March 28, 2011
DoD Environmental Monitoring and Data Quality (EMDQ) Workshop

Introduction to Nanotechnology
for Defense Environment, Health & Safety (EHS) and Research Professionals in Support of the Acquisition Process

Carole A. LeBlanc, Ph.D.
Chemical and Material Risk Management (CMRM) Directorate
Office of the Deputy Under Secretary of Defense for Installations and Environment
Tel.: 703-604-1934   For DoD EHS 'Nano' Work Group information   Email: carole.leblanc@osd.mil

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **28 MAR 2011**	2. REPORT TYPE	3. DATES COVERED **00-00-2011 to 00-00-2011**

4. TITLE AND SUBTITLE **Introduction to Nanotechnology for Defense Environment, Health & Safety (EHS) and Research Professionals in Support of the Acquisition Process**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Office of the Deputy Under Secretary of Defense (Installations & Environment),Chemical and Material Risk Management Directorate,3400 Defense Pentagon, Room 3B856A,Washington,DC,20301-3400**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the 2011 DoD Environmental Monitoring & Data Quality Workshop (EMDQ 2011), 28 Mar ? 1 Apr, Arlington, VA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**29**	

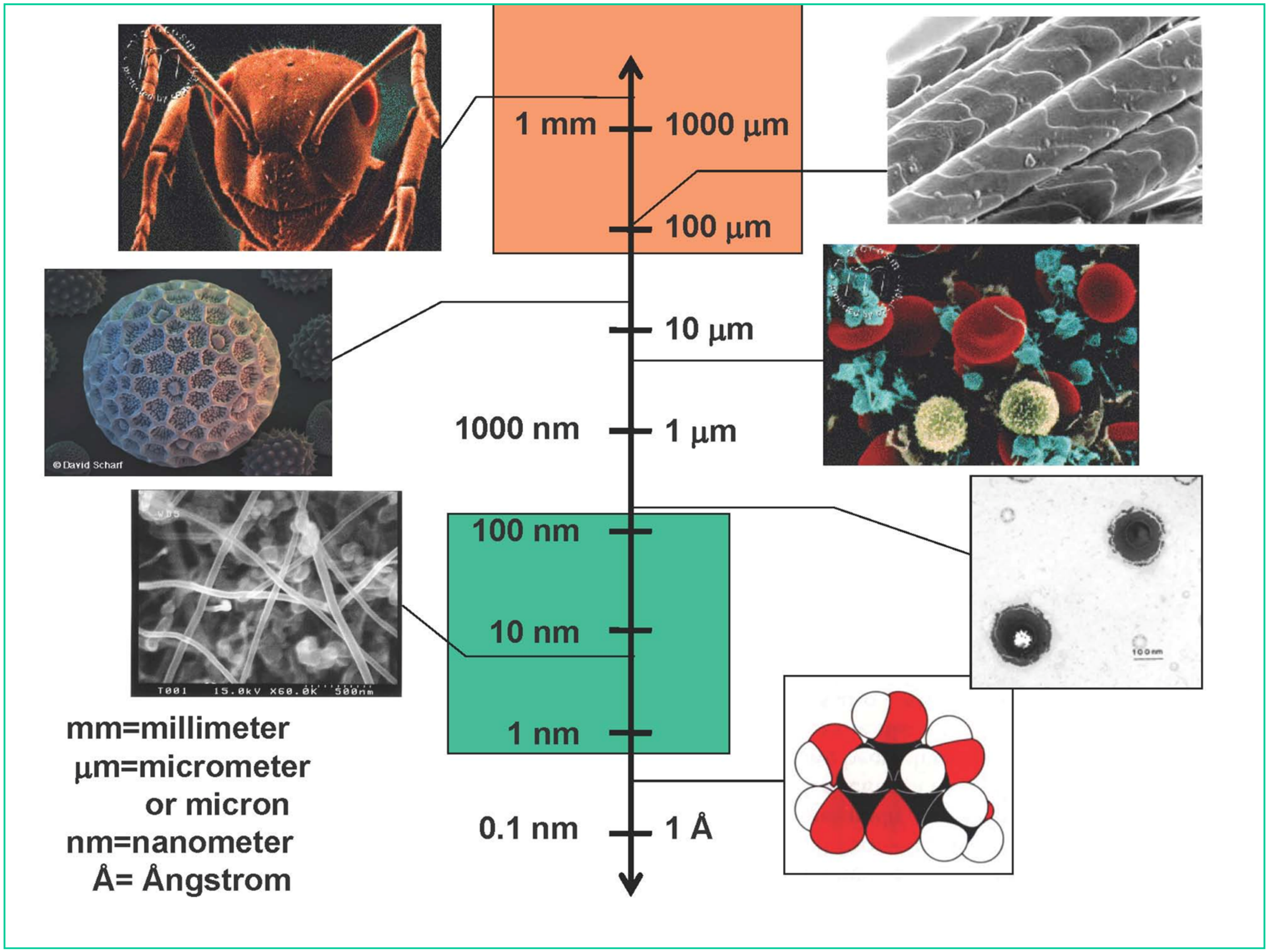
Nanotechnology 101
Course Outline

- **Overview of DoD CMRM**
- **Introduction to Nanotechnology (this briefing)**
  - Includes the status of local, federal and international regulation
    - » What science and technology (S&T) and acquisition specialists need to know
- **Plan: National Nanotechnology Initiative (NNI) 2011 EHS Research Strategy**
- **Practice: The Defense Mission and Nanomaterials**
  - EHS Research Case Studies from Subject Matter Experts (SMEs) throughout the Services and CMRM update on nanomaterials
    - » Problem statement
    - » Research goals and objectives
    - » Results and observations
    - » Conclusions
      - Future research needs
    - » Additional resources, references, etc.

Some 'Wiki-like' Definitions
For educational purposes only

- Nanotechnology **('nanotech') is the study of manipulating matter on an atomic and molecular scale. In general, nanotechnology deals with structures sized between 1 to 100 nanometers (nm), i.e., at the 'nanoscale' in at least one dimension, and involves developing materials or devices within that size. Quantum mechanical effects are very important at this scale.**
- Nanoengineering **is the *practice of engineering at the nanoscale*.**
- Nanomaterials **is the field that takes a materials science-based approach to nanotechnology. It studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions such as large surface area.**

How Small Is Small?
Very Small!

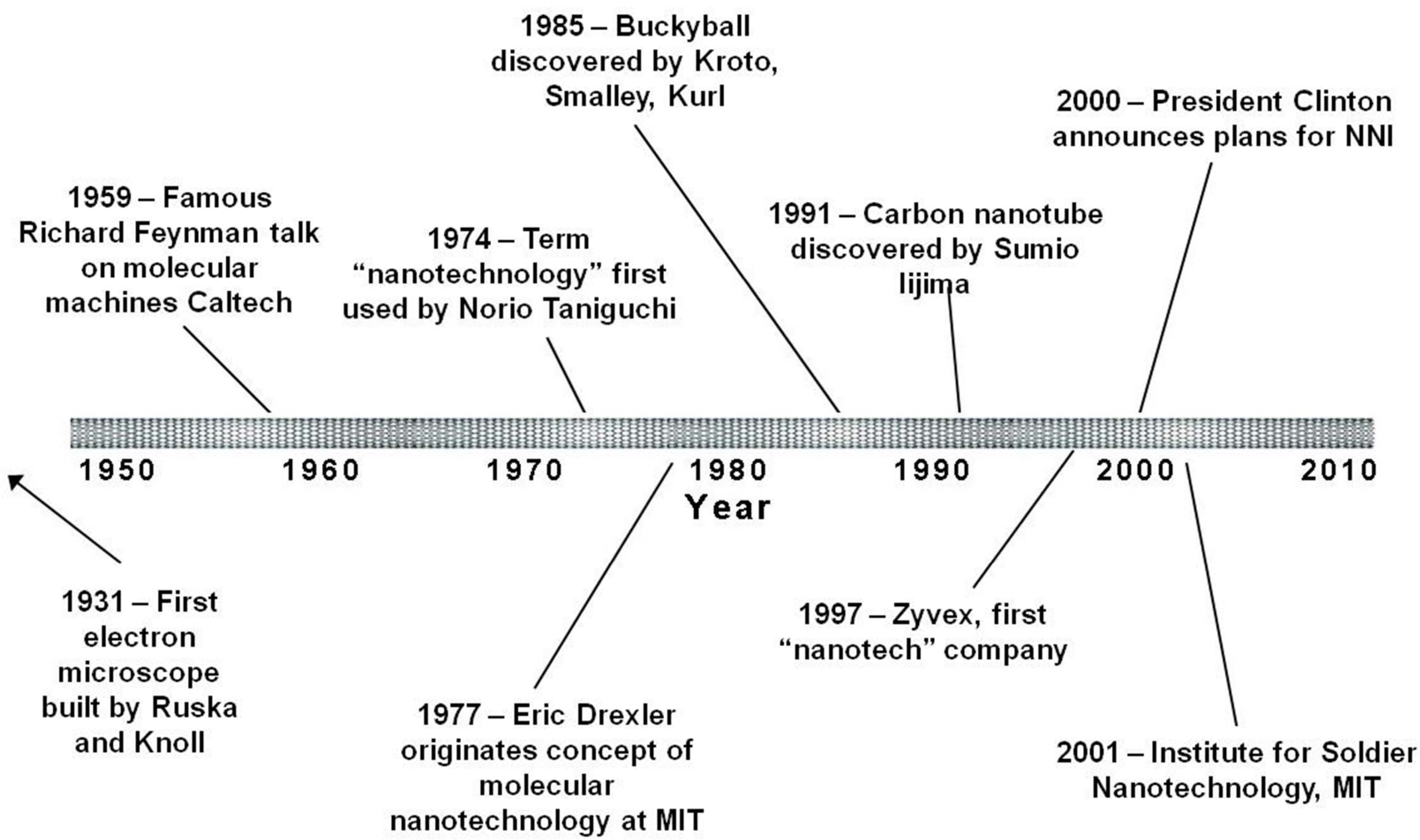


George Whitesides, Chemistry and Chemical Biology Department, Harvard University, Cambridge, MA

History of Nanotechnology
Not actually a 'new' science

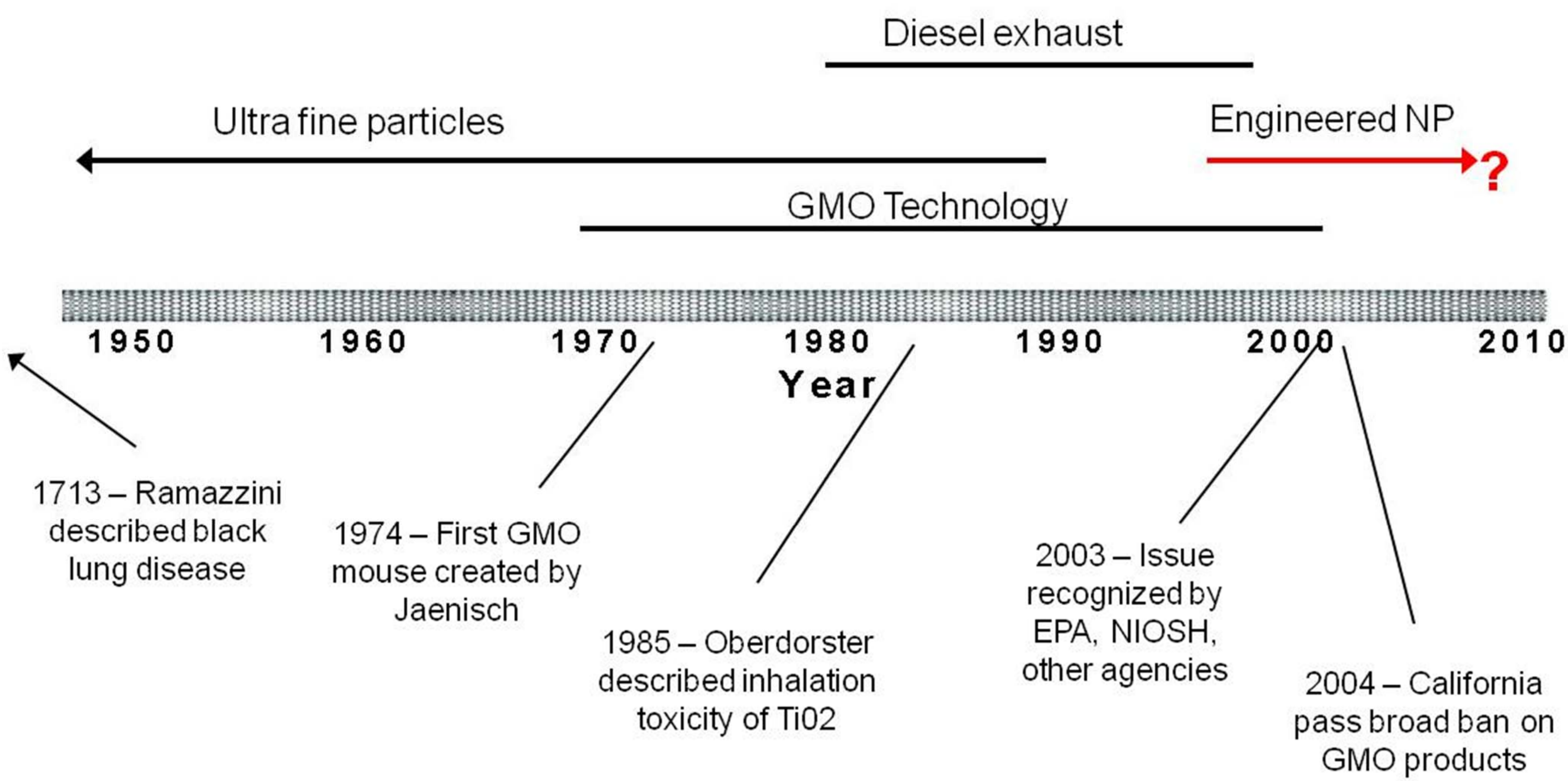
- **Concept in, *"There's Plenty of Room at the Bottom,"* a talk given by Richard Feynman, American Physical Society, Caltech, 1959**
  - Gravity would become <u>less</u> important, *and*
  - Surface tension and van der Waals attraction would become <u>more</u> important
- **Term first defined by Norio Taniguchi, Tokyo Science University, 1974**
  - Further refined by K. Eric Drexler by 1986 in his books
    - » **Engines of Creation: The Coming Era of Nanotechnology**
    - » **Nanosystems: Molecular Machinery, Manufacturing, and Computation**

Development of Nanotechnology



www.foresight.org

History and Development of Nanotoxicology



Courtesy of Jeff Steevens, ACoE

Growing Body of EHS Research
Far-reaching implications or singular exceptions?

- **Nanoparticles induced skin aging in mice through oxidative stress (Chinese study, 2009)**
- **Nano-titanium dioxide (TiO_2) consumed by mice *linked to* DNA and chromosome damage (two-year UCLA School of Public Health study)**
- **Some forms of carbon nanotubes may be as harmful as asbestos, *if inhaled in sufficient quantities* (major study published in Nature Nanotechnology)**

Consequences and Concerns
A few examples

INTENDED CONSEQUENCES	POTENTIAL UNINTENDED CONSEQUENCES
Passing through the blood brain barrier or placenta	Passing through the blood brain barrier or placenta
In vivo drug delivery	Interference with other biological pathways (for example, enzymatic activity)
Bioremediation (only one illustration of an intended environmental release)	Little understood fate and transport mechanisms could lead to deleterious ‘sinks’ and cumulative effects
Antimicrobial activity	Inability to differentiate between beneficial and harmful bacteria

WE STILL DON’T KNOW WHAT WE DON’T KNOW.

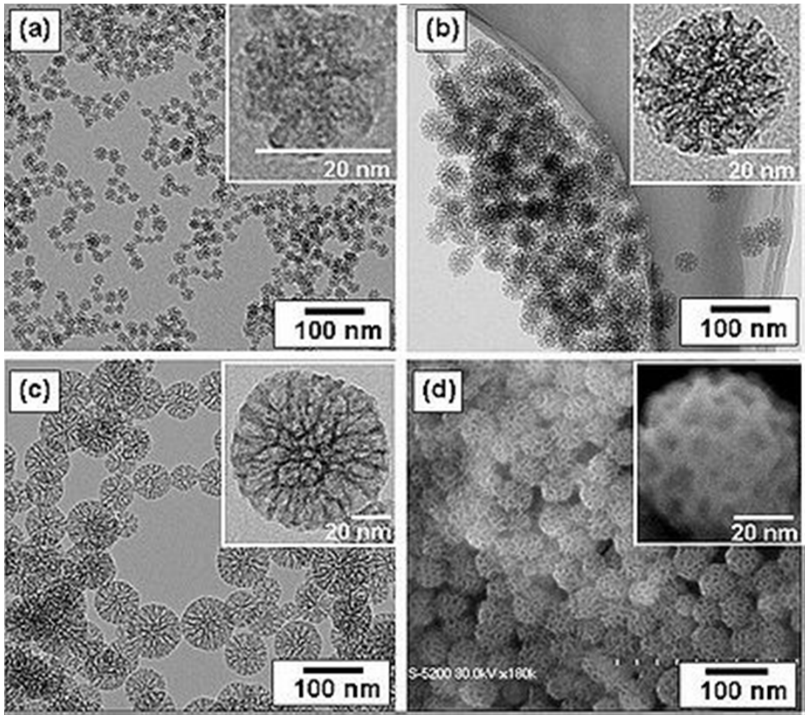
Kinds of Nanomaterials

- Nanoparticles
- Fullerenes
- Nanotubes

A researcher harvests single-walled nanotubes from a carbon arc reactor. Source: National Nanotechnology Initiative 2011 EHS Research Strategy.

Nanoparticles
Used as powders, in sol gel, colloids, etc.

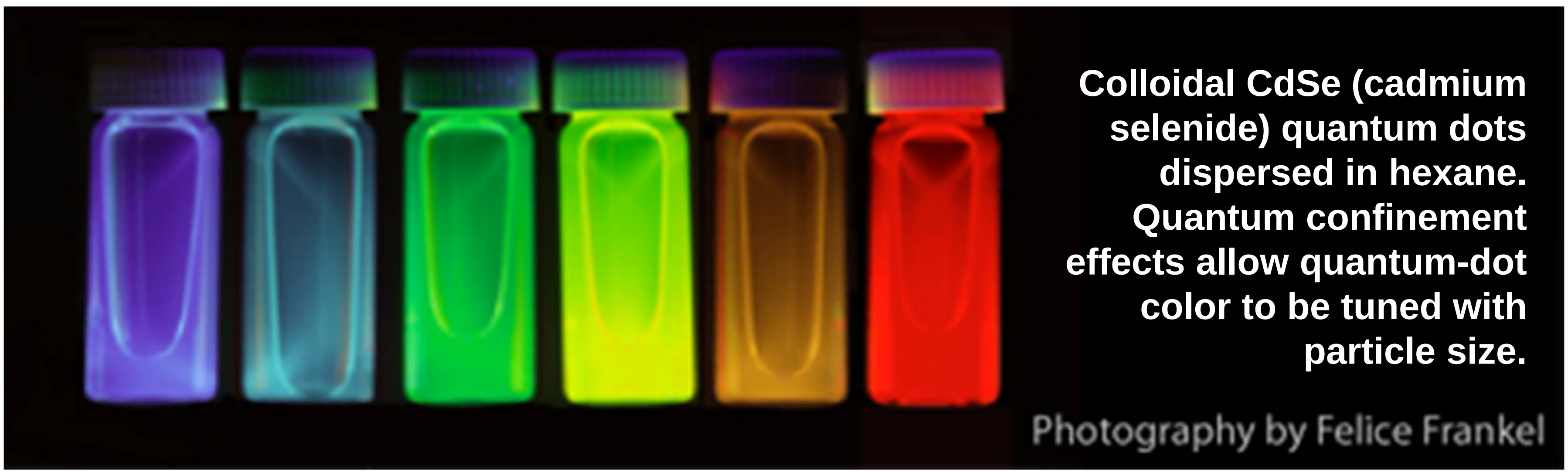
- **Properties exploited by artists as early as the 9th century**
  - 'Glitter' paint
- **Synthesis**
  - **Attrition**
    - » Macro- or micro-scale particles are ground in a ball mill or other reducing mechanism
  - **Pyrolysis**
    - » A vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned
  - **Thermal plasma**
    - » Delivers the energy necessary to cause evaporation of the mm-size particles
- **Modern applications involve quality control (QC) issues of uniformity and agglomeration**



Microscopic images of mesoporous silica nanoparticles of various diameters.

Unique Properties of Nanoparticles

MACROSCALE PROPERTY		NANOSCALE PROPERTY	
Aluminum:	Stable	Aluminum:	Combustible
Copper:	Opaque	Copper:	Transparent
Gold:	Insoluble	Gold:	Soluble

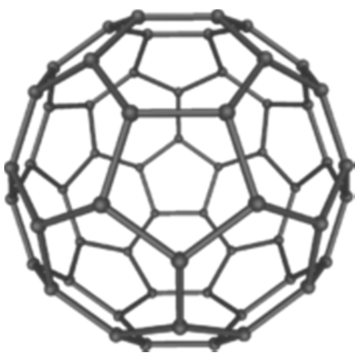


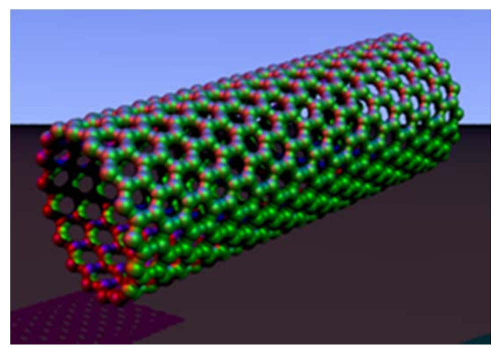
Colloidal CdSe (cadmium selenide) quantum dots dispersed in hexane. Quantum confinement effects allow quantum-dot color to be tuned with particle size.

Courtesy of scientist doing work for the Army as part of the Institute for Soldier Nanotechnology (ISN), Massachusetts Institute of Technology

Fullerenes

- **A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube**
  - Spherical fullerenes are called **buckyballs**
  - Cylindrical fullerenes are called **nanotubes**





Buckminsterfullerene C_{60} **Carbon nanotube**

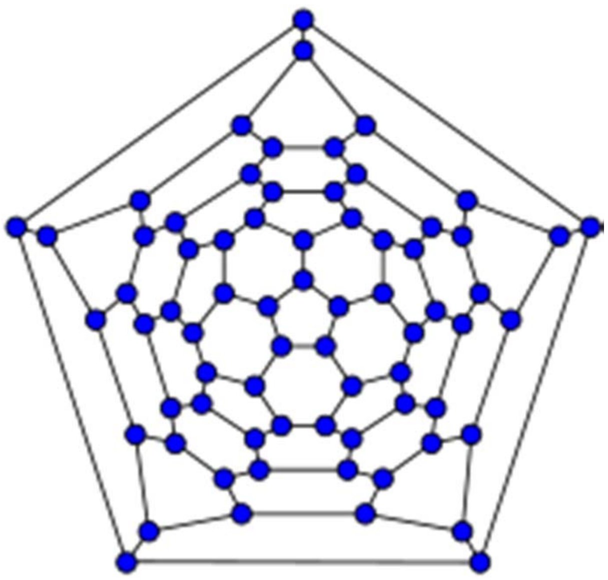
smallest fullerene molecule in which no two pentagons share an edge (occurs naturally in soot)

Scientific Discovery
Of the fullerene

- **Predicted by Eiji Osawa of Toyohashi University of Technology, 1970**
- **Prepared by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University, 1985**
  - Named in honor of Buckminster Fuller, whose geodesic dome designs (soccer/volleyball-like) it resembled
  - Curl, Kroto and Smalley received Nobel Prize in Chemistry for discovery of fullerenes, 1996
    - » **Smalley's work partially funded by Army Research Organization**
- **Detected recently in outer space**
  - According to at least one astronomer, "It's possible that buckyballs from outer space provided seeds for life on Earth."

Many Sizes/Configurations
Of fullerenes possible

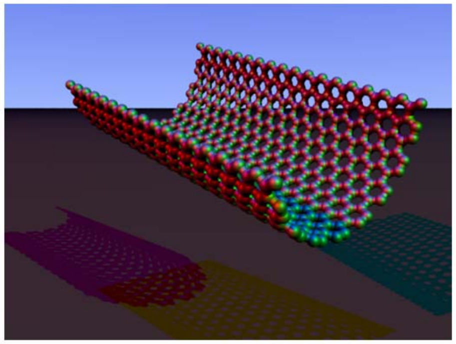
- Another common fullerine is C_{70}
- Fullerenes with 72, 76, 84 and even up to 100 carbon atoms are possible
- Smallest fullerene is C_{20}



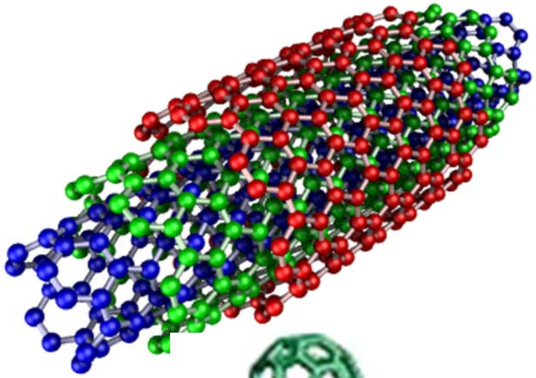
Fullerene C_{70}

Nanotubes

- Single-walled carbon nanotubes (SWCNT)



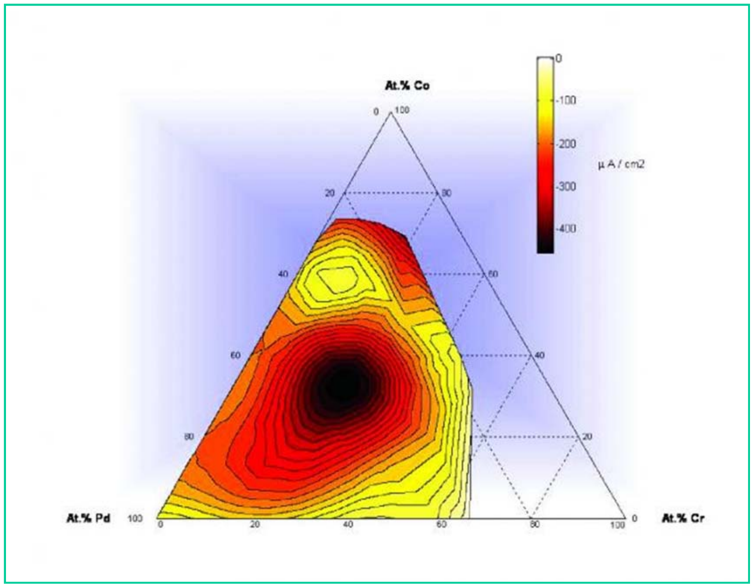
- Multi-walled carbon nanotubes (MWCNT)



- Nanobud (obtained by adding a buckminsterfullerene)

'Extreme' Nanomaterials

- **The longest, the shortest, the thinnest…**
- **Manipulation to impart functionality**
  - **Important to control properties such as**
    - » Hardness and strength
    - » Catalysis
    - » Chirality
    - » Superconductivity



Electrode materials screening by Ilika Technologies, Chilworth, UK, shows high activity for previously undiscovered alloy.

Preparing Nanomaterials
Material and molecular perspectives

- **Larger to smaller**
  - Physical phenomena become pronounced as size decreases
    - » What's at stake: statistical and quantum mechanical effects
- **Simple to complex**
  - Molecular self-assembly
    - » What's at stake: synthetic chemistry, pharmaceuticals, polymers

Preparing Nanomaterials
Approaches and illustrations

- **Bottom-up**
  - Seeks to arrange smaller components into more complex assemblies (chemical self-assembly)
    - » DNA nanotechnology utilizing specificity of base-pairing
- **Top-down**
  - Seeks to create smaller devices by using larger ones to direct their assembly (no atomic-level control)
    - » Giant magnetoresistance-based hard drives
- **Functional**
  - Seeks to develop components of a desired functionality ***without regard to assembly methodology***
    - » Single-molecule components in nanoelectronic devices
- **Biomimicry**
  - Seeks to apply biological methods and systems found in nature
    - » Possible use of viruses
- **'Anticipatory' approaches include nanorobotics, etc.**

Unique Uses

- **Megatubes: larger in diameter than nanotubes, and prepared with walls of different thicknesses**
  - Potentially used for the transport of a variety of molecules of different sizes
- **Fullerites: solid-state manifestation of fullerenes, and related compounds and materials**
  - ‘Ultrahard fullerite’ is a term used to describe material produced by high-pressure high-temperature (HPHT). Such treatment converts fullerite into a nanocrystalline form of diamond which has been reported to exhibit remarkable mechanical properties.
- **‘Nano onions’: spherical particles based on multiple carbon layers surrounding a buckyball core**
  - Proposed for lubricants
- **Silicon buckyballs**
  - Created around metal ions

Defense Applications

- **Carbon nanotubes**
  - EMI hardened electronics
  - Lightweight composites
  - Filtration
  - Infrared obscurants
  - Textiles
  - Reactive coatings
  - Light weight/hi energy batteries
- **Metals**
  - Reactive/dynamic coatings
  - Propellants, wear resistant surfaces, reactive coatings (Al)
  - Sensing

Natick Soldier Center

Chemically and Biologically Protective Shelter

Courtesy of Jeff Steevens, ACoE

Summary of Nanomaterial Regulation

U.S. Federal Regulations	U.S. State Regulations	International Regulations
• U.S. Environmental Protection Agency (EPA) has proposed regulation of nanomaterials through the **Toxic Substances Control Act (TSCA)** • With respect to statutes such as the Clean Air Act (CAA) or Clean Water Act (CWA), the USEPA maintains the authority to regulate nanomaterials as pollutants	• California has taken the lead in addressing nanomaterials as an EC, largely through voluntary reporting efforts • California and several other states have listed nanomaterials as a priority contaminant of concern	• The European Union (EU) is regulating nanomaterials under the **Regulation, Evaluation, Authorization, and Restriction of Chemicals (REACH)** legislation. Will involve: (1) **Labelling** to identify products containing nanomaterials; and (2) **Listing** nanomaterial content in Safety Data Sheets (SDSs), the equivalent of Material Safety Data Sheets (MSDSs) in the U.S. • Individual countries are also reviewing their regulatory regimes with respect to nanomaterials

More on U.S. Regulation

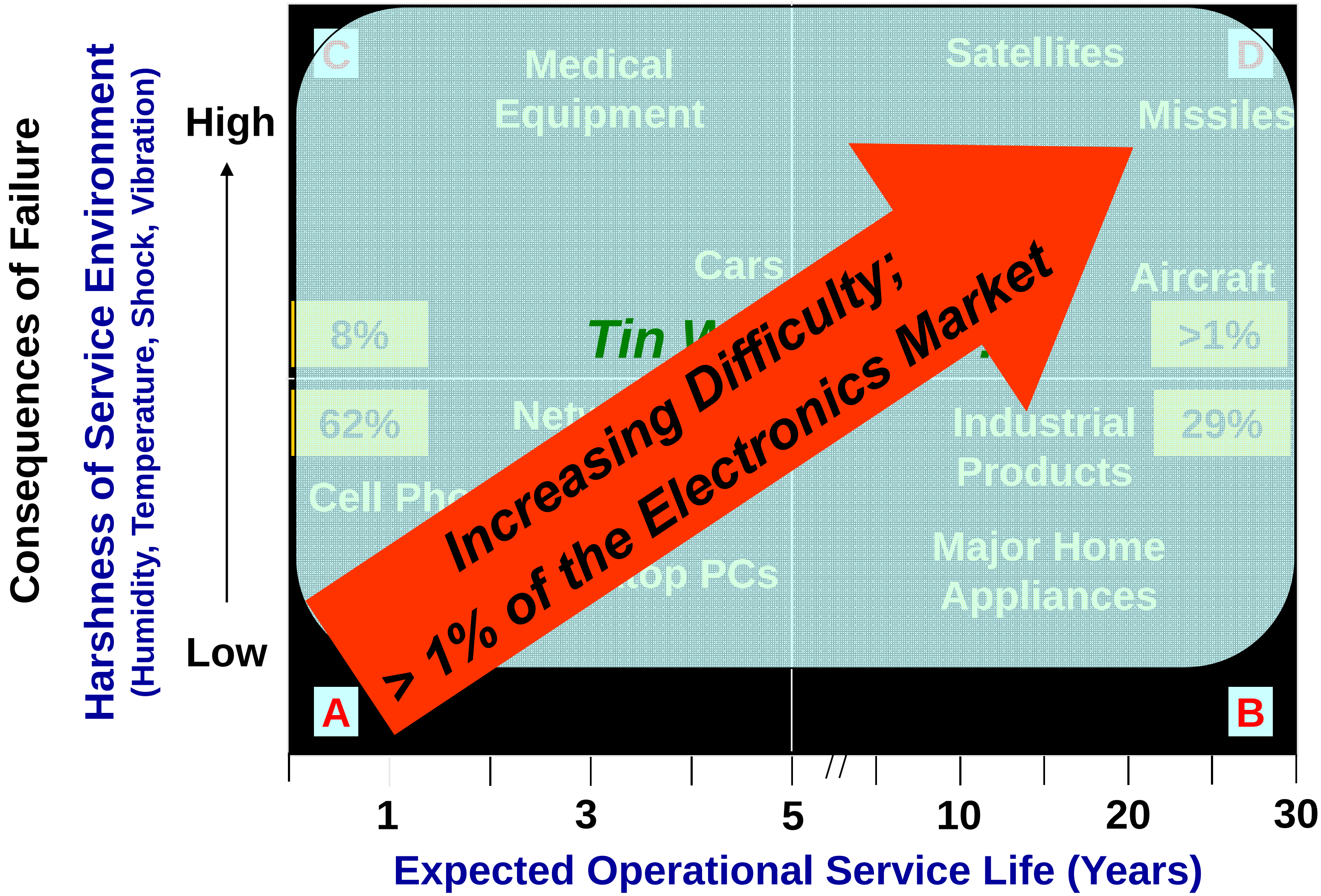
- **U.S. EPA (as of December 20, 2010)**
  - » Test rule for certain nanomaterials, including MWCNT, under TSCA Section 4(a)
    - Intent to issue notice of proposed rulemaking (NPRM) by April 2011
  - » Proposal to set reporting requirements for certain nanomaterials under TSCA Section 8(a)
    - Intent to issue NPRM by February 2011
  - » 2nd Significant New Use Rule (SNUR) under TSCA Section 5(a)(2)
    - Intent to issue NPRM by February 2011
    - 1st SNUR on MWCNT and SWCNT went into effect in October 2010

More on EU Regulation

- **‘REACH’ was enacted in June 2007 to replace some 40 pre-existing laws**
  - Covers all 27 EU Member States and some neighboring states
- **Focus is on**
  - High-volume (most exposure) chemicals
  - Will also require application-specific authorization to use
    - » Substances of Very High Concern (SVHCs)
      - Very persistent, very bio-accumulative (vPvB)
      - Carcinogens, mutagens and reproductive toxins
      - Risks adequately controlled OR benefits outweigh risks AND no alternatives exists
- **REACH is far more sweeping than EU’s Restriction of Hazardous Substances (RoHS)**
  - <u>Six</u> RoHS-regulated chemicals vs. <u>thousands</u> of chemicals already REACH-registered

RoHS and Lead-free Electronics
A cautionary tale

Courtesy of E. Morris,
Lockheed-Martin



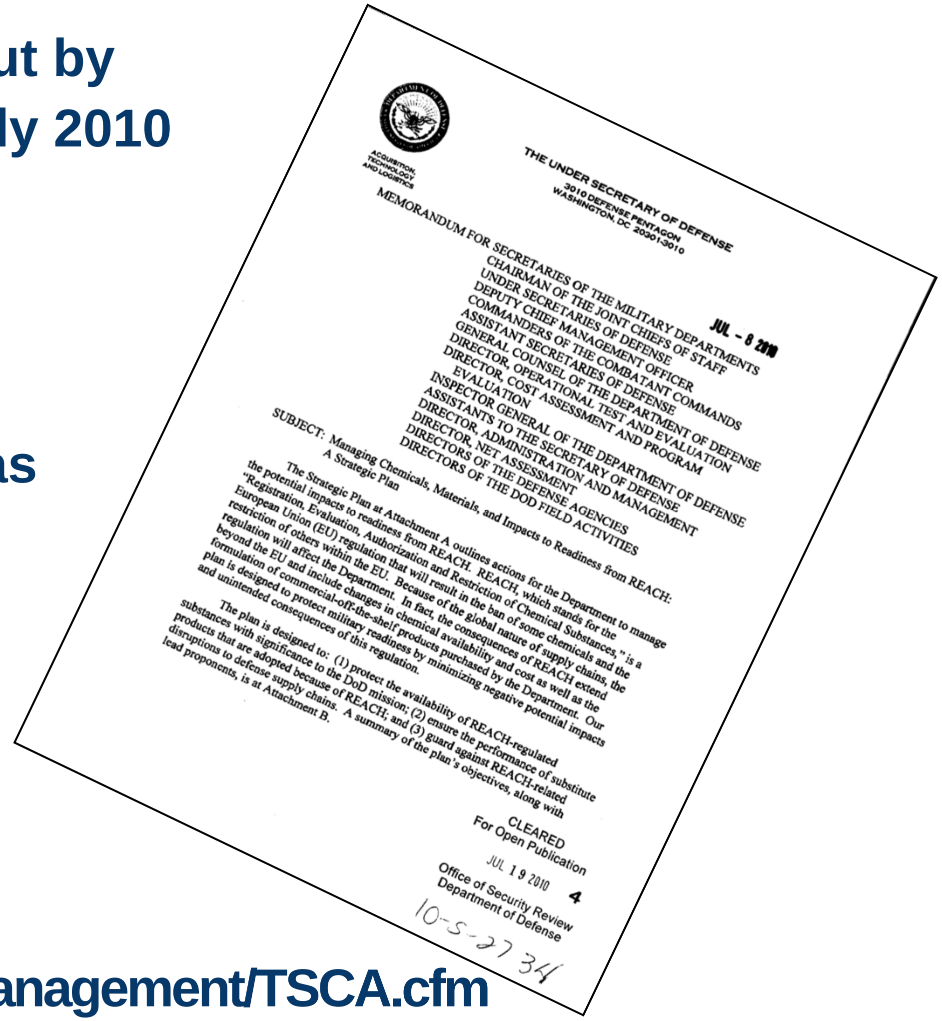
Operating Environment vs. Operational Life-time

Effects of REACH on Product Innovation

- **Military chemical uses were not considered, and there is no blanket defense exemption**
  - Different EU Ministries of Defence have different opinions on applying REACH to their militaries, and can issue narrow, performance-based exemptions for defense-unique products
  - Companies might find it economically infeasible to continue providing these materials, if DoD is the only user
    - May mean more expensive defense products
- **REACH will incentivize companies to develop substitute (i.e., safer and greener) commercial chemicals and materials**
  - Some of them will be nanomaterials (also covered by REACH)
  - All of them should require toxicological/environmental testing

DoD: The Only Federal Agency with a Plan

- **Strategic Plan for REACH signed out by Principal Deputy USD for AT&L[1] July 2010**



THE UNDER SECRETARY OF DEFENSE
3010 DEFENSE PENTAGON
WASHINGTON, DC 20301-3010

ACQUISITION, TECHNOLOGY AND LOGISTICS

JUL - 8 2010

MEMORANDUM FOR SECRETARIES OF THE MILITARY DEPARTMENTS
CHAIRMAN OF THE JOINT CHIEFS OF STAFF
UNDER SECRETARIES OF DEFENSE
DEPUTY CHIEF MANAGEMENT OFFICER
COMMANDERS OF THE COMBATANT COMMANDS
ASSISTANT SECRETARIES OF DEFENSE
GENERAL COUNSEL OF THE DEPARTMENT OF DEFENSE
DIRECTOR, OPERATIONAL TEST AND EVALUATION
DIRECTOR, COST ASSESSMENT AND PROGRAM EVALUATION
INSPECTOR GENERAL OF THE DEPARTMENT OF DEFENSE
ASSISTANTS TO THE SECRETARY OF DEFENSE
DIRECTOR, ADMINISTRATION AND MANAGEMENT
DIRECTOR, NET ASSESSMENT
DIRECTORS OF THE DEFENSE AGENCIES
DIRECTORS OF THE DOD FIELD ACTIVITIES

SUBJECT: Managing Chemicals, Materials, and Impacts to Readiness from REACH: A Strategic Plan

The Strategic Plan at Attachment A outlines actions for the Department to manage the potential impacts to readiness from REACH. REACH, which stands for the "Registration, Evaluation, Authorization and Restriction of Chemical Substances," is a European Union (EU) regulation that will result in the ban of some chemicals and the restriction of others within the EU. Because of the global nature of supply chains, the regulation will affect the Department. In fact, the consequences of REACH extend beyond the EU and include changes in chemical availability and cost as well as the formulation of commercial-off-the-shelf products purchased by the Department. Our plan is designed to protect military readiness by minimizing negative potential impacts and unintended consequences of this regulation.

The plan is designed to: (1) protect the availability of REACH-regulated substances with significance to the DoD mission; (2) ensure the performance of substitute products that are adopted because of REACH; and (3) guard against REACH-related disruptions to defense supply chains. A summary of the plan's objectives, along with lead proponents, is at Attachment B.

CLEARED
For Open Publication
JUL 19 2010 4
Office of Security Review
Department of Defense
10-S-2734

- **Defense Logistics Agency (DLA) has major role in identifying Service-specific supply concerns**

- **Plan available at www.denix.osd.mil/cmrmd/ChemicalManagement/TSCA.cfm**

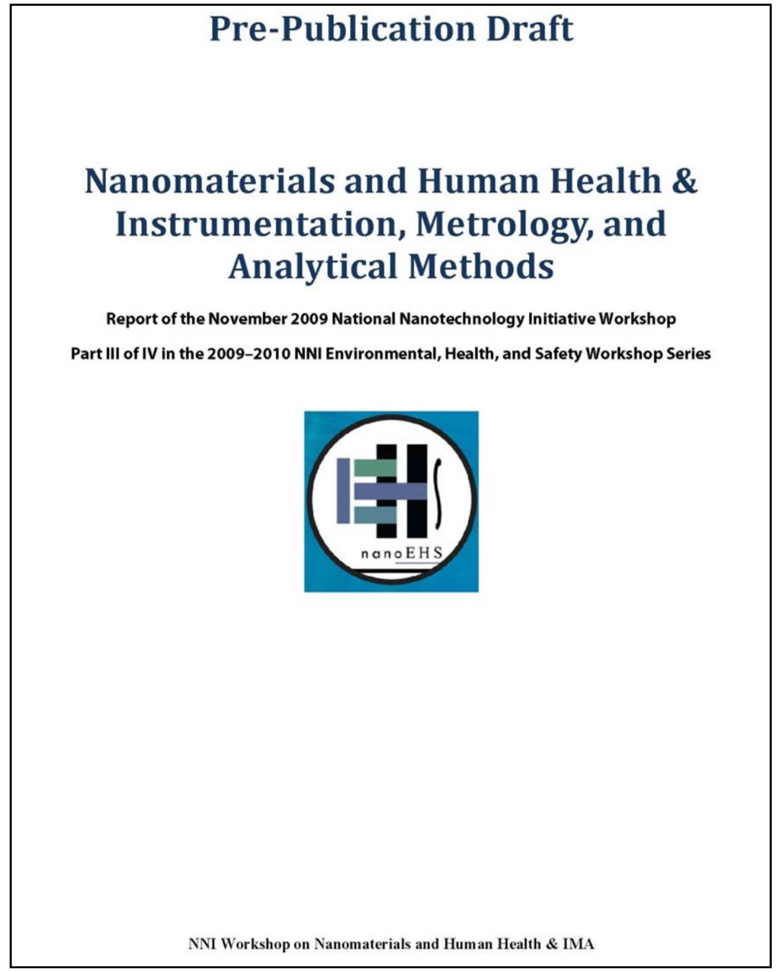
[1] Under Secretary of Defense for Acquisition, Technology and Logistics.

Goals of DoD's Strategic Plan for REACH

1. Protect the availability of substances with significant mission impact
2. Ensure the performance of substitutes
3. Guard against disruptions to the supply chain
4. Encourage partners to pursue defense exemptions
5. Capitalize on ESH improvements
6. Capitalize on chemical management opportunities
7. Assure acquisition strategies
8. Plan for future regulations
9. Minimize negative impacts to Foreign Military Sales

Requirements of a Developing Science

- **During the SME presentations, keep in mind**
  - **Opportunities for professional growth and career development**
    - » For S&T
      - What analytical skills and scientific instruments are needed?
    - » For acquisition
      - What skill sets are needed to ensure timely, well-understood and authoritative delivery of this powerful new technology to the Warfighter?



Pre-Publication Draft

Nanomaterials and Human Health & Instrumentation, Metrology, and Analytical Methods

Report of the November 2009 National Nanotechnology Initiative Workshop

Part III of IV in the 2009–2010 NNI Environmental, Health, and Safety Workshop Series

nanoEHS

NNI Workshop on Nanomaterials and Human Health & IMA

Report available at: www.nano.gov/html/meetings/humanhealth