POLITECNICO
MILANO 1863

Advances in Pulsed Laser Deposition of ultra-low density carbon foams

Alessandro Maffini
Department of Energy, Politecnico di Milano, Italy

E-MRS Spring Meeting, Strasbourg
Symposium X :Photon-assisted synthesis and processing of materials in nano-microscale

18/06/2018

ERC-2014-CoG No.647554
ENSURE

NanoLab

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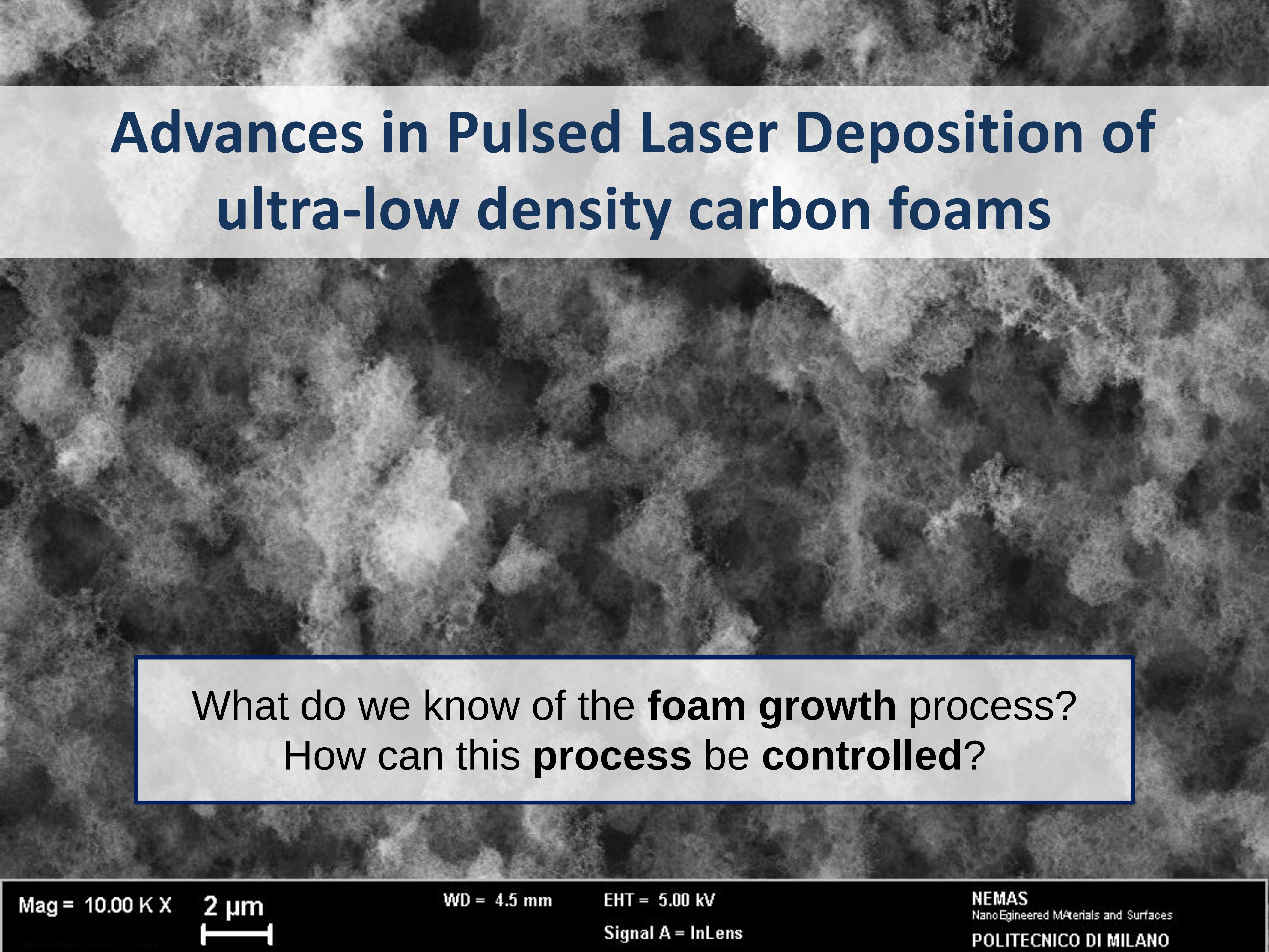
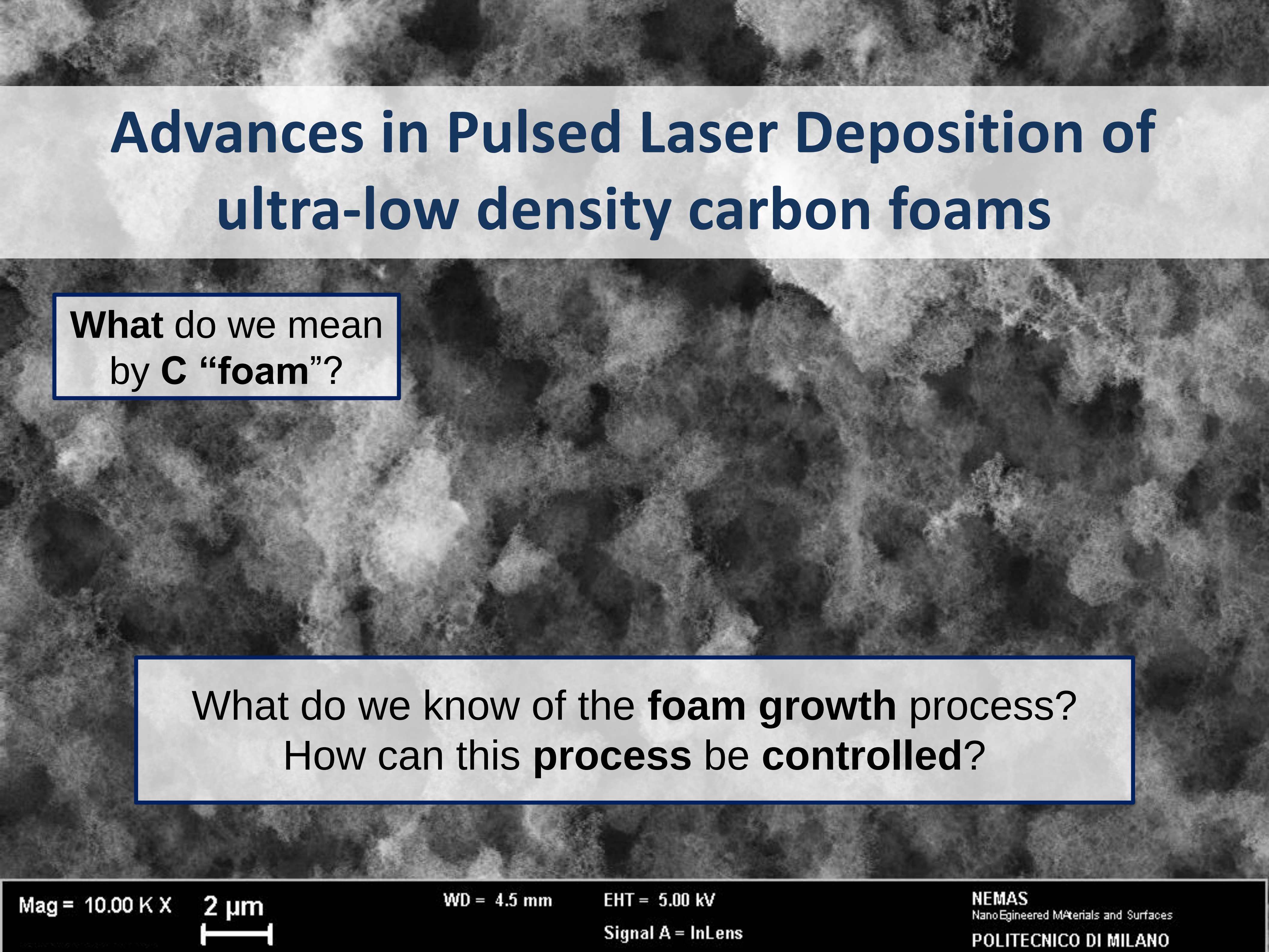


What do we know of the **foam growth** process?
How can this **process** be **controlled**?

Advances in Pulsed Laser Deposition of ultra-low density carbon foams



What do we mean by **C “foam”**?

What do we know of the **foam growth** process?
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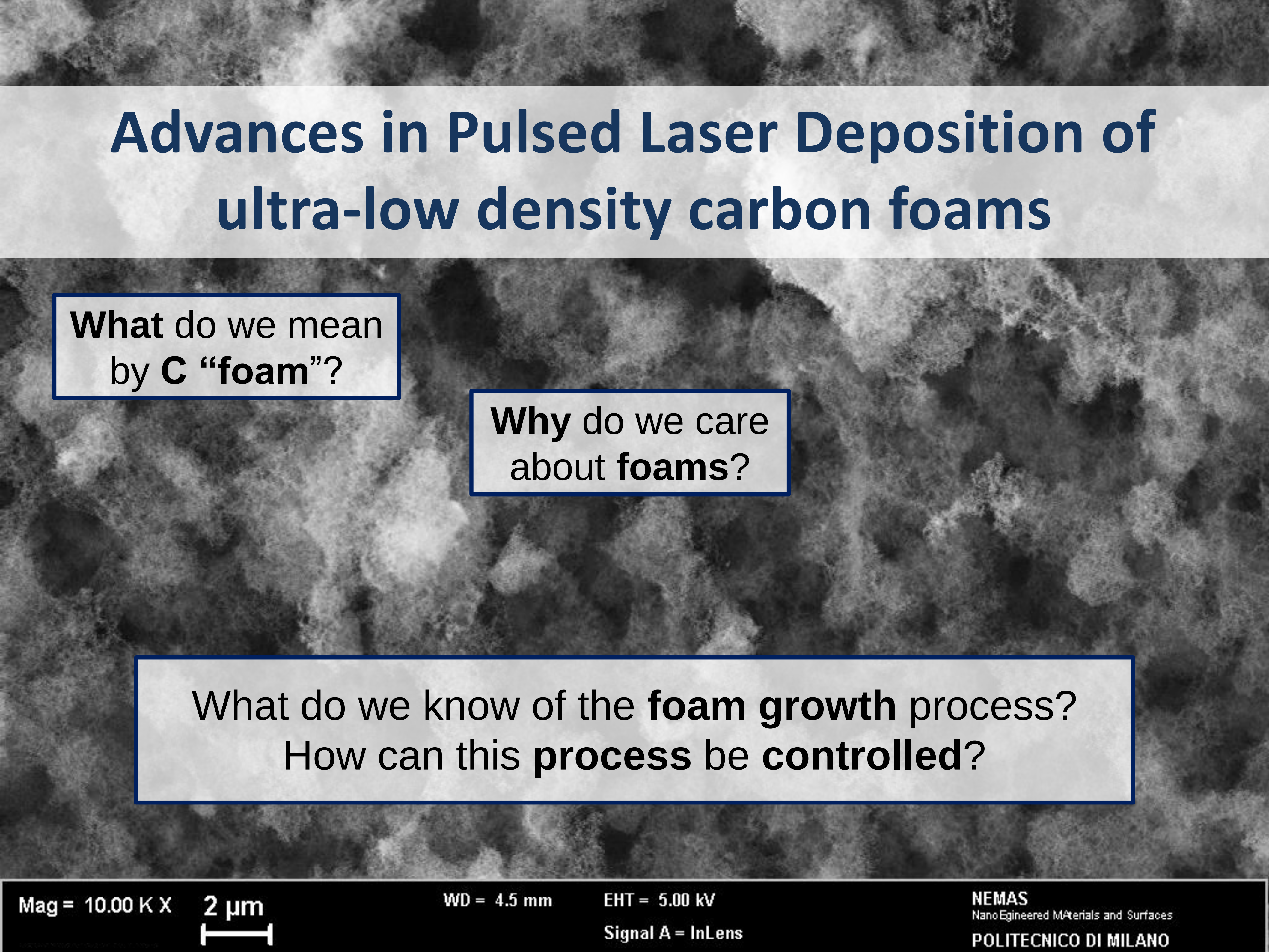

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Why do we care about **foams**?

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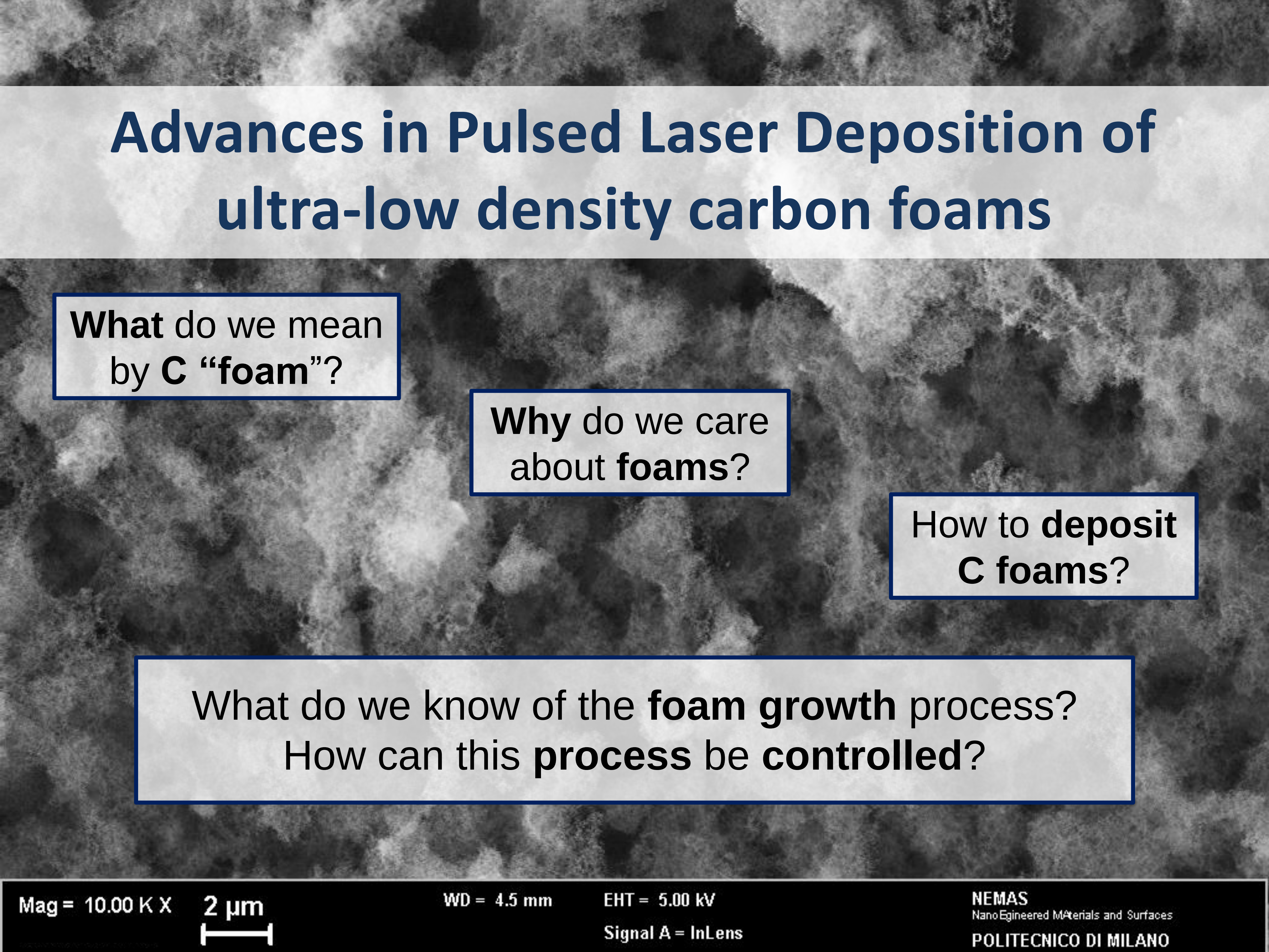

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Why do we care about **foams**?

How to **deposit C foams**?

What do we know of the **foam growth** process?
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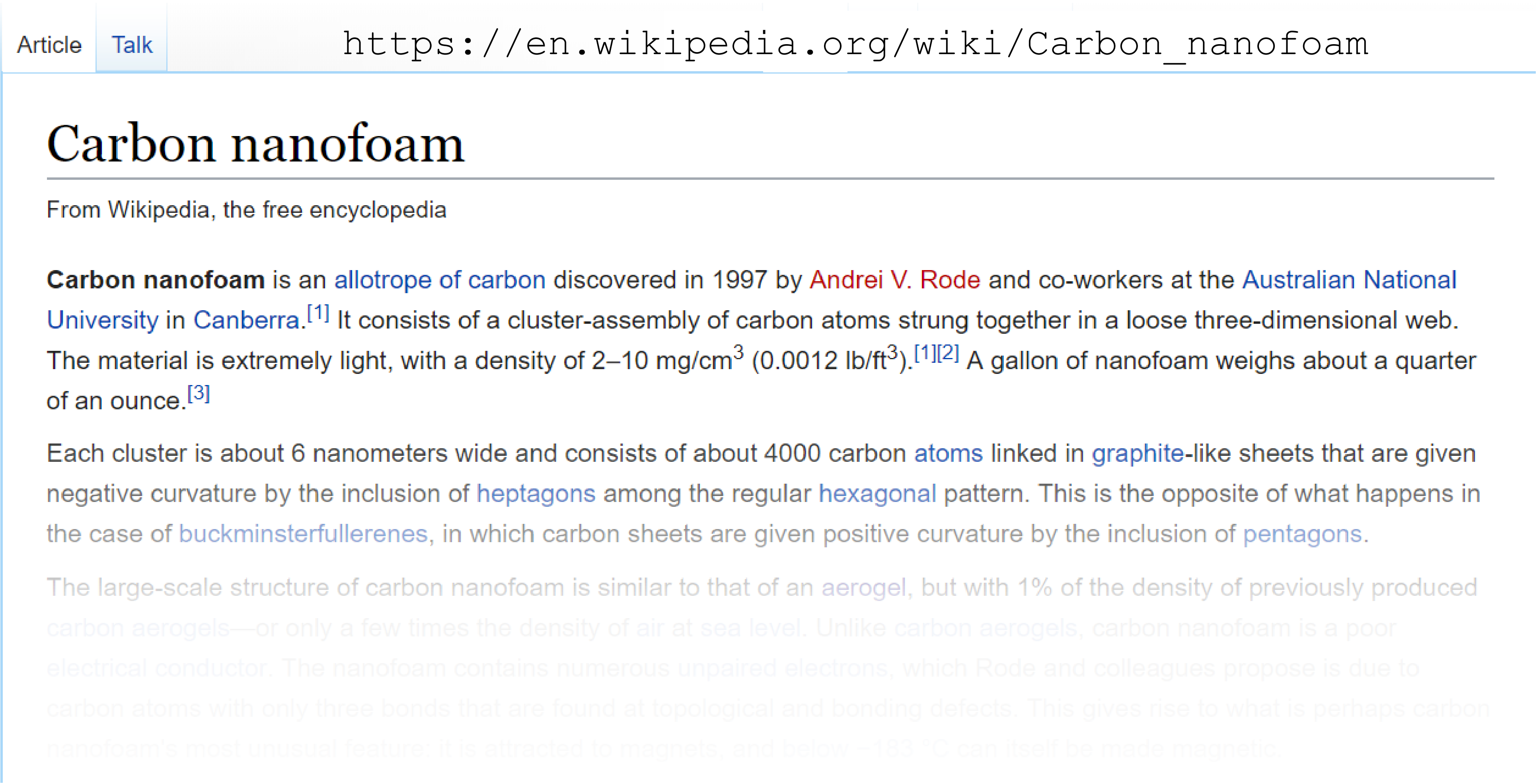
What do we mean by “carbon foams” ?



https://en.wikipedia.org/wiki/Carbon_nanofoam

Carbon nanofoam

From Wikipedia, the free encyclopedia

Carbon nanofoam is an allotrope of carbon discovered in 1997 by Andrei V. Rode and co-workers at the Australian National University in Canberra.[1] It consists of a cluster-assembly of carbon atoms strung together in a loose three-dimensional web. The material is extremely light, with a density of 2–10 mg/cm^3 (0.0012 lb/ft^3).[1][2] A gallon of nanofoam weighs about a quarter of an ounce.[3]

Each cluster is about 6 nanometers wide and consists of about 4000 carbon atoms linked in graphite-like sheets that are given negative curvature by the inclusion of heptagons among the regular hexagonal pattern. This is the opposite of what happens in the case of buckminsterfullerenes, in which carbon sheets are given positive curvature by the inclusion of pentagons.

The large-scale structure of carbon nanofoam is similar to that of an aerogel, but with 1% of the density of previously produced carbon aerogels—or only a few times the density of air at sea level. Unlike carbon aerogels, carbon nanofoam is a poor electrical conductor. The nanofoam contains numerous unpaired electrons, which Rode and colleagues propose is due to carbon atoms with only three bonds that are found at topological and bonding defects. This gives rise to what is perhaps carbon nanofoam's most unusual feature: it is attracted to magnets, and below −183 °C can itself be made magnetic.

A.V. Rode et al., *Formation of cluster-assembled carbon nano-foam by high-repetition-rate laser ablation*, Appl. Phys. A **70** 135 (2000)

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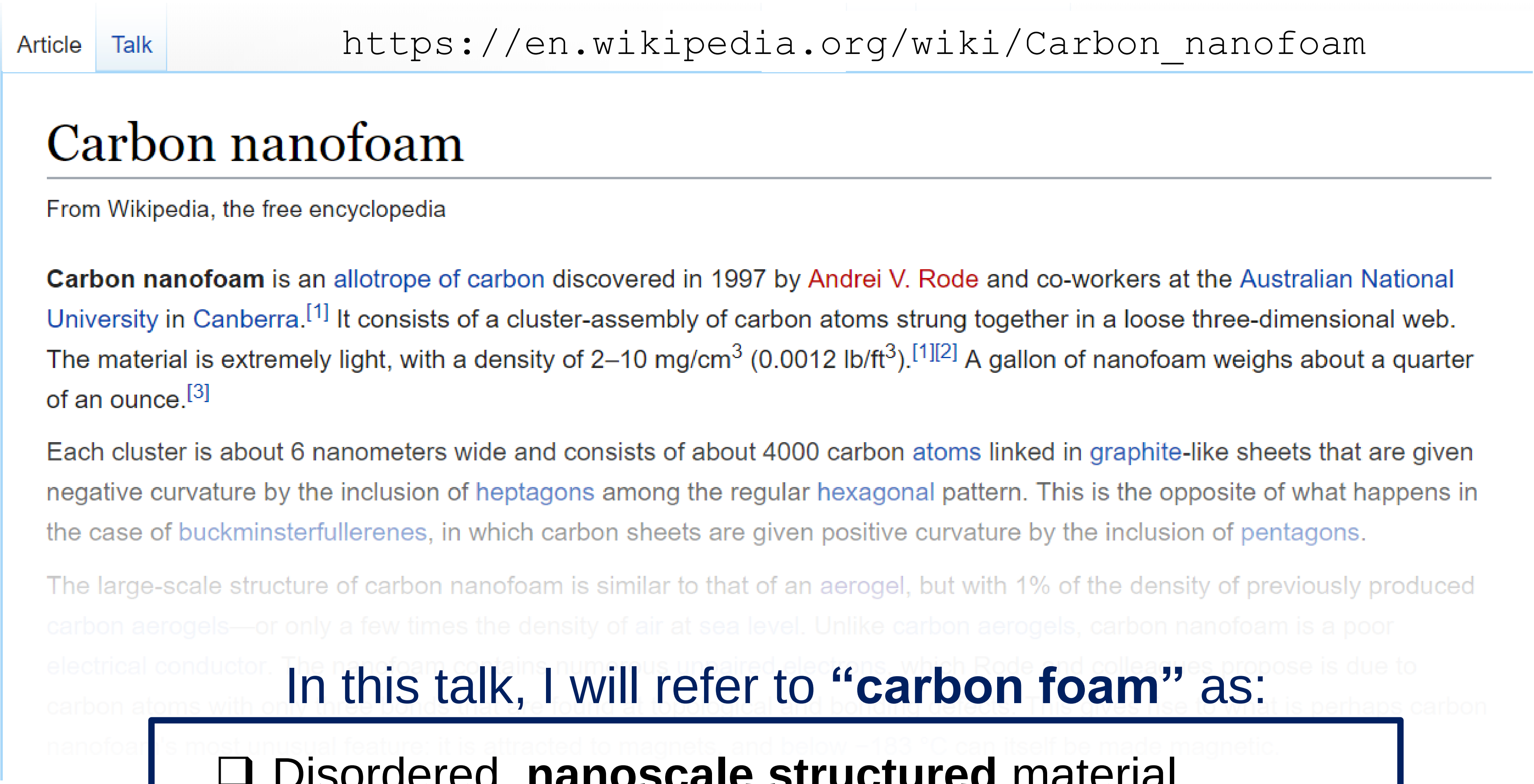

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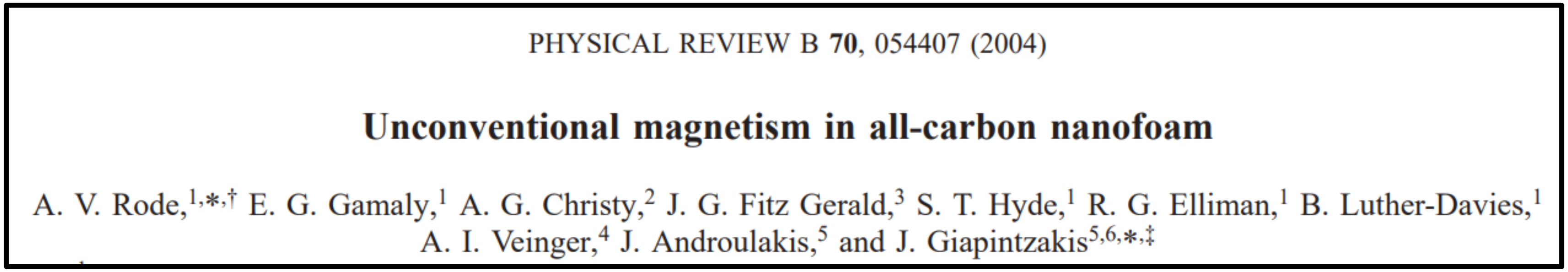
In this talk, I will refer to “**carbon foam**” as:

- ❑ Disordered, **nanoscale structured** material
- ❑ (almost) **pure carbon**
- ❑ Void fraction ≈ 99% → **density** ≈ 10 mg/cm^3

A.V. Rode et al., *Formation of cluster-assembled carbon nano-foam by high-repetition-rate laser ablation*, Appl. Phys. A **70** 135 (2000)

Why do we care?



PHYSICAL REVIEW B **70**, 054407 (2004)

Unconventional magnetism in all-carbon nanofoam

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Journal of Biomedical Materials Research Part A / Volume 85A, Issue 3

Pore structure engineering for carbon foams as possible bone implant material

Gursel Turgut, Ayhan Eksilioglu, Nagehan Gencay, Emre Gonen, Nezih Hekim, M. F. Yardım, Damlanur Sakiz, Ekrem Ekinci ✉

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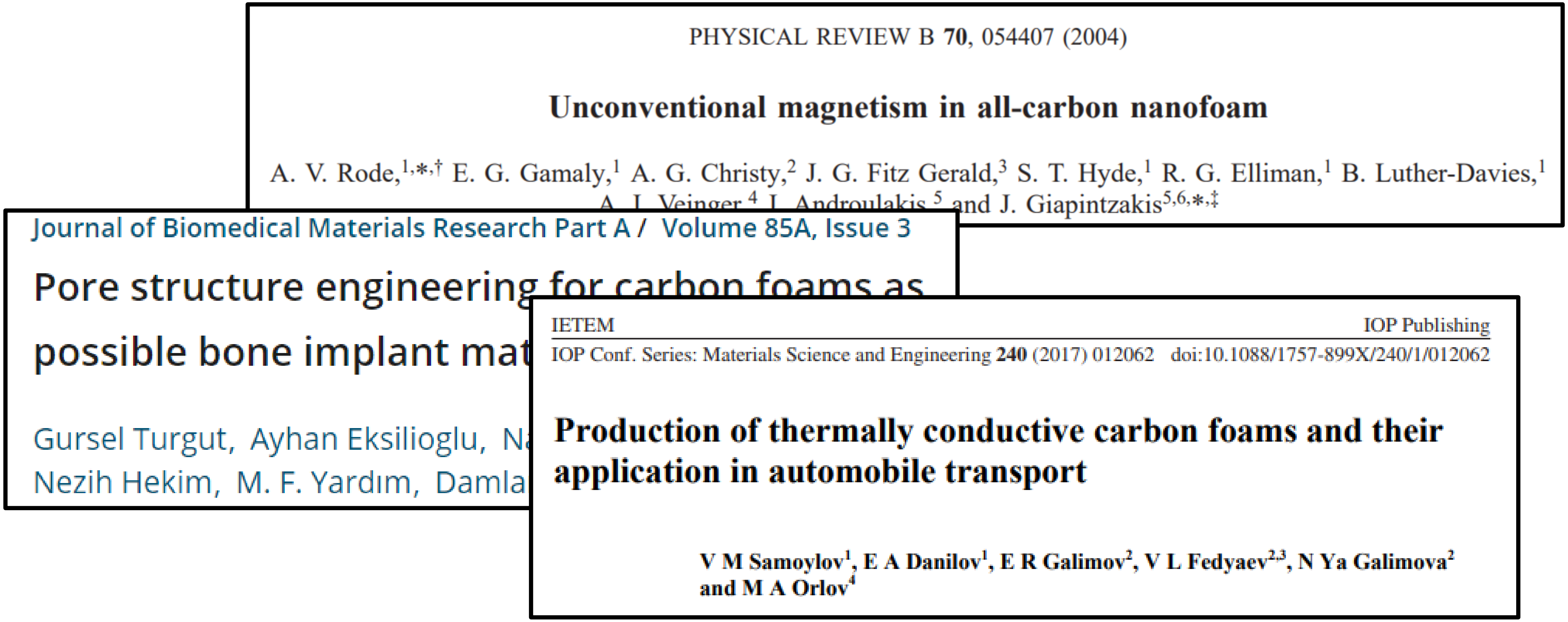

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IETEM IOP Publishing
IOP Conf. Series: Materials Science and Engineering **240** (2017) 012062 doi:10.1088/1757-899X/240/1/012062

Production of thermally conductive carbon foams and their application in automobile transport

V M Samoylov[1], E A Danilov[1], E R Galimov[2], V L Fedyaev[2,3], N Ya Galimova[2] and M A Orlov[4]

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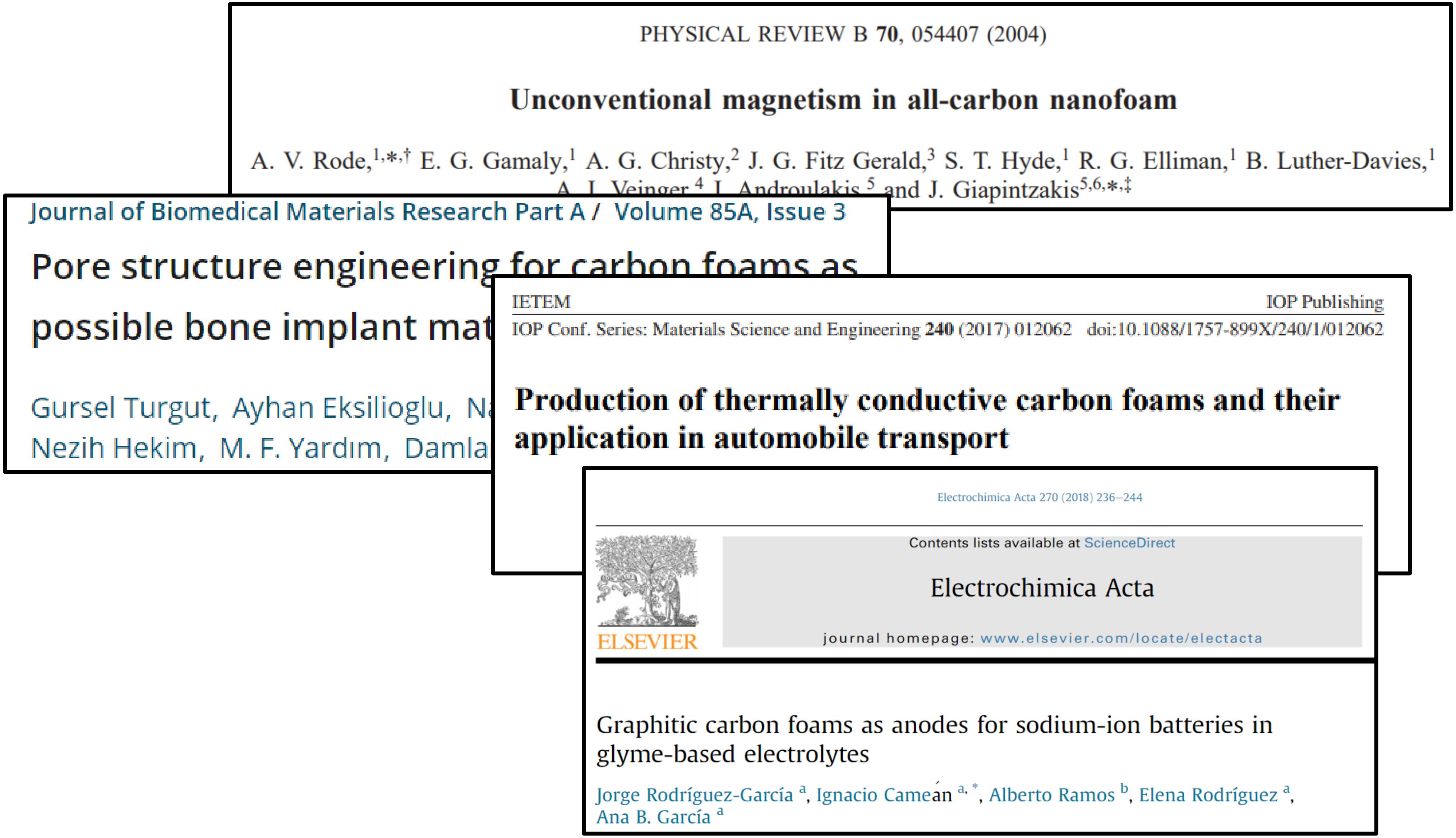

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Electrochimica Acta 270 (2018) 236–244

Contents lists available at ScienceDirect

Electrochimica Acta

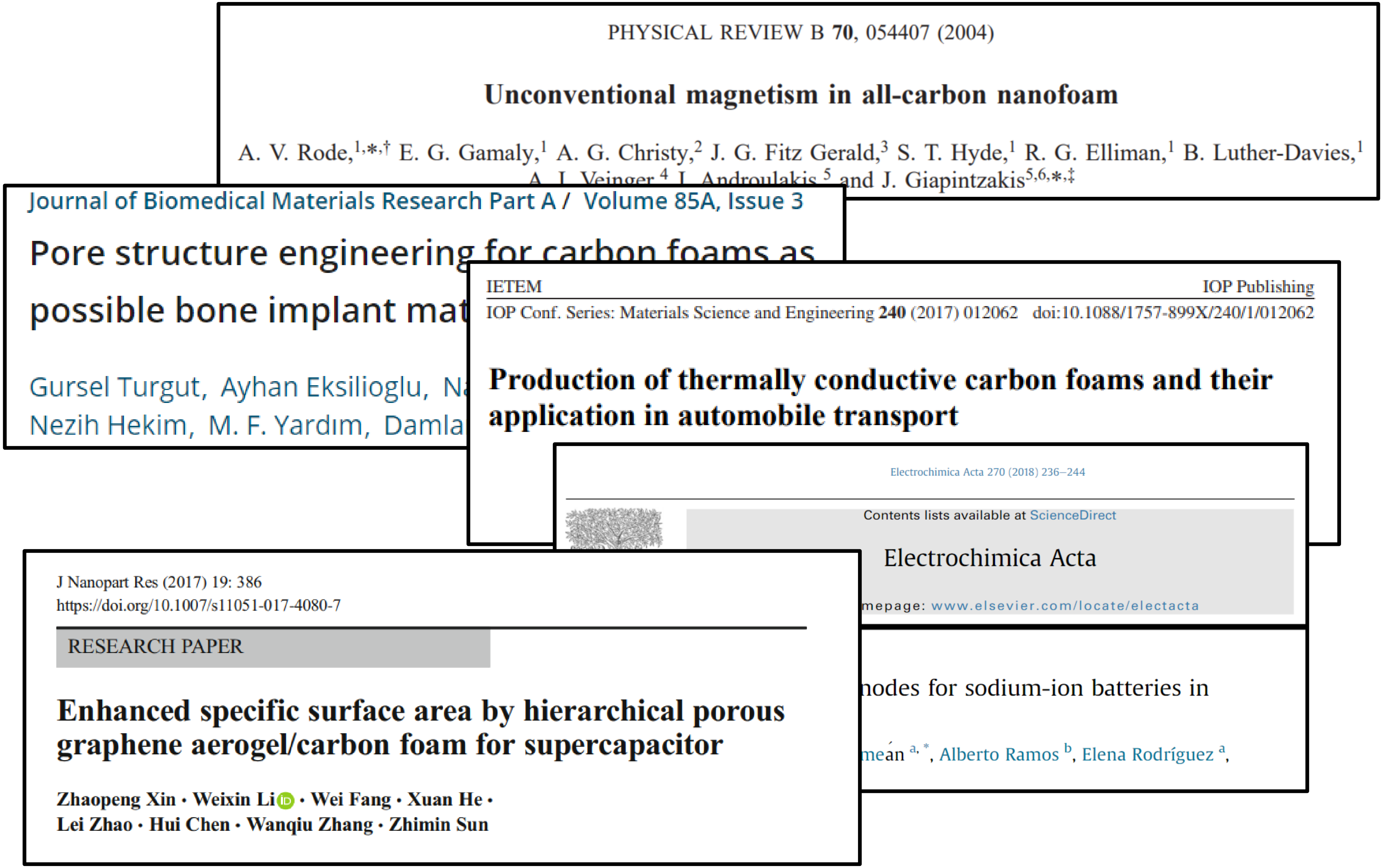
journal homepage: www.elsevier.com/locate/electacta

ELSEVIER

Graphitic carbon foams as anodes for sodium-ion batteries in glyme-based electrolytes

Jorge Rodríguez-García [a], Ignacio Cameán [a, *], Alberto Ramos [b], Elena Rodríguez [a], Ana B. García [a]

Why do we care?



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meán [a,*], Alberto Ramos [b], Elena Rodríguez [a],

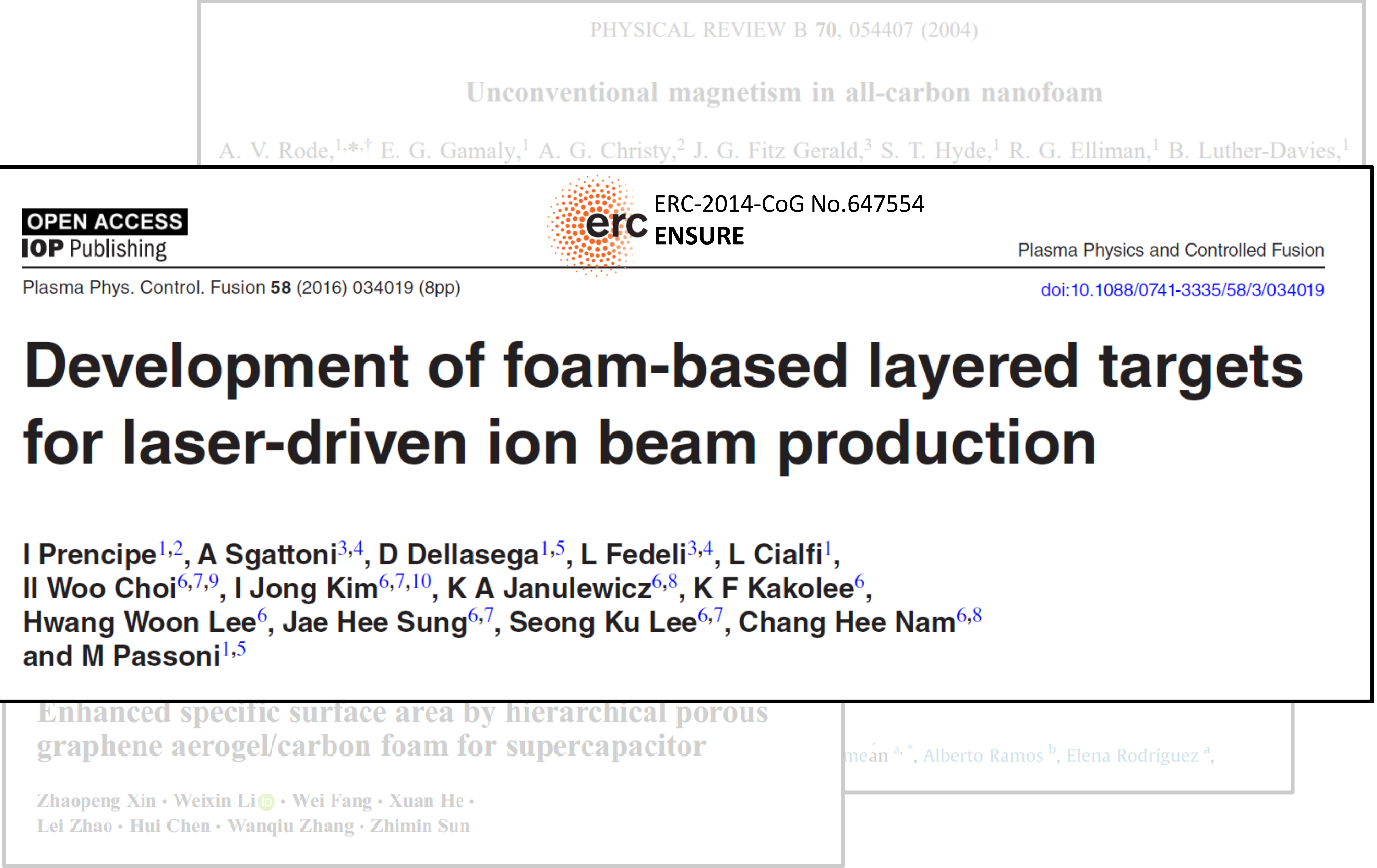
J Nanopart Res (2017) 19: 386
https://doi.org/10.1007/s11051-017-4080-7

RESEARCH PAPER

Enhanced specific surface area by hierarchical porous graphene aerogel/carbon foam for supercapacitor

**Zhaopeng Xin · Weixin Li · Wei Fang · Xuan He ·
Lei Zhao · Hui Chen · Wanqiu Zhang · Zhimin Sun**

Why do we care?



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ENSURE

Plasma Physics and Controlled Fusion

Plasma Phys. Control. Fusion **58** (2016) 034019 (8pp)

doi:10.1088/0741-3335/58/3/034019

Development of foam-based layered targets for laser-driven ion beam production

I Prencipe[1,2], A Sgattoni[3,4], D Dellasega[1,5], L Fedeli[3,4], L Cialfi[1], Il Woo Choi[6,7,9], I Jong Kim[6,7,10], K A Janulewicz[6,8], K F Kakolee[6], Hwang Woon Lee[6], Jae Hee Sung[6,7], Seong Ku Lee[6,7], Chang Hee Nam[6,8] and M Passoni[1,5]

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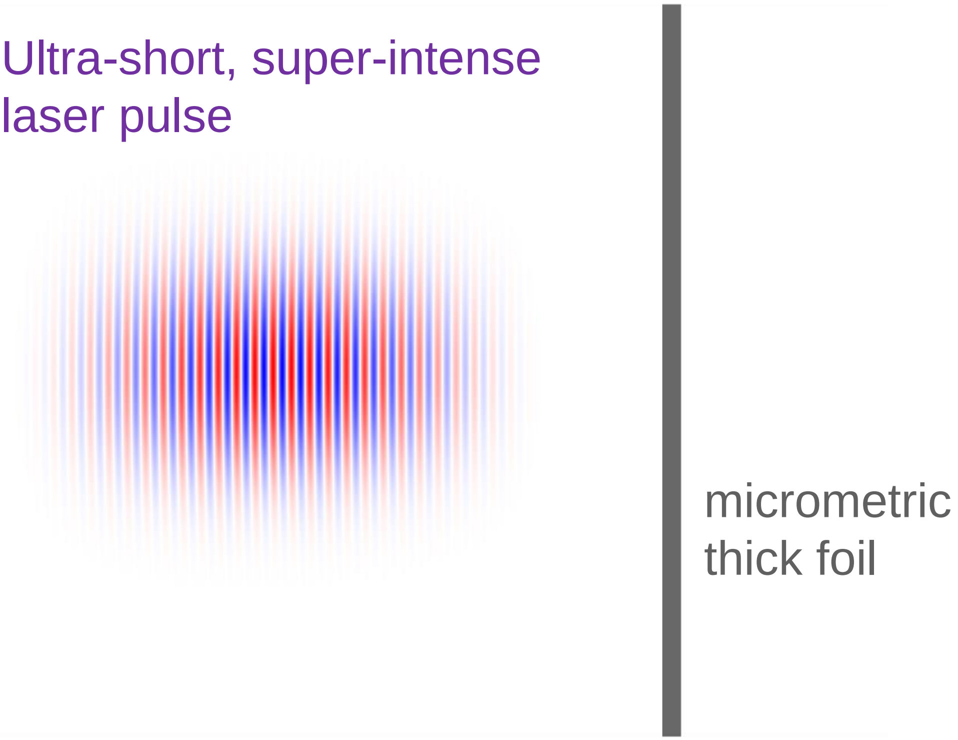
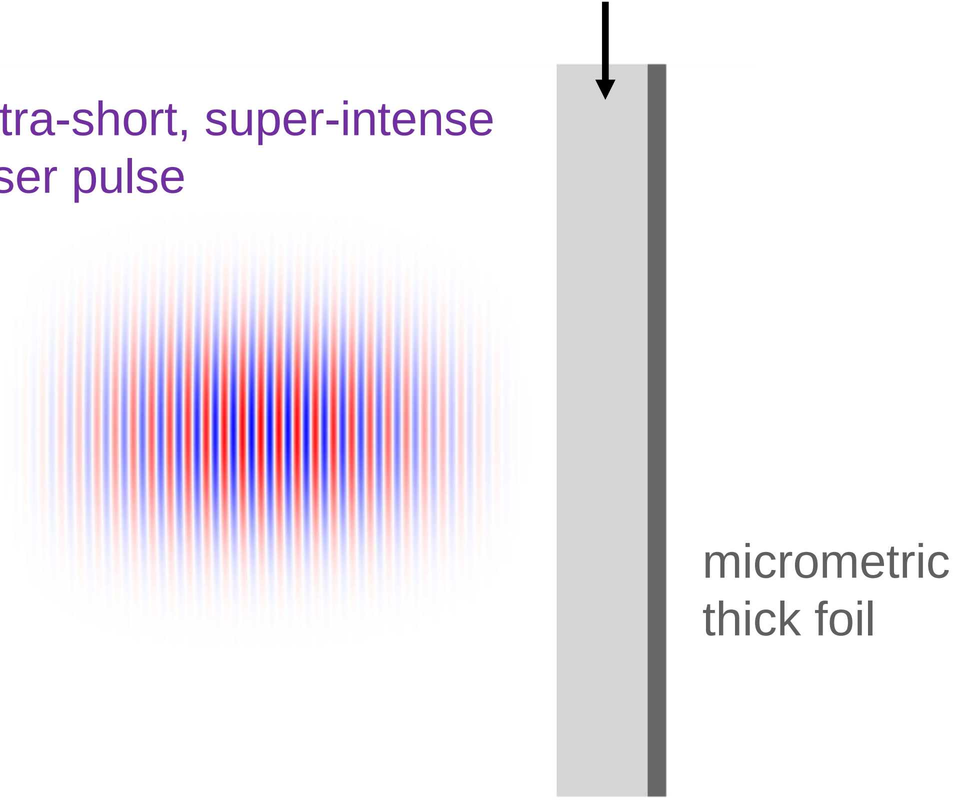
Carbon foam for laser-plasma ion acceleration



Ultra-short, super-intense
laser pulse

micrometric
thick foil

Conventional scheme



Low density C foam

Ultra-short, super-intense
laser pulse

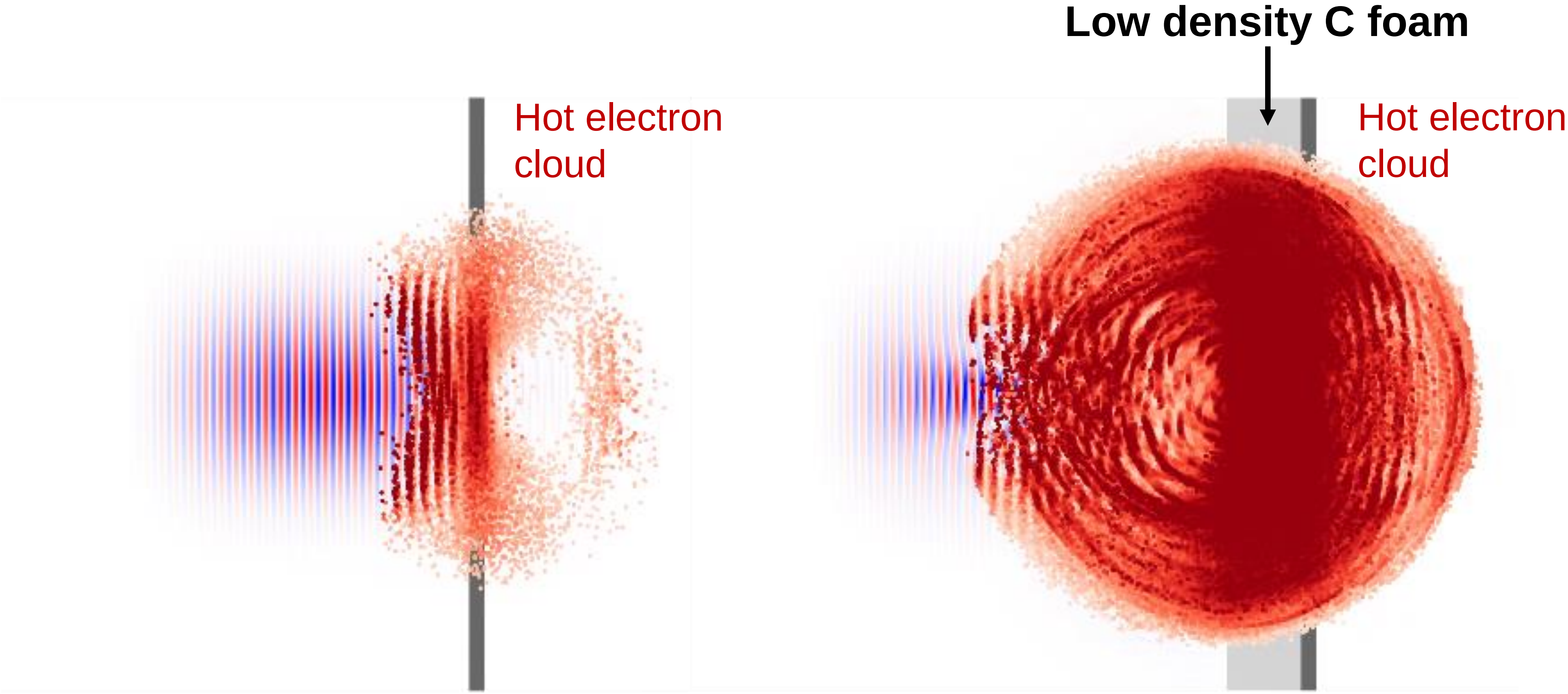
micrometric
thick foil

Advanced target

- ~10 mg/cm^3 C foam onto a μm-thick foil

M. Passoni et al. *Phys Rev Acc Beams* **19.6** (2016)

Carbon foam for laser-plasma ion acceleration



Conventional scheme

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- ☐ ~10 mg/cm^3 C foam onto a μm-thick foil
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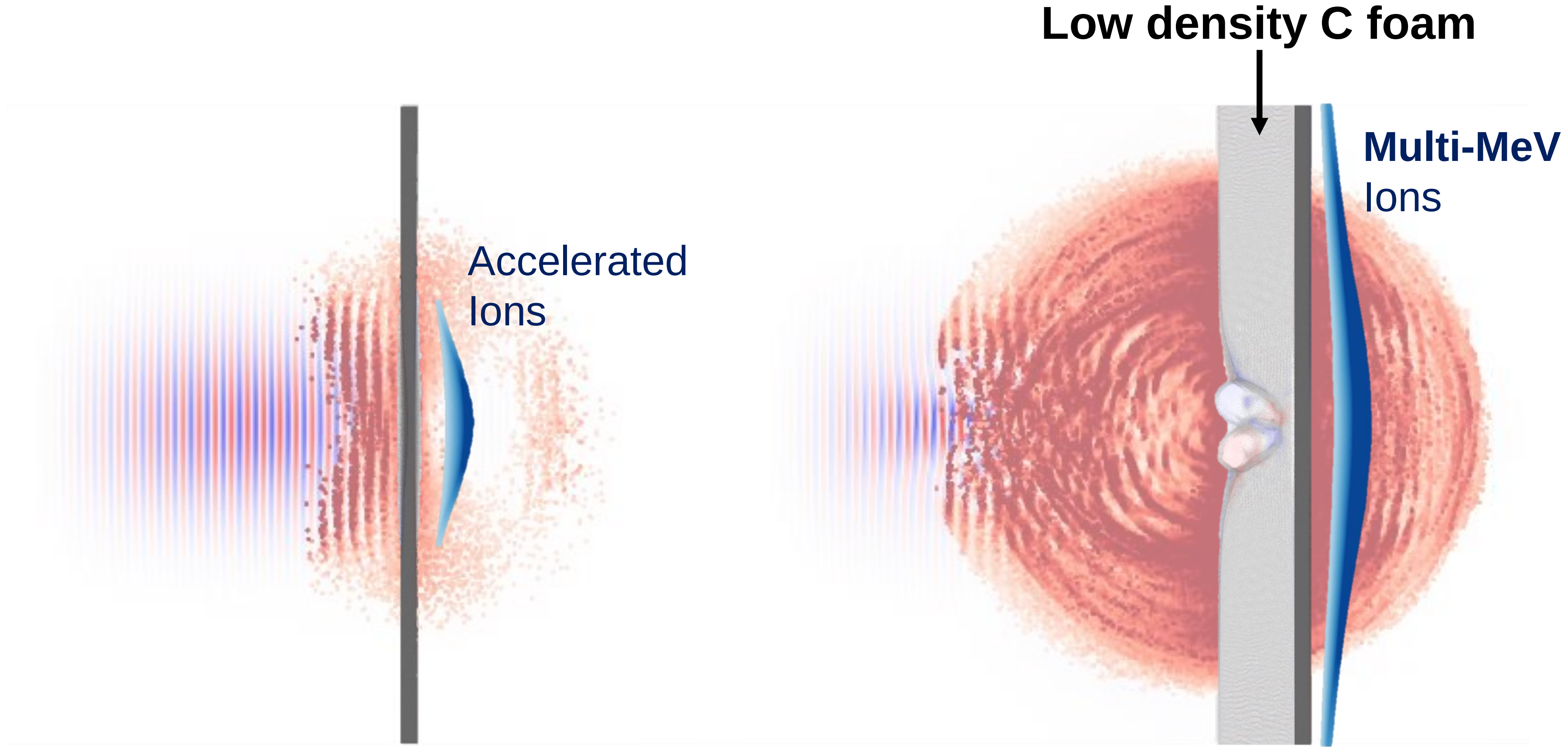

Conventional scheme

Advanced target

- ❑ ~10 mg/cm^3 C foam onto a μm-thick foil
- ❑ Foam enhances laser-plasma coupling
- ❑ **More ions at higher energy**

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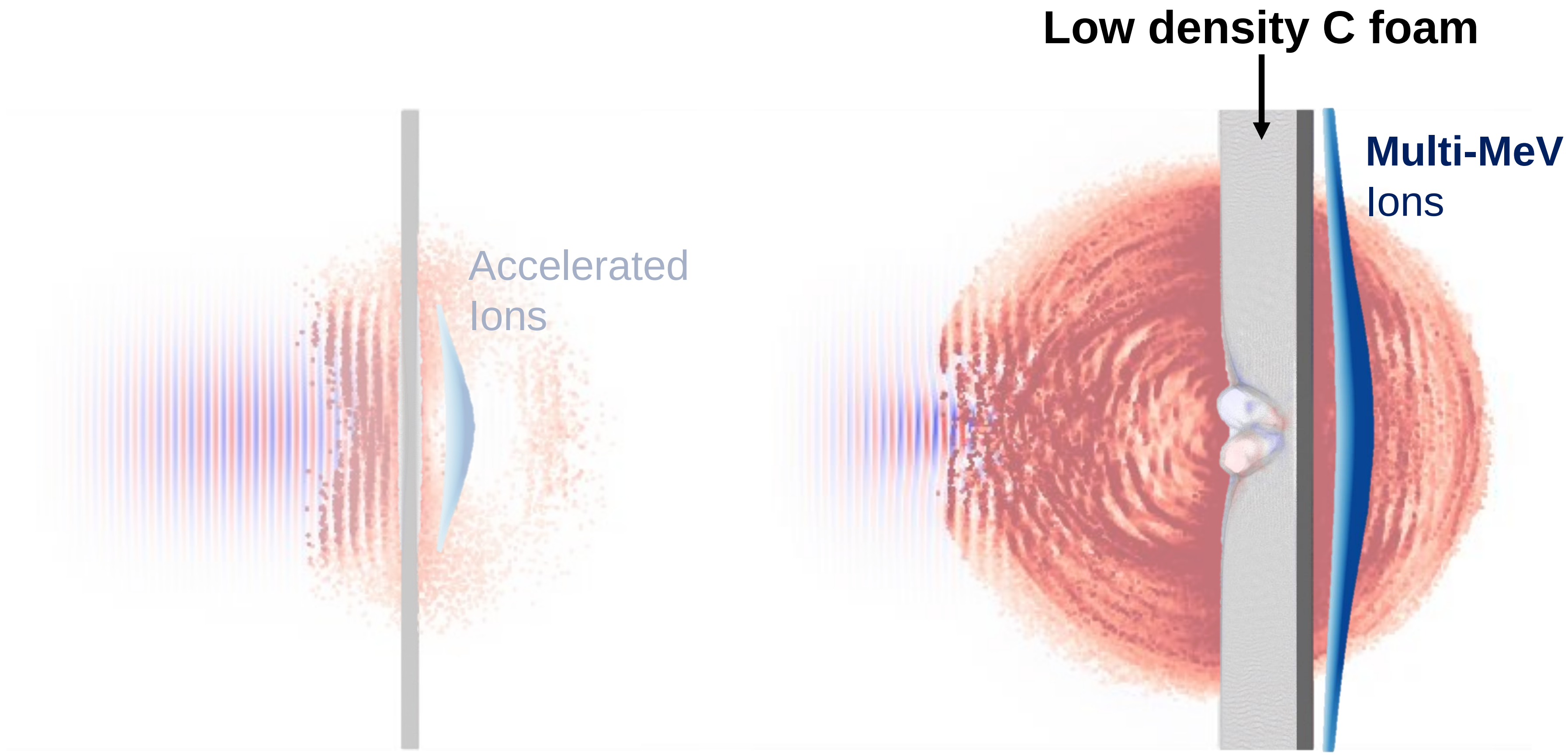
Carbon foam for laser-plasma ion acceleration



Advanced target

TARGET IS THE KEY!

ERC-2014-CoG No. 647554

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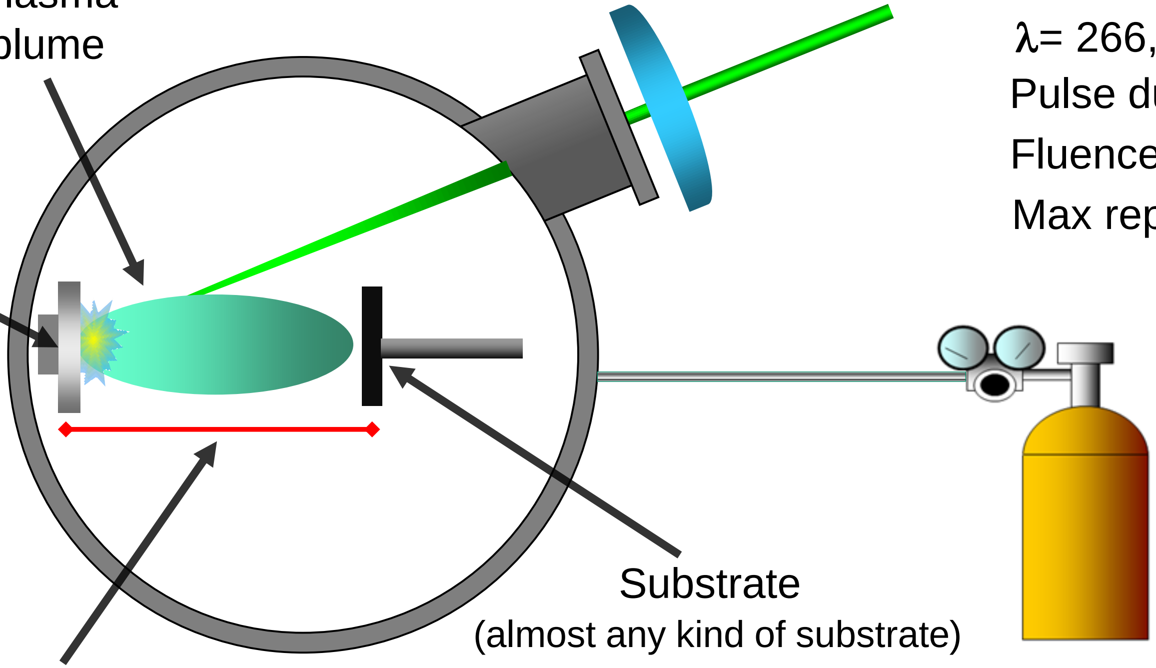
- ☐ ~10 mg/cm^3 C foam onto a μm-thick foil
- ☐ Foam enhances laser-plasma coupling
- ☐ **More ions at higher energy**

How to produce C foams : Pulsed Laser Deposition (PLD)



Plasma plume

Target

Substrate
(almost any kind of substrate)

target-to-substrate distance

Laser Beam

λ= 266, 532, 1064 nm

Pulse duration= 7ns, energy= 0.1-2 J

Fluence: 0.1 - 20 J/cm^2

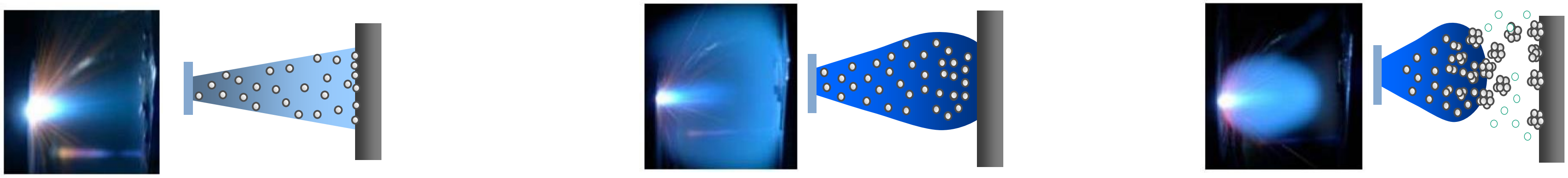
Max rep. rate= 10 Hz

Background Gas

- Inert (He, Ar..)
- Reactive (O_2)

Laser fluence

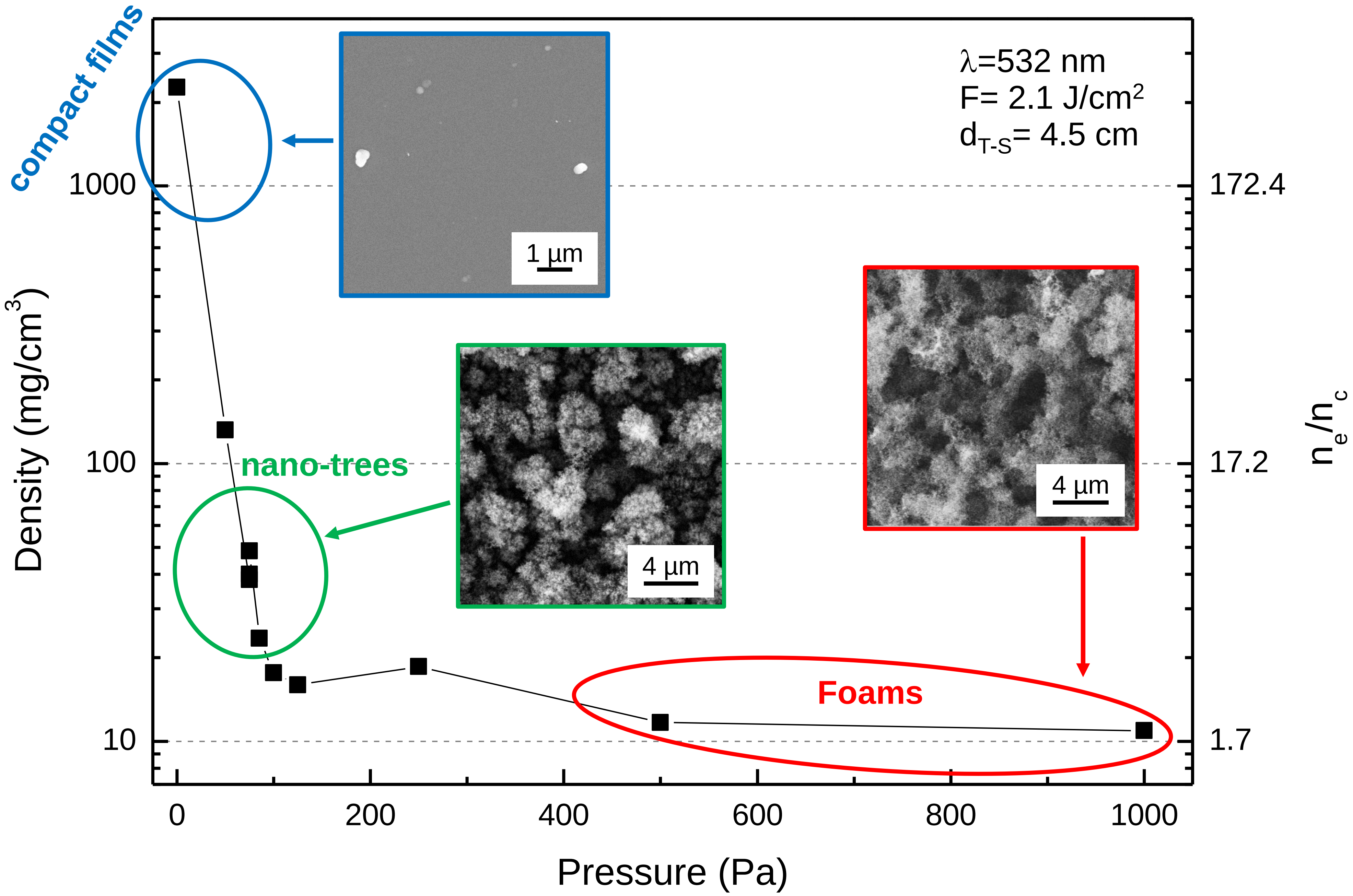
Gas pressure



“atom by atom” deposition

“Nanoparticle” deposition

How to produce carbon foams



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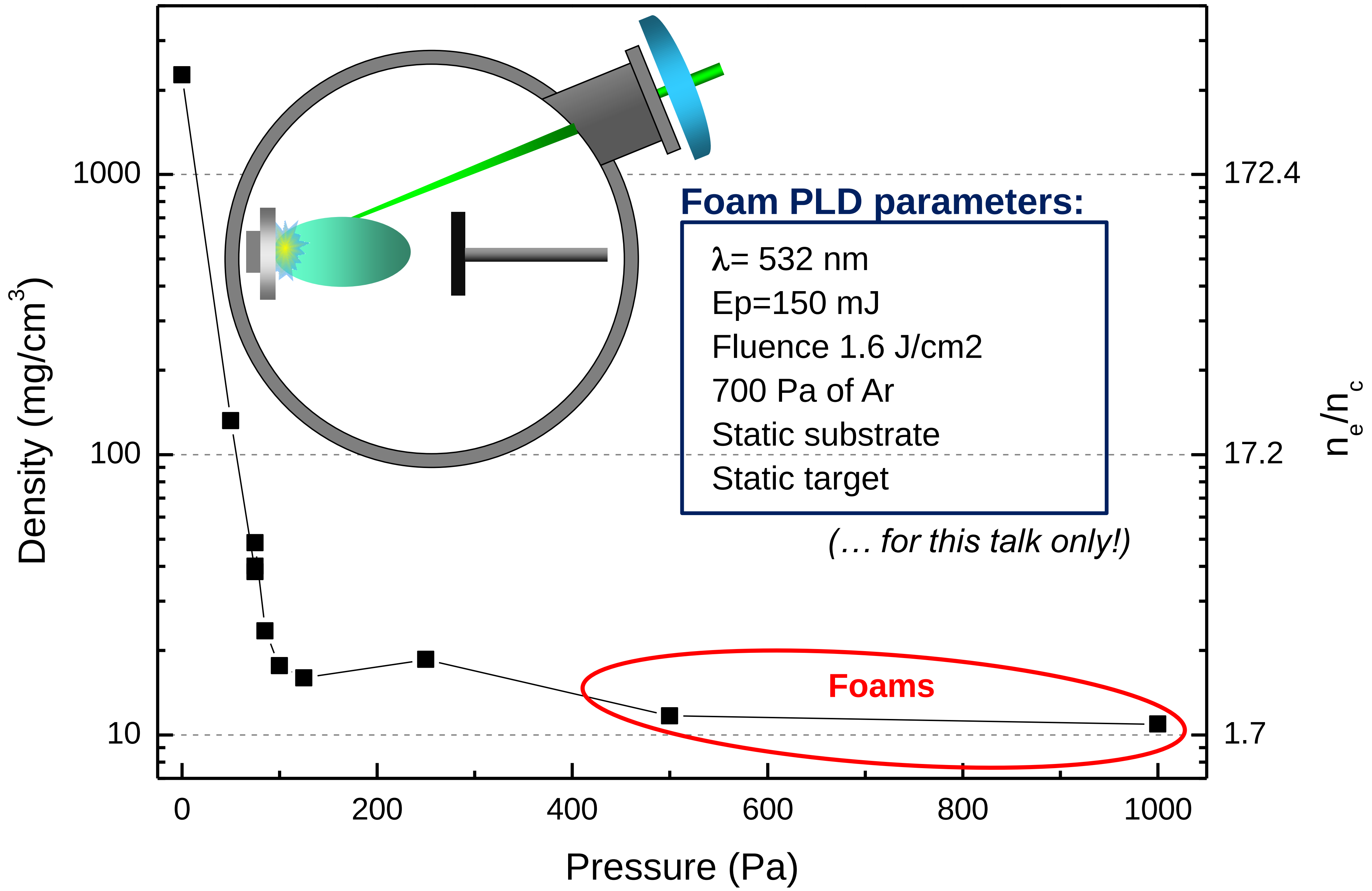
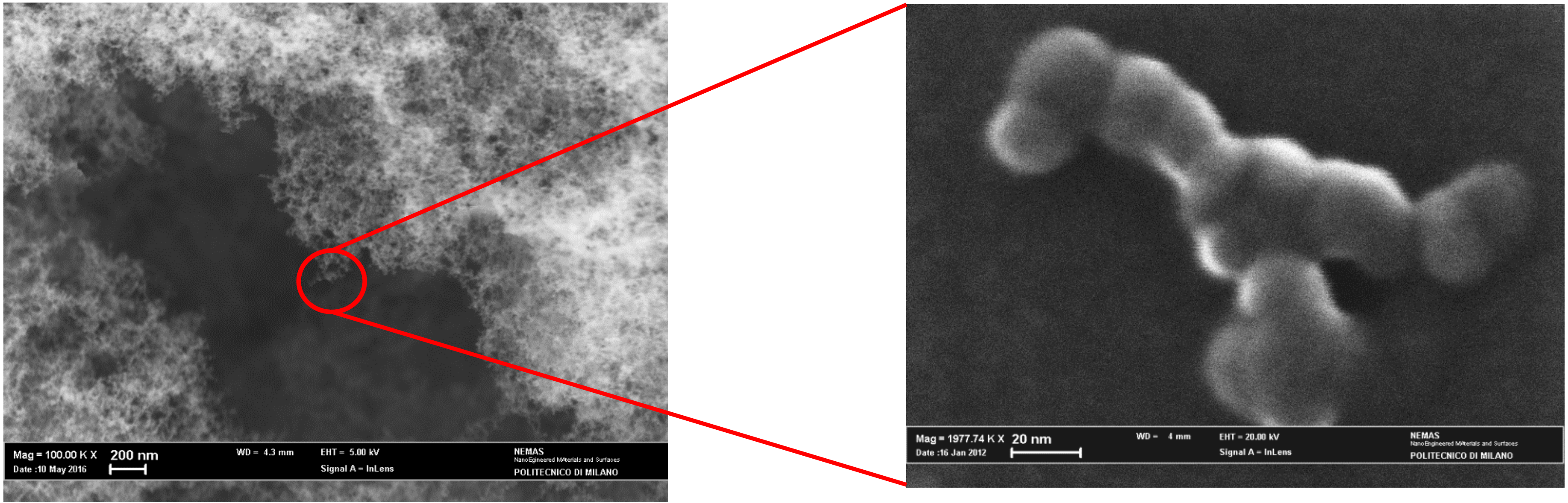


Foam PLD parameters:

λ= 532 nm
Ep=150 mJ
Fluence 1.6 J/cm2
700 Pa of Ar
Static substrate
Static target

(… for this talk only!)

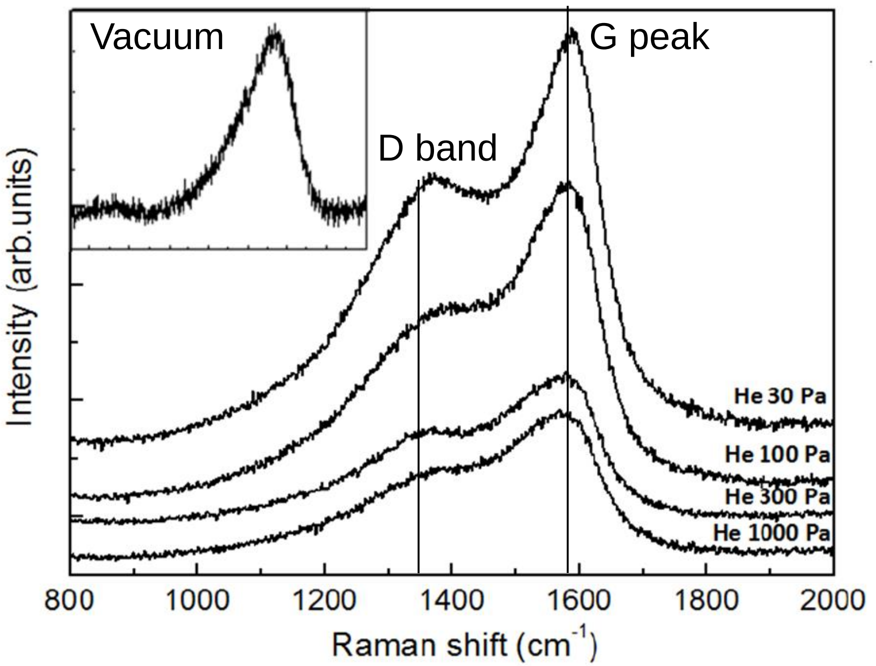
What are “foams” made of?



Elementary constituents:
10-20 nm **C nanoparticles**

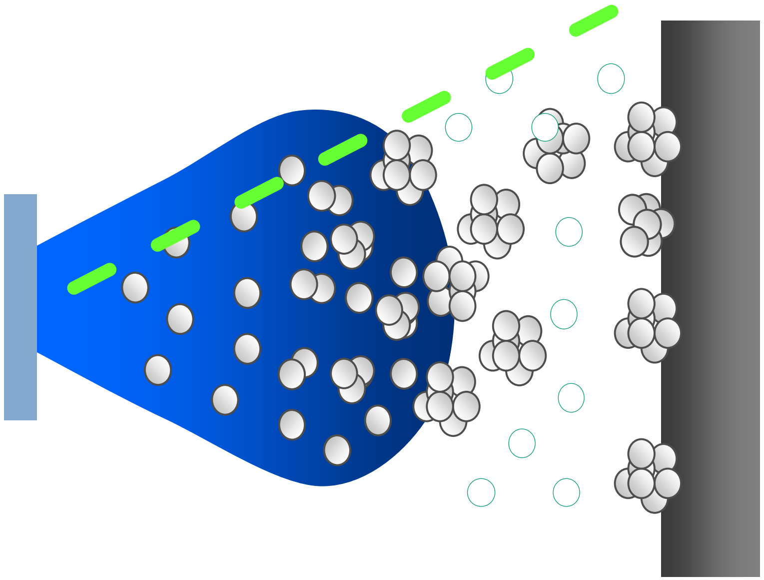
C-C bonding:
Nearly pure sp^2
odd-membered rings and
few chain-like structures

Crystalline structure:
Topologically disordered domains,
Size ~ 2nm

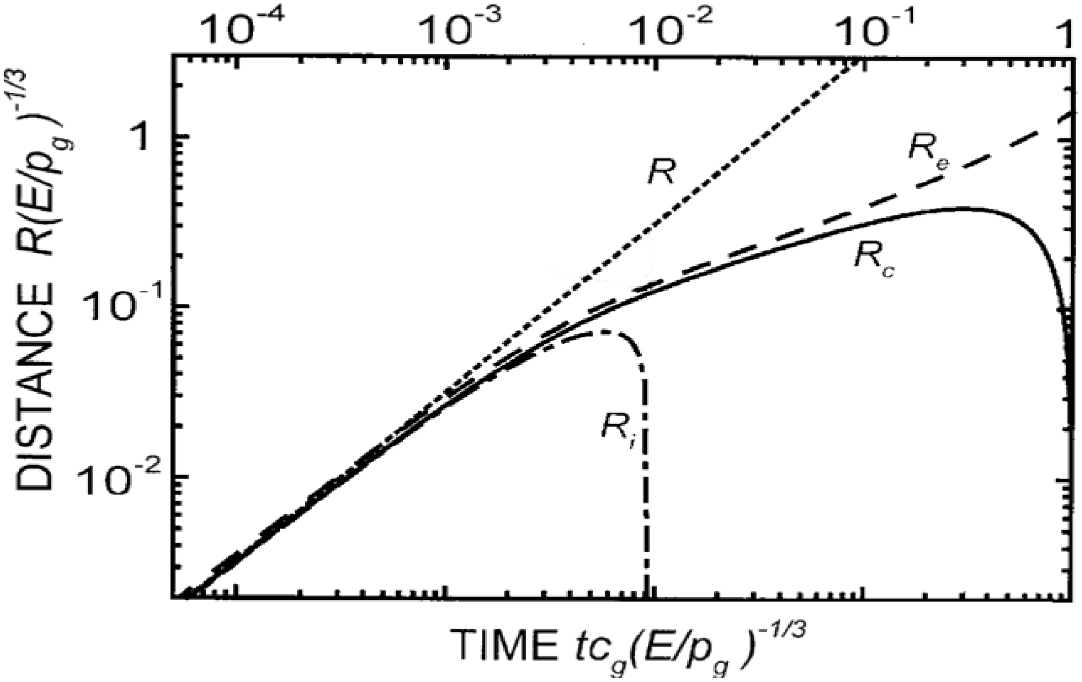


A. Zani *et al.*, Carbon, 56 358 (2013)

Plume expansion and NPs synthesis



PLD plume dynamics & NP production are open research topics!



Adapted from: Arnolds et al., *Appl. Phys. A* 69 S87–S93 (1999)

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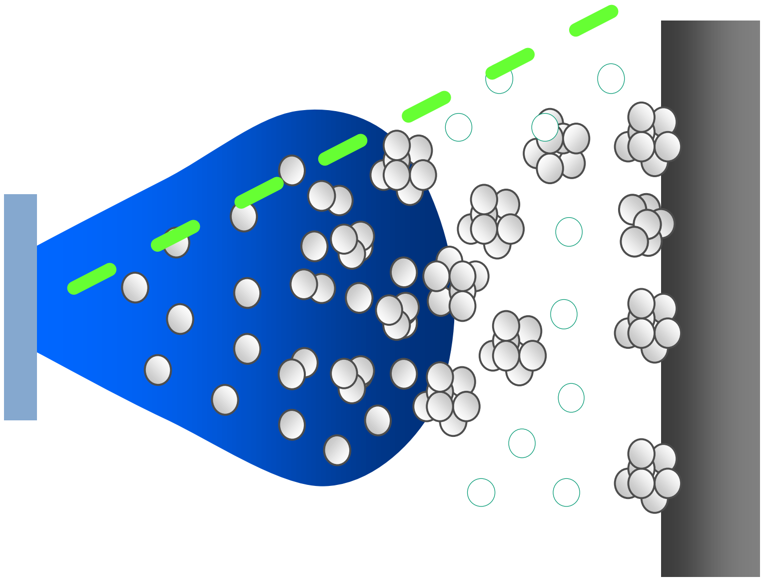

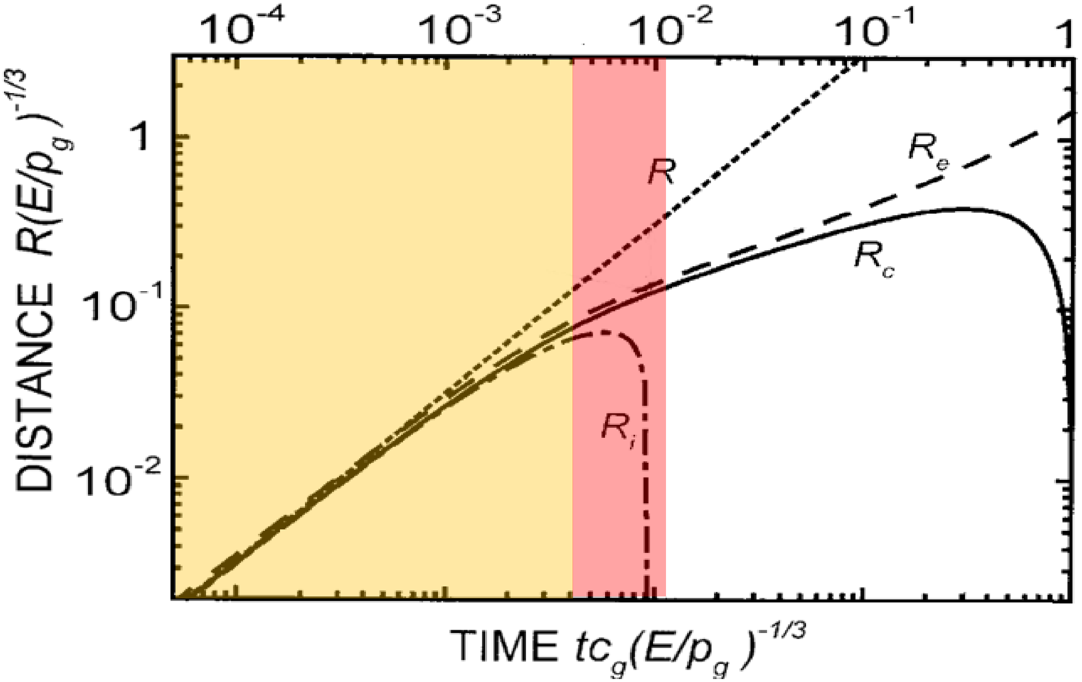

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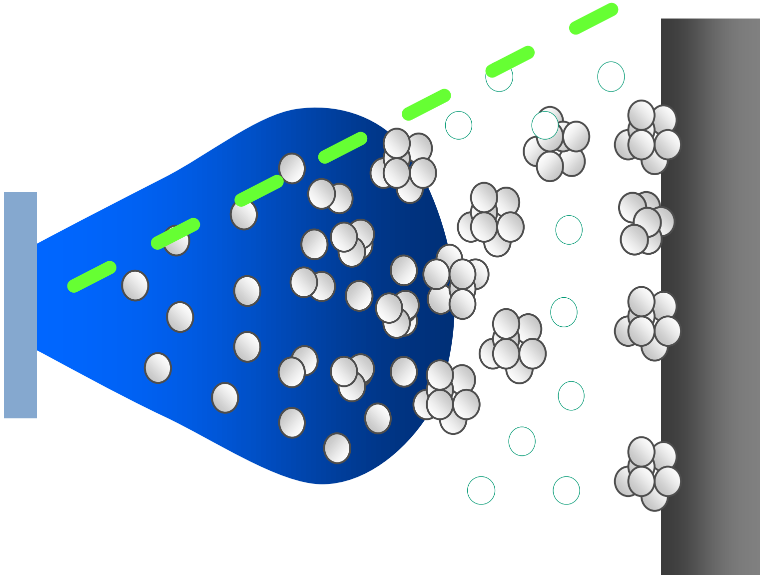
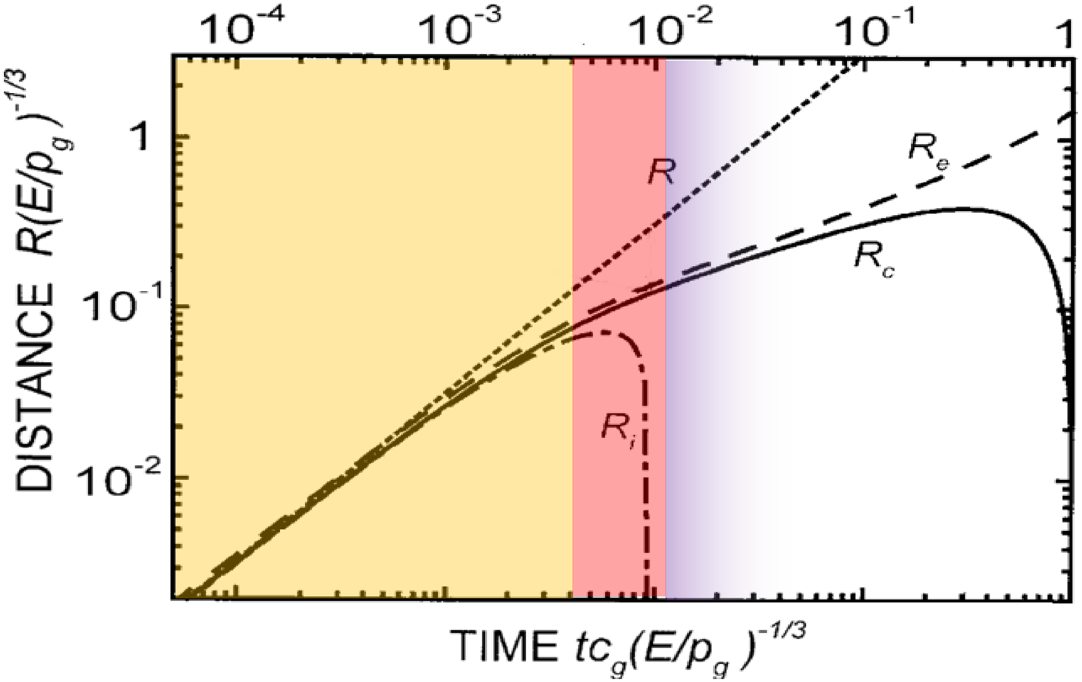
A sketch of plume dynamics:

1) Adiabatic Expansion
2) Shock wave formation

Plume expansion and NPs synthesis





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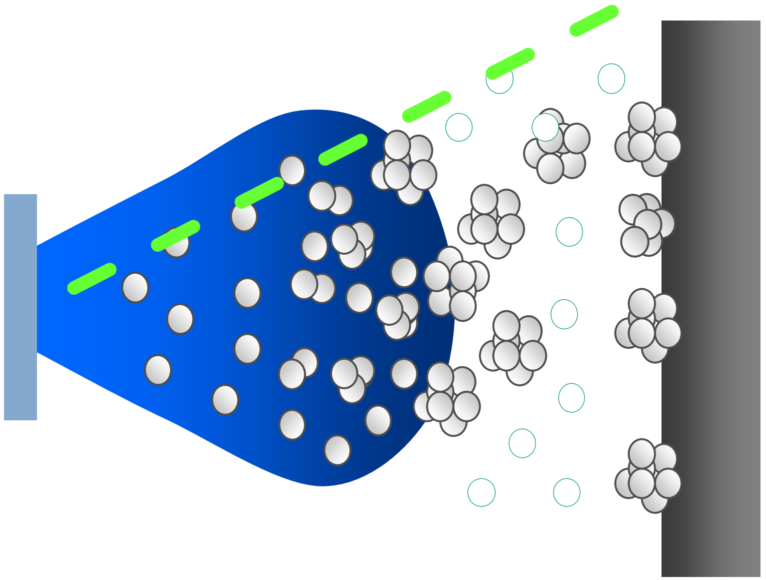

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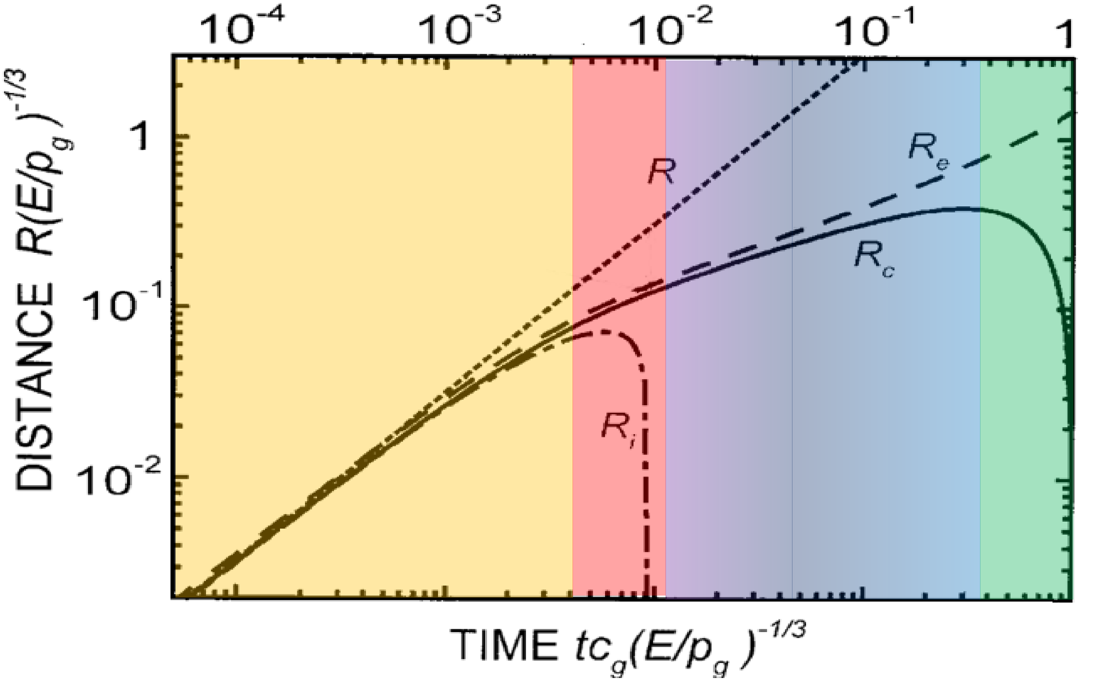

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5) Landing on substrate

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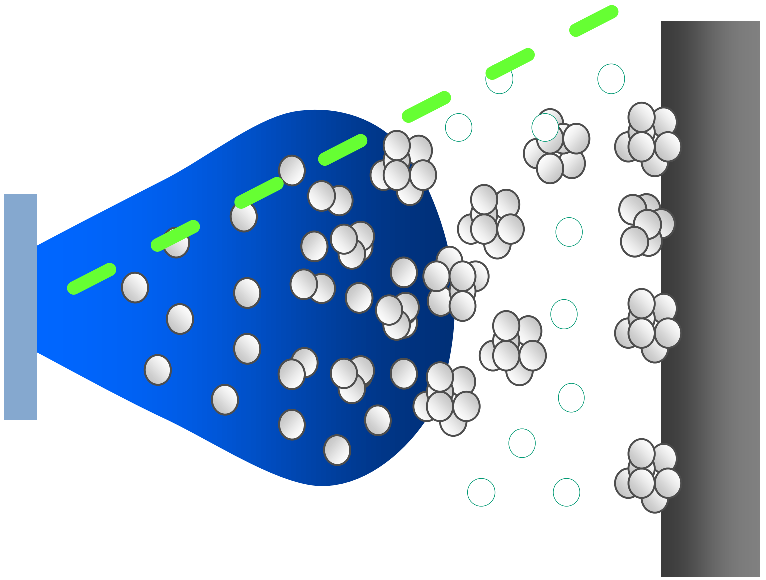

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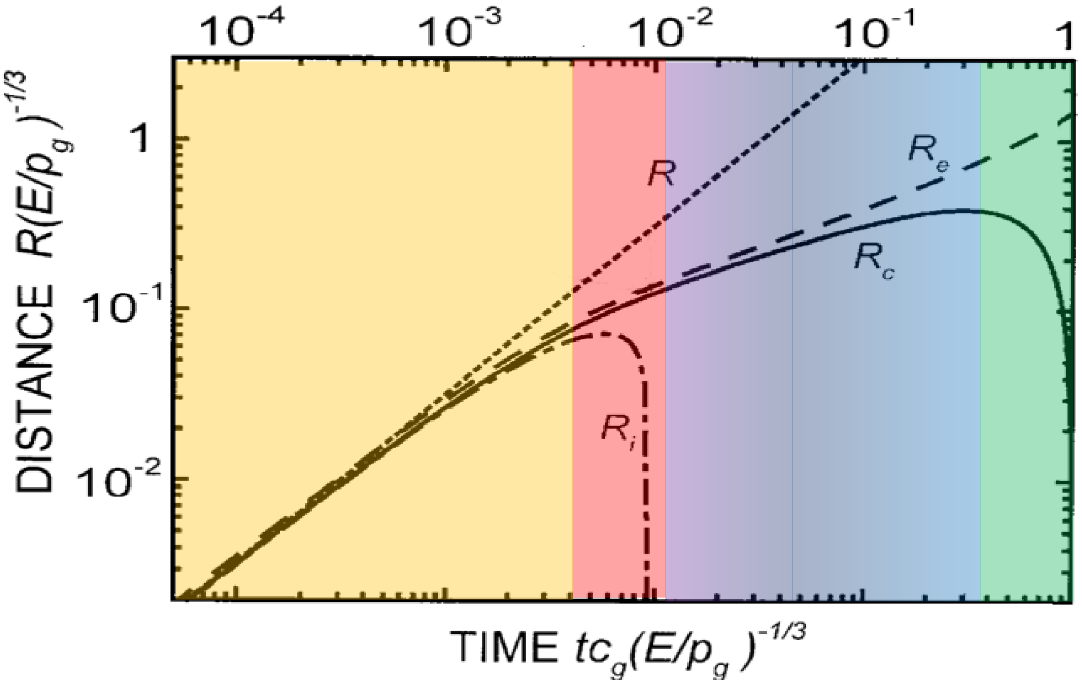

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- I'll consider C NPs as "LEGO bricks" to play with

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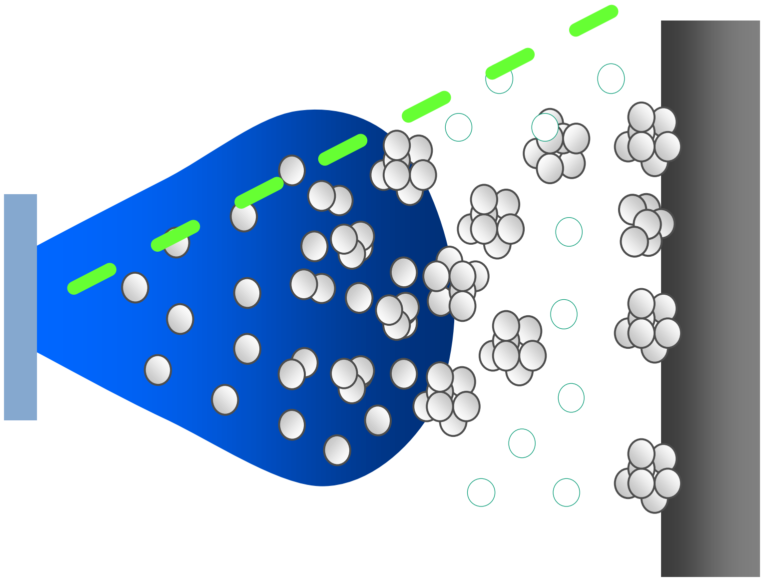

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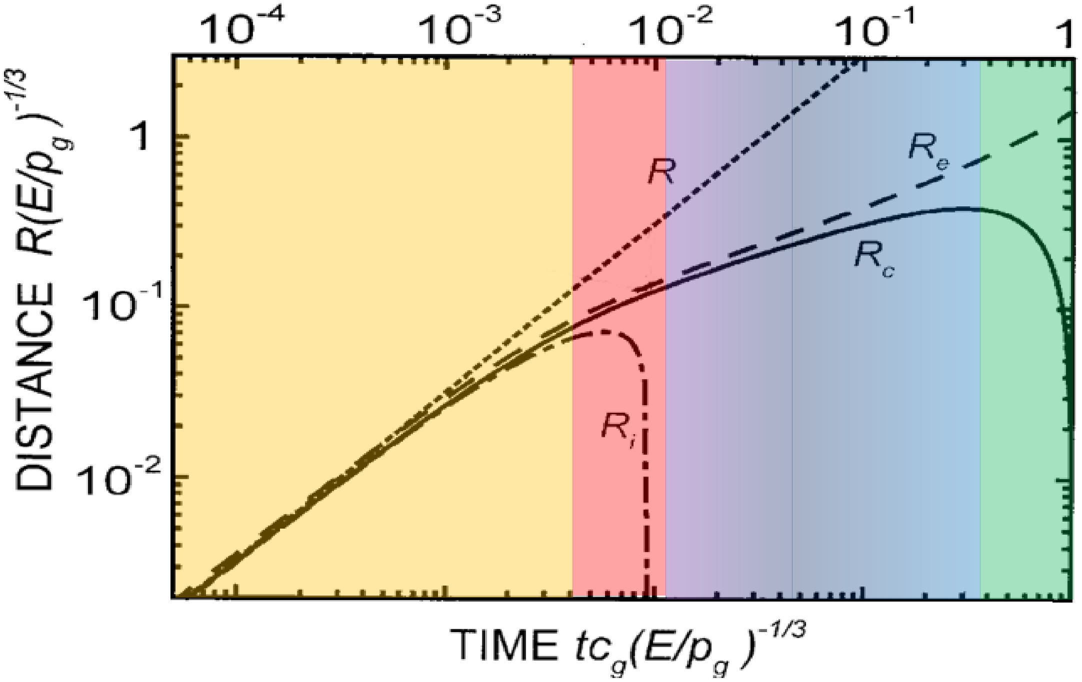

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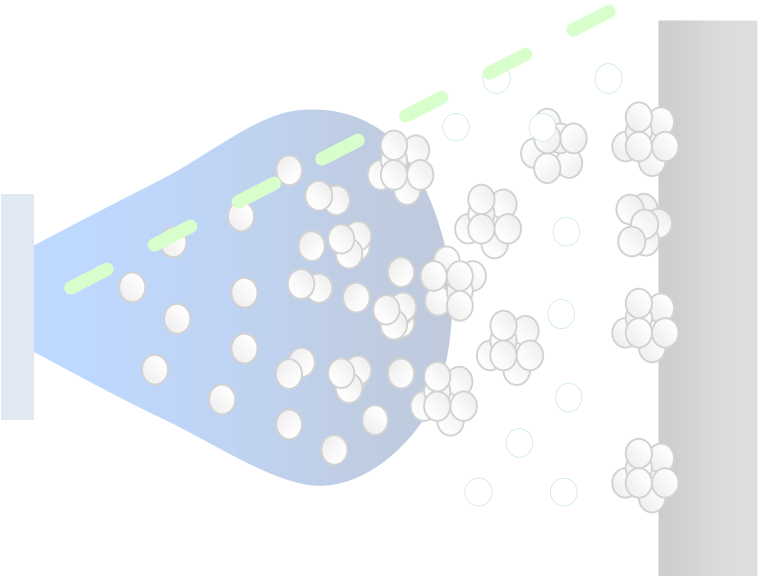
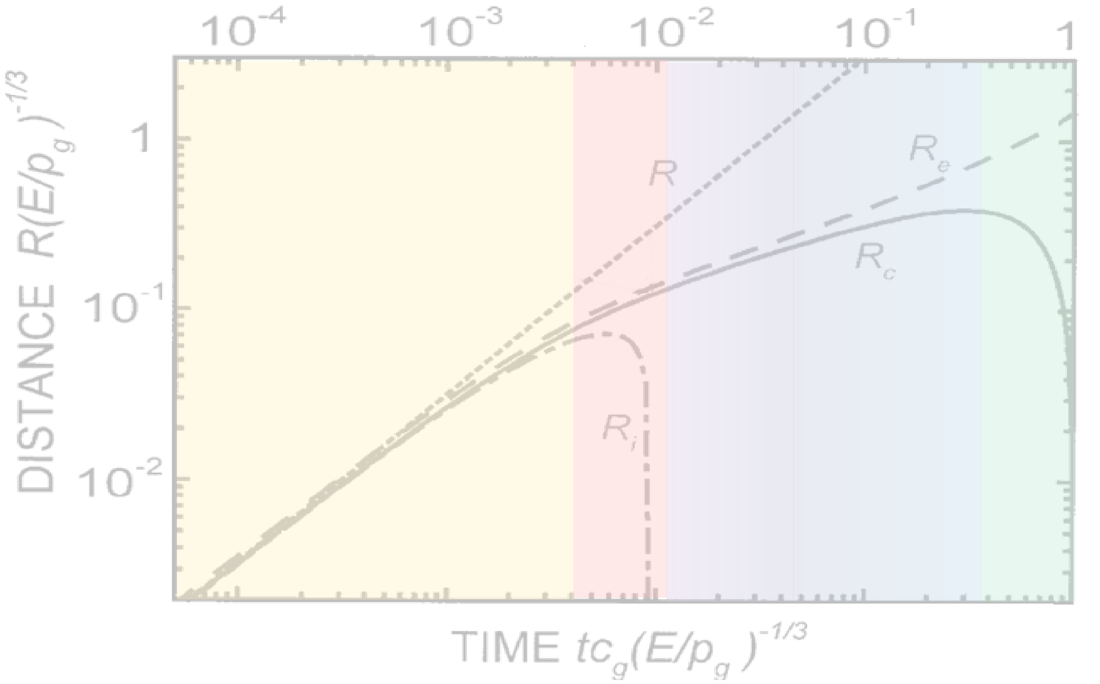
I'll try to answer these questions:

- What is the **NPs aggregation dynamics ?**
- How **aggregation dynamics** controls **foam properties?**

The aim of this talk



PLD plume dynamics in background gas is still an open research topic!



Adapted from: Arnolds et al., *Appl. Phys. A* 69 S87–S93 (1999)

A sketch of plume dynamics:

1) Adiabatic Expansion
2) Shock wave formation
3) Nanoparticle synthesis
4) Nanoparticle aggregati
5) Landing on substrate

For the purpose of this talk:

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I'll try to answer to these questions:

☐ What is the **NPs aggregation dynamics ?**

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What is said in the literature?

- ☐ The **growth of fractal structures** has been observed **since earliest PLD** experiments
- ☐ Different **aggregation models** (DLA, DLCCA, RLA,…) in **numeric simulation** of growth
- ☐ Diffusion Limited Aggregation on the substrate (**2D-DLA**) is the **most employed**

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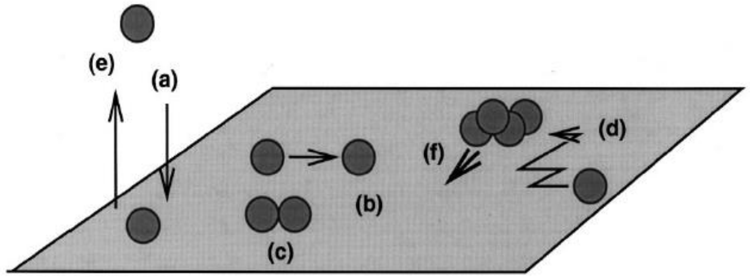
The physics in a 2D-DLA model



Diffusive motion (“**random walk**”) of **NPs**

Sticking of **NP** and **aggregation**

Diffusion on **substrate** → **2D physics**

P. Jensen, *Rev. Mod. Phys.* **71** 1695 (1999)

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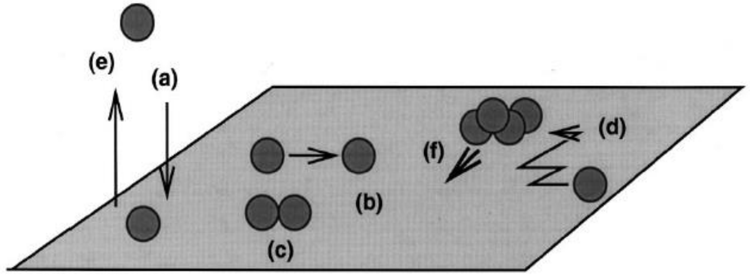

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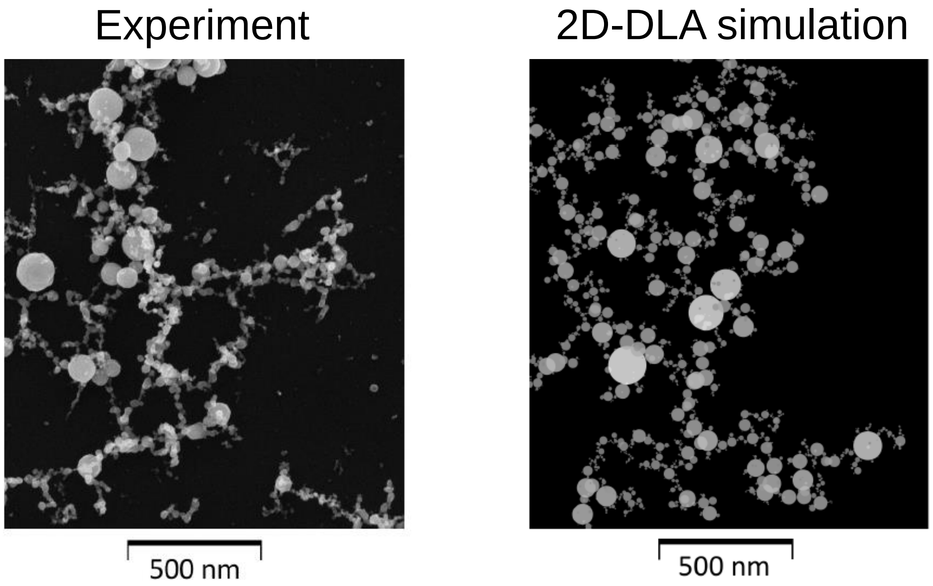

G. L. Celardo et al., *Mater. Res. Express* **4** (2017) 015013

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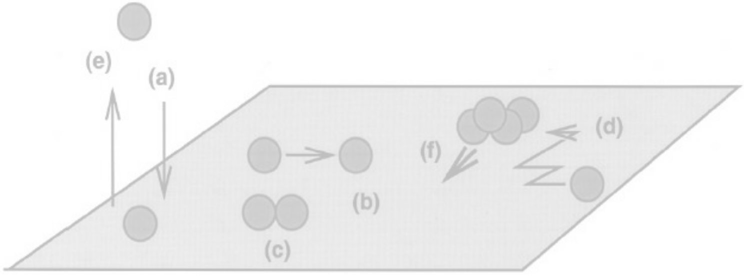

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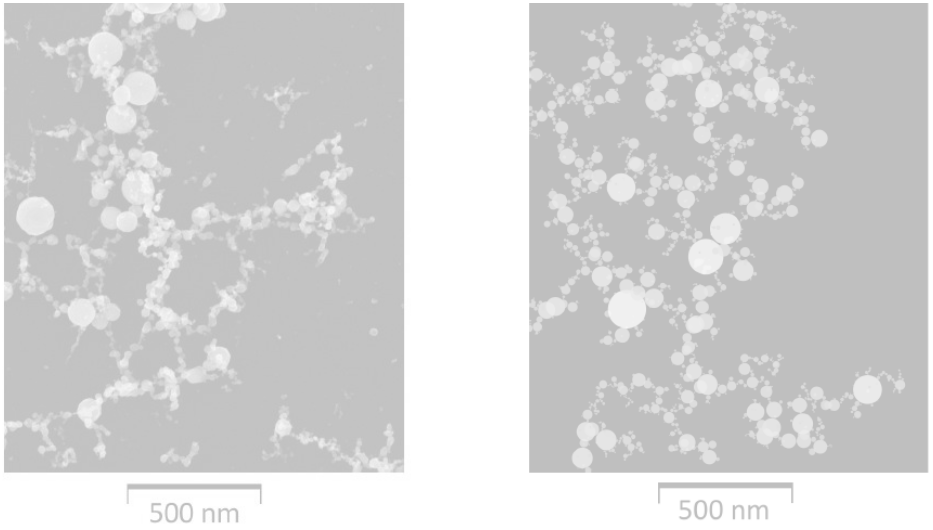

Experiment | 2D-DLA simulation

G. L. Celardo et al., *Mater. Res. Express* **4** (2017) 015013

..Is 2D-DLA ok also to describe the growth of C foams?

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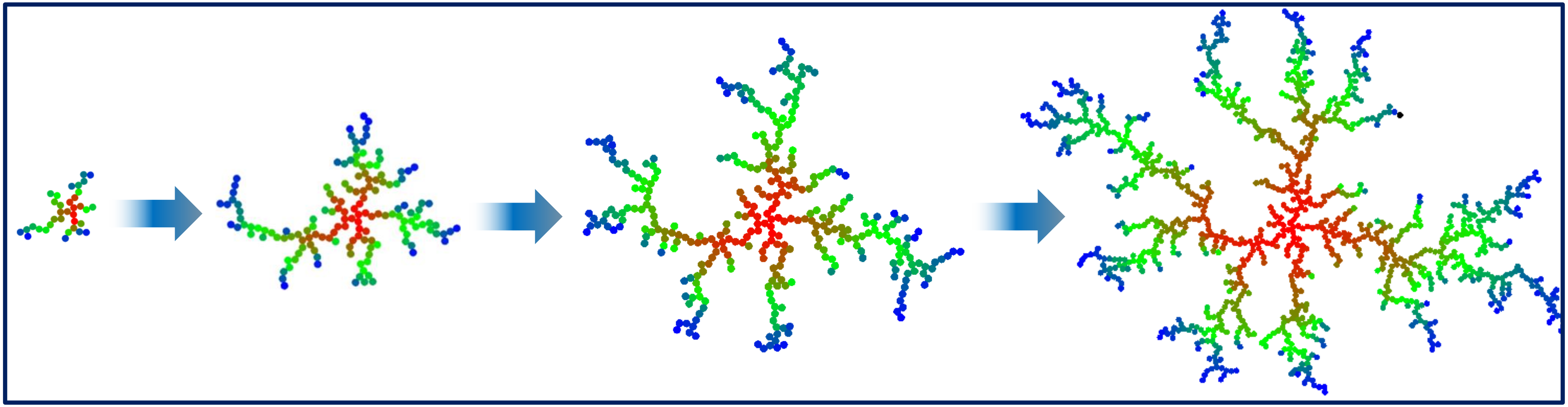
With **2D-DLA**, **aggregate grow** like this:



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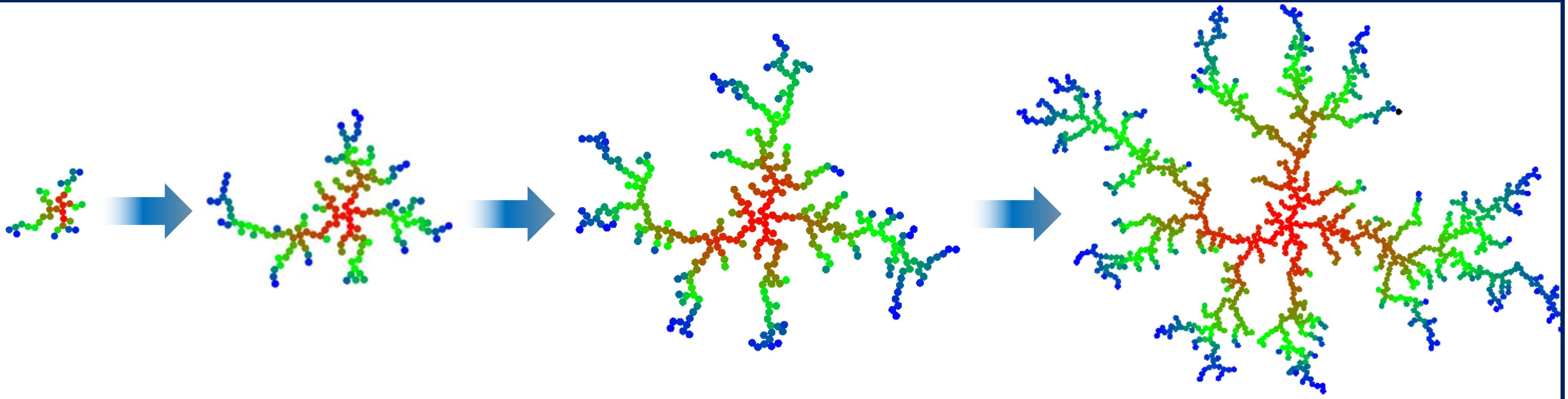

2D-DLA predicts:

1) Very **small aggregates** for **few shots**

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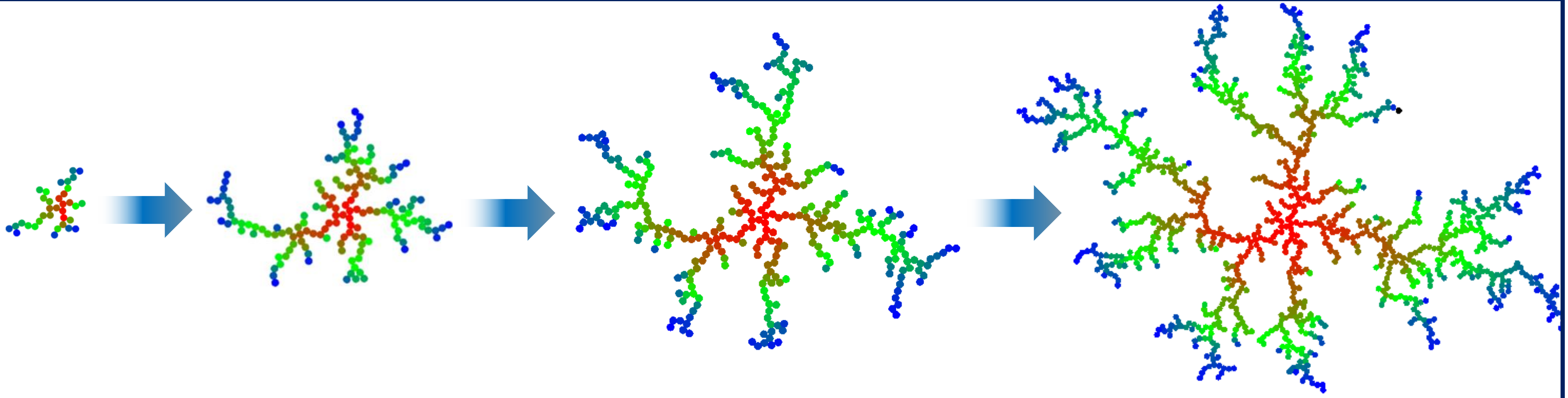

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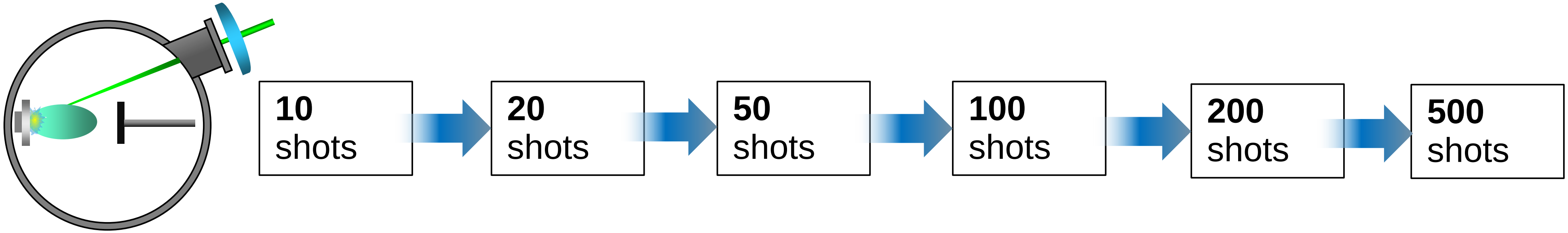
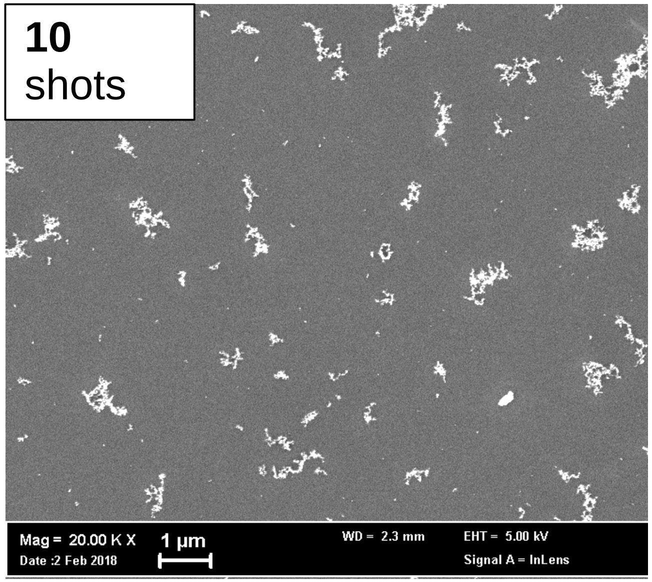
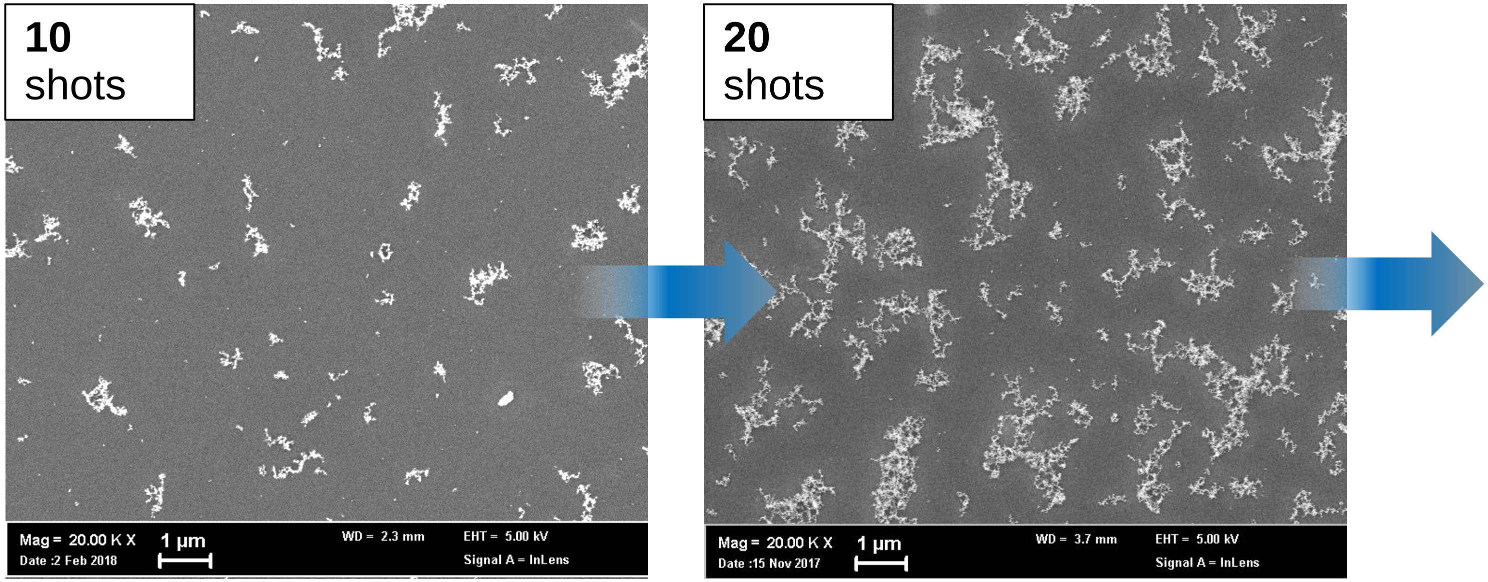
We can **test experimentally** if 2D-DLA is ok:



10 shots → **20** shots → **50** shots → **100** shots → **200** shots → **500** shots



1) Few shots: **large**, μm-sized **aggregates** (~ 100s NPs!)



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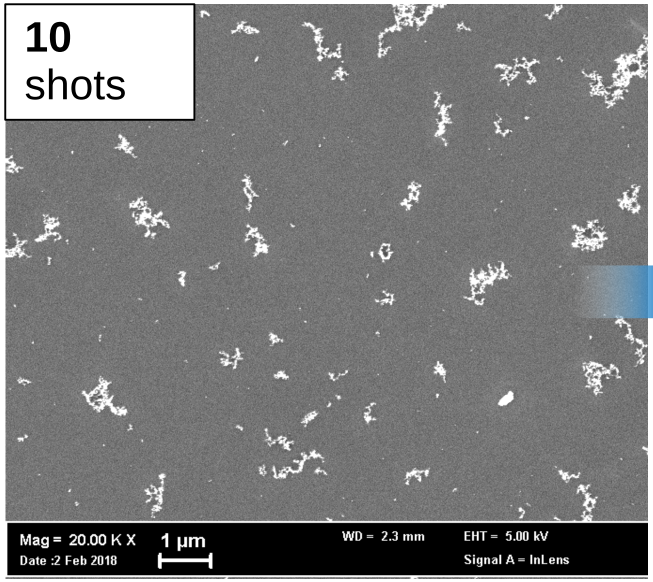
2) Aggregates **coalesce**



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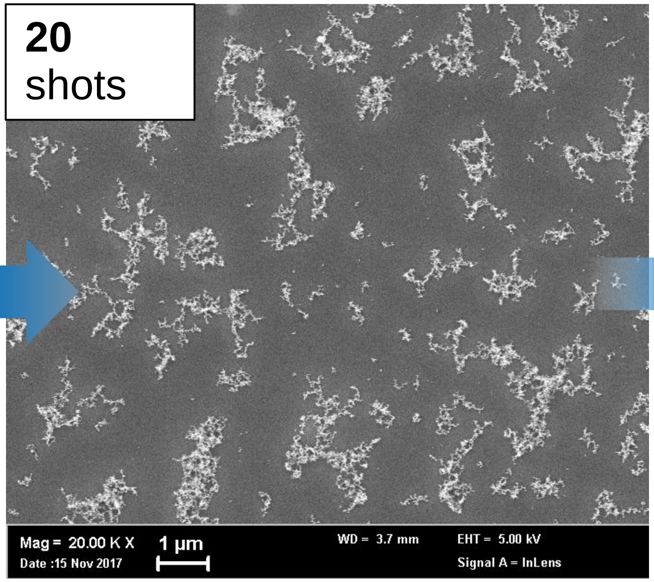

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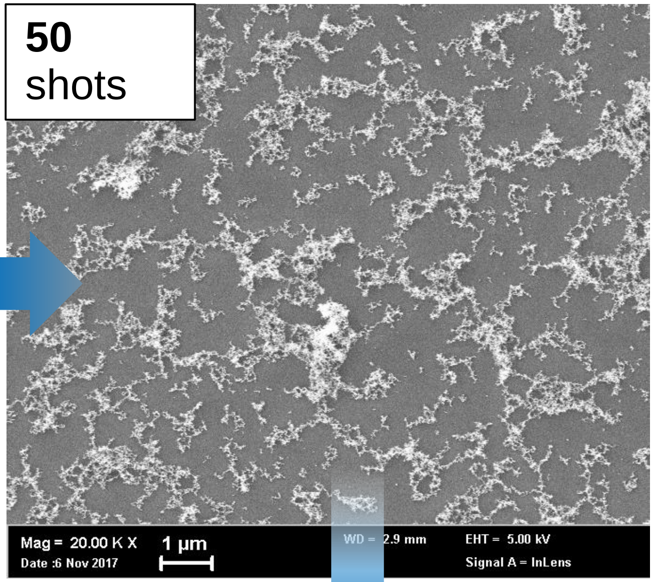
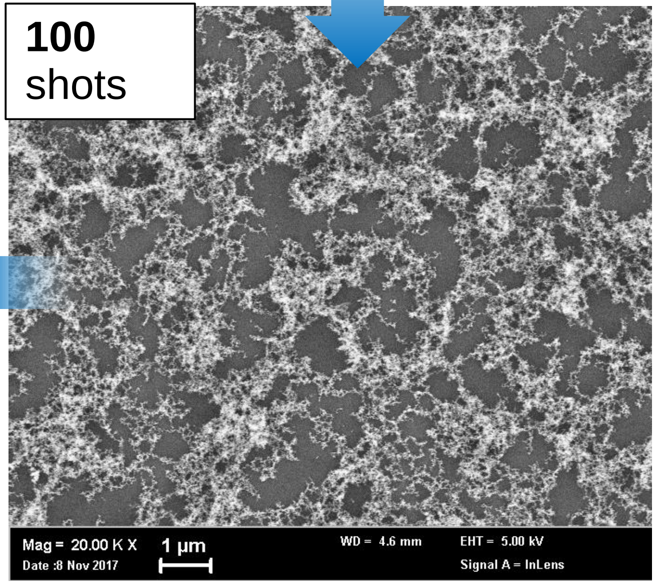


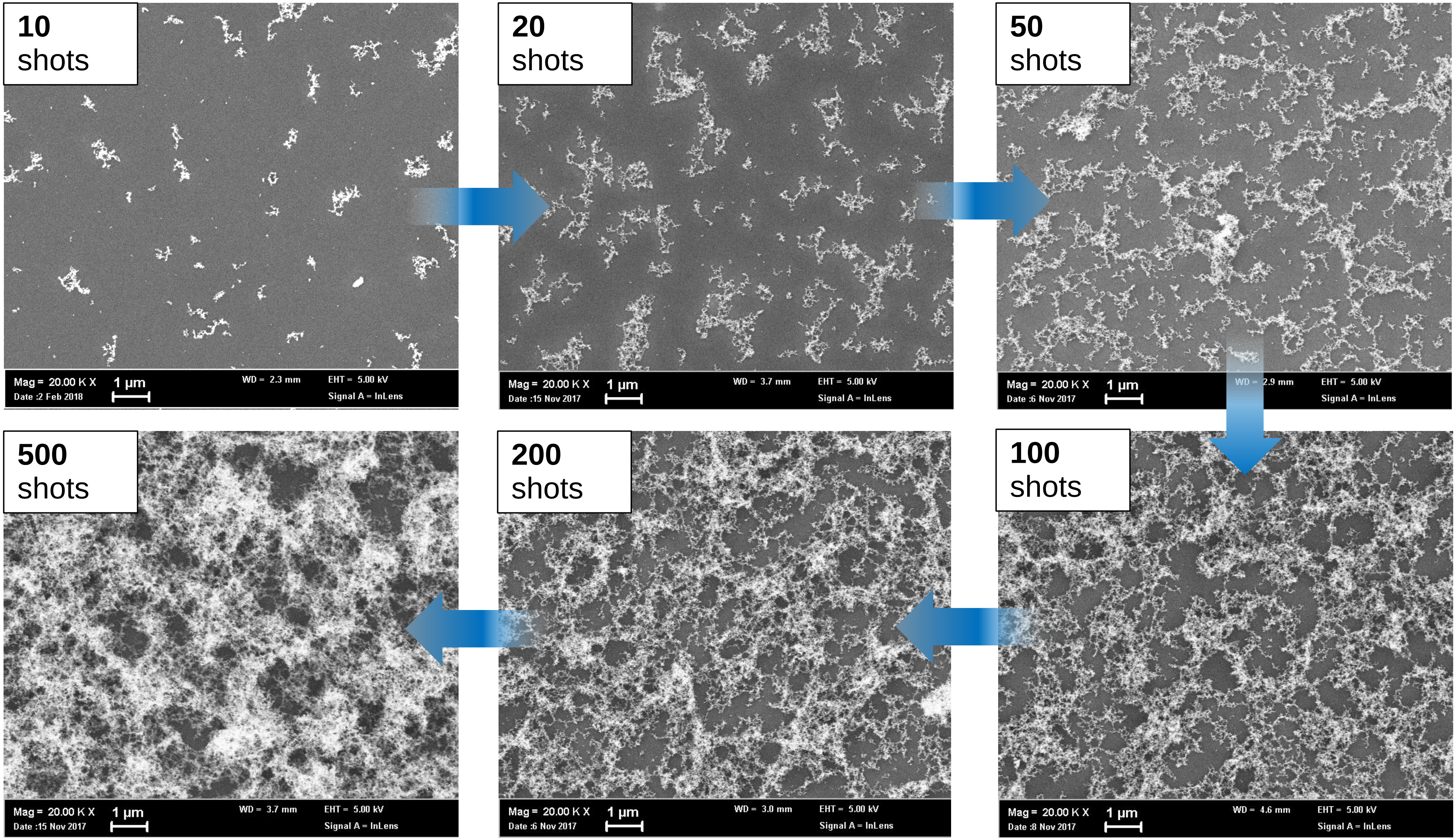
50 shots



100 shots

1) Few shots: **large**, µm-sized **aggregates** (~ 100s NPs!)

2) Aggregates **coalesce** but having almost **constant size**



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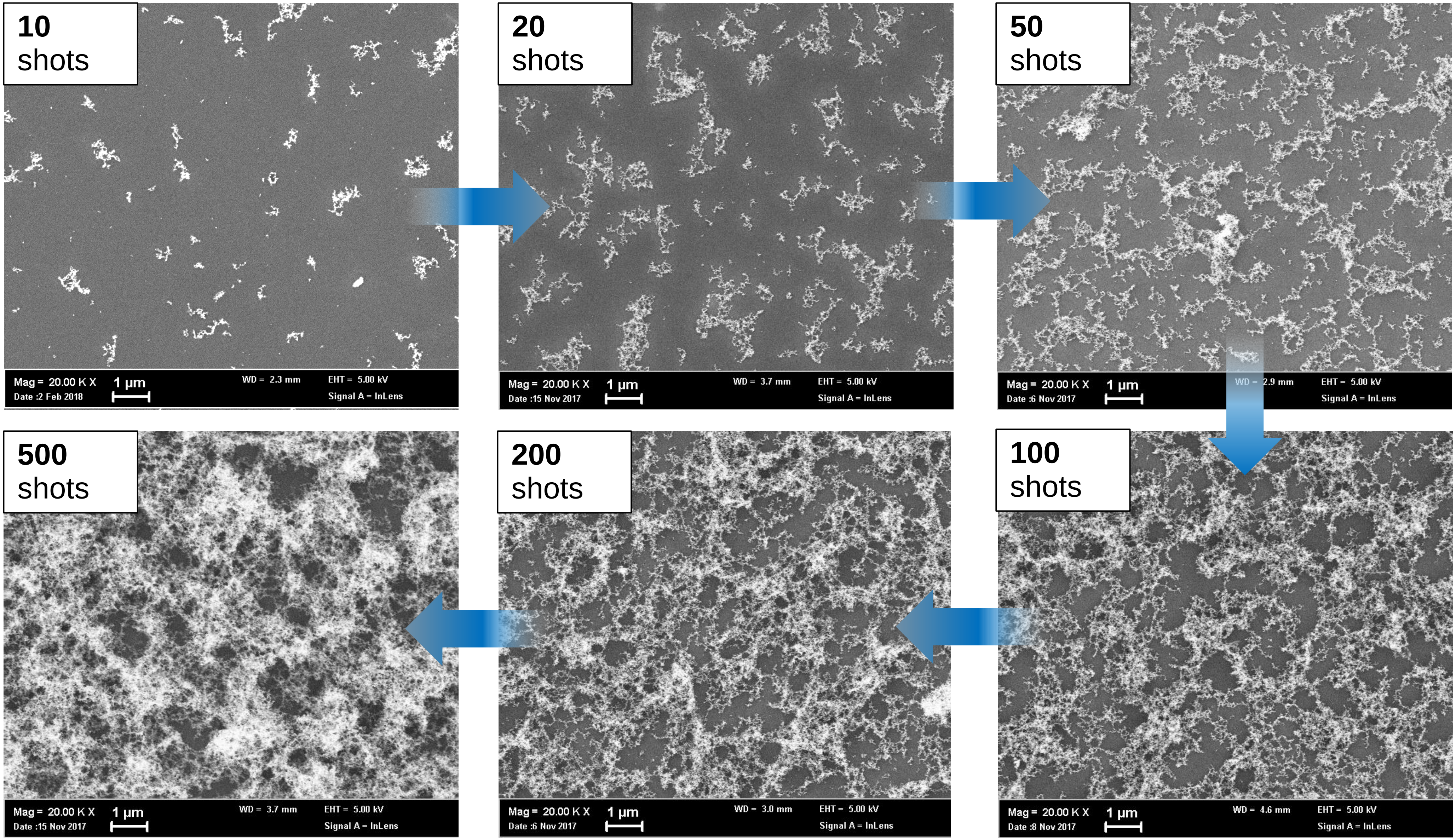

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2D-~~DLA~~ fails!

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Smoluchowski coagulation equation (1916)

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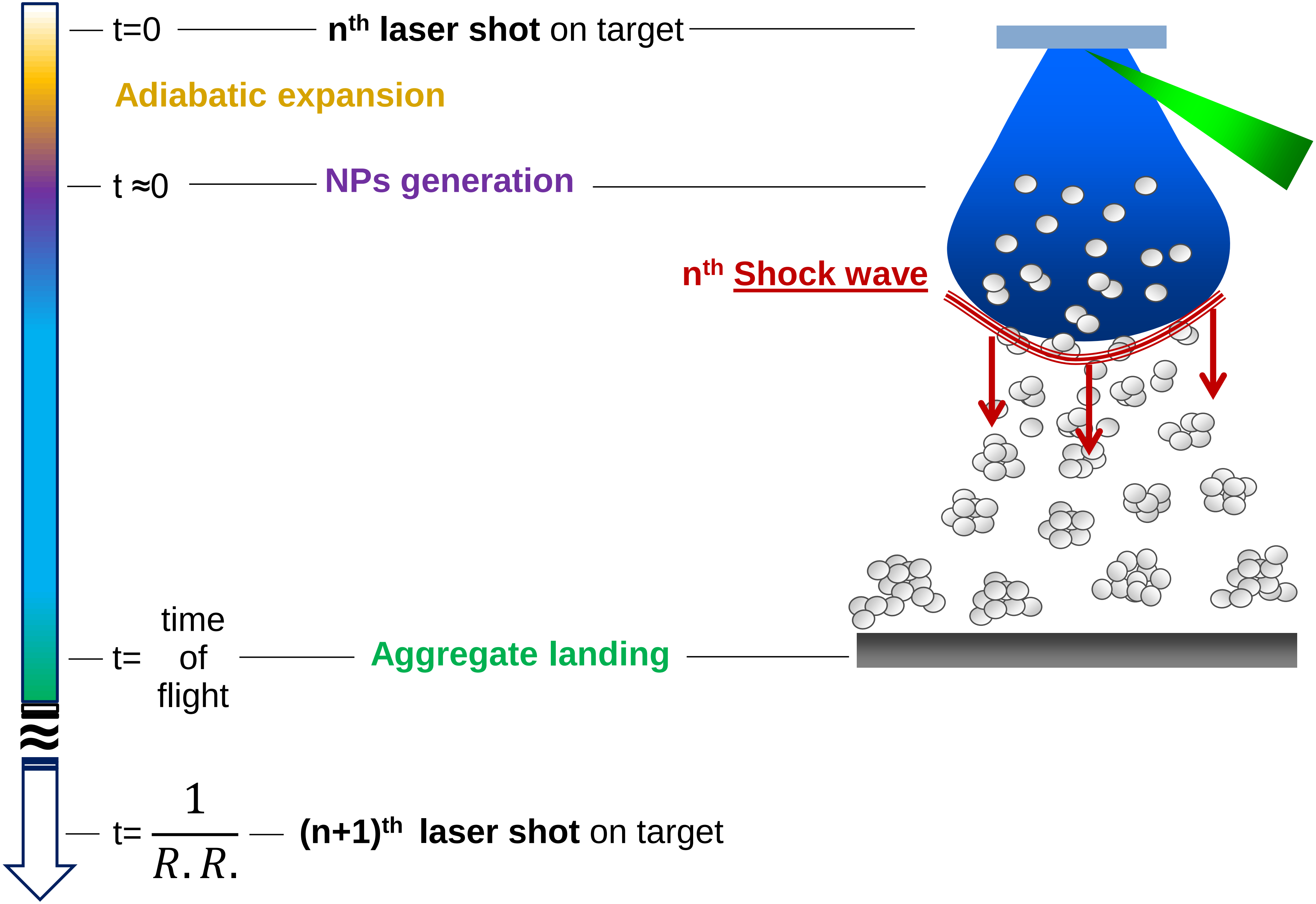

t=0 — **nth laser shot** on target

Adiabatic expansion

t ≈0 — **NPs generation**

nth Shock wave

t= time of flight — **Aggregate landing**

$t=\frac{1}{R.R.}$ — **(n+1)th laser shot** on target

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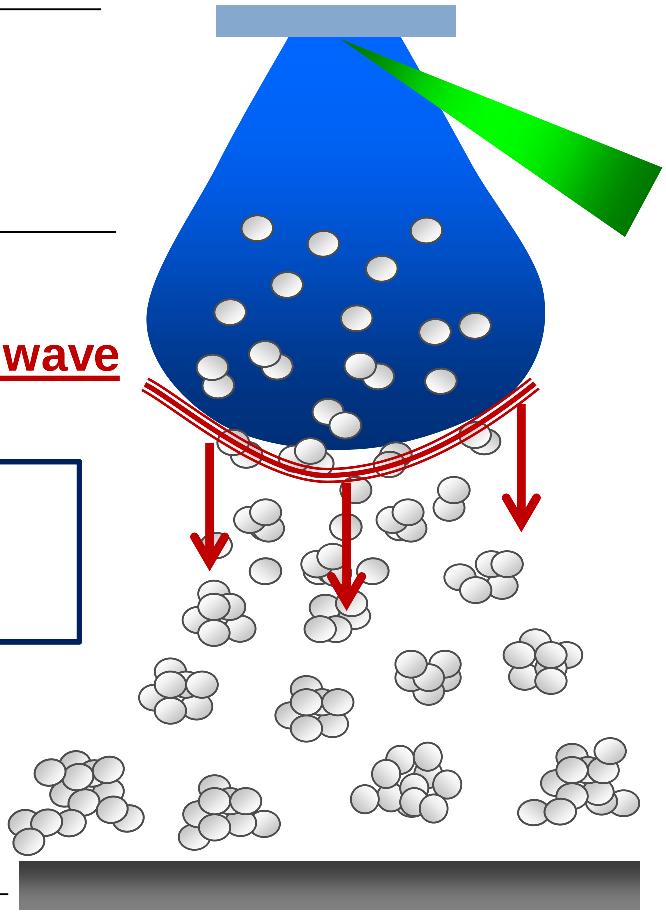

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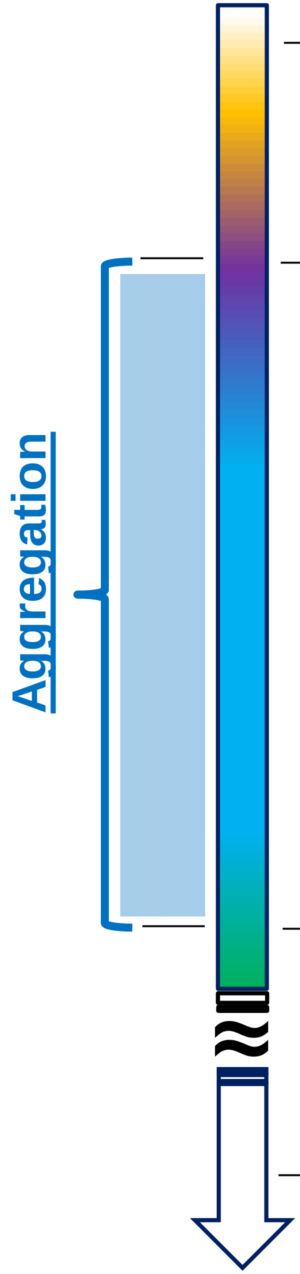

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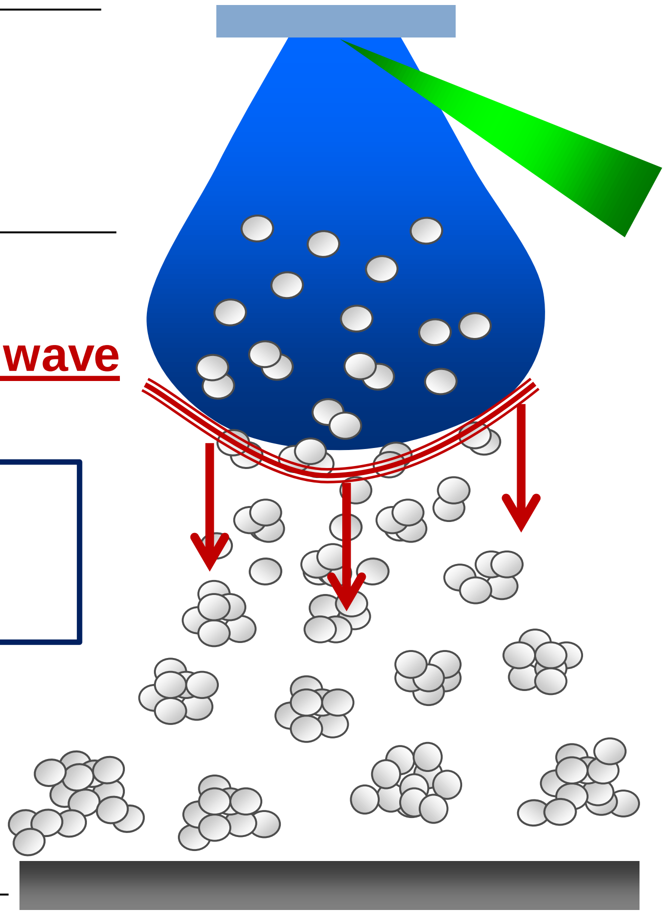

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- ☐ Aggregates drag force by Stokes-Einstein eq.
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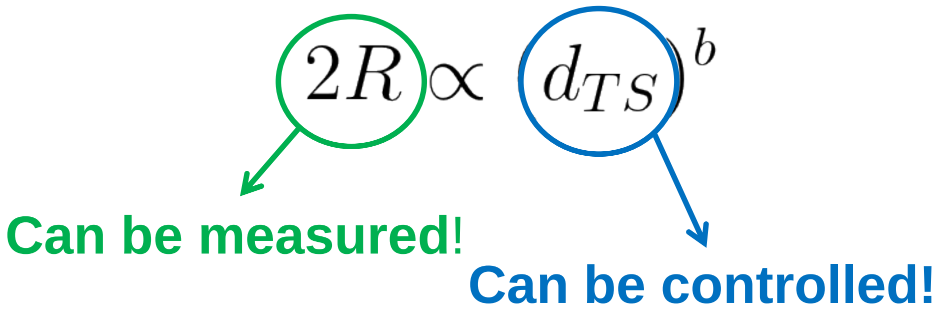
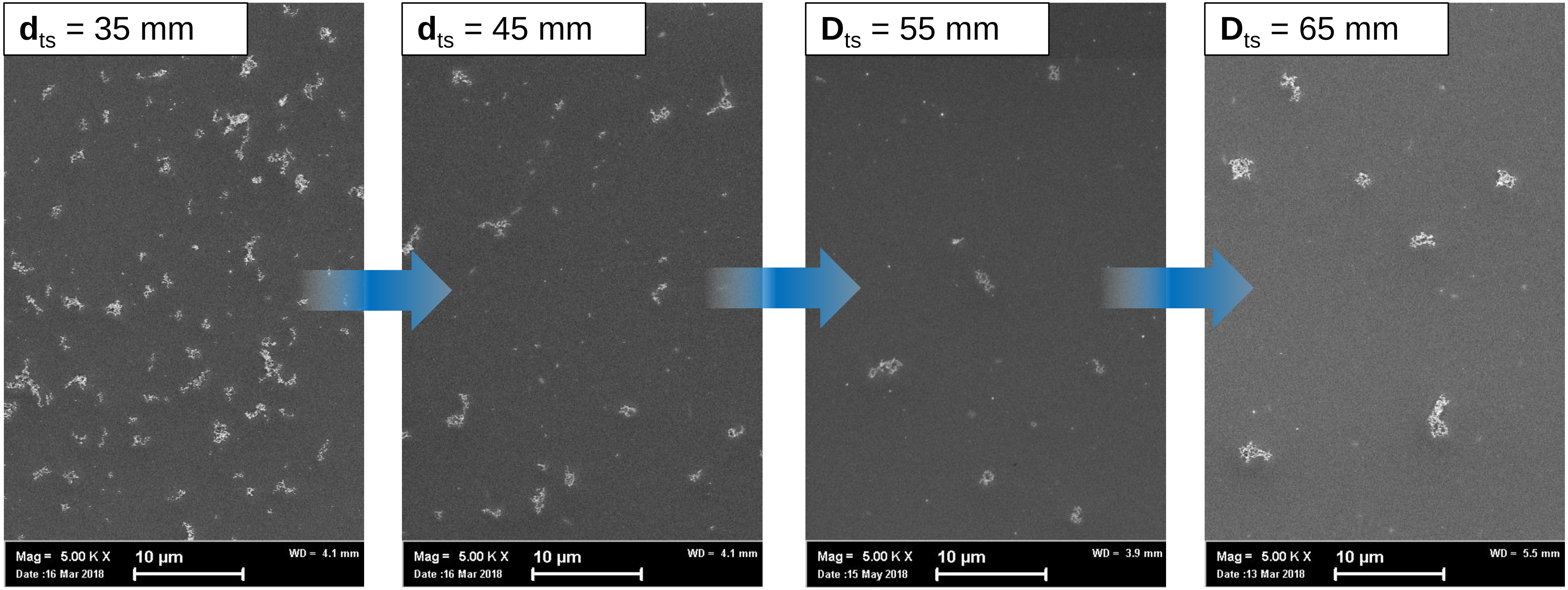


$$2R \propto (d_{TS})^b$$

Can be measured!

Can be controlled!

Let’s test the t.o.f. hypotesis…



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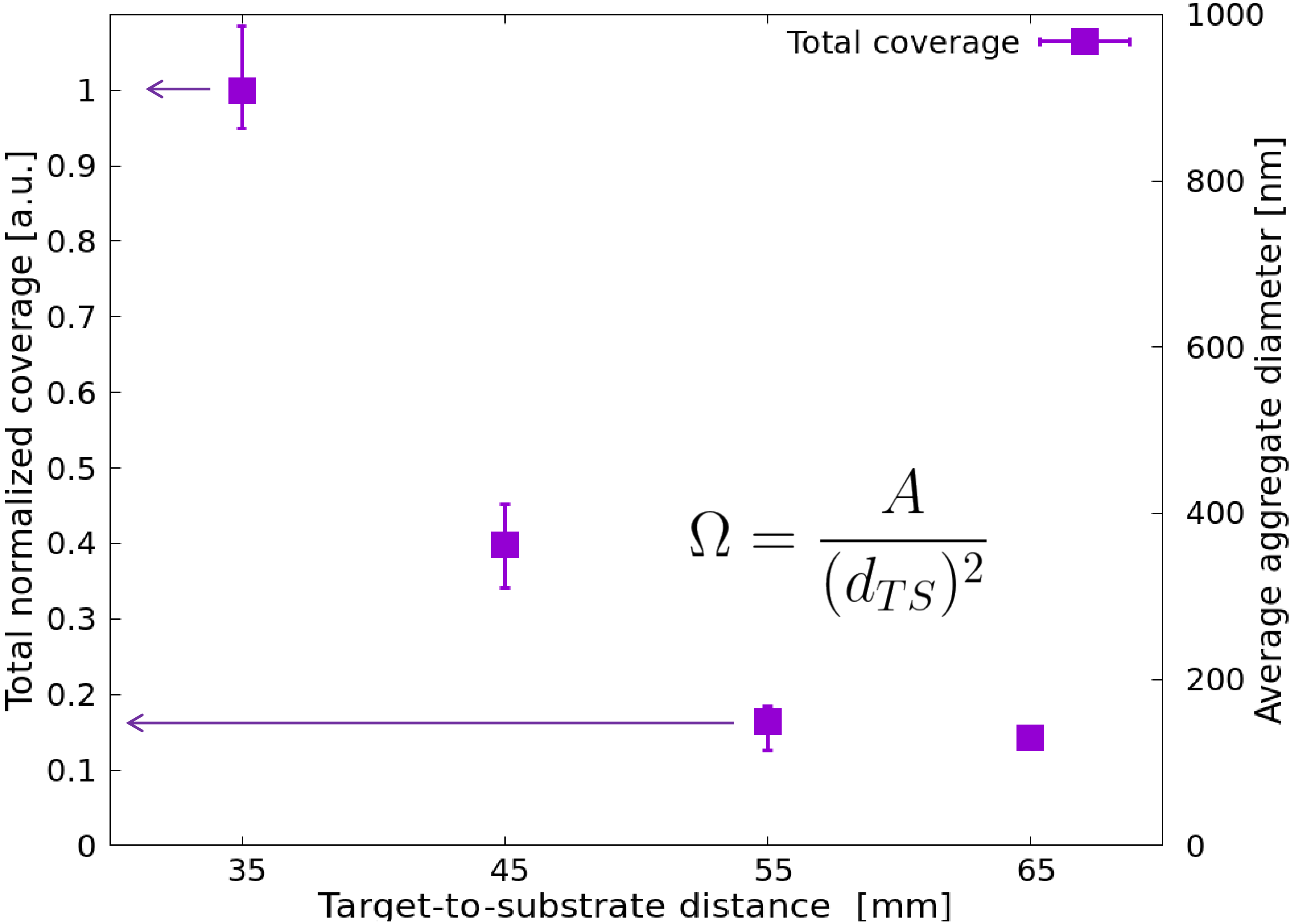

$$\Omega = \frac{A}{(d_{TS})^2}$$

- Less coverage because of solid angle reduction

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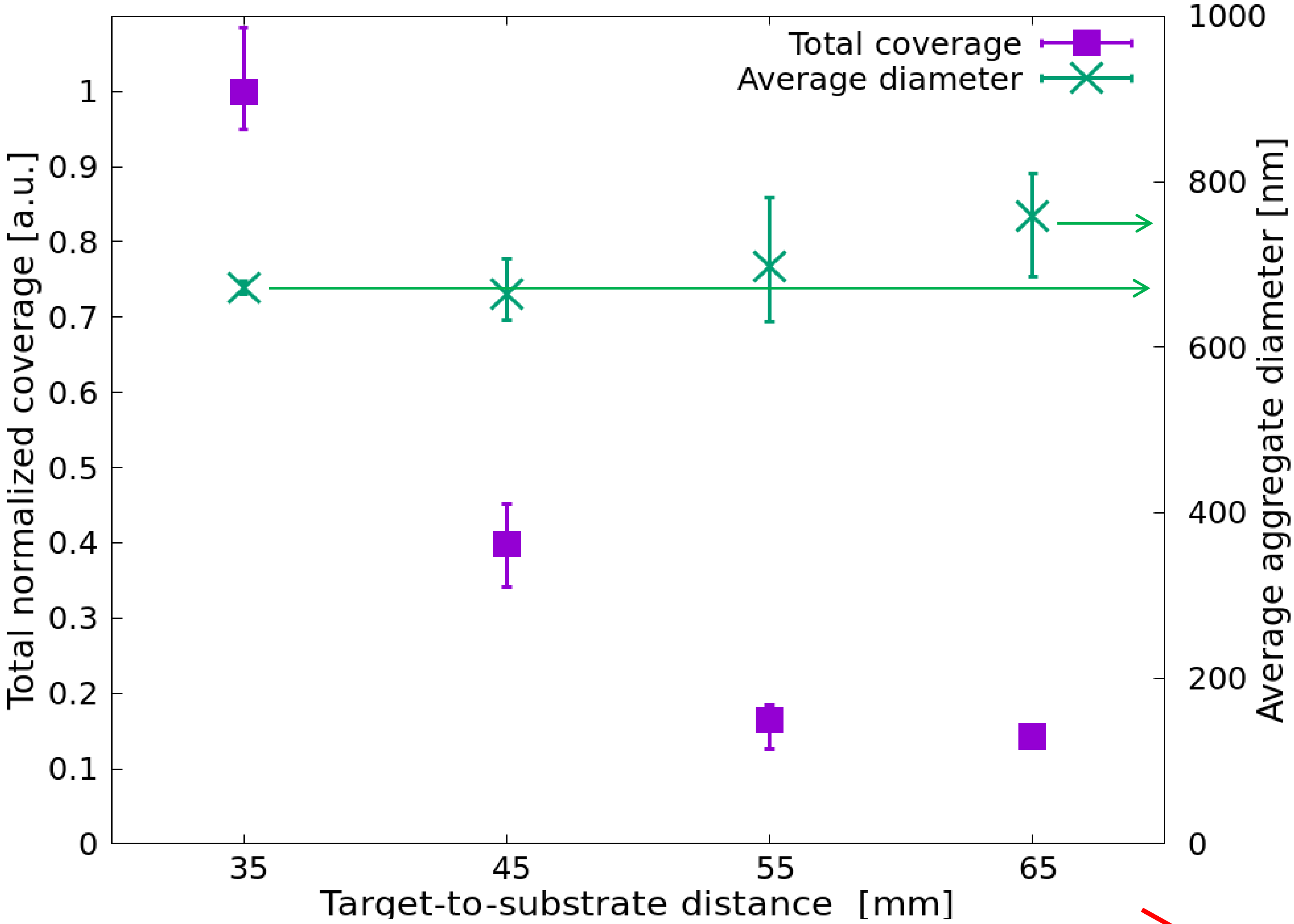

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- **Size almost independent from *d_{ts}***

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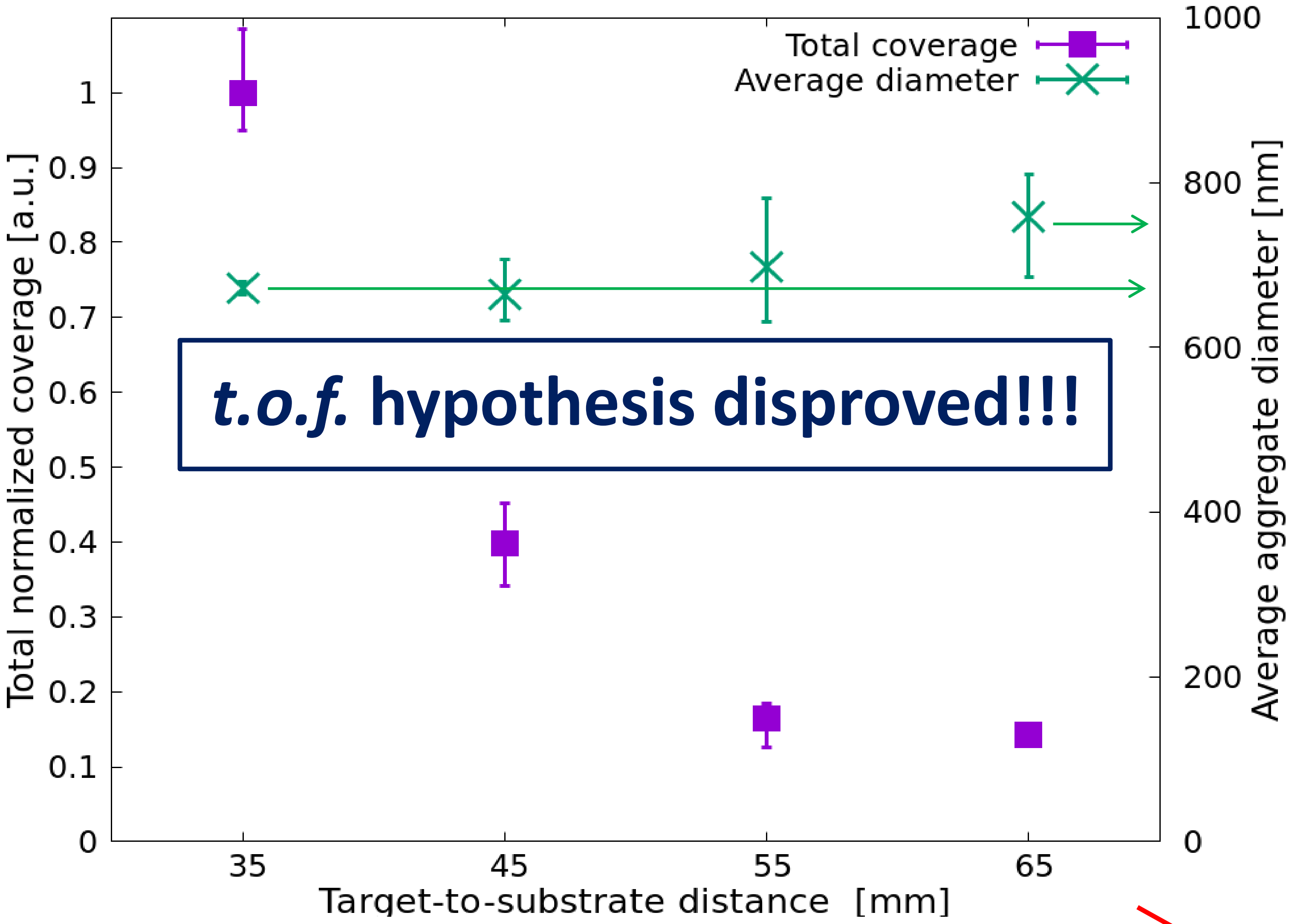

***t.o.f.* hypothesis disproved!!!**

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I) ~~t_{aggr} ≈ time-of-flight~~

A model (II) to find the aggregation time

t=0 — **n^{th} laser shot** on target

Adiabatic expansion

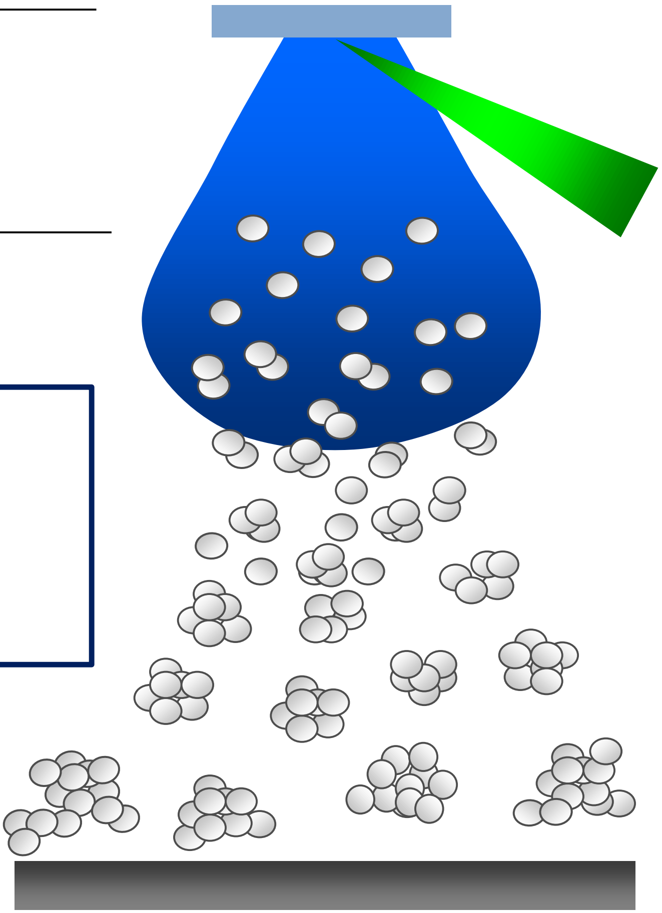
t ≈0 — **NPs generation**

Hypotheses (II):

1) n^{th} SW too quick to drag aggregates

≈

$t = \frac{1}{R.R.}$ — **$(n+1)^{th}$ laser shot** on target



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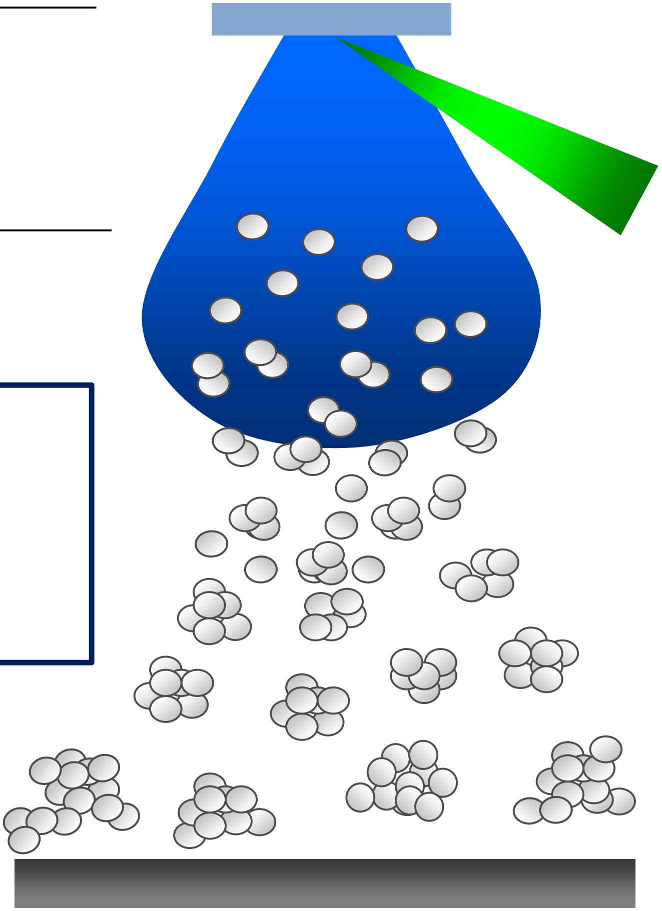
(Adiabatic expansion + NPs generation)

↓↓ **$(n+1)^{th}$ Shock wave** ↓↓



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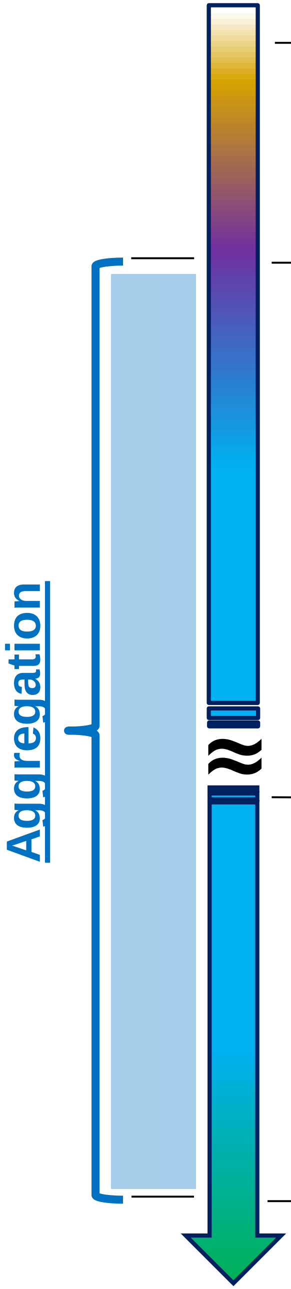

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$$t = \frac{1}{R.R.}$$

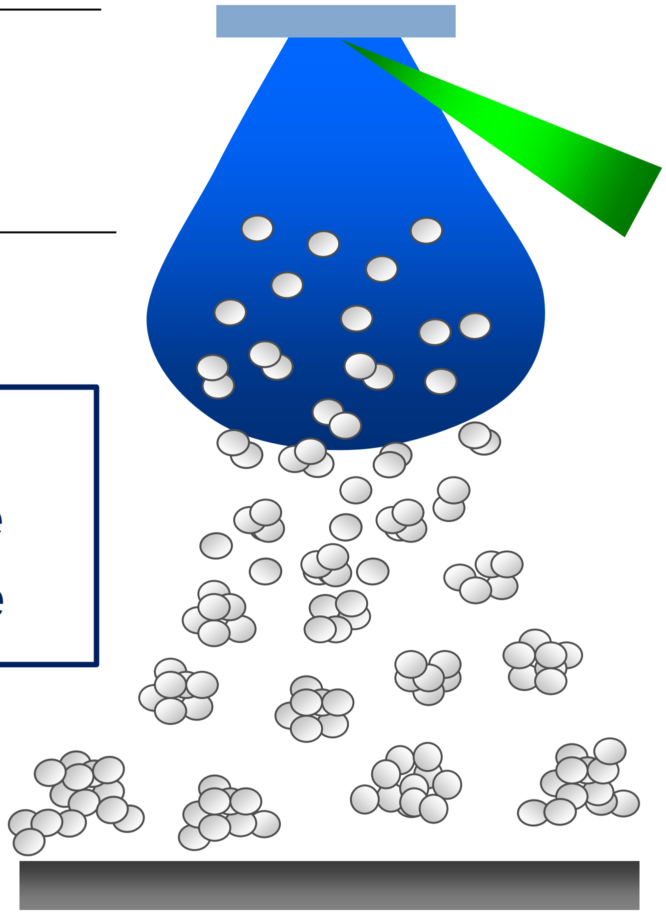
$(n+1)^{th}$ laser shot on target

(Adiabatic expansion + NPs generation)

$(n+1)^{th}$ Shock wave

$$t = \frac{1}{R.R.} + tof \approx \frac{1}{R.R.}$$

Aggregate landing



$$\boxed{t_{aggr} \approx \frac{1}{R.R.}}$$

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Hp 3: (n+1)th SW drags aggregates to substrate

$\mathbf{t_{aggr}}$ **≈ shot-to-shot time**

3rd step: experimental test

$$2R \propto \left(\frac{1}{R.R.}\right)^b \equiv (t_{sts})^b$$

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Hp 1: nth SW too quick to drag aggregates

Hp 2: Aggregates coalesce after nth SW is gone

Hp 3: (n+1)th SW drags aggregates to substrate

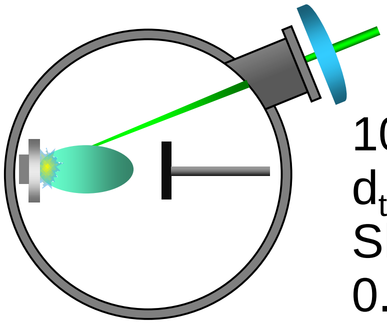
$\mathbf{t_{aggr}}$ **≈ shot-to-shot time**

3rd step: experimental test

$$2R \propto \left(\frac{1}{R.R.}\right)^b \equiv \left(t_{sts}\right)^b$$

Can be measured!

Can be controlled!



PLD parameters:

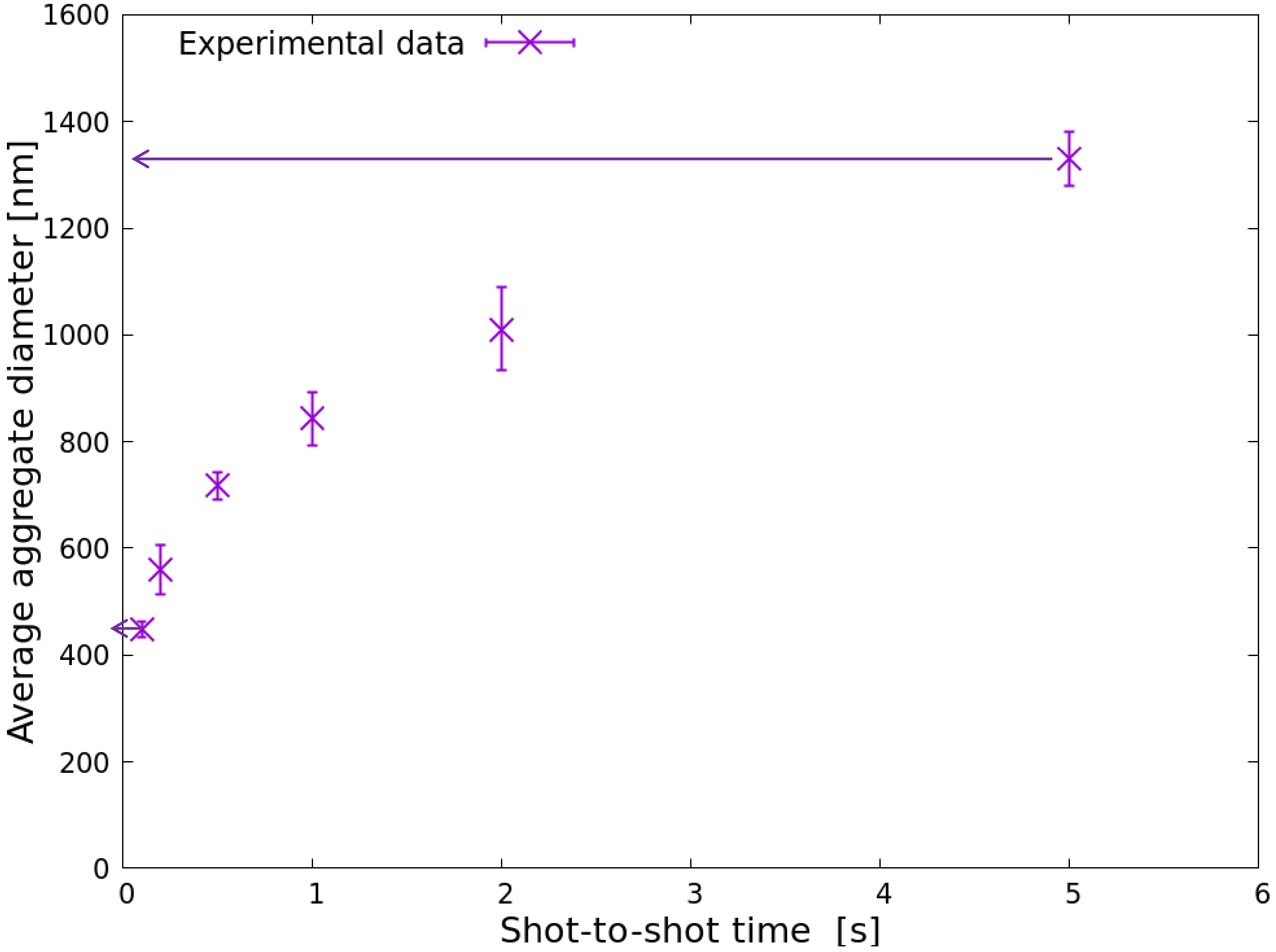
10 shots

d_{ts} = 45 mm

Shot-to-shot time=

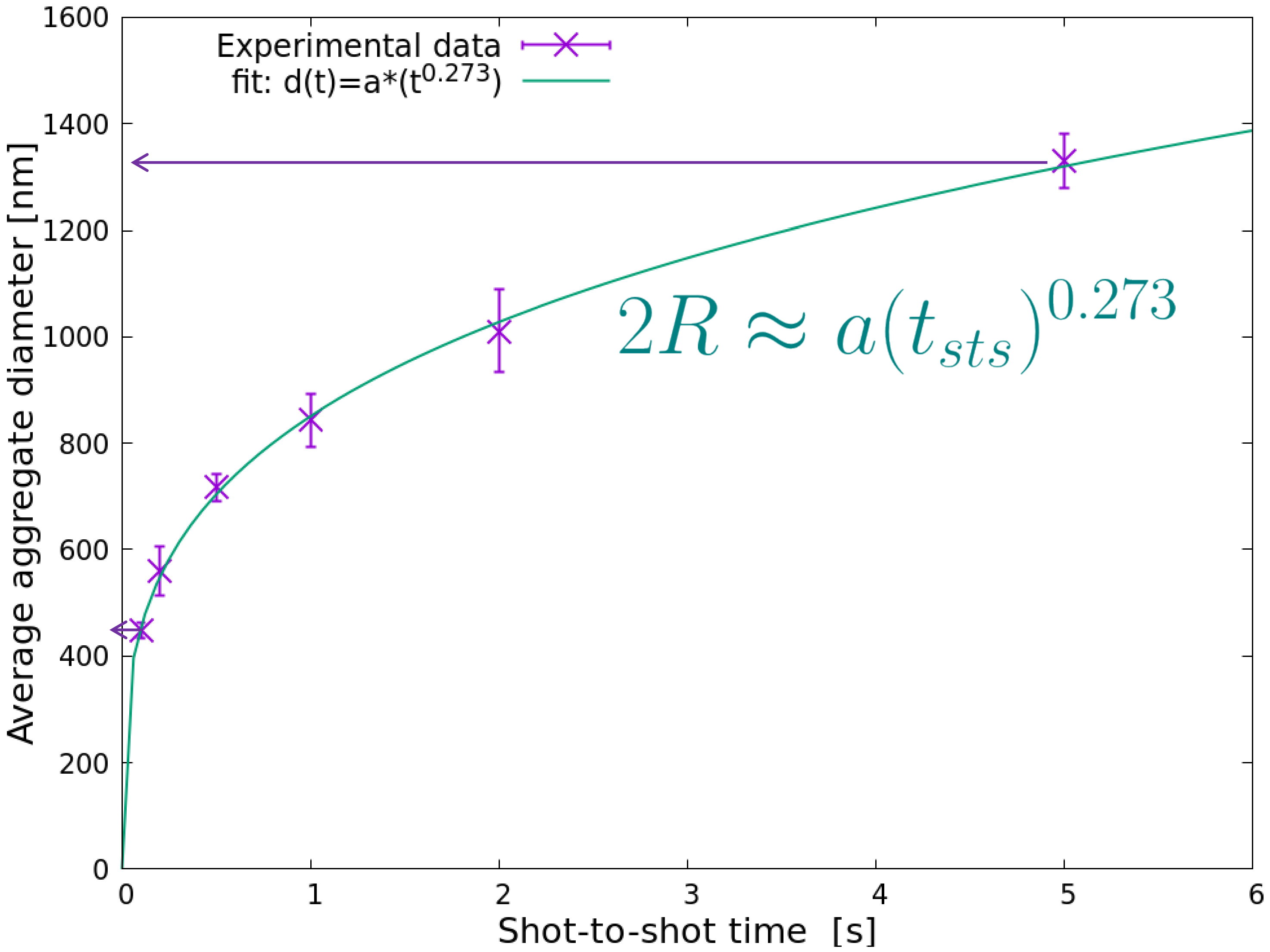
0.1s, 0.2s, 0.5s, 1s, 2s, 5s

Let’s test the “repetition rate” hypothesis…



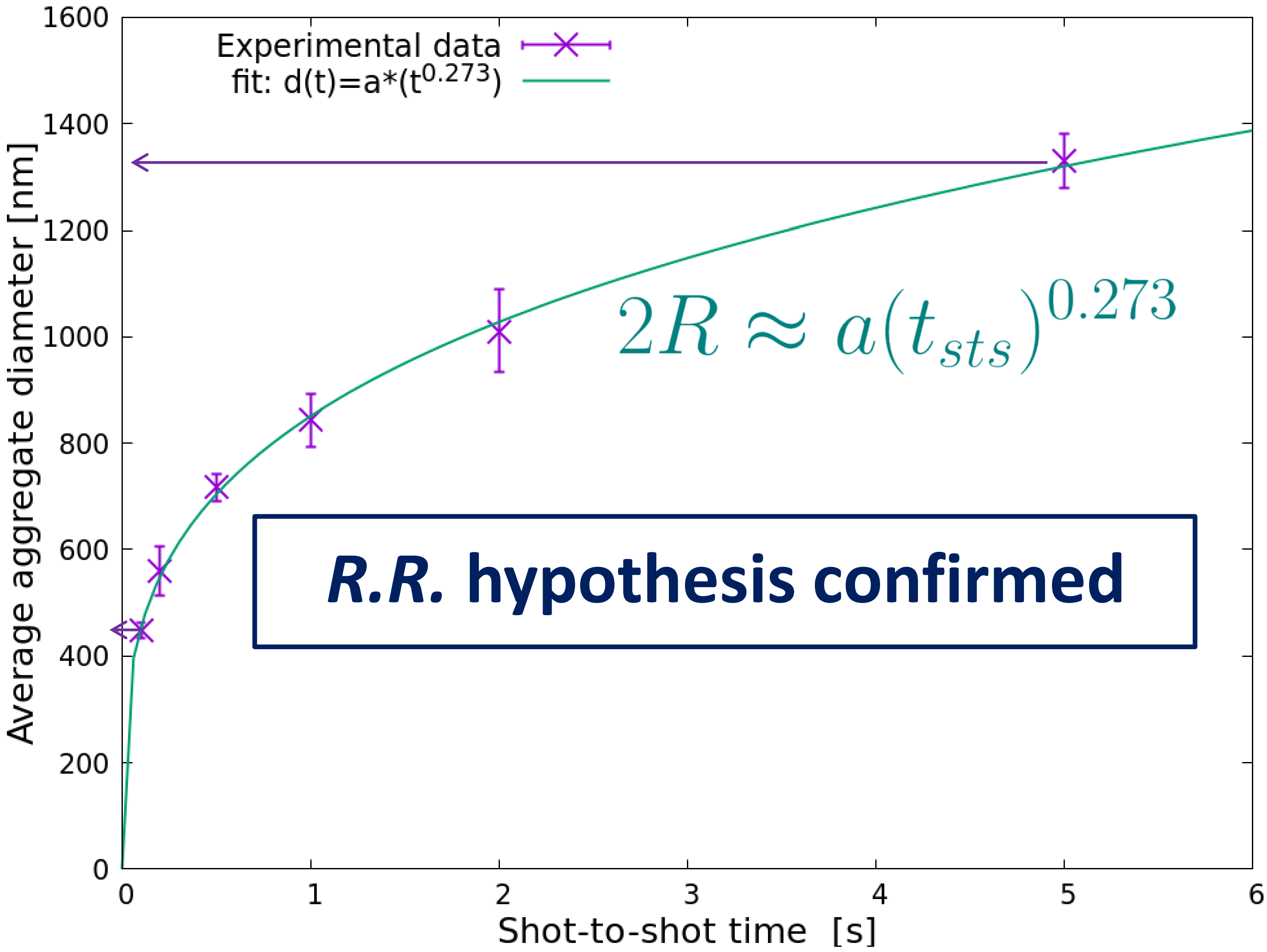
- Average size 2R significantly affected by shot-to-shot time

Let’s test the “repetition rate” hypothesis…



- ➢ Average size 2R significantly affected by shot-to-shot time
- ➢ **Experimental points nicely fitted by a power law!**

Let’s test the “repetition rate” hypothesis…



$$2R \approx a(t_{sts})^{0.273}$$

R.R. **hypothesis confirmed**

- Average size 2R significantly affected by shot-to-shot time
- **Experimental points nicely fitted by a power law!**

A summary:

We tried to answer to these questions:

How NPs aggregate and produce a foam?

How aggregation dynamics controls foam properties?

In the literature, mostly **2D-DLA**

2D diffusion-limited aggregation on substrate **cannot describe** foam growth

A **model** to describes **aggregation dynamics**

Aggregates generated by the nth shot are dragged by (n+1)th shock wave

Aggregation timescale is given by the shot-to-shot interval

Aggregates size depends on Rep. Rate and not on d_{ts}

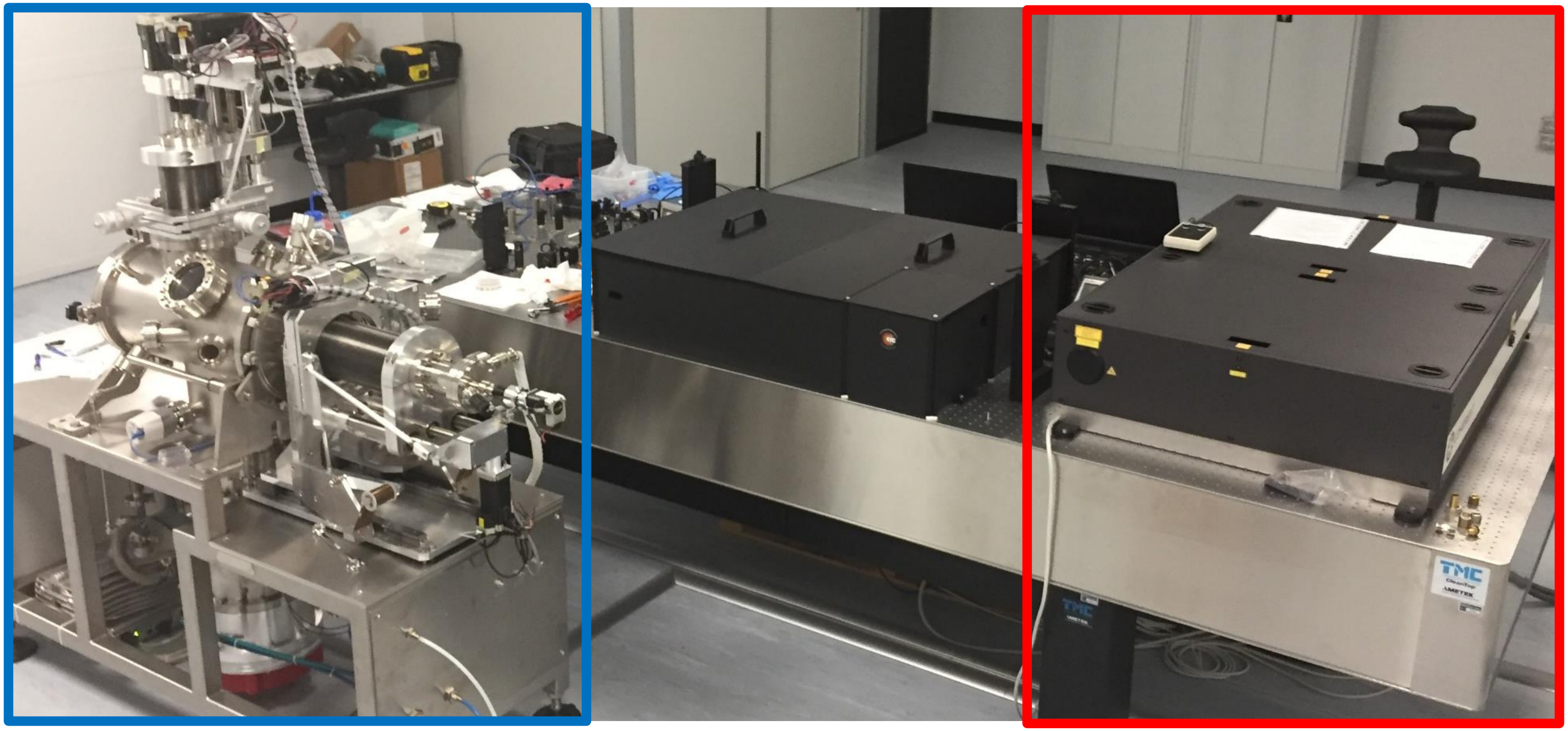
There's still **work to do**

Why **the exponent in 2R scaling** law is roughly half than expected?

Does the model work for **other materials** and **deposition conditions**?

… **even in different PLD regimes?**

A brand new fs-PLD system



fs-PLD interaction chamber

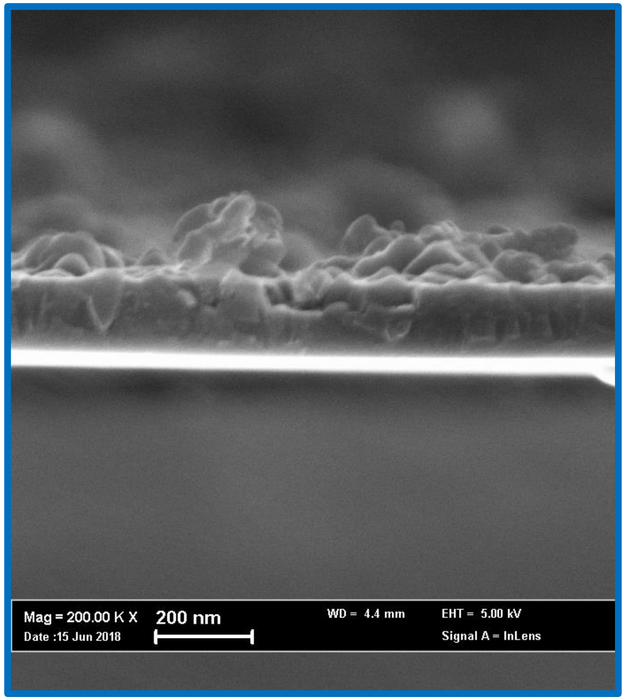
- ☐ PLD mode + Laser processing
- ☐ up to 4 targets
- ☐ Upstream + downstream pressure control
- ☐ Fast substrate heater
- ☐ Fully automated software

Coherent Astrella ™

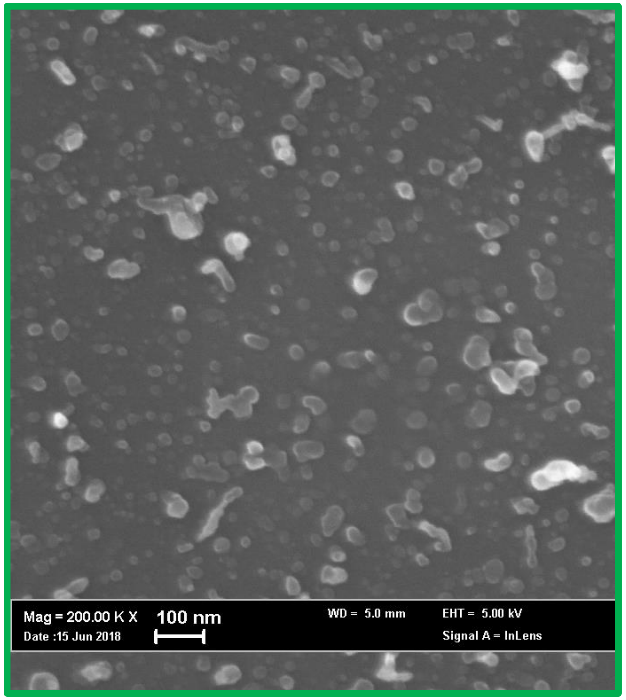
- ☐ Ti:Shappire, λ=800 nm
- ☐ **Ep > 5 mJ**
- ☐ **Pulse duration < 100 fs**
- ☐ Peak Power > 50 GW
- ☐ Rep Rate = 1000 Hz

fs-PLD of carbon materials

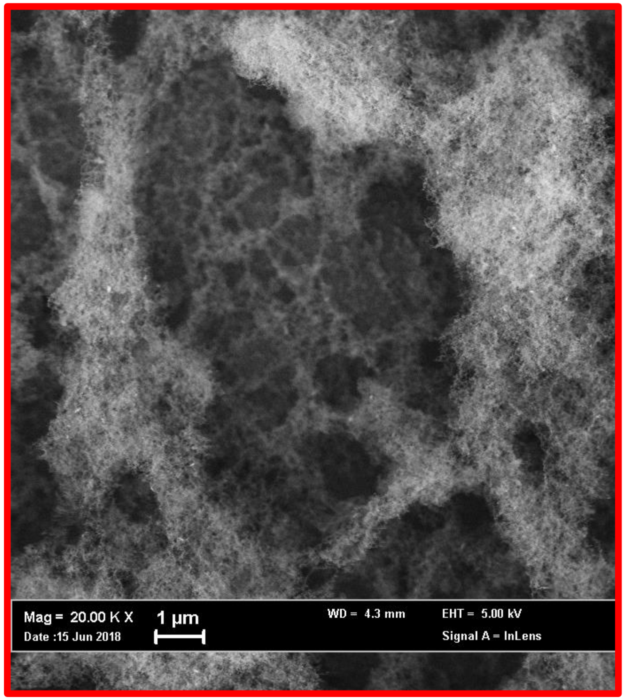
Compact film

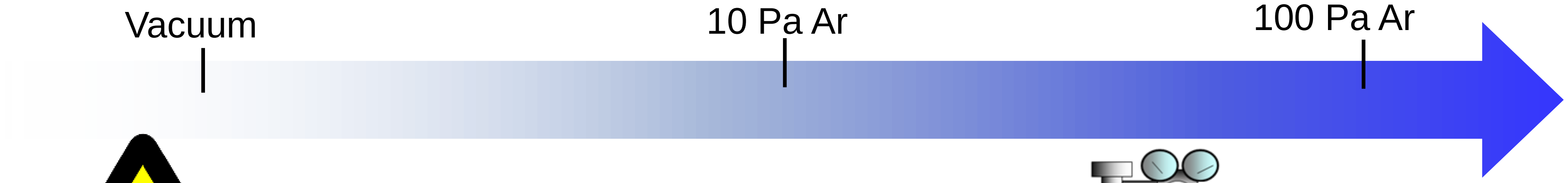


Nanoparticles



Carbon foam





Work in progress

Gas pressure

Argon

Acknowledgment

The “ENSURE” team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….Thank you for your attention!

More info on our website

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Exploring the **N**ew **S**cience and engineering unveiled by
Ultraintense ultrashort **R**adiation interaction with matt**E**r

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