Consiglio Nazionale delle Ricerche

Istituto per l'Energetica e le Interfasi – Milano ***ITALY***

Experimental Correlation between Particle Size and Laser-Induced Incandescence (LII) Time Decay in TiO_2 Flame Synthesis

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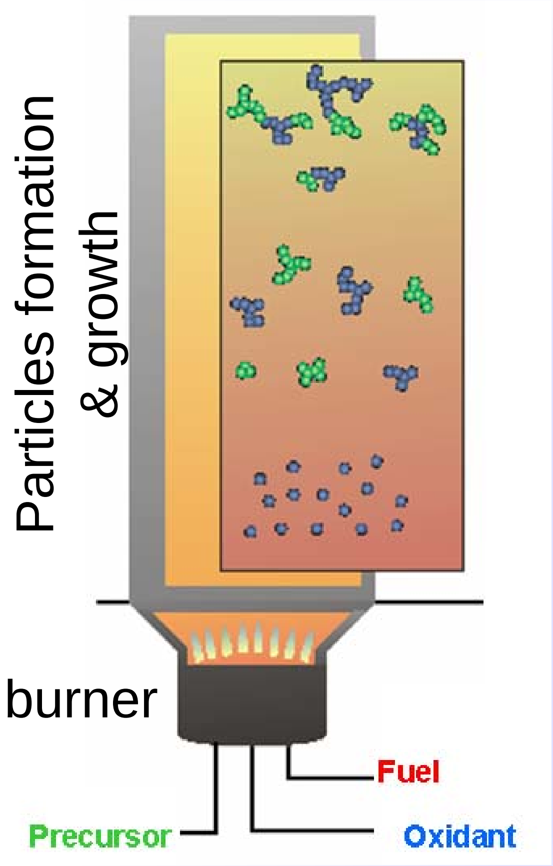
Particles 2008
Particle-Based Advanced Materials
nanoparticles.org

FLAME SYNTHESIS:

AN OUTSTANDING METHOD TO PRODUCE NANOPARTICLES

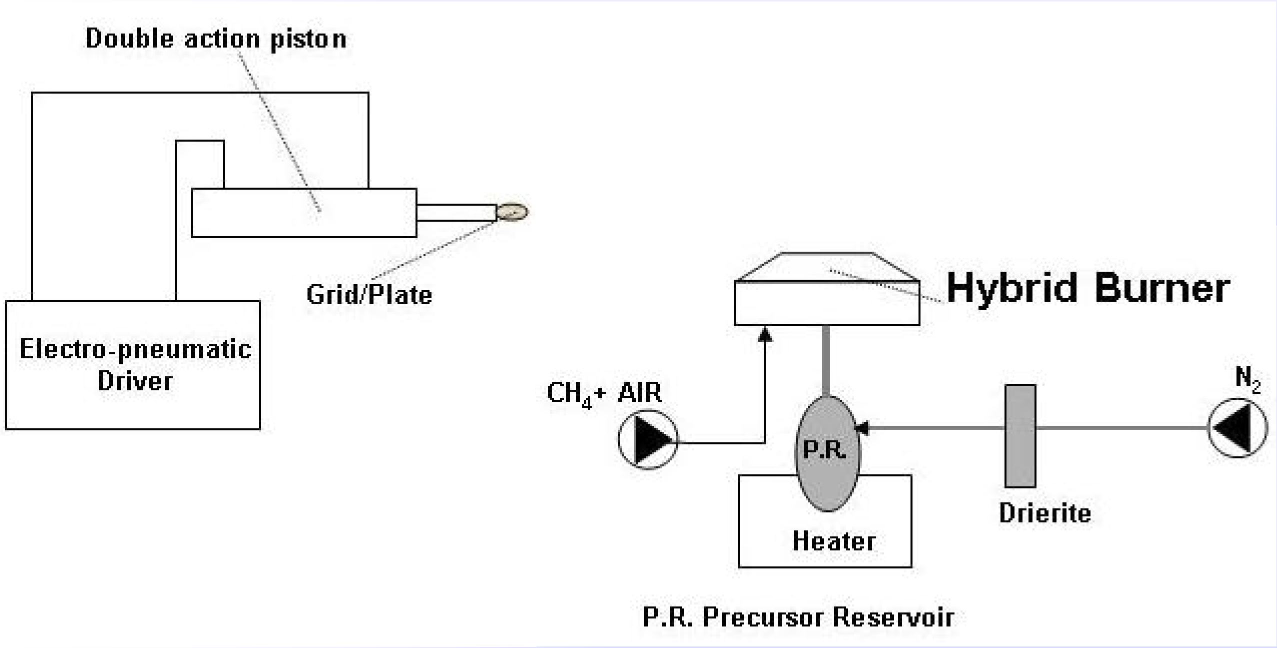


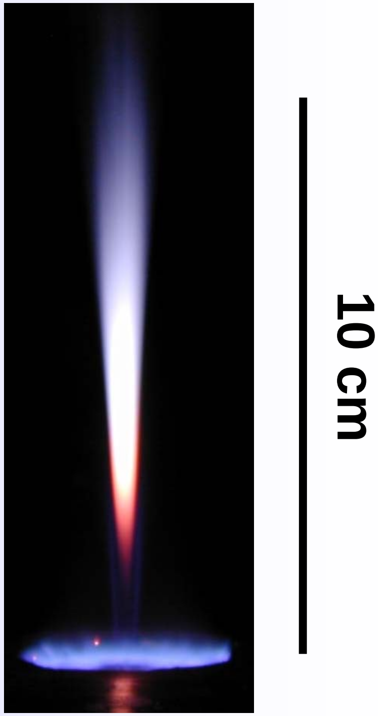
Flame manufacturing of nanoparticles:

Product powders	Volume (Mt/year)	Value (B$/year)
Carbon Black	8	8
Titania	2	4
Fumed silica	0.2	2

After Wegner et al., Chemical Engineering Science 58 (2003) 4581

Reaction Burner and Sampling set-up





$V_{CH4} = 0.7$ Nl/min;
$V_{AIR} = 8$ Nl/min;
$\Phi = 0.81$;

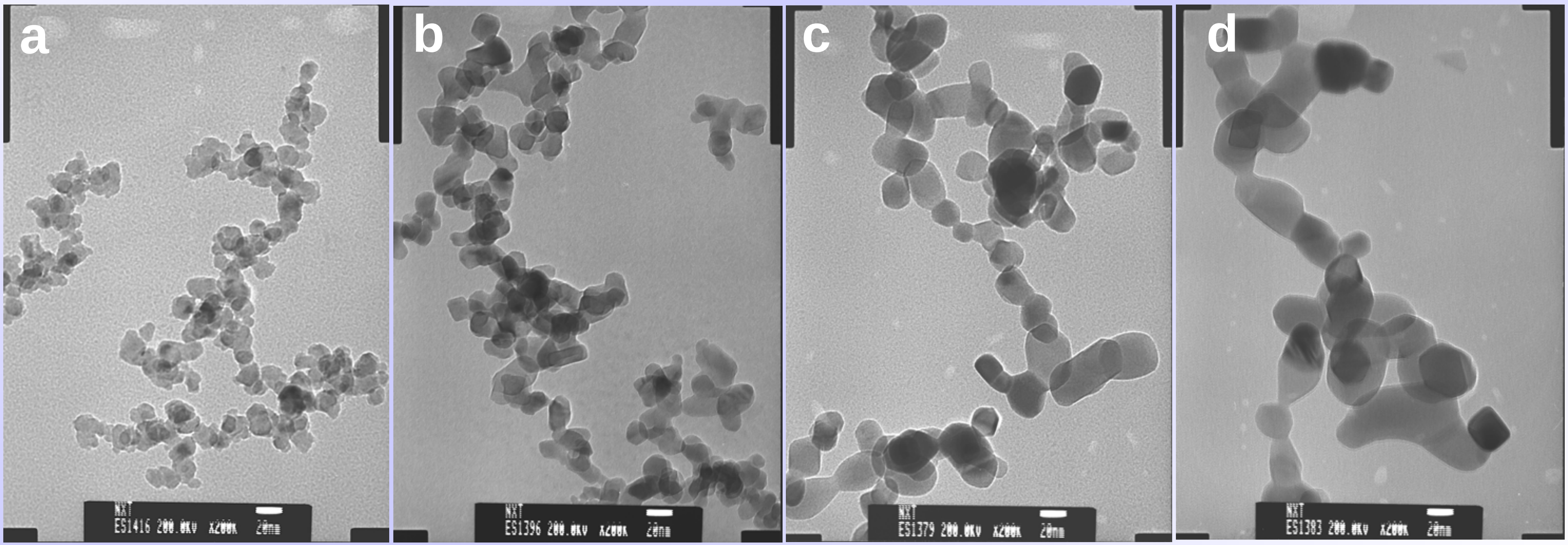
$V_{N2} = 0.2$ Nl/min

➢ $Ti(OC_3H_7)_4 \longrightarrow TiO_2$

TiO_2 size evolution along the reaction flame

TEM images of particles collected at:

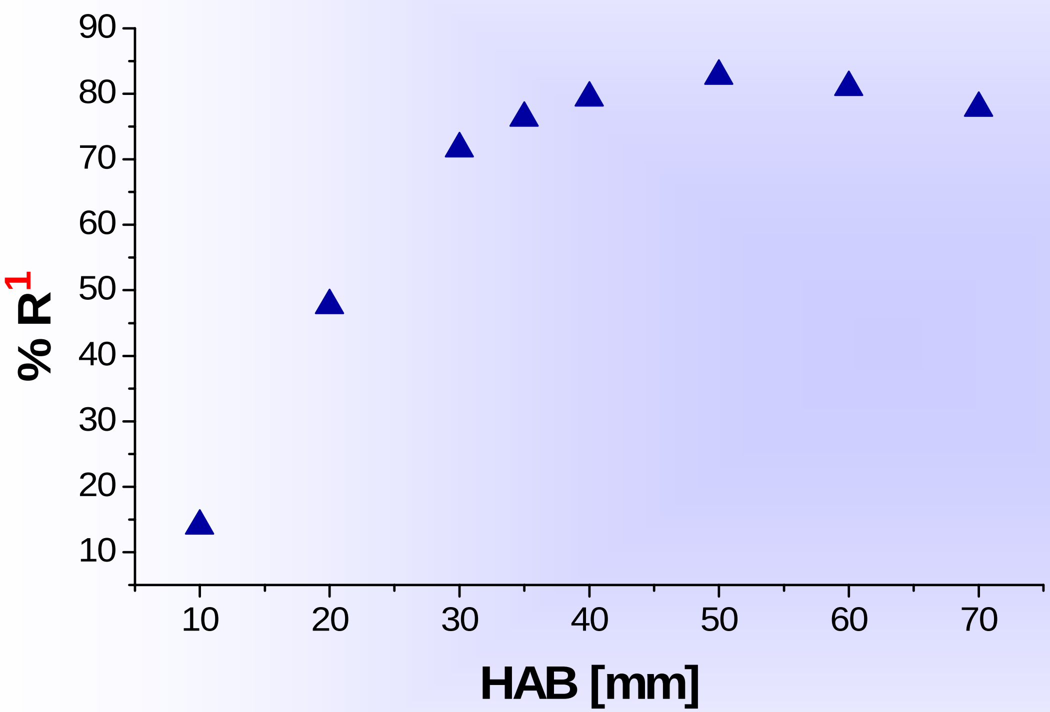
a) 5mm HAB b) 15mm HAB c) 25mm HAB d) 50mm HAB



20 nm

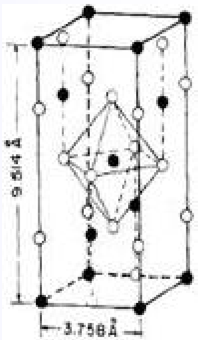
HAB =**H**eight **A**bove the **B**urner

TiO_2 phase evolution along the reaction flame

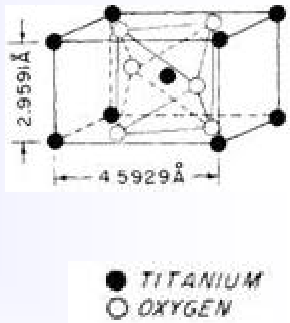


Phase composition from XRD spectra

ANATASE
(A)



RUTILE
(R)



[1]
$$\%R = \frac{1}{\left(\frac{A}{R} \times 0.884\right) + 1} \times 100$$

It would be very useful the availability of a diagnostic technique allowing insights in the particle formation and growth process. In particular, an

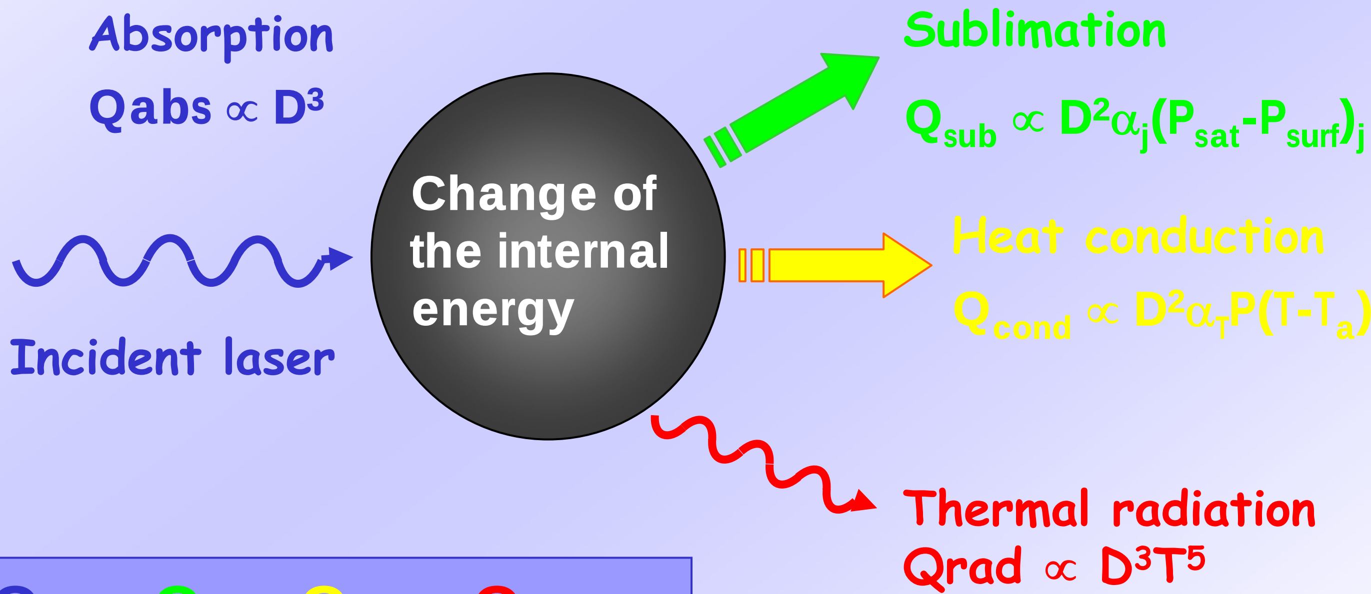
ON-LINE DIAGNOSTICS

would be very attractive :

- ✓near real-time response;
- ✓spatial resolution;
- ✓non-intrusive.

in gas-phase reaction some chance…

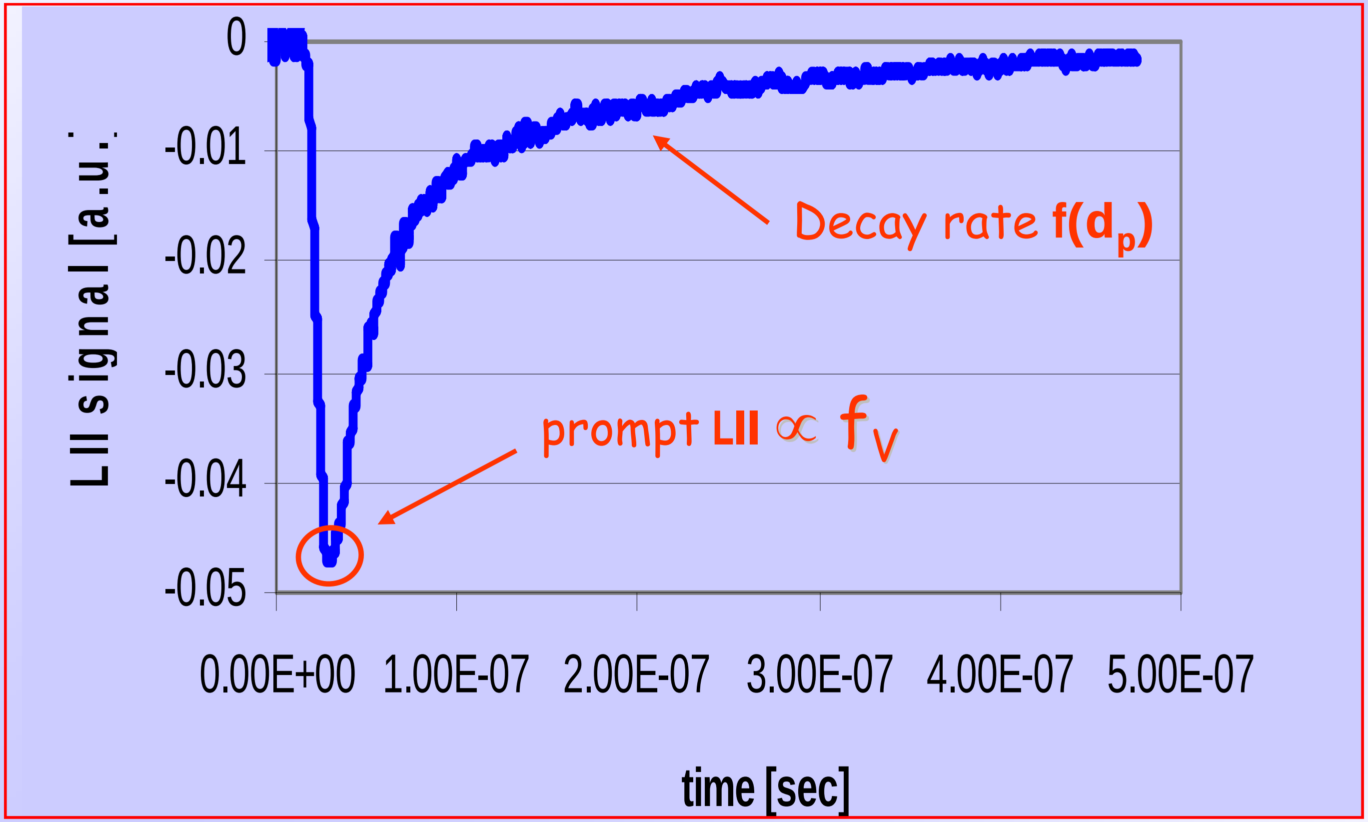
Laser Induced Incandescence: PRINCIPLES



$$Q_{int} = Q_{abs} - Q_{sub} - Q_{cond} - Q_{rad}$$

The LII signal is based on the energy and mass balance between a single particle and its surrounding

LII signal: A powerful tool in SOOT diagnostic



FROM SOOT TO OTHER NANOMATERIALS…

How could react particles different from soot to strong laser irradiation?

R.L. Vander Wal et al., 1999 → Laser Induced Emission (LIE)

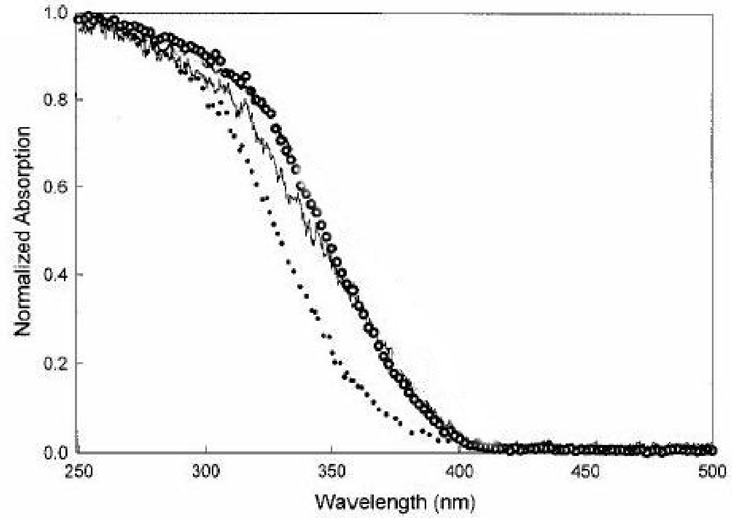
LII on Non-Carbonaceous particles: STATE OF THE ART

- ✓ Metals nanoparticles by laser ablation (R.L. Vander Wal et al., **1999**)
- ✓ Various nanoparticles at room T in a cell (A.V. Filippov et al., **1999**)
- ✓ Oxides np by laser evaporation reactor (A. Leipertz, S. Danckers, **2003**)
- ✓ Manganese oxide by laser evaporation reactor (T. Lehre et al., **2005**)
- ✓ Fe from a hot-wall reactor (B. F. Kock et al., **2005**)
- ✓ TiO_2 flame synthesis (S. Maffi et al., **2008**)

LII ON TITANIA FLAME

LIE and TIRE-LII : Operative Condition

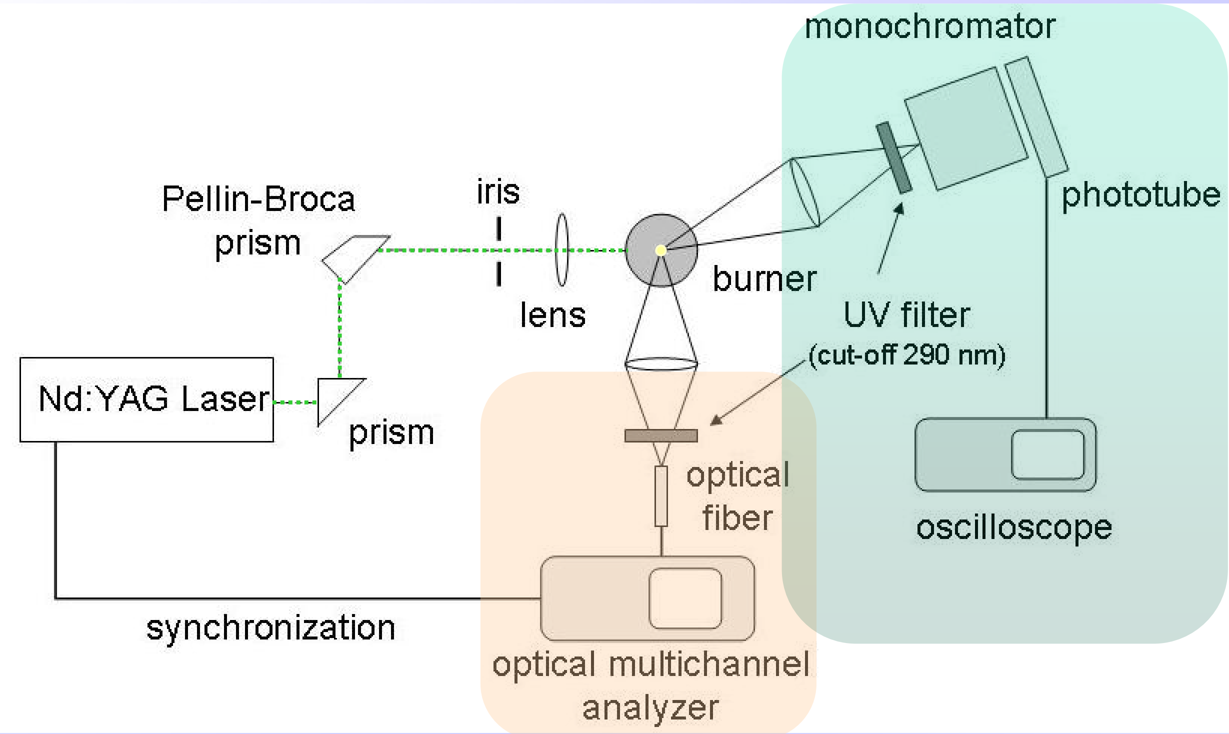
- Excitation Wavelength
- Laser Fluence
- Detection Wavelength



Uv–vis absorption spectra of flame-synthesized TiO_2 powders of different particle sizes. ●, 6 nm; ——, 12 nm; ○, 30 nm.

✓266 nm (4° harmonic of the Nd:YAG laser)

TIRE-LII and LIE set up



TEMPORAL ANALYSIS

SPECTRAL ANALYSIS

Excitation wavelength:

✓266 nm

Detection wavelength:

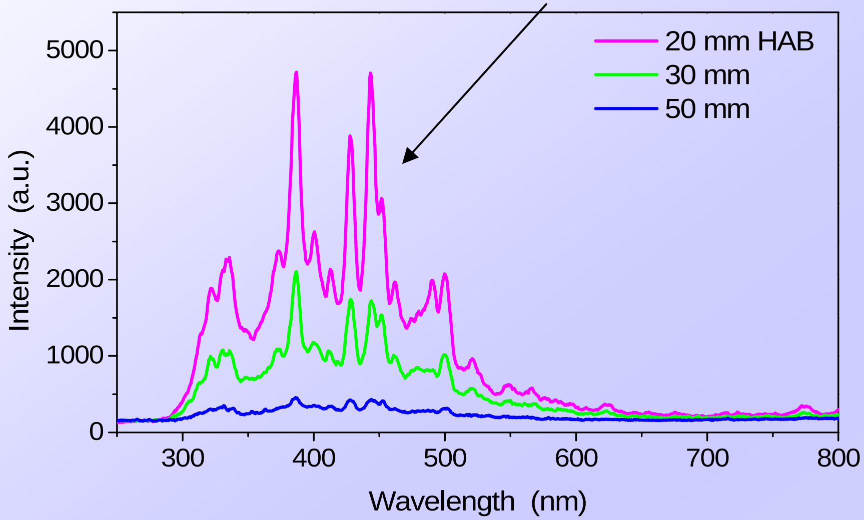
✓300nm-600 nm (20 nm step)

At different laser fluences:

- On time and delayed LIE spectra
- LII signals at different HAB

LIE spectra at High Laser Fluence

Highly structured shape

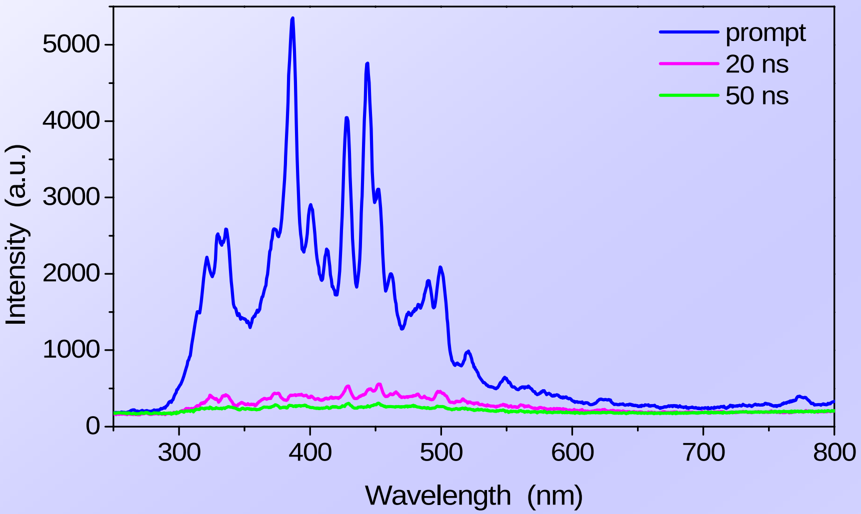


at different HAB

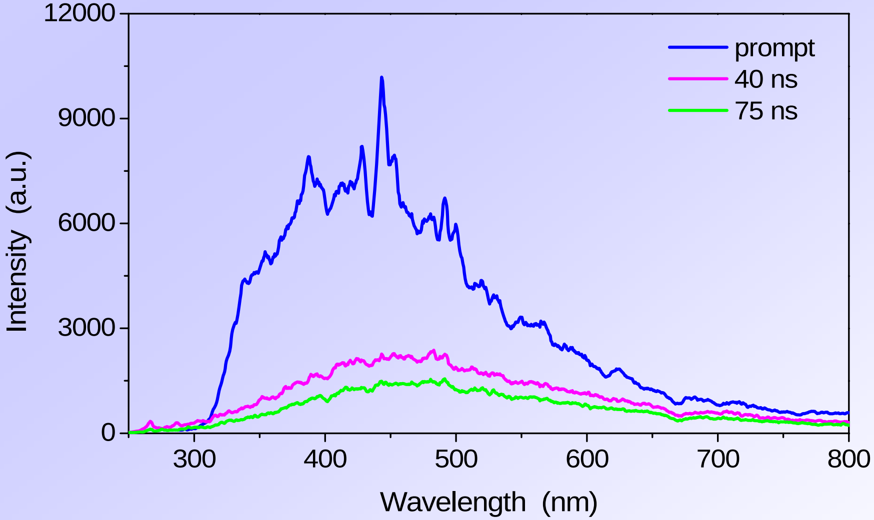
- ✓ Excitation: 266 nm
- ✗ Fluence: 600 mJ/cm^2

LIE spectra at different Laser Fluences: TIME EVOLUTION

600mJ/cm^2

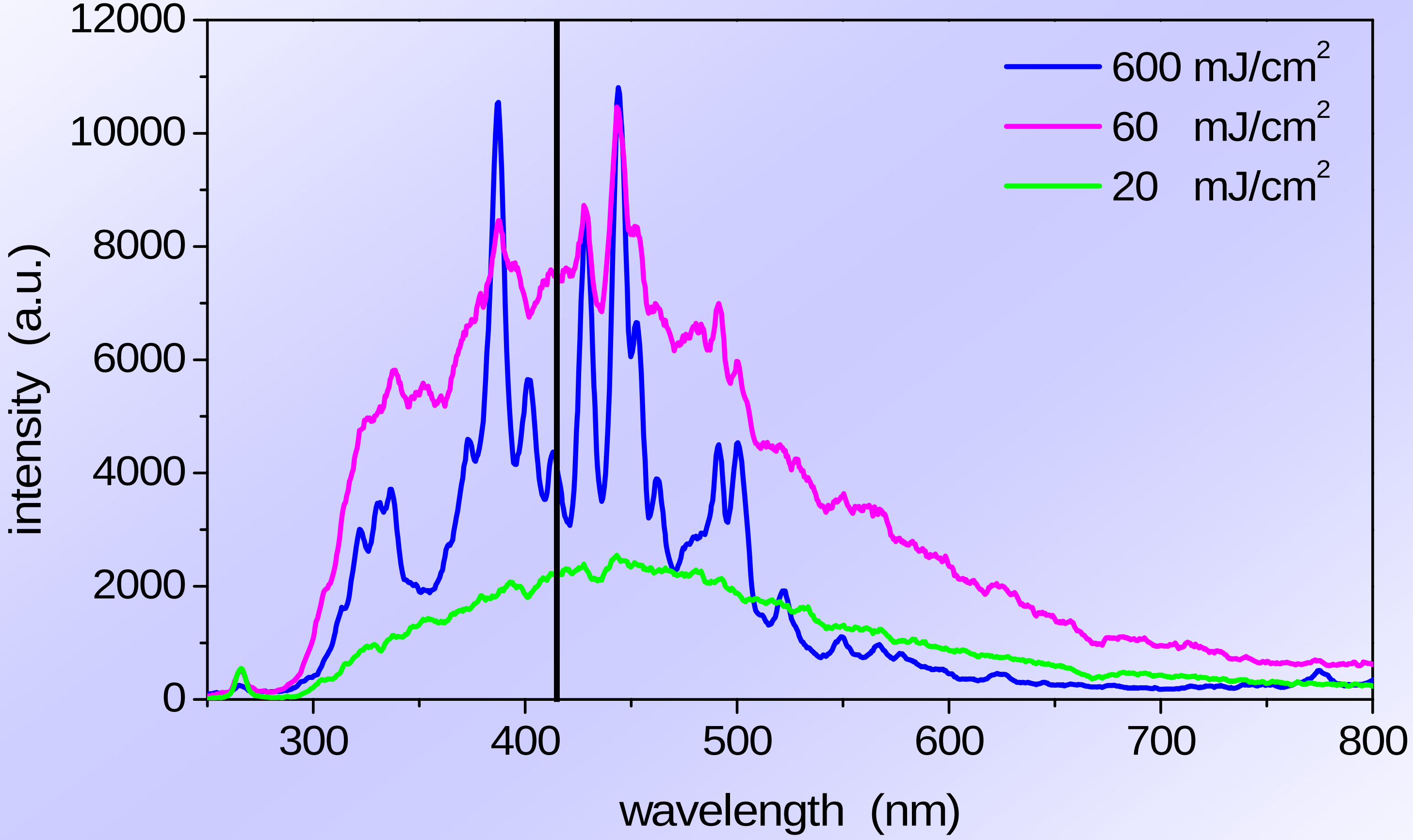


60mJ/cm^2



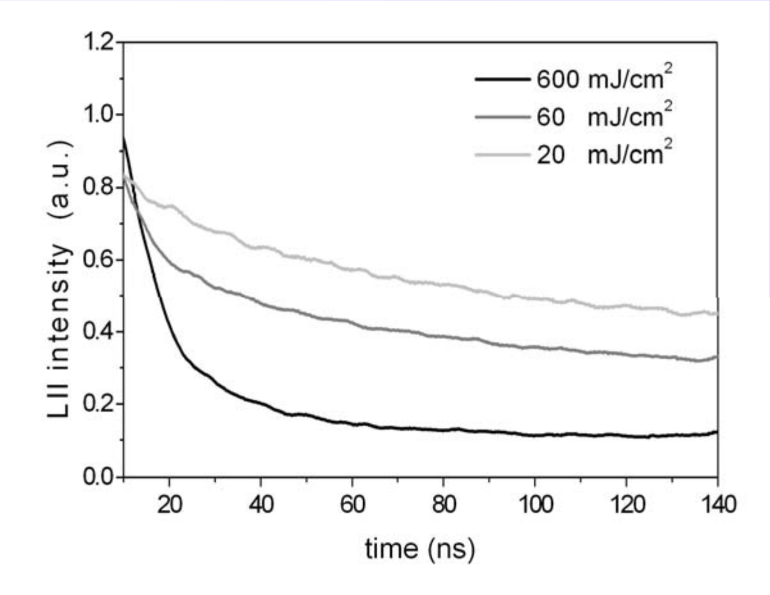
- Particles destroyed
- Spectrum is less structured

Prompt LIE spectra at Different Laser Fluences



✓ fluence values up to about 40 mJ/cm^2 give satisfactory results for titania at 266 nm

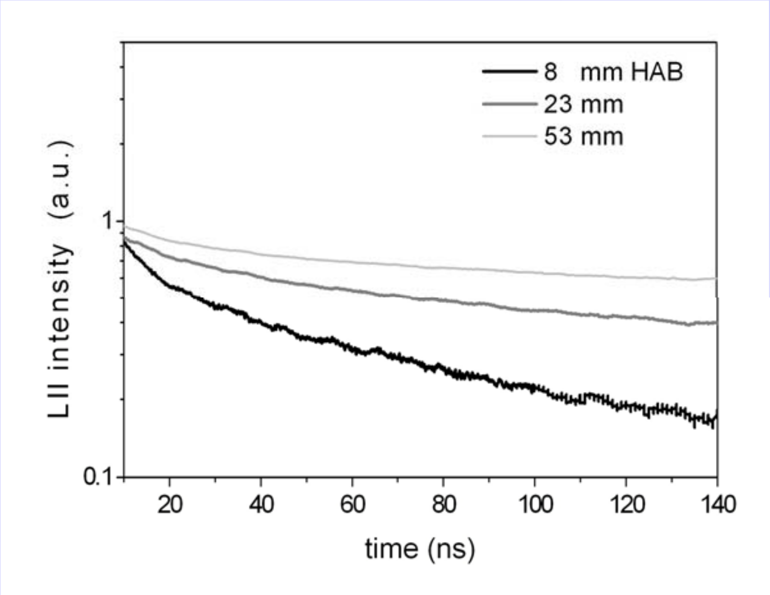
Time decay of the emission signal at Different Laser Fluences



- ✓Excitation: 266 nm
- ✓Detection: 415 nm
- ✓HAB: 20 mm
- ✓dp= 20 nm (by TEM)

LII signals at Different HAB

- ✓ Excitation: 266 nm
- ✓ Detection: 415 nm
- ✓ Fluence: 20 mJ/cm^2



✓ LII signal is sensitive to particle size

S. Maffi, F. Cignoli, C. Bellomunno, S. De Iuliis, G. Zizak, Spectrochim. Acta Part B (2008)

Operative procedure

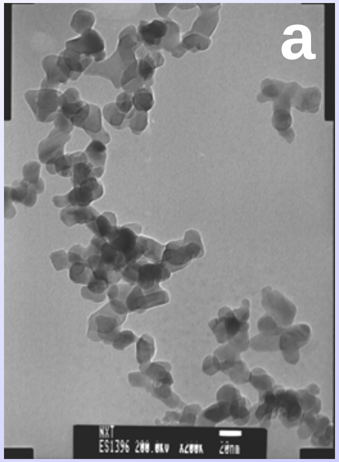
TEM - IA

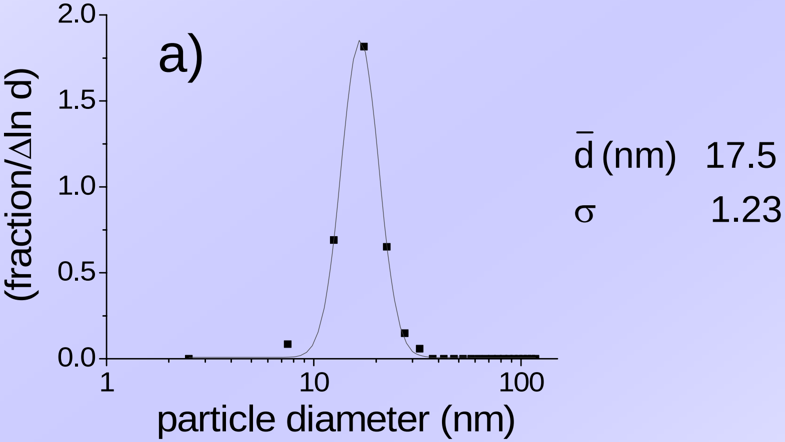
- particle sampling on TEM grids at different location in the flame;
- TEM images;
- image analysis;
- particle size statistics and lognormal distribution of particles for the whole flame

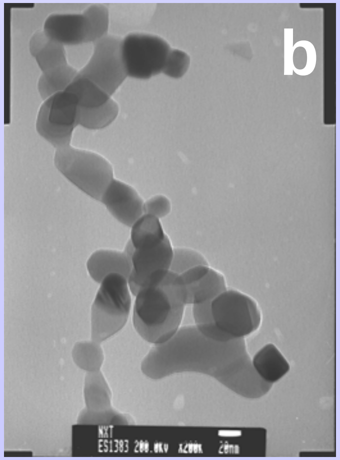
LII

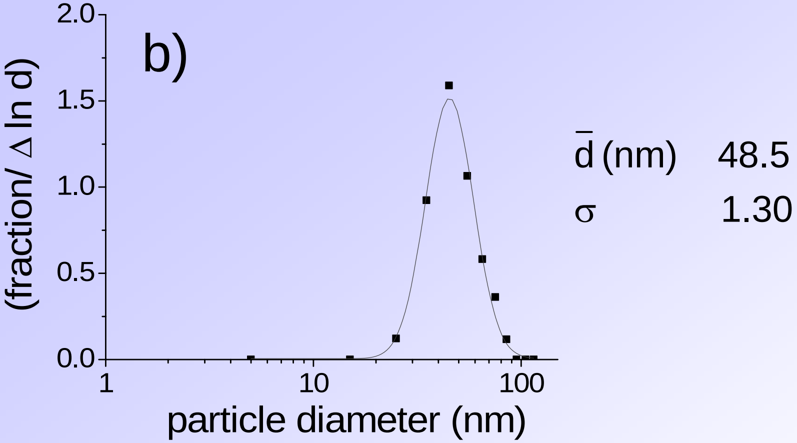
- choice of the suitable LII operative conditions (best detection wavelength, trade-off between SNR, probe volume size, spectral integration, dynamic range);
- TIRE-LII recording and processing for the whole flame

TEM – IA – Particle Size Statistics



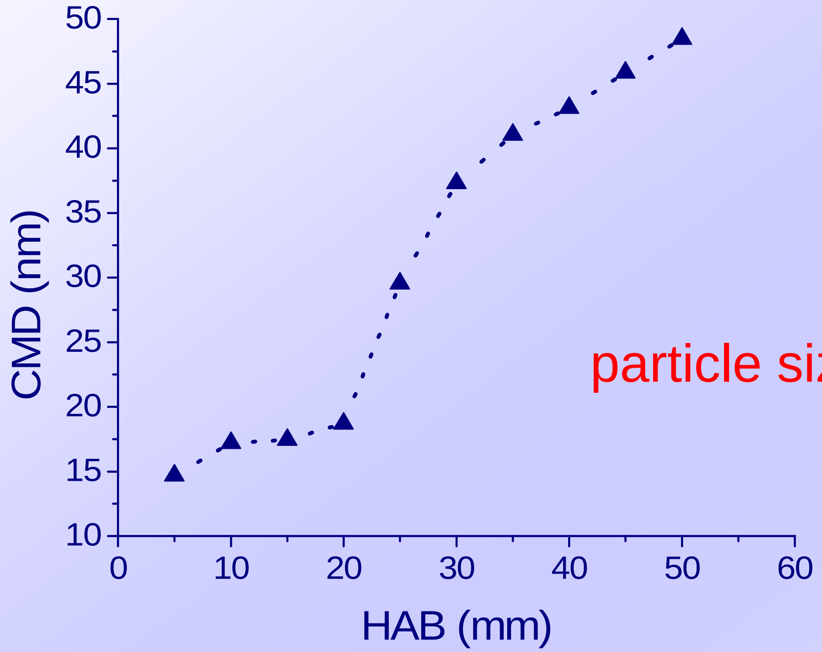






TEM images and lognormal distribution of particles at 15 mm a) and 50 mm b)

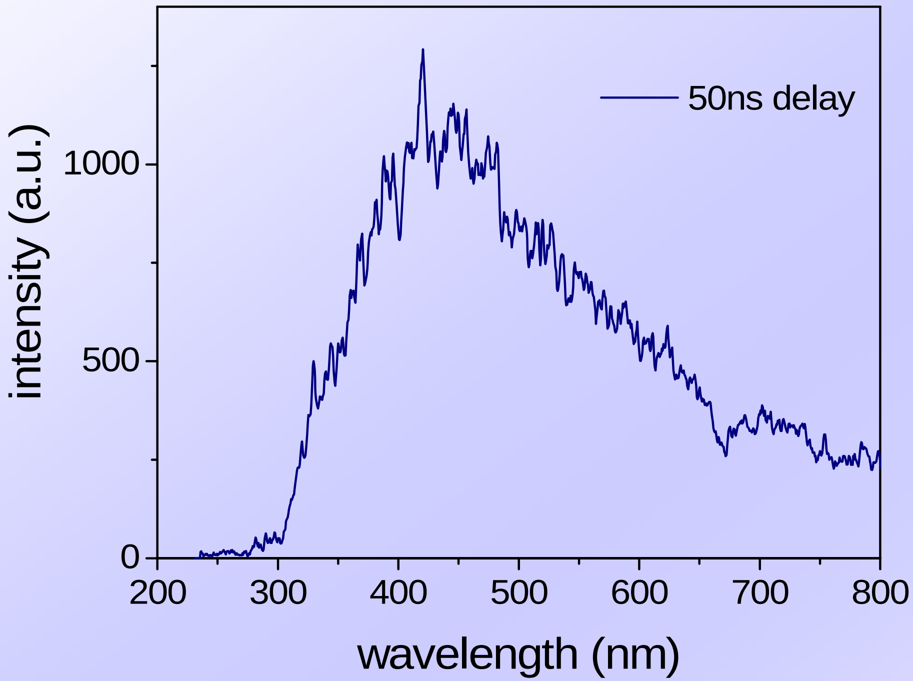
Counter Median Diameter (CMD) of titania particles in the reaction flame

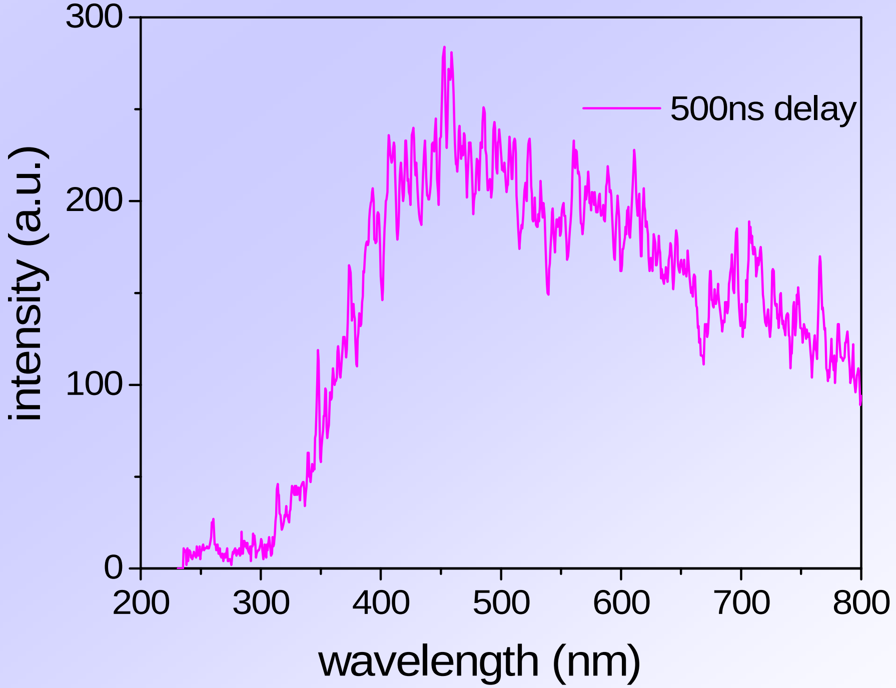


particle size INCREASES along the flame

- counter median diameter obtained by the lognormal distribution of particles

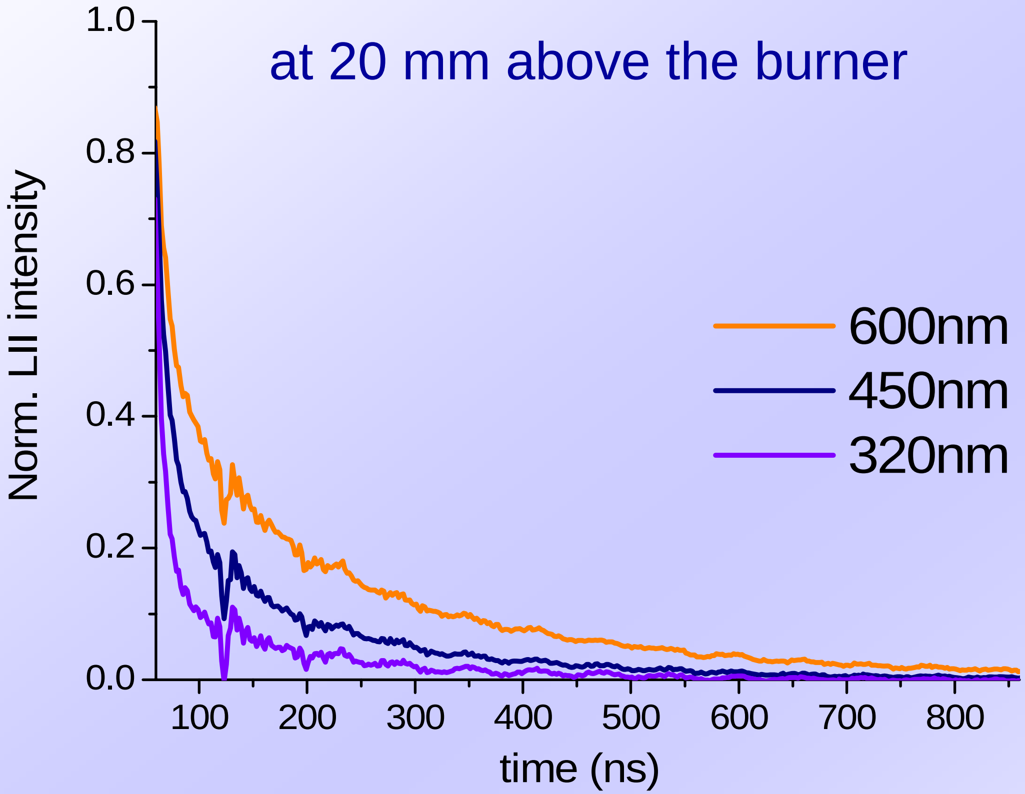
Temporal evolution of the Emission spectrum
(uncorrected for system spectral response)





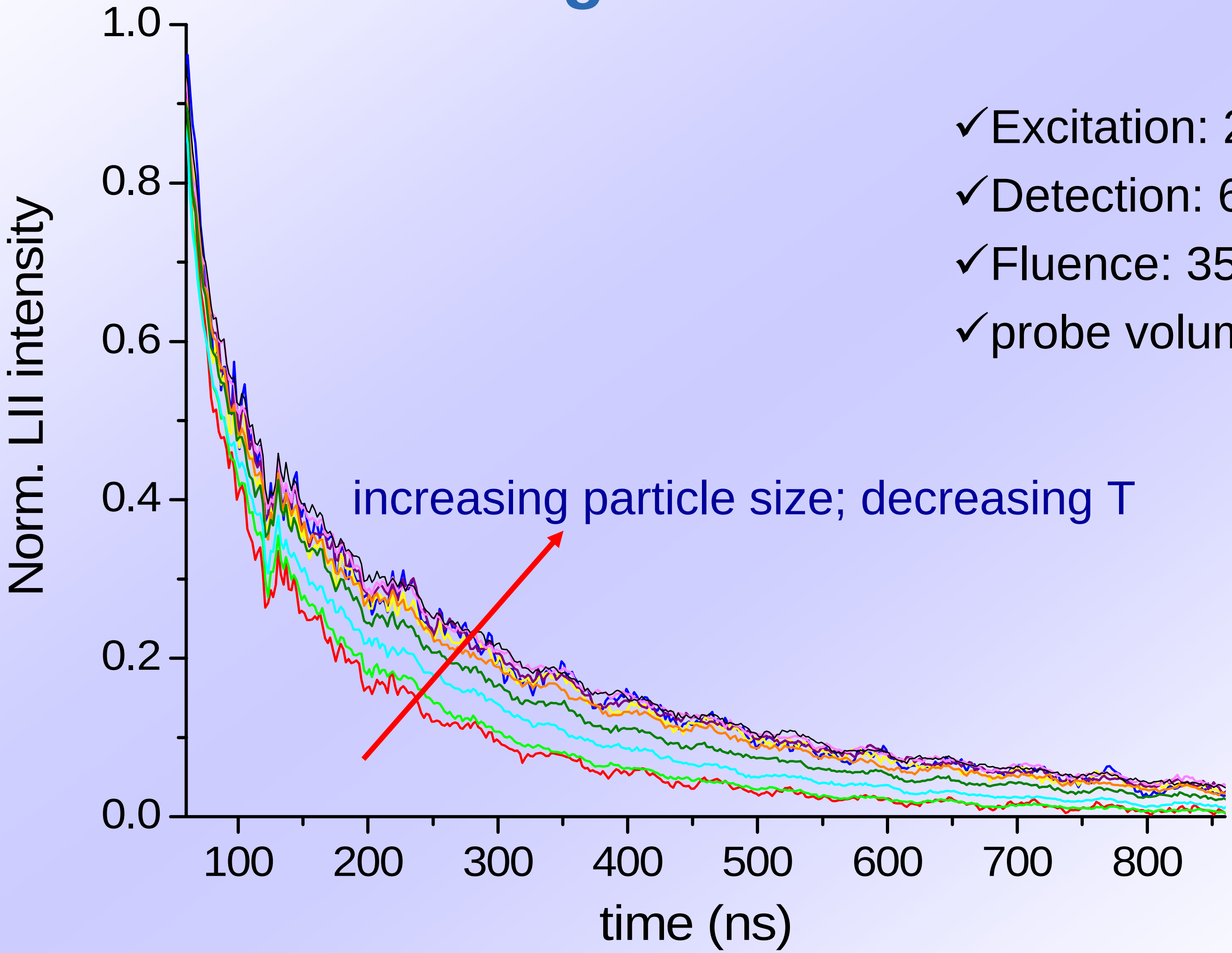
just after the laser pulse the maximum signal is at short wavelengths (higher temperature) but…

LII signal at different detection wavelengths



…at longer wavelengths the signal drops more slowly allowing better SNR at longer times

LII signal taken with a 5mm step along the titania flame



- ✓Excitation: 266 nm
- ✓Detection: 600 nm
- ✓Fluence: 35mJ/cm^2
- ✓probe volume: 1x2x3 mm^3

Conclusion, Problems and Perspectives

- ✓ LII signal can be rather safely obtained in flame reactors;
- ✓ LII decay time is clearly and continuously depending on particle size;
- ✓ Suitable LII operative conditions should be selected:
  1. Excitation wavelength in the UV region
  2. Laser fluence carefully determined through spectral test
  3. Detection wavelength
- ➢ Signal quality can be further increased;
- ➢ a real-time measurement is in principle feasible (as it is for soot already) at least for TiO_2. A suitable model seems to be mandatory and TiO_2 parameters must be well known.

If successful, the method offers unique advantages

Thanks for your attention!

Milano

$$Q_{\mathrm{abs}}\frac{\pi d_{\mathrm{p}}^2}{4}E_{\mathrm{i}} - \Lambda(T - T_0)\pi d_{\mathrm{p}}^2 + \frac{\Delta H_v}{M}\cdot\frac{dm}{dt}$$

$$-\pi d_{\mathrm{p}}^2 \int \varepsilon(d_{\mathrm{p}},\lambda)M_\lambda^b(T,\lambda)d\lambda - \frac{\pi d_{\mathrm{p}}^3}{6}\rho C\frac{dT}{dt} = 0$$

•ABSORPTION OF LASER IRRADIATION

Q_{abs}: absorption efficiency

E_i: laser irradiance

•HEAT LOSS DUE TO CONDUCTION

Λ: heat transfer coeff.

T: particle temperature

T_0: gas temperature

•VAPORIZATION

ΔH_v: heat of vaporization

M: molar mass

•RADIATION

ε: emission coeff.

M^b_λ: blackbody spectral radiant exitance

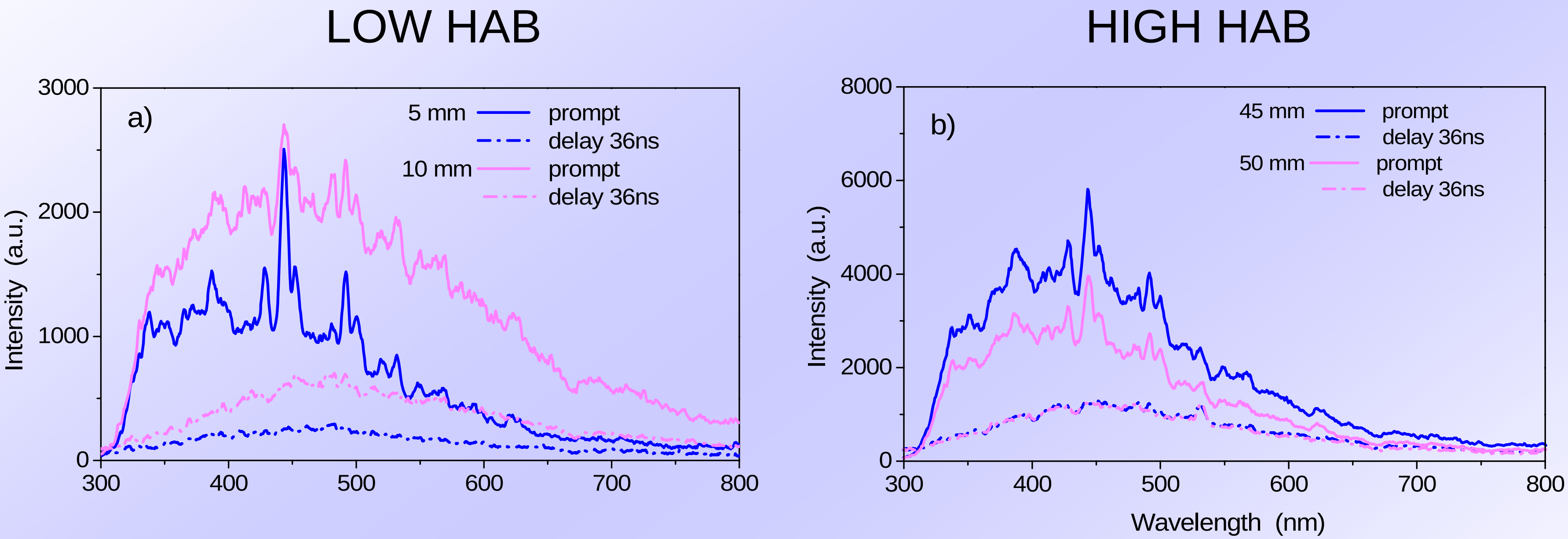
λ: wavelength

•CHANGE IN INTERNAL ENERGY

ρ: density

C: specific heat

LIE spectra at Medium Laser Fluence



Young particles seem to be more sensitive to the fluence value

✓Excitation: 266 nm

✓Fluence: 60 mJ/cm^2