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# On light extinction spectrometry (LES) for the characterization of nano to microparticles in large to microscale systems

F. R.A. Onofri

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F. R.A. Onofri. On light extinction spectrometry (LES) for the characterization of nano to microparticles in large to microscale systems. International Workshop on Optoelectronic Perception (IWOP2021), Oct 2022, Xi'An, Shaanxi, China. hal-03808060

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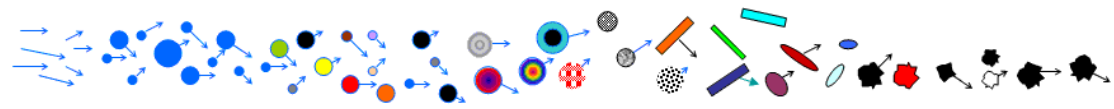
Submitted on 10 Oct 2022

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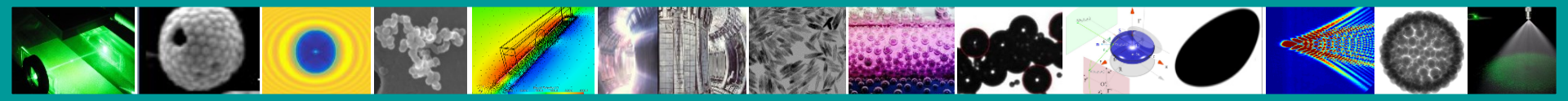
# On light extinction spectrometry (LES) for the characterization of nano to microparticles in large to microscale systems



**Fabrice R.A. ONOFRI** and collaborators:

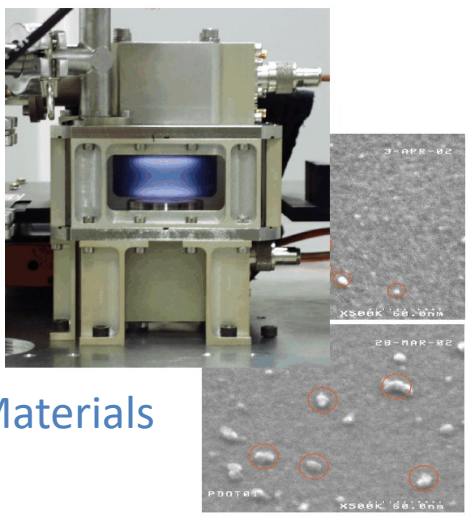
C. Arnas, L. Couedel, S. Barbosa, F. Lamadie, I. Rodriguez-Ruiz, M. Wozniak....

Laboratory IUSTI, UMR n°7343  
 CNRS/Aix-Marseille University, Marseille, France.

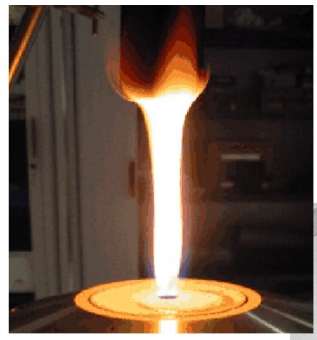


# Nano & microparticles are everywhere....

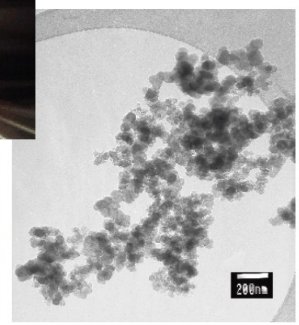
Nanocrystals



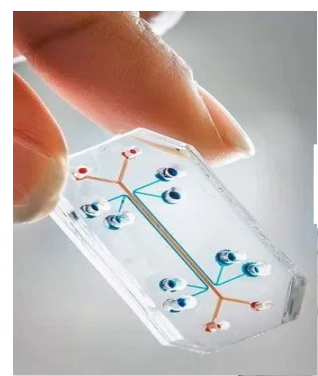
Dust



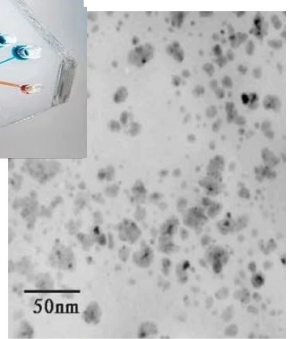
Aerosols



Colloids

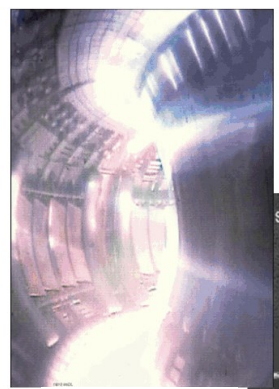


Nanofluids

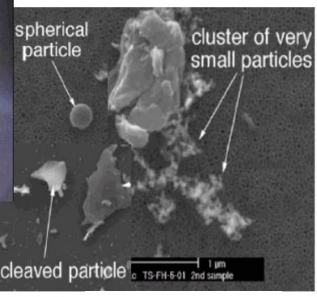


Materials

Environment



Energy



Safety

Process

Filtration

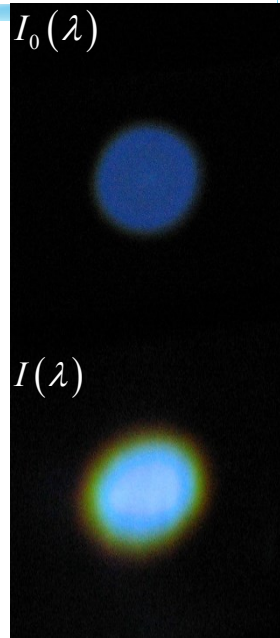
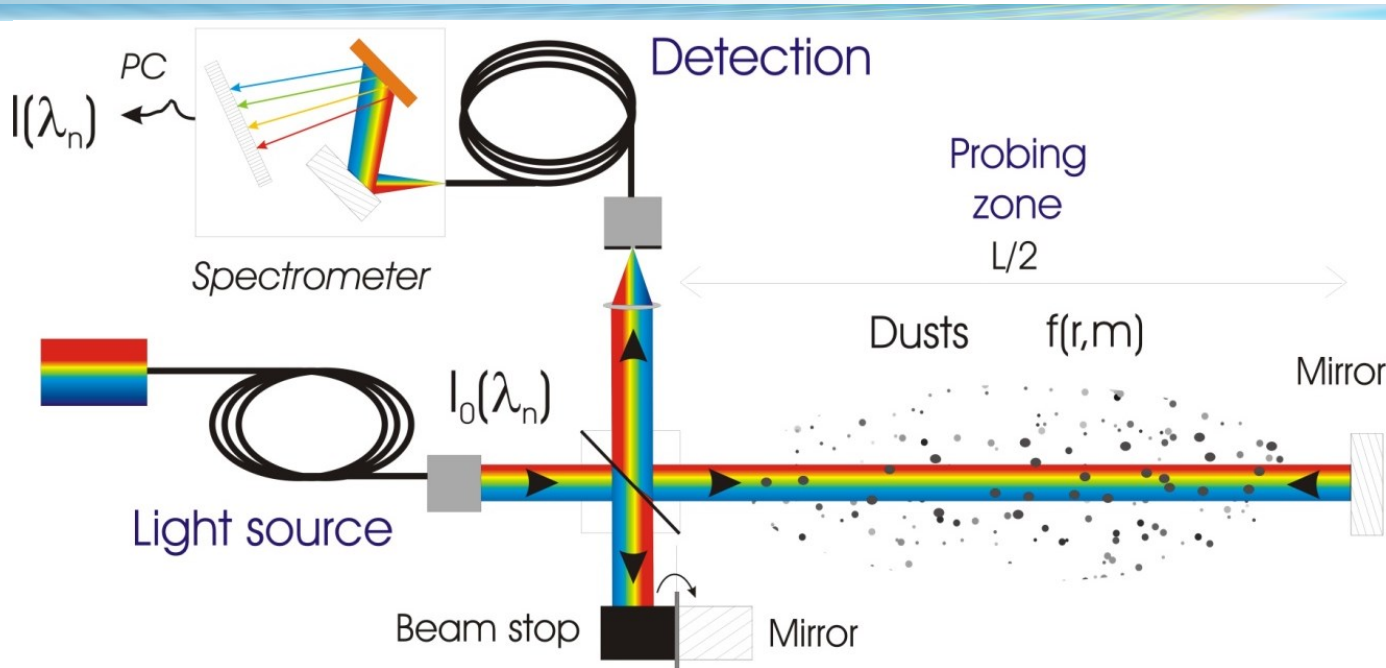
x 10 cm

x 10 m

x 10μm

# Light extinction spectrometry

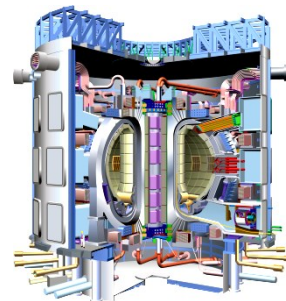
## Basic setup



### Optical setup : UV-NIR extinction

- Stabilized UV-NIR light source
- Achromatic collimating optics
- Optical and spatial filters
- Optical choppers
- High efficiency and low noise spectrometer
- Proprietary acquisition and processing software

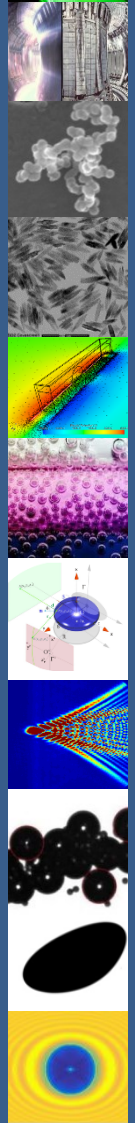
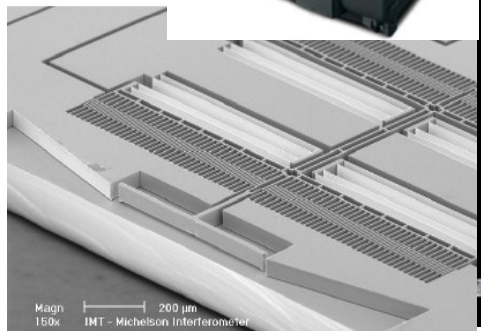
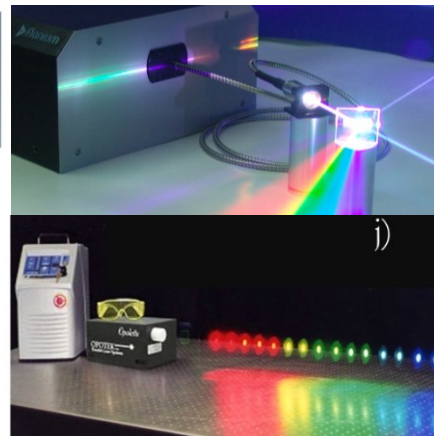
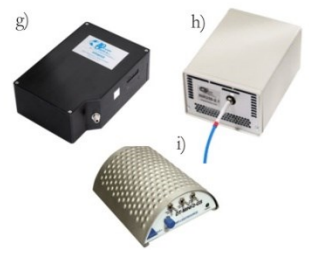
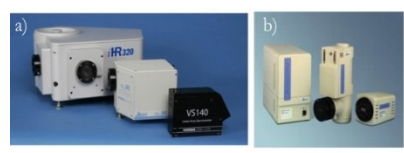
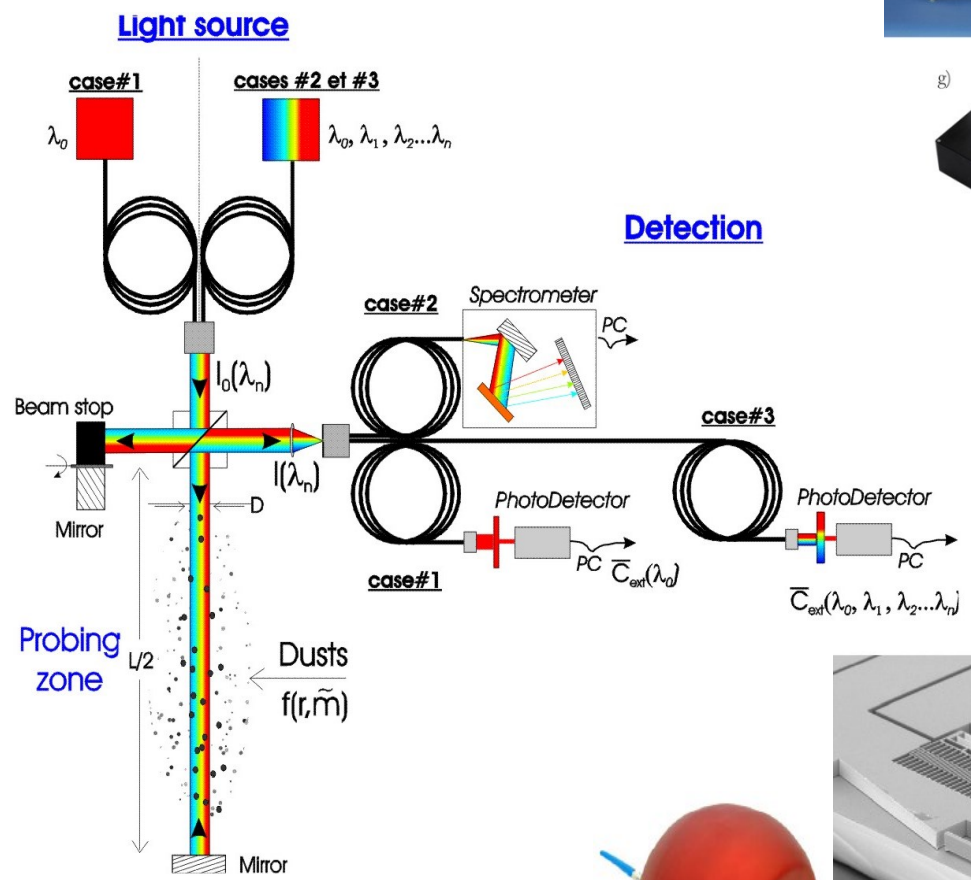
$$T(\lambda) = \left( \frac{I(\lambda)}{I_0(\lambda)} \right) = \exp[-N\bar{C}_{ext}L]$$



# Light extinction spectrometry

## Other setups

Units, laser, distance...:



# Light extinction spectrometry

Basic equations for optically diluted medium, small particles, no collection of multi-scattered photons, ...

Barbosa et al. J. Plasma Phys 82, 2016

## Measurement of the spectral transmission of a collimated beam

### Linearized form of the discrete transmission:

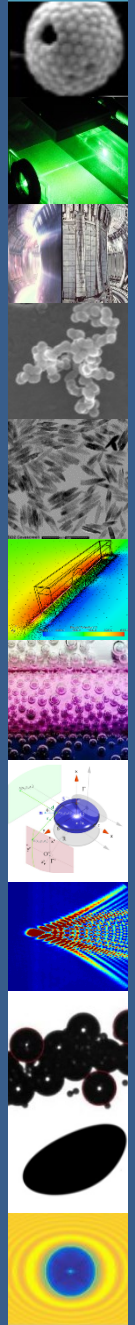
$$\underbrace{\ln[T(\lambda_i)]}_{\bar{T}} = -NL \sum_{j=1}^m \bar{C}_{i,j} n_j$$

$N$  : particle number concentration

$L$  : probed length

$\bar{C}_{i,j}$  : extinction coeff. particle size  $j$  wavelength  $i$

$n_j$  : PSD coefficient particle of size  $j$



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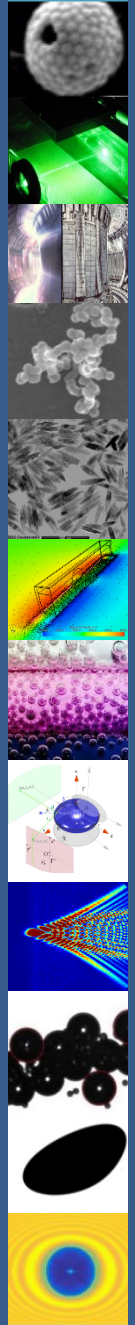
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### Algebraic equation to solve in the concentration was known:

$$\bar{\mathbf{C}} \times \mathbf{n} + \bar{\mathbf{T}} / (NL) = \mathbf{0} \text{ where } n_{j=1 \dots m} \geq 0 \text{ + continuity, mono mode, ...}$$



# Light extinction spectrometry

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### PSD & concentration:

$$\frac{\bar{\mathbf{C}} \times \mathbf{n}}{\|\bar{\mathbf{C}} \times \mathbf{n}\|} + \frac{\bar{\mathbf{T}}}{\|\bar{\mathbf{T}}\|} = \mathbf{0} \Rightarrow \mathbf{n} \Rightarrow N = - \frac{\|\bar{\mathbf{T}}\|}{NL \sum_{j=1}^m \bar{C}_{i,j} n_j}$$

An inversion technique is necessary to get n !!!



# Light extinction spectrometry

Inversion with "no" PSD model assumption

## Phillips-Twomey regularization and NNLSQ inversion:

$$\text{Min}_{\mathbf{n}>0} \left\{ \|\mathbf{C}\mathbf{n} - \bar{\mathbf{T}}\|^2 + \lambda^2 \|\mathbf{L}(\mathbf{n} - \mathbf{n}_0)\|^2 \right\}$$

## Tikhonov regularization and NNLSQ inversion (or SVD...)

$$\text{Min}_{\mathbf{n}>0} \left\{ \left\| (\mathbf{C}^T \mathbf{C} + \gamma \mathbf{H}) \mathbf{n} - \mathbf{C}^T \bar{\mathbf{T}} \right\|^2 \right\}$$

where

$\bar{\mathbf{T}}$ : Measured transmission spectrum

$\mathbf{C}$ : Extinction matrix (core of the fredholm integral)  $\Leftarrow$  part. & scatt. models

$\mathbf{n}_0$ : Initial guess for the PSD ( $\mathbf{n}_0 = \mathbf{0}$ )

$\mathbf{n}$ : Unknown PSD

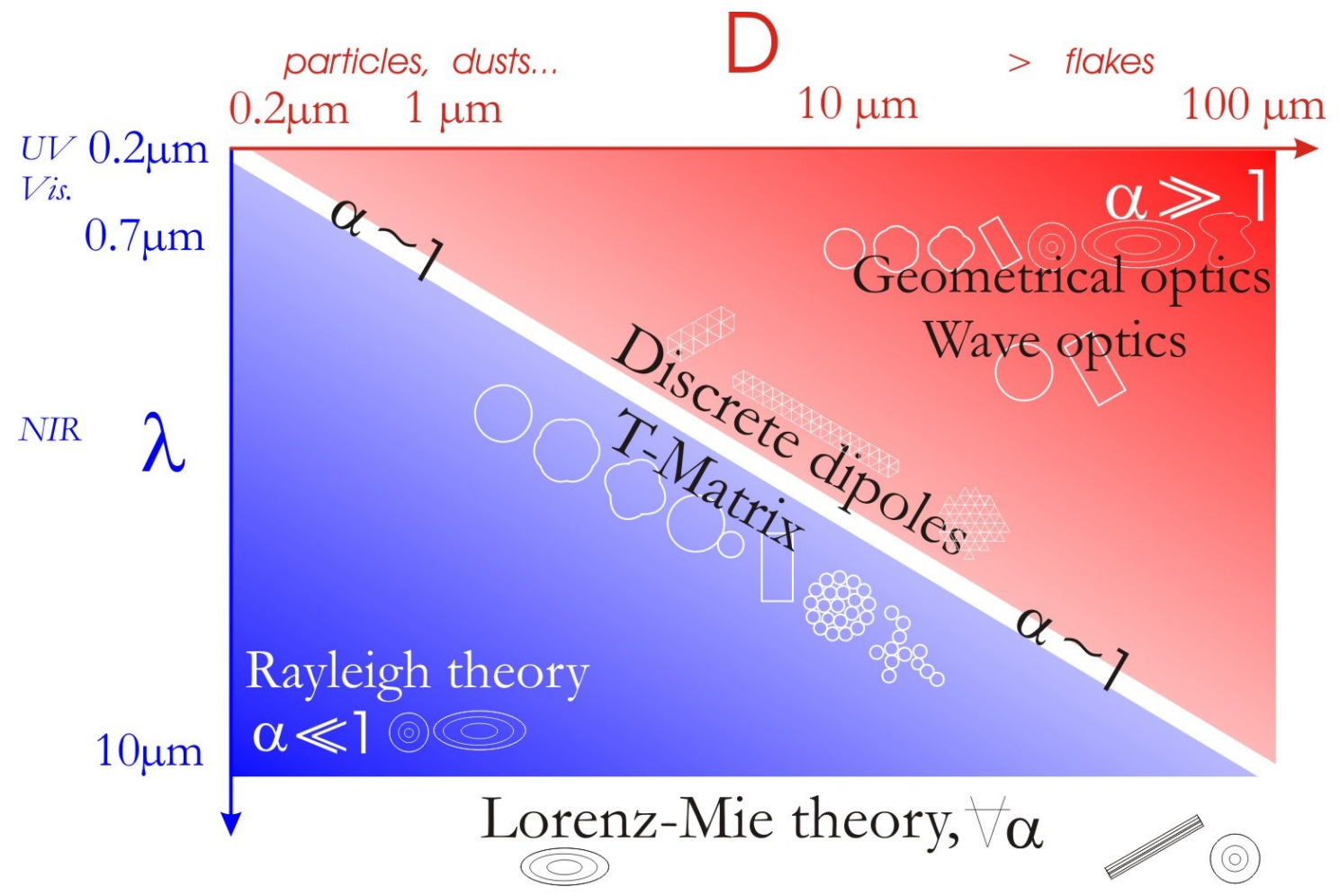
$\mathbf{H}, \mathbf{L}$ : Smoothing/continuity matrices (identity, firsts derivatives, &)

$\gamma, \lambda$ : Regularization parameters (truncated singular values, L-Curve,...),

$\| \|$ : L2 norm

# Light extinction spectrometry

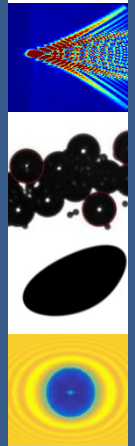
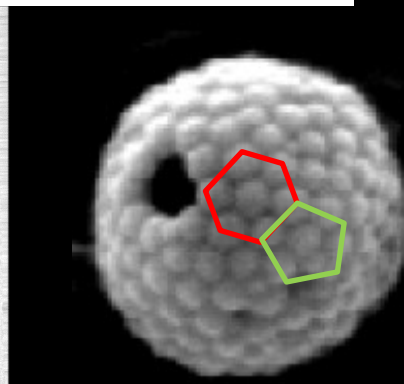
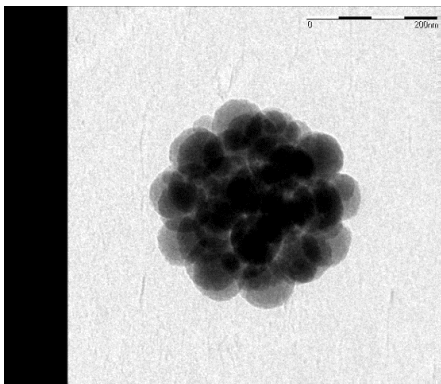
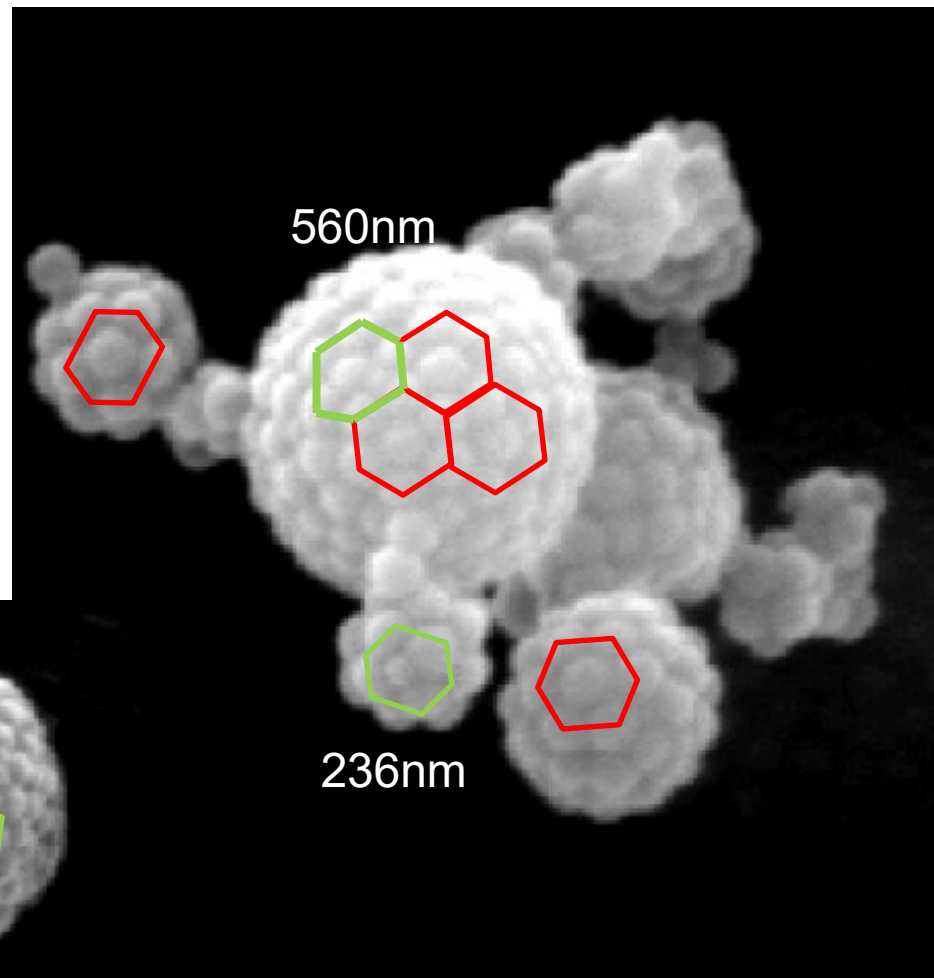
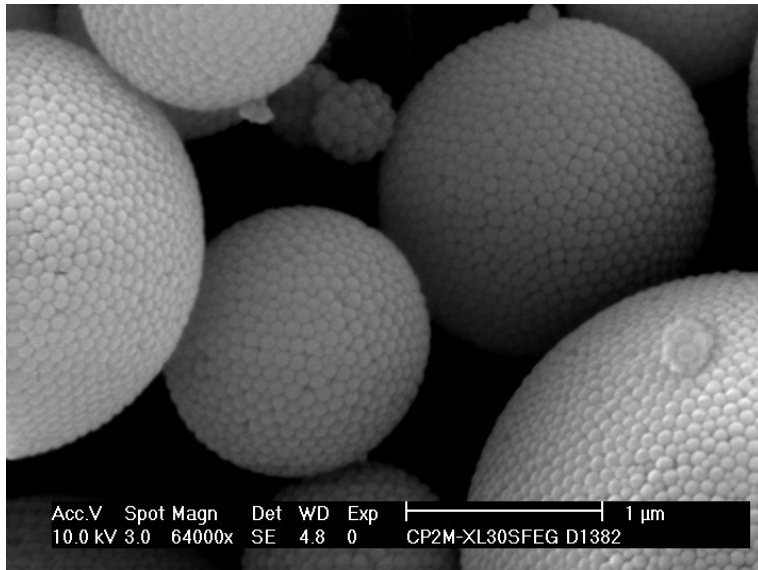
Scattering models



# Models to describe the morphology of particles

## Buckyball-shaped aggregates

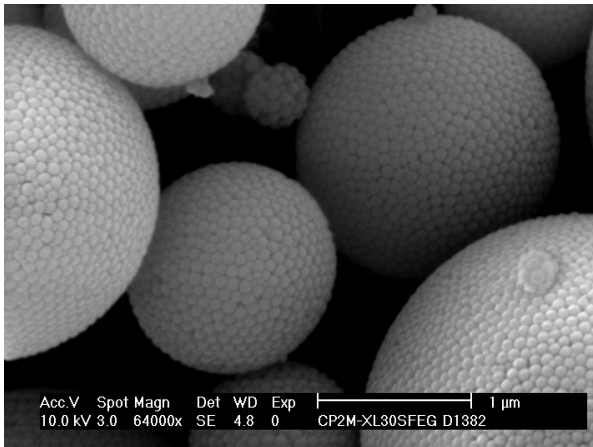
Colloidal suspensions sprayed: a regular pentagonal-hexagonal surface lattice



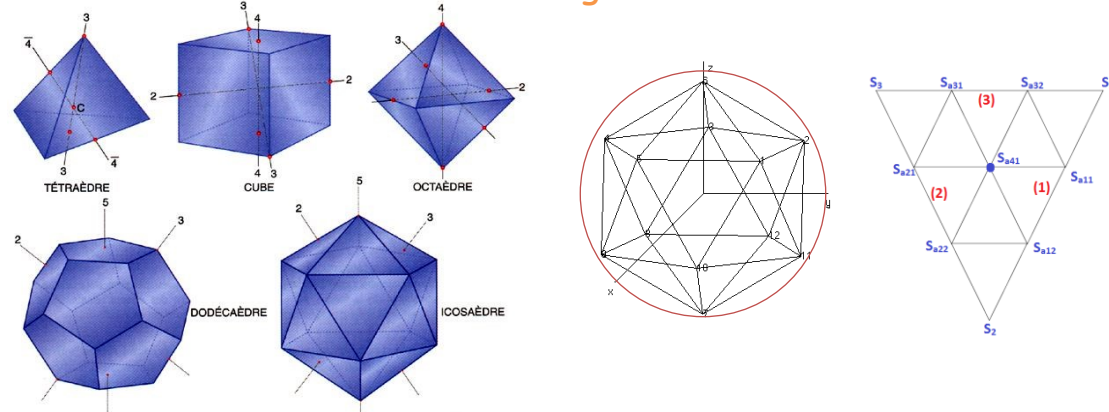
# Models to describe the morphology of particles

## Buckyball-shaped aggregates

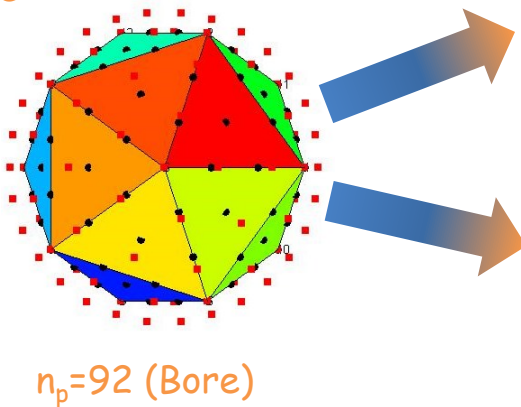
Silica aggregates of nanoparticles



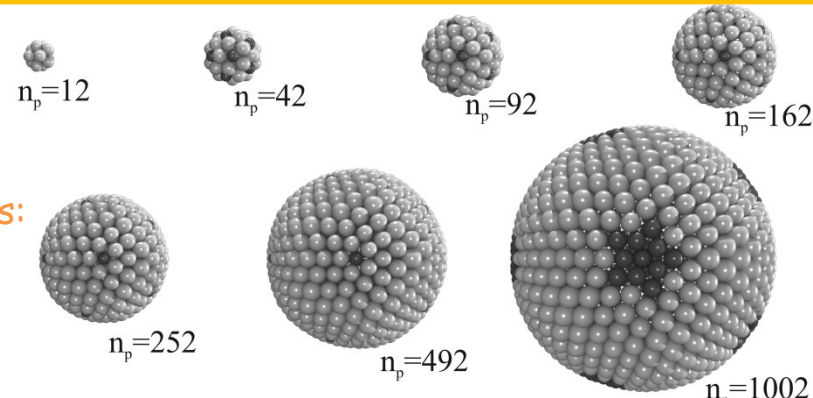
(1) Geodesic dome model starting with the icosahedron



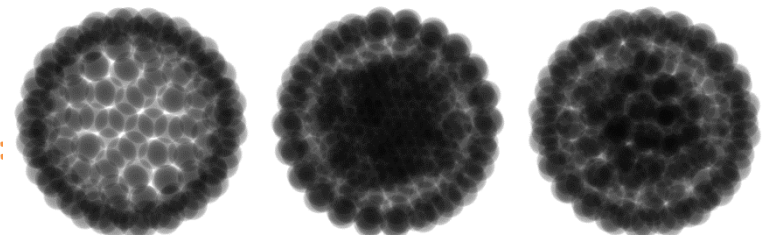
(2) Projection onto circumscribed sphere:

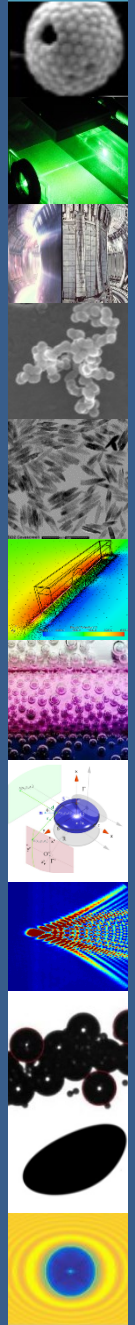


(3) Synthetic SEM images:



(4) Synthetic TEM images:

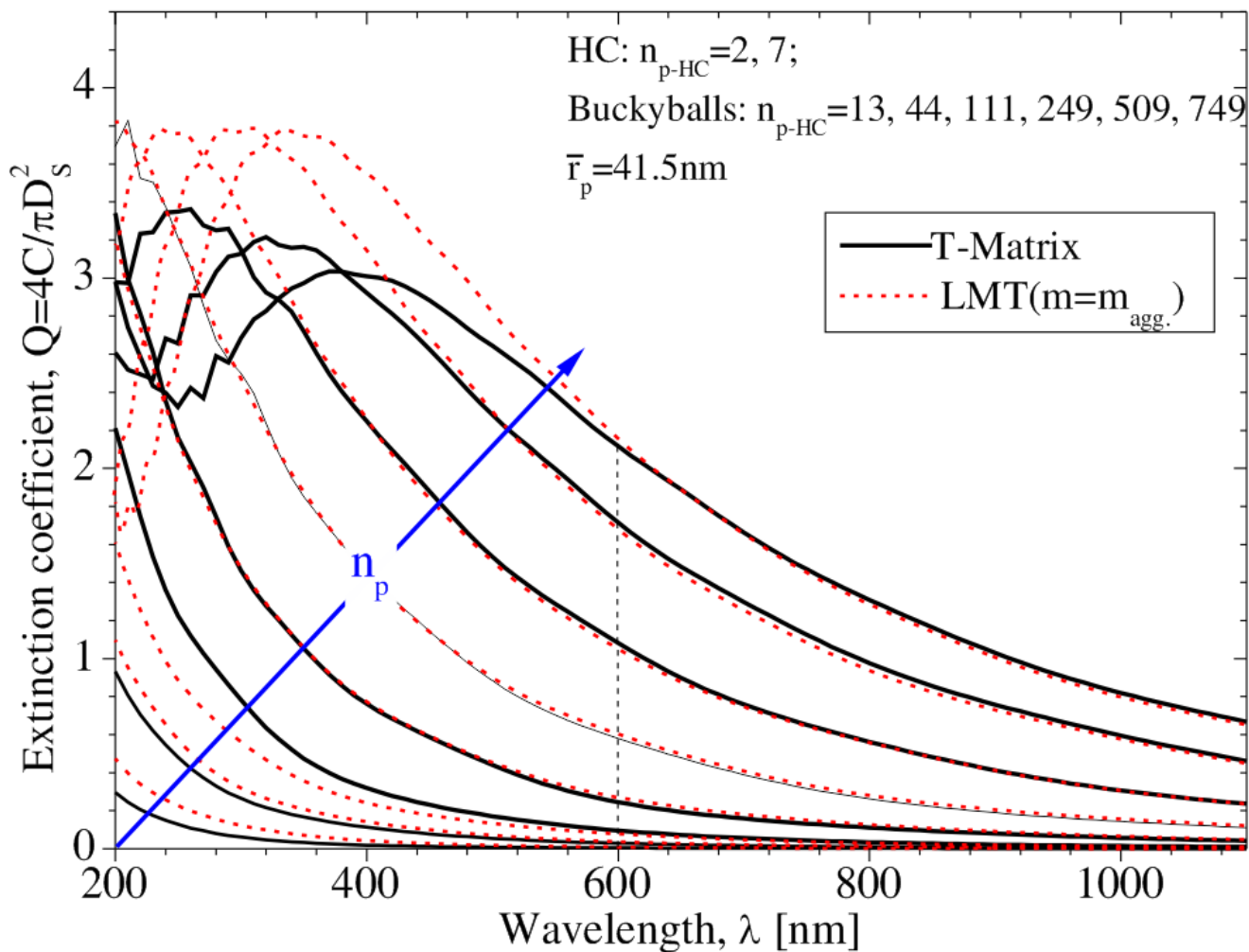


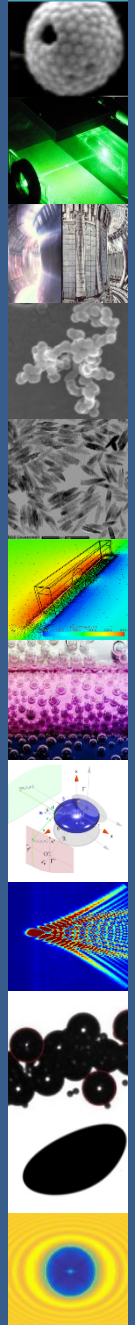


# Light extinction spectrometry

Scattering models : T-Matrice vs. Lorenz-Mie Theory with "effective refractive index"

For aggregates of other sizes & geometrical volume fraction:





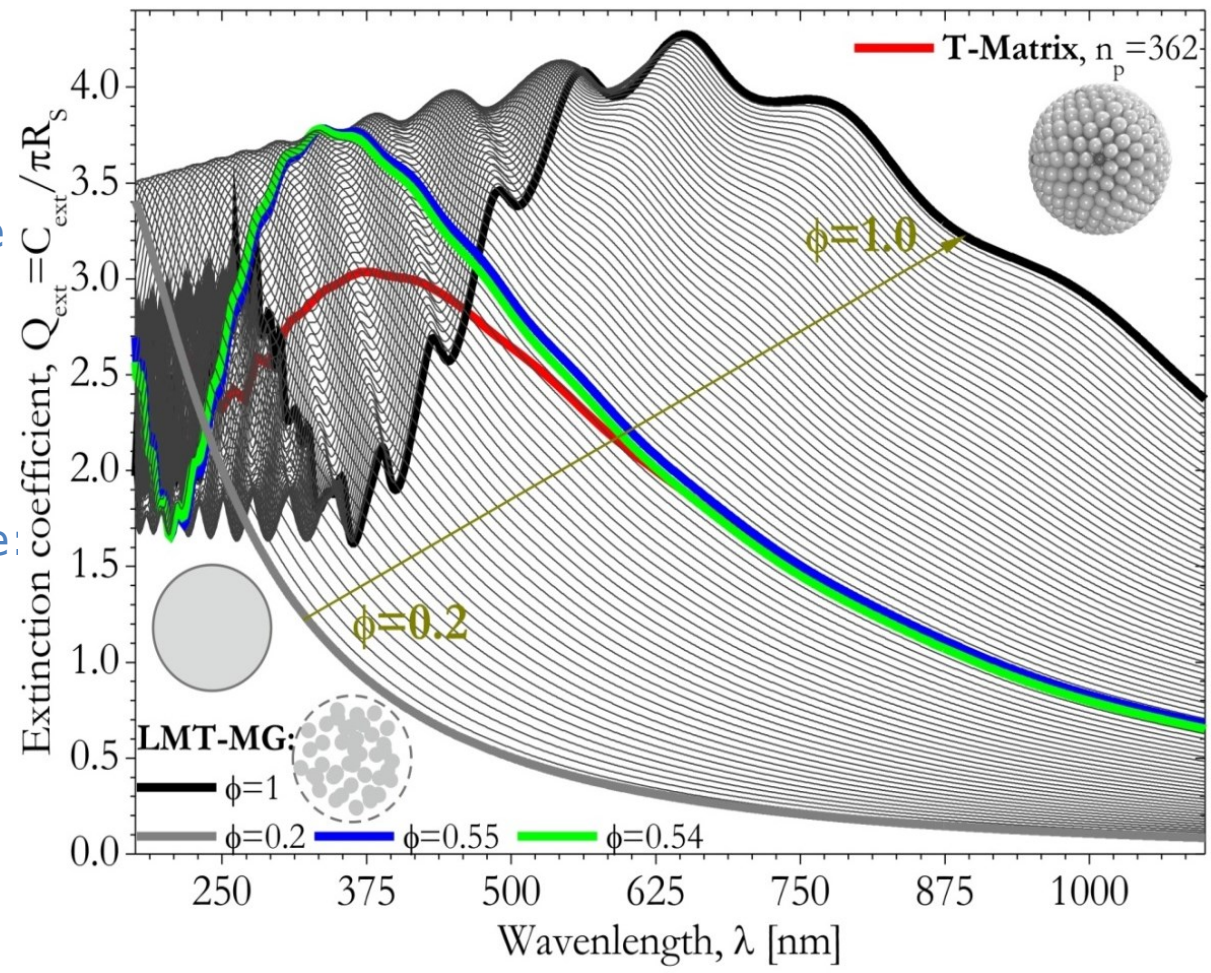
# Light extinction spectrometry

Scattering models : T-Matrice vs. Lorenz-Mie Theory with "effective refractive index"

Good agreement with T-Matrix results for large buckyballs

The optimal volume fraction is very close to the morphological one:

$$\phi_{LMT-MG} \approx 0.545; \phi_{Morph.} \approx 0.54!$$



# Input data: refractive index...

## Light-scattering calculations:

- Particle agregats (nano-spheres, clusters, effective medium)
- Mixed dipoles (arbitrary shapes)



→ limited in size and complexity (references ?)

## Kramers-Koning relations:

$$m(\lambda) = 1 + \frac{c}{\pi} \int_0^{\infty} \frac{\alpha(\lambda')}{\lambda'^2 - \lambda^2} d\lambda'$$



→ Compacted powder & Absorption measurements (integrating sphere + FTIR)

## Extinction measurements:

- Experiments
- Reference technique for the PSD (electron microscopy...)
- Accurate light scattering model

→ Iterative process with minization of a residu

# Light extinction spectrometry

In-situ characterization of dust mobilized by laser cleaning methods and loss of vacuum accident

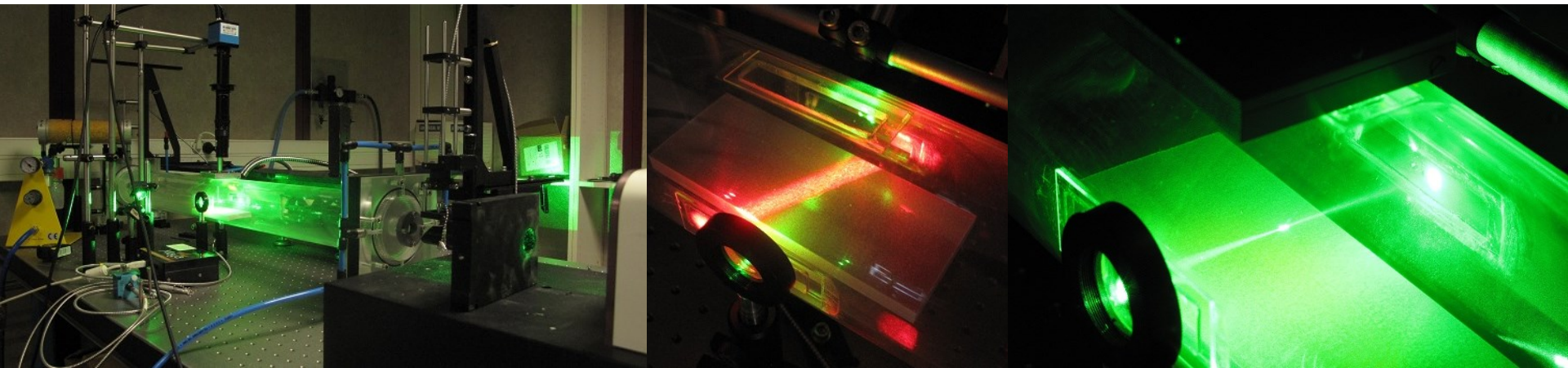
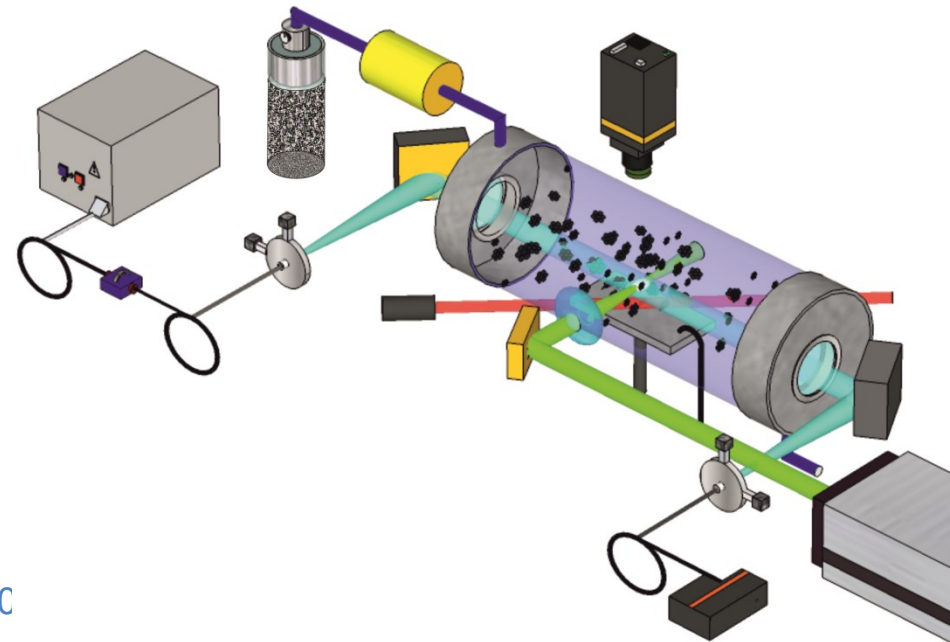
## Tungsten aggregates

### Investigations:

- Sizing with LES (fractal model & T-Matrix)
- Effect of wall proximity
- Effect of laser ablation techniques  
(*broadband emittance, shock wave*)

### Test & setup:

- Spraying tungsten nanopowders
- Mobile wall
- YAG laser (laser-induced breakdown of air, 24C)

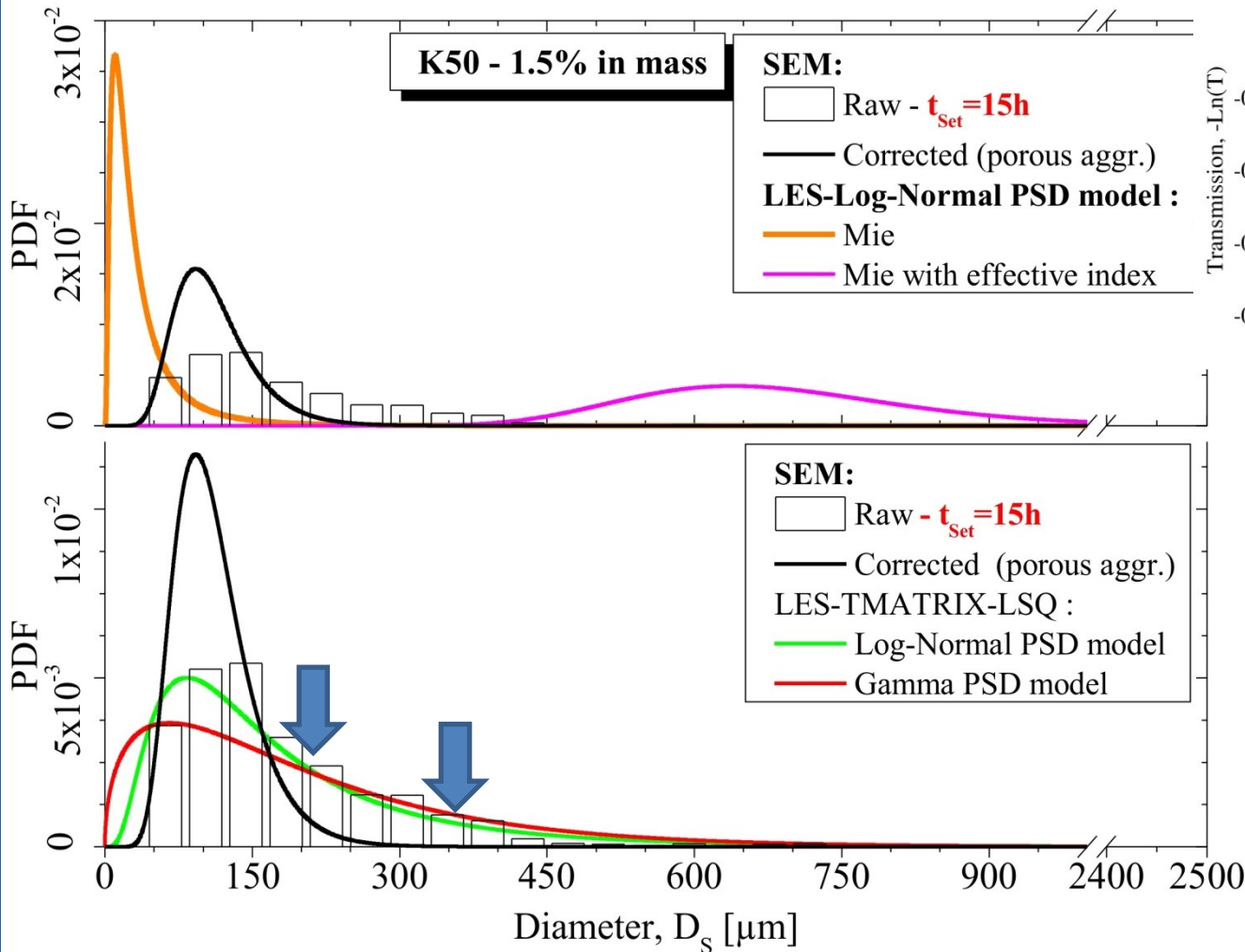




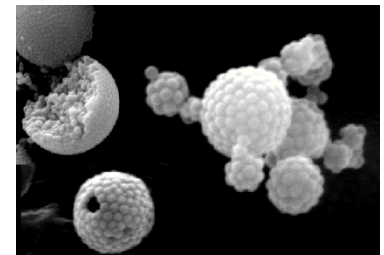
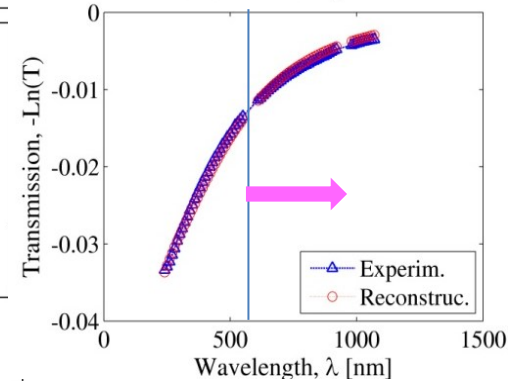
# Light extinction spectrometry

e.g. Application to Buckyball-shaped silica nanoaggregates

**Example:** sedimentation time of 24 h

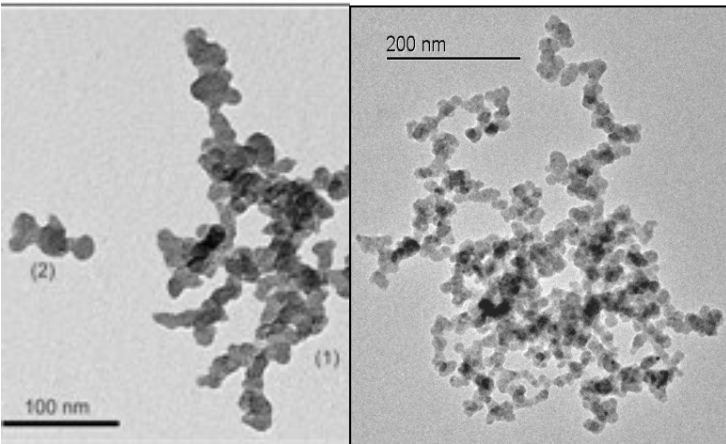


Extinction spectra

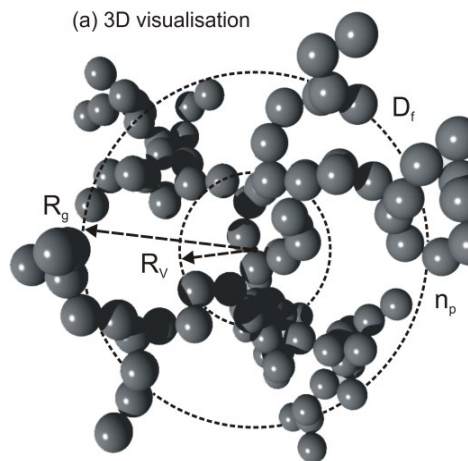


# Models to describe the morphology of particles Fractal-like aggregates

## Soot and Silicone-Carbide aggregates



## (1) Model of the fractal aggregate



$$n_p = k_f \left( R_g / r_p \right)^{D_f}$$

**Primary particles:**

- $n_p$  number
- $R_p$  mean radius

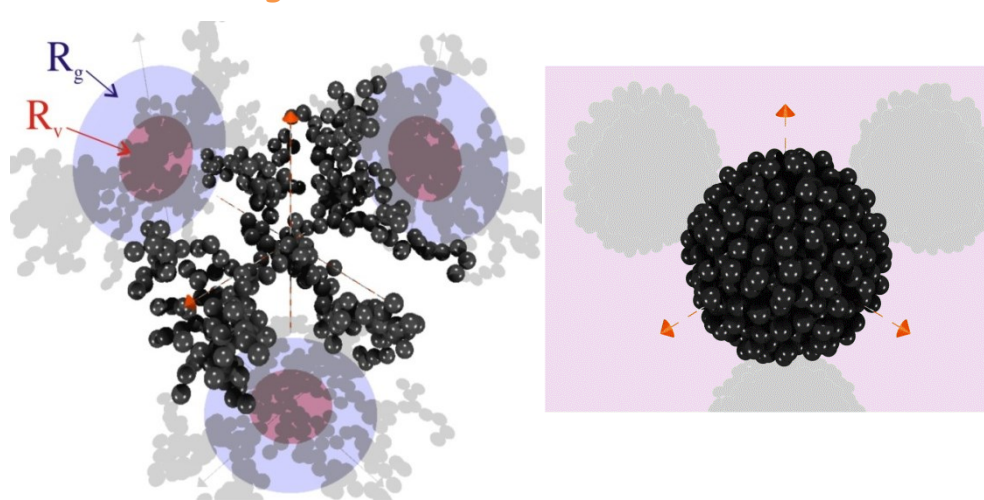
**Aggregate:**

- $D_f$  fractal dimension
- $R_g$  radius of gyration
- $k_f$  struct. coefficient

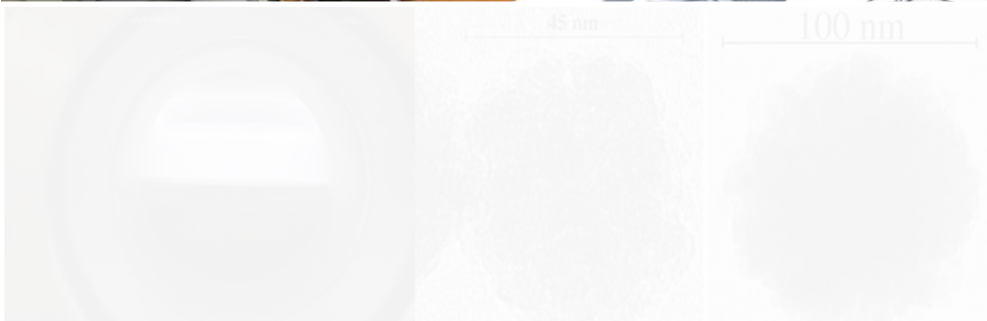
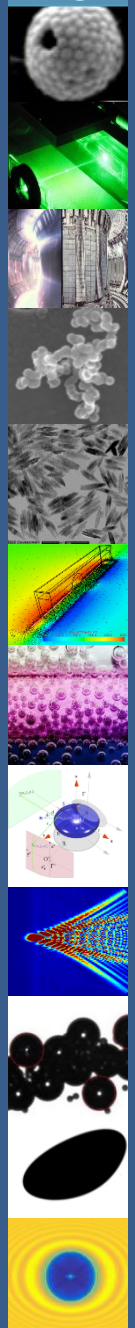
## (2) Diffusion limited aggregation code

| No. | X               | Y              | Z               | Current Df    | Theoretical Rg | Current Rg    | Appearance sphere |
|-----|-----------------|----------------|-----------------|---------------|----------------|---------------|-------------------|
| 1   | 0               | 0              | 0               | 0             | 0              | 0             | 0                 |
| 2   | -0.969307415078 | 0.624181939179 | 1.63427049226   | 1.75          | 1.17867362032  | 1             | 12.9277002188     |
| 3   | 1.4310472558    | 1.17276721687  | -0.759421363068 | 1.49599428914 | 1.49599428914  | 1.49599428914 | 12.9277002188     |
| 4   | -1.40220220203  | 1.32650778163  | 1.8095271515    | 1.737121841   | 1.7515226586   | 1.73442766736 | 15.715605217      |
| 5   | -0.735870125732 | 1.04357187523  | 3.67478800247   | 1.7514154979  | 1.98970116599  | 1.98958517639 | 16.6514730246     |
| 6   | -1.74710703195  | -2.1589806916  | 2.65841736792   | 1.74882094321 | 2.20817902735  | 2.2082855047  | 16.3879993396     |
| 7   | 0.775150391482  | 2.2732771959   | 4.12702545144   | 1.7504361823  | 2.4115228815   | 2.41102347304 | 16.9616784051     |
| 8   | 0.93017631742   | -0.85240460412 | -1.6932055781   | 1.76985325759 | 2.4672228489   | 2.46209466202 | 17.3882719784     |
| 9   | 3.12385653505   | 0.144105463368 | -1.0358532028   | 1.74962509211 | 2.78392709182  | 2.78453793079 | 17.7982785466     |
| 10  | -2.80478053334  | -1.29075962078 | 4.11885022597   | 1.74919100761 | 2.95668456975  | 2.95816735351 | 18.7964021838     |
| 11  | 1.98313266445   | -2.3054736276  | -1.91428445941  | 1.74952280471 | 3.12218014643  | 3.12302787845 | 19.6409040338     |

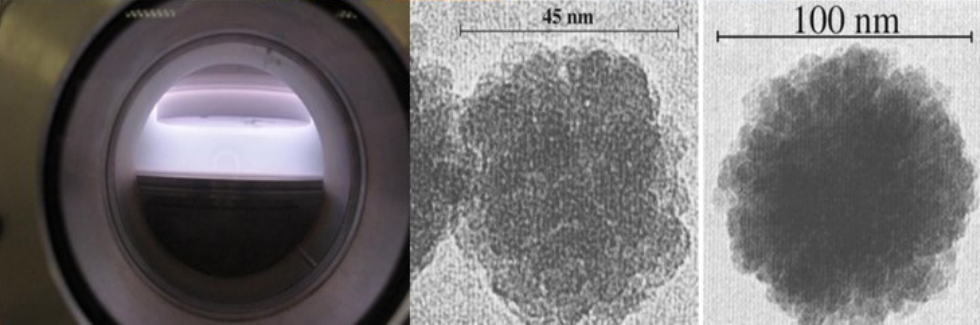
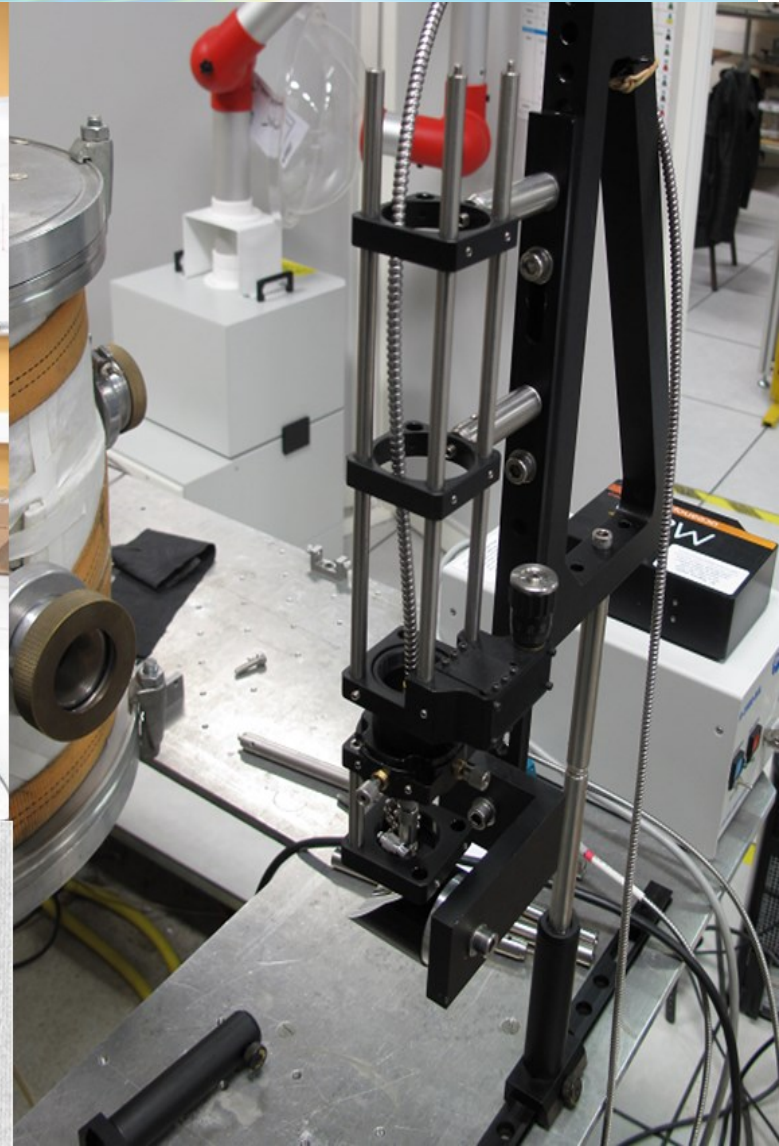
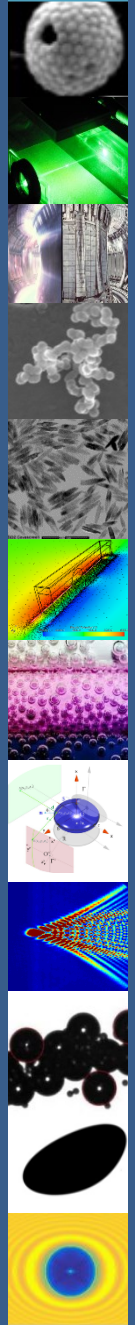
## (3-4) Rendering views (SEM/TEM)

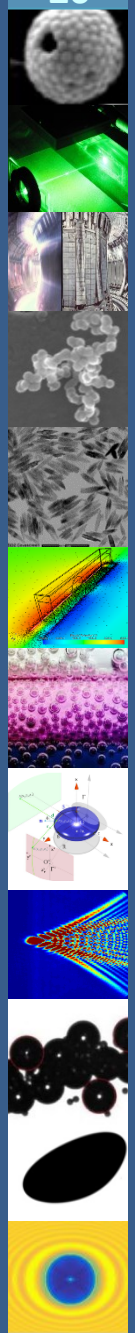


# In-situ characterization of dust mobilized by laser cleaning methods and loss of vacuum accident



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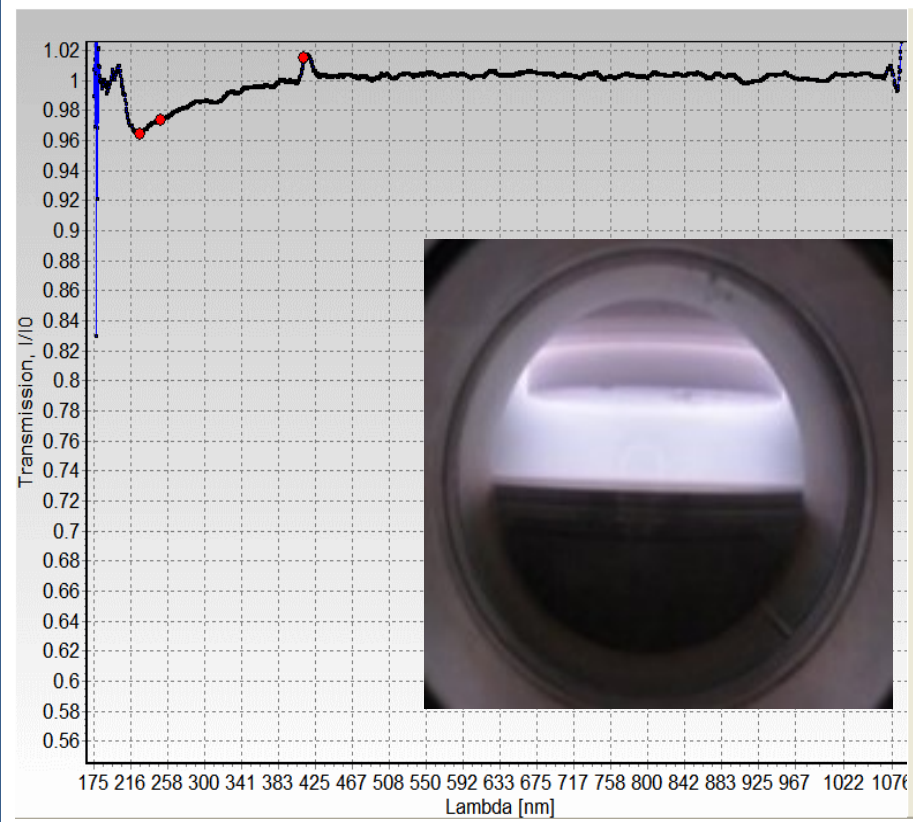




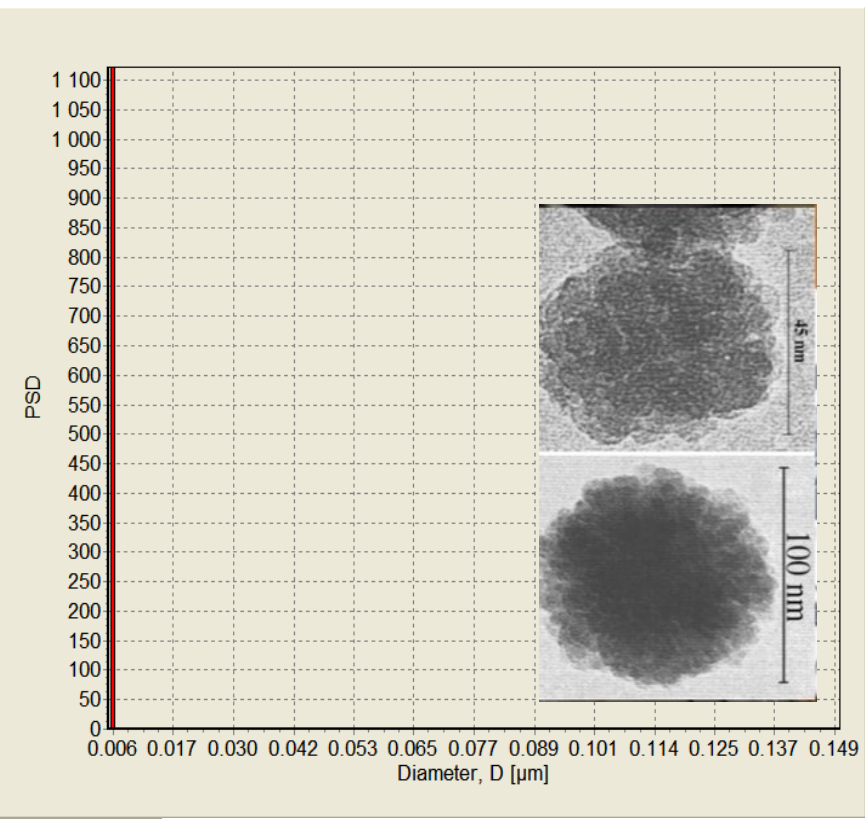
# Light extinction spectrometry

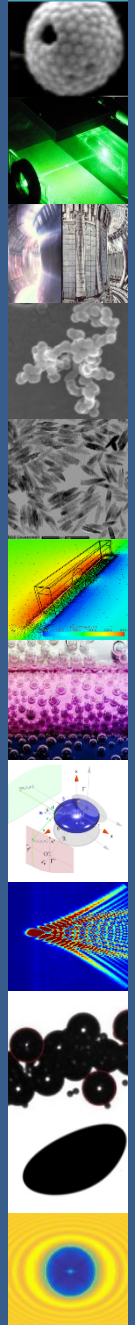
Particle nucleation and growth in a low-pressure Argon/Silane discharge

### Corrected spectra



### Measured PSD

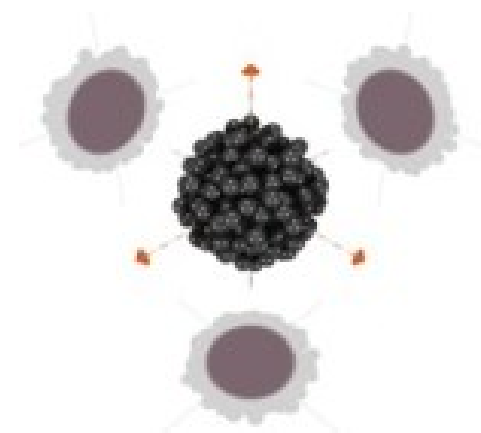
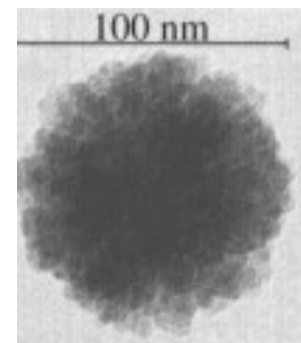
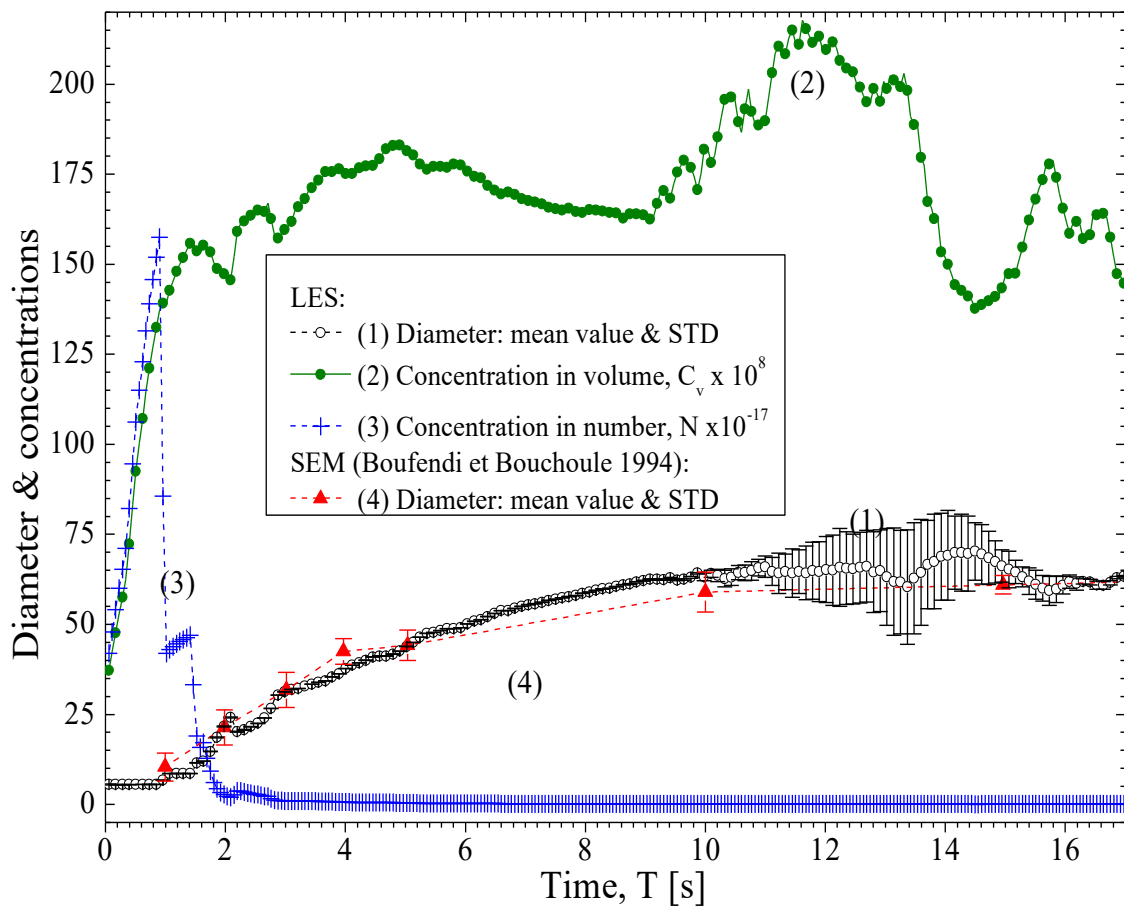


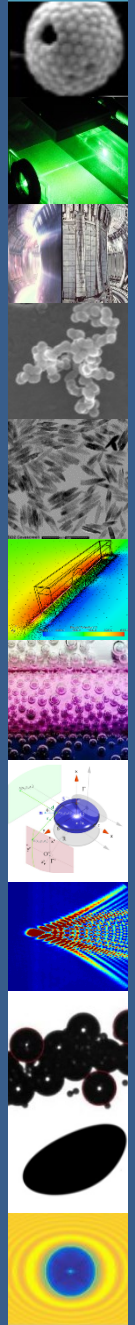


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Particle nucleation and growth in a low-pressure Argon/Silane discharge

*Barbosa et al. J. Phys. D: Appl. Phys. 49 045203 (2016)*

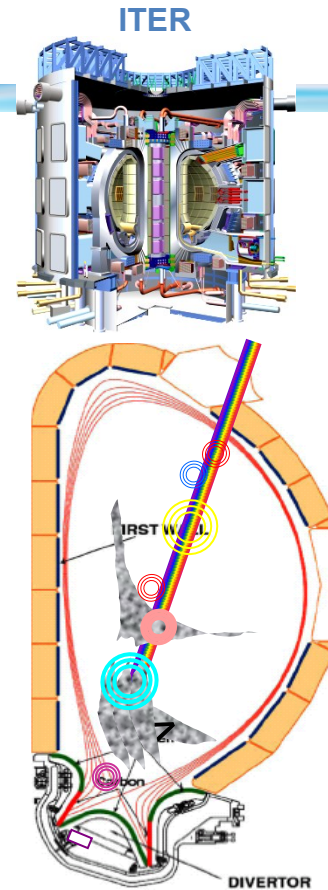
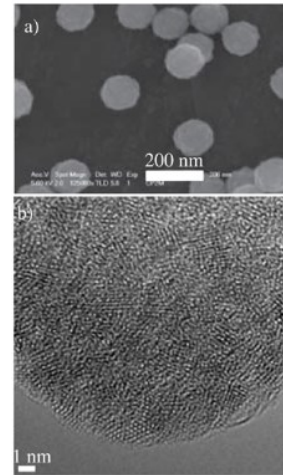
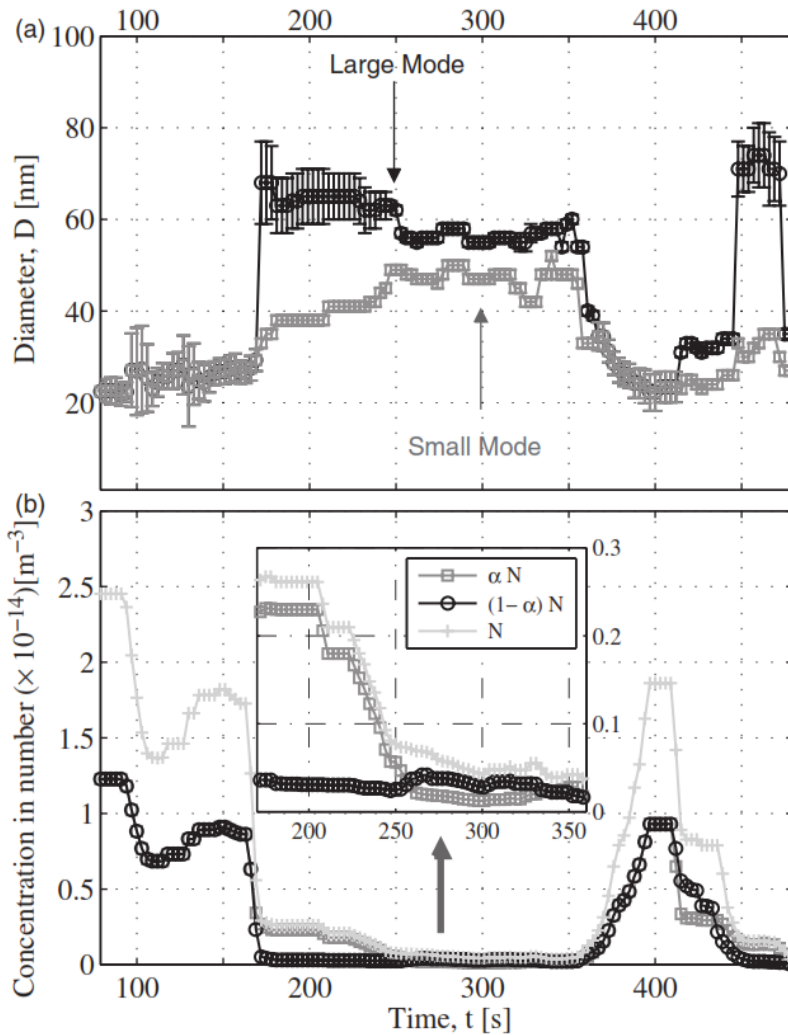




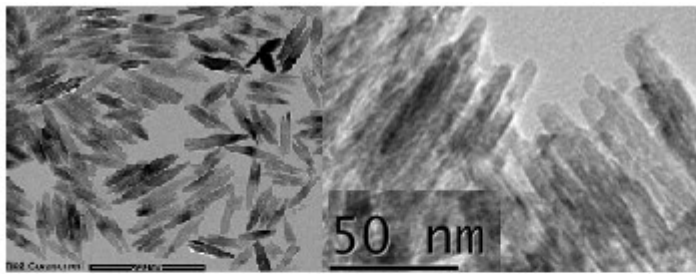
# Light extinction spectrometry

Particle nucleation and growth in a low-pressure Argon/Tungsten RF discharge

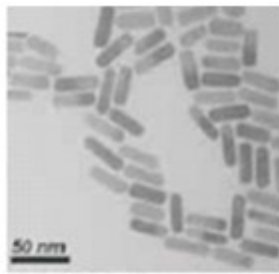
Barbosa et al. *J. Phys. D: Appl. Phys.* 49 045203 (2016)



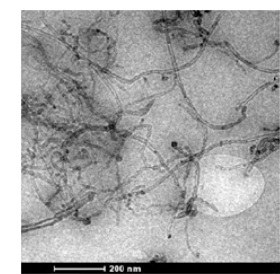
# LES : nanotubes, nanorods and needle shapes particle characterization in suspensions



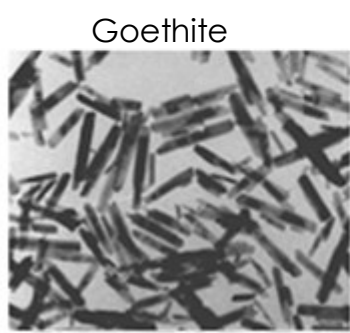
Acicular TiO<sub>2</sub>



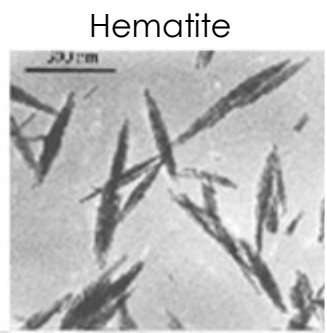
Gold nanorods



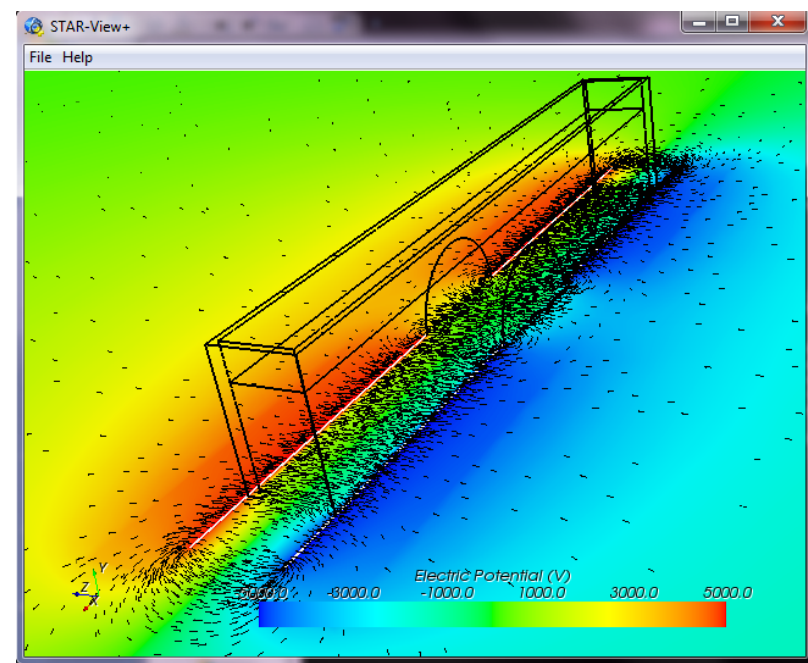
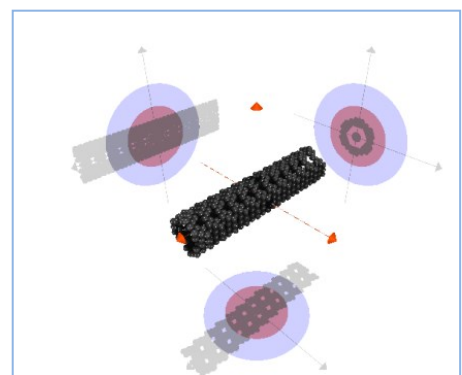
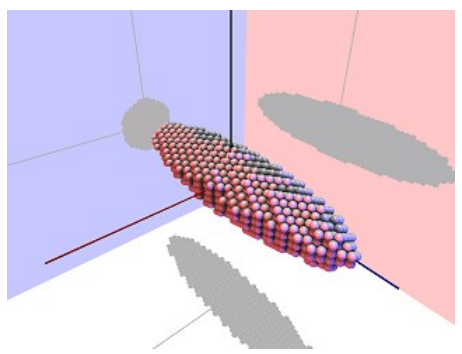
Carbon nanotubes



Goethite



Hematite





# Characterization of colloids at the Microscale

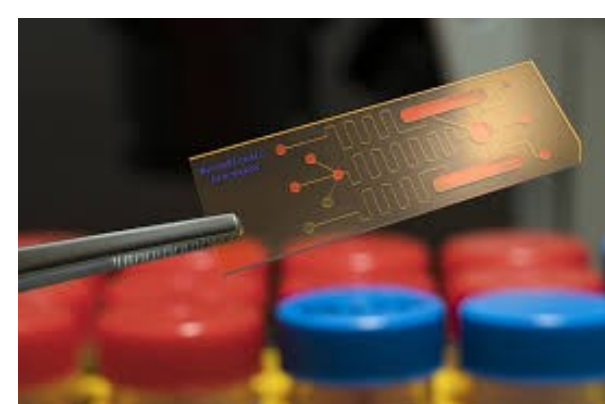
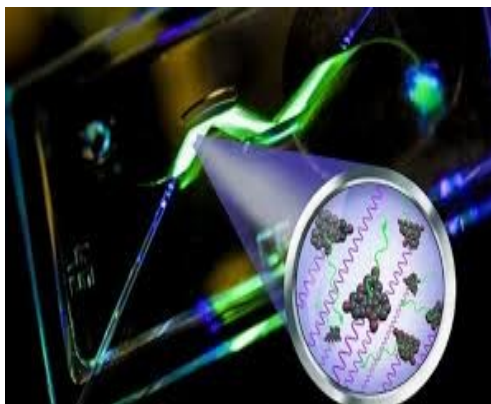
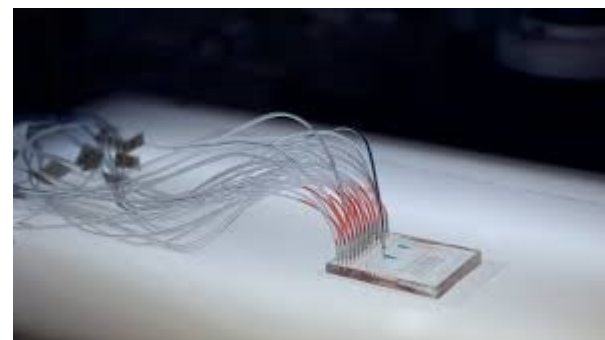
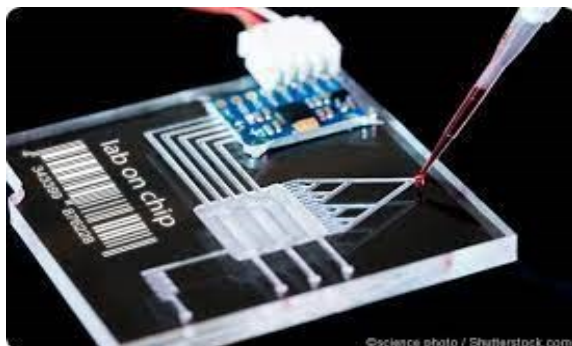
## Photonic Lab-on-a-Chip (PLOC)

### Why?

Reduced costs & dimensions

Improve space–time yields, selectivity, reaction residence times and conversions capabilities

Highly demanding fields: Biology, chemical engineering, chemistry...



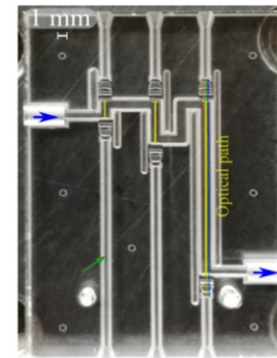
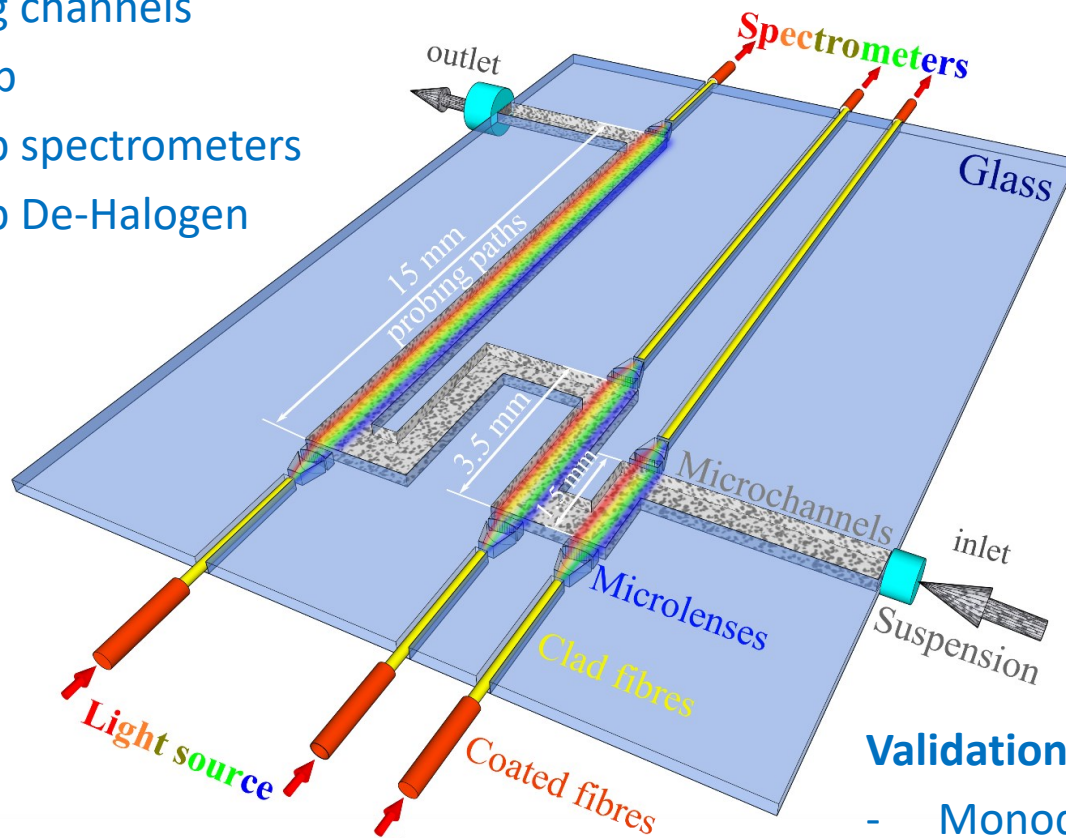
# LES at the Microscale

## Photonic Lab-on-a-Chip (PLOC)

*Onofri et al., Optics Express (Submitted 2021)*

### First prototype

- 3 probing channels
- Glass chip
- Benchtop spectrometers
- Benchtop De-Halogen source

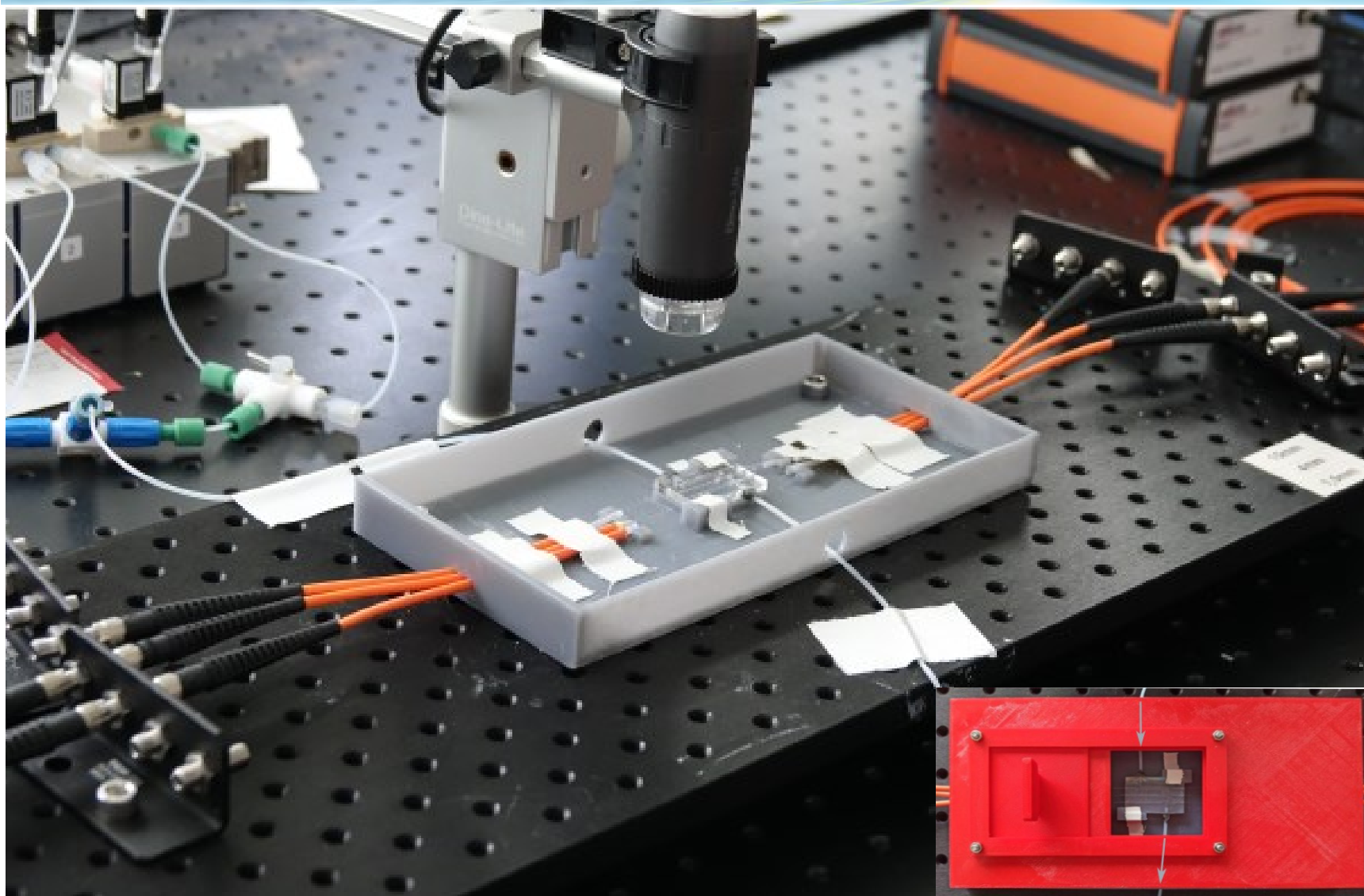


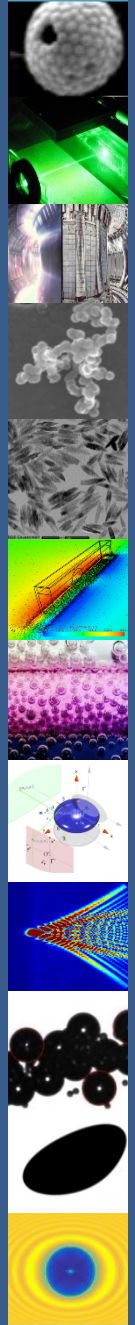
### Validations:

- Monodisperse 30-750nm
- Silica & Glass beads
- Concentraions: 1-1000ppm

# LES at the Microscale

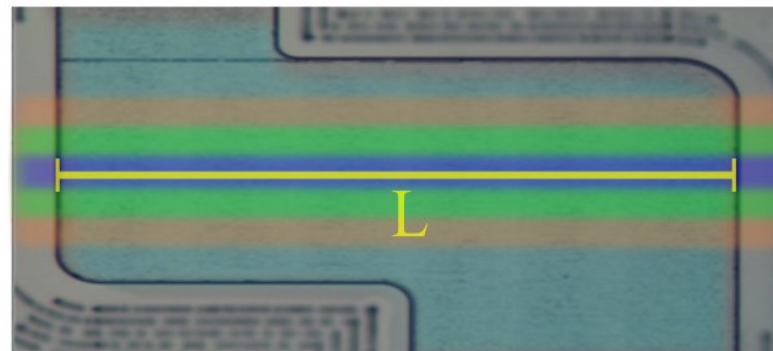
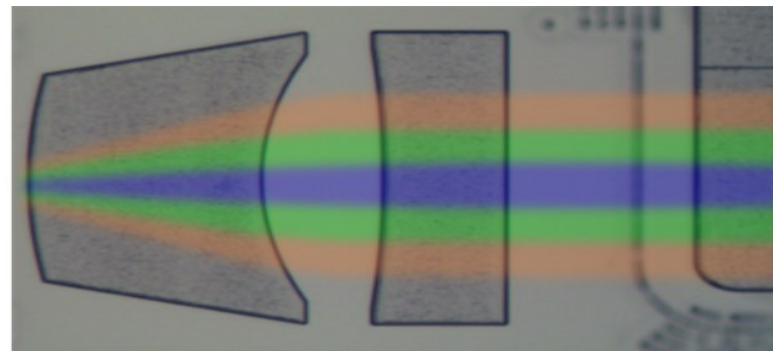
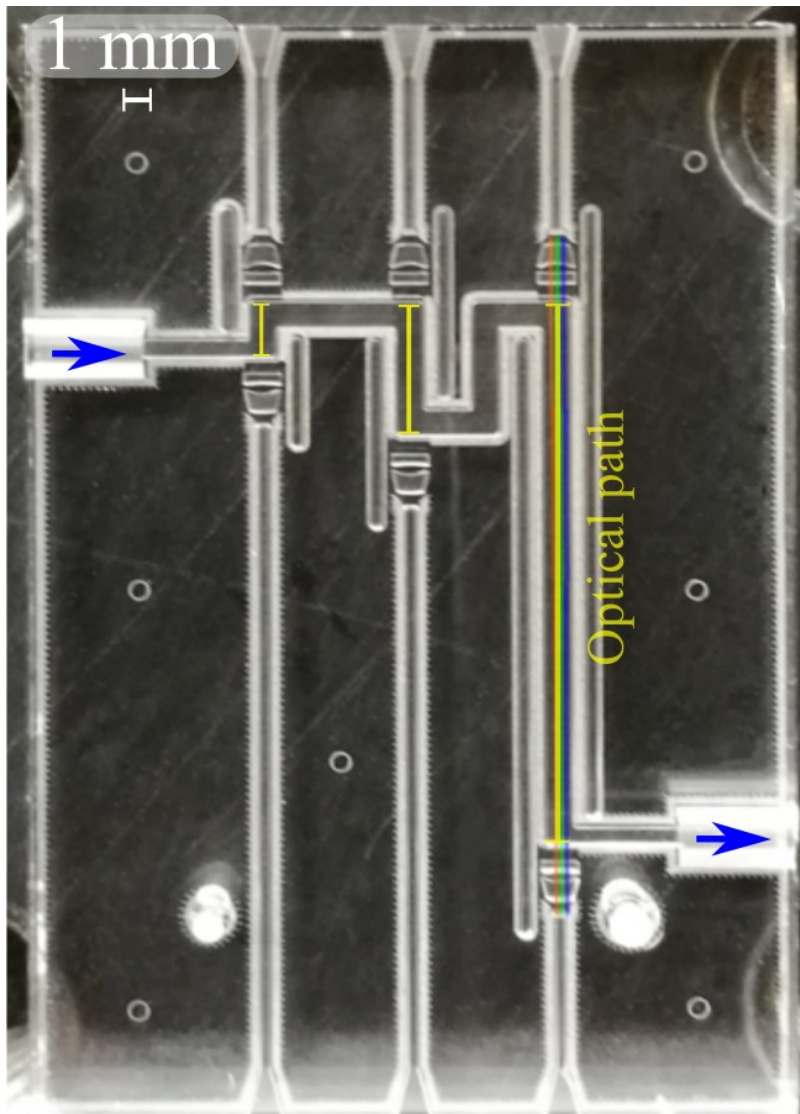
First prototype - Photonic Lab-on-a-Chip (PLOC)





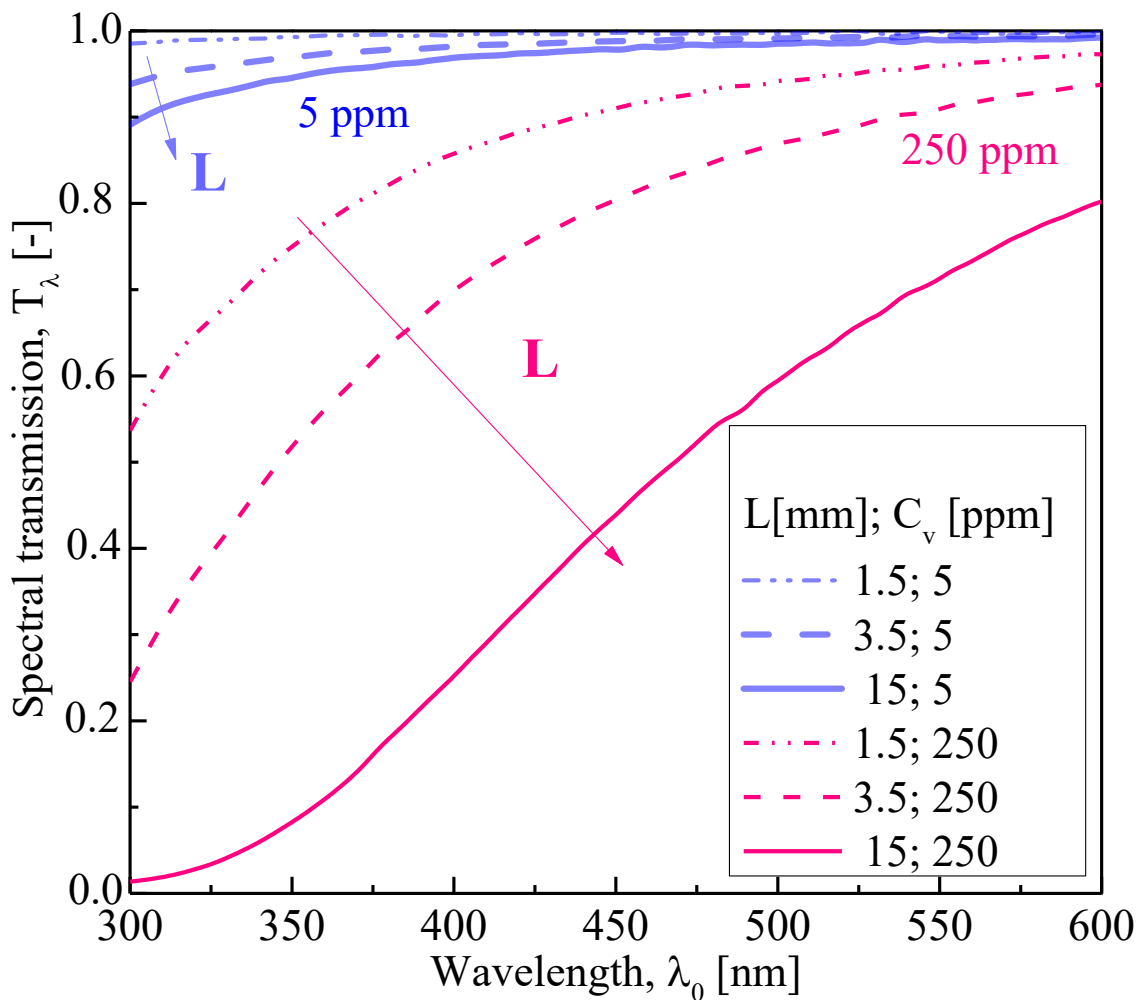
# LES at the Microscale

First prototype - Photonic Lab-on-a-Chip (PLOC)



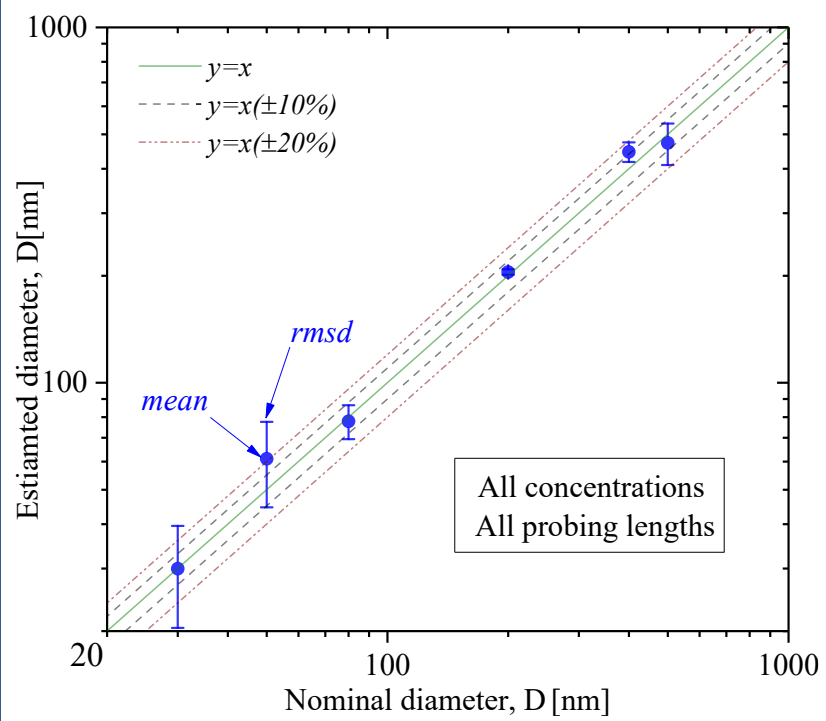
# LES at the Microscale

Example: signals for 80nm silica suspensions in two concentrations

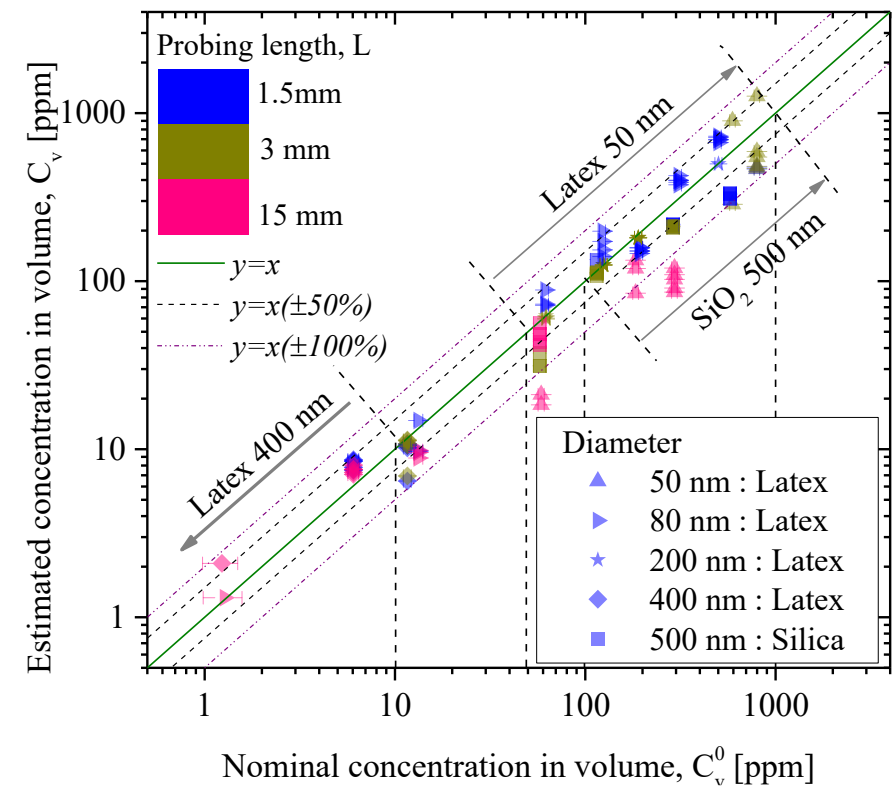


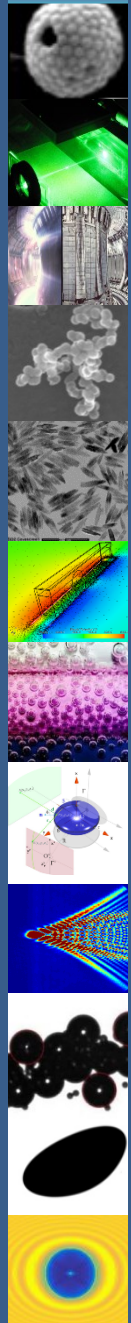
# LES at the Microscale - PLOC

## Comparison of size and concentration measurements



References:  
 Size : MEB (NIST)  
 Concentrations: Weighings





# Preliminary conclusions for LES at microscale

## Experimental results are already very promising

- Size from 30 nm to 0.5  $\mu\text{m}$
- Volume concentrations from 1 to 1000 ppm

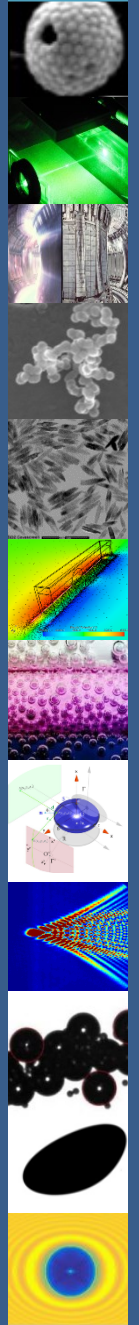
## Works for both stationary suspensions and dynamic particulate flows

## Straight improvements:

- Channels could be further optimized to fit the optical properties, size and concentration of the particles
- Better control the SNR of the transmittance signals.

## Perspectives

- Increasing the optical path length with wave guide s
- Integrating a microfluidic-controlled optical router for multiplexed analyses



End.