DoD Industrial Hygiene Forum, 5 June 2007

ENGINEERED NANOMATERIALS:

What you might need to know!

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Service IH SMEs

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Nanotechnology:

The Next Technological Revolution?

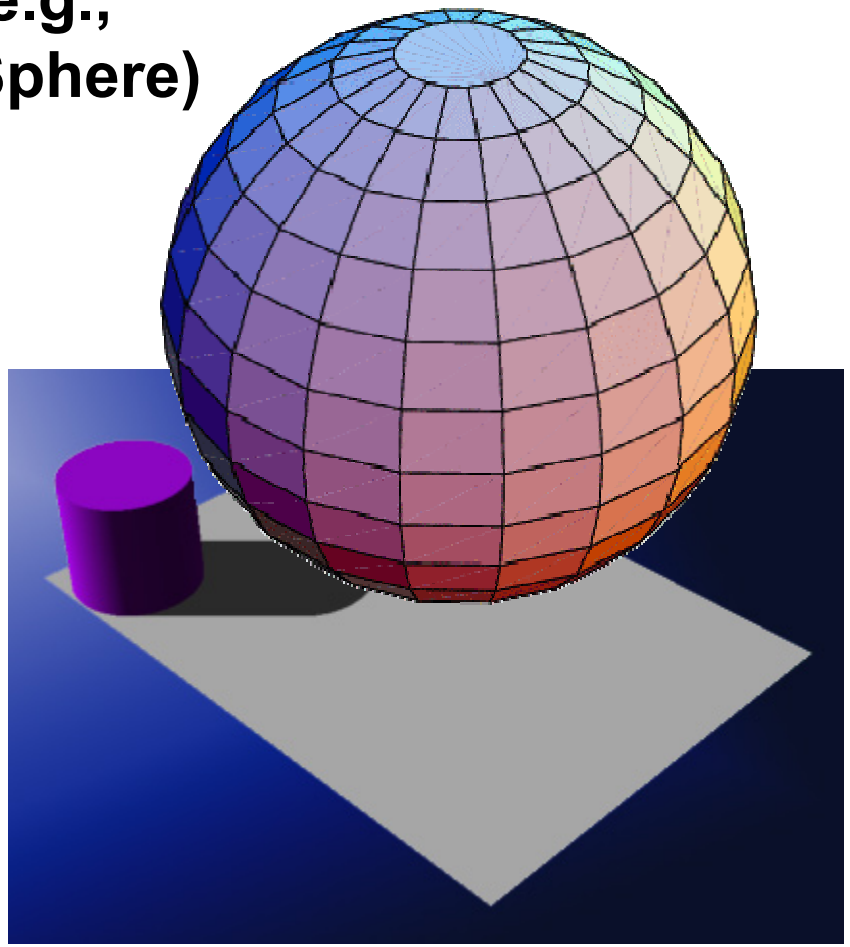
Why Should You Care?

- **DoD and other Federal Departments investing a lot of money in R&D**
- **More and more products down the road**
- **May see nanomaterial regulations from EPA, OSHA, FDA, DoD, etc. in years ahead**

Definitions: Nanoparticle or Nanoscale Object or Particle?

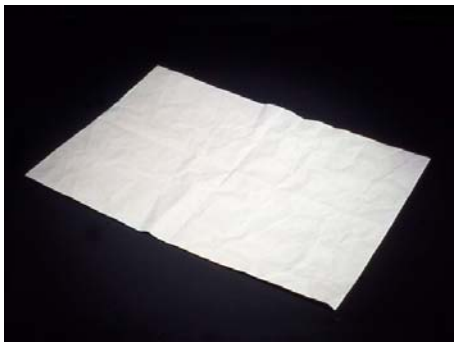
< 100 nm in one, two, or three dimensions?

3-D Object (e.g., Sphere)



2-D Object (e.g., Cylinder)

1-D Object (e.g., Plate)



Nanotechnology Definition

- **Nanoscale science, engineering, and technology encompassing any of the following:**

- **1. Understanding and control of matter at dimensions approximately less than 100 nm (in one or more dimensions)**

- **2. Using the physical, chemical, and biological properties of materials that differ in fundamental and valuable ways from the properties of individual atoms, molecules and bulk matter to create improved materials, devices and systems that exploit these new properties**

- **3. Imaging, measuring, modeling, and manipulating matter at the nanoscale**

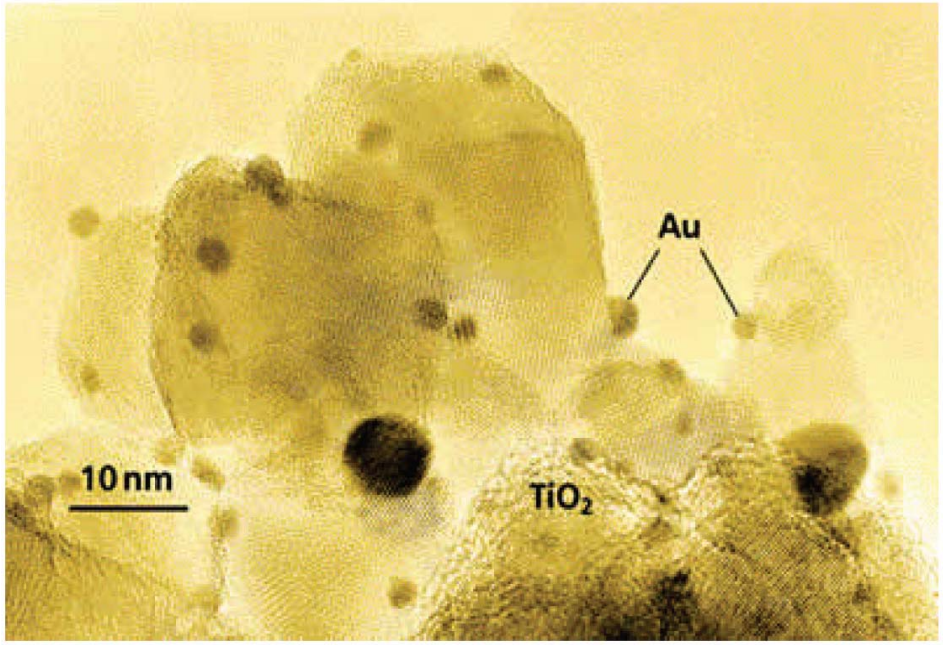
Nanoscale materials are made from either of two approaches:
"*bottom-up*" (e.g., beginning with atoms or molecules)
"*top-down*" (refining or reducing bulk materials)

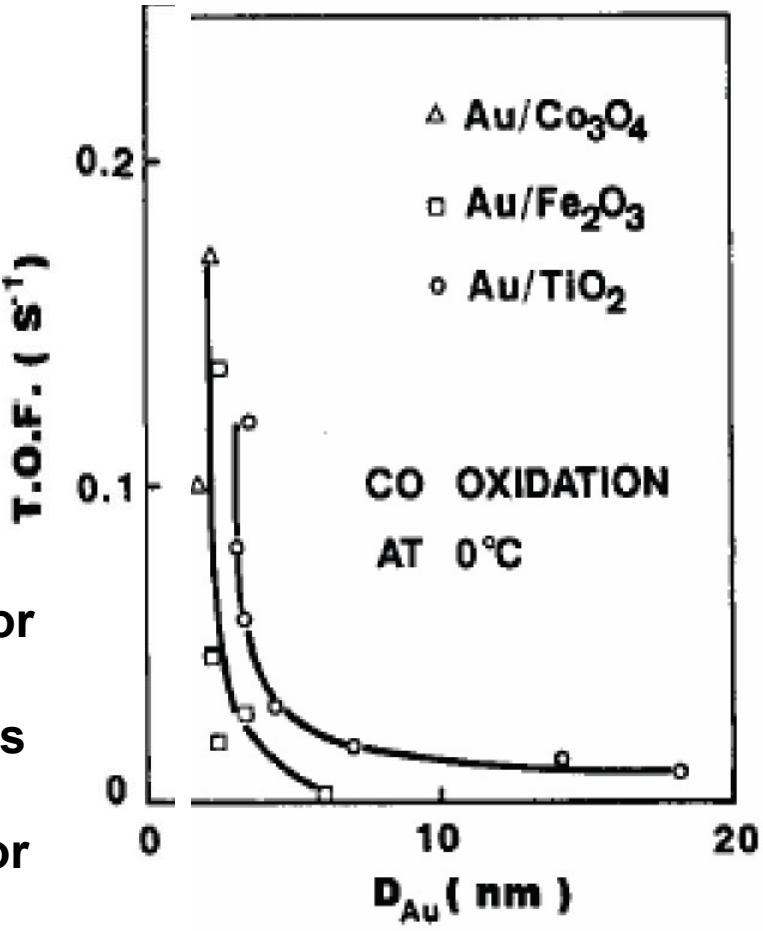
Bulk Form of Gold

Inert – not a catalyst

used in dental fillings, corrosion-resistant coatings.

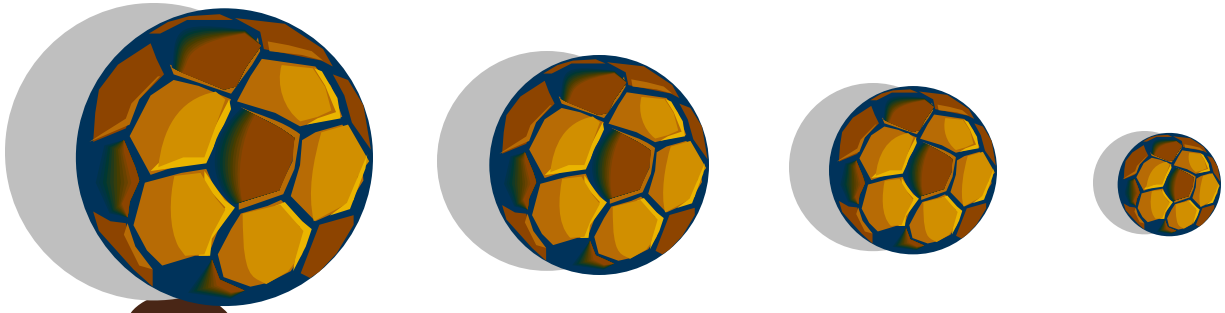
Gold Nanoparticle Catalytic Behavior





Source: NNI Report, Nanoscience Research for Energy Needs. Transmission electron micrograph of gold (Au) nanoparticle catalysts on a titania (TiO2) support. The remarkable catalytic behavior of the gold nanoparticles for CO oxidation is shown on the right as a function of their size

Person becomes a stronger Person
NON-TRANSITIVE NANOPARTICLE



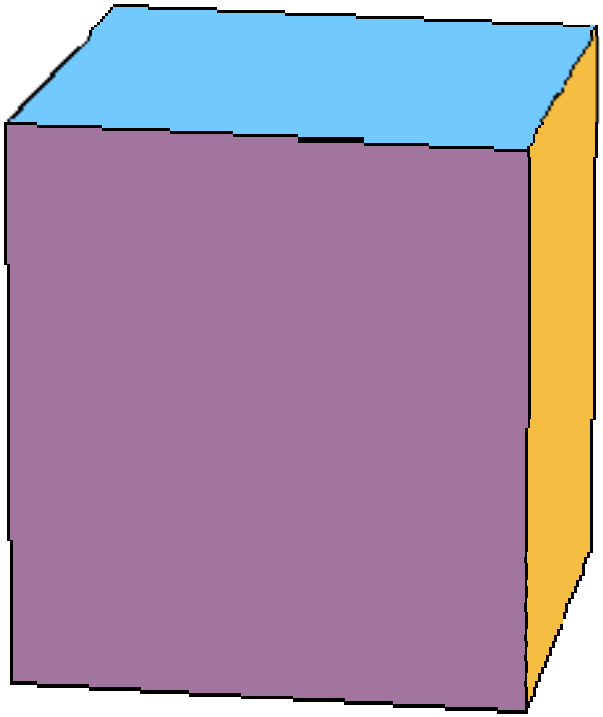
e.g., nanocrystalline Al 2X stronger than larger Al particles

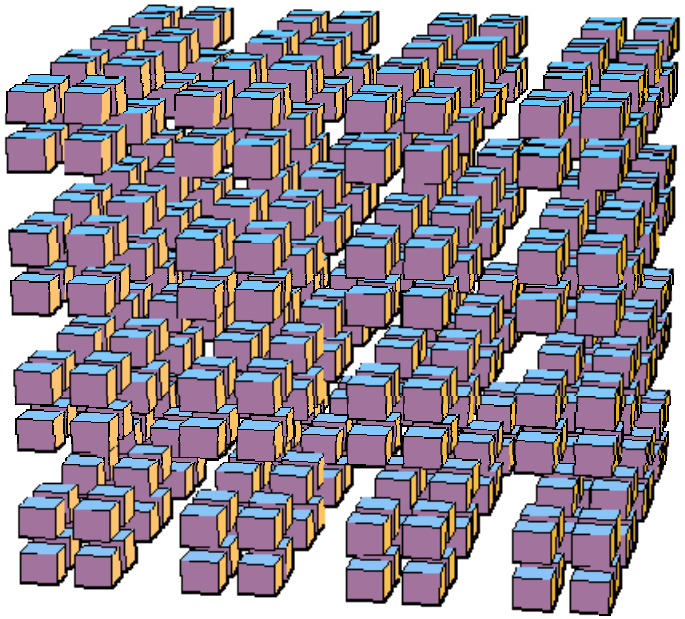
e.g., nanocrystalline Ni as strong as steel

Does NOT exhibit size-related intensive properties

Has properties that fall on a continuum that can be smoothly extrapolated from the behavior of the larger particles

Surface Area and Health Implications





Source: Maynard, NIOSH

Toxicology

- **Toxicology Studies Have Found:**

- **Certain Insoluble Nanoparticles are More Toxic and Tumorigenic than Larger Particles of Similar Composition**

Penetration (Inhalable/Thoracic/Respirable) and Deposition

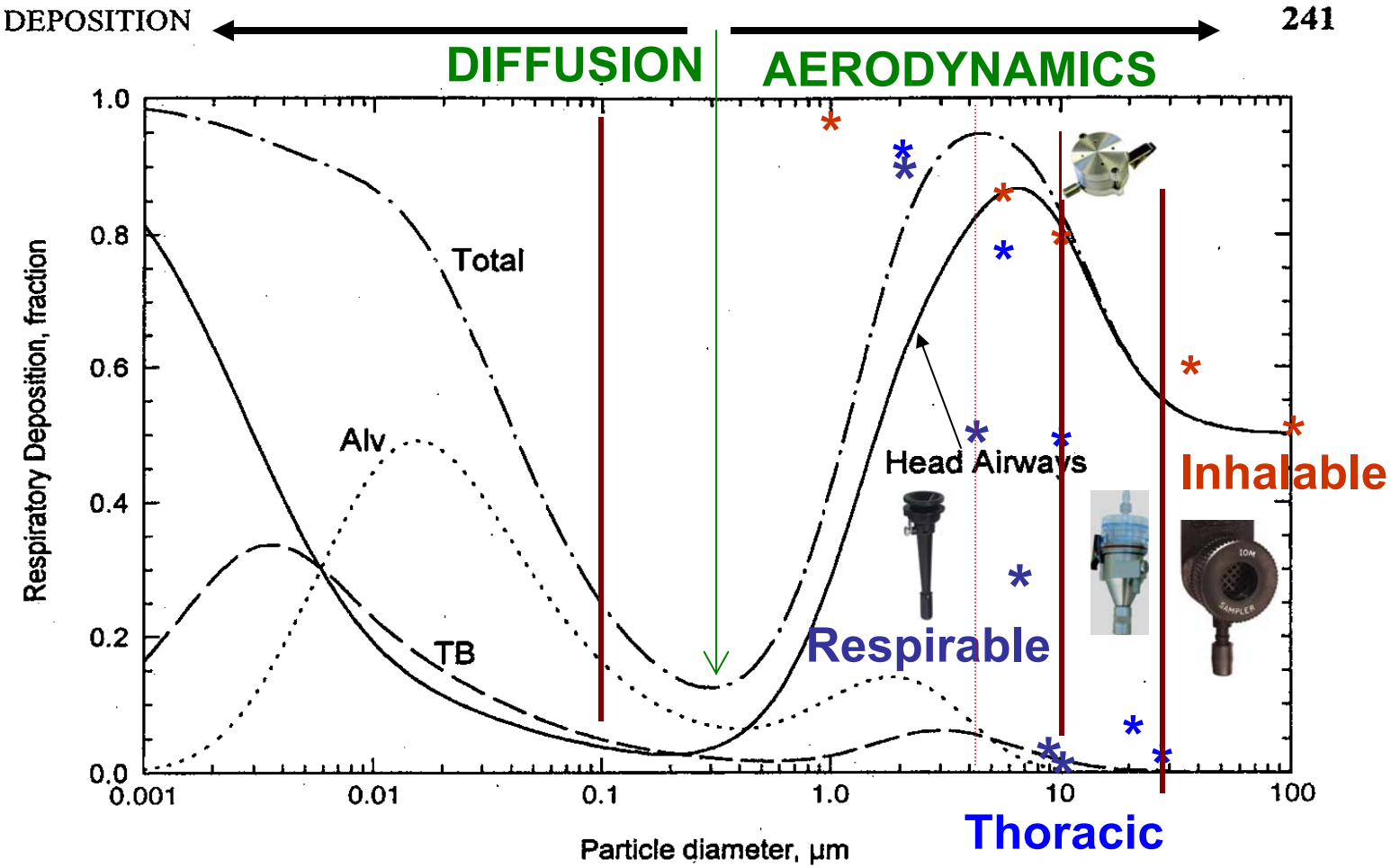


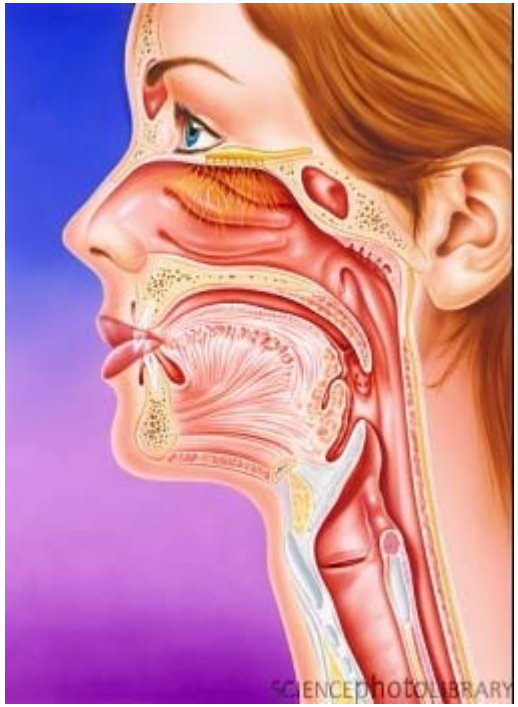
FIGURE 11.3 Predicted total and regional deposition for light exercise (nose breathing) based on ICRP deposition model. Average data for males and females.

Adapted from Hinds, W.C., Aerosol Technology, 2nd Edition, 1999

Colored information is NOT from Hinds.

Will Nanoparticles Travel Along Sensory Nerves in Respiratory Tract to Ganglionic and CNS Structures (e.g., brain)?

Olfactory Nerves



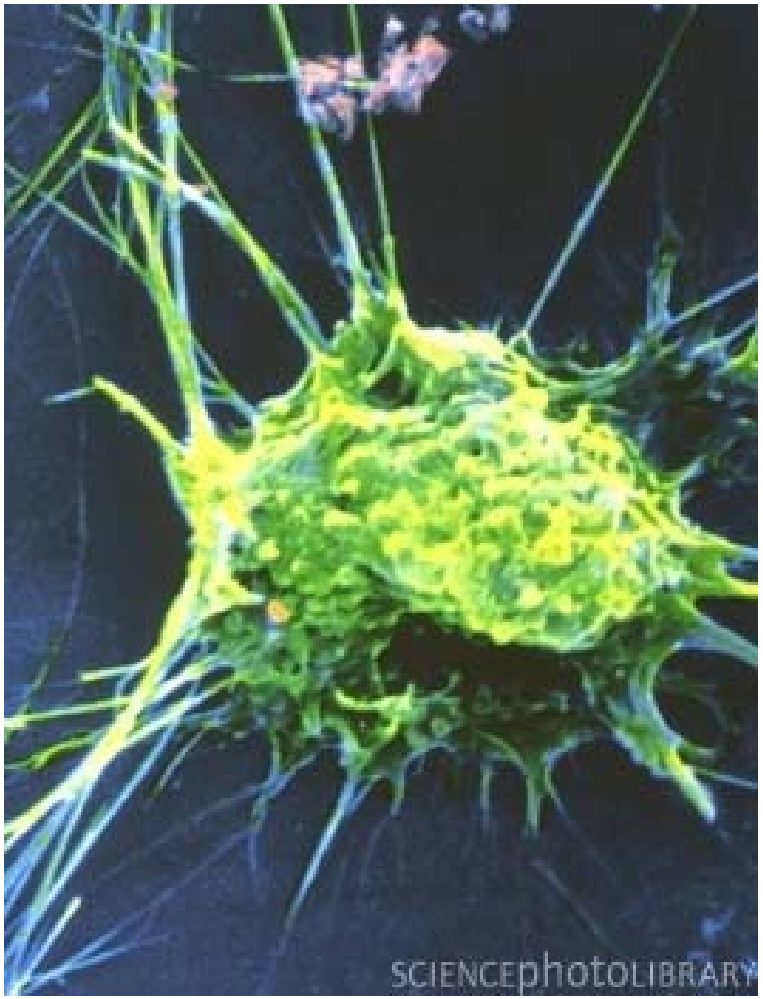
JOHN BAVOSI / SCIENCE PHOTO LIBRARY

Trigeminal Nerve

D. ROBERTS / SCIENCE PHOTO LIBRARY

Tracheobronchial

Alveolar Macrophages Capture Larger Particles, but Nanoparticles Evade Them



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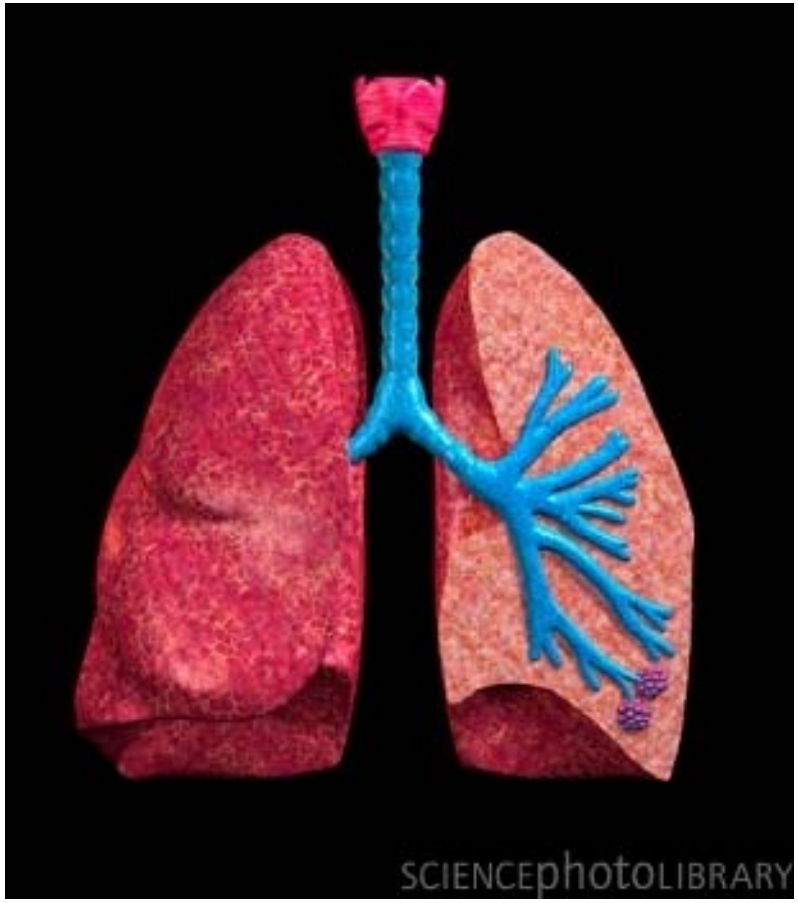

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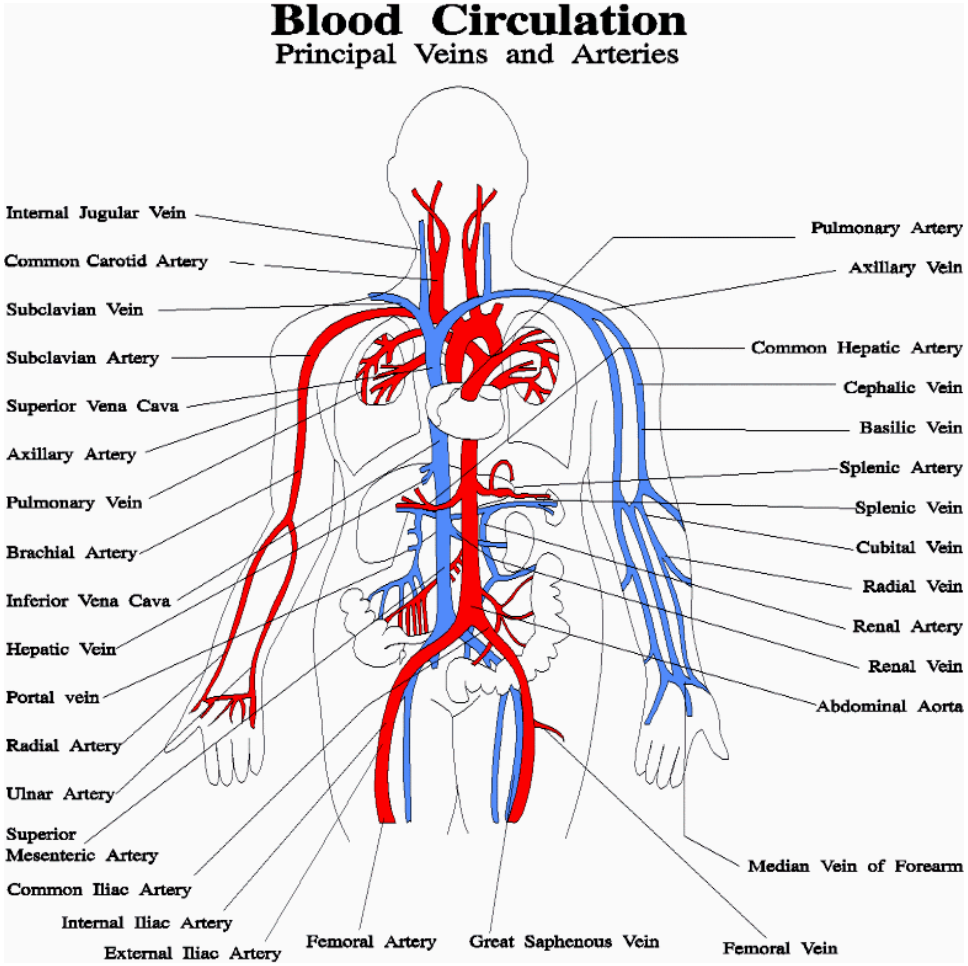
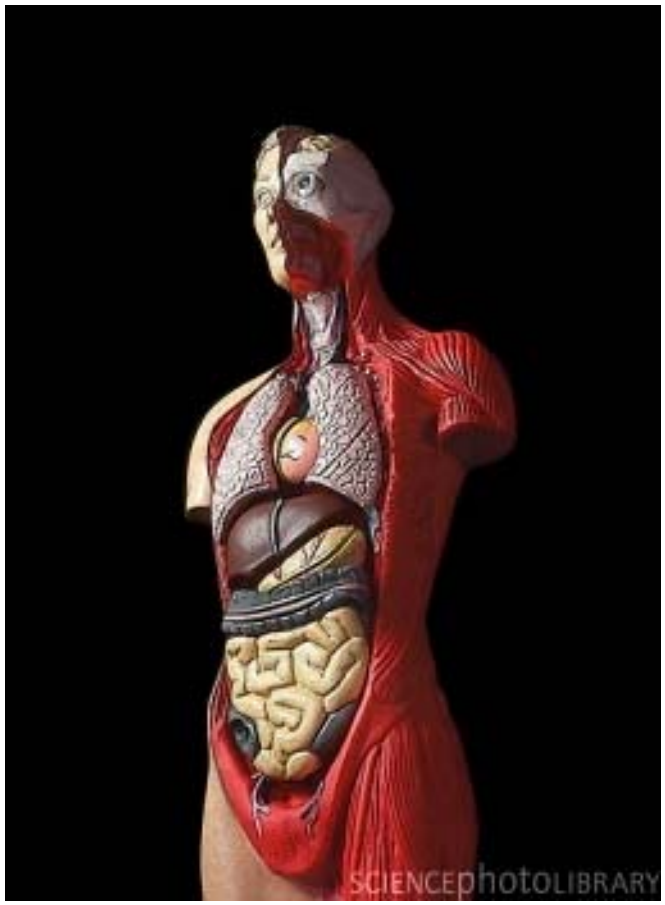
Nanoparticles May Translocate from Lungs to other Organs





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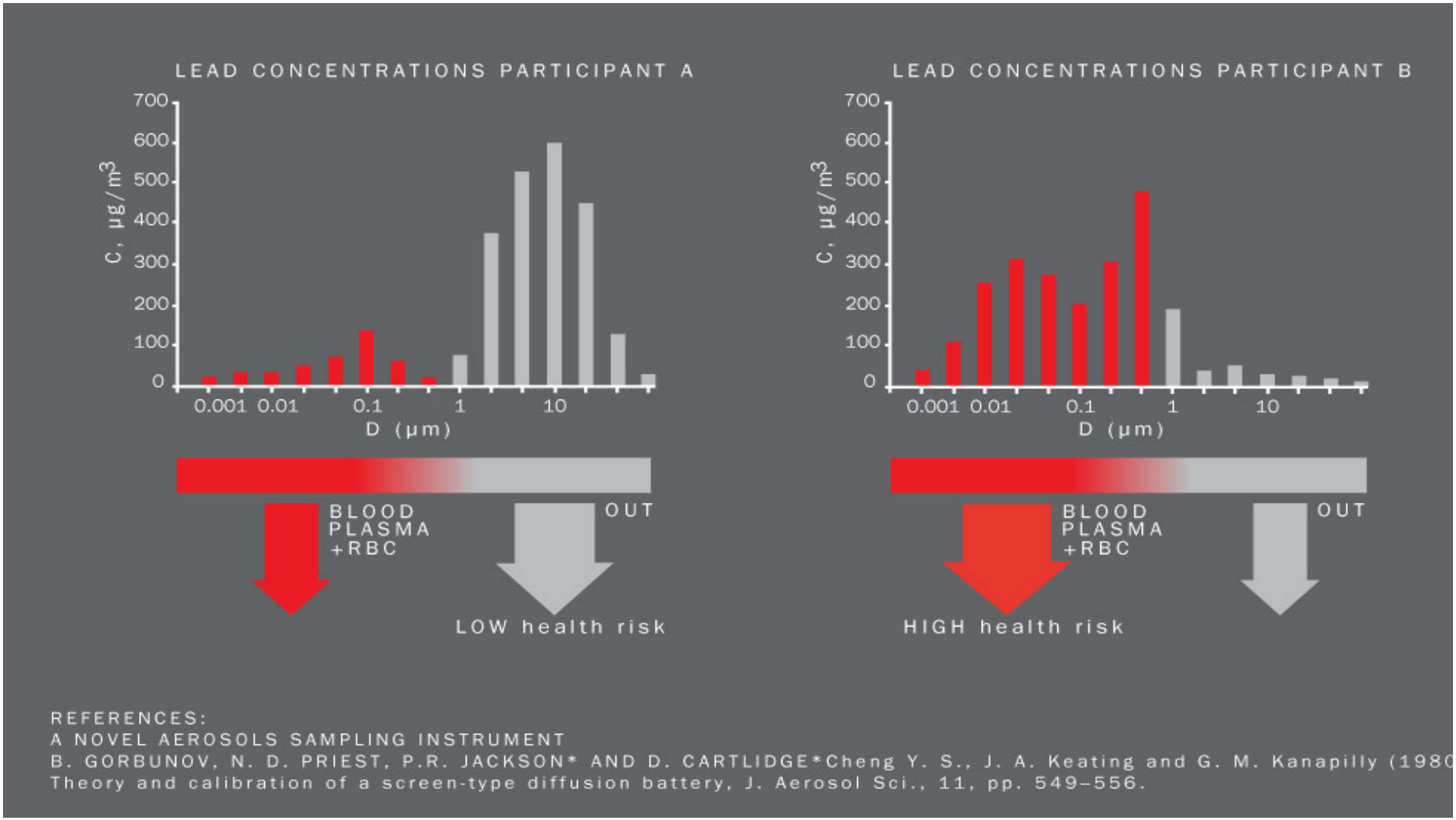
European Crystal Glass Industry Studies of Lead Concentration, Particle Size, and Lead in Blood



REFERENCES:
A NOVEL AEROSOLS SAMPLING INSTRUMENT
B. GORBUNOV, N. D. PRIEST, P.R. JACKSON* AND D. CARTLIDGE*Cheng Y. S., J. A. Keating and G. M. Kanapilly (1980
Theory and calibration of a screen-type diffusion battery, J. Aerosol Sci., 11, pp. 549–556.

Highly correlated (R2 = 0.95) blood lead with particles < 200 nm but not as total dust (R2 = 0.58), PM10 (R2 = 0.61), or respirable fraction (R2 = 0.59).

Naneum
Wide Range Aerosol Sampler
WRAS Technologies

- Wide Range Aerosol Sampler based on research and development of particulate behaviour (proprietary)
- Separates airborne particulates by size from 2 nm to 30μ
- Funded by EU and developed in collaboration with ceramics and glass industries to address occupational health problems

Exposure Limits and Nanomaterials

- Nanoscale particles of existing materials (Ag, Al, Au, ZnO, TiO_2, C, Fe, MgO, etc.) are being manufactured or researched
- TLVs, PELs, WEELs, IDLHs, ERPGs, may not be relevant, adequate for poorly-soluble or insoluble nanoscale particles
- Consult PEL, TLV, and IDLH documentation for basis!

Titanium Dioxide

- **ACGIH**
  - 10 mg/m^3, 8-hour TWA, total dust
- **NIOSH** 11/05 Draft Recommendations (NIOSH 0600, Respirable Particles):
  - Potency associated with surface area
  - Fine: 1.5 mg/m^3, 10-hour TWA
  - Ultrafine: 0.1 mg/m^3, 10-hour TWA, 40-hr/wk
- **National Research Council** (1999), Military Smokes and Obscurants:

  - Respirable: 2 mg/m^3, 8-hour TWA, 5 d/week

  - Ultrafine: 0.25 mg/m^3 8-hour TWA, i.e., 2/8

Incident Investigations

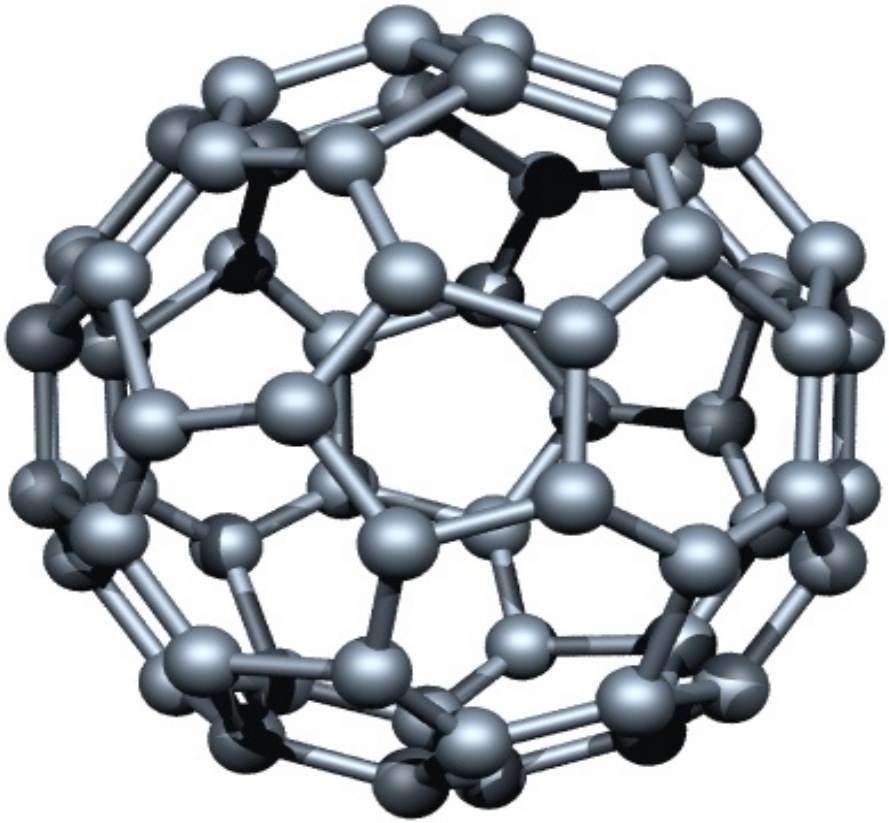
- **Think out of the box** if investigating reasons for adverse signs and symptoms!

- Current mass-based TLVs for poorly-soluble or insoluble particles may not necessarily be a good means for predicting health effect for nanoscale particles!

Smaller Diameter Fibers

- Nanowires (e.g., Co, Au, Cu, silicon)
- Carbon nanofibers

C_{60} Fullerene



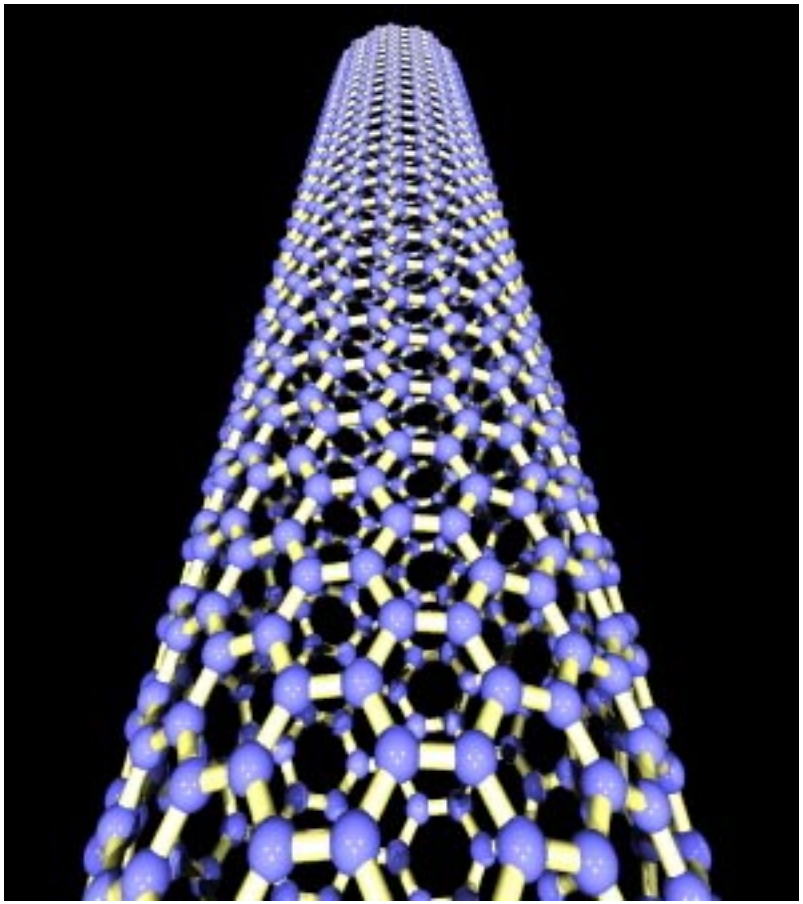
About 1 nm diameter

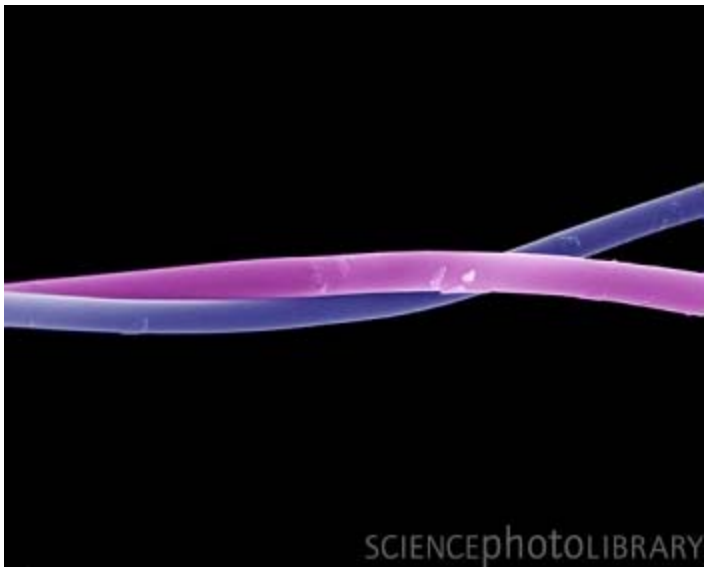
Fullerene C_{60} molecules seen with a scanning tunneling microscope ***(Image: Swiss Re)***

Single-Walled Carbon Nanotubes (SWCNT)

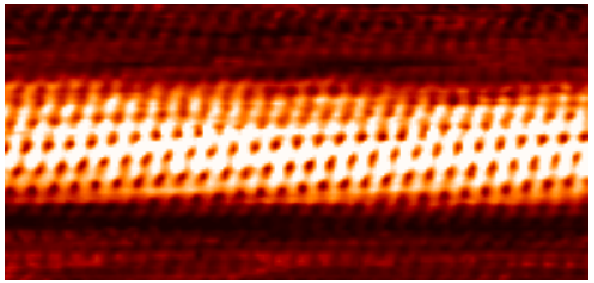
0.7-3 nm diameter
Length: widely variable, up to tens of microns

10-times as strong as steel, 1.2 times as stiff as diamond



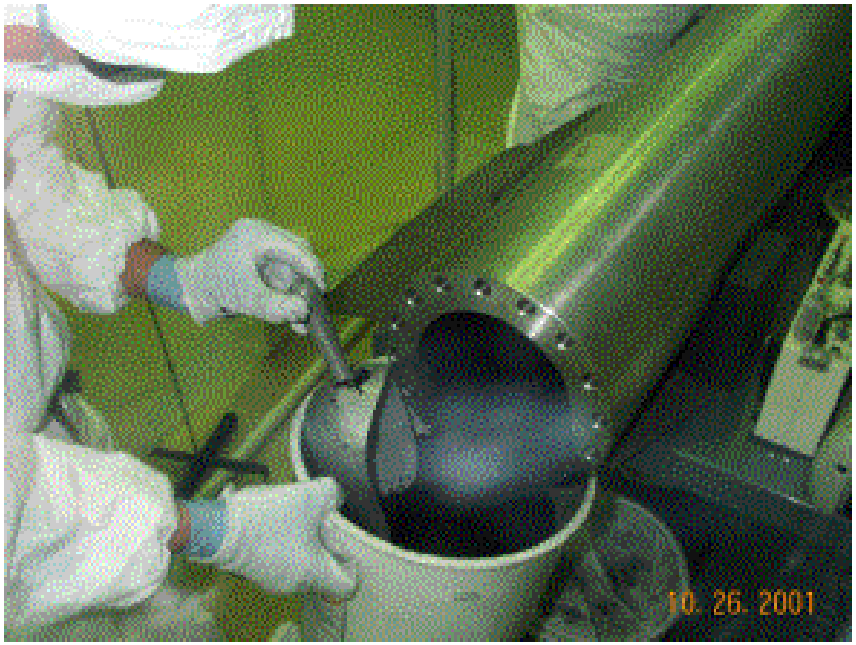


SEM Image. DR KOSTAS KOSTARELOS & DAVID MCCARTHY/ SCIENCE PHOTO LIBRARY

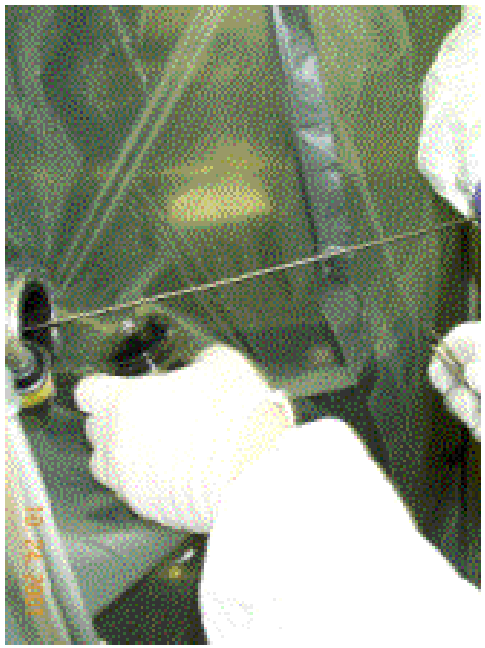


STM Image, American Institute of Physics

Carbon Nanotube Manufacture



Material removal from HiPCO reactor

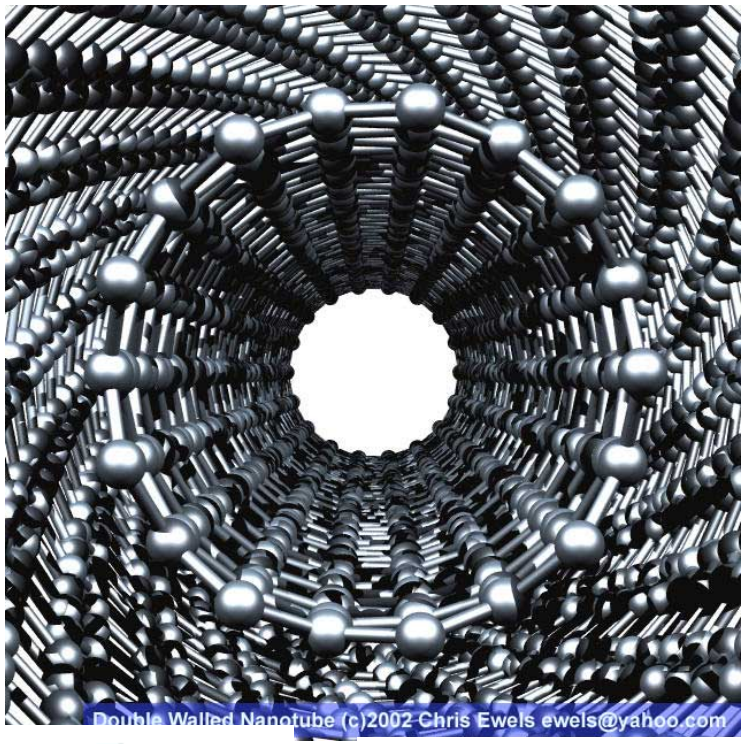


Removing material from laser ablation reactor

Source: A. Maynard

Multi-Walled Carbon Nanotube (MWCNT)

10 to 200 nm diameter
Length: widely variable, up to tens of microns

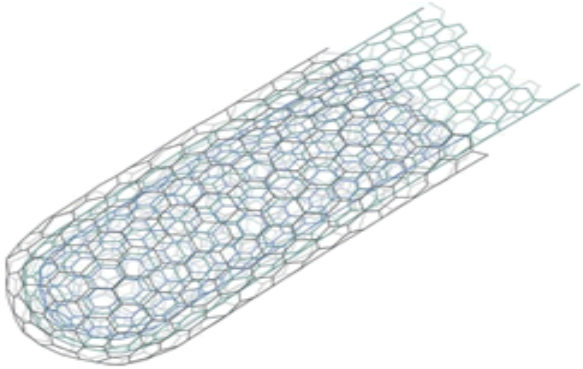


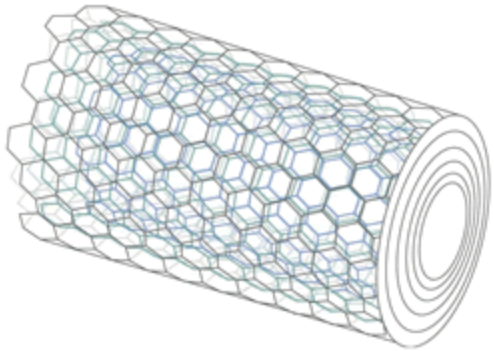
Test tube

Automobile plastics (i.e.. fenders, door handles, mirror housings)

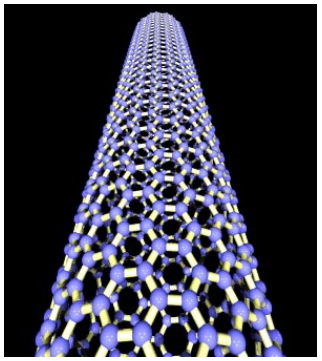
Automobile fuel systems (i.e.. fuel lines, quick connects, O-rings, filter housings, pump modules)

Potential use:
1. flame retardant
2. flat-panel displays, advanced batteries and fuel cells

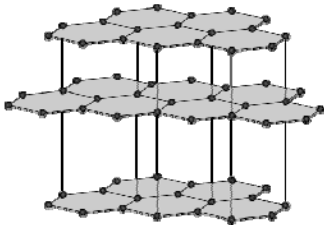




Carbon Nanotubes

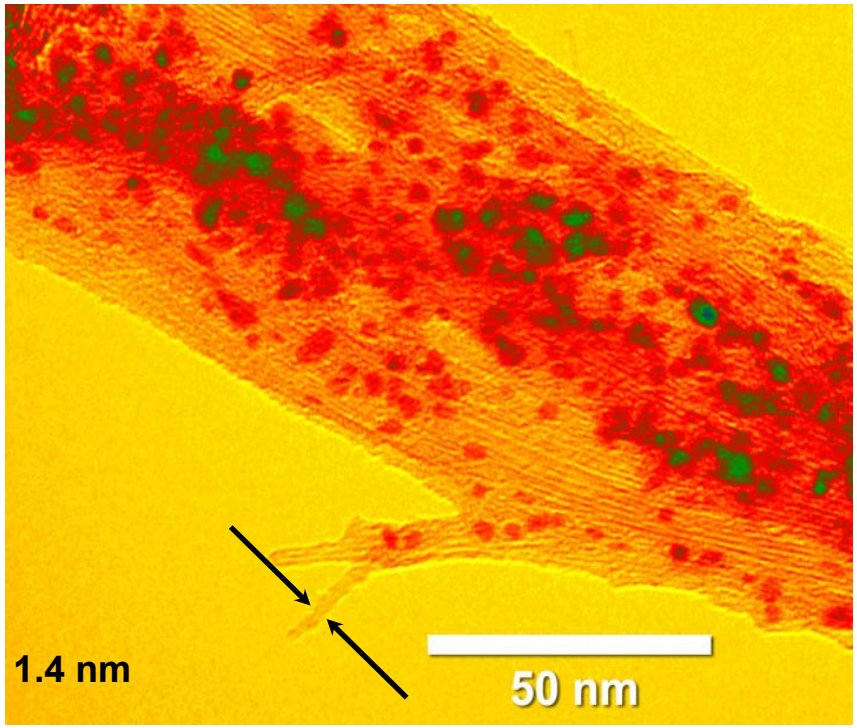


- **Carbon black** (disordered graphite sheets)
  - ACGIH: 3.5 mg/m^3, 8-hr TWA, as “total dust”
- **Graphite**
  - ACGIH: 2 mg/m^3, 8-hr TWA, respirable fraction
- **Crystalline silica**
  - ACGIH: 0.025 mg/m^3, 8-hr TWA, respirable
- **Graphite/carbon fibers** (strands of layered graphite): 1 f/cc, 8-hr. TWA, respirable, NIOSH 7400 Method, “B” Rules
- **Chrysotile asbestos**: 0.1 f/cc, 8-hr. TWA, NIOSH 7400 Method, “A” Rules (> 5 um length, ≥ 3:1 aspect ratio, etc.)



Trace Contaminants/Impurities

- **Metals used in carbon nanotube synthesis: Co, Fe, Ni, Mo**
- **Carbon nanotube organic trace contaminants: carbon black, PAHs**



Source: Maynard, NIOSH

Exposure Assessment Metrics for Engineered Nanoparticles

- **Concentration**

  Example:

  Surface area concentration

  Particle number concentration

  Mass concentration

- **Other physicochemical parameters**

  Particle size distribution

  Particle chemistry

  Aggregation/Agglomeration state of particles

Nanoparticle Measurement

- For the time being, will have to rely more on GA or hand-held samplers for nanoparticle measurement
- Companies looking at developing real-time personal samplers for particle number, size, and surface area
- Some existing personal samplers still relevant

Where TLVs and PELs exist for an insoluble/poorly-soluble nanomaterial

- Sample per the TLV/PEL criteria (e.g., “total,” inhalable, thoracic, respirable)
- Sample for submicron fractions (e.g., less than 100/200/300/400/500 nm????)
- Take samples for particle number, surface area, and mass for smaller particle sizes
- Consider that the mass-based TLVs/PELs may possibly not be adequate

Where TLVs and PELs Do NOT exist for an insoluble/poorly-soluble nanomaterial

- Take samples for particle number, surface area, and mass for smaller particle sizes
- Consider toxicological findings and physicochemical characteristics
- Sample inhalable, thoracic, respirable, submicron fractions (e.g., less than 100/200/300/400/500 nm????)

Subtract Out Background

- **Number (particles per cc):**

p/cc (during process) – p/cc (background)

- **Surface Area (μm²/cc):**

$\mu m^2/cc$ (during process) - $\mu m^2/cc$ (background)

- **Mass (μg/m³):**

$\mu g/m^3$ (during process) - $\mu g/m^3$ (background)

Surface Area Concentration Monitors, Diffusion Charger – Direct-Reading, Non-Specific

Measures active surface area,

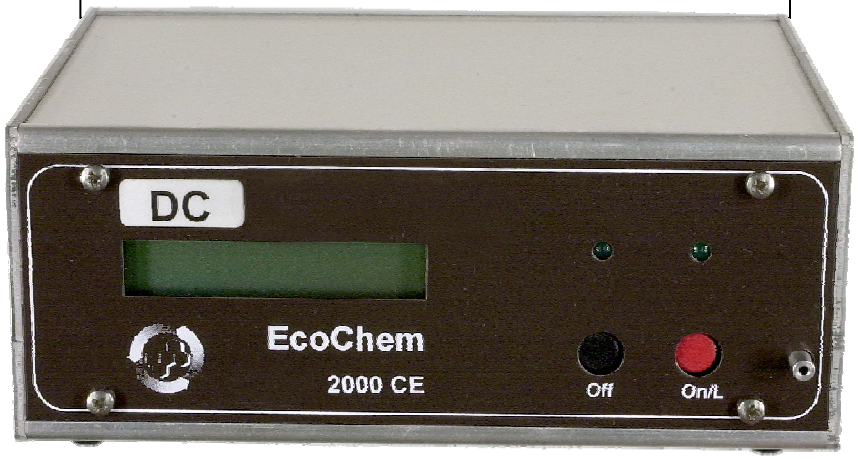
External Surface Area

Generally insensitive to particle porosity

< 100 nm mobility diameter: correlates well with TEM-derived surface area

> 100 nm, surface area is underestimated

Charge on Aerosol $\propto$ **Surface Area**



DC2000 CE Diffusion Charger *EcoChem*

Particle size range: 10 nm to 1,000 nm

Cost: $10,000

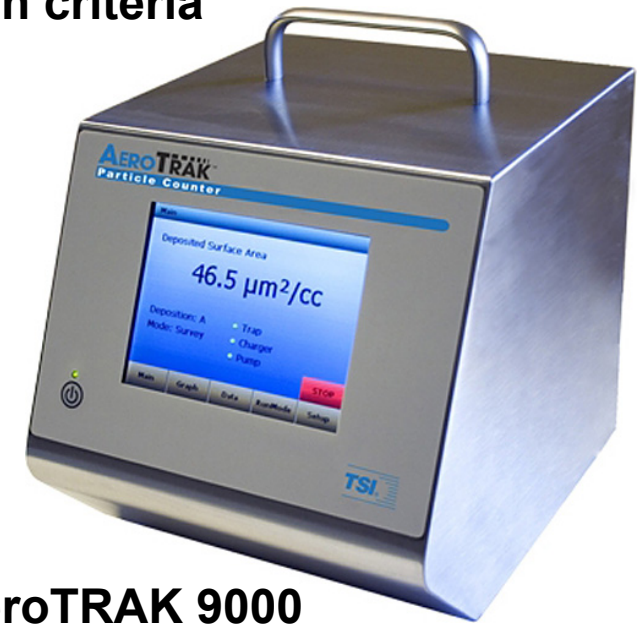
Surface Area Concentration Monitors, Diffusion Charger, Direct-Reading, Non-Specific

User selectable response modes indicate lung deposited surface area of nanoparticles deposited in the tracheobronchial (TB) and alveolar (A) regions of the lung, corresponding to the ICRP lung deposition criteria

TSI Model 3550 **Cost; $16,000**

Concentration range:
TB:1 to 2,500 µm²/cc
A: 1 to 10,000 µm²/cc

Size range: 10 to 1000 nm (with 1µm cyclone on inlet)



TSI AeroTRAK 9000
Battery-Operated
Cost: $10,000

Generally insensitive to particle porosity

Measures active DEPOSITED surface area in the TB or A regions of the lung

Measures Deposited External Surface Area Within the Lung

Particle Number Concentration, Direct-Reading Hand-Held Condensation Particle Counters (CPC), Non-Specific, < 1,000 nm

Cost: $6,000

TSI P-Trak

20 nm to 1,000 nm

0 to 500,000 particles/cc

Cost: $8,000

TSI Model 3007

10 nm to 1,000 nm

0 to 100,000 particles/cc

Without a nanoparticle pre-separator, they are not specific to the nanometer size range.
(no suitable pre-separators are currently available)

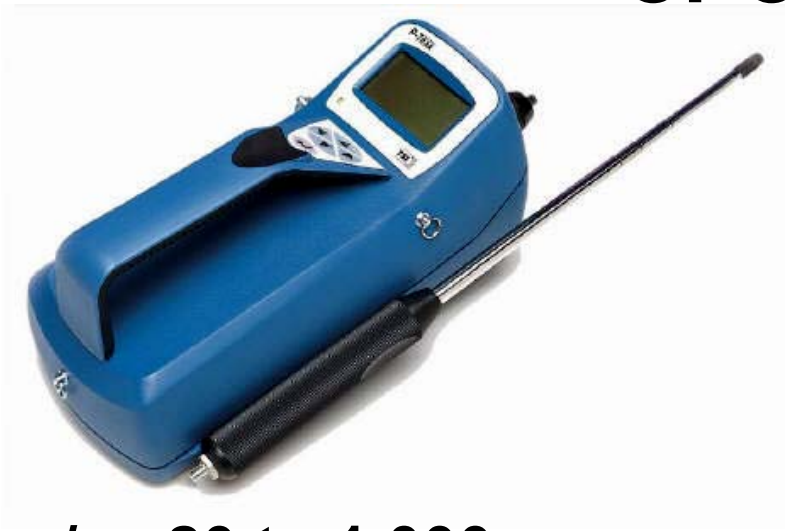
Particle Number Concentration,

Optical Particle Counter (OPC):

> 300 nm diameter

Counts in 1 to 6 user-adjustable bin sizes from 0.3 to 10 microns

Particle Number Concentration,
Particles 10 or 20 nm to 300 nm
CPC minus OPC



p/cc 20 to 1,000 nm

p/cc 10 to 1,000 nm

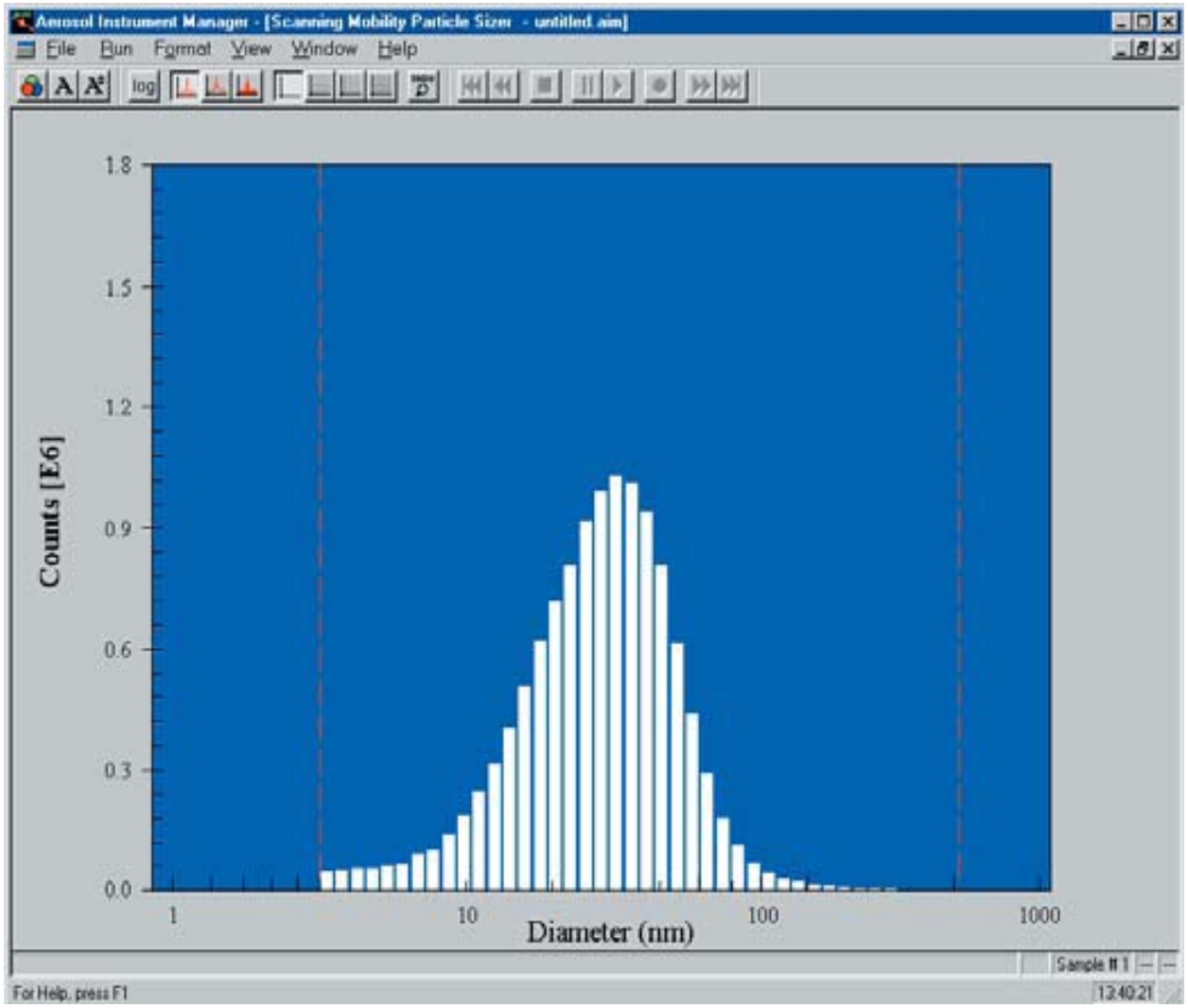
SUBTRACT

p/cc > 300 nm

NIOSH monitoring of a worker during a nanomaterial powder production and collection operation

Source: NIOSH

Size and Size Distribution



Portable (Hand-held) Particle Detector/monitor

Naneum Selector and Counter (SAC) 1

$30-40K
Available Fall, Winter 07?

Specification:

- **Battery/mains operated,**
- hand-held ,
- on-line measurement
- Sample time <2 minutes
- **Size range covered 2/3nm-10 µm**
- Several months untended operation (mains)
- (Blue-tooth/wireless connection to laptop)

Properties measured:

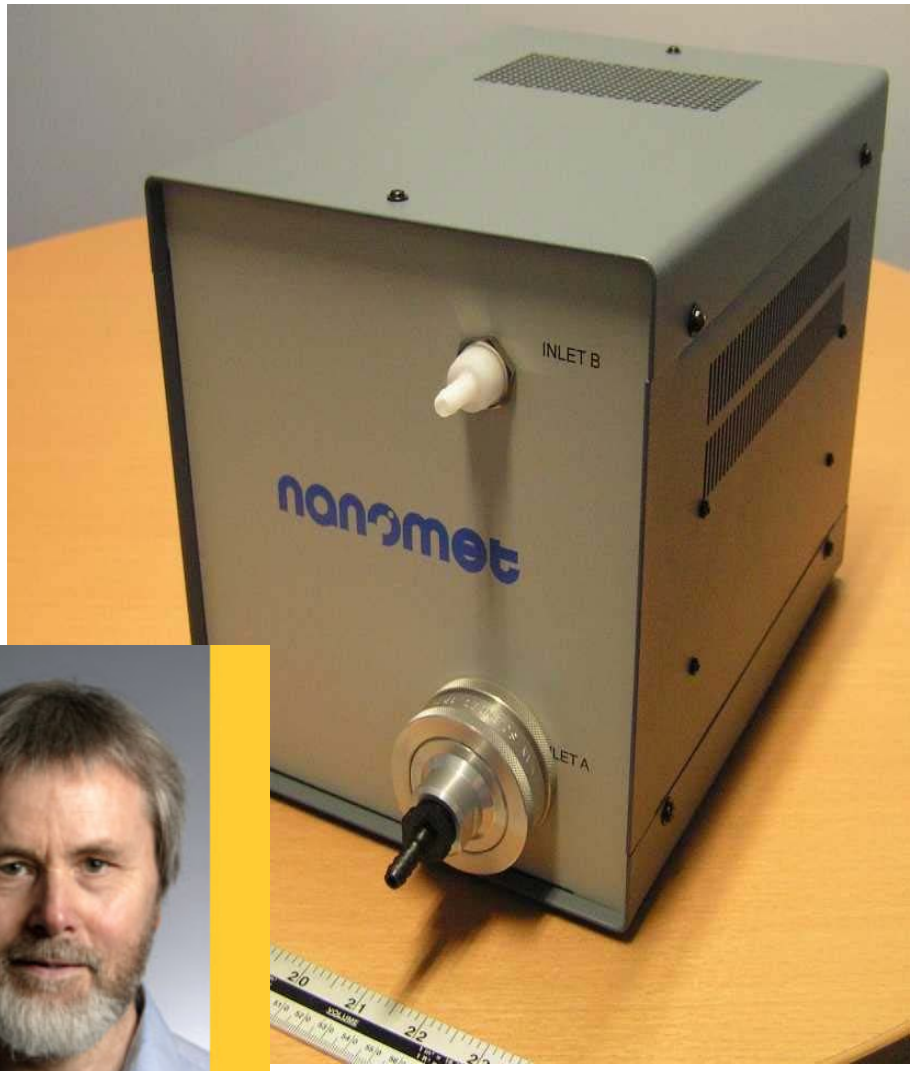
Total particle number
Particle size distribution, number concentration

Applications

- Particle distribution mapping
- Identify “hot spots”
- Background from engineered particles
- Continuous monitoring
- Identify “events”
- Exposure/dose

Intellectual property

- EU Application
- Patents in preparation but not yet filed



www.naneum.com

Mass Concentration (mg/m^3), Photometers Non-Specific, Personal Sampling

PHOTOMETERS: Calibration only valid for the specific calibration aerosol and can differ as much as a factor of ten when used with an aerosol from a different source, different composition, and size distribution

Built-in impactors: "none," 1.0, 2.5 or 10-micron cut off

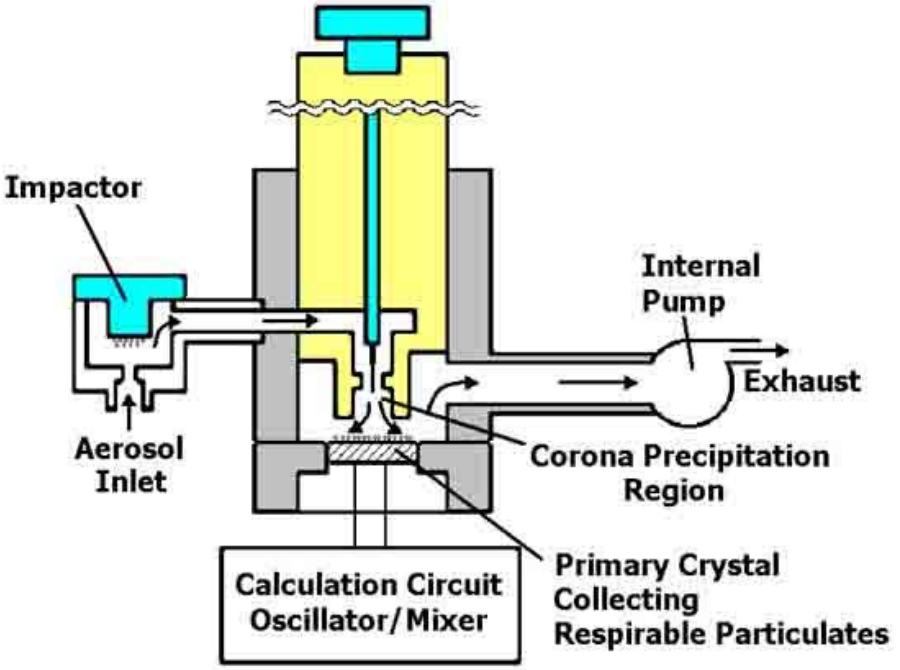
Light Scattering, 670 nm Laser Diode

Size range: 100 nm to 10 micron

Concentration Range: 0.001 to 20 mg/m3

Mass Concentration (mg/m^3), Piezobalance Dust Monitor, Non-Specific, General Area

KANOMAX USA, INC.



Size range: < 10 microns

Concentration: 0.02-10 mg/m3

Accuracy: +/-10% of reading +/-1 digit

Mass Concentration (mg/m^3), Filter for Collecting Particles,

Personal Sampling

Utility for carbon nanotubes, fullerenes, carbon nanofibers, etc.??

< 1 µm: 1.7 lpm

< 400 nm: about 3 lpm

Theoretical:

< 200 nm: about 6 lpm

< 100 nm: about 10 lpm

SKC: Diesel Particulate Matter (DPM) Cassette

At 1.7 to 2.0 LPM, particles less than 1.0 µm aerodynamic diameter are collected on heat-treated low carbon quartz filters. Samples are analyzed for organic and elemental carbon content using a highly sensitive Evolved Gas Analysis (EGA) technique with thermal-optical analyzer as specified in NIOSH Method 5040.

Meets specs for NIOSH 5040 for analysis of elemental carbon (EC) to determine total carbon (organic and elemental) in a sample. Total carbon represents more than 80% of diesel particulate emissions.

Size Distribution
Mass, Chemistry, Personal Sampling

Size Distribution	50% cut-points:
> 2.5 µm	2.5 µm
1 µm – 2.5 µm	1.0 µm
500 nm – 1 µm	500 nm
250 nm – 500 nm	250 nm
< 250 nm	<250 nm (after filter)

Aerodynamic diameter

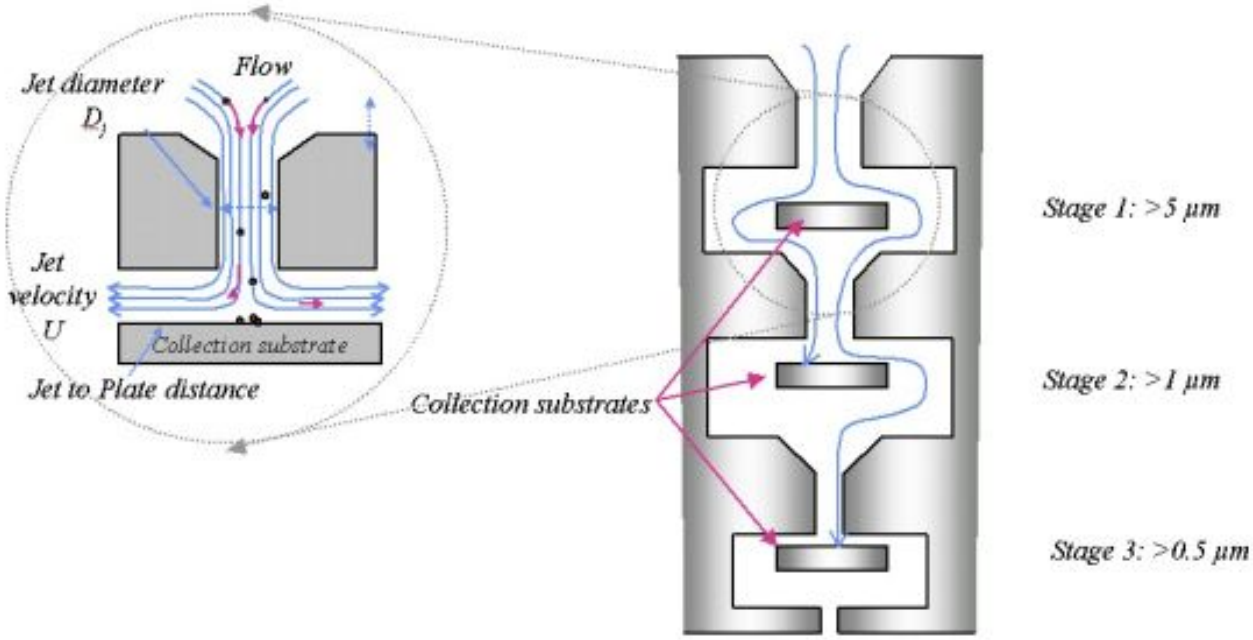
Sioutas Cascade Impactor; teflon filters recommended

Analysis: gravimetrically, chemically, and microscopically

Size Distribution, Mass Concentration, Chemistry,

Dekati Low Pressure Impactor

$20,000



Aerodynamic diameter from 30 nm up to 10 µm. With the filter stage accessory, particles below 30 nm can be collected on a 47 mm filter.

Naneum Wide range Aerosol sampler (WRAS)

$38,000

- **Specification:**
  - Mains operated portable sampler weighing approx 10kg
  - Continuous collection of size resolved samples on custom substrate
  - **Up to 15 size "bins" from 2/3nm-30µm**
  - Flow rates from 5lpm-1000lpm
  - Samples suitable for off-line analysis using SEM/TEM, MS, Atomic Adsorption,HPLC etc.
- **Properties measured:**
  - **Size resolved chemical composition**
  - **Size resolved morphology**
- **Technical Principles**
  - **Inertial deposition (300 nm to 30 µm)and Diffusion (2 -300 nm)**
  - Integrated to give seamless size resolution across aerosol range
- **Intellectual property**
  - 2 granted UK patents
  - USA application

Transmission Electron Microsopy

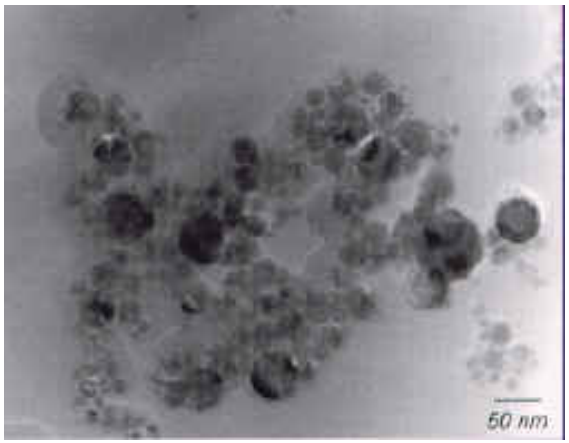
- **Size:** projected area of particles
- **Shape and structure**
- **Number distribution**
- **Surface area:** projected area may be related to geometric area for some particle shapes
- **Aggregation/agglomeration state**
- **Chemistry:** Combined with Energy Dispersive X-Ray Analysis (EDX), can provide spatially resolved information on particle elemental composition and compositional heterogeneity

Sampling for TEM Analysis

- Sample long enough for analysis, but avoid particle overloading
- Preferable to sample directly onto a TEM support grid
- Place grid on the face of a filter, or
- Pull air through lacy carbon film, or
- Thermal precipitation: particles migrate from a hot region to a cold region
- Electrostatic precipitation: efficient for > 20 nm sizes

Particle Chemistry, Mass, Number, Surface Area

Titanium Dioxide



Iron

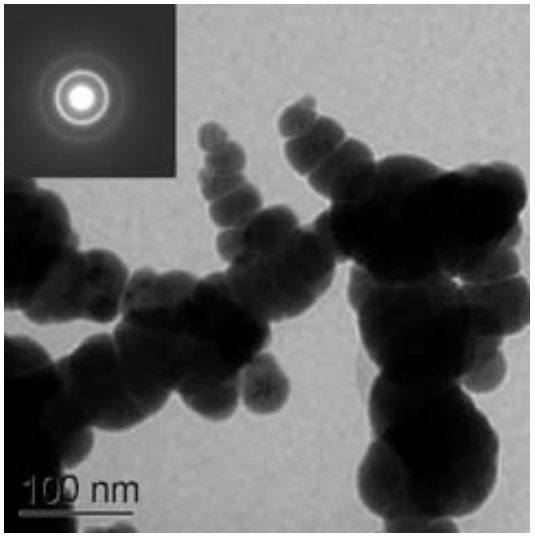
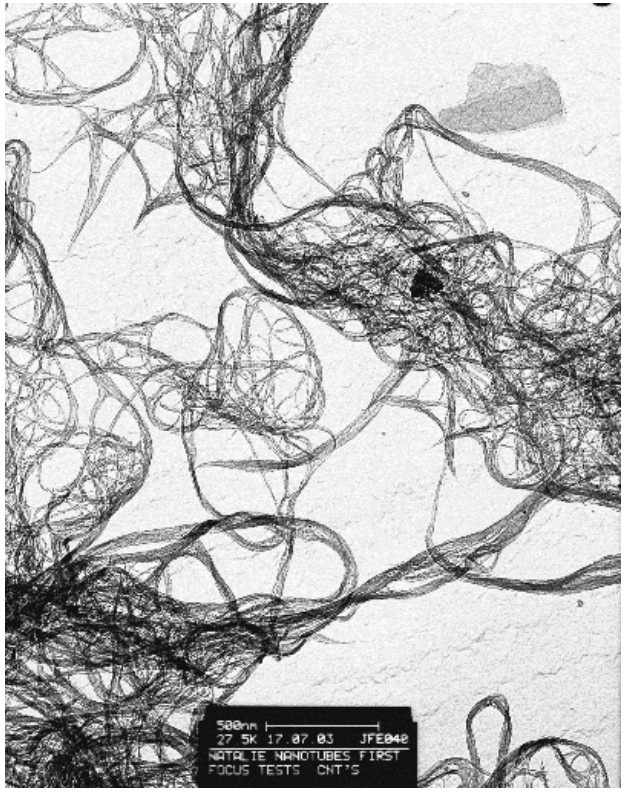


Photo Chongmin Wang, Pacific Northwest National Laboratory)

TEM

Single-Walled Carbon Nanotubes



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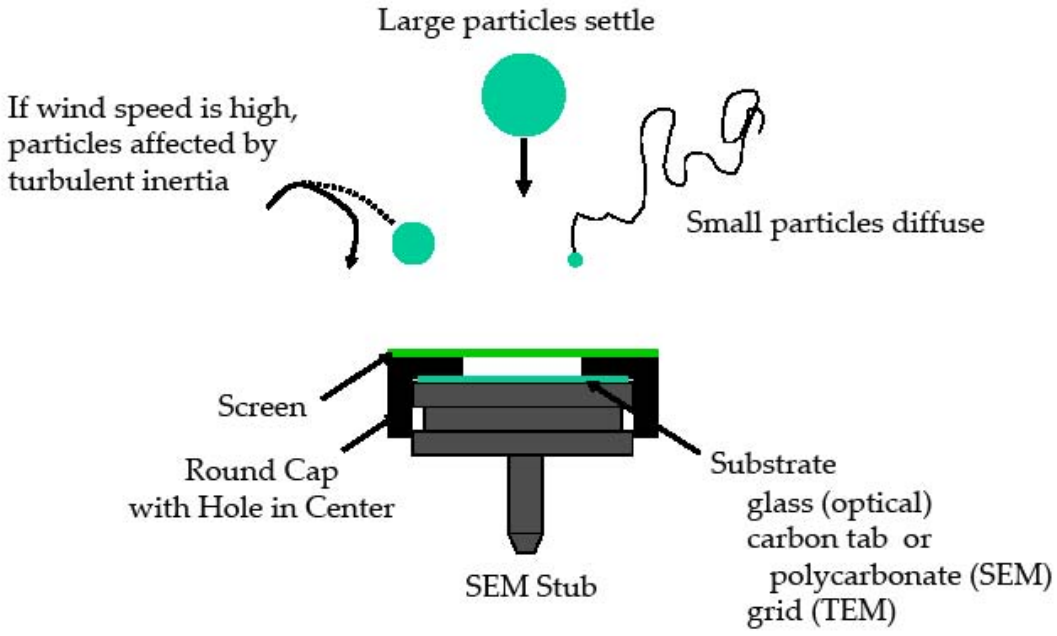
Wagner-Leith
Passive Aerosol Sampler

Wagner-Leith Passive Aerosol Sampler

How It Works



Engineering Controls

Local exhaust ventilation controlling fugitive emissions during precursor mixing at a primary nanoscale metal oxide Production facility

Source: NIOSH

Engineering Controls

Enclosing hood with HEPA exhaust constructed to control possible emission of nylon nanofibers during destructive testing

Source: NIOSH

Sampling and data collection during a mixing operation

Source: NIOSH

How Effective Are Respirators?

A flat plate test system for measuring respirator filter penetration of 3 to 20 nm silver particles

Source: NIOSH

How Effective is Personal Protective Clothing Against Nanoparticles?

Controls

- Controls may have to be more stringent for nanomaterial than for the insoluble/poorly-soluble micro- or macro-scale material of same chemical composition

- For instance, if 10-x above a TLV or PEL, and you use a ½ facepiece APR to get down to the TLV or PEL, consider ratcheting up to a full-face APR with HEPA

Questions?

GENERAL INTRODUCTION TO NANOTECHNOLOGY

- **Booker, R. and Boysen, E, Nanotechnology for Dummies,** Wiley Publishing, Inc., 2005, http://www.wiley.com/WileyCDA/WileyTitle/productCd-0764583689.html

- **Luther, Wolfgang (Ed.), Industrial Application of Nanomaterials - chances and risks,** Future Technologies Division of VDI Technologiezentrum GmbH, Germany, 2004

Top documents of relevance, in the order of suggested priority to read as a practicing IH

- **1. NIOSH, Approaches to Safe Nanotechnology -- An Information Exchange with NIOSH.** Available at: http://www.cdc.gov/niosh/topics/nanotech/safenano/

- **2. Maynard, A.D. and Aitken, R.J., Assessing exposure to airborne nanomaterials: Current abilities and future requirements**, Nanotoxicology, Volume 1:1, 26-41, March 2007. Available at: http://www.informaworld.com/smpp/title~content=t716100760

- **3. ISO, Workplace Atmospheres - Ultrafine, nanoparticle and nano-structured aerosols - Exposure characterization and assessment.** Geneva: Switzerland: International Standards Organization. Document no. ISO/TR 27628, 2007. Available for purchase from ANSI, http://www.ansi.org/

Top documents of relevance, in the order of suggested priority to read as a practicing IH

- **4. ASTM, WK8985 New Standard Guide for Handling Unbound Engineered Nanoscale particles in Occupational Settings.** Under development: http://www.astm.org/cgi-bin/SoftCart.exe/COMMIT/SUBCOMMIT/E5603.htm?L+mystore+cprk8709+1177117315

- **5. NIOSH, Progress Toward Safe Nanotechnology in the Workplace,** February 2007. Available at: http://www.cdc.gov/niosh/docs/2007-123/pdfs/2007-123.pdf

- **6. NIOSH, Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide, DRAFT Current Intelligence Bulletin"** Online, available: http://www.cdc.gov/niosh/review/public/TIo2/

On-line databases of relevance

- **ICON, Online EHS journal and database:** http://icon.rice.edu/virtualjournal.cfm
- **NIOSH, Nanoparticle Information Library:** http://www.cdc.gov/niosh/topics/nanotech/NIL.html
- **Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars, Health and Environmental Implications: an inventory of current research:** http://www.nanotechproject.com/index.php?id=18

Websites

- **American Industrial Hygiene Association (AIHA):** http://www.aiha.org/Content/Topics/nano/
- **ASTM E56 Nanotechnologies**: http://www.astm.org/cgi-bin/SoftCart.exe/COMMIT/COMMITTEE/E56.htm?L+mystore+cprk8709+1179181259
- **Defense Nanotechnology Research and Development Programs, May 17, 2005:** http://www.nano.gov/html/res/DefenseNano2005.pdf
- **DoD laboratory research and development:** http://www.nanosra.nrl.navy.mil/
- **DoD NNI Centers, Networks, and Facilities:** http://www.nano.gov/html/centers/nnicenters.html

Websites

- **Environmental Protection Agency (EPA):** http://es.epa.gov/ncer/nano/

- **Food and Drug Administration (FDA):** http://www.fda.gov/nanotechnology/

Websites

- **International Conference on Nanotechnology: Occupational and Environmental Health & Safety, 4-7 December 2006, Cincinnati, OH. Slide presentations online, available:** http://www.uc.edu/noehs/conference_program.asp.

- **International Council on Nanotechnology (ICON):** http://cohesion.rice.edu/centersandinst/cben/industry.cfm?doc_id=5023

- **International Organization for Standardization (ISO) TC 229 Nanotechnologies:** http://www.iso.org/iso/en/CatalogueListPage.CatalogueList?COMMID=5932&scopelist=PROGRAMME

Websites

- **National Institute for Occupational Safety and Health (NIOSH):** http://www.cdc.gov/niosh/topics/nanotech/
- **Occupational Safety and Health Administration (OSHA):** http://www.osha.gov/
- **Organization for Economic Co-operation and Development (OECD):** http://www.oecd.org/department/0,2688,en_2649_37015404_1_1_1_1_1,00.html

Websites

- **National Nanotechnology Initiative (NNI):** http://www.nano.gov/
- **NNI, Research and Development Leading to a Revolution in Technology and Industry (Supplement to the President's FY 2007 Budget), July 2006: http://www.nano.gov/NNI_07Budget.pdf**
- **NNI, EHS research needs for Engineered nanoscale materials: http://www.nano.gov/NNI_EHS_research_needs.pdf)**

Websites

- **Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies:** http://www.nanotechproject.org/

- **National Cancer Institute (NCI):** http://nano.cancer.gov/

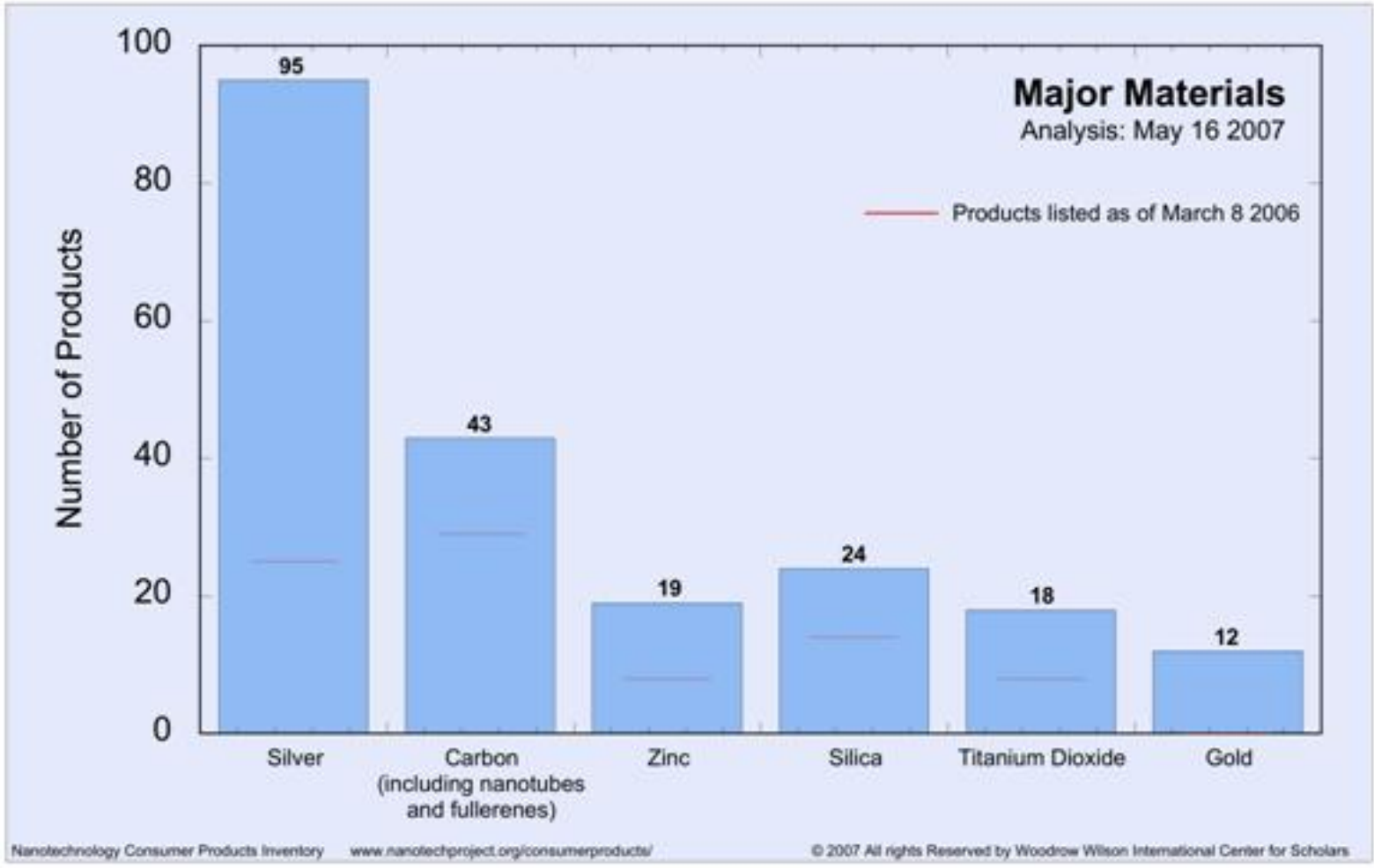
- **Note: The NIOSH, ASTM, ISO, and OSHA links should be regularly consulted for the latest developments related to occupational health and safety**

Major Materials

Over 475 commercial products contain engineered nanomaterials

Used with Permission

Source: Woodrow Wilson International Center for Scholars

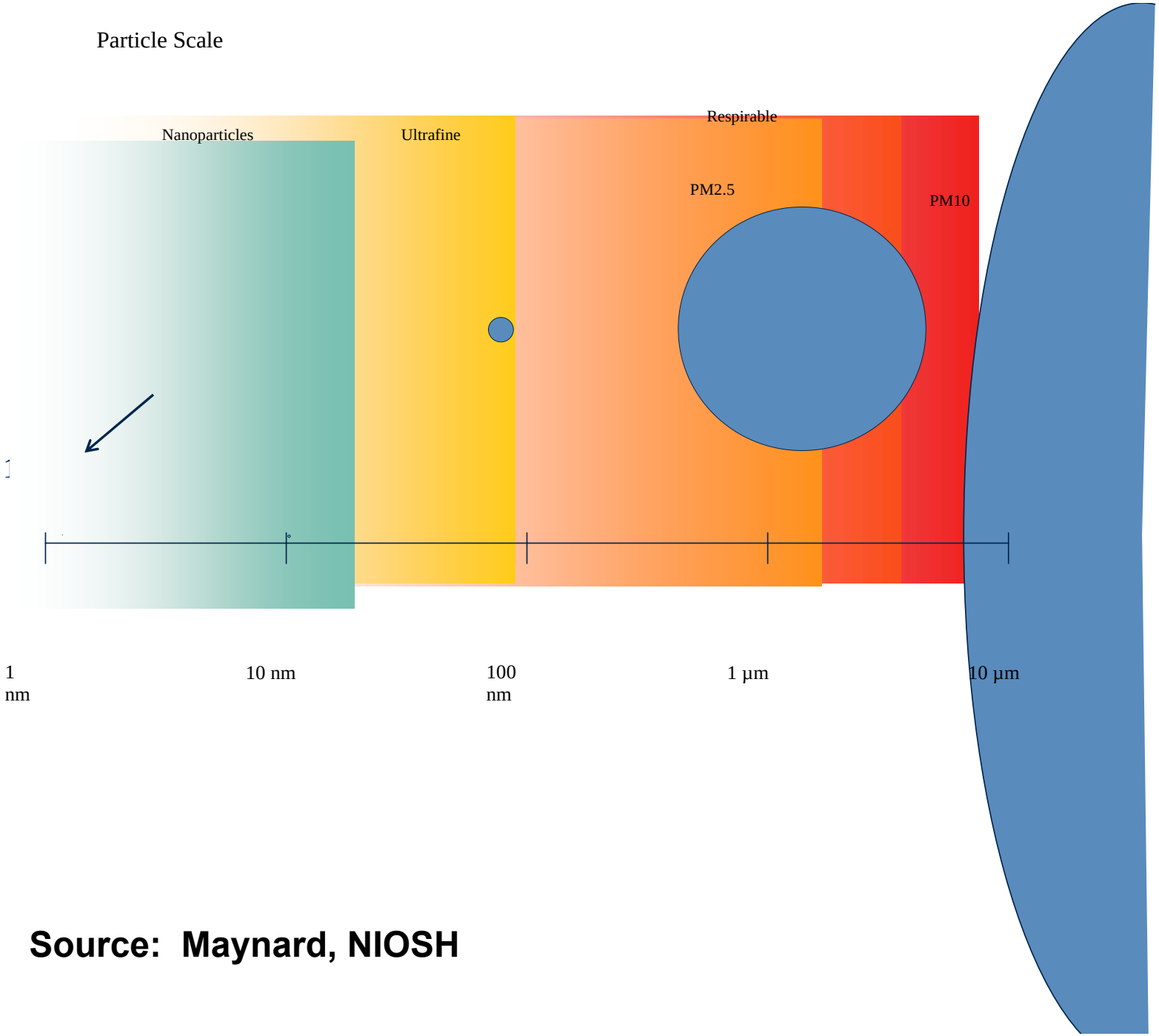


Why Should You Care?

- Industrial hygiene sampling and analytical equipment will get much lighter, have greater sensitivity, specificity, and response time
- PPE will become lighter and more effective
- Health impacts of insoluble/poorly-soluble nanoscale particles may not be the same as for larger respirable micron-size particles of IDENTICAL chemical composition

Fire and Explosion

- Nanoscale combustible material could present a higher risk than coarser material of similar quantity.
  - Decreasing particle size can reduce minimum ignition energy, increase combustion potential, combustion rate
  - Relatively inert materials may become combustible
- Some metals
  - Explosion risk can increase significantly as particle size decreases



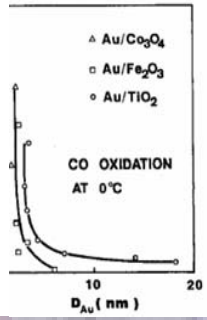
Source: Maynard, NIOSH

Nanotechnology Description

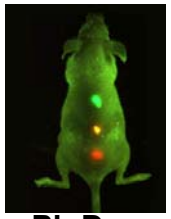
- **Fundamental properties can be adjusted/changed** from the corresponding coarser bulk material by only reducing the size of the particles, **with no change in substance** . Adjustable properties of nanomaterials –
- **Biological:** Increased permeability through biological barriers
- **Catalytic:** Better catalytic efficiency through higher surface-to-volume ratio
- **Sterical:** Increased selectivity, drug transportation and controlled release
- **Optical:** optical absorption and fluorescence properties
  increased quantum efficiency of semiconductor crystals
- **Electrical:** electrical conductivity and resistance
- **Magnetic:** Superparamagnetic behavior.
- **Mechanical:** Improved hardness and toughness of metals

Cat becomes/behaves like a Dog

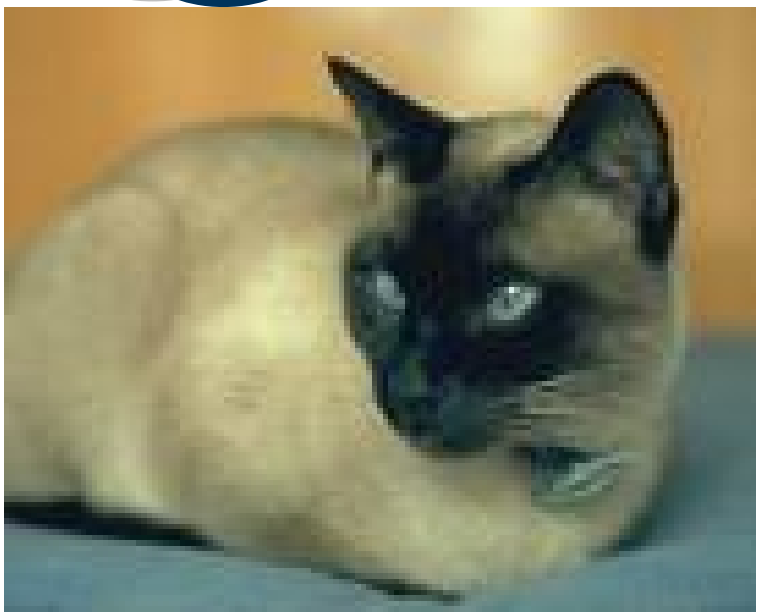
TRANSITIVE NANOPARTICLE

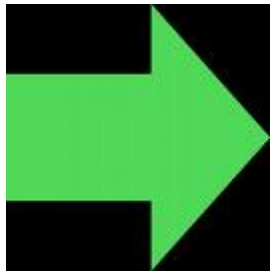


Quantum-Tagged Prostate Cancer Cells



Shuming Nie, Ph.D., Georgia Institute of Technology.

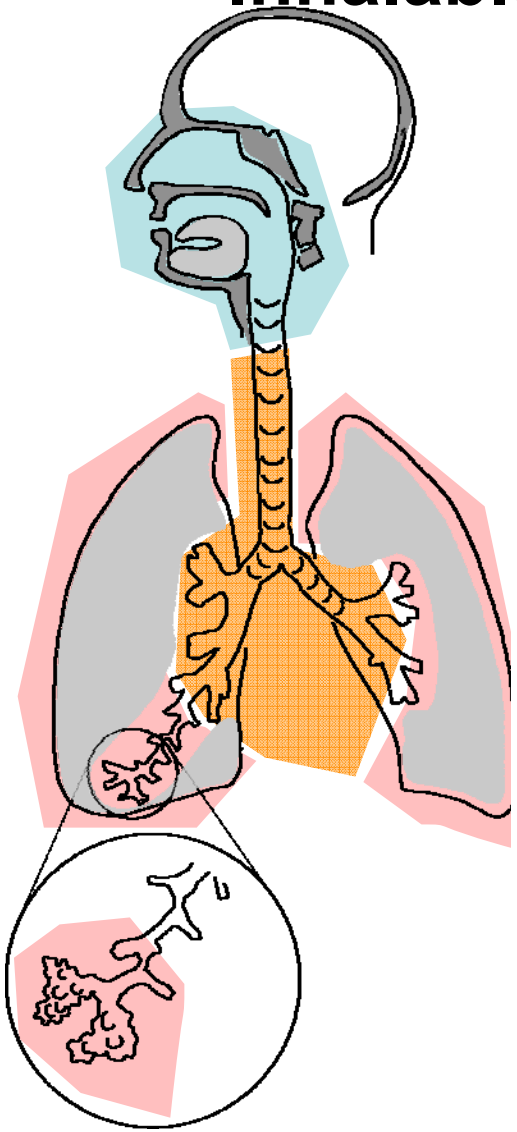


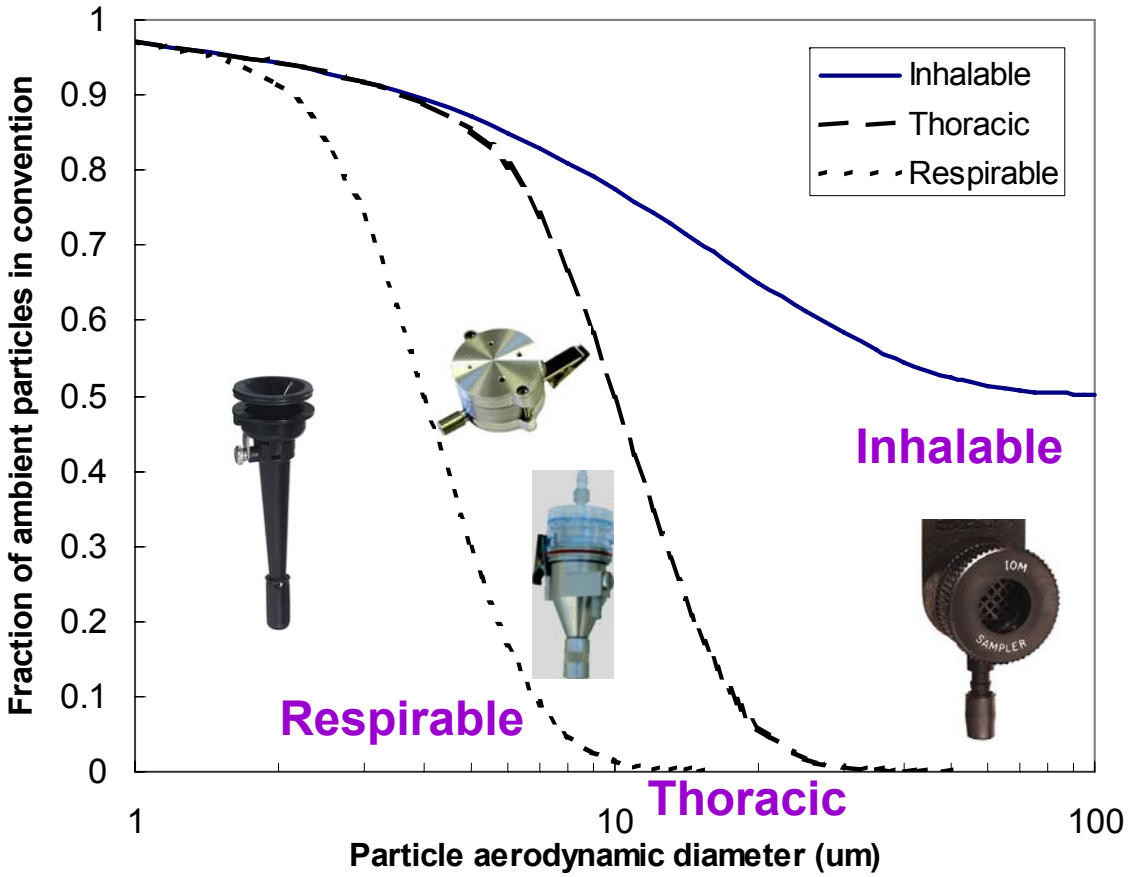


Exhibits size-related intensive property that differs significantly from larger particles

Behavior that is not smoothly or simply extrapolated from the larger particles

Penetration into the Respiratory Tract
Size-Selective Sampling:
Inhalable/Thoracic/Respirable





Source: Maynard, NIOSH

“Nano” Copper Oxide Powder?

- Apply fume TLV instead of dust TLV?
- Copper fume TLV-TWA: 0.2 mg/m^3
- Dusts and mists, as Cu: 1 mg/m^3

Nano ZnO

- Is current 2 mg/m^3 TLV-TWA, 10 mg/m^3 TLV-STEL, adequate?
- Respirable fractions
- Basis – metal fume fever

Nanoaluminum

- Is current 2007 TLV-TWA adequate?
  - 10 mg/m^3 metal dust, 5 mg/m^3 pyro powders; “total”
- Is 2007 NIC TLV-TWA adequate?
  - 1 mg/m^3, metal and insoluble compounds; respirable?

Nanosilver

- Apply TLV-TWA for “metal” or soluble compounds (as Ag)?
  - TLV-TWA of 0.1 mg/m^3, metal, “total”
  - TLV-TWA of 0.01 mg/m^3, soluble compounds, as Ag, “total”

Titanium Dioxide

- **Is it possible to have one ultrafine exposure limit that applies to all polymorphs, shapes, sizes, etc?**
- Different Crystalline Polymorphs (anatase, rutile),
- Coatings (e.g., Ag)
- Particle Size Distributions, Shapes
  - Different Surface areas
  - Different Deposition Probabilities in Respiratory Tract
  - Different Translocation Potentials?

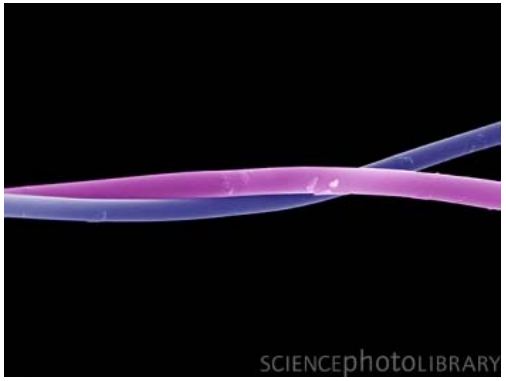
Local and Systemic Effects

- Increased local effects on a mass-basis?

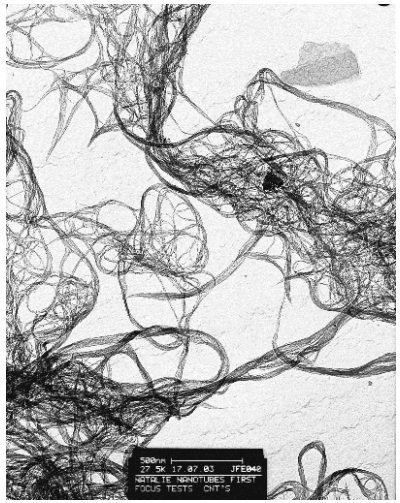
- Systemic effects?
  - Where TLVs or PELs were based upon avoidance of a localized respiratory health effect (e.g., fibrosis of deep lung), be aware that smaller sizes of the same particle may possibly cause effects beyond localized effects – i.e., systemic effects!

Carbon Nanotube Toxicity Factors?

Structure, Shape



SEM Image. DR KOSTAS KOSTARELOS & DAVID MCCARTHY/ SCIENCE PHOTO LIBRARY



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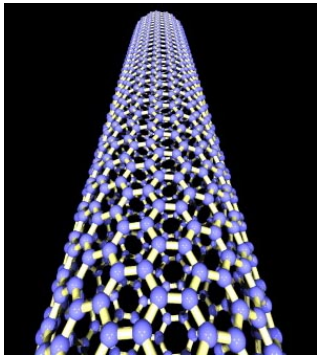
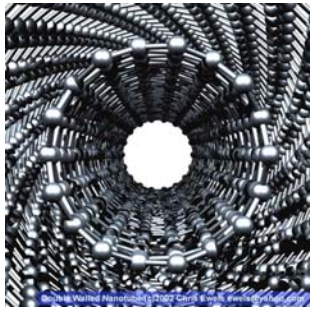
Diameter, SW, MW

0.7-3 nm



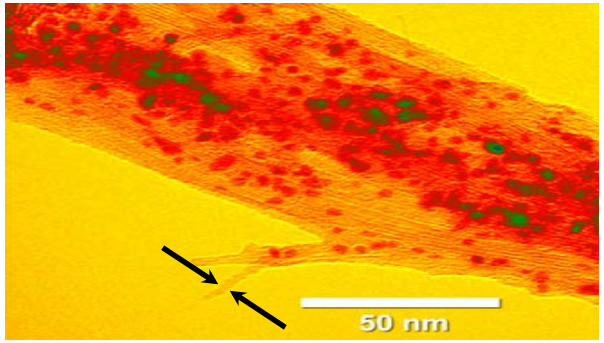
10 to 200 nm



Aspect Ratio:

length to width

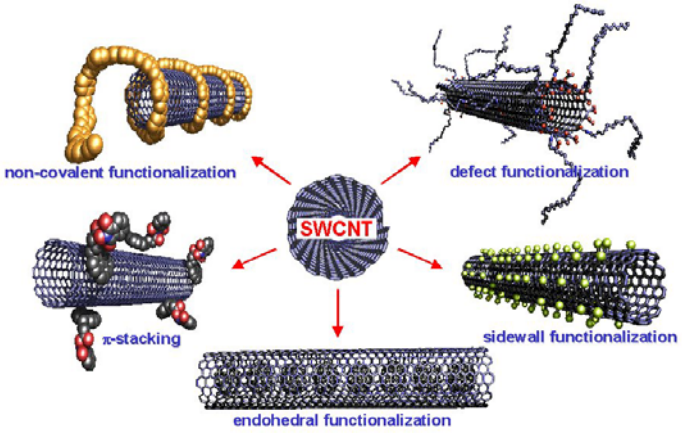
Trace Contaminants



1.4 nm

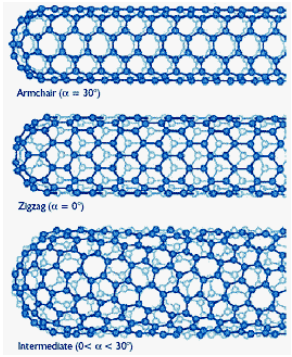
Source: Maynard, NIOSH

Functionalization



Computer Chemistry Center
University of Erlangen-Nuremberg

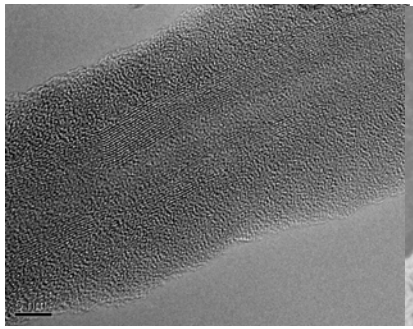
Chirality



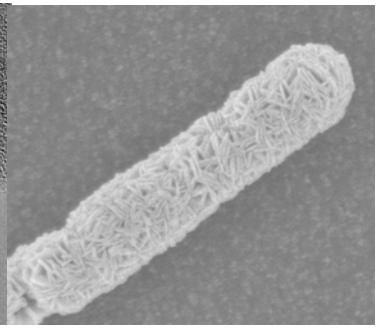
American Institute of Physics

Surface Coatings

SiO_2 Coated



Ag Coated



Trace Contaminants Possible in Carbon Nanotube Powders

- **Co:** 0.02 mg/m^3, “total” TLV-TWA
- **Fe oxide:** 5 mg/m^3, respirable TLV-TWA
- **Ni (insoluble inorganic):** 0.2 mg/m^3, inhalable TWA-TLV
- **Carbon black:** 3.5 mg/m^3, “total” TLV-TWA
- **PAHs**

Nanoparticle Toxicity Determinants

- Size and size distribution
- Shape
- Surface area: external, internal
- Surface chemistry: composition, charge, reactivity, energy/wettability, adsorbed species, contamination
- Chemical composition: spatially averaged (bulk), spatially resolved heterogenous composition
- Crystallinity: amorphous or crystalline
- Crystalline form (e.g., rutile or anatase TiO2)
- Porosity: nonporous, microporous, mesoporous
- Trace impurities/contaminants (e.g., metal catalysts, PAHs, etc)
- Agglomeration/aggregation state
- Biopersistence/durability/solubility

Sampling for airborne nanoparticles during a drum hanging operation in a commercial nanomaterial production facility

Source:
NIOSH