIAL CHEMICALS



UNEP

PCBs: Polychlorinated biphenyls
Trade Names for different mixtures (partial list): Aroclor, Pyranol, Pyroclor, Phenochlor, Pyralene, Clophen, Elaol, Kanechlor, Santotherm, Fenchlor, Apirolio, Sovol

HCB: Hexachlorobenzene
White monoclinic crystals or crystalline solid



UNEP

We have encountered new technologies before…











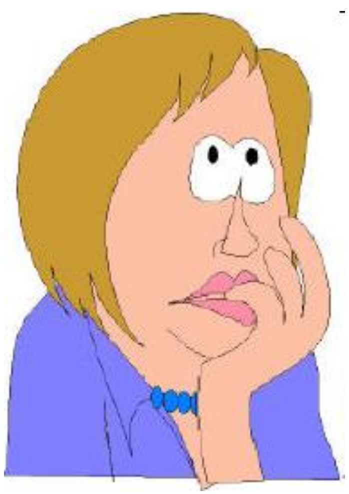


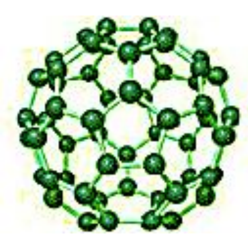
What's different this time?

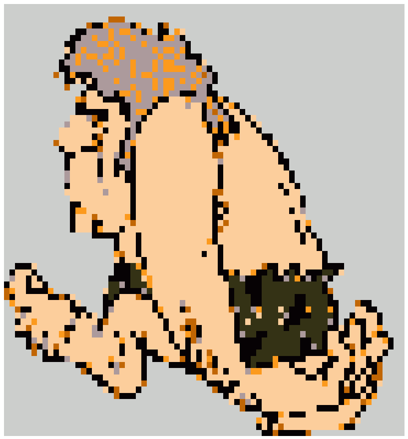
We have evolved in our thinking

Is it harmful? Can it be made without pollution?
How will it affect society? Do we have an adequate
Infrastructure to handle it? Is it economically feasible?
What are the risks? Is it green?
Is it sustainable?

Stone Age to Copper







20th Century Technologies to Nanotechnologies

Compared to chemistry, this is where nanotechnology is today

No Periodic Table

Absence of standards

Not much worker protection

Reliance on empiricism

Lack of instrumentation

Primitive Models/low predictive capabilities

Nanotechnology can help alleviate sustainability problems

Climate change/Energy

Water

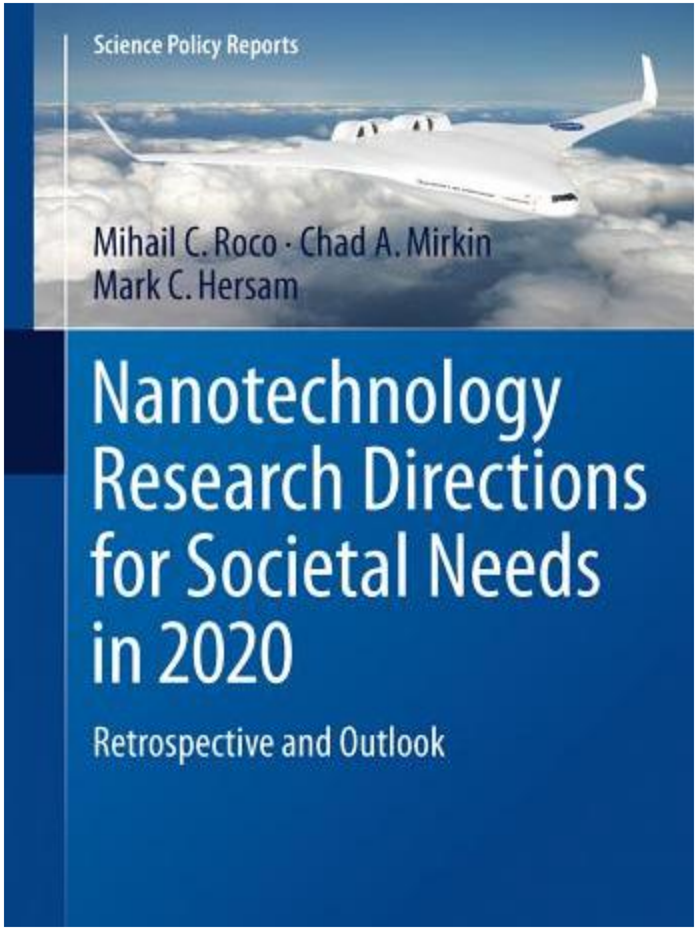
Infectious disease

Food production

Toxics/Pollution

Opportunity!!

Make nanomaterials without the old pollutants



Nanotechnology research moves to sustainability

Safe and sustainable development of nanotechnology for responsible and effective management of its potential; this includes environmental, health, and safety (EHS) aspects and support for a sustainable environment in terms of energy, water, food, raw materials, and climate

Four fundamental routes to making nano materials.

Form in place
These techniques incorporate lithography, vacuum coating and spray coating.

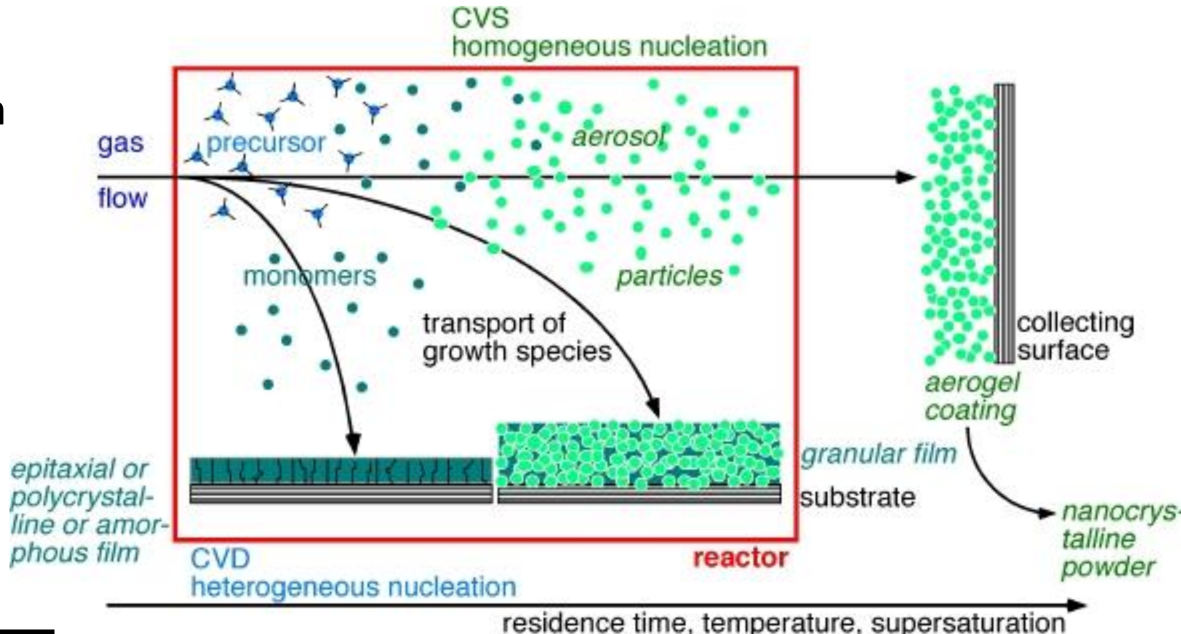
Mechanical
This is a ‘top-down’ method that reduces the size of particles by attrition, for example, ball milling or planetary grinding.

Gas phase synthesis
These include plasma vaporization, chemical vapor synthesis and laser ablation.

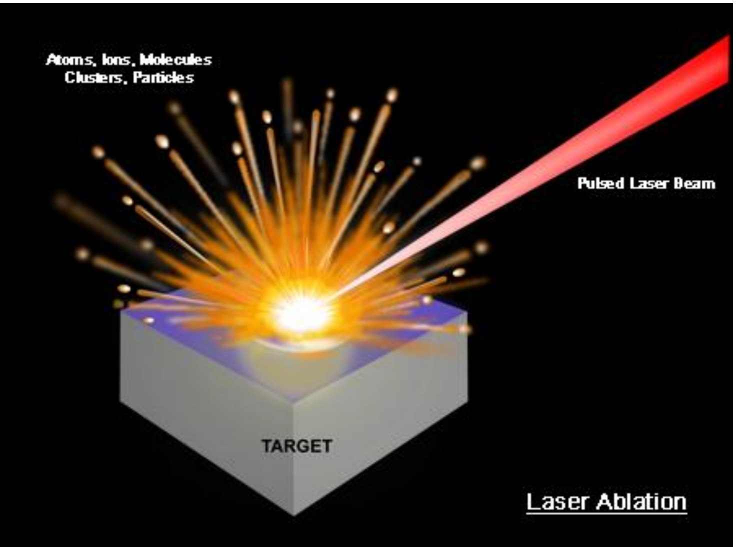
Wet chemistry
This is the range of techniques that are most applicable for characterization by light scattering techniques. These are fundamentally ‘bottom-up’ techniques, i.e. they start with ions or molecules and build these up into larger structures.

Most nanomaterials are produced by chemical processes

Chemical Vapor deposition



Laser ablation



Wet chemistry

Green Nano Processes

Producing nanomaterials and products without harming the environment or human health

Incorporates the source reduction principles of environmentally benign chemistry and engineering and focuses on the processes of making nanomaterials without emitting harmful pollutants and using nanotechnology to make current processes greener
Managing and designing nanomaterials and their production to minimize potential environmental, health, and safety risks

Other names: Clean production, P2, clean tech, environmentally benign manufacturing

Examples of Making Current Processes Greener

<u>Nano Membranes</u>

Separate out metals

Clean process solvents

Product separations

<u>Nano Catalysts</u>

Increased efficiency and *selectivity*

<u>Process Energy</u>

More Efficient

Lower use

Green Chemistry Principles applied to Nanoscience

Green Chemistry Principles	
P1.	Prevent waste
P2.	Atom economy
P3.	Less hazardous chemical synthesis
P4.	Designing safer chemicals
P5.	Safer solvents/reaction media
P6.	Design for energy efficiency
P7.	Renewable feedstocks
P8.	Reduce derivatives
P9.	Catalysis
P10.	Design for degradation/Design for end of life
P11.	Real-time monitoring and process control
P12.	Inherently safer chemistry

Designing Greener Nanomaterial and Nanomaterial Production Methods		Practicing Green Nanoscience
Design of safer nanomaterials (P4,P12)	→	Determine the biological impacts of nanoparticle size, surface area, surface functionality; utilize this knowledge to design effective safer materials that possess desired physical properties; avoid incorporation of toxic elements in nanoparticle compositions
Design for reduced environmental impact (P7,P10)	→	Study nanomaterial degradation and fate in the environment; design material to degrade to harmless subunits or products. An important approach involves avoiding the use of hazardous elements in nanoparticle formulation; the use of hazardless, bio-based nanoparticle feedstocks may be a key.
Design for waste reduction (P1,P5,P8)	→	Eliminate solvent-intensive purifications by utilizing selective nanosyntheses - resulting in greater purity and monodispersity; develop new purification methods, e.g. nanofiltration, that minimize solvent use; utilize bottom-up approaches to enhance materials efficiency and eliminate steps
Design for process safety (P3,P5,P7,P12)	→	Design and develop advanced syntheses that utilize more benign reagents and solvents than used in "discovery" preparations; utilize more benign feedstocks, derived from renewable sources, if possible; identify replacements for highly toxic and pyrophoric reagents
Design for materials efficiency (P2,P5,P9,P11)	→	Develop new, compact synthetic strategies; optimize incorporation raw material in products through bottom-up approaches, use alternative reaction media and catalysis to enhance reaction selectivity; develop real-time monitoring to guide process control in complex nanoparticle syntheses
Design for energy efficiency (P6,P9,P11)	→	Pursue efficient synthetic pathways that can be carried out at ambient temperature rather than elevated temperatures; utilize non-covalent and bottom-up assembly method near ambient temperature, utilize real-time monitoring to optimize reaction chemistry and minimize energy costs

Dahl et al Greener Nano Synthesis, Chem. Rev. 2007 107:2228.

Greener Techniques to make nanomaterials

Self-assembly

Molten Salt or Ionic Liquid Synthesis

Bottom up Manufacturing

Improved synthesis, fewer steps

Bio-inspired nanoscale synthesis

Use of non-toxic solvents like supercritical CO2

Renewables in Nanocomposites

Microwave techniques

Aqueous processing

Photochemical synthesis

Renewable starting materials

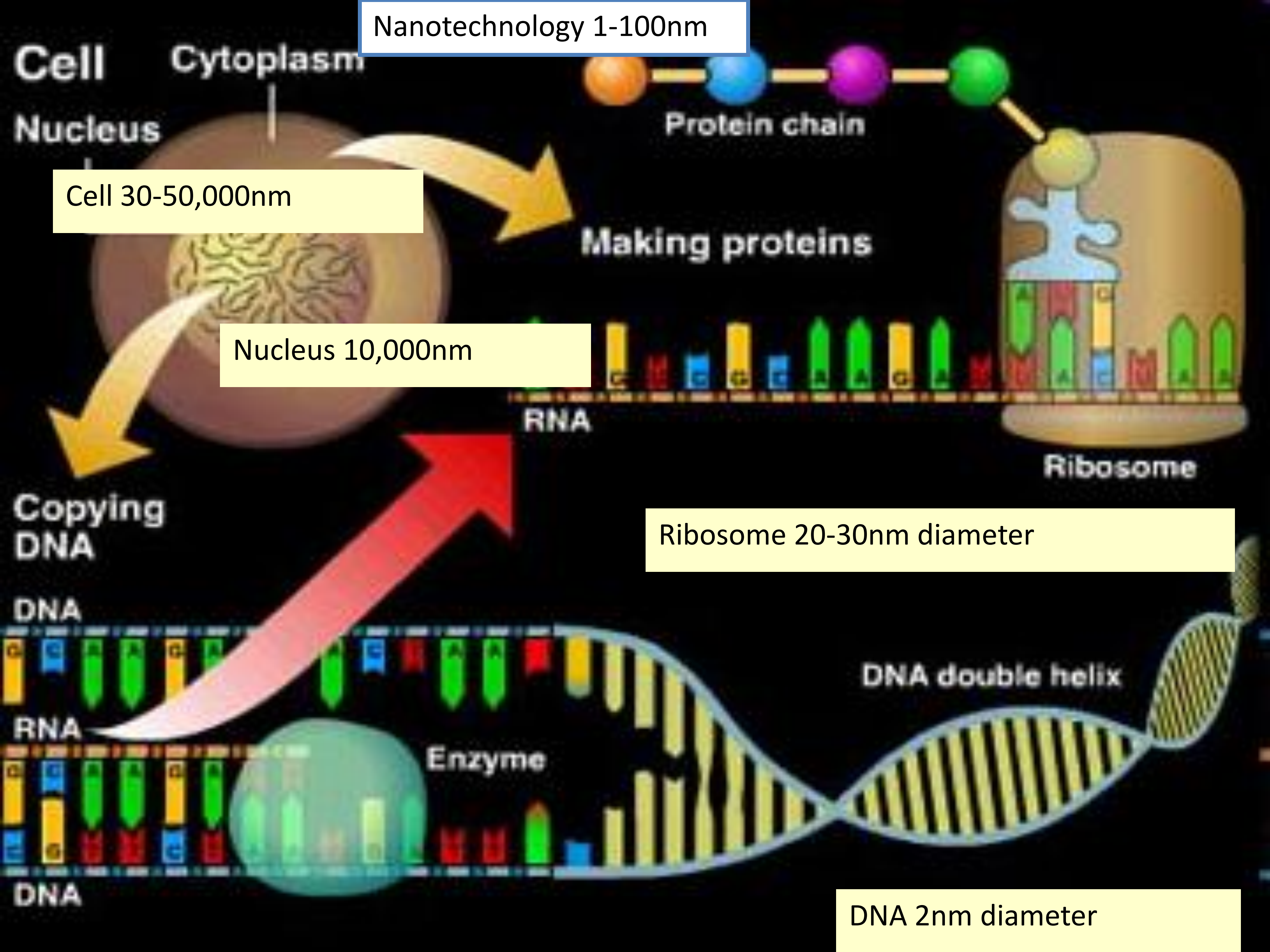
Solvothermal/hydrothermal Processes

Templating processes

Non-toxic starting materials

Use of solid state/solventless processes

Nanocatalysis


Nanotechnology 1-100nm
Cell
Cytoplasm
Nucleus
Protein chain
Cell 30-50,000nm
Making proteins
Nucleus 10,000nm
RNA
Ribosome
Copying DNA
Ribosome 20-30nm diameter
DNA
DNA double helix
RNA
Enzyme
DNA
DNA 2nm diameter

Nanotech is both top down and bottom up—like Nature

The Cell is a Nano Factory

A. Uses “natural” ingredients-simple atoms
B. at room temperature,
C. With small machines for assembling,
D. in non-toxic solvents,
E. With complex feedback loops, smart controls,redundancy for safety
F. And the end of life disposal is accounted for

Breaking no laws of chemistry, physics, biology

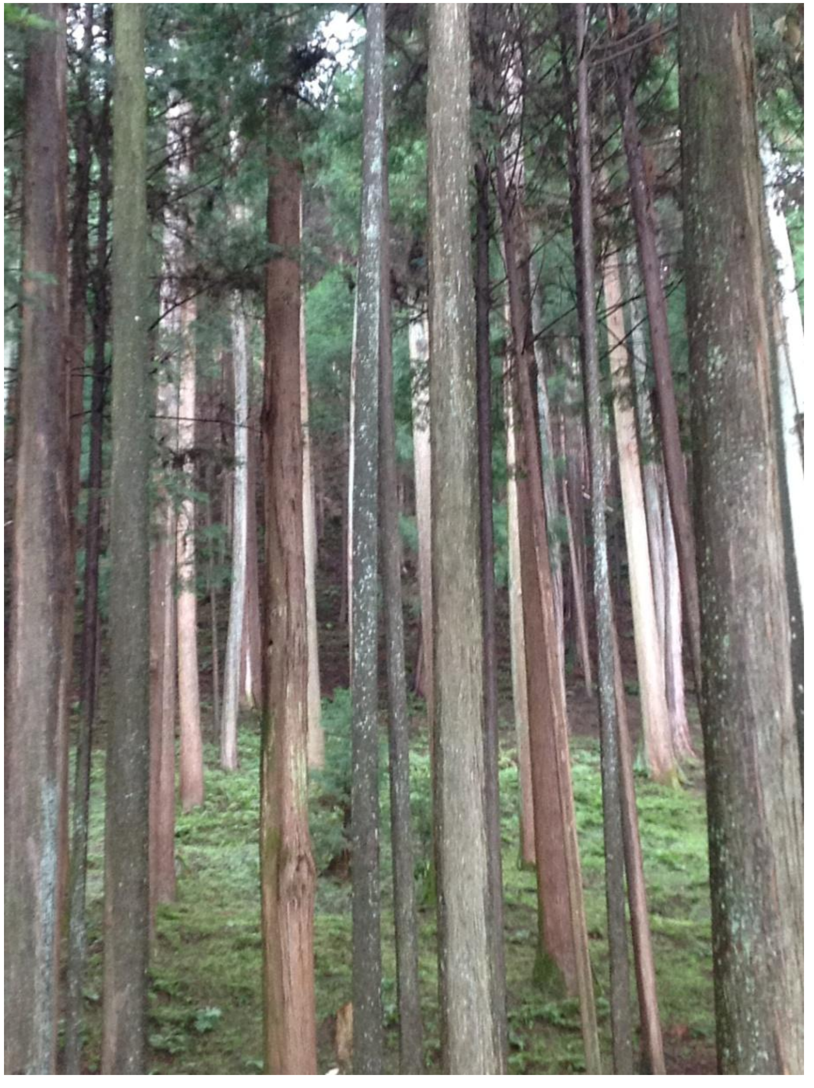
If nature, working at the nanoscale, can accomplish a sustainable world, then surely humans can minimize their risks and help accomplish sustainability through this new scientific approach, nanotechnology

Take Home Message

Nanotechnology is a powerful tool
to aid sustainability

Engineers and scientists have the
responsibility to use this tool

Because they can



Thanks!

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"When you fully understand the situation, it is worse than you think"

Barry Commoner

Producing without harm

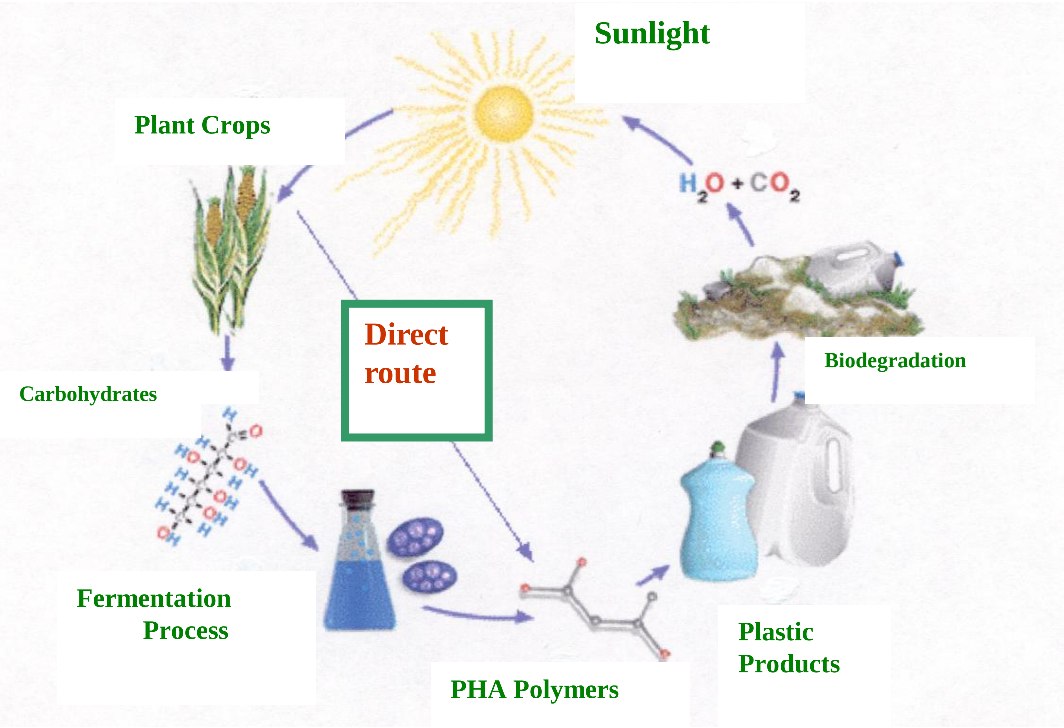
Membranes
Catalysts
Green chemical synthesis
Green engineering
Atomically Precise manufacturing

Green nanomaterials

Green ingredients:

- renewable
- non-toxic
- degradable

Green routes to nanocomposites



Bacterial polyester nanoparticles

Mohanty, Parulekar, Drzal

Manipulating Matter at the Nanoscale

Three methods

1. Pick them up and move them

2. Pattern them (lithography)

3. Use self-assembly

Green Nanotechnology Framework

1. Production/Processes

Making nanomaterials and their products cause no harm

Making NanoX "greenly"

e.g., Green chemistry, Green engineering, DfE, Smart business practices

Using NanoX to "green" up production

e.g., Nanomembranes, nanoscaled catalysts

Pollution Prevention Emphasis

2. Products

Using nanomaterials and their products help the environment

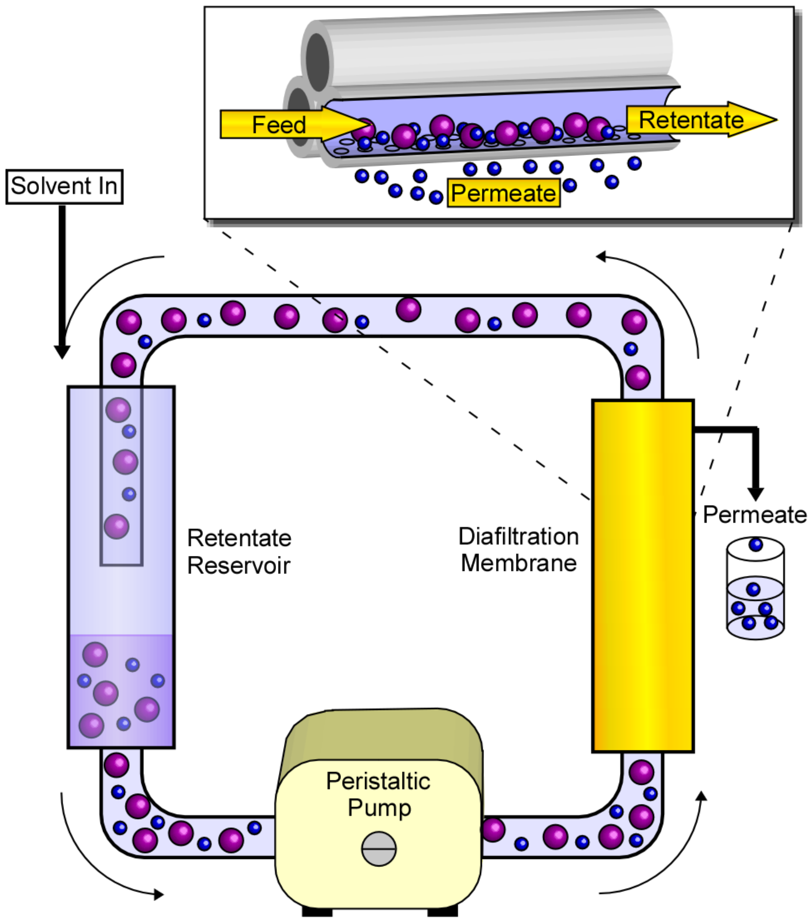
Direct Environmental Applications — e.g., environmental remediation, sensors

Indirect Environmental Applications — e.g., saved energy, reduced waste,

Anticipating full life cycle of nanomaterials and nanoproducts

NEXT STEPS: Policies that offer incentives for developing green nanoproducts and manufacturing techniques

Reducing solvent waste in the purification of nanoparticles



Benefits of diafiltration

Rapid purification
and
Reduces solvent use

Rapid approach to removal of small molecules

Size selection is possible

Some Green NanoSynthesis Processes

Self-Assembly of nanomaterials using:

Film formation

Solvent evaporation

Hydrophobic interactions

Magnetic properties

Templating

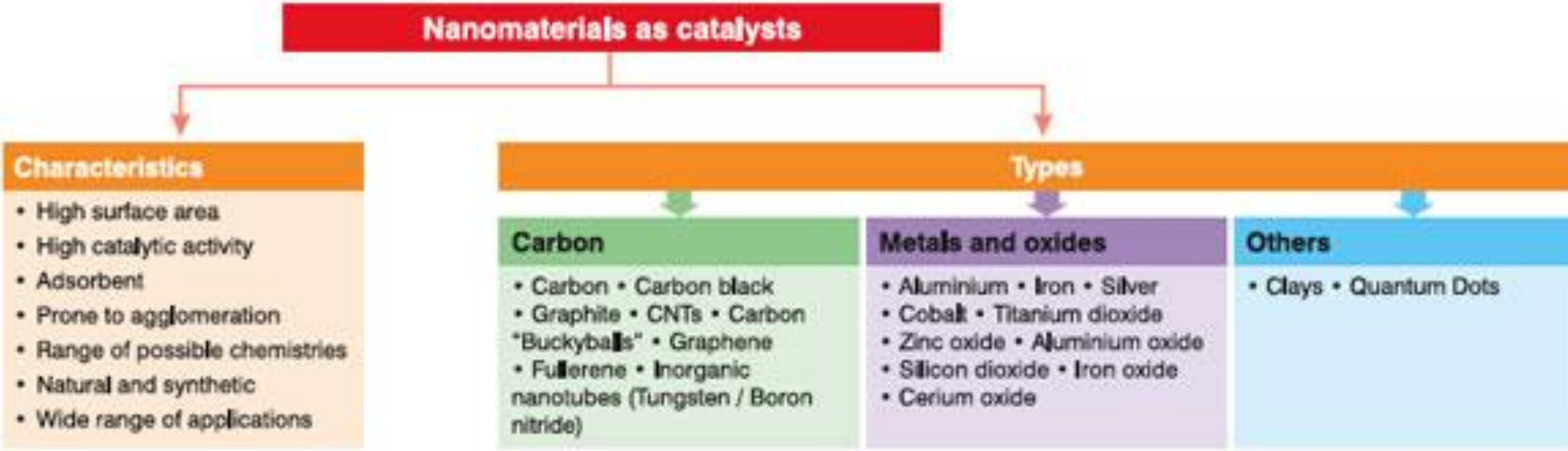
Electrostatic

Oil-water micelles

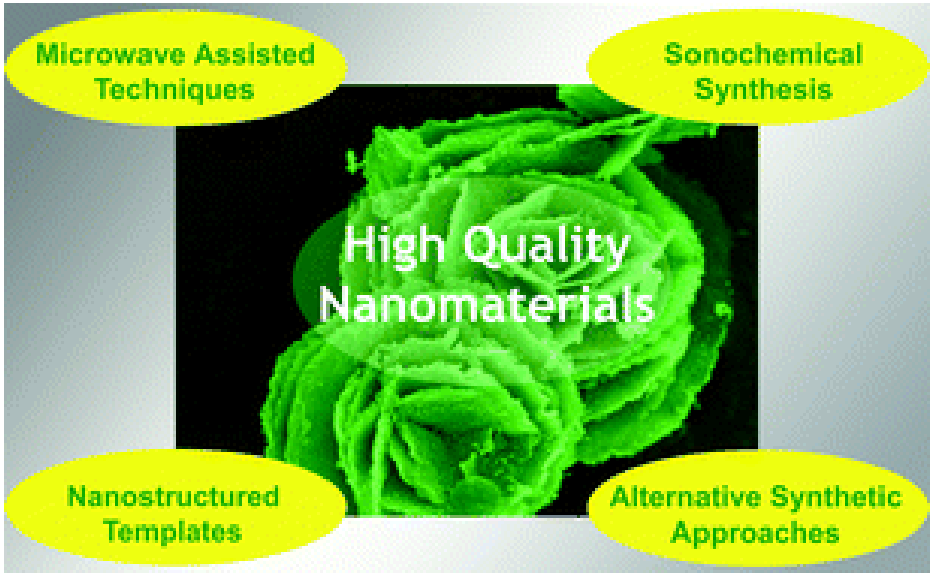
Nano-Catalysis

Emulating Nature

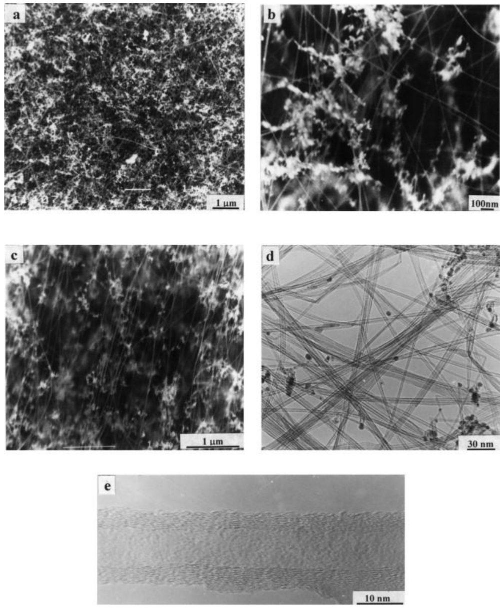
Nanocatalysts



Moving from efficiency to specificity



Patete, J. M.; Peng, X.; Koenigsmann, C.; Xu, Y.; Karn, B.; Wong, S. S. *Green Chemistry* **2011,** 13, (3), 482-519

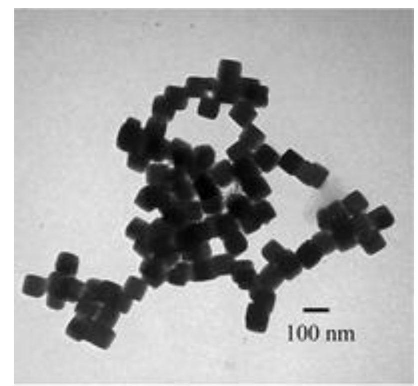


Carbon nanofibers at purity levels of 98.5% can now be produced in bulk with as much as a 8200 weight percent yield on water-soluble, nontoxic sodium chloride supports.

Ravindra, R.; Bhat, B. R. *J. Nanoengin. Nanomanuf.* **2012,** 2, 31-35.

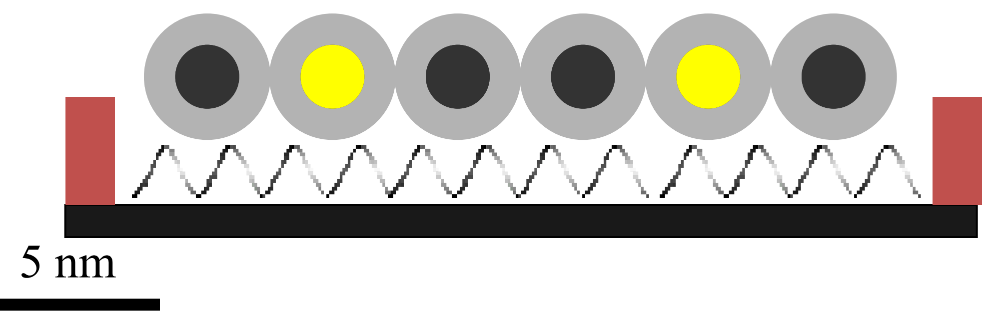
Highly uniform Cu_2O nanocubes can be prepared by using a simple solution approach. Copper(II) salts in water are reduced with ascorbic acid in air in the presence of polyethylene glycol (PEG) and sodium hydroxide. The average edge length of the cubes can be controlled from 25 to 200 nm by changing the order of addition of reagents, and the PEG concentration.

Gou, L.; Murphy, C. J. *Journal of Materials Chemistry* **2004,** 14, 735-738



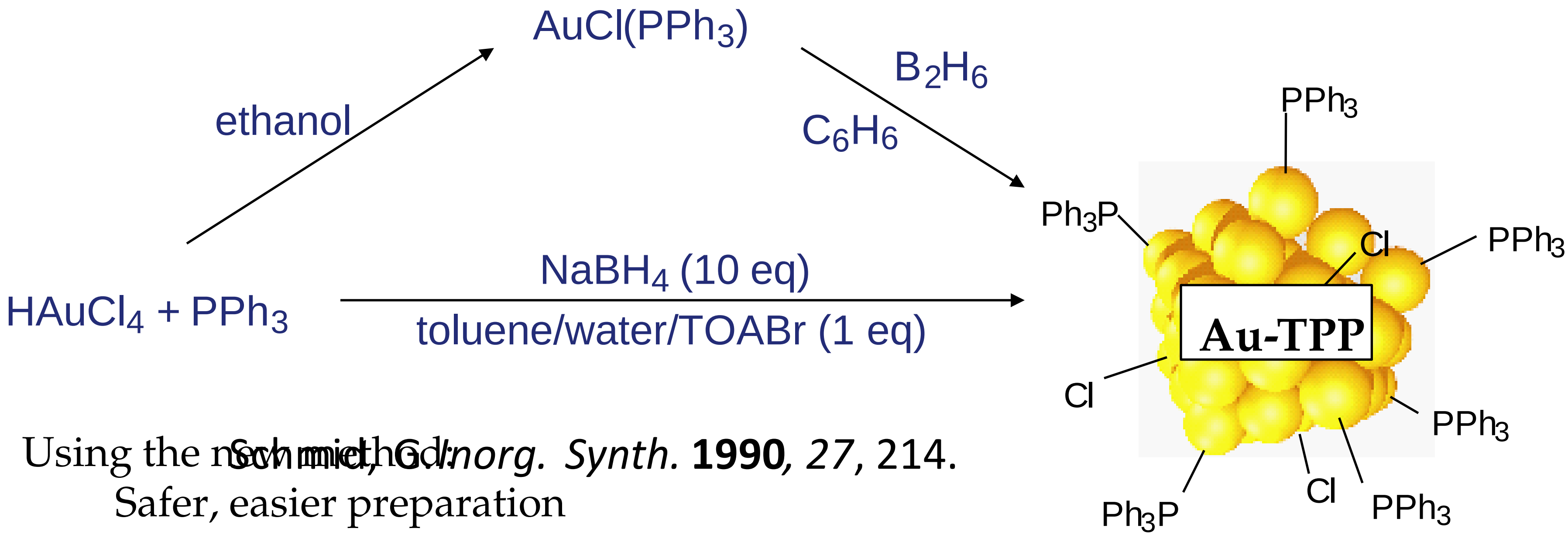
Microwave functionalization of nanotubes

Reduced reaction time
number of reaction steps
Wang, Iqbal, Mitra



Biomolecular nanolithography for bottom-up assembly of nanoscale electronic devices Kearns, Hutchison

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



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")

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

Weare, Reed, Warner, Hutchison *J. Am. Chem. Soc.* **2000**, *122*, 12890.
Hutchison, et al. *Inorg. Syn*. **2004**, *34*, 228.
US Patent # 6,730,537: Issued May 4, 2004.

Greener reagents and solvents

Questions to consider

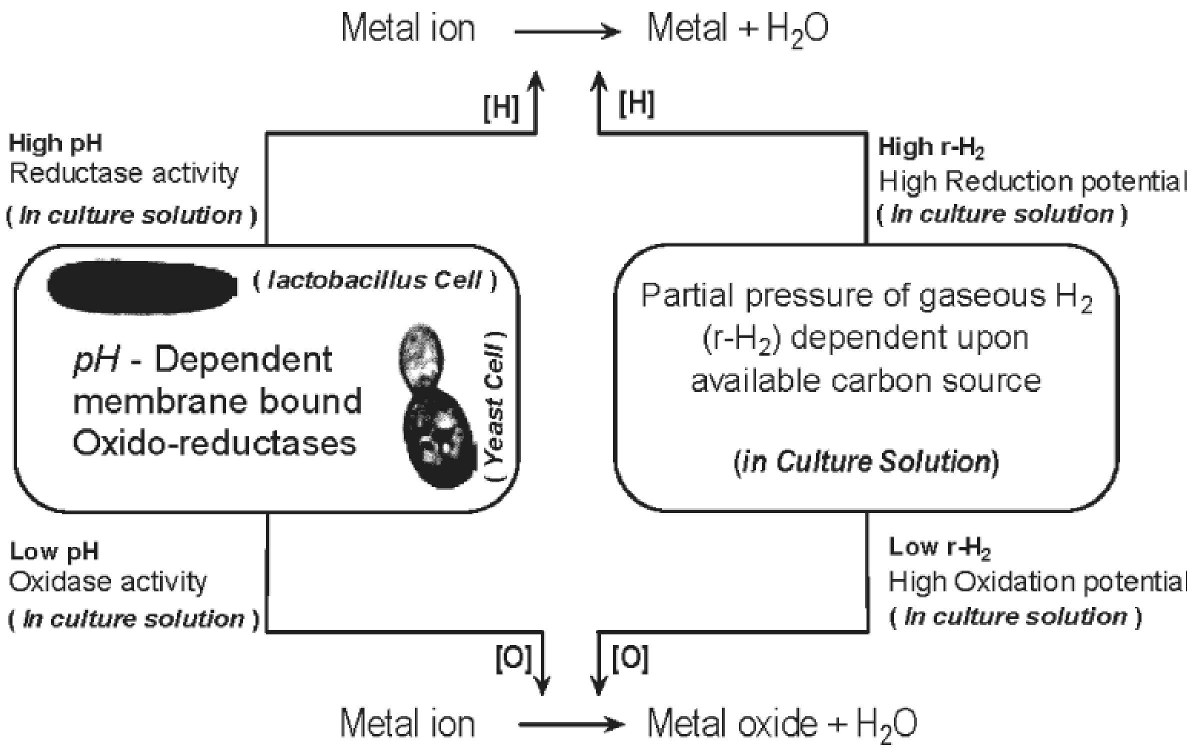
Is it produced greenly?

low energy
fewer steps
non-toxic starting materials
non-volatile solvents
self assembled--not chemical soup

Is it benign in its use?

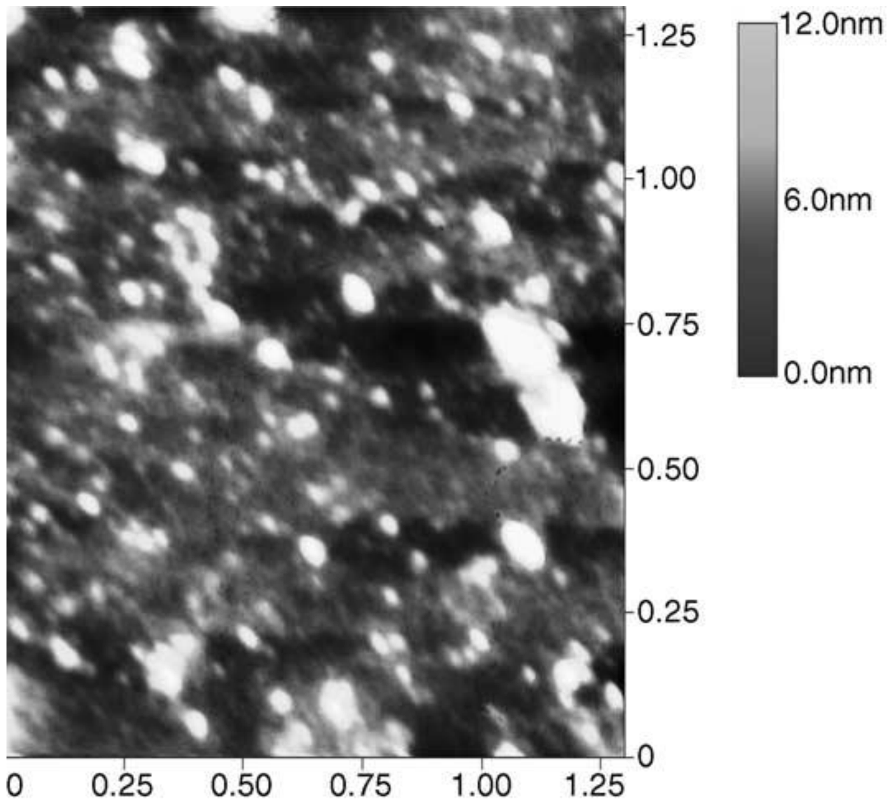
exposure controlled
energy efficient
helpful to the environment
Full life cycle considered

Bio-assisted syntheses of Ti nanospheres (40-60 nm) have been initiated using *Lactobacillus,*



Prasad, K.; Jha, A. K.; Kulkarni, A. *Nanoscale Res. Lett.* **2007,** 2, 248-250.

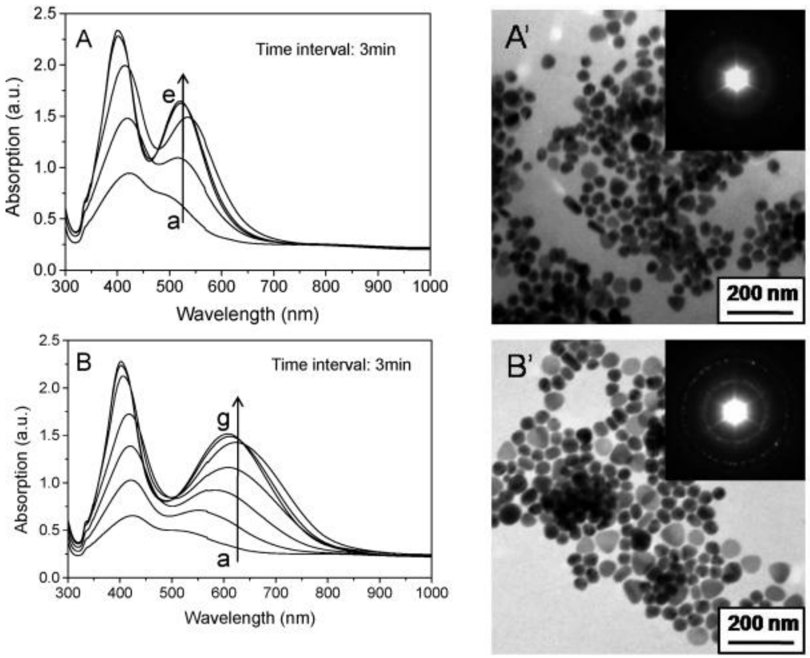
CdS nanoparticles



AFM image of starch capped CdS nanoparticles on mica

~10 nm capped CdS nanoparticles have been successfully manufactured by stirring a solution of cadmium nitrate with an aqueous solution of soluble starch at room temperature, adjusting pH conditions, and ultimately adding in an aqueous solution of sodium sulfide, followed by stirring for 5 h and aging for an additional 12 h, prior to isolation of a yellow precipitate, coupled with acetone washing and low-temperature drying steps.

Wei, Q.; Kang, S.-Z.; Mu, J. *Colloids and Surfaces A* **2004,** 247, 125-127

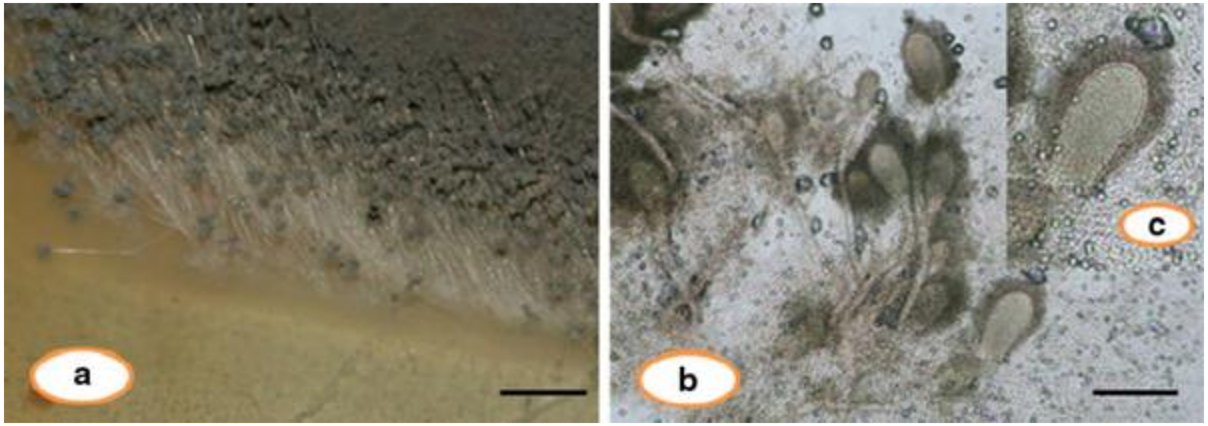


Silver nanoplates

Time-dependent UV-vis spectra of silver nanoparticles on the molar ratio of sodium citrate to silver ions: (A) 6 and (B) 12.
Corresponding TEMimages (A0 and B0) when the maximum absorption intensity is reached.

Citrate ions have been used as reducing agents, stabilizers, and complexing agents in the presence of surfactants to form Ag nanoplates measuring from 100 to 350 nm under ambient conditions.

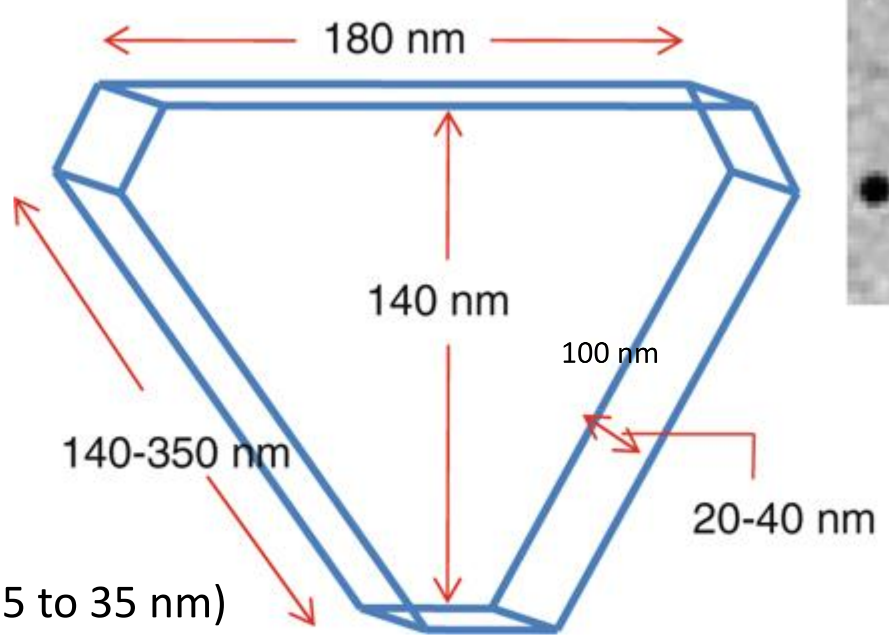
Jiang, X. C.; Chen, C. Y.; Chen, W. M.; Yu, A. B. *Langmuir* **2010,** 26, (6), 4400-4408.

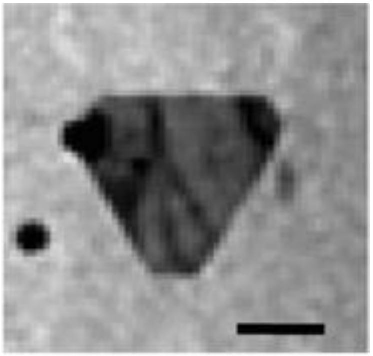


Aspergillus clavatus

The endophytic *Aspergillus clavatus* , isolated from surface sterilized stem tissues *Azadirachta indica* A. Juss. **a** Bunches of conidiophores as visualized onto petriplate, **b** the club-shaped conidiophores, **c** stipes smooth walled and hyaline (*Bar* represents magnifications ×40 for **a** and **b**, while ×100 for **c**).

Relatively large, single-snipped gold nanotriangles





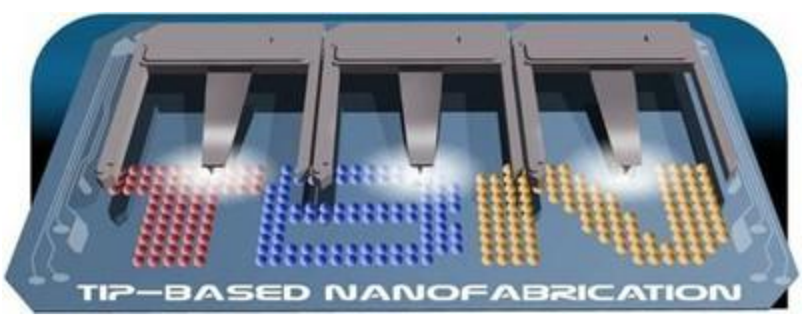
anisotropic Au nanotriangles (25 to 35 nm)

Verma, V. C.; Singh, S. K.; Solanki, R.; Prakash, S. *Nanoscale Res. Lett.* **2011,** 6, 16.

Atomically Precise Manufacturing

The basis of this technology…is building with molecular building blocks and precise positional control. This molecule-by-molecule control can become the basis of a manufacturing technology that is cleaner and more efficient than anything we know today. It is a fundamentally different way of processing matter to make products that people want.

-Eric Drexler, 1992



Molecular Manufacturing—Ultimate Nanotechnology

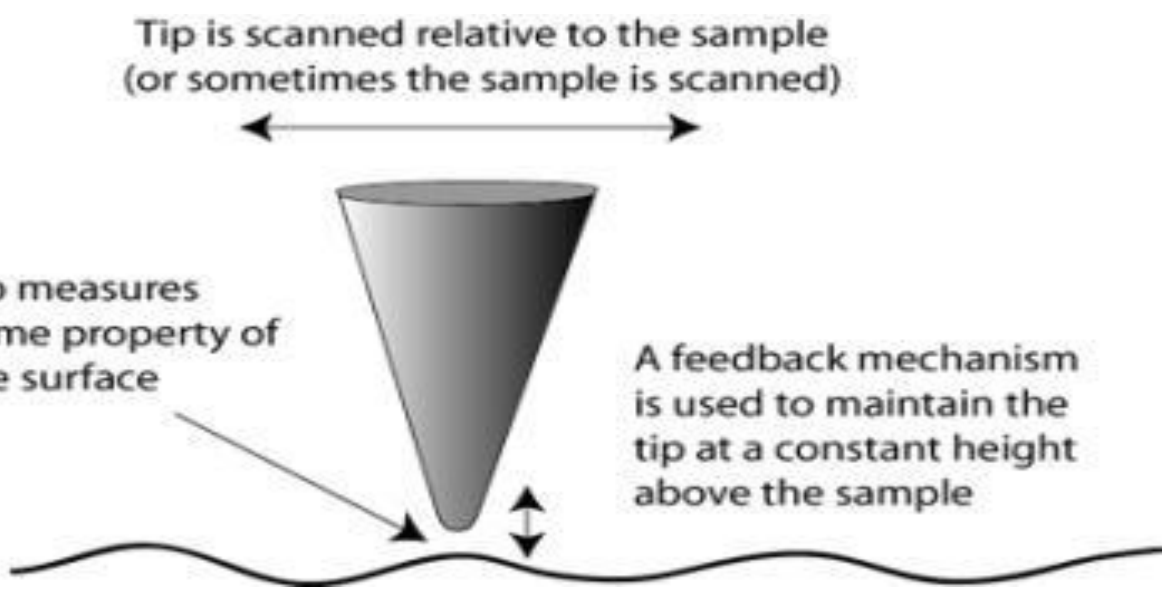
Will it revolutionize our industries? Can we do it?
Will it decrease risks?

It is possible to

Use molecular machines	Biology
Synthesize diverse molecules	Chemistry
Model designs	Physics
Build systems from component parts	Engineering

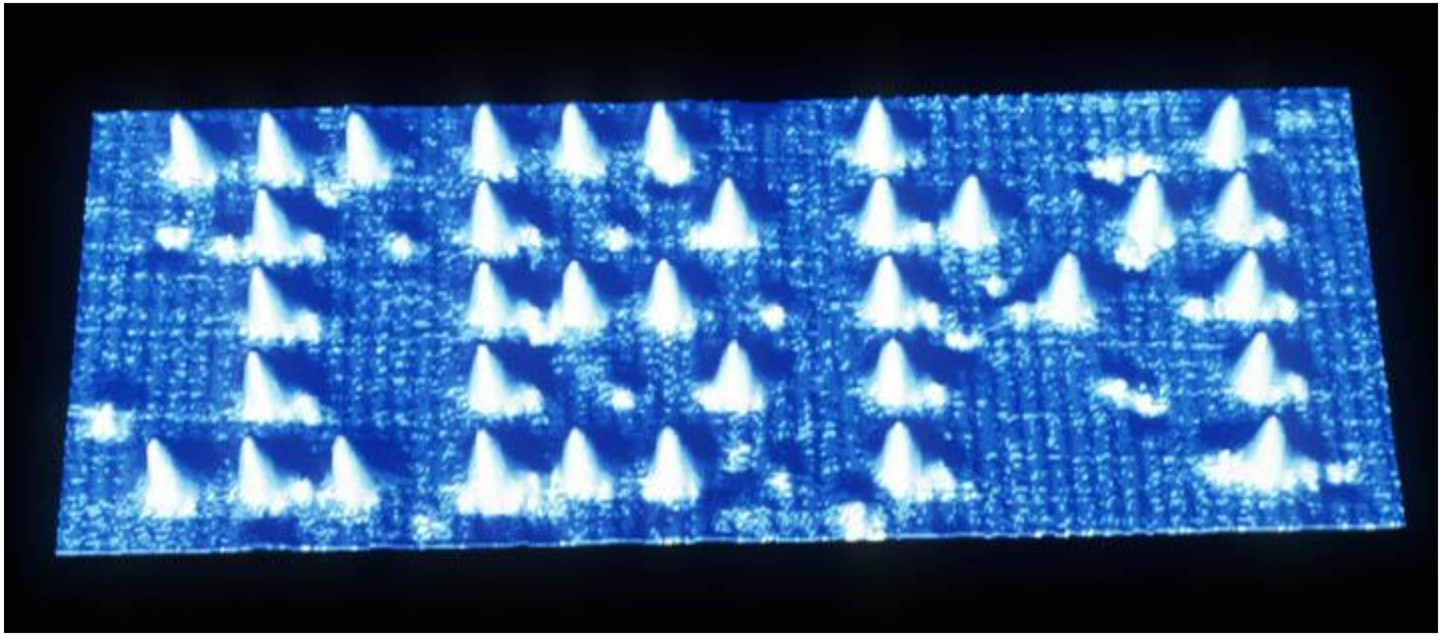
Adapted from Drexler,2005

1. Pick Them Up



The tip of an AFM can be used to move a molecule if you can figure out how to 'pick up' and then release the molecule or element.

A famous ‘real’ image of nanotechnology



November, 1989, IBM spelled their logo using thirteen xenon atoms.

Each atom was picked up using an AFM tip and moved into place.

While the picture suggests a very nice stable arrangement the atoms were in fact continuously moving, and the ‘letters’ were short lived.

2. Lithography

- All nanometer sized electronic components are made using a process called lithography.
- Alois Senefelder of Munich discovered the basic principle of lithography, “printing on stone”, around 1798.
- It is based upon the notion that oil and water do not mix.
- Photolithography involves using energy (e.g., light or electrons) to change the solubility of a material.
- Photolithography literally means *light-stone-writing* in Greek.
- An image can be produced on a surface by drawing with light or electrons much the same way that you might scratch away the crayon on a scratch board

Photolithography

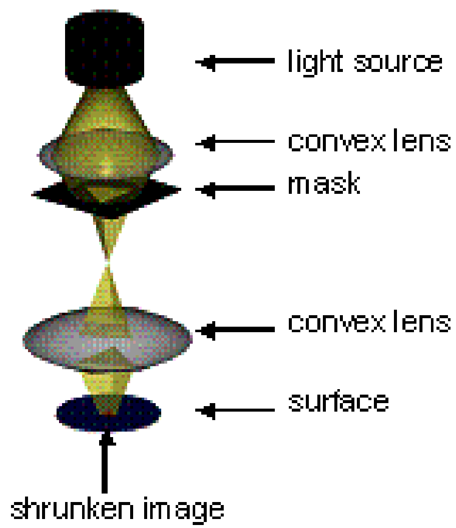


Figure 5. Lenses and light used to shrink images, http://foodmicro.foodsci.cornell.edu/fmlab/personnel/cady.htm

Scientists use photolithography to make computer chips and other devices that have very small features, as small as 100 nanometers.

3. Self-assembly

Molecules self-assemble when the forces between these molecules are sufficient to overcome entropy. Entropy drives molecules to a low energy state.

Common examples

- Snow flakes
- Salt crystals
- Soap bubbles