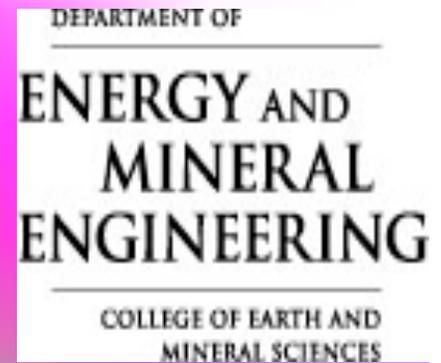


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# Engineered Nanomaterials for NASA: Managing Health and Safety Concerns (a user's perspective)

**Dr. Randy L. Vander Wal**

[www.psu.edu](http://www.psu.edu)

**Acknowledgements:**

**The 2009 NASA Occupational Health Meeting for the Invitation and Support**

**The NSC c/o OAI, July  
13-17<sup>th</sup>, Cleveland OH**

*"Even technophobes will enjoy this introduction to nanotechnology—it actually makes sense!"* —James Tour, Professor of Chemistry, Rice University

# Nanotechnology

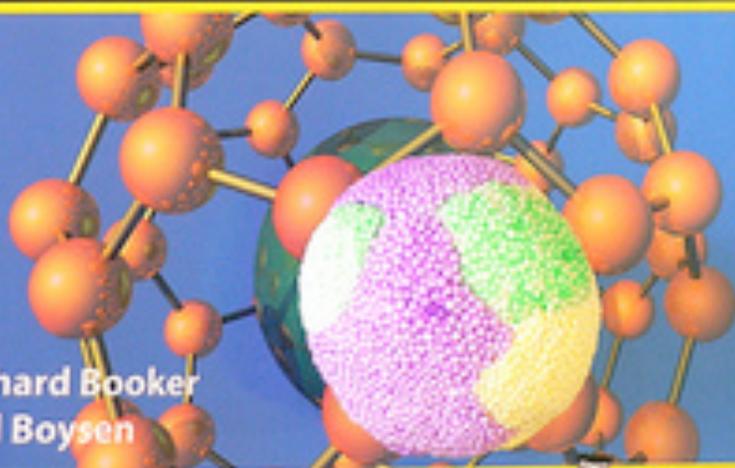
FOR

# DUMMIES

Richard Booker  
Earl Boysen

*A Reference for the Rest of Us!*

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## **Outline**

**I. Applications**

**II. Production**

**III. Illustrations of Engineered Nanomaterials**

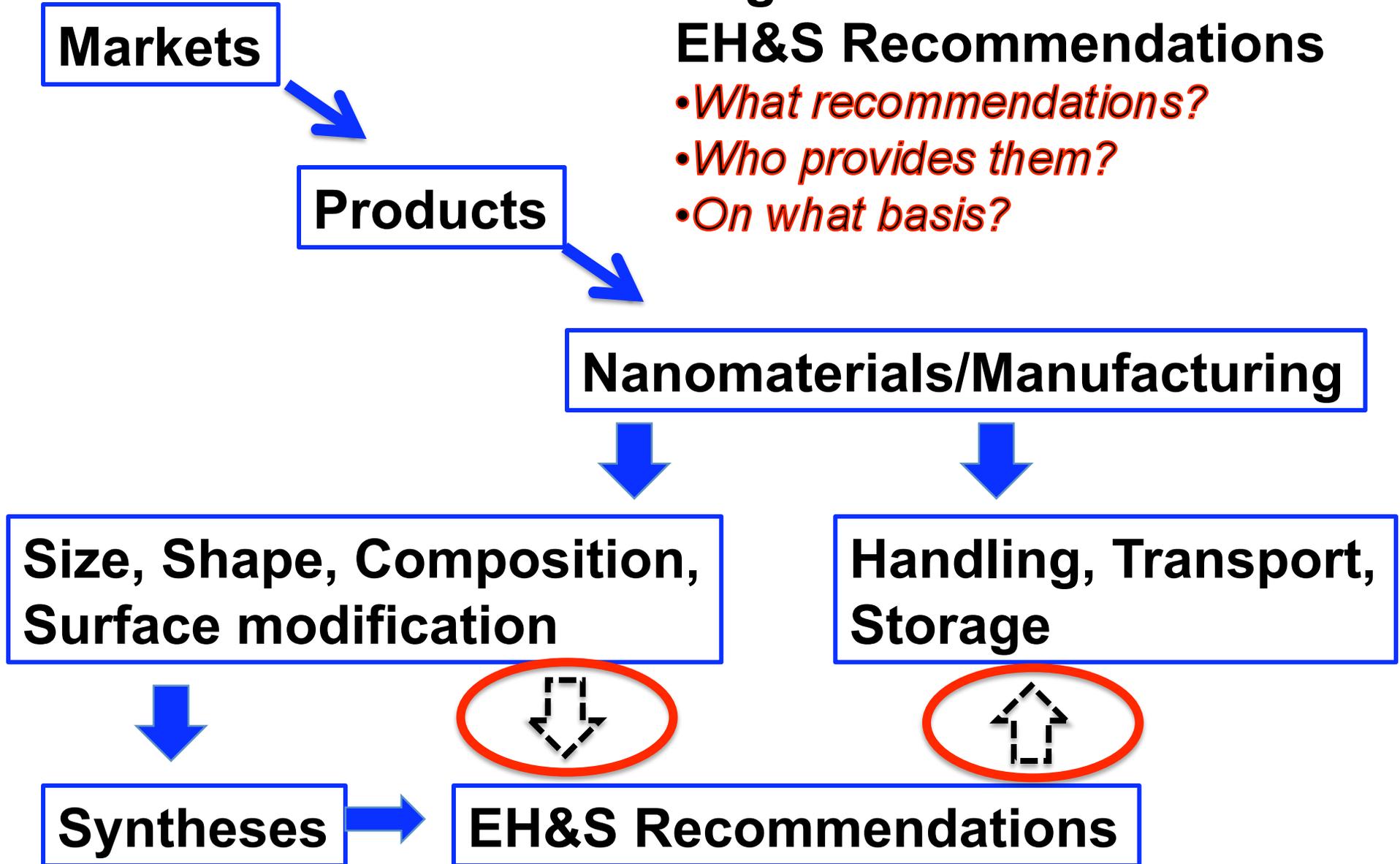
**IV. Status Overview – (present day headlines)**

**V. Managing Health and Safety Concerns**

**VI. Conclusions**

# Engineered Nanomaterials EH&S Recommendations

- *What recommendations?*
- *Who provides them?*
- *On what basis?*





**Dust mite**  
200  $\mu\text{m}$



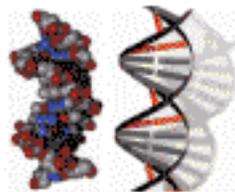
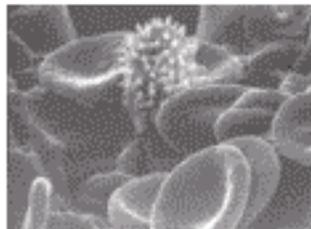
**Ant**  
 $\sim 5 \text{ mm}$



**Human hair**  
 $\sim 10\text{-}50 \mu\text{m}$   
wide

**Red blood cells with white cell**

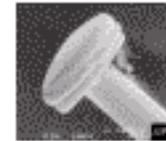
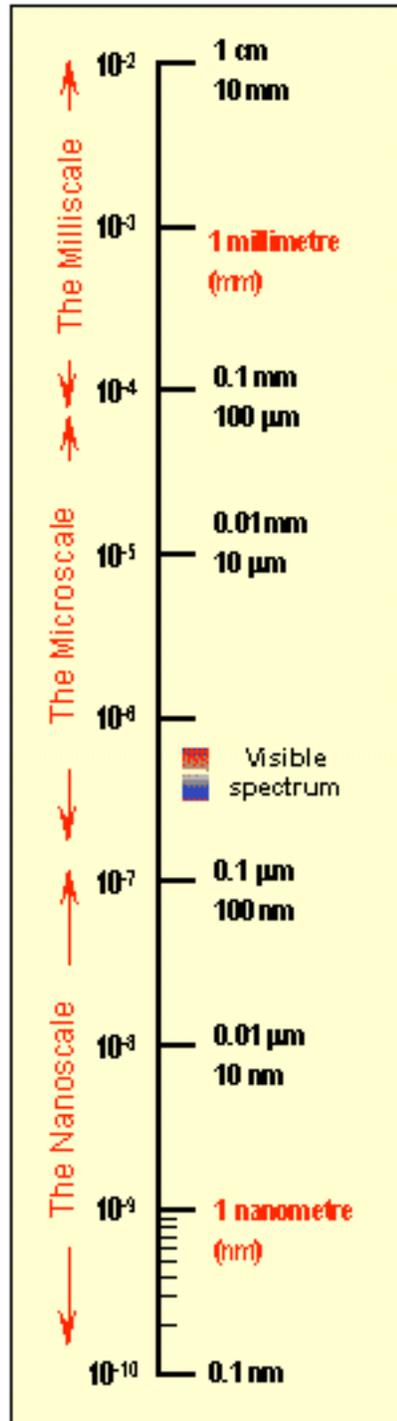
$\sim 2\text{-}5 \mu\text{m}$



**DNA**  
 $\sim 2\text{-}1/2 \text{ nm}$



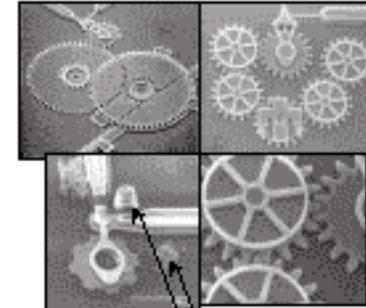
**5 Atoms of silicon**  
1 nm



**Head of a pin**  
1-2 mm

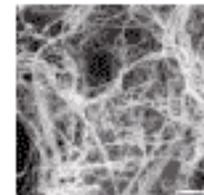
**Micro Electro Mechanical Devices**

10 -100  $\mu\text{m}$  wide



Pollen grain

Red blood cells



**Cellulose nanofibrils**  
20-100nm wide



**Stacks of clay mineral platelets, each platelet with  $\sim 1 \text{ nm}$  thickness**



**Carbon nanotube**  
 $\sim 2 \text{ nm}$  diameter

# NanoTech Markets

## Nanotechnology – Definition

Nanotechnology is the ability to measure, see, manipulate and manufacture things usually between 1 and 100 nanometers

e.g. a human hair is roughly 10,000 nanometers wide.

## Market Forecasts

In 2007, the global market for goods incorporating nanotechnology totaled \$147 billion.

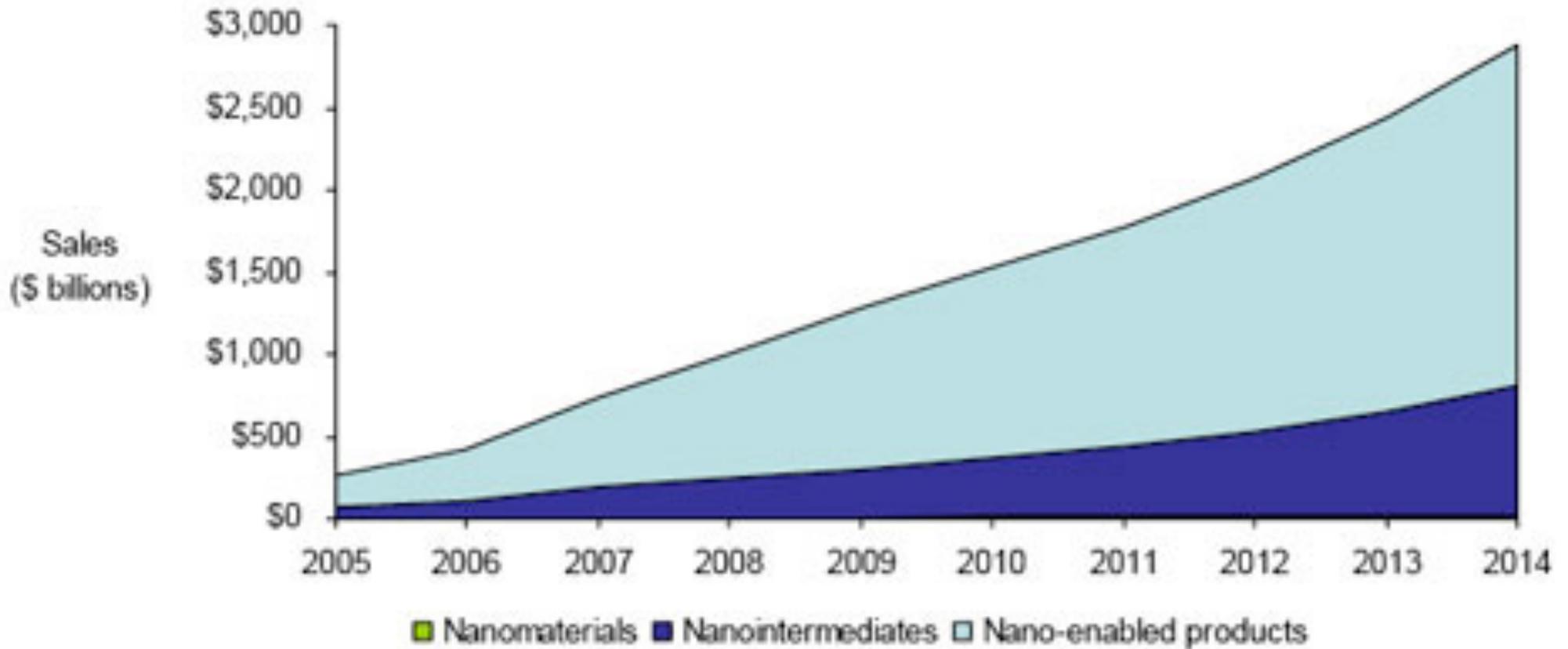
- \* Lux Research projects that figure will grow to \$3.1 trillion by 2015.
- \* National Science Foundation's (NSF) "\$1 trillion by 2015",

*Evolutionary or Revolutionary Nanotechnology?*

# Nanomaterials: Application Fields



# Nanomaterials: Markets



## **NanoTechnology for the Better**

### **Cheap and clean energy**

- ✓ Wind turbine blades
- ✓ Solar panels
- ✓ Battery technology

### **Clean Water**

- ✓ Purification
- ✓ Detection of impurities

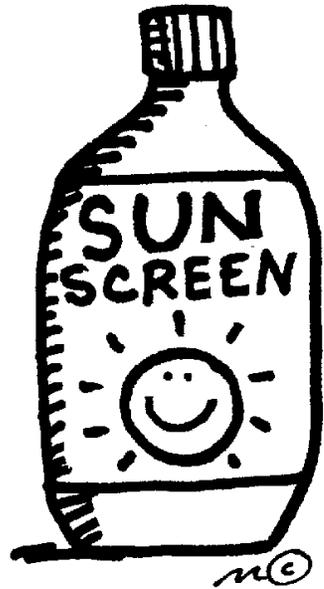
### **Pollution Reduction and Environmental Progress**

- ✓ Nanoscale Ag with antibacterial properties

### **Improved Materials and New Products**

- ✓ Baseball bats, tennis rackets &
- ✓ Thin films to make them water-repellent, anti-reflective, self-cleaning, ultraviolet or infrared-resistant, antifog, anti-microbial, scratch-resistant, or electrically conductive.

# Nanomaterials: Commercial Products

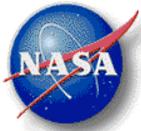


EED 9000 X

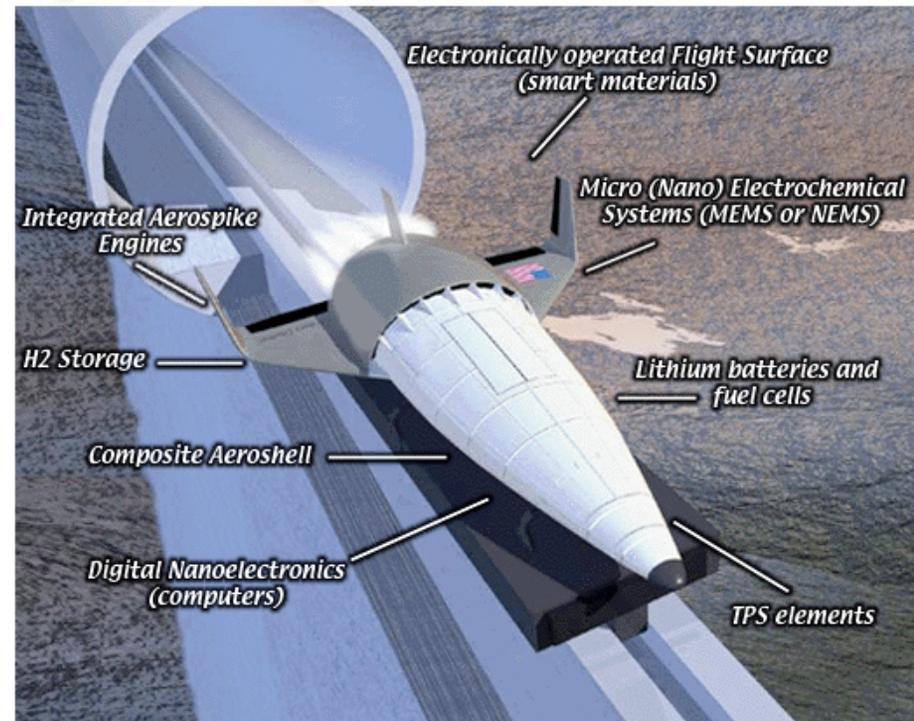


## ***Nanomaterial Enabled Technologies***

Area	Under Development	In Market	Well-Established
<b>Power/Energy</b>	<p>Nanocrystalline Ni and Metal hydrides for batteries</p> <ul style="list-style-type: none"> <li>* Dye sensitized solar cells</li> <li>* Anode/Cathode materials for fuel cells</li> <li>* Thermal control fluids</li> </ul>	<p>Environmental Catalysts</p> <p>Diesel additives</p>	<p>Automotive catalysts</p>
<b>Healthcare/medical</b>	<ul style="list-style-type: none"> <li>* Drug delivery</li> <li>Inhalable drugs</li> <li>* Bone growth promoters</li> </ul> <p>Virus detection</p> <p>Anticancer treatments</p> <p>Coatings for implants</p>	<p>Sunscreens using ZnO, TiO<sub>2</sub></p> <p>Molecular tagging</p> <p>Quantum dots</p> <p>Drug carriers</p>	<p>Ag antibacterial wound dressings</p> <p>ZnO fungicide</p> <p>Au for biolabelling and detection</p> <p>MRI contrast agents</p>



## *Faster, Better, Cheaper Space Transportation with Nanotubes*



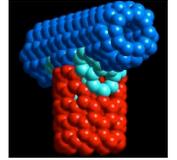
### **NASA Nanotechnology Goals**

1. Mass reduction and miniaturization,
2. Robotic exploration of the solar system
3. Small economical spacecraft with high autonomy and improved capabilities.
4. Medical diagnostics and therapy procedures for life support systems

*Long-term and more complex manned space missions*



# NASA Nanotechnology Program Content



- Nanotechnology Program Elements
  - Nanoelectronics and Computing
  - Sensors
  - Structural Materials

## Nanoelectronics and Computing

- Molecular electronics & photonics
- Computing architecture
- Assembly

## Sensors

- Life detection
- Crew health & safety
- Vehicle health

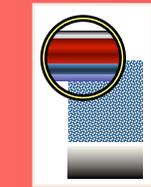
## Structural Materials

- Composites
- Multifunctional materials
- Self healing

# NASA Nanotechnology Roadmap

## C A P A B I L I T Y

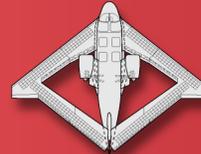
### Multi-Functional Materials



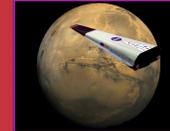
**High Strength Materials**  
( $>10$  GPa)



**Reusable Launch Vehicle** (20% less mass, 20% less noise)



**Revolutionary Aircraft Concepts**  
(30% less mass, 20% less emission, 25% increased range)



**Autonomous Spacecraft**  
(40% less mass)

**Bio-Inspired Materials and Processes**



**Adaptive**

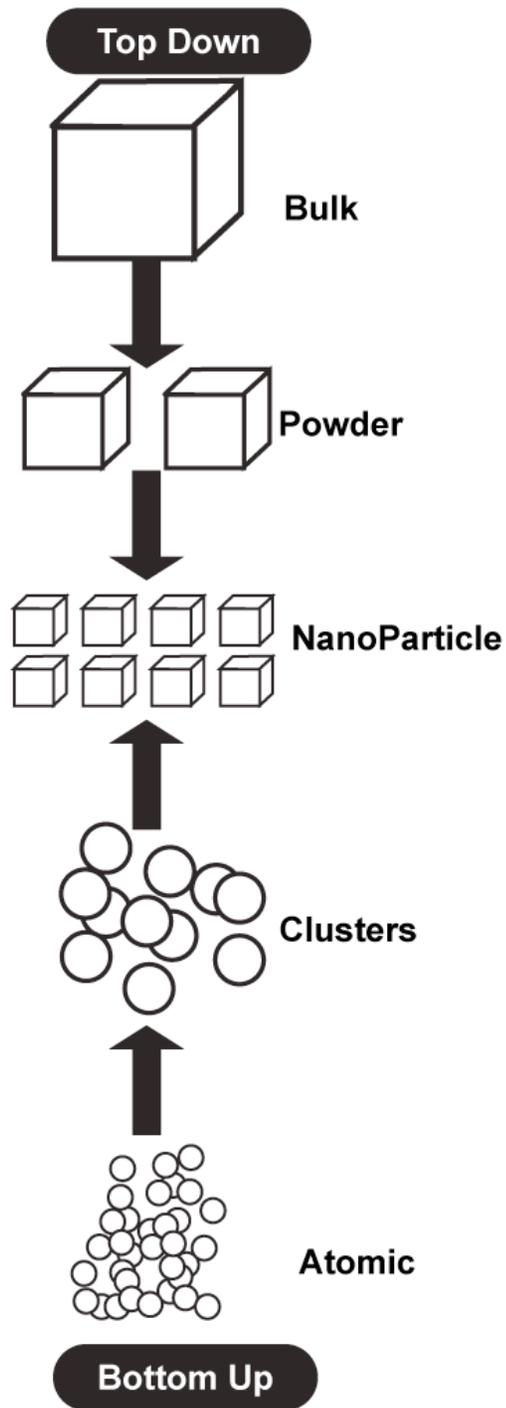
**Self-Repairing Space Missions**



Increasing levels of system design and integration →

	2002	2004	2006	2011	2016
<b>Materials</b>	• Single-walled nanotube fibers	• Nanotube composites	• Integral thermal/shape control	• Smart "skin" materials	• Biomimetic material systems
<b>Electronics/computing</b>	• Low-Power CNT electronic components	• Molecular computing/data storage	• Fault/radiation tolerant electronics	• Nano electronic "brain" for space Exploration	• Biological computing
<b>Sensors, s/c components</b>	• In-space nanoprobes	• Nano flight system components	• Quantum navigation sensors	• Integrated nanosensor systems	• NEMS flight systems @ $1 \mu\text{W}$

# Nanomaterial Synthesis Approaches



## Top Down Methods

Mechanical Grinding

Erosion

## Bottom Up Methods

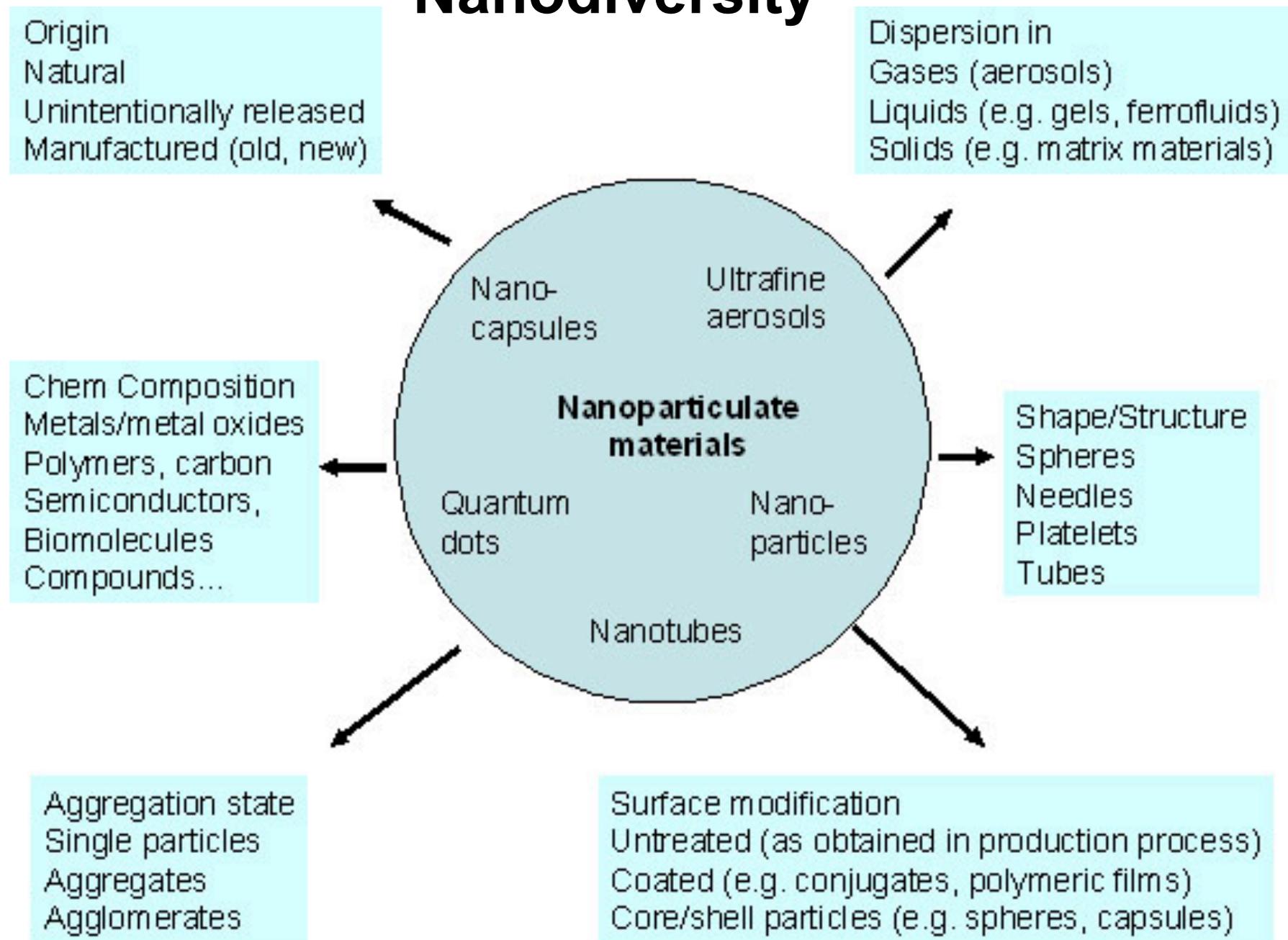
Aerosol Techniques

Chemical Precipitation

Gas Phase Agglomeration

Self Assembly

# Nanodiversity



# Nanotech Safety

***NRC report blasts federal research strategy for addressing risks of nanomaterials***

**[Britt E. Erickson](#)**

**THE FEDERAL GOVERNMENT'S** research plan for assessing the potential environmental, health, and safety (EHS) risks of nanomaterials is **inadequate**, concludes a new report from the **National Research Council**.

**Nanotech safety high on Congress' priority list**

***New House bill addresses need for more risk research, oversight***

Washington, DC – The House Science and Technology Committee today introduced legislation that highlights the growing attention on Capitol Hill to the need to strengthen federal efforts to learn more about the potential environmental, health and safety (EHS) risks posed by engineered nanomaterials. *January 2009*

# Nanotech Safety

## 1. Warheit et al. Dupont, 2003

- \* Administered a bolus via intratracheal instillation of CNTs in buffered saline solution
- \* Rats died within minutes of injection

(Toxicity of CNTs or Suffocation?)

## 2. Donaldson et al. University of Edinburgh, 2007

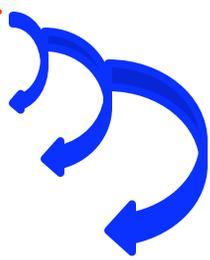
- \* SWNTs injected into the peritoneal cavity of mice invoked an immune reaction with inflammation and lesions developing (failed phagocytosis).
- \* Used 0.5% wt. of BAL to maintain suspended CNTs
- \* Study only lasted 7 days.

# Nanotech Safety

*Nanocarbons – a partial listing:*

*SWNTs, DWNTs, MWNTs, Nanofibers, Micro-coils, Nano-onions, Fullerenes, Nanohorns, Graphene, Carbon dots, Nano-diamonds*

## ***Related Issues:***

- 1. Metallic impurities*
  - 2. Functional groups*
  - 3. Disordered carbon*
  - 4. Varied lengths*
  - 5. Dispersing agents*
- 

*Purity of CNTs – size, type, composition and morphology*

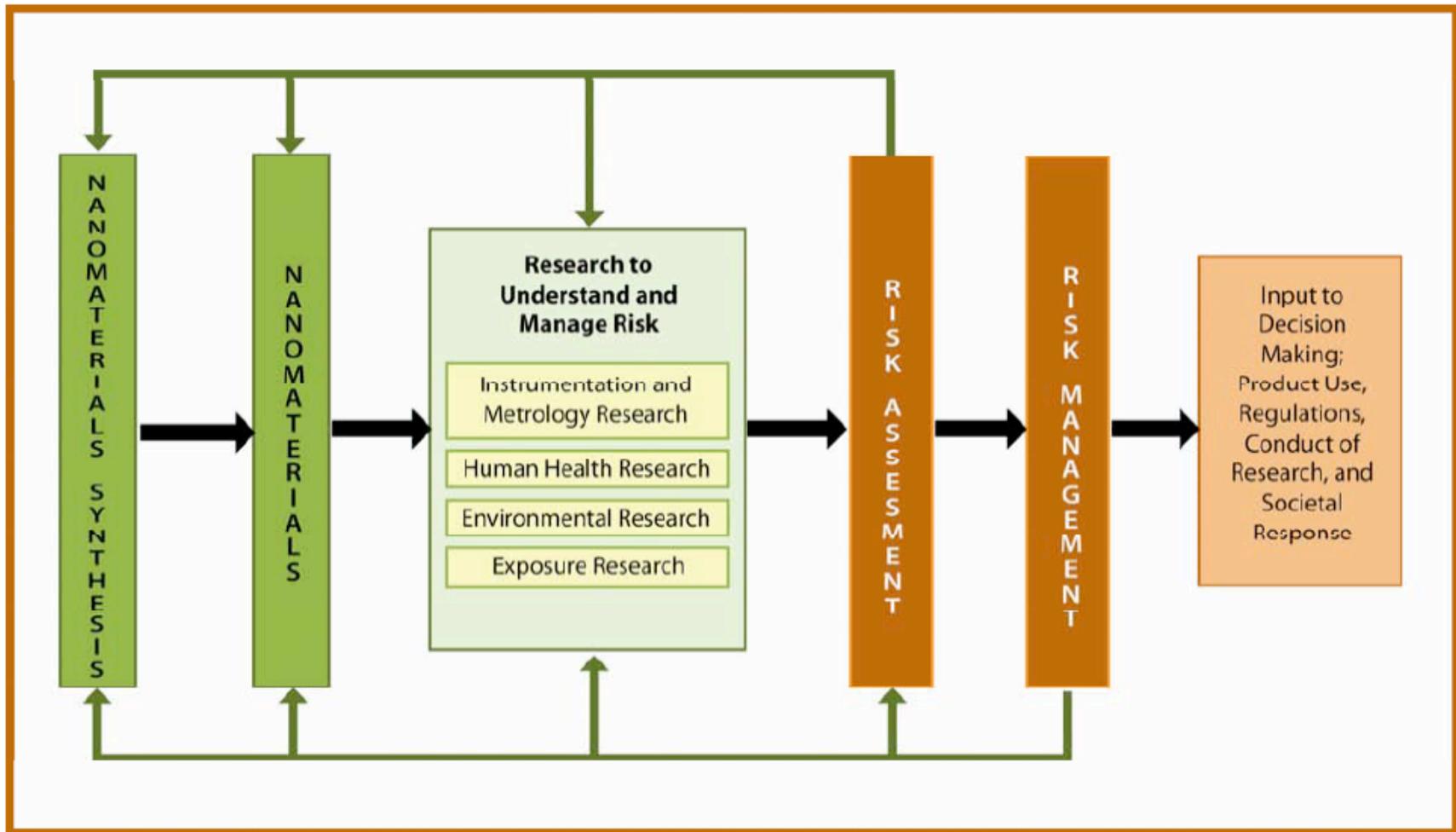
# Present Day Status – EH&S

- Non-governmental initiatives such as the [GoodNanoGuide](#) and the [ResponsibleNanoCode](#) are helping businesses address nanomaterial safety.
- **But there is an absence of standards and toxicology results vary widely.**
- Agency requests for voluntary information largely have failed, e.g. Canada, & U.S. Potential in Europe to require mandatory reporting for > 1 kg quantities.
- On 29 June, the EPA tightened its regulatory oversight on specific types of carbon nanotubes.

*How to predict and manage the potential risks associated with existing nanomaterials?*

“Get this right, and consumers and industry stand to gain from the development of safe, sustainable new technologies. But get it wrong, and everyone is likely to lose out.” (*Nature* **460**, 174, published online 9 July 2009).

# Role of Nanotechnology EHS Research in Risk Management of Nanomaterials



Source: The National Nanotechnology Initiative

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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- ❖ Engineered nanoparticles: one dimension between 1 and 100 nanometers.
- ❖ Unique physical and chemical properties
- ❖ Little is known about effects on human health.
- ❖ Research has shown physicochemical including particle size, shape, surface area, charge, chemical properties, solubility, oxidant generation potential, and degree of agglomeration have biological consequences.

*Until the results from research studies can identify characteristics posing health risks, precautionary measures are warranted.*

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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## Research Results to-date

- ◆ Uptake via respiratory system, skin contact or ingestion
- ◆ Nanoparticles can enter the blood stream, and translocate to other organs.
- ◆ Equivalent mass doses of nanoparticles are more potent than large particles *in causing pulmonary in-flammation and lung tumors.*
- ◆ Composition, crystal structure and size of particles can influence their oxidant generation properties and cytotoxicity.

*Research is needed to determine the key physical and chemical characteristics of nanoparticles that determine their hazard potential.*

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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## **Working with Nanomaterials - Exposure routes**

- Working with nanomaterials in liquids during pouring or mixing operations, or where a high degree of agitation is involved without adequate protection (e.g., gloves)
- Generating nanoparticles in non-enclosed systems
- Handling (e.g., weighing, blending, spraying) powders of nanomaterials
- Maintenance on equipment and processes used to produce or fabricate nanomaterials
- Cleaning up spills, waste material & dust collection systems used to capture nanoparticles
- Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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## Exposure Assessment and Characterization

- *Until more information becomes available* (on the mechanisms underlying nanomaterial toxicity), it is uncertain what measurement technique should be used to monitor exposures in the workplace.
- Mass and bulk chemistry may be less important than particle size and shape, surface area, and surface chemistry (or activity) for some nanostructured materials.
- Current airborne nano-aerosol measurement techniques
  - \* vary in complexity
  - \* *can provide* useful information for evaluating occupational exposures
  - \* *yet fail* to provide a comprehensive characterization with respect to particle size, mass, surface area, number concentration, and composition
  - \* *few* of these techniques are readily applicable to routine exposure monitoring.

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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## Precautionary Measures – To minimize exposure

- 1) Evaluate the hazard based on available physical and chemical property data, toxicology, or health-effects data
- 2) Assess the potential for exposure
- 3) Education and training in proper handling of nanomaterials (e.g., good work practices)
- 4) Establish criteria and procedures for installing and evaluating engineering controls (e.g., exhaust ventilation).
- 5) Systematically evaluating exposure potential to ensure that control measures are working

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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## Precautionary Measures – To minimize exposure

- ✓ *Who is responsible? (for evaluating, educating, establishing....*
- ✓ *Are they qualified?*
- ✓ *What are the metrics?*
- ✓ *Are there related hazards?*
- ✓ *If time and/or money are inadequate, then what?*

***Are the hazards associated with raw materials, synthesis, storage, handling, transport or processing?***

# Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

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## **Risk Mitigation - Control Measures for Preventing Exposure**

Presently: No guidelines on clothing or other ap-parel (e.g., gloves) *but reasonable lab attire!*

Future: Procedures for selecting proper personal protective equipment (e.g., clothing, gloves, respi-rators).

✓ Implement engineering control techniques:

- source enclosures
- local exhaust ventilation systems
- HEPA filters should effectively re-move nanomaterials.

✓ Good work practices can help to minimize worker exposures to nanomaterials.

- cleaning of work areas using HEPA vacuum pickup, wet wiping
- no consumption of food or beverages in workplaces where
- nanomaterials are handled, providing facilities for hand-washing
- showering and changing clothes

*Safe Handling?* **Common Sense!**



## *Unwarranted Fear?*



Flickr: brainsluice

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***Comments  
Suggestions  
Welcomed!***

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# Post-script: NanoTech Safety – Perspective

\* Chemists & Biologists have dealt with naturally occurring nanoparticles all along.

e.g. molecules or viruses.

\* Toxicologists have dealt with nanoparticles, e.g. carbon particles in combustion engine exhaust

\* Tire manufacturers used nanoparticles, carbon black, to improve the performance of tires as early as the 1920s.

\* Medieval artists used gold nanoparticles to achieve the bright red color in church windows (gold particles in nanometer size are red, not golden).

*We are surrounded by, and made of, nanostructures – atoms and molecules are nanoscale.*

*So what is all the fuss about, and where do the risk issues come from all of a sudden?*