The only thing worse than

NO Metrology

is

BAD Metrology

Addressing some misconceptions in materials characterization

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Condensed Matter National Laboratory (CMNL), IPM

Outline

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A brief introduction

2

The coming age of advanced materials

3

The case of Carbon Nanotubes

3

Determining the size: Challenges and Opportunities

A brief introduction

The need for materials characterization

Material characterization enables researchers to determine the structure of a material, how this structure relates to its macroscopic properties, and how it will behave in technological applications.

Beware of FAKE Materials!!!

Consistent quality!!!

Reproducible functionalities

The coming age of advanced materials

Or is it???

Advanced Materials

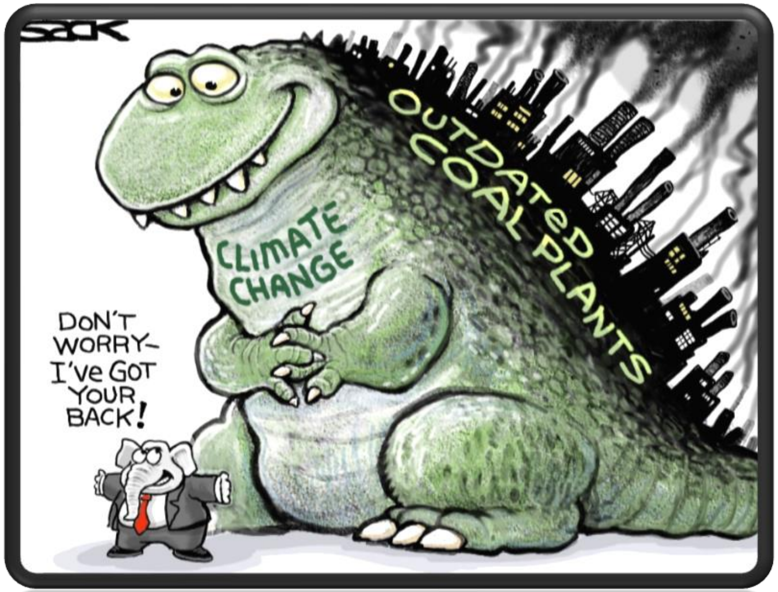


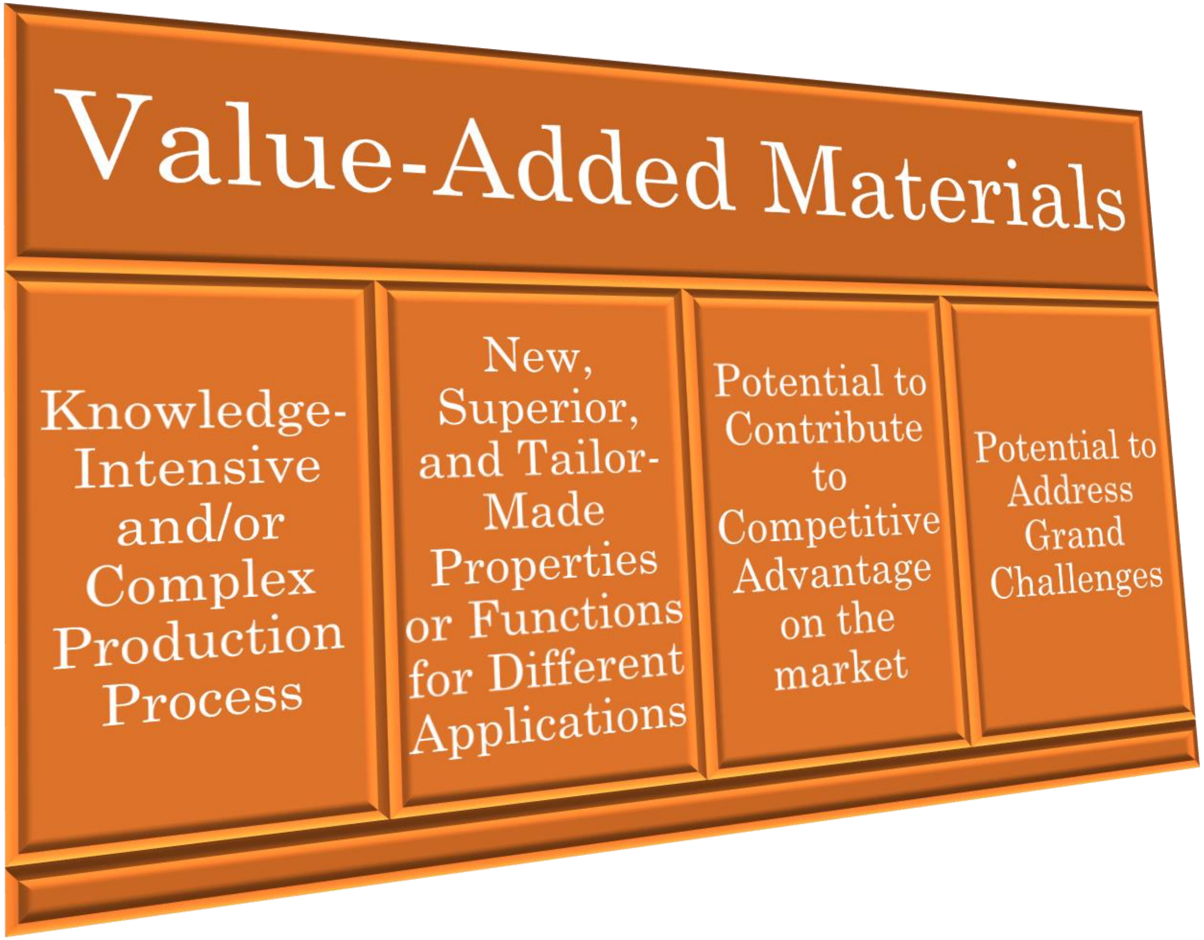
Image Credit: Star Tribune

Image Credit: Jantoo Cartoons

"YOU MEAN YOU NEVER HEARD OF CARS WITH FIBERGLASS BODIES BEFORE?"

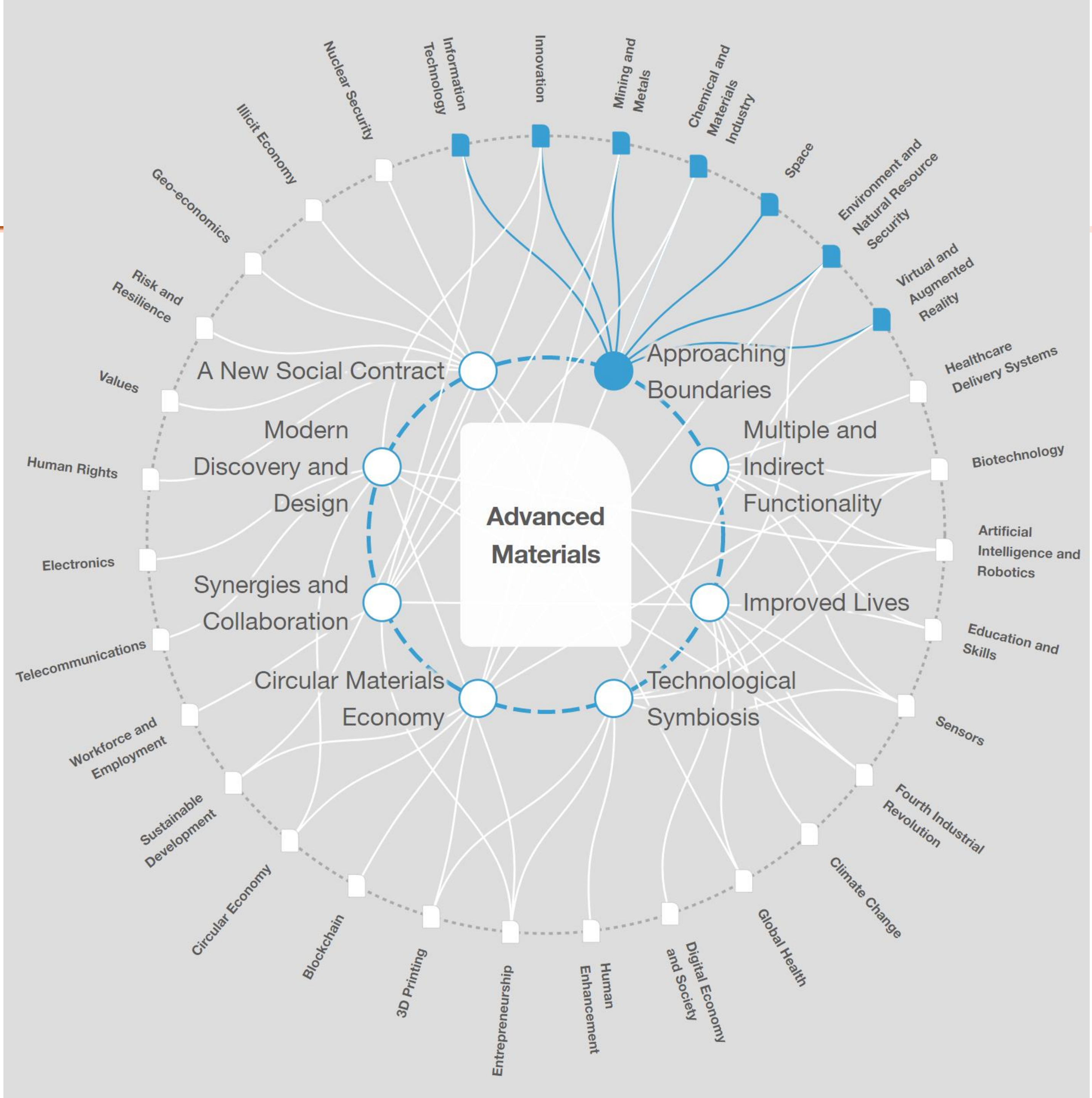
More new materials are made in the last 20 years compared to the rest of the history!!!

Advanced Materials



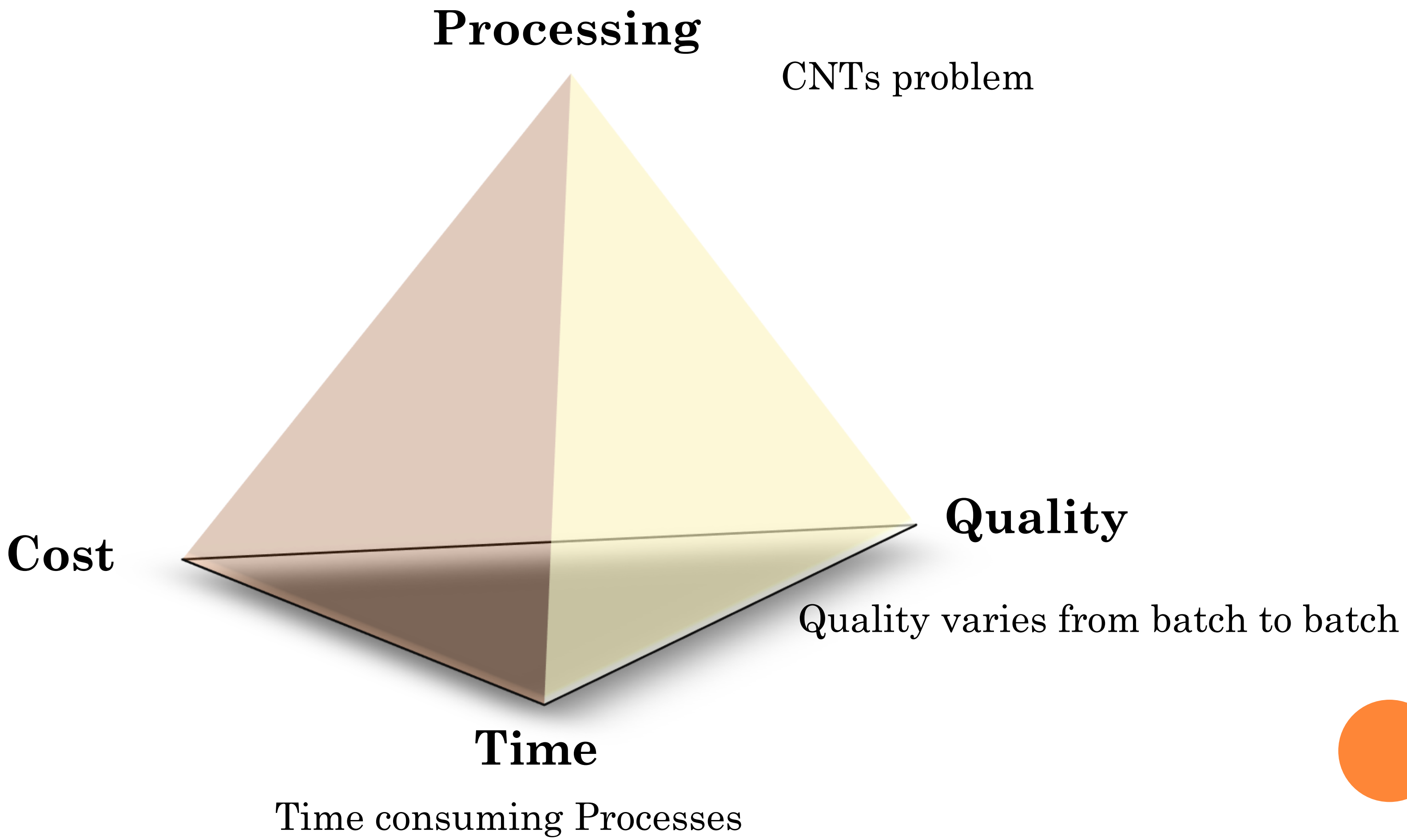
Porter, M. E. *The Competitive Advantage: Creating and Sustaining Superior Performance*. NY: Free Press, 1985. (Republished with a new introduction, 1998.)

Advanced Materials



World Economic Forum

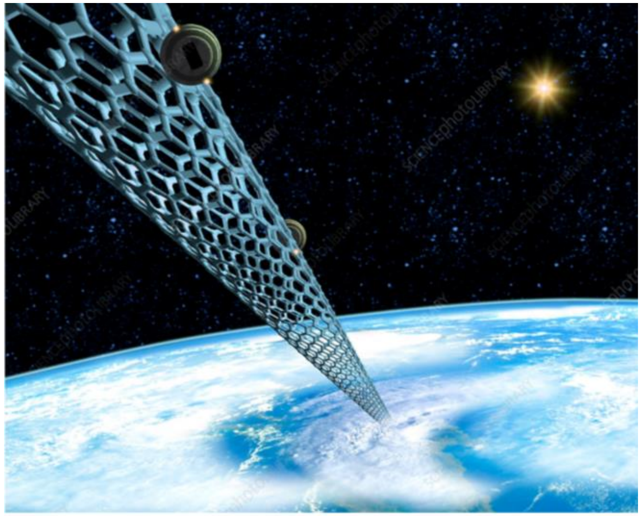
The Problem


Processing
CNTs problem
Quality
Cost
Quality varies from batch to batch
Time
Time consuming Processes

The case of CNTs

The Gold Rush

The case of Carbon Nanotube: The Gold Rush



Credit: VICTOR HABBICK VISIONS / SCIENCE PHOTO LIBRARY

The end of gold rush!!!

A complete disaster!!!

Basically, nothing matched anything else!!!

History

2000-2005

Significant difference in CNT response

Extraordinary CNT properties

Unique electronic properties

The main Challenge

The case of Carbon Nanotube

The end of the golden age of CNT electrochemistry

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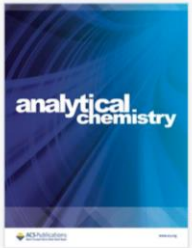
Basal Plane Pyrolytic Graphite Modified Electrodes: Comparison of Carbon Nanotubes and Graphite Powder as Electrocatalysts

Ryan R. Moore, Craig E. Banks and Richard G. Compton

View Author Information

Cite This: *Anal. Chem.* 2004, 76, 10, 2677-2682
Publication Date: April 20, 2004
https://doi.org/10.1021/ac040017q



Analytical Chemistry

Issue 16, 2004

Previous Article | Next Article

From the journal:
Chemical Communications

Investigation of modified basal plane pyrolytic graphite electrodes: definitive evidence for the electrocatalytic properties of the ends of carbon nanotubes

Craig E. Banks,[a] Ryan R. Moore,[a] Trevor J. Davies[a] and Richard G. Compton*[a]

THE CASE OF CARBON NANOTUBE

It is all done with Metals!!!

RETURN TO ISSUE | < PREV ARTICLE NEXT >

Iron Oxide Particles Are the Active Sites for Hydrogen Peroxide Sensing at Multiwalled Carbon Nanotube Modified Electrodes

Biljana Šljukić, Craig E. Banks and Richard G. Compton

Copper oxide nanoparticle impurities are responsible for the electroanalytical detection of glucose seen using multiwalled carbon nanotubes

Christopher Batchelor-McAuley [a], Gregory G. Wildgoose [a], Richard G. Compton [a], Lidong Shao [b], Malcolm L.H. Green [b]

Carbon Nanotubes Contain Metal Impurities Which Are Responsible for the "Electrocatalysis" Seen at Some Nanotube-Modified Electrodes

Craig E. Banks Dr., Alison Crossley Dr., Christopher Salter, Shelley J. Wilkins Dr., Richard G. Compton Prof. Dr.

Communication | Full Access

Bioavailability of Nickel in Single-Wall Carbon Nanotubes†

X. Liu, V. Gurel, D. Morris, D. W. Murray, A. Zhitkovich, A. B. Kane, R. H. Hurt

Angew Chem Int Ed 45 (16):2533

The case of Carbon Nanotube

Metallic impurities can be washed by HNO3

- Residual Metallic catalyst impurities cannot be washed out!!!

Reduction of Hydrogen peroxide

- Fe-based impurities are responsible!!!

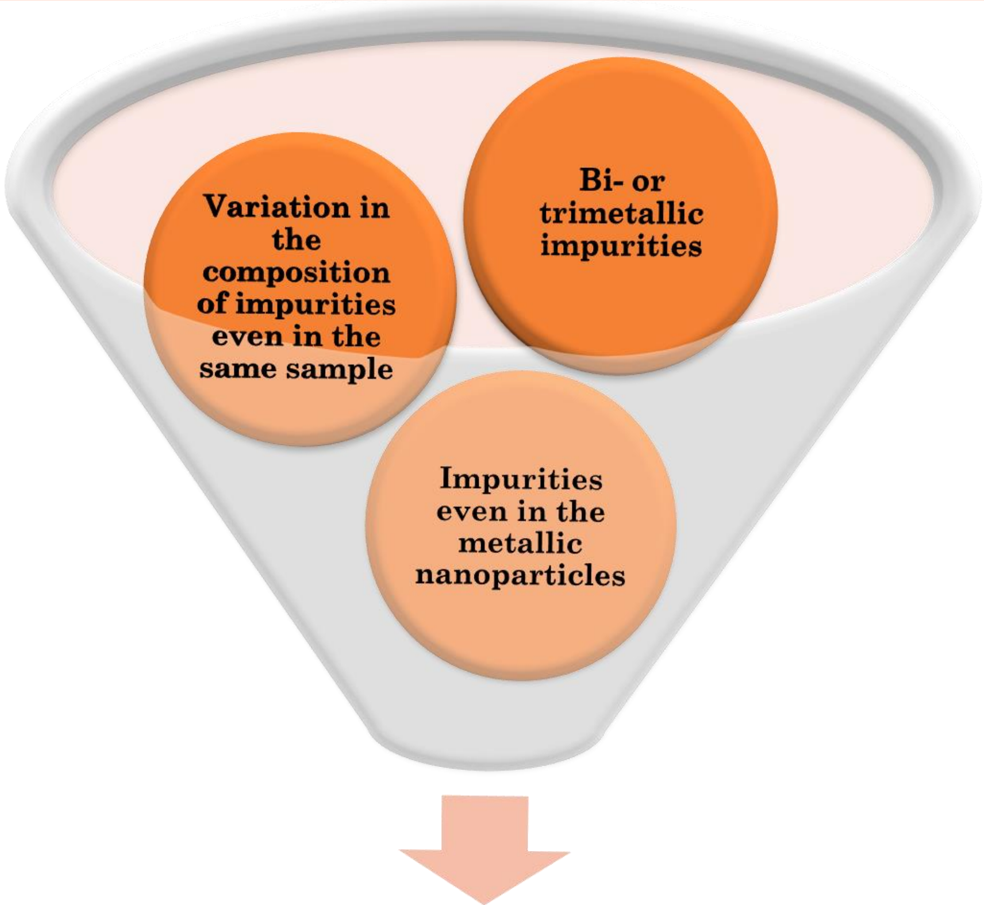
Glucose Oxidation

- Cu-based and Fe-based impurities are responsible!!!

Electrocatalytic oxidation of amino acids, and sulfides

- Ni-based impurities are responsible!!!

The case of Carbon Nanotube: The biggest Challenge

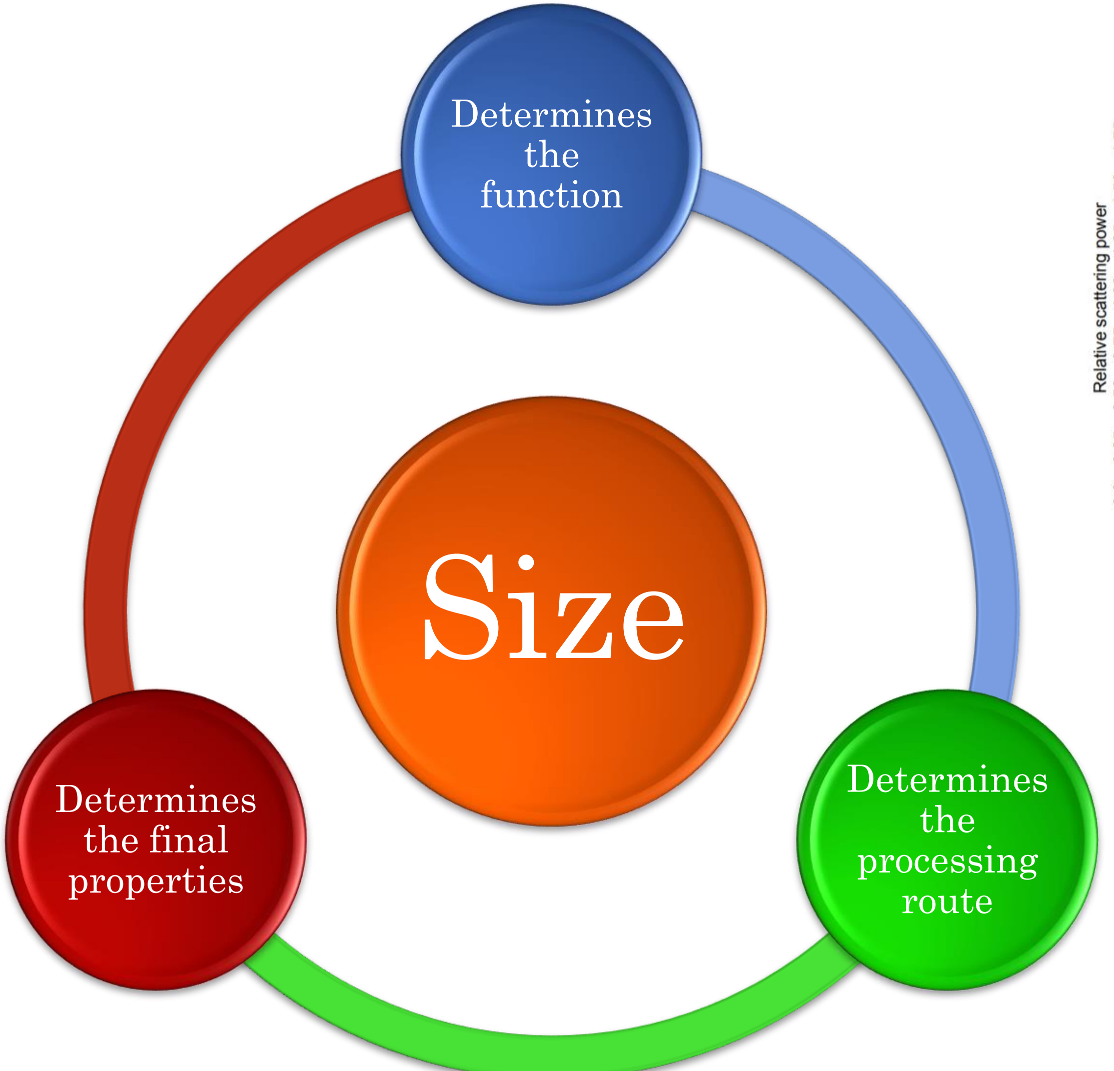


There is no standard method recommended by IUPAC or any other authority body for determining the amount of impurities!!!

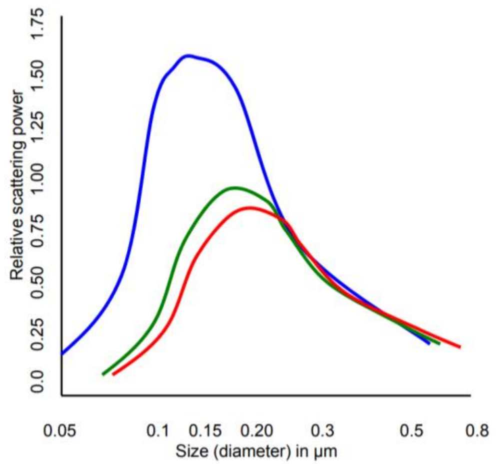
Size

Size is everything, at least from the particles' point of view!!!

The importance of size



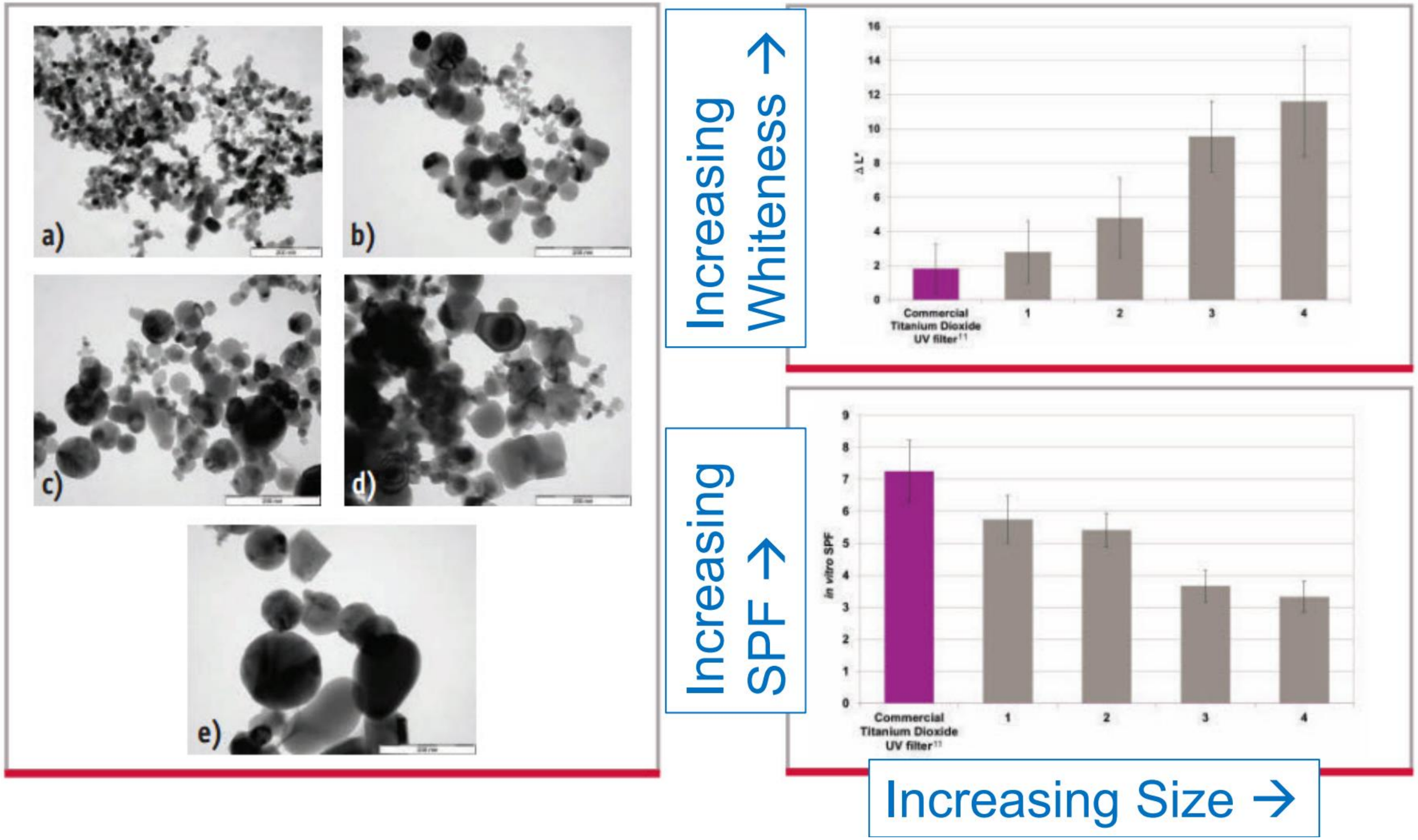
Relative scattering power rutile TiO_2 vs. size



The importance of size

Ceramics	Soil science	Cosmetics and pigments	Catalysts	Minerals
• Affects sintering and compressibility • Determines bonding, curing, final strength, and pore distribution	• Moisture holding capacity • Drainage rate • Ability to hold nutrients	• Efficacy • Color, tint, strength, brightness	• Catalytic activity	• Reactivity • Exposed surface area

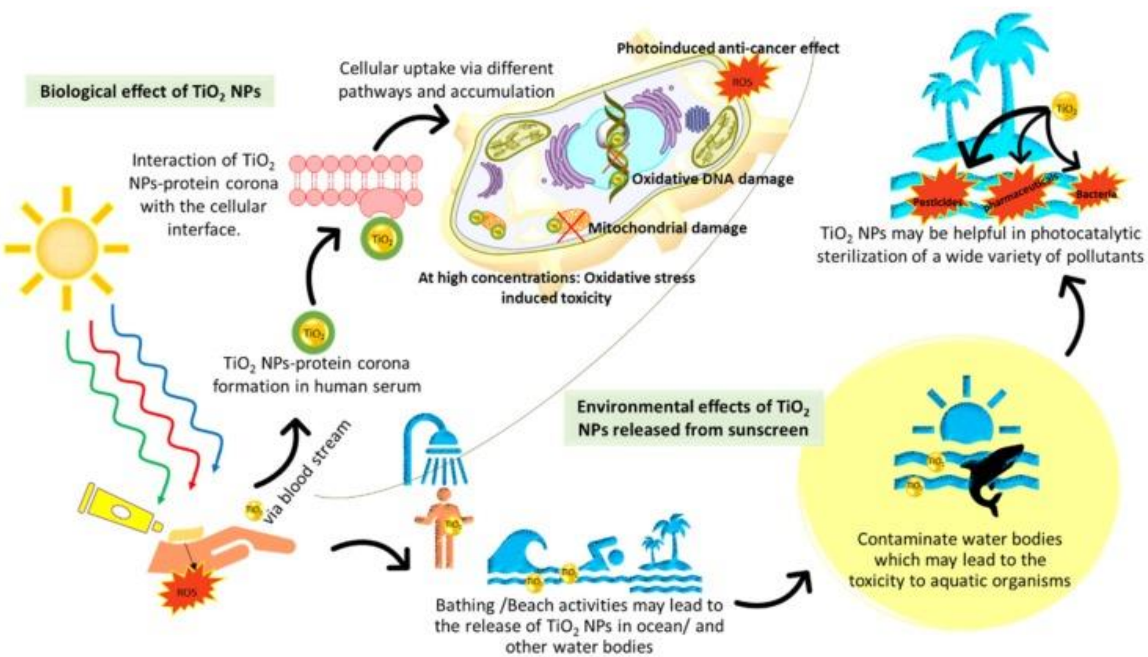
The importance of size: the case of sunscreens



Evonik Study, 2013

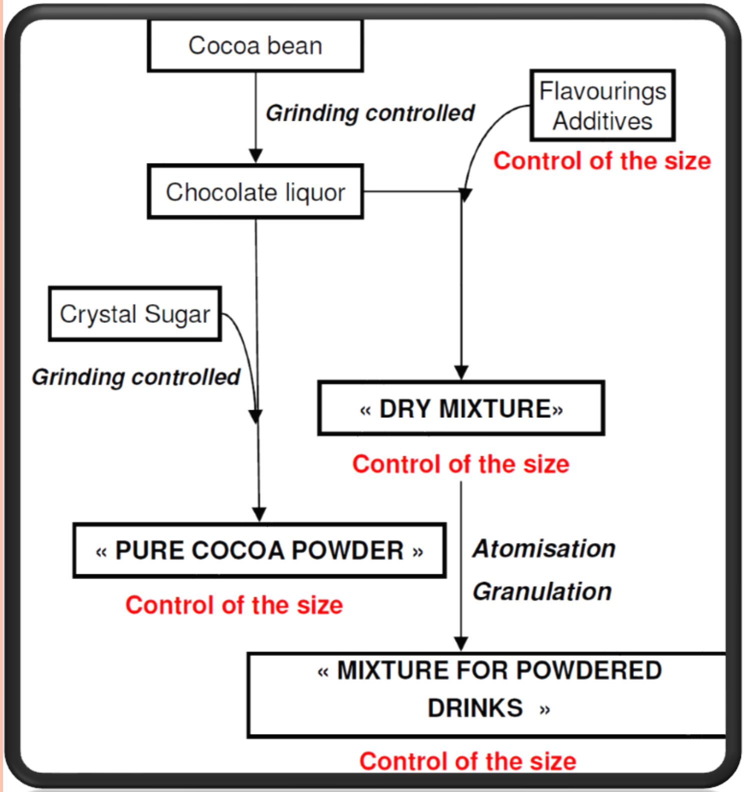
The importance of size: the case of sunscreens

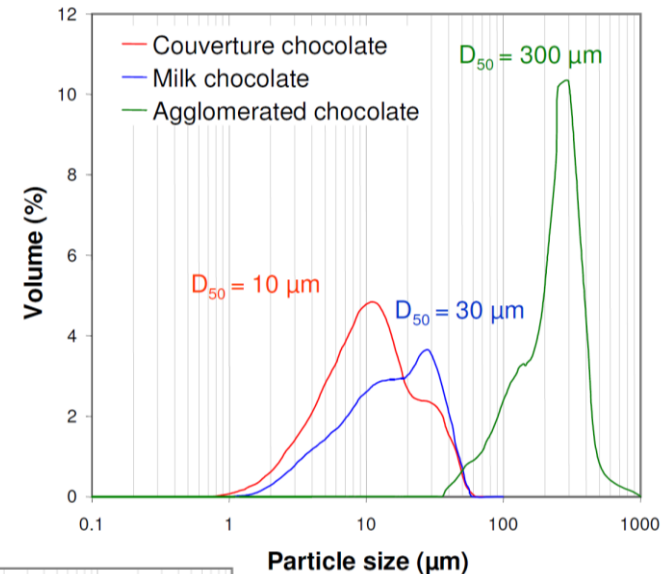
Size increase	More opaque finish
	Less in vitro SPF
	Less efficiency

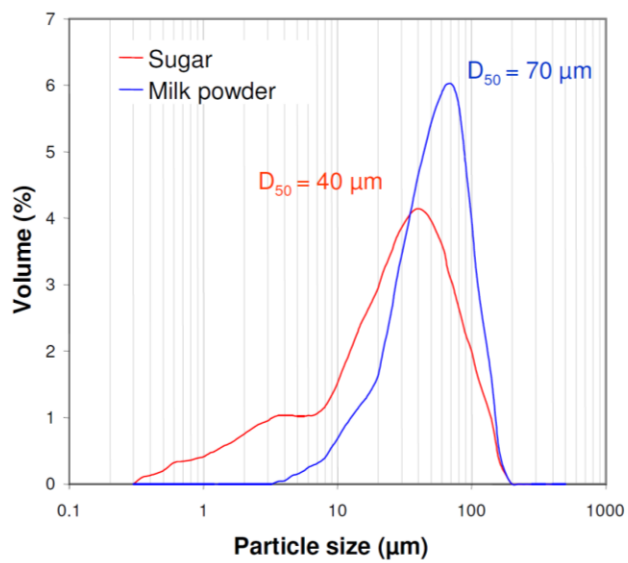


Materials **2019**, *12*(14), 2317

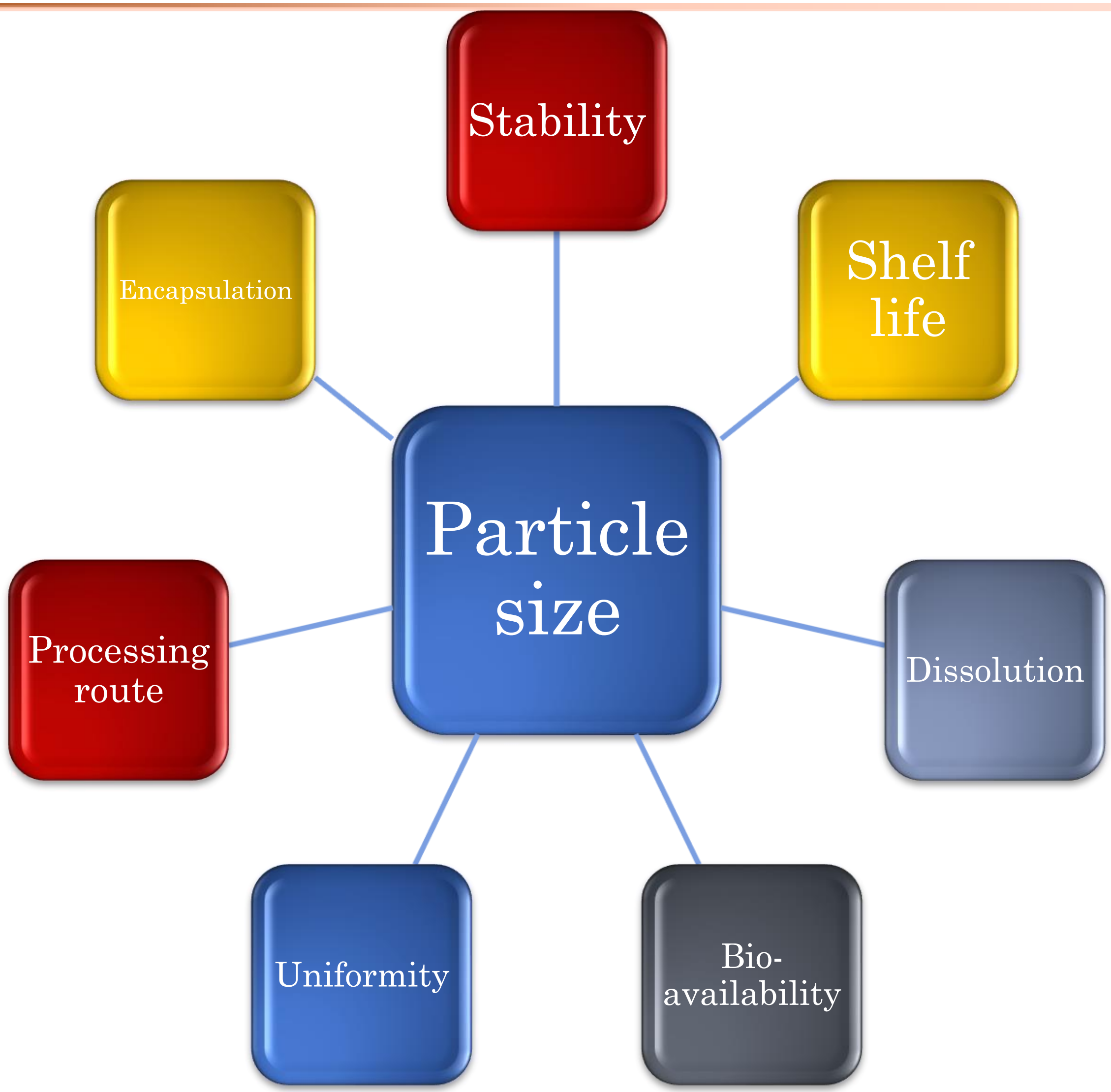
Size Matters: The case of Chocolate Manufacturing Industry







Particle Size Analysis For The Pharmaceutical Industry



Particle Size Analysis For The Pharmaceutical Industry

Smaller particle size

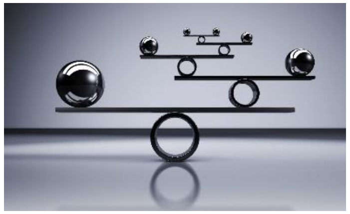
Greater Surface area → Higher dissolution rate → Higher Bio-availability → Rapid drug absorption

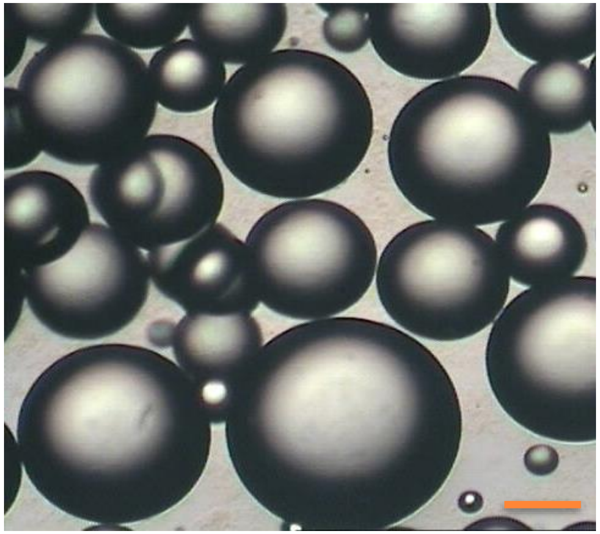
Larger particle size

Better Flowability → Improved product shape → Better appearance → Increased shelf life

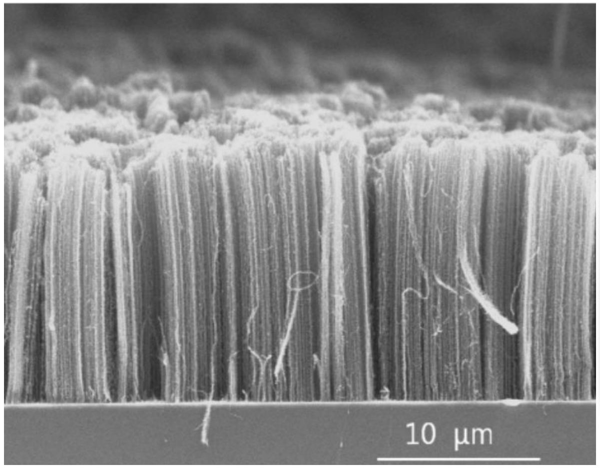
How can we calculate the size?

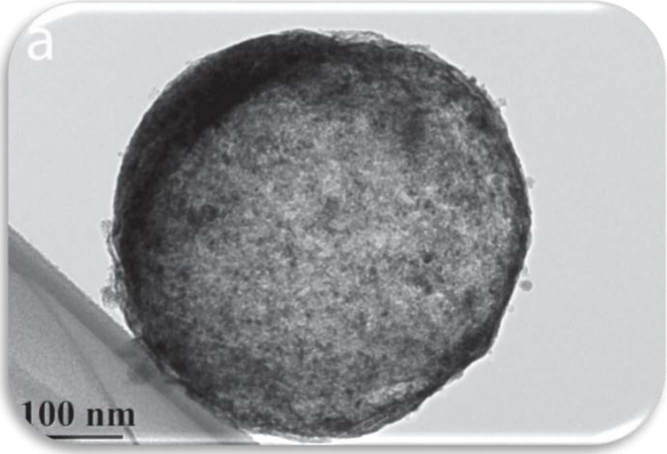
WHAT IS SIZE?

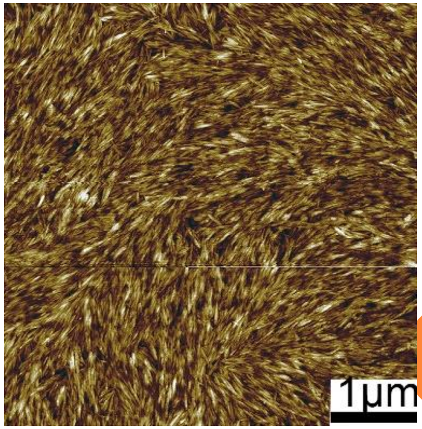




Regular shapes	Fairly easy to describe
	High sphericity particles: 1 value is needed
	Rods, cubes and regular shapes can be defined by 2 values







Energy & Environmental Science, **5**(1): p. 5236-5240.

What about irregular shapes

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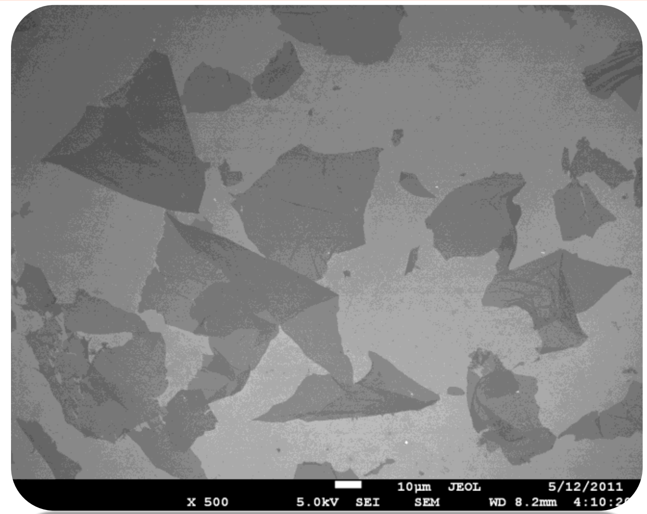
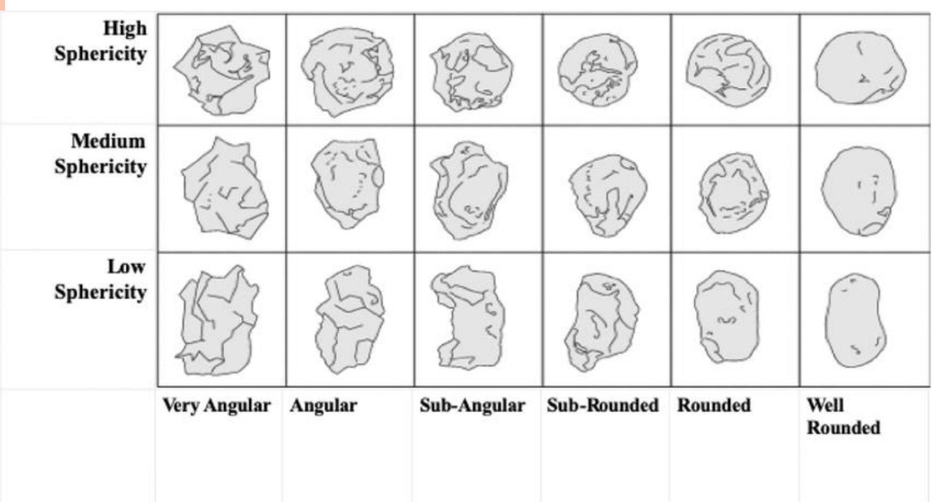
Irregular shapes

- Can we describe them with just 1 number?
- Medium sphericity and Low sphericity
- 2D materials and angular materials



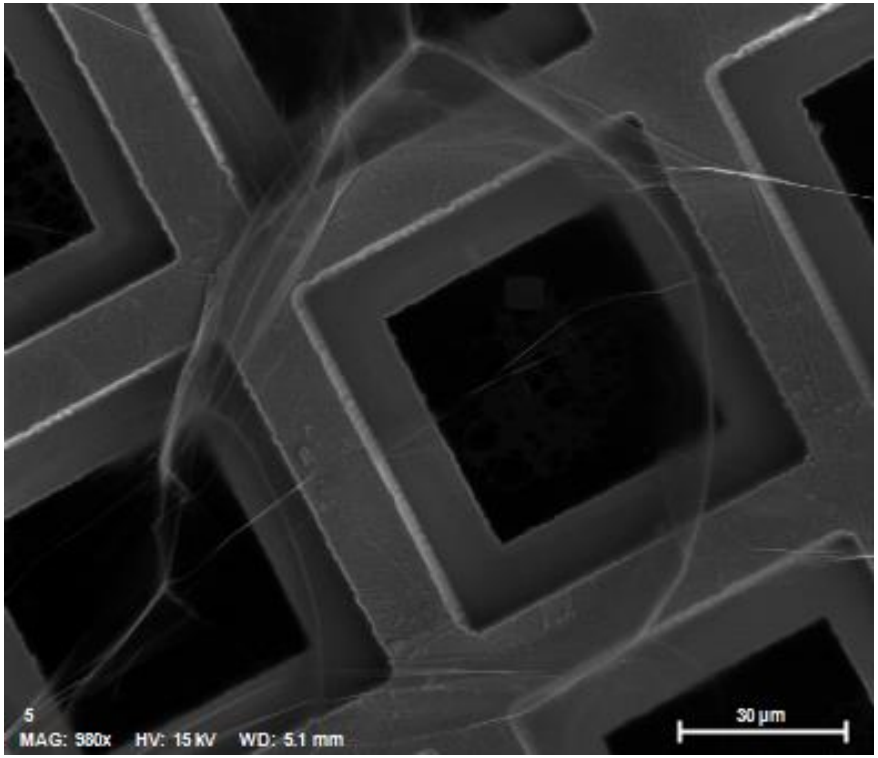
Advanced Functional Materials 21 (15), 2978-2988

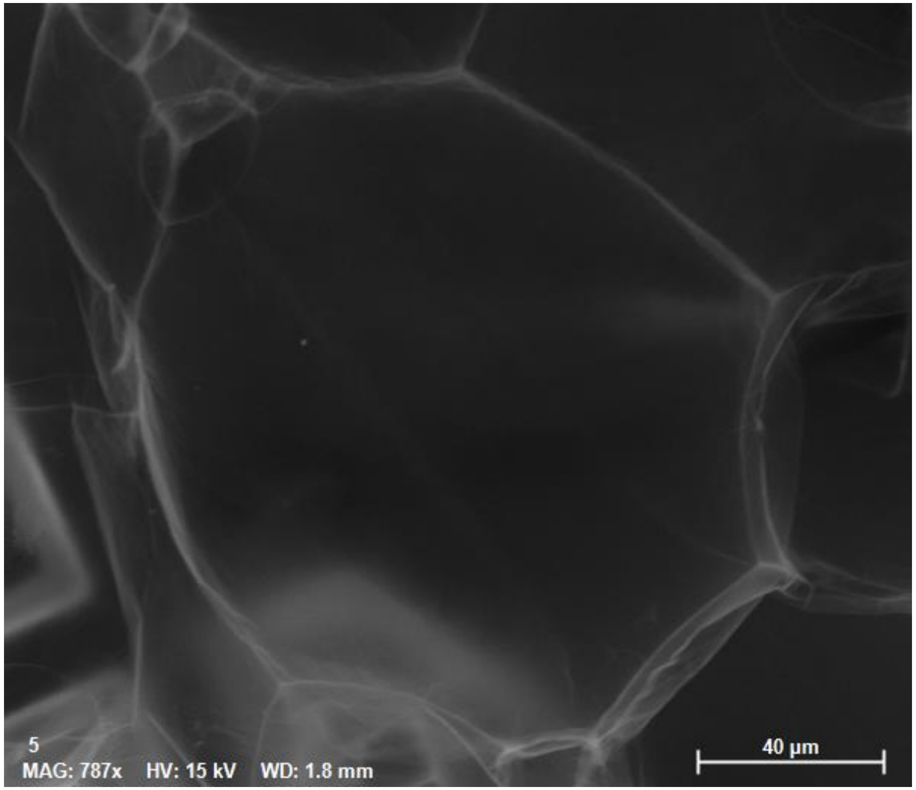


http://dx.doi.org/10.2139/ssrn.3417470

Image credit: http://mail.ipb.ac.rs/~vrhovac/sloba/science/gs.html

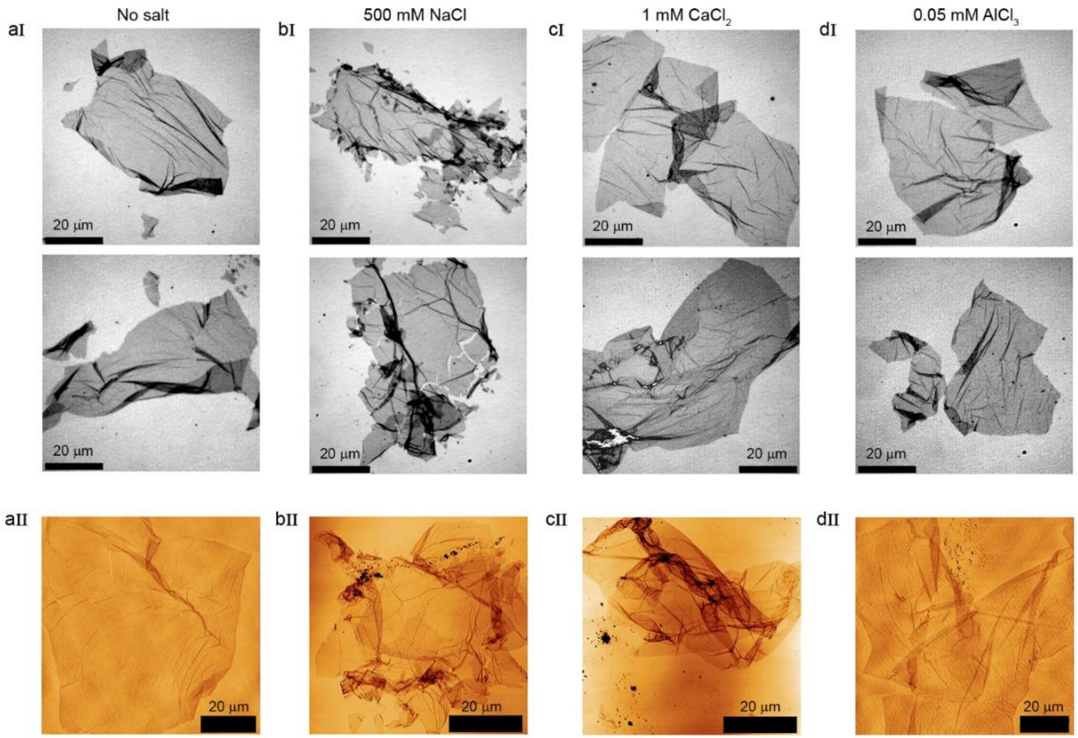
And even more complex than that





Unpublished work

And even more complex!!!



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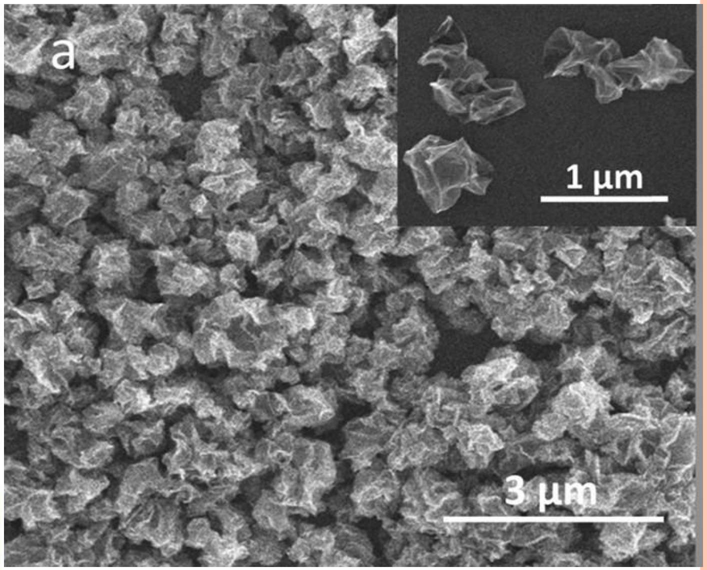
J. Mater. Chem. A, 2021, Accepted Manuscript



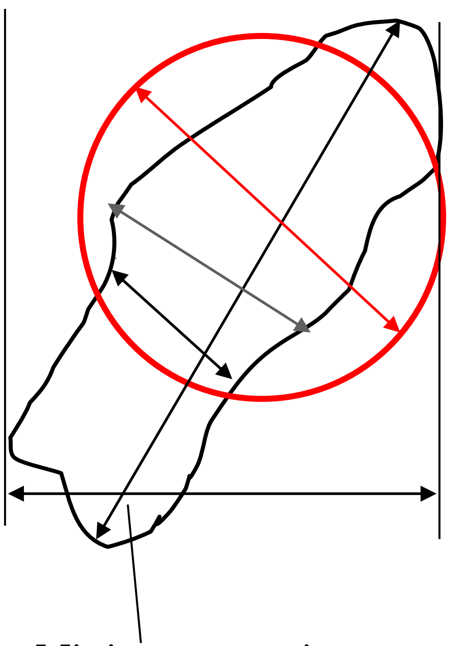
Crumpled

DOI: (10.1021/acsomega.7b01647)

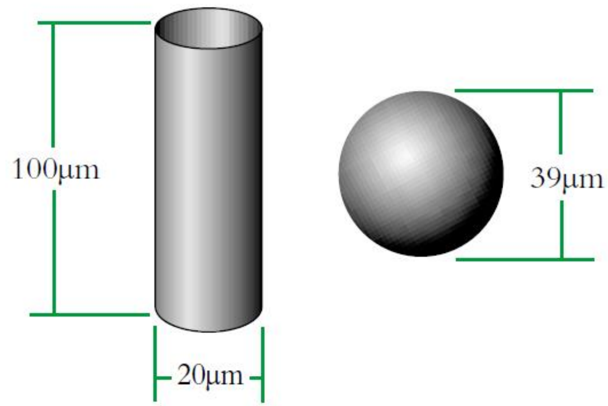
So why does it matter?

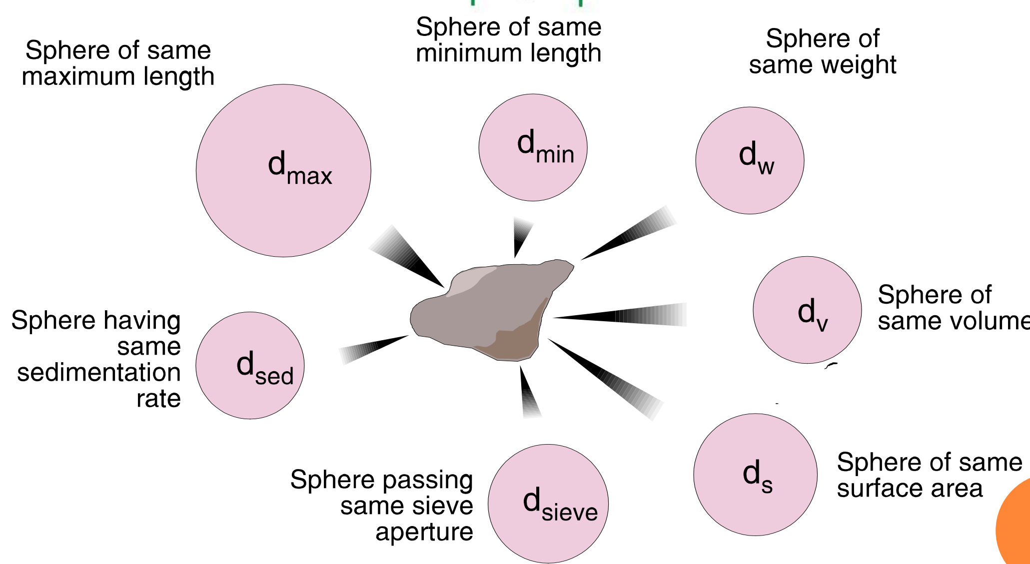
THE PARTICLE SIZE DILEMMA: THE EQUIVALENT SPHERE

Equivalent sphere (volume) diameter



Minimum, maximum diameters





Aspect ratio: longest /shortest diameter

So why does it matter?

Image Credit: Malvern application note

THE PARTICLE SIZE DILEMMA: THE EQUIVALENT SPHERE

Sauter mean diameter: It is defined as the diameter of a sphere that has the same volume/surface area ratio as a particle of interest.

Application: wherever the active surface area is important including catalysis and fuel combustion.

$$SD = D[3,2] = d_{32} = \frac{d_v^3}{d_s^2}.$$

$$\frac{V_p}{A_p} = \frac{\frac{4}{3}\pi(d_v/2)^3}{4\pi(d_s/2)^2} = \frac{(d_v/2)^3}{3(d_s/2)^2} = \frac{d_{32}}{6}$$

$$d_{32} = 6\frac{V_p}{A_p}.$$

The **De Brouckere mean diameter** is the mean of a particle size distribution weighted by the volume (also called volume-weighted mean diameter, volume moment mean diameter.

Application: Mining and milling industries

$$D[4,3] = \frac{\Sigma n_i D_i^4}{\Sigma n_i D_i^3}$$

The particle size dilemma: The equivalent sphere

$$X_{nl} = D[1,0] = \frac{1+2+3}{3} = \underline{2.00}$$

$$X_{ns} = D[2,0] = \sqrt{\frac{1+4+9}{3}} = \underline{2.16}$$

$$X_{nv} = D[3,0] = \sqrt[3]{\frac{1+8+27}{3}} = \underline{2.29}$$

$$X_{ls} = D[2,1] = \frac{1+4+9}{1+2+3} = \underline{2.33}$$

$$X_{lv} = D[3,1] = \sqrt{\frac{1+8+27}{1+2+3}} = \underline{2.45}$$

$$X_{sv} = D[3,2] = \frac{1+8+27}{1+4+9} = \underline{2.57}$$

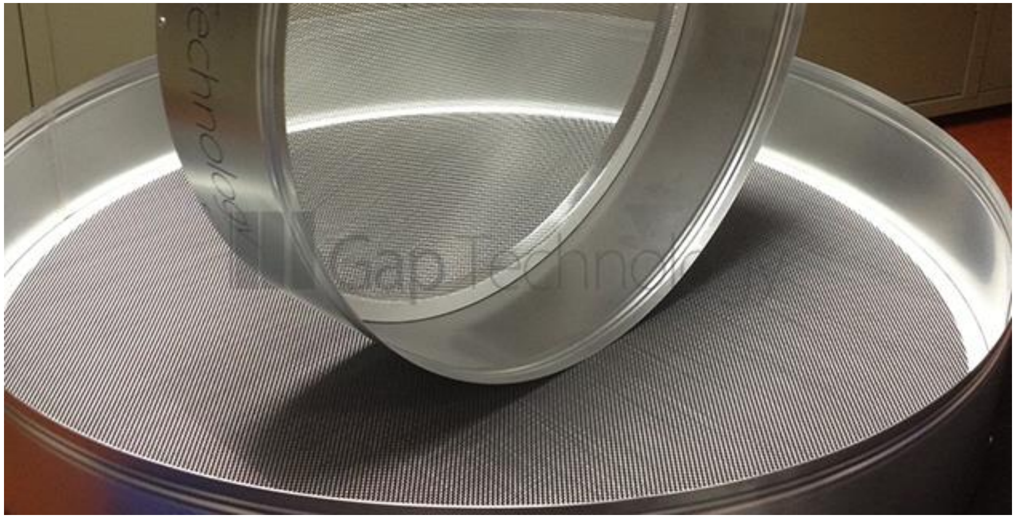
$$X_{vm} = D[4,3] = \frac{1+16+81}{1+8+27} = \underline{2.72}$$

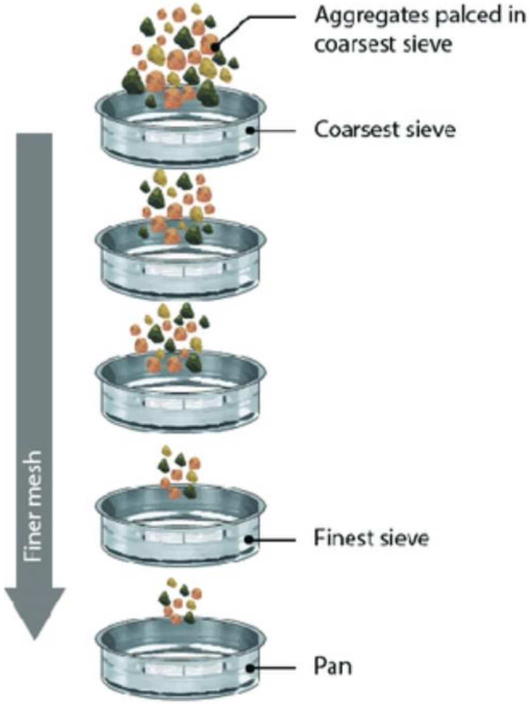
There are simply no right or wrong answers.

Determined by application!!!

Measurement methods: Sedimentation

- Not possible to measure sprays or emulsions
- Measurement for dry powders under 400# (38µ) is very difficult.
- Cohesive and agglomerated materials e.g. clays are difficult to measure.
- The method is not inherently high resolution.
- The longer the measurement, the smaller the answer as particles orientate themselves to fall through the sieve.
- Funny results for rod-shaped materials.

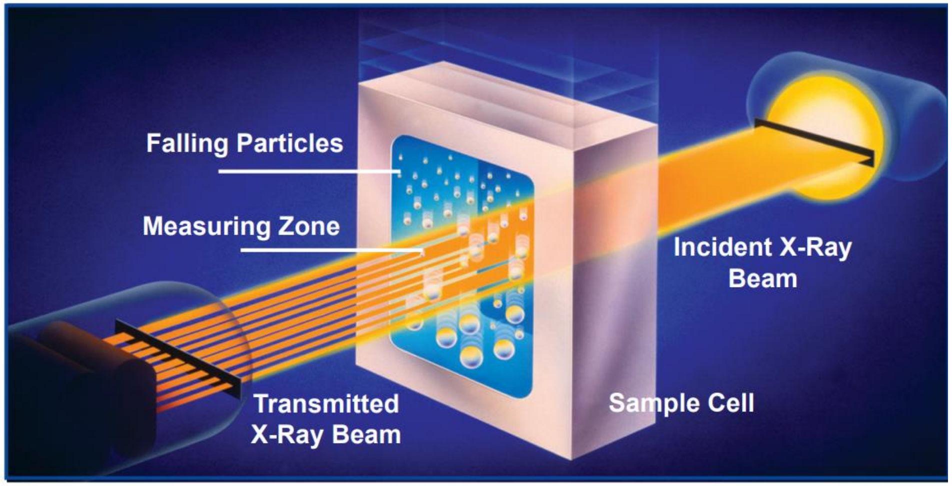




Indispensable method in mining industries!

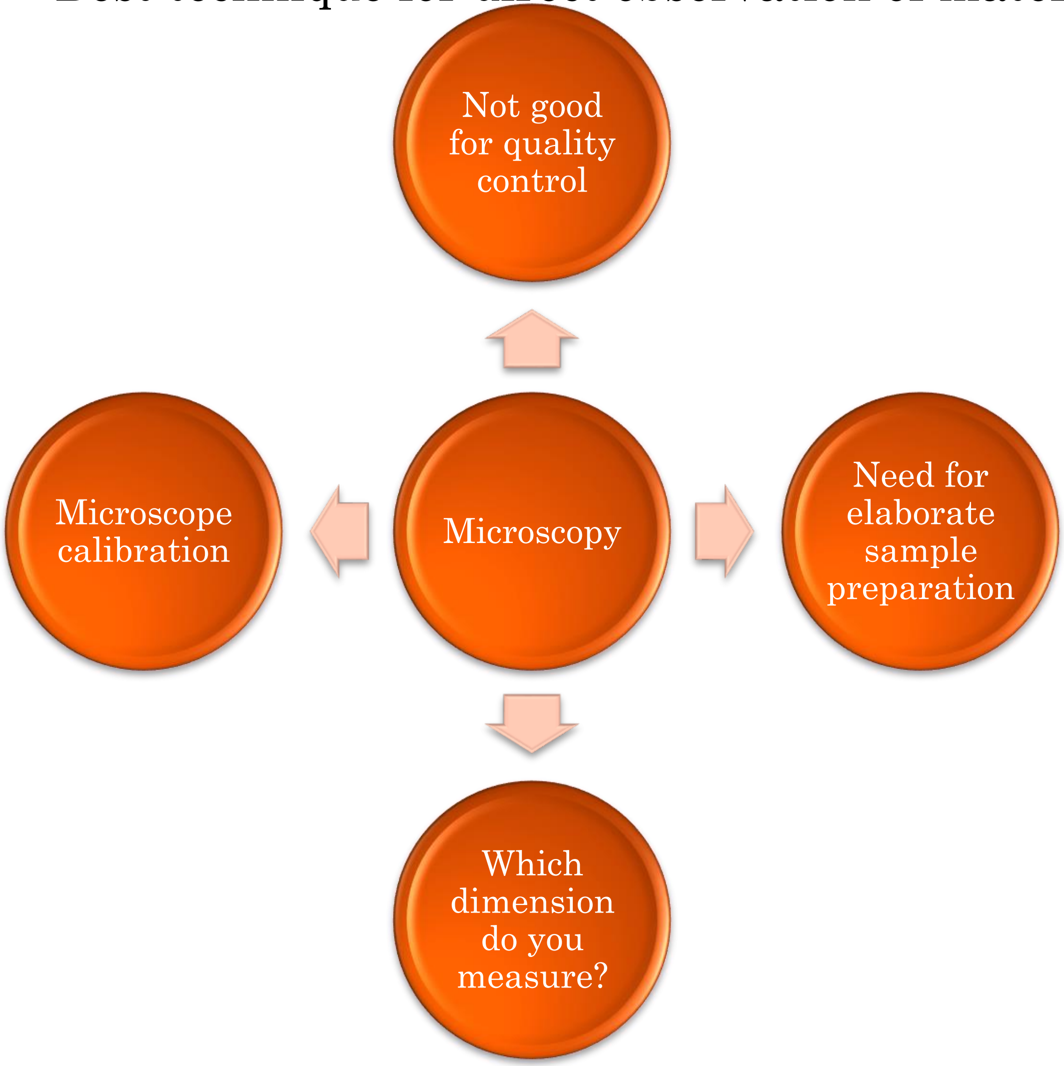
MEASUREMENT METHODS: SEDIMENTATION

- Low speed of measurements leaves room for agglomeration
- Need for accurate temperature control better than 1 kelvin
- Disk-shaped materials are almost impossible to measure
- Limited-range 2-50 μm.



MEASUREMENT METHODS: MICROSCOPY

Best technique for direct observation of materials!!!

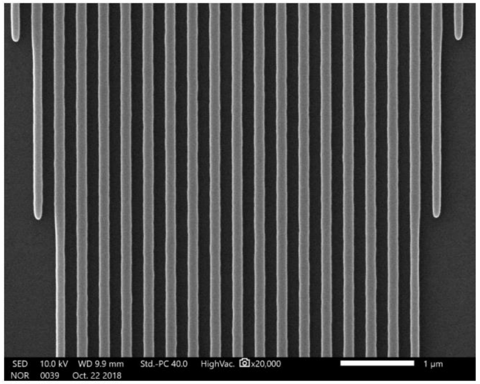


MEASUREMENT METHODS: MICROSCOPY

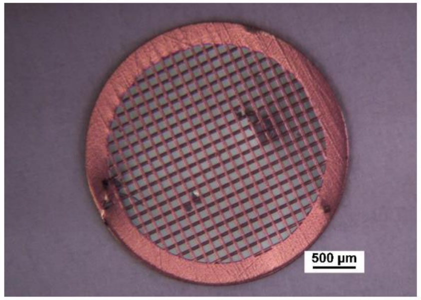
SEM Magnification Calibration and Verification

What features make a good calibration tool?

- Chemically and structurally stable
- Sharp edges that don't use a lot of pixels
- Something periodic spanning ~4 orders of magnitude (100 nm to 1 mm)
  - Pitch doesn't deviate too much from the mean at any point
  - Pitch is constant over a wide range of length scales



- Some things to avoid using for calibration or verification:



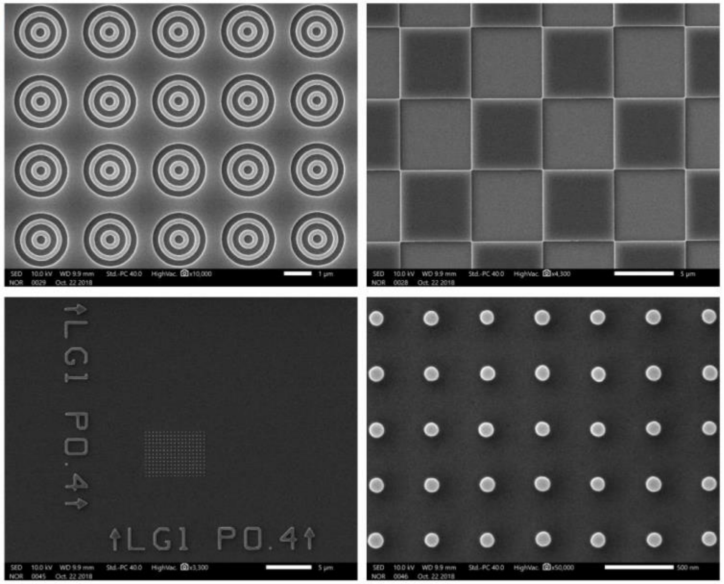
You have no frame of reference other than the trust that the instrument was accurately calibrated.

Measurement methods: Microscopy

SEM Magnification Calibration and Verification

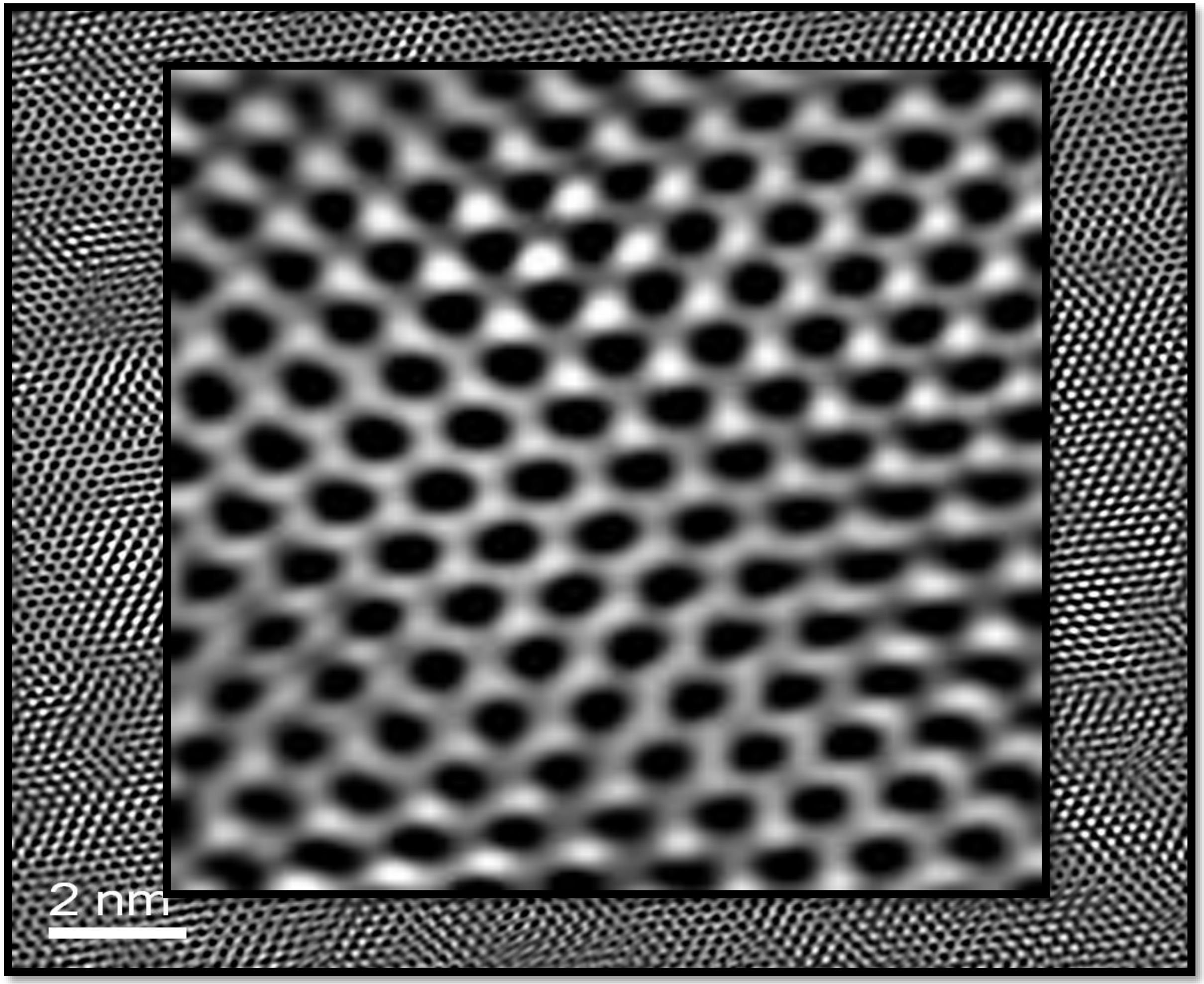
What Standard Reference Material Should You Use?

- Best sources for SRMs are National Metrological Institutes (NMI)
  - United States: NIST www.nist.gov/iaao/national-metrology-laboratories
  - United Kingdom: NPL (National Physical Laboratory)
  - France: LNE (Laboratoire National d'Essais)
  - Germany: PTB (Physikalisch-Technische Bundesanstalt)
- An SRM that is **traceable** back to an NMI like NIST
  - Unbroken chain of validation from processing to measurement
  - Sample-to-sample uncertainties are known and acceptable
  - Measurement uncertainties are known and acceptable
  - These are the requirements to satisfy Category I traceability for an ISO 17025 accreditation body
- Some good SRM examples:
  - MetroBoost's MetroChip (SEM)
  - NIST RM 8820 (SEM)
  - MAG*I*CAL (TEM)



MEASUREMENT METHODS: MICROSCOPY

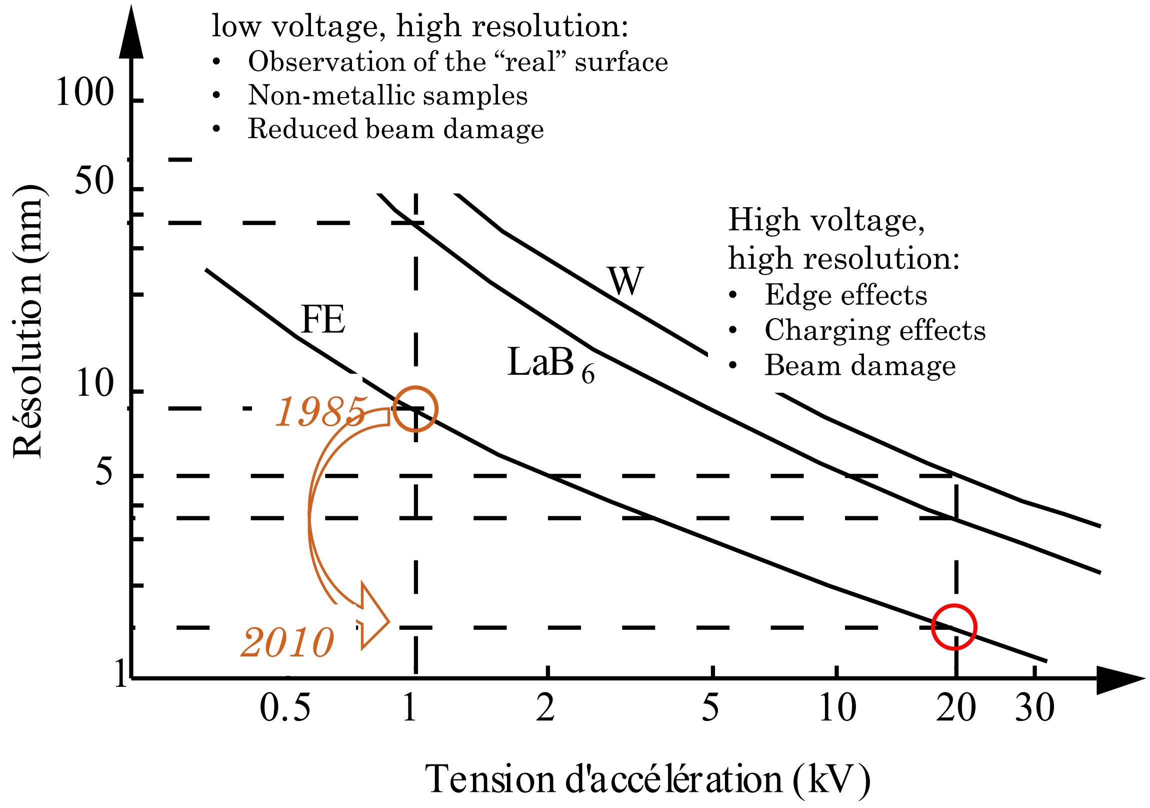
HRTEM Magnification Calibration and Verification



MEASUREMENT METHODS: MICROSCOPY

SEM or FESEM? Image correction

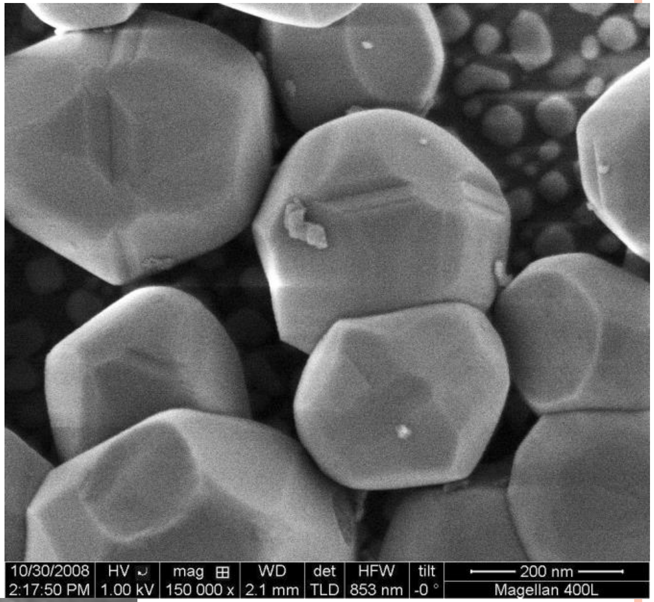
Avoid artefacts!!!
Avoid artefacts!!!
Avoid artefacts!!!

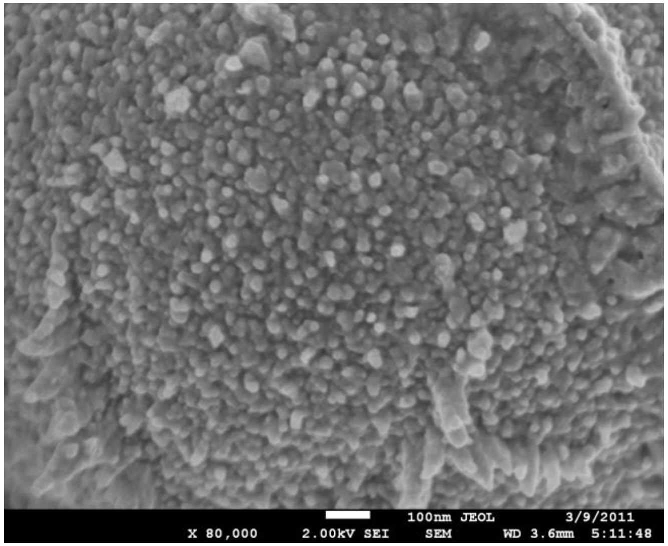


Measurement methods: Microscopy

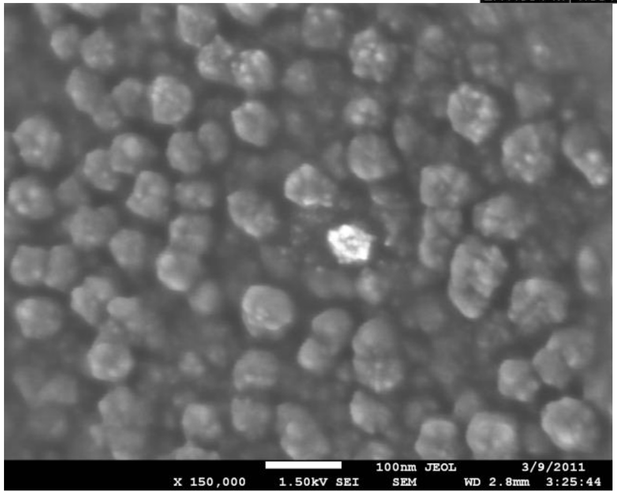
Avoid artefacts!!!
Avoid artefacts!!!
Avoid artefacts!!!

Al2O3 crystals





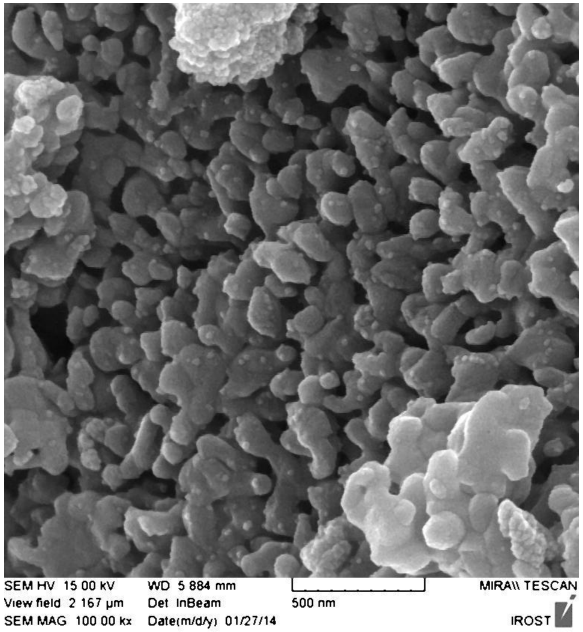
NiO Nano-crystals

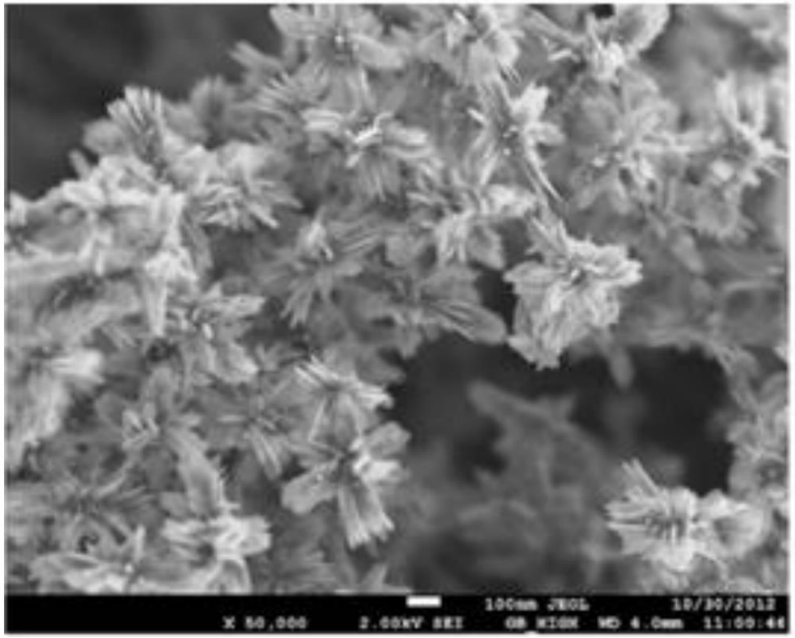


MEASUREMENT METHODS: MICROSCOPY

Avoid artefacts!!!
Avoid artefacts!!!
Avoid artefacts!!!

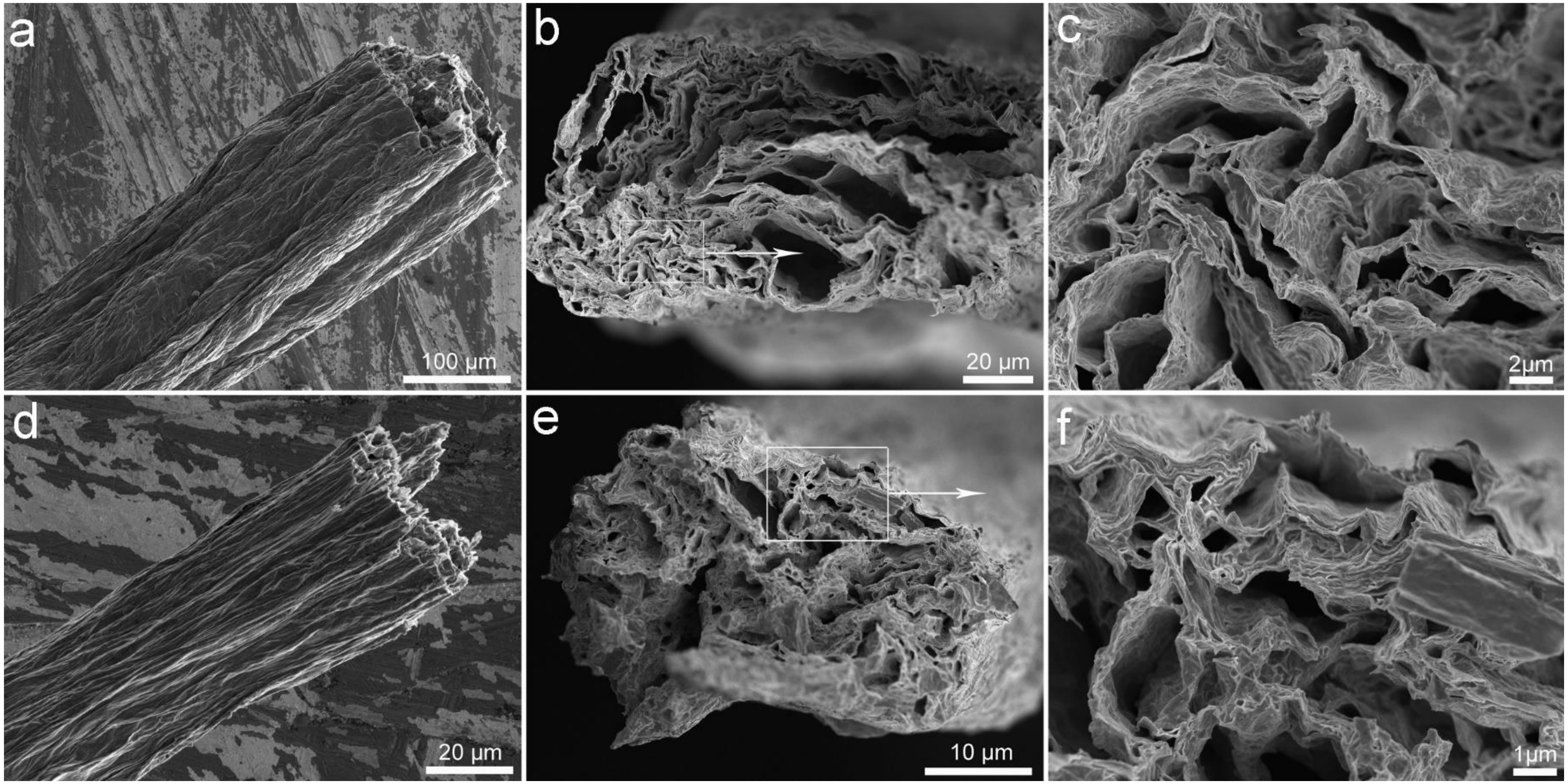
- contamination “spoils” imaging at low kV
- How to avoid:
  - Plasma cleaning of the sample before inserting
  - Plasma clean the chamber at each insertion (multi-user environment)



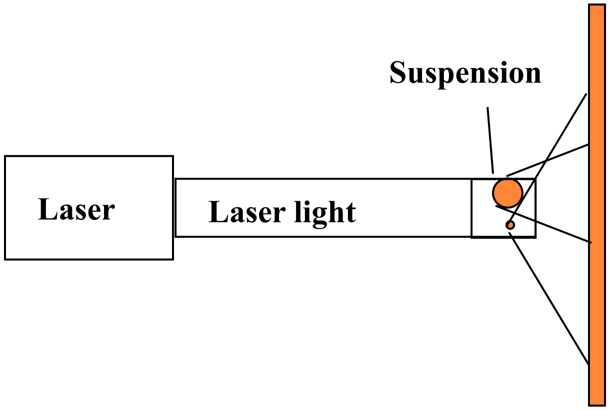


Measurement methods: Microscopy

Avoid artefacts!!!
Avoid artefacts!!!
Avoid artefacts!!!

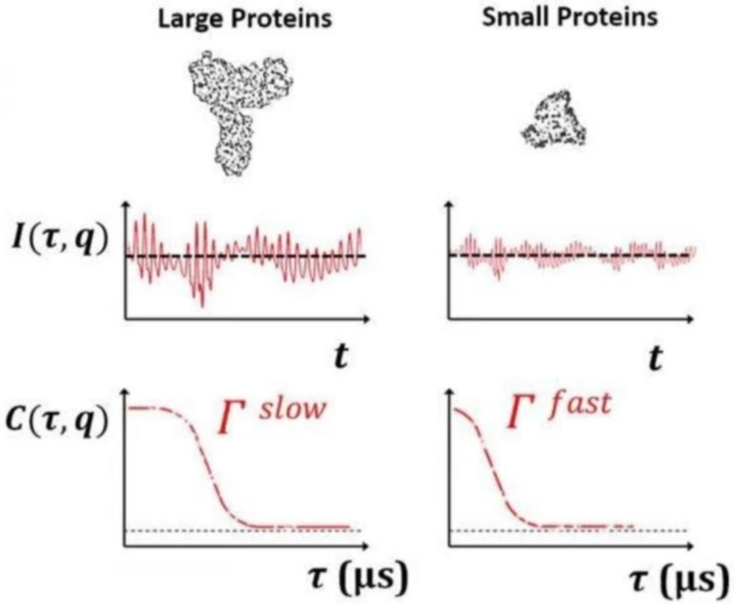


MEASUREMENT METHODS: LASER DIFFRACTION



+ Good statistics (measuring >10^9 particles at once)
+ Analysis can be conducted in solution with minimal effect on the sample.

- Data is fit to a model (multiple structures or completely unknown structures can be very problematic)



$$q = 4\pi n/\lambda_o \sin(\theta/2)$$

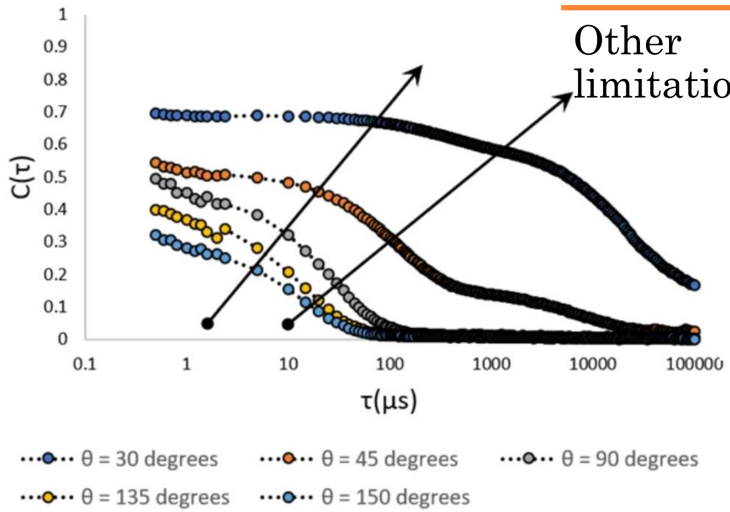
$$\Gamma = D_t q^2$$

$$D_t = k_B T / 3\pi\eta d_h$$

Measurement methods: Laser diffraction

Notes to consider

- Refractive index of solvents and particles should be known
- A configurable correlator lay-out is needed
- Generalized Stokes-Einstein equation is only applicable for spherical particles
- Detectors at multiple angles are needed to get a correct estimation



Correlation functions obtained at five separate scattering angles, θ = (30,150°). The existence of a second decay becomes obvious at the two lowest angles. Image Credit: Brookhaven Instrument Corporation

Other limitations

- Cannot measure the size of turbid solutions.
- Cannot measure the size of aggregating or sedimenting particles.
- Polyelectrolyte materials are difficult to analyse and require salt additives.
- Surfactant-like molecules that promote the formation of bubbles can be problematic.

Measurement methods: Laser diffraction

Other notes of concern

First and foremost DLS just gives D(4,3) diameter and is limited to a maximum size of 8µm where two phases have similar density and usually less than 600-700 nm for carbon-based materials where the theoretical density is calculated to be 2.2 g cm^{-3}.

It can only calculate the hydrodynamic radius of a spherical particle or at least a 3D particle through the Stokes–Einstein equation and not the real dimension.

The hydrodynamic diameter of a nonspherical particle is the diameter of a sphere that has the same translational diffusion speed as the particle. If the shape of a particle changes in a way that affects the diffusion speed, then the hydrodynamic size will change. For example, small changes in the length of a rod-shaped particle will directly affect the size, whereas changes in the rod's diameter, which will hardly affect the diffusion speed, will be difficult to detect.

The technique is developed based on Rayleigh Scattering and Mie Theory. Essentially, it means that the technique is more biased towards larger particle sizes and scattering intensity of larger particles might swamp the smaller ones

Take-away lessons

- Data analysis and quality control even for the simplest property of materials, i.e. size is complicated.
- There is no absolute method to measure particle sizes.
- Many characterization methods should be used in conjunction to other techniques.

Thanks!!!

Aberration corrected scanning TEM