Engineered Nanomaterials and Occupational Health

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Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars

THE PEW CHARITABLE TRUSTS

Society of Toxicology, National Area Chapter. November 2nd 2005, Washington DC

Focus on the Workplace

Consumer perspective

www.eastonbike.com

Nano-based and nano-enabled products.

Nanomaterials not readily accessible biologically in many cases.

Example: Multi-walled carbon nanotube composites

Occupational perspective

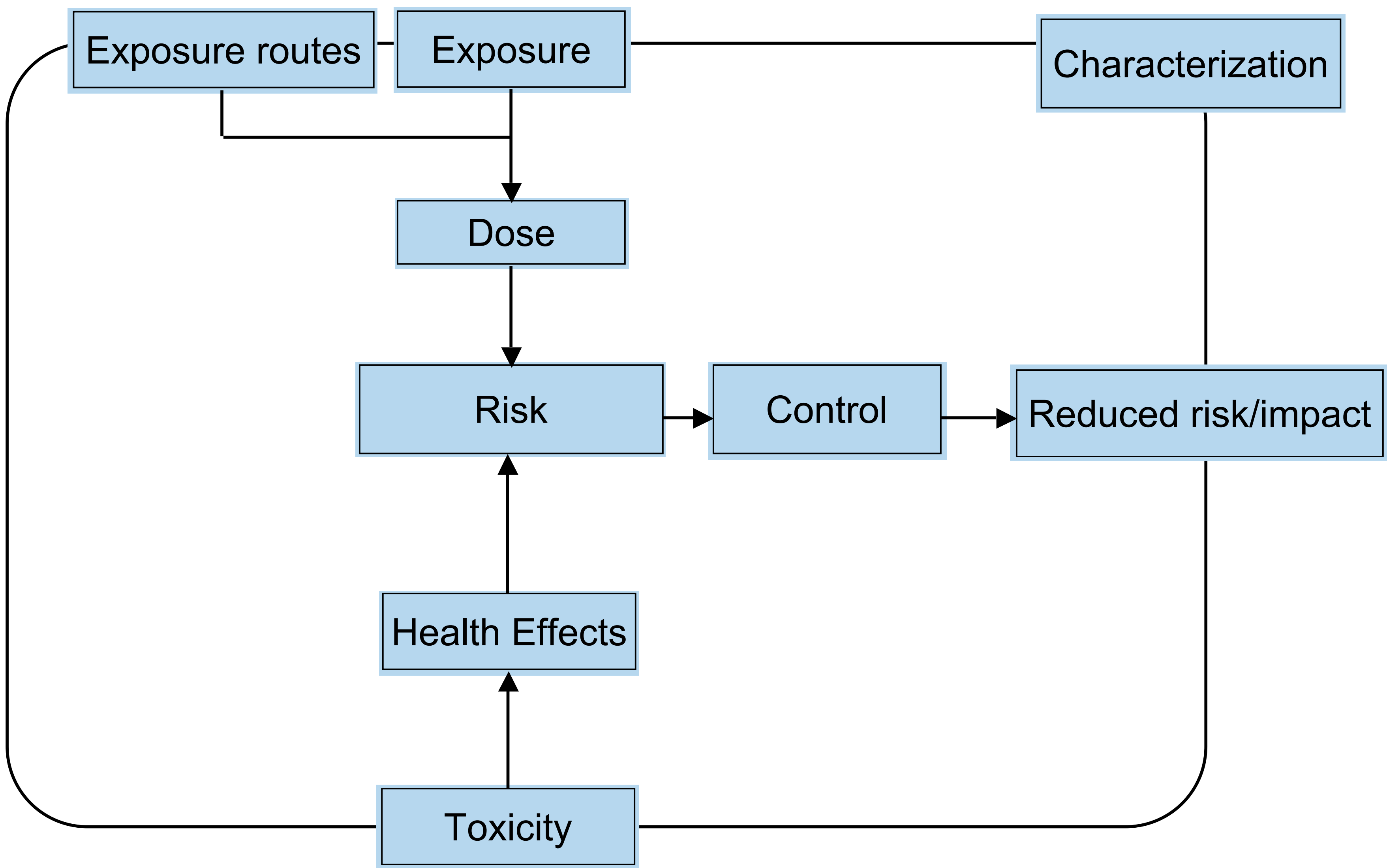
Production, handling and use of engineered nanomaterials.

Exposure potential likely to be higher than in final products.

Example: Handling single-walled carbon nanotubes

Note: additional hazard potential may exist over the lifecycle of nano-enabled products

Addressing Occupational Impact



Characterization and nano-toxicity screening

"Appropriate physicochemical characterization of nanomaterials used in toxicity screening tests is essential, if data are to be interpreted in relation to the material properties, inter-comparisons between different studies carried out, and conclusions drawn regarding hazard."

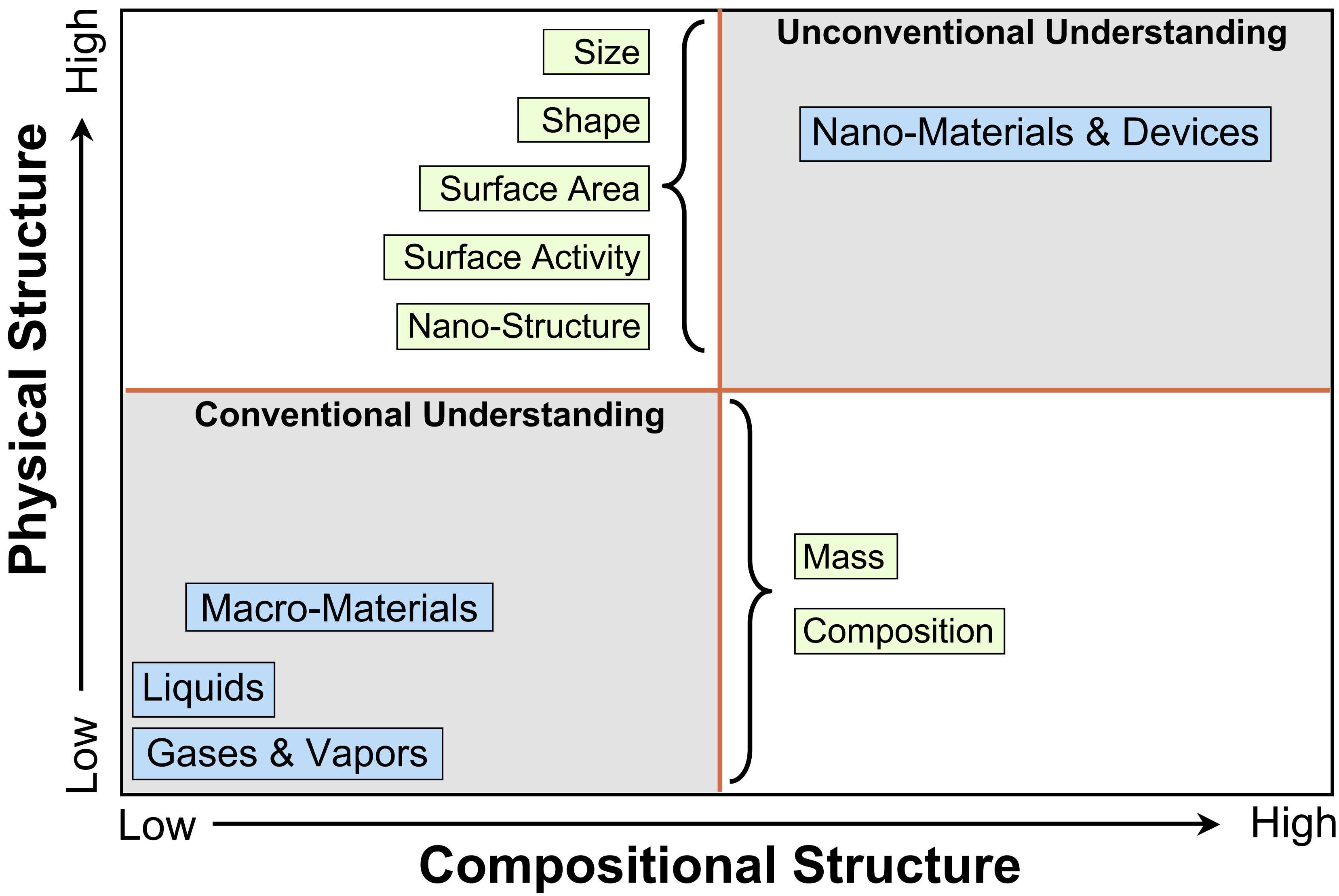
Principles for characterizing the potential human health effects from exposure to nanomaterials: Elements of a screening strategy.

Oberdörster *et al.* Particle and Fibre Toxicology **2**:8 (2005)

Potential Health Impact

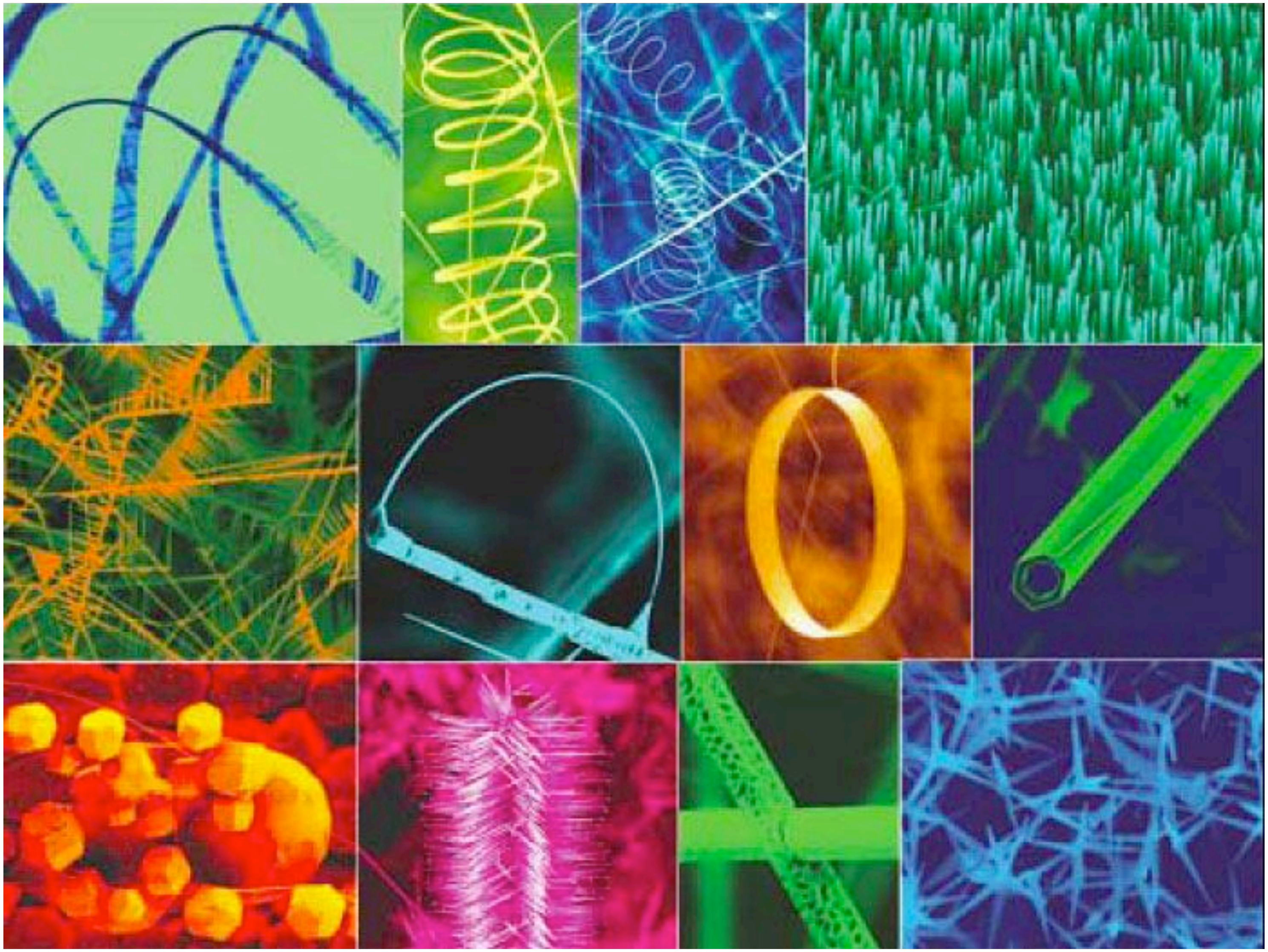
What makes 'nano' different?

Influence of structure on potential health impact



Engineered Nanomaterials - Structure is Important

Example: Zinc Oxide nanostructures

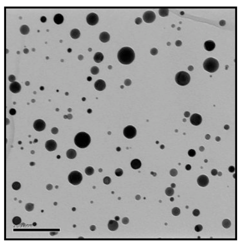


Materials Today June 2004. Zhong Lin Wang, Georgia Institute of Technology

Setting Boundaries

Engineered nanomaterials which potentially present new challenges

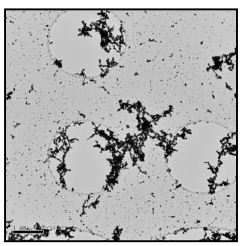
- Criteria:
  - Nanomaterials capable of entering or interacting with the body
  - Nanomaterials which potentially exhibit nanostructure-dependent biological activity



Nanoparticles
Simple, complex, “smart”. Aerosols, powders, suspensions, slurries

www.osha.gov

Comminution
Aerosols from grinding, cutting, machining nanomaterials



Agglomerates
or aggregates of nanoparticles

www.picturearts.comov

Degradation/Failure
Aerosols and suspensions resulting from degradation and failure of nanomaterials

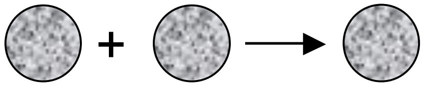
Aerosolized suspensions
Including slurries and solutions of nanomaterials

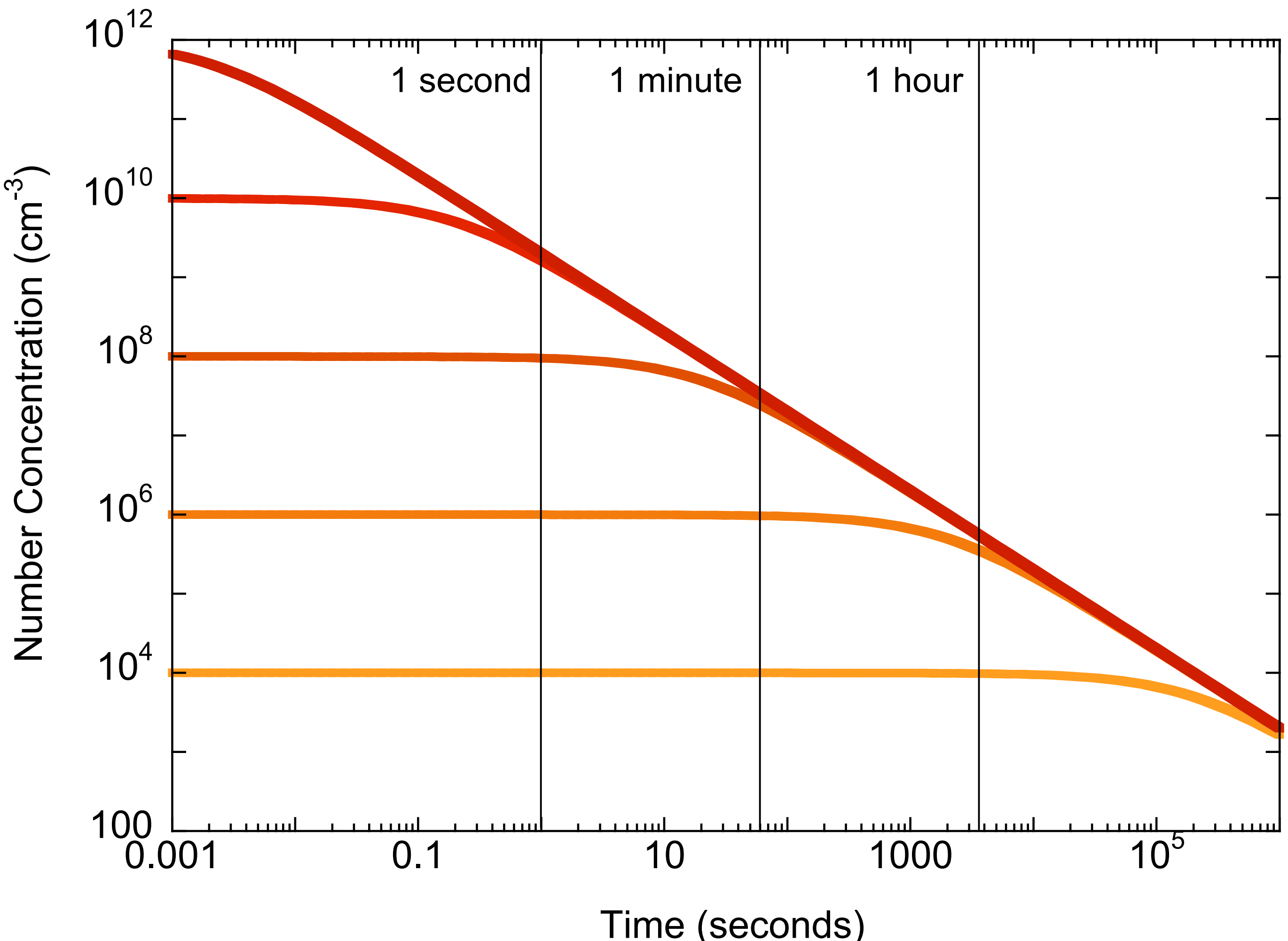
?

Unintentional use
Potential exposure from unanticipated/unintentional use

Airborne nanomaterials transformation

Monodisperse coagulation

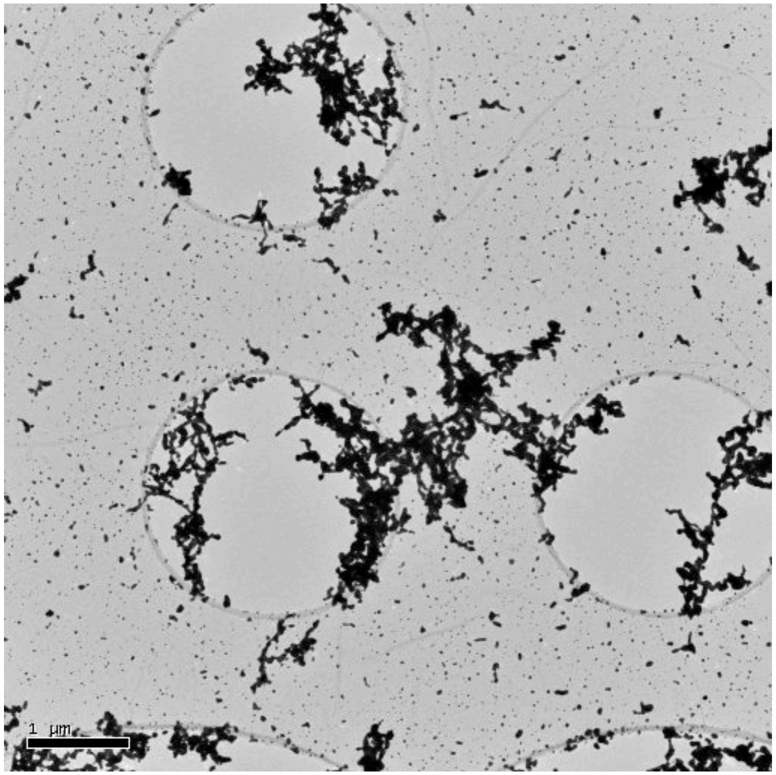




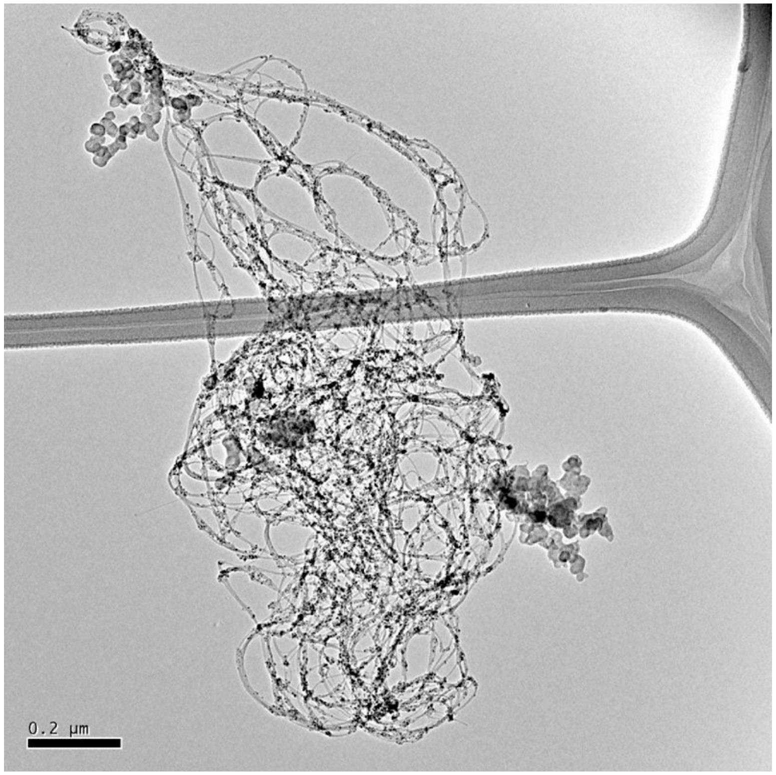
Adapted from Hinds (1999)

Agglomeration

How does it affect particle biological activity?



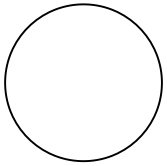
Agglomerated silver particles



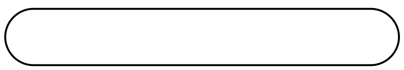
"Agglomerated" single walled carbon nanotubes

Particle Categories

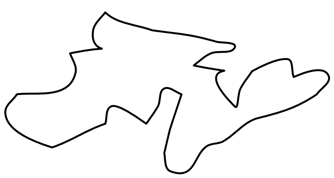
Classes of engineered nanoparticles



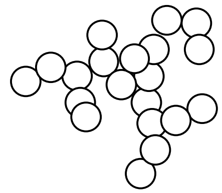
A. Spherical homogeneous



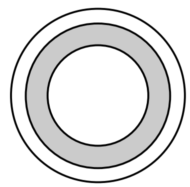
B. Fibrous homogeneous



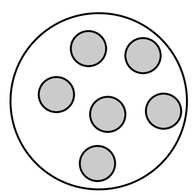
C. Non-spherical homogeneous



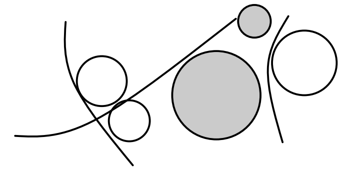
D. Agglomerate homogeneous



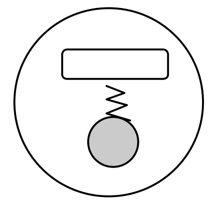
E. Heterogeneous concentric



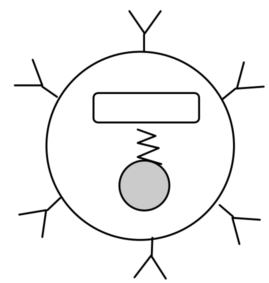
F. Heterogeneous distributed



G. Heterogeneous agglomerate



H. Active particle



I. Multifunctional particle

(not necessarily inclusive)

Measuring exposure

Attribute + related physical quantity → exposure metrics

Attribute	Particle Type								
	A	B	C	D	E	F	G	H	I
Size / size distribution	■	■	■	■	■	■	■	■	■
Shape		■	■	■	■	■	■	■	■
Chemical Composition	■	■	■	■	■	■	■	■	■
Surface Chemistry	■	■	■	■	■	■	■	■	■
Size dependent properties	■	■	■	■	■	■	■	■	■
Morphology dependent properties		■	■	■	■	■	■	■	■
Physicochemical structure-dependent properties				■	■	■	■	■	■
Solubility	■	■	■	■	■	■	■		
Charge (in lung fluid)	■	■	■	■	■	■	■	■	■
Crystallinity	■	■	■	■	■	■	■		
Physicochemical structure					■	■	■	■	■
Inter-particle adhesive forces				■			■		
Physical re-structuring potential				■			■		
Size distribution				■			■	■	■
Temporal changes in physicochemical structure			■	■	■		■	■	■
Component particle dissociation (in body)				■			■	■	■
Differential component dissociation (in body)					■	■		■	■
Synergistic interactions							■		
Stimulus-associated behavior								■	■
Functional response to environment									■

Associated metrics

Mass

Surface Area

Number

(Indicative only)

Monitoring nanoscale aerosol exposures

Options

- **Monitor mass concentration**
  - Continuity with the past
  - Sensitivity and relevance issues
- **Monitor number concentration**
  - Relatively simple
  - Difficult to differentiate between process-related and background aerosols
  - Relevance?
- **Monitor aerosol surface area concentration**
  - Relevant for some materials
  - Is this achievable?

Mass

Mass-based Exposure Measurement

- Relevance
  - Provides continuity with historic measurements/methods
  - Over 50 years experience in measuring mass concentration
  - When is mass concentration relevant to the health implications of exposure to nanomaterials?
- Conversions
  - Can mass concentration measurements be converted to other metrics?
  - Possible, but additional information is needed (such as aerosol size distribution)
  - Conversions are heavily biased by larger particles
- Sensitivity
  - Is the limit of quantification of mass-based methods sufficient for nanomaterials?

Gravimetric analysis - sensitivity

Example.

- Conventional material: 5 mg/m^3 OEL
- Nanomaterial:
  - Particles are 100 times smaller
  - Surface area is 100 times larger
  - Possible nano-OEL is 100 times lower - 50 $\mu g/m^3$
- Gravimetric analysis
  - Limit Of Quantification between 5 - 50 µg [est].
  - 8 hour sample at 2 l/min: 48 µg collected at nano-OEL
  - Just within LOQ - with a good balance system
- Problems if the conventional OEL is significantly lower than 5 mg/m^3.
- Chemical speciation is an option

Number

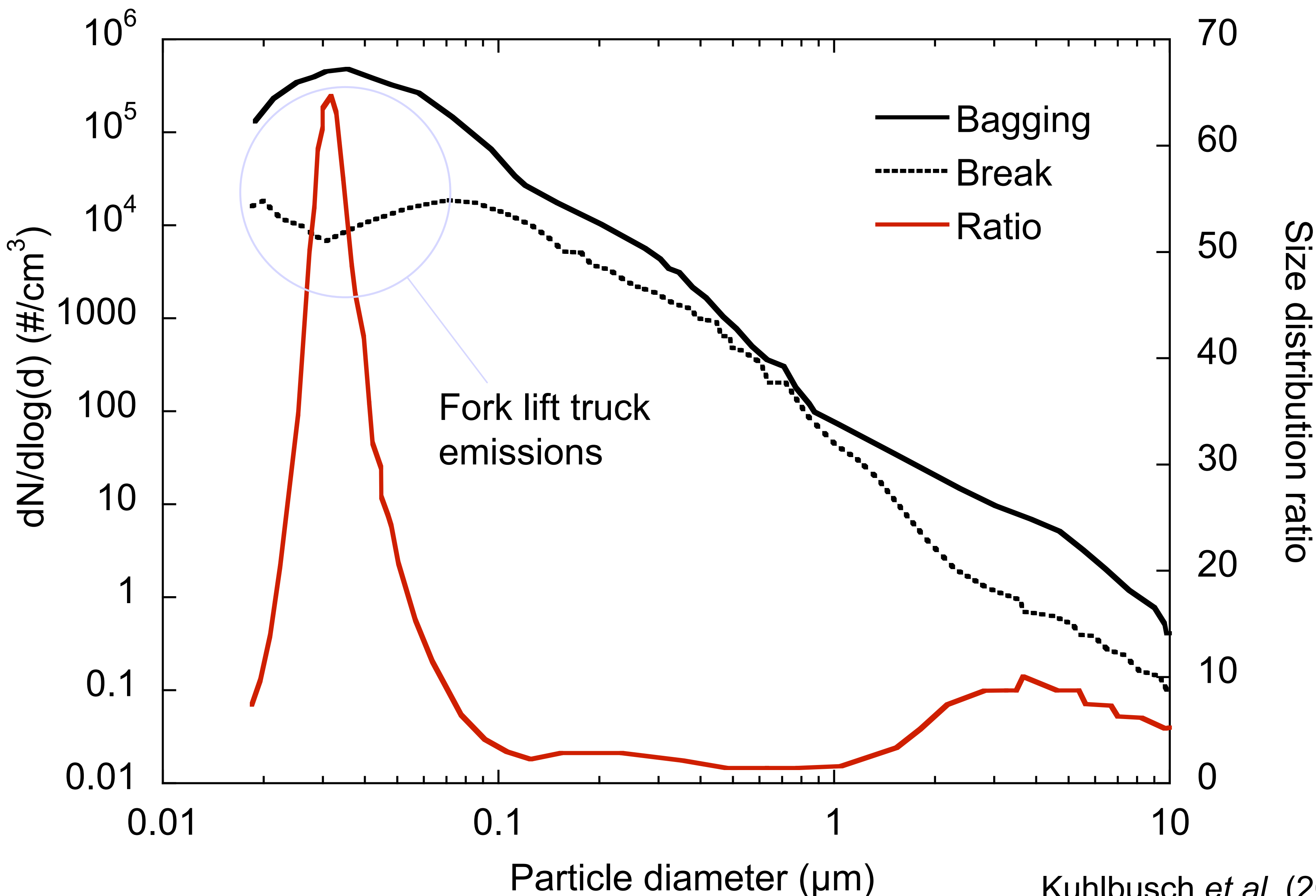
Number-based Exposure Measurement

- Portable Condensation Particle Counter
  - Responds to particles larger than ~10 nm
  - Very sensitive to low concentrations. Limited at high concentrations (10^5 particles/cm^3 for the TSI 3007)
  - Background counts: can be as high as 10^6 particles/cm^3 and above
  - Not material-specific
  - Good for ‘sniffing out’ sources

3007 Portable CPC, www.tsi.com

Example - non-specificity of number concentration

Carbon black production - bag filling areas



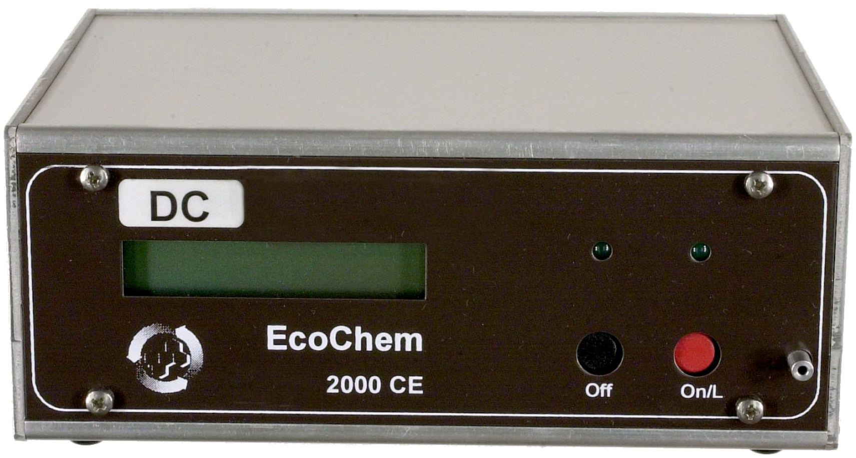
Kuhlbusch *et al.* (2004)

Surface Area

Aerosol surface-area measurement

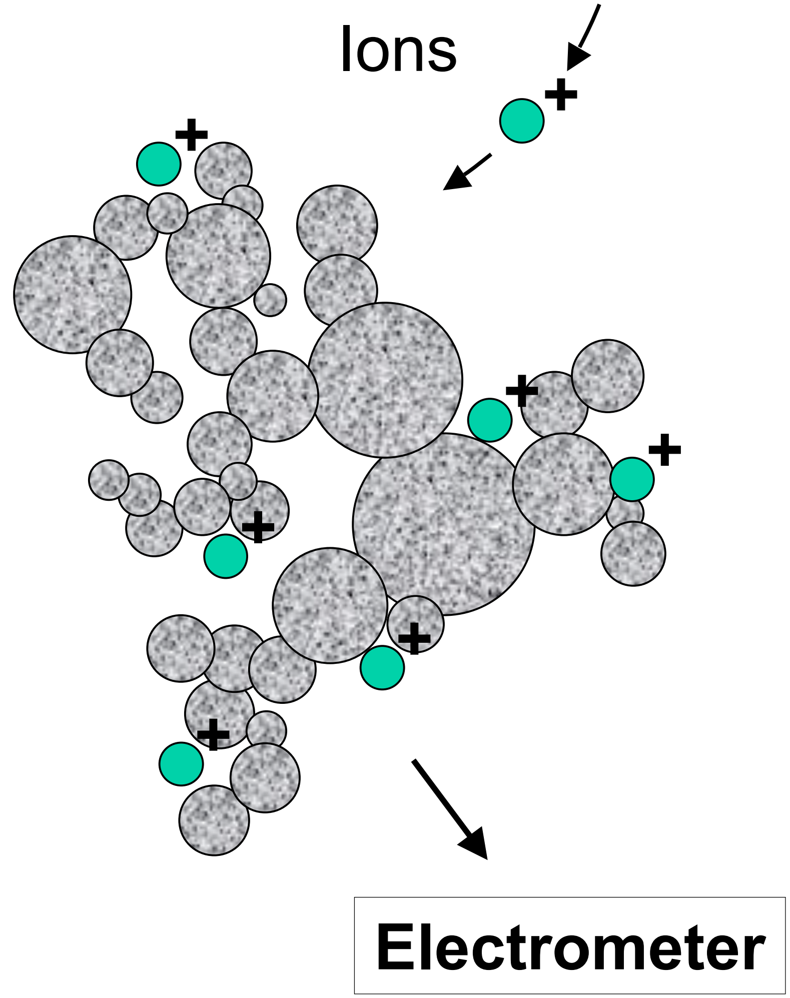
Using attachment rate

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

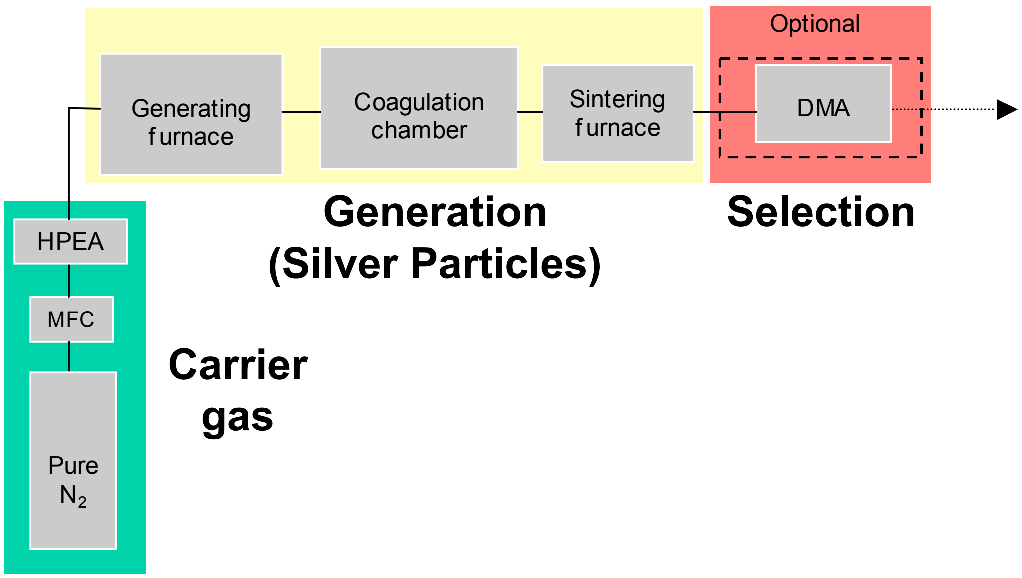


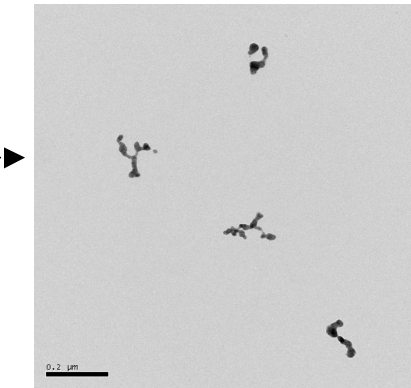
DC2000 CE Diffusion Charger

EcoChem

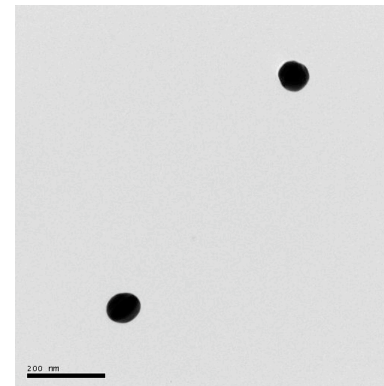


Monodisperse Test Particles



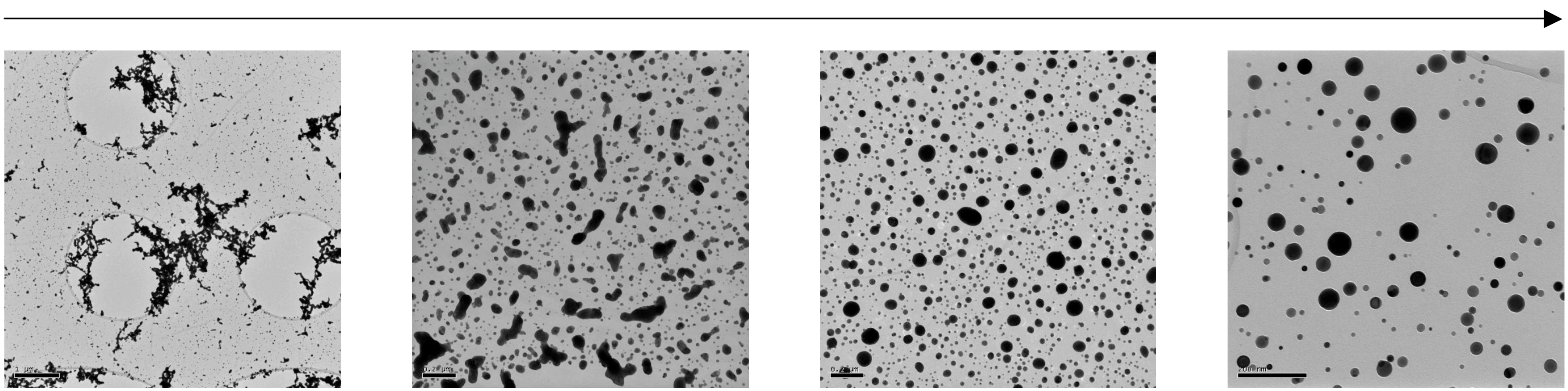


Fractal-like particles



Spherical particles

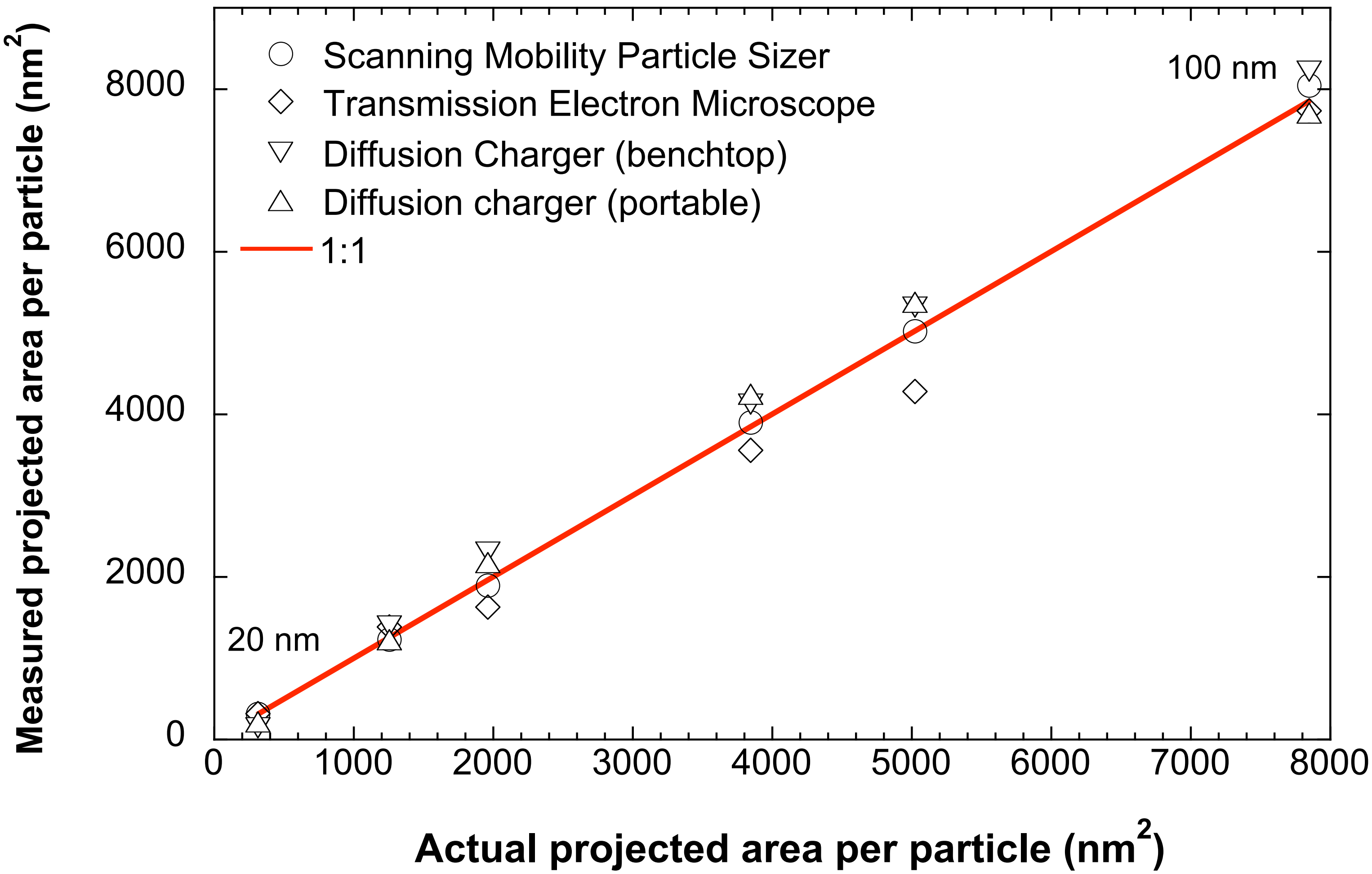
Increasing sintering temperature



Ku, B. K. and Maynard, A. D. *J. Aerosol Sci.* 36 (9), 1108-1124, 2005.

Comparison of measurement methods

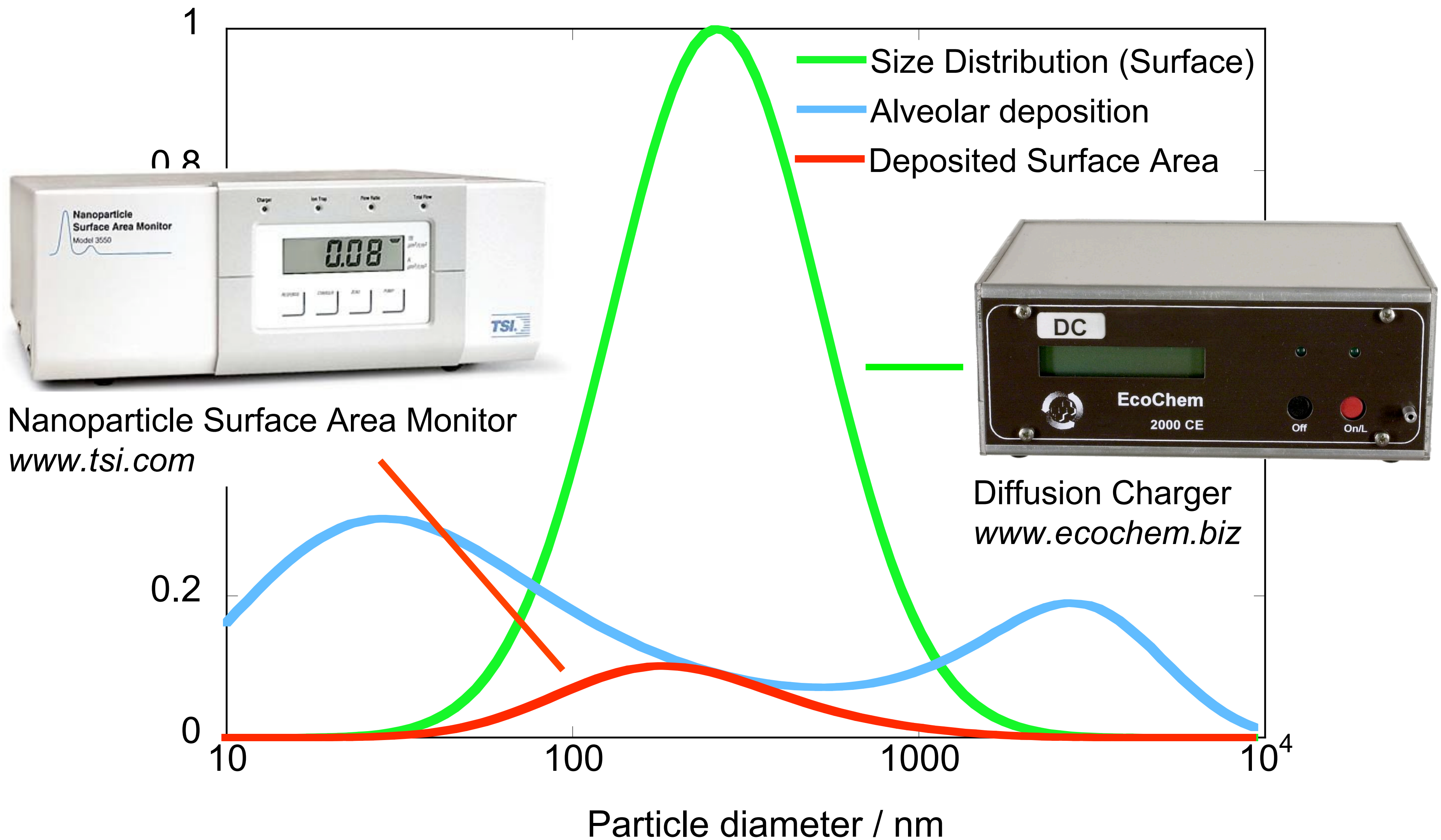
Monodisperse particles < 100 nm, fractal-like



Ku, B. K. and Maynard, A. D. *J. Aerosol Sci.* 36 (9), 1108-1124, 2005.

Emerging Measurement Technologies

Surface Area



Nanoparticle Surface Area Monitor
www.tsi.com

Diffusion Charger
www.ecochem.biz

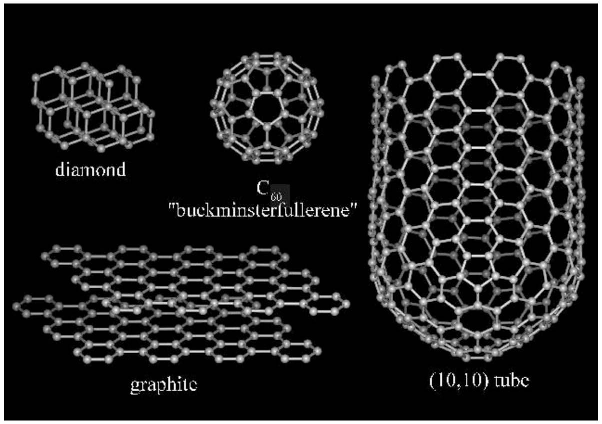
Wilson, W. E., in *Proceedings of the 2004 Air and Waste Management Association Conference*, 2004.

Example: Handling nanotube material

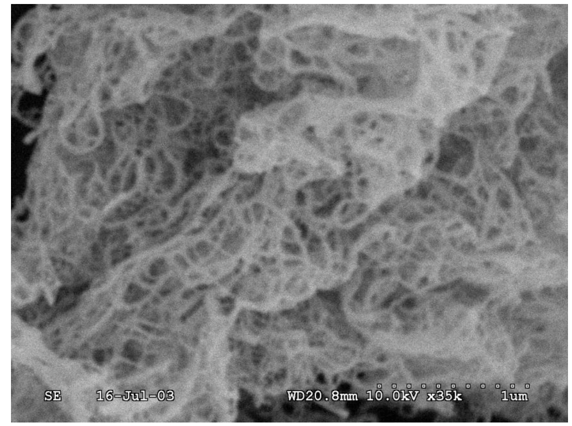
Unprocessed single walled nanotube material

Aerosol characterization

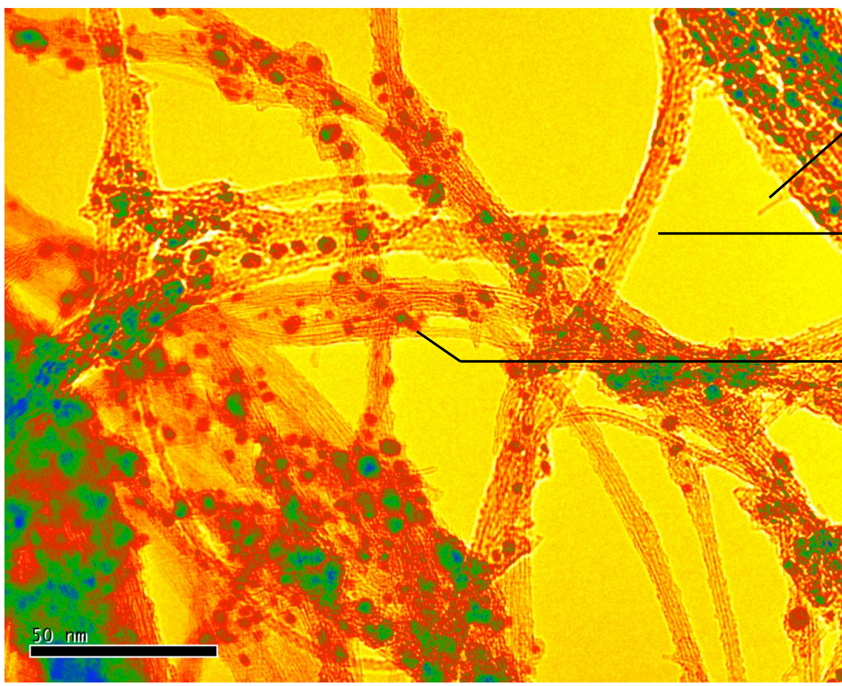
Single Walled Carbon Nanotubes



Allotropes of carbon



'Tangles' of nanotubes and nanoropes



Nanotubes

Nanoropes

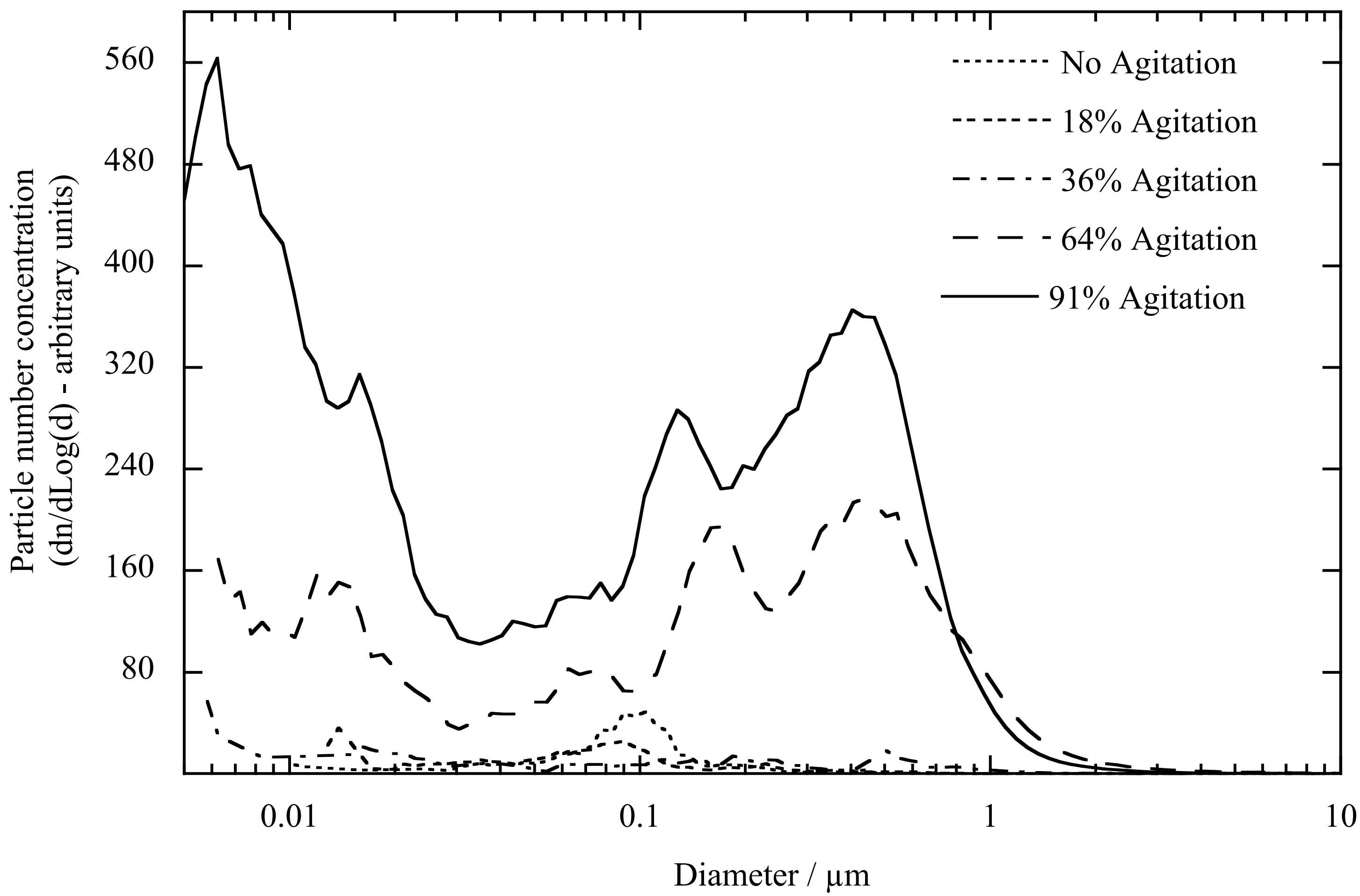
Catalyst particles

Non-tubular carbon

Raw single walled carbon nanotube material.

Laboratory generation of nanotube aerosol

Agitation of unprocessed material in an airflow

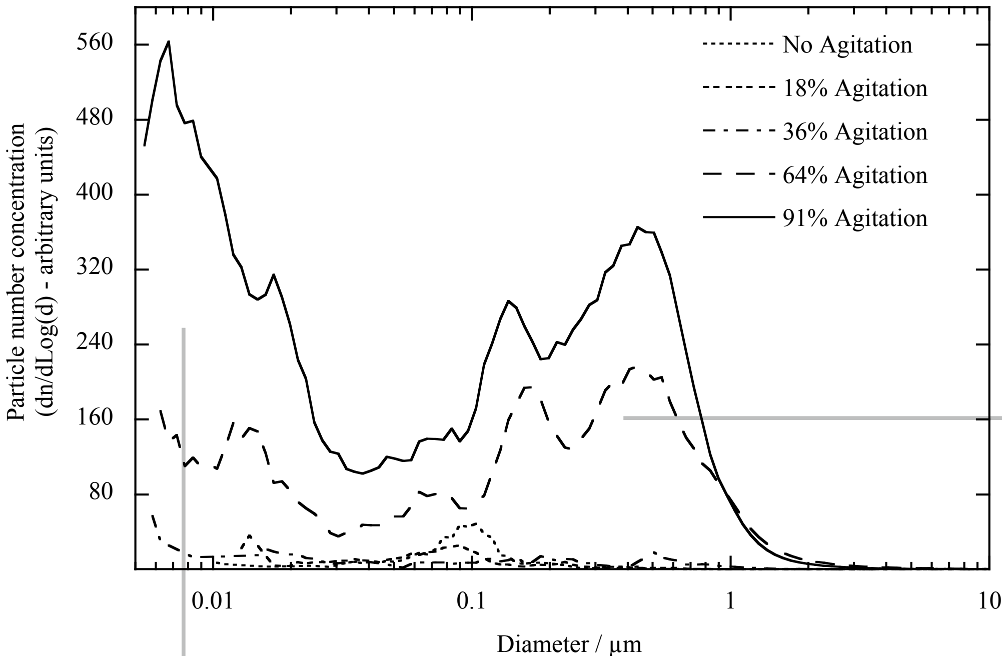


Agitation of unprocessed material in an airflow

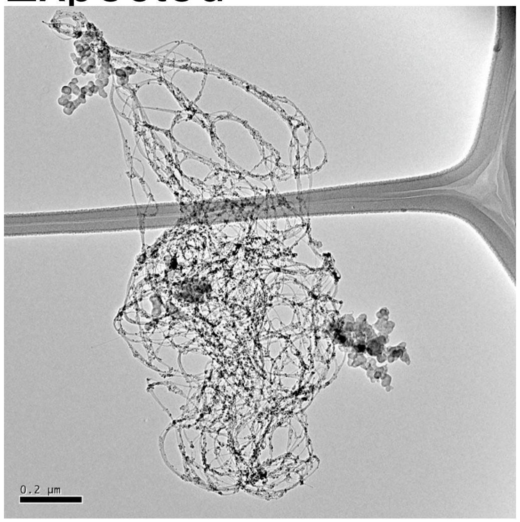
Maynard, A. D., P. A. Baron, et al. (2004). *J. Toxicol. Environ. Health* **67**(1): 87-107.

Aerosol characterization

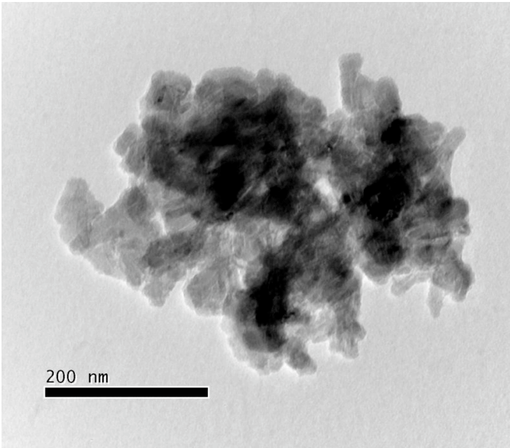
Physical characteristics of airborne carbon nanotubes



Expected



Measured

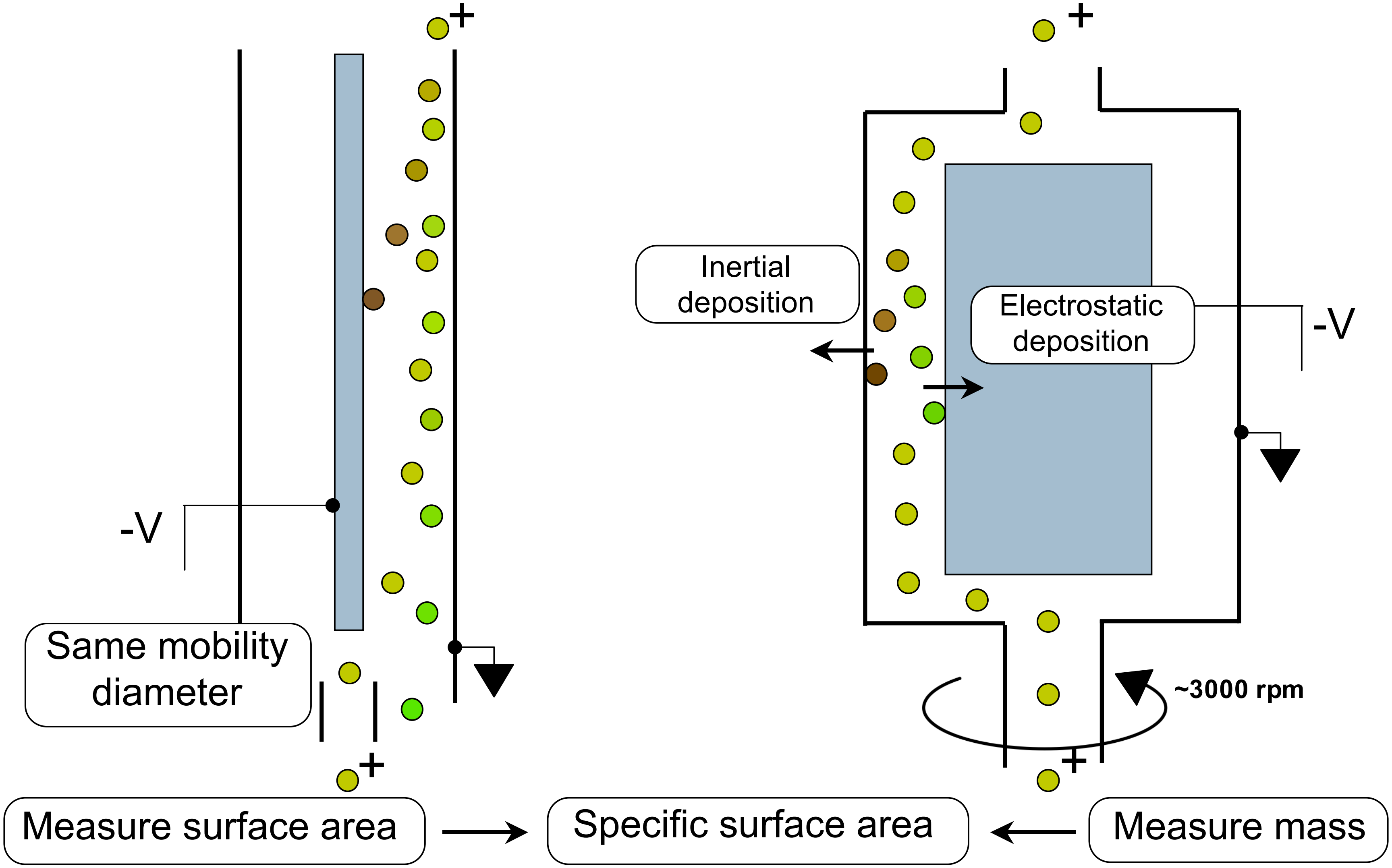


- Physical/Chemical Characteristics?
    - Discrete carbon nanotubes or nanoropes?
    - Transition metal catalyst particles?
    - Non-tubular carbon?

Aerosol Characterization

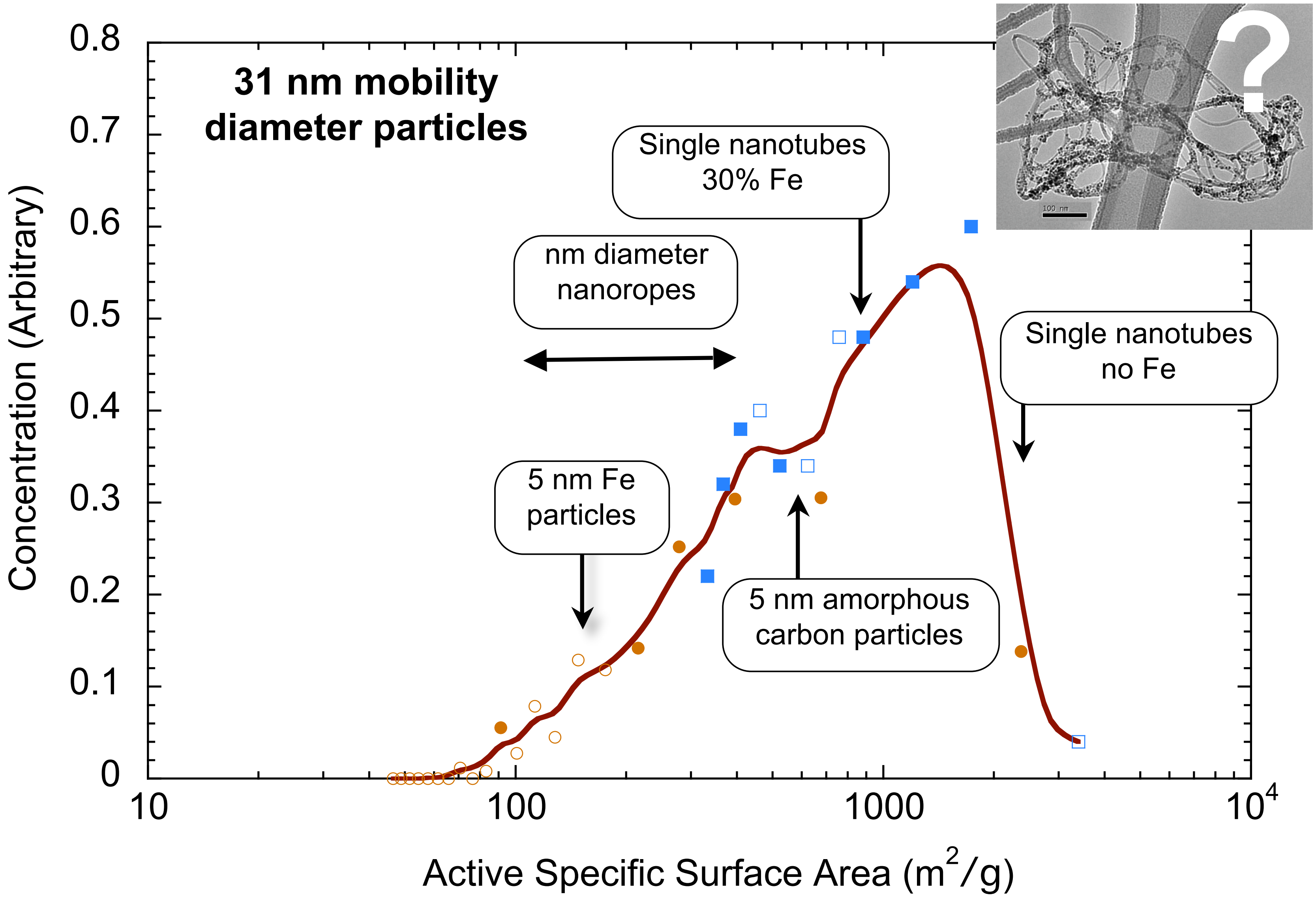
‘Active specific surface area’ measurements

Differential Mobility Analysis   Aerosol Particle Mass Analysis



Aerosol Characterization

'Active' specific surface area



Summary

- Physical and chemical structure strongly influence the properties of engineered nanomaterials
- Engineered nanomaterial hazard potential will likely be higher in the workplace than many other areas
- Characterizing engineered nanomaterials in a health context presents many challenges, but is essential to understanding and managing potential impact.
- Mass, surface-area and number concentration remain important exposure metrics
- Inter-disciplinary collaboration is essential to understanding and managing potential risk

Contact Information

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