Sustainable
Nanotechnology
Organization
Research | Education | Responsibility

# Research in Sustainable Synthesis of Nanomaterials

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# Green Nanotechnology

**1. Production** of nanomaterials and products does not harm the environment

**Making** NanoX "greenly"

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

**Using** NanoX to "green" production

e.g., Nanomembranes, nanoscaled catalysts

Pollution Prevention Emphasis

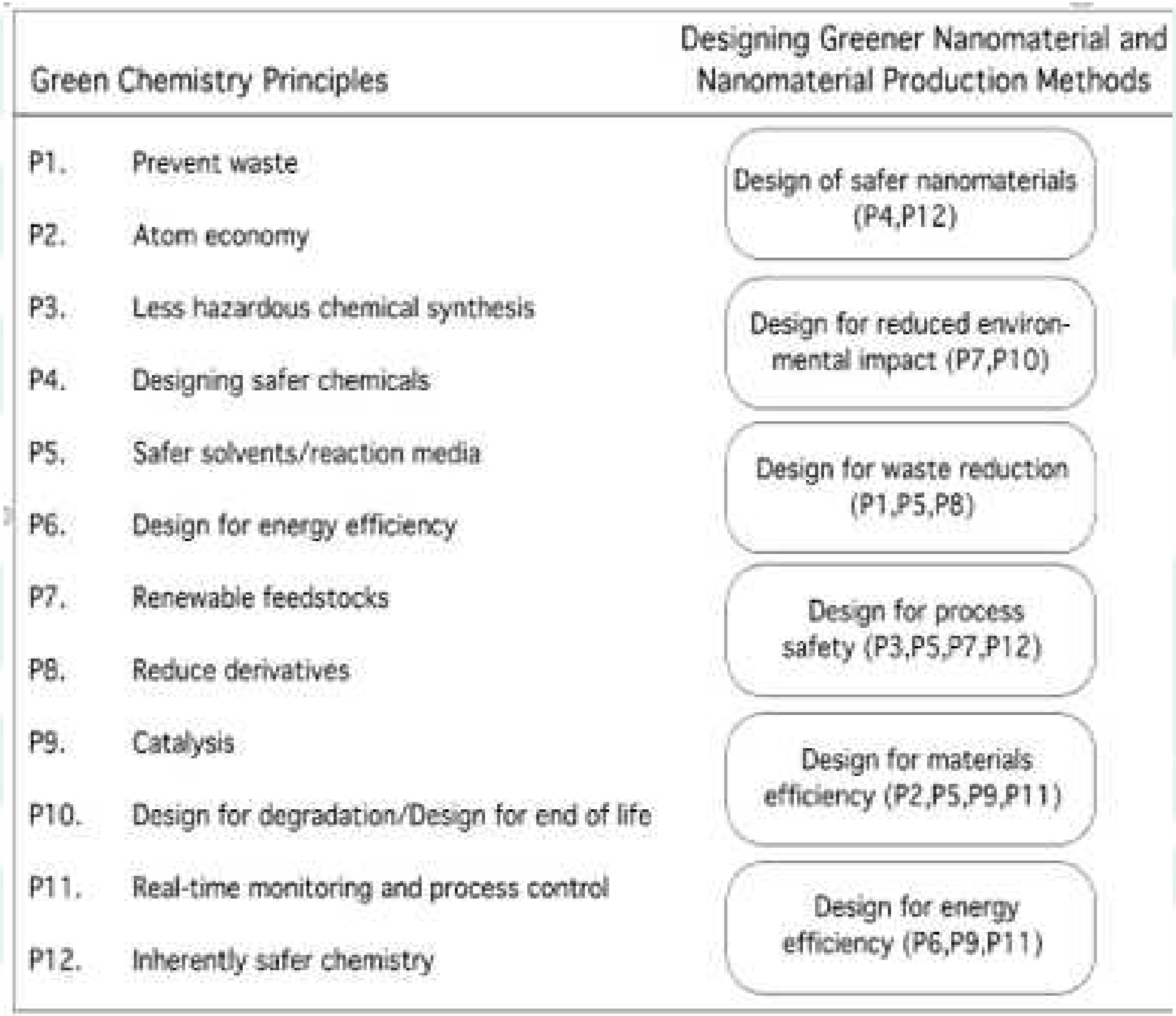
**2. Products** of nano help the environment

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

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

**Addressing a full systems approach to nanomaterials and nanoproducts**

# 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**

- Design of safer nanomaterials (P4,P12)
- Design for reduced environmental impact (P7,P10)
- Design for waste reduction (P1,P5,P8)
- Design for process safety (P3,P5,P7,P12)
- Design for materials efficiency (P2,P5,P9,P11)
- Design for energy efficiency (P6,P9,P11)

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

| 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 |

# Four fundamental routes to making nano materials.

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

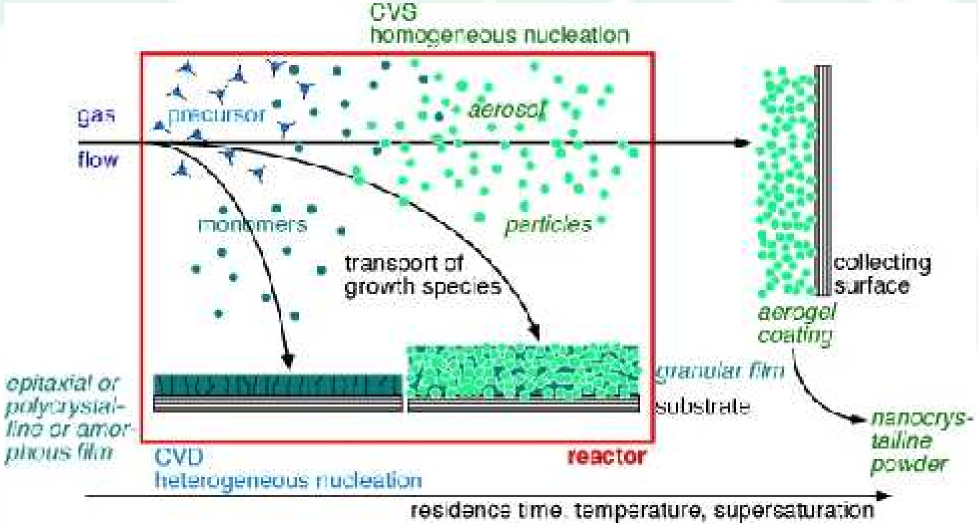
**Mechanical**
This is a ‘top-down’ method that reduces the size of particles by attrition, for example, ball milling or planetary grinding.

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

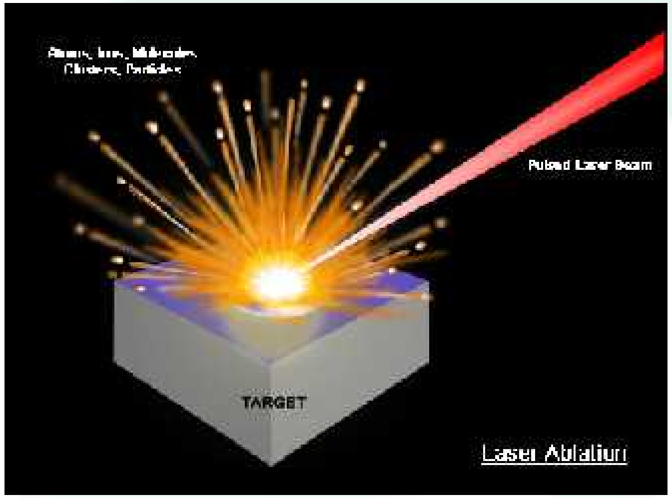
**Wet chemistry**
This is the range of techniques that are most applicable for characterization by light scattering techniques. These are fundamentally ‘bottom-up’ techniques, i.e. they start with ions or molecules and build these up into larger structures.

# Most nanomaterials are produced by chemical processes

**Chemical Vapor deposition**



**Laser ablation**



**Wet chemistry**

# Toolbox of Greener Techniques to make nanomaterials

Molten Salt or Ionic Liquid Synthesis

Self-assembly

Improved synthesis, fewer steps

Bottom up Manufacturing

Bio-inspired nanoscale synthesis

Use of non-toxic solvents like supercritical CO2

Aqueous processing

Microwave techniques

Renewables in Nanocomposites

Renewable starting materials

Photochemical synthesis

Solvothermal/hydrothermal Processes

Templating processes

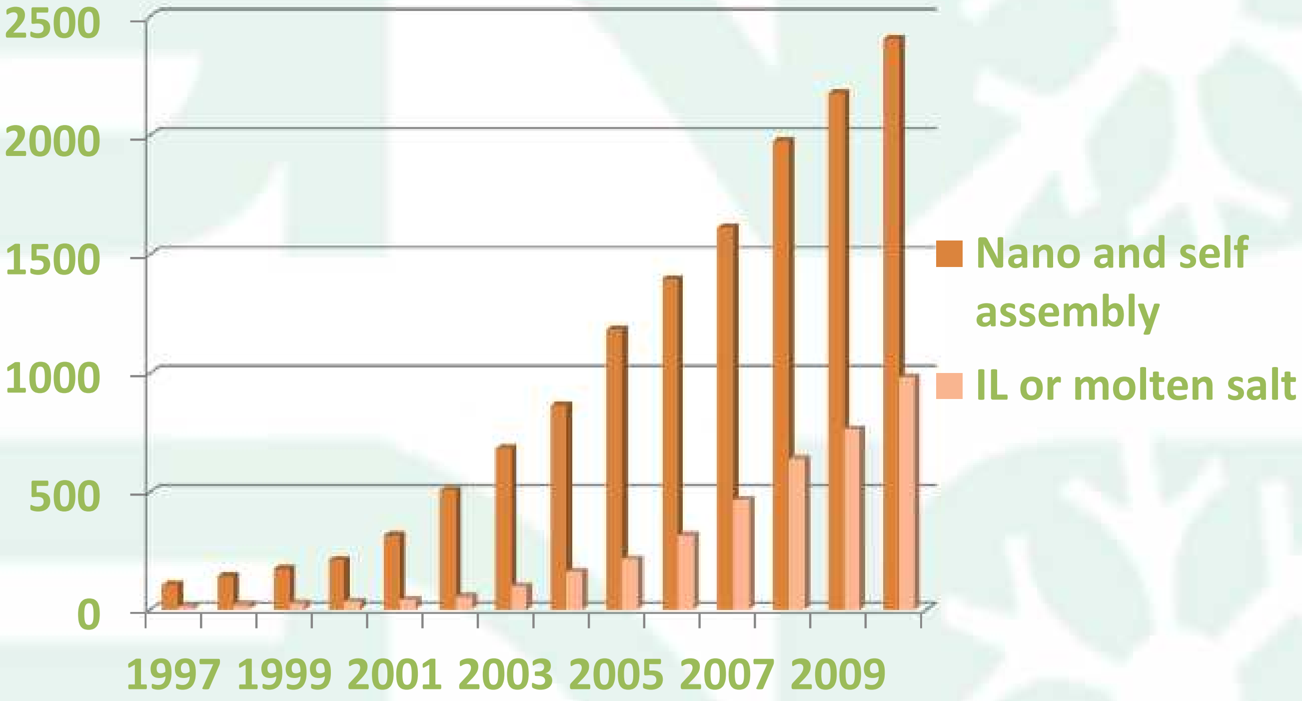
Non-toxic starting materials

Use of solid state/solventless processes

Nanocatalysis

# Growth in publications—2 green nano methods

2014:
SA 879
IL 1133

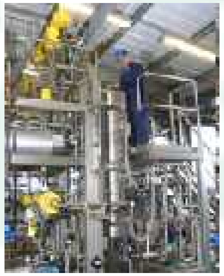


**Totals 1997 to 2014: 62,442 Self-assembly 68,089 IL/Molten salt**

# Green Nano Processes

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

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

# Greener processes via nanotechnology

Nano Membranes

- Separate out metals and byproducts
- Clean process solvents
- Product separations

Nano Catalysts

- Increased efficiency and *selectivity*

Process Energy

- More Efficient
- Lower use

# Presidential Green Chemistry Awards

- promote the environmental and economic benefits of developing and using novel green chemistry.
- recognize chemical technologies that incorporate the principles of green chemistry into chemical design, manufacture, and use.

**Alternative solvents**
**Biopolymers**
**Biotechnology**

**Carbon Dioxide as Solvent**

**Chemical Catalysts**
**Chemical Polymers**
**Genetic Engineering**
**Polymers**

**Renewable Resources**

**Safer Chemical Feedstocks**

**Safer Chemical Products**

**Solvents**

**Solvent-free Processes**

**Synthetic Processes**

**Use of Isolated Enzymes**

**Water as Solvent**

**Analysis**

GREEN
CHEMISTRY
A U.S. EPA Program

**Three Examples (from Presidential Green Chemistry Awards)**

# Sustainable nanomaterial synthesis in industry

2007 Headwaters Technology Innovation

2010 Dow BASF

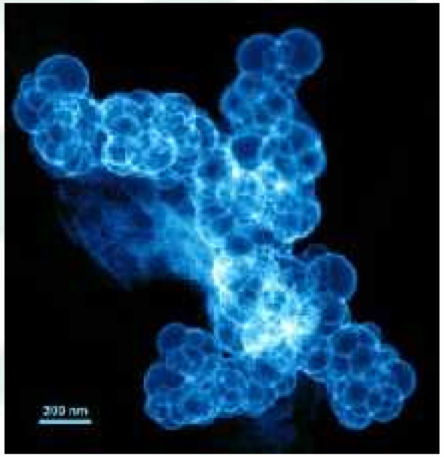
2014 QD Vision

# Headwaters Technology Innovation (2007)

The Problem :The existing manufacturing process for $H_2O_2$ is complex, expensive, and energy-intensive. This process requires an anthraquinone working solution containing several toxic chemicals

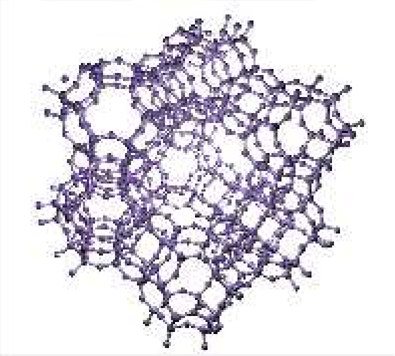
The Nano-solution: palladium-platinum catalyst that eliminates all the hazardous reaction conditions and chemicals of the existing process, along with its undesirable byproducts

The Award: Engineered a set of molecular templates and substrates that maintain control of the catalyst's crystal structure, particle size, composition, dispersion, and stability. This catalyst has a uniform 4-nanometer feature size that safely enables a high rate of production with a hydrogen gas concentration below 4 percent in air (i.e., below the flammability limit of hydrogen). It also maximizes the selectivity for $H_2O_2$ up to 100 percent.



The Outcome: Degussa AG commercial production 2009

# Dow and BASF (2010)



***Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide***

The Problem: Propylene oxide is one of the biggest volume industrial chemicals in the world. It is a chemical building block for a vast array of products including detergents, polyurethanes, de-icers, food additives, and personal care items. Its manufacture creates byproducts, including a significant amount of waste.

The Nano Solution: catalyst is a ZSM-5-type zeolite with channels of about 0.5 nm in diameter. In this catalyst, titanium replaces several percent of the silicon of the zeolite in a tetrahedral coordination environment.

The Award: high conversions of propylene and high selectivity for propylene oxide. Hydrogen peroxide is completely converted to product. In contrast with processes using organic peroxides, the HPPO process uses substantially less peroxide and eliminates the need to recycle peroxide. Production facilities are up to 25 percent cheaper to build because there is no need for equipment to collect and purify the coproduct.
The HPPO process also provides substantial environmental benefits. It reduces the production of wastewater by as much as 70–80 percent and the use of energy by 35 percent over traditional technologies.

The Outcome: Plants in 2008 and 2011

# QD Vision (2014)

The Problem: 150,000 liters (40,000 gallons) of highly toxic solvent per year and 100 kilograms of cadmium waste in production in the United States from QD production

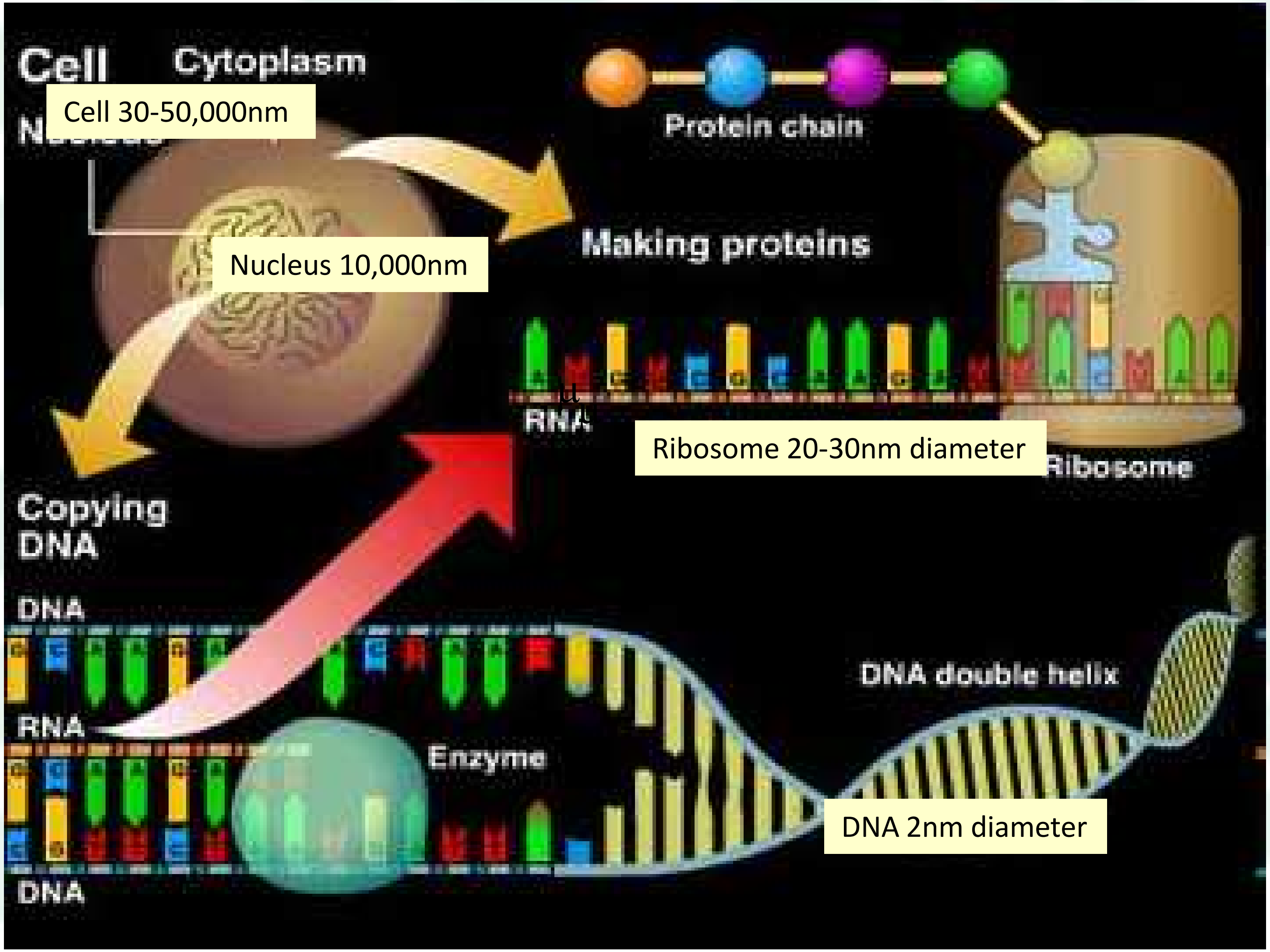
The Nano-Solution: Semiconductor nanocrystal quantum dot technology offers high-quality color to the solid-state lighting (LED light bulbs) and liquid-crystal display (TVs, mobile devices) markets with high system efficiency.

The Award: improvements by replacing alkyl phosphine- and alkyl phosphine oxide solvents with long-chain hydrocarbons, reducing both the hazard and amount of solvent used. They also replaced highly hazardous organo-cadmium and organo-zinc building blocks with less hazardous precursors. Finally, they improved their purification by switching from centrifugation to filtration saving time and energy, and reducing waste.

The Outcome: These quantum dots were the first to be implemented in mainstream commercial devices, including ten different models of Sony TVs in 2013. Using QD Vision Color IQ$^{TM}$ components in 20 million TVs (equivalent to roughly 10 percent market penetration) is projected to save 600,000,000 kilowatt-hours (kWh) of electricity per year worldwide—enough electricity to power 50,000 average U.S. homes. Although QD Vision quantum dots do still use cadmium, the amount of cadmium used in a device is less than the amount of cadmium emissions prevented through reduced electricity production, resulting in a net decrease in cadmium waste.

# The ultimate in sustainable nanosynthesis

Nanotechnology 1-100nm



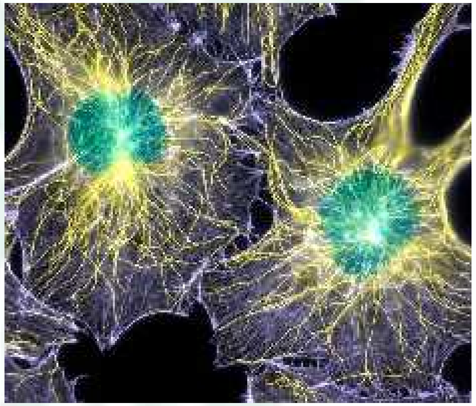
Cell 30-50,000nm

Nucleus 10,000nm

Ribosome 20-30nm diameter

DNA 2nm diameter

# 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

**Can nanotechnology emulate this process?**

**Ultimate green nano!**

So—

Why don't we practice green/sustainable synthesis??

Technical Barriers

Non-technical Barriers

# Technical Barriers

- Data gap:

Producers are not required to investigate and disclose sufficient information on the hazard traits of chemicals to government, the public, or businesses that use chemicals.

Need information on potential health and environmental hazards

Michael P. Wilson and Megan R. Schwarzman, EHP, 2009

# Technical Barriers

- Safety gap:

Government lacks the legal tools it needs to efficiently identify, prioritize, and take action to mitigate the potential health and environmental effects of hazardous chemicals.

Safety of chemicals for human health and the environment is undervalued relative to chemical function, price, and performance.

Michael P. Wilson and Megan R. Schwarzman, EHP, 2009h

# Technical Barriers

- Technology gap:

Industry and government have invested only marginally in green chemistry research, development, and education.

Need green chemistry research, development and education

Michael P. Wilson and Megan R. Schwarzman, EHP, 2009h

## Non-technical barriers

Switching to more sustainable processes, practices, and products often involves disruptive changes for a manufacturing plant

Within the context of conventional business practices, changes can be difficult to justify.

## Issues

higher upfront costs,

slow return on investment

limited incentives

inflexible regulations

customer demand that sustainable alternatives must also be superior to existing products

Satterfield et al, 2009

Classes of non-technical barriers:

(A) *Economic and Financial;

(B) *Regulatory: Environment, Health, Safety,and Product Quality;

(C) Educational: Students and Professionals;

(D) *Organizational and *Cultural.

Satterfield et al, 2009

Breaking down nontechnical barriers to sustainability:

- establish a clear, measurable, actionable, and universally accessible definition of sustainability;
- create and disseminate better information for better decision-making;
- reframe sustainability as an opportunity, investment, and pathway to innovation so it becomes a top priority;
- tear down silos within and among organizations and build cross functional teams
- develop forward-thinking, collaborative regulations or incentives that can adapt to changing circumstances.

Satterfield et al, 2009

Scientists and engineers have the knowledge to promote change and practice sustainable synthesis and processing of nanomaterials

Together, we can make nanotechnology sustainable and use it to reach sustainability of the future.

Thanks

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Abstract: The basis of nanotechnology is the manufacture, characterization and use of new nanomaterials with properties that replace, improve, or create useful products.  However, in order to be sustainable, these new materials must be made in sustainable ways—without generating the old pollutants, without using more energy, and without causing environmental impacts at any of their life stages. Research into the sustainable synthesis of nanomaterials is a beginning step into making the whole enterprise sustainable.  Less polluting means of synthesis such as using non-toxic solvents (e.g., supercritical CO2, water), self-assembly, microwave technologies, photochemical syntheses, renewable starting materials,  molten salts/ionic liquids, etc. are several ways in which nanomaterials can be made in a more sustainable manner.  This talk will track and discuss research in sustainable synthesis of nanomaterials and barriers to its use.