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**COLA 2024**  
*17<sup>th</sup> International  
Conference on Laser  
Ablation*

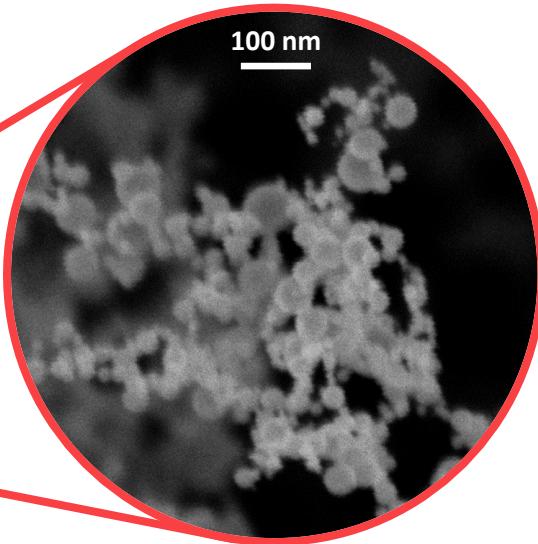
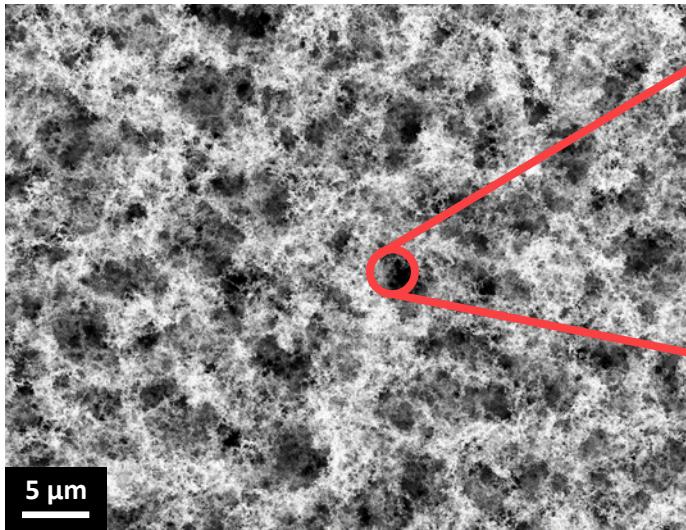
# Femtosecond pulsed laser deposition as a universal tool for nanofoam synthesis

**Davide Orecchia,**  
Alessandro Maffini,  
Alessandro Milani,  
Margherita Zavelani-Rossi  
and Matteo Passoni



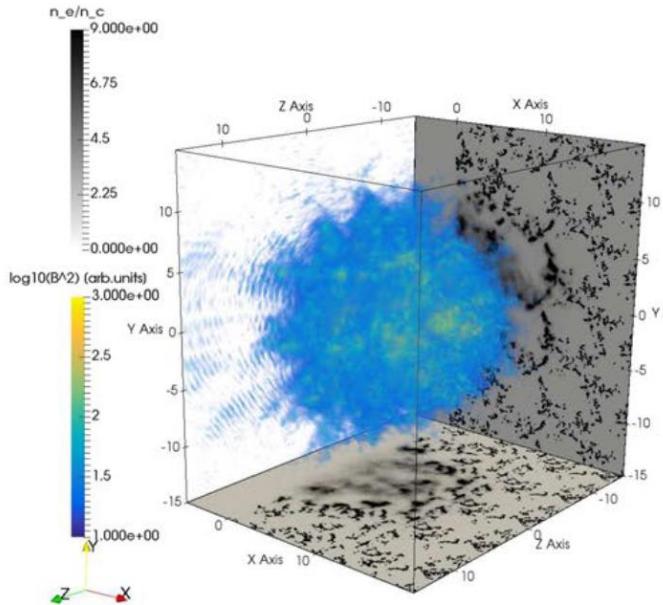
Hersonissos – 4 oct 2024

# Nanostructured materials and nanofoams



Disordered **web-like** structures  
Substantial **surface area**  
Density as low as a **few mg/cm<sup>3</sup>**

- Supercapacitors
- Catalysis
- Gas sensing
- High intensity **laser-matter interaction**



**Efficient**  
laser energy  
absorption

▼  
**Nanostructure effect**

# Nanostructured materials synthesis

- Nanostructure properties **control**
- **Flexibility**



**Chemical techniques**

Top-down

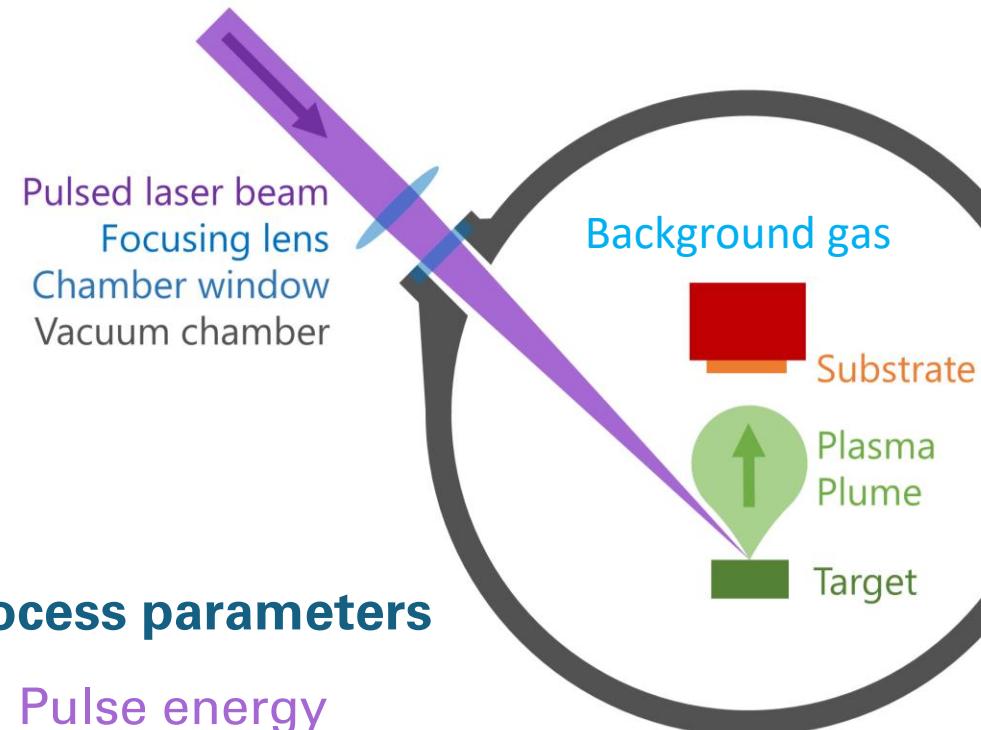


**Bottom-up**



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## Pulsed Laser Deposition (PLD)



### Process parameters

- Pulse energy
- Target-substrate distance
- Background gas pressure
- Substrate

**Laser pulse duration**

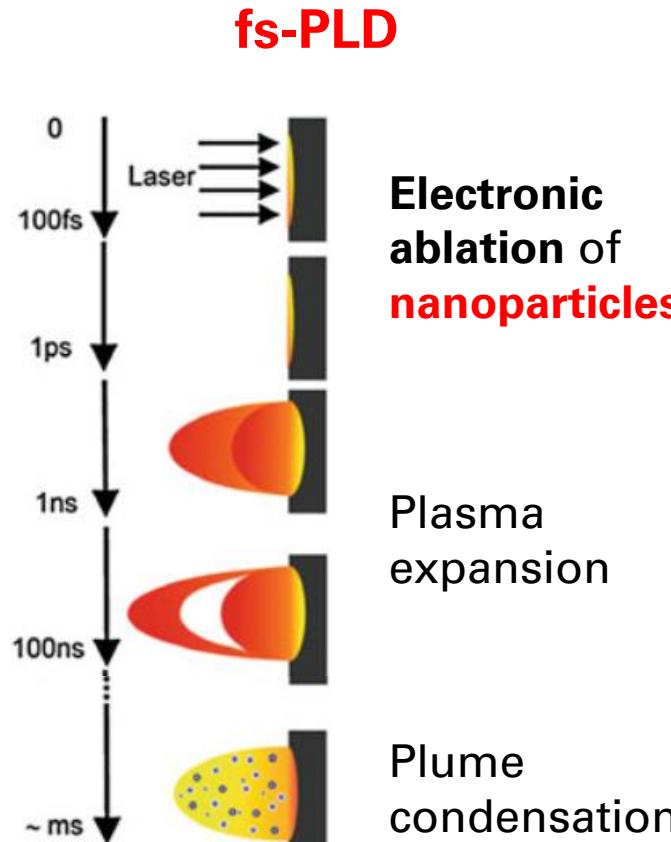
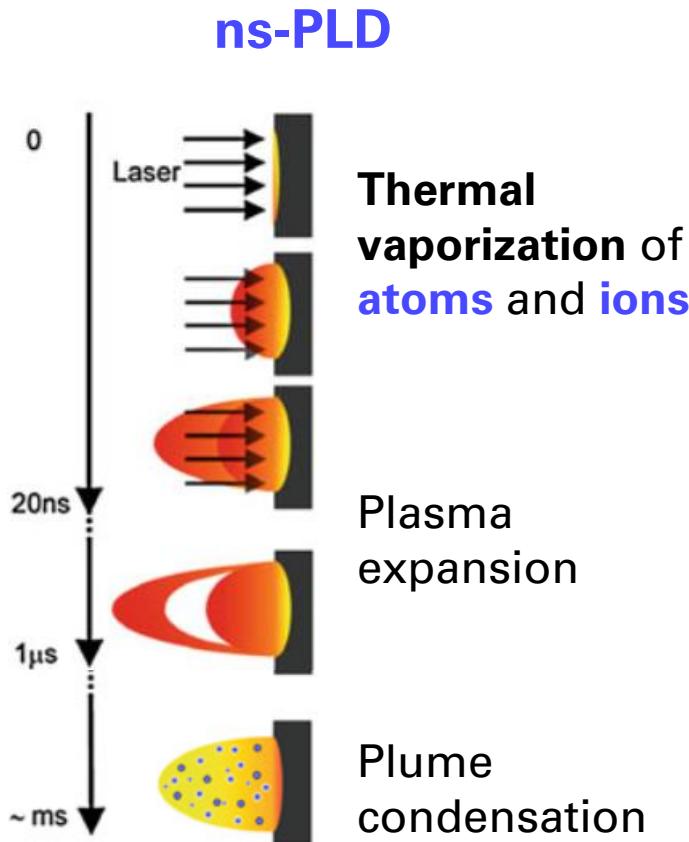


**Introduction**

2

# ns-PLD and fs-PLD techniques

Different ablation regimes



- ns-PLD**
- Well-established
  - Better thickness uniformity
  - Atom-by-atom deposition
  - Gas-mediated nanoparticle synthesis
- fs-PLD**
- Direct nanoparticle synthesis
  - High ablation efficiency
  - Technically challenging
  - Great flexibility in material choice

Harilal S.S. et al., in "Laser-induced breakdown spectroscopy", ch. 6, 2014

# Outline and methods

1

Comparative investigation of carbon nanofoams through ns and fs-PLD

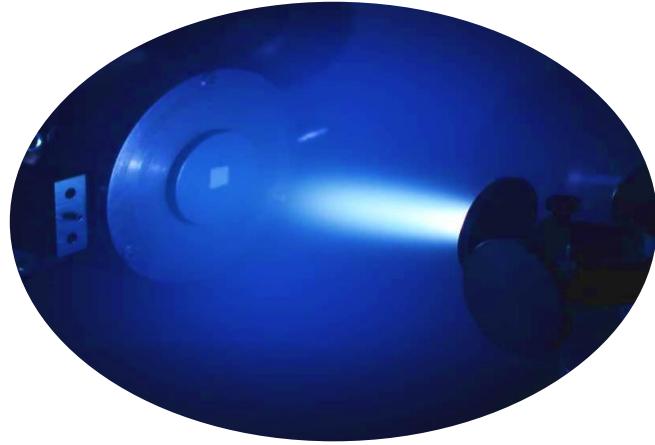
ns-PLD



fs-PLD



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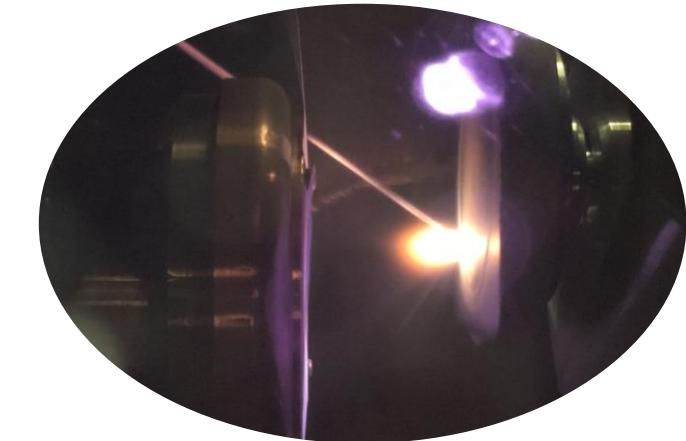


ns-PLD

- Nd:YAG (SH @ **532 nm**)
- **5 – 7 ns** pulse duration
- 100 – 600 mJ per pulse
- **100 – 600 mJ/cm<sup>2</sup>**
- 10 Hz

fs-PLD

- Ti:Sapphire (**800 nm**)
- **~80 fs** pulse duration
- 1 – 4 mJ per pulse
- **100 – 600 mJ/cm<sup>2</sup>**
- 1 kHz



Outline & methods

# Outline and methods

1

# Comparative investigation of carbon nanofoams through ns and fs-PLD

ns-PLD



# fs-PLD

2

# fs-PLD synthesis of different elements nanofoams



# Investigate the **deposition and** **growth process**

3

# Development of **application-tailored** nanostructured materials

Laser-driven  
**particle acceleration**

Inertial confinement  
fusion (**ICF**)

**Proton-boron** fusion

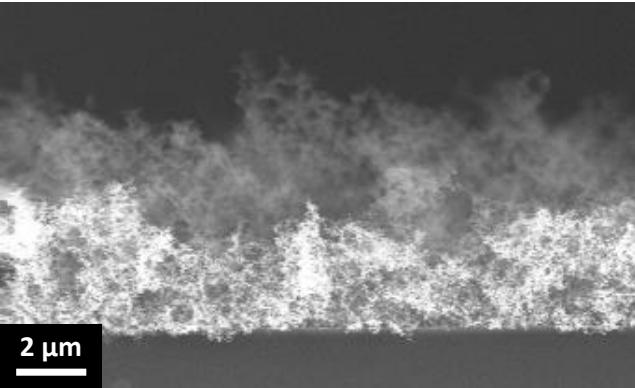
# Bone tissue engineering (BTE)



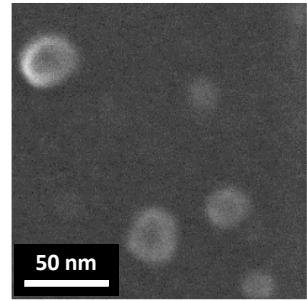
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# Outline & methods

# Carbon nanofoams



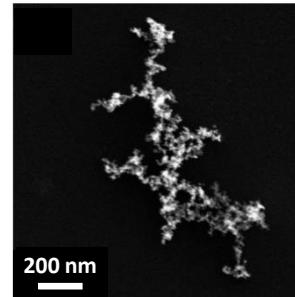
Argon background pressure



Nanoparticle production

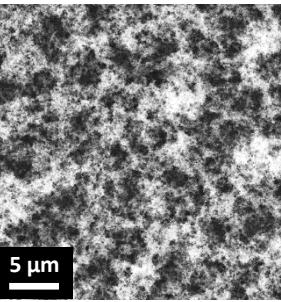
2

In-flight interaction and fractal aggregate formation



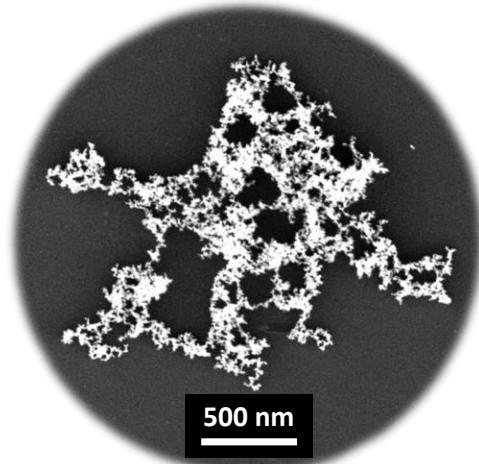
3

Deposition on the substrate and foam growth



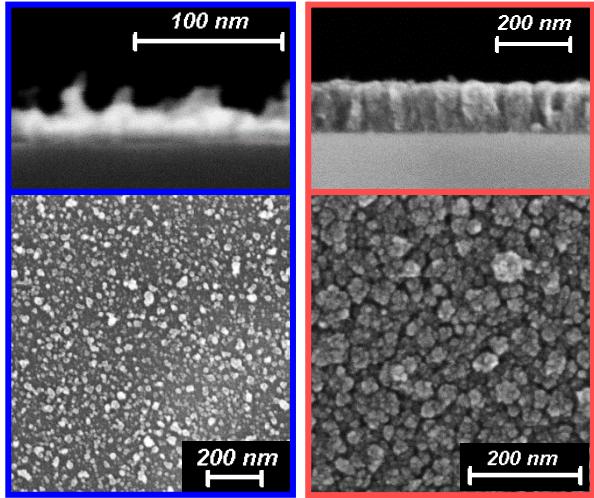
ns-PLD  
fs-PLD

Fractal aggregates study

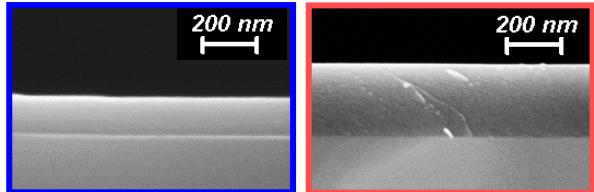


# Density and morphology

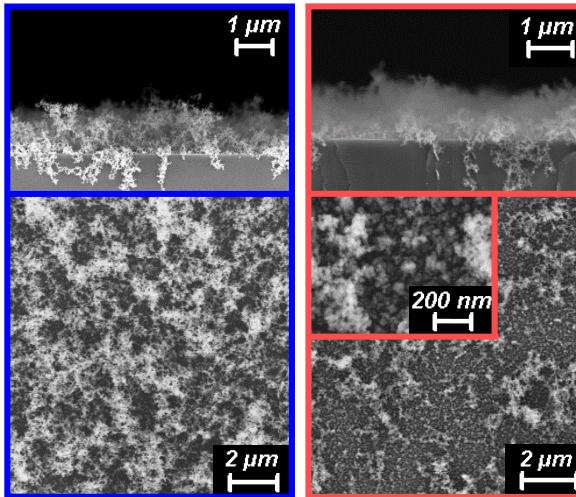
25 Pa



< 10<sup>-3</sup> Pa

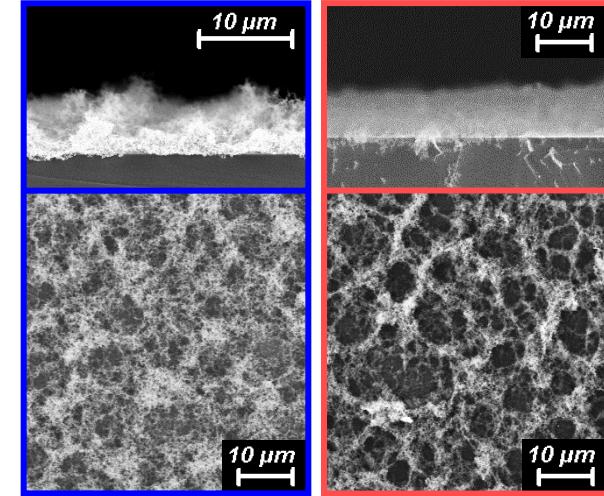


50 Pa

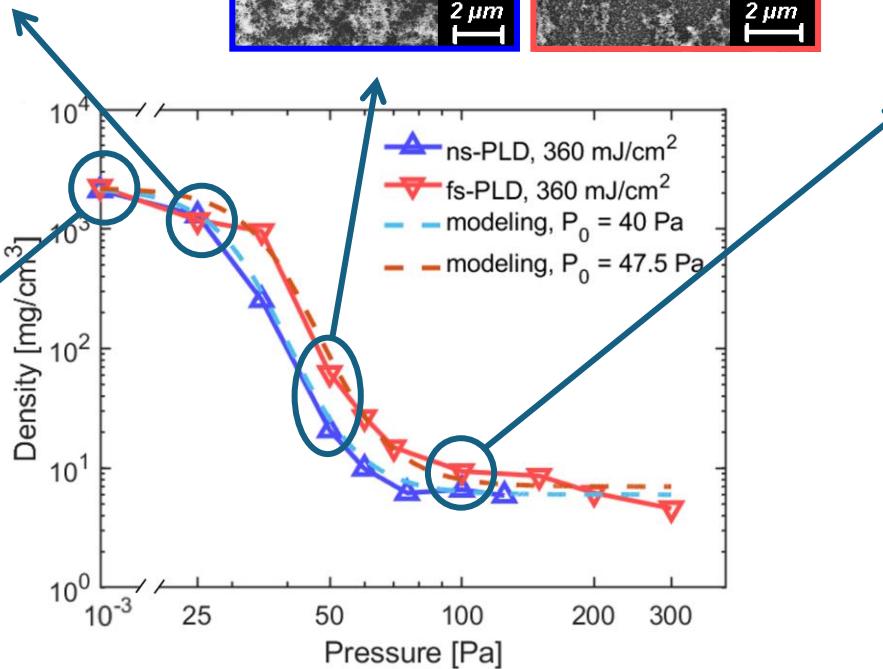


Mixed morphology  
for fs-PLD

100 Pa



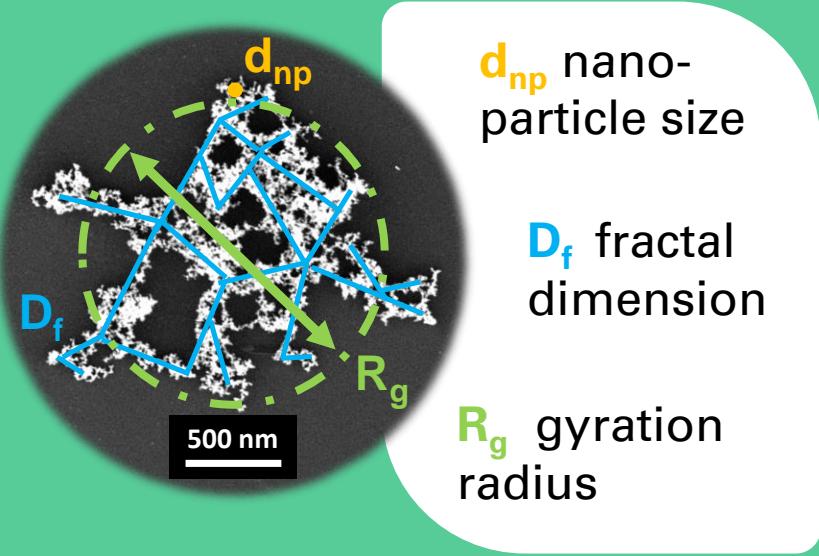
Analogous density  
evolution



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Carbon  
nanofoams

# Fractal aggregate study



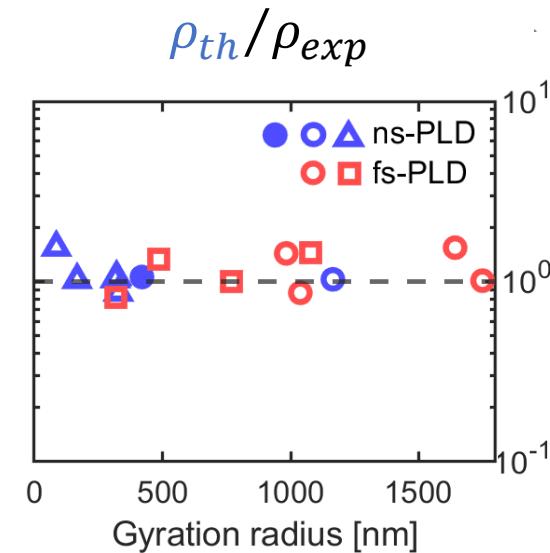
$$\rho_{th} \approx k \rho_{np} \left( \frac{d_{np}}{2R_g} \right)^{3-D_f}$$



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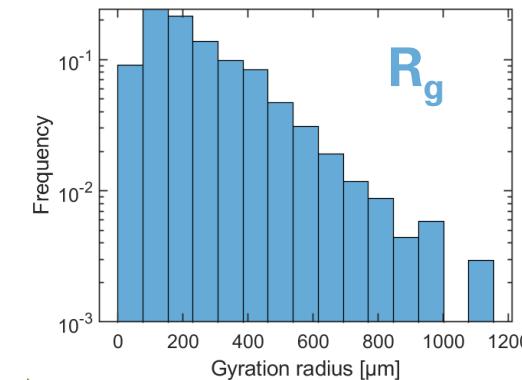
|  $d_{np} \approx 8 \text{ nm} / 10 \text{ nm}$

|  $D_f \approx 2$  in all conditions

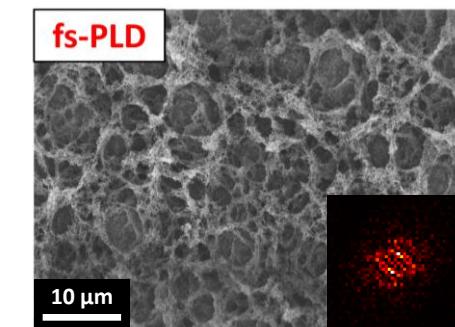
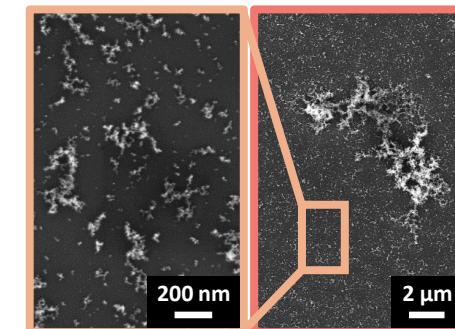
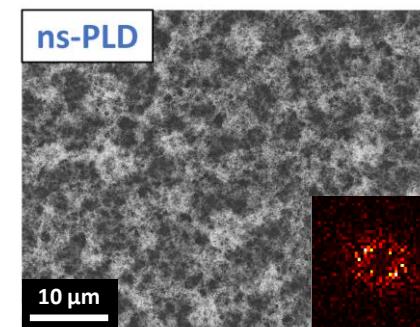
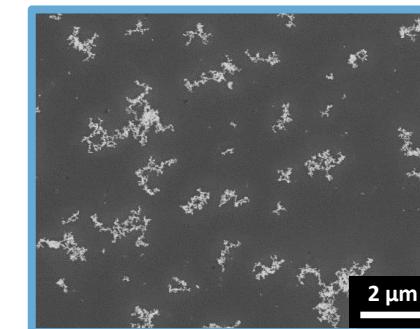
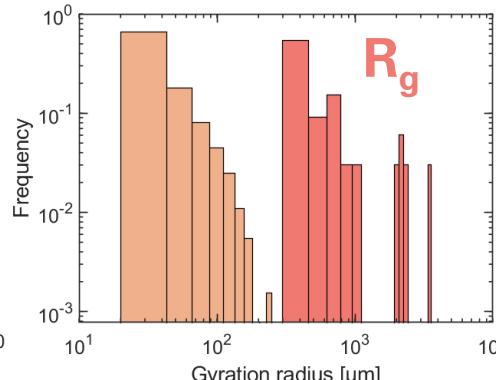


| Great agreement

ns-PLD

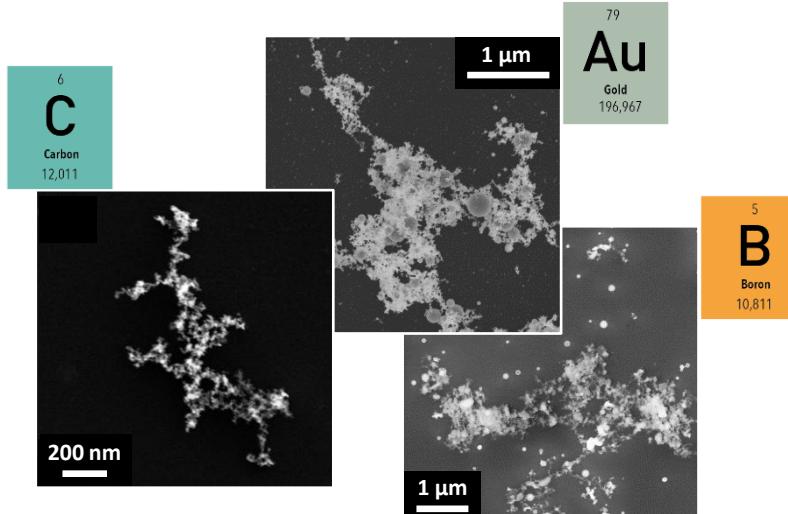
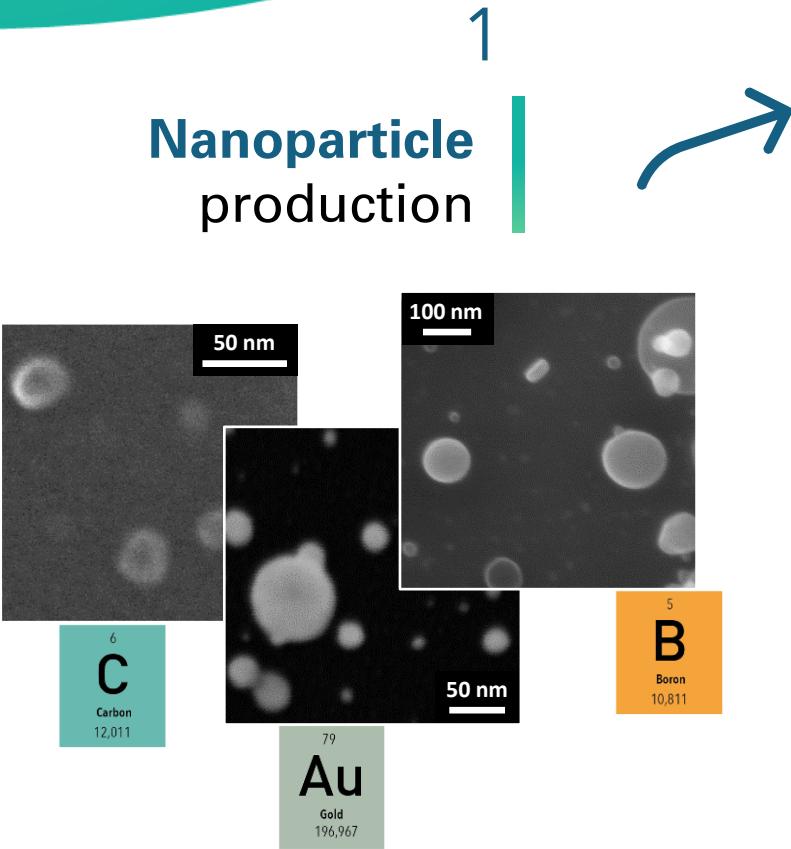


fs-PLD



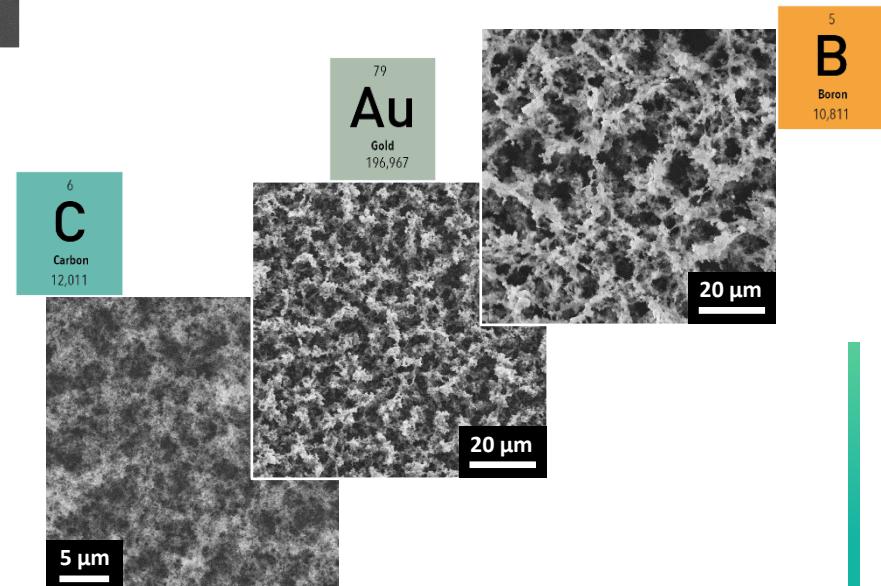
Carbon  
nanofoams

# fs-PLD nanofoams synthesis

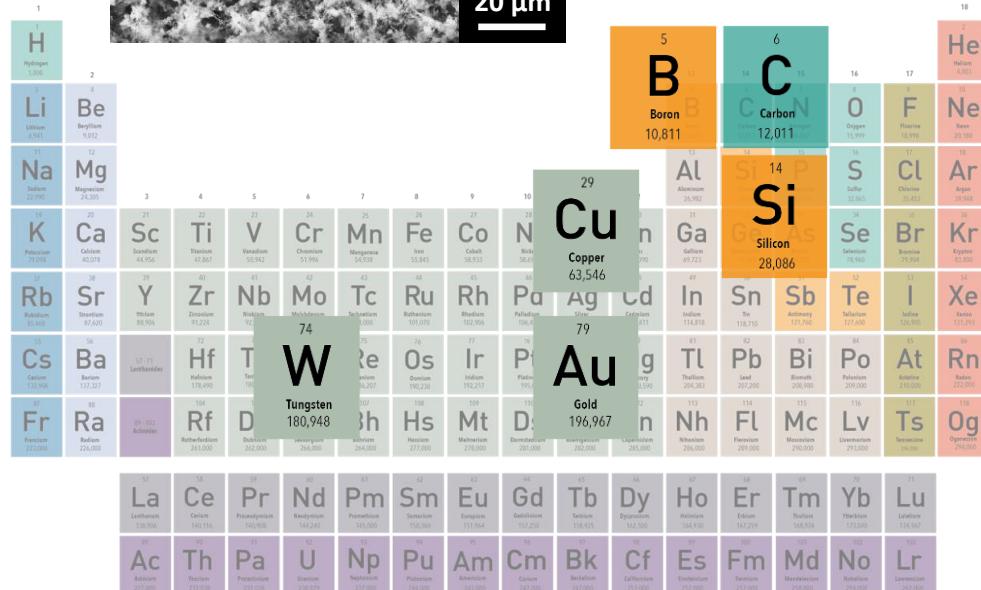
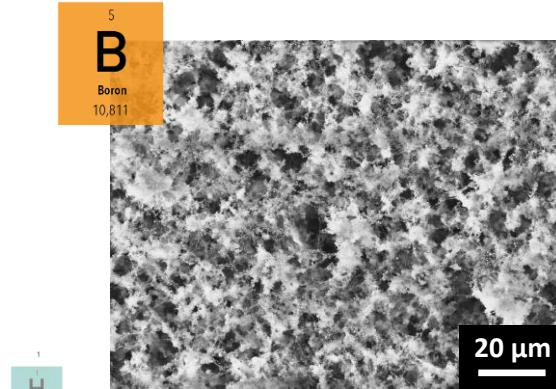
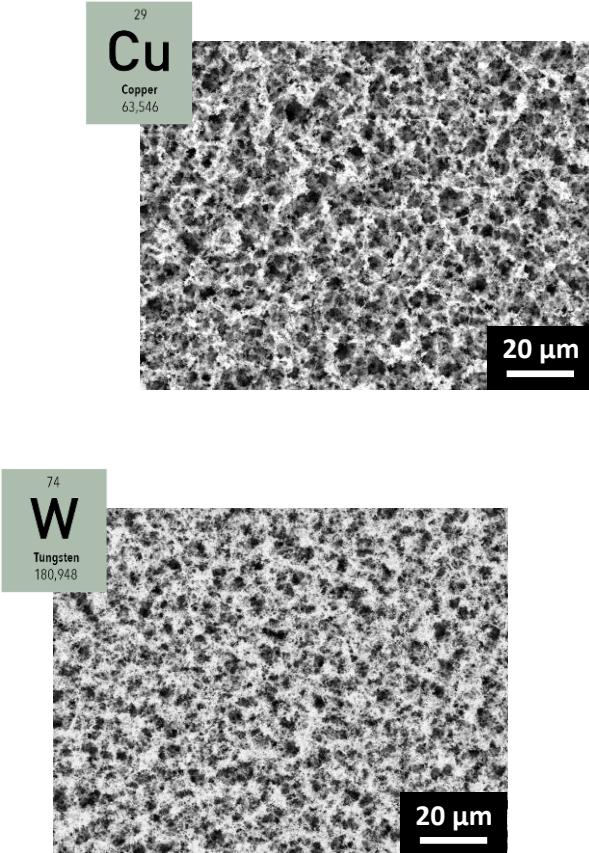


3

Deposition on the substrate and foam growth

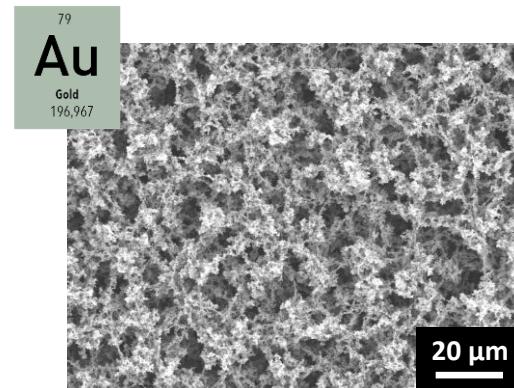
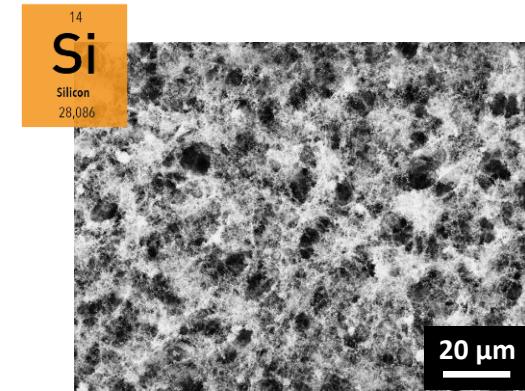
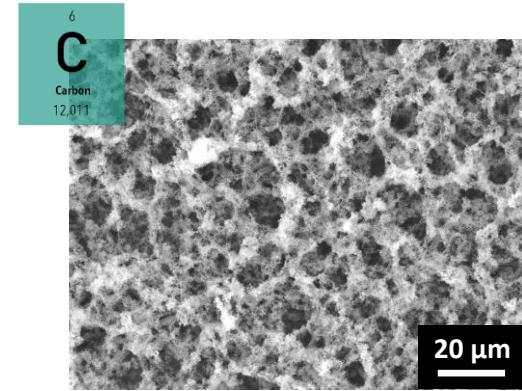


# Versatile nanofoam production through fs-PLD

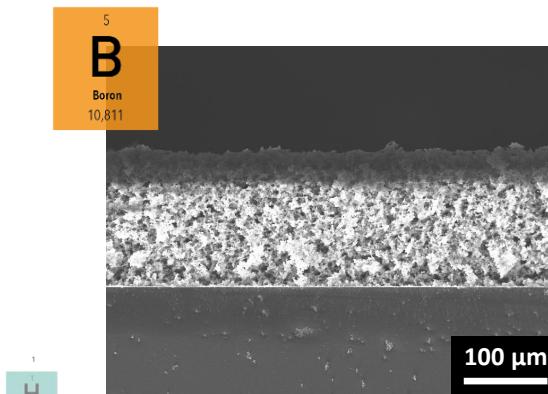
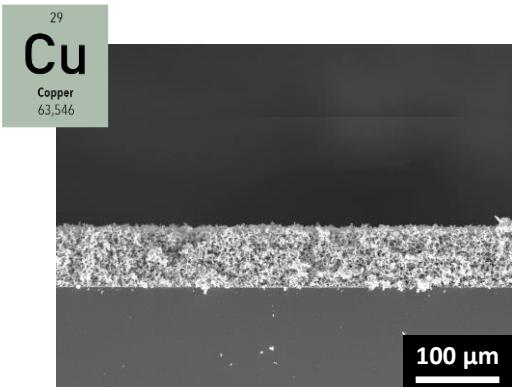
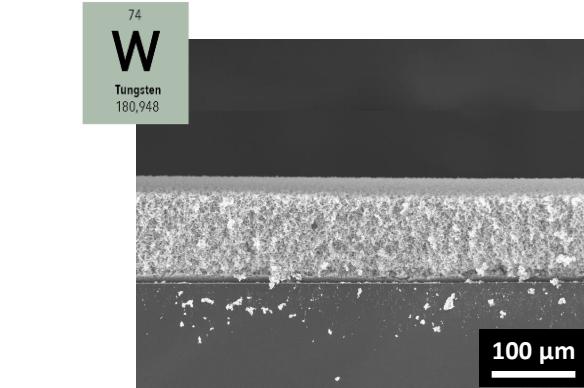


Same ablation  
fluence  $\sim 0.1 \text{ J/cm}^2$

Analogous  
morphology



# Versatile nanofoam production through fs-PLD

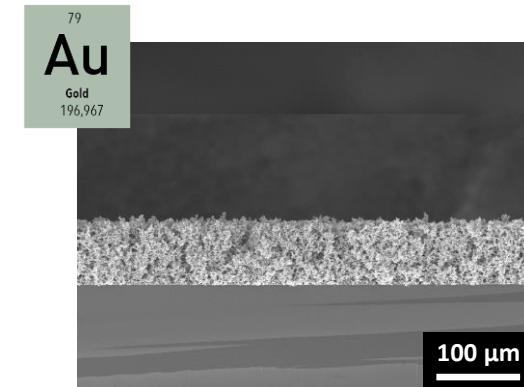
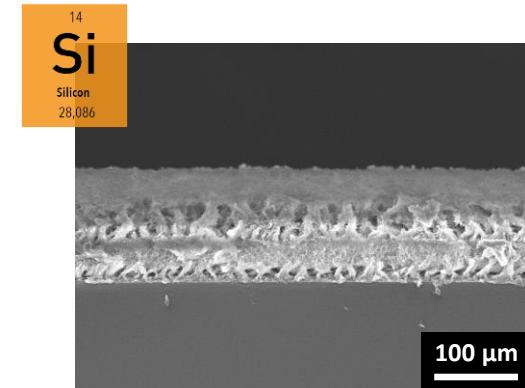
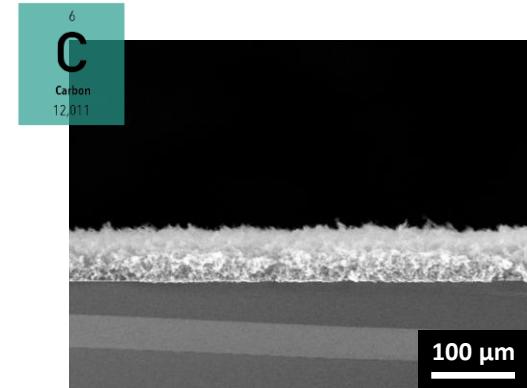


The periodic table highlights several elements used in the study:

- Boron (B):** Atomic number 5, mass 10.811.
- Carbon (C):** Atomic number 6, mass 12.011.
- Tungsten (W):** Atomic number 74, mass 180.948.
- Copper (Cu):** Atomic number 29, mass 63.546.
- Silicon (Si):** Atomic number 14, mass 28.086.
- Gold (Au):** Atomic number 79, mass 196.967.

Same ablation  
fluence  $\sim 0.1 \text{ J/cm}^2$

Analogous  
morphology



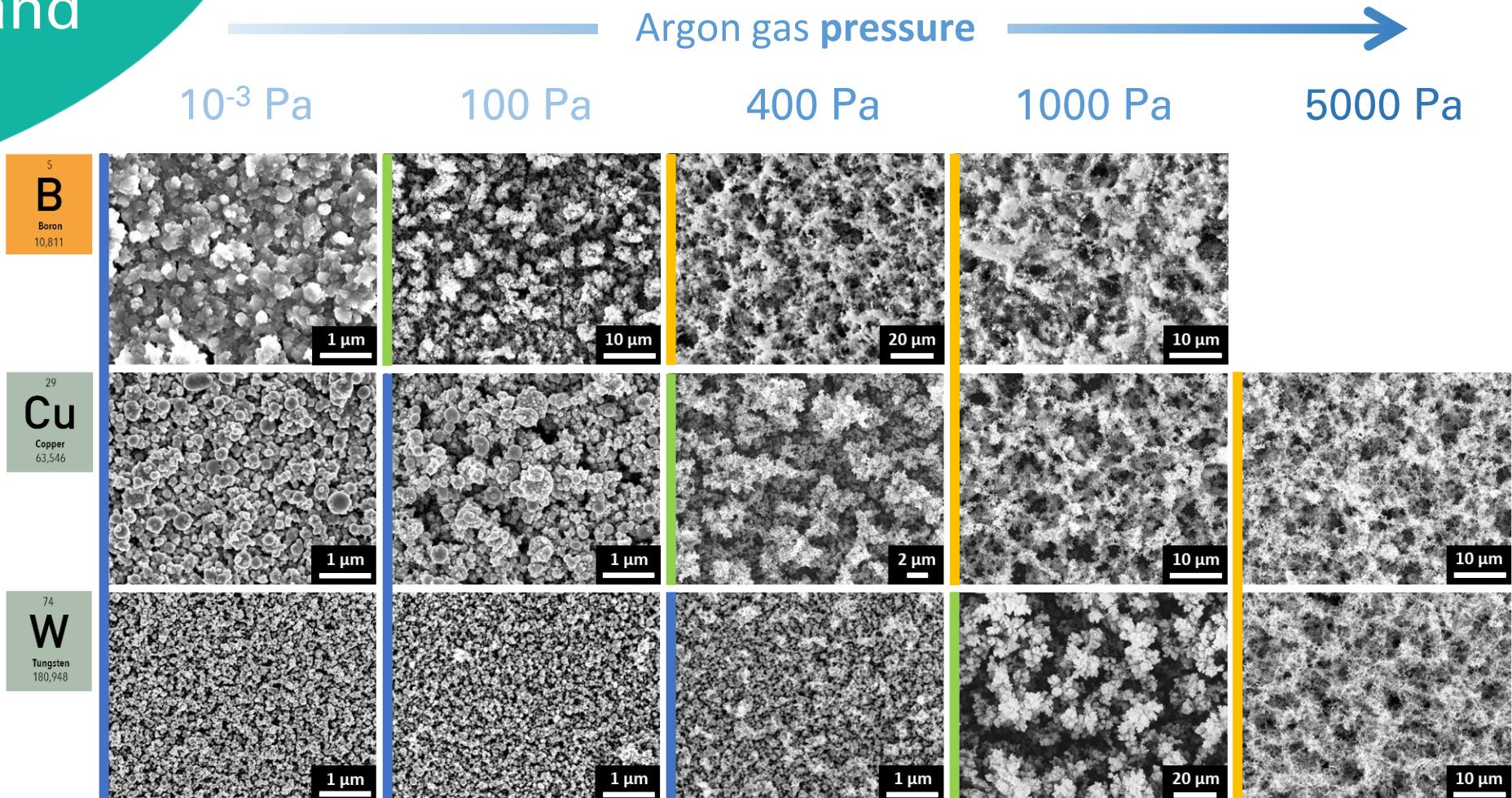
Exceeding 100  
μm thickness

# Morphology and gas pressure

Same morphology evolution



Different pressure thresholds



Nanoparticle-assembled  
compact film

Tree-like  
nanostructured film

Web-like  
nanofoam

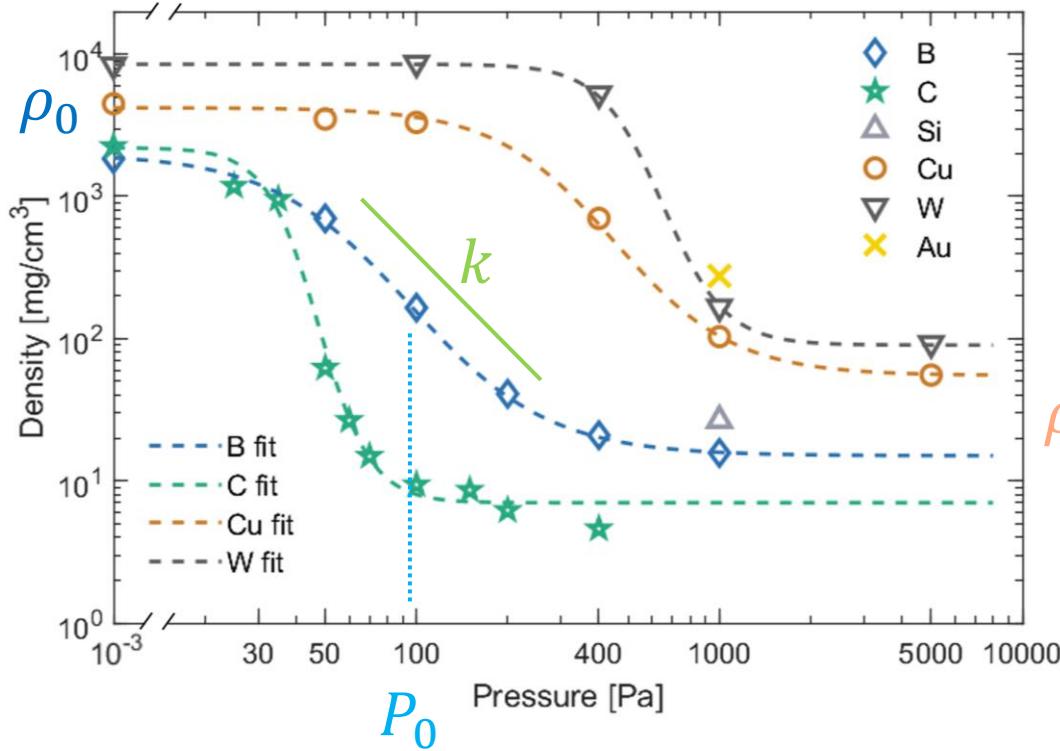


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# Average density and gas pressure

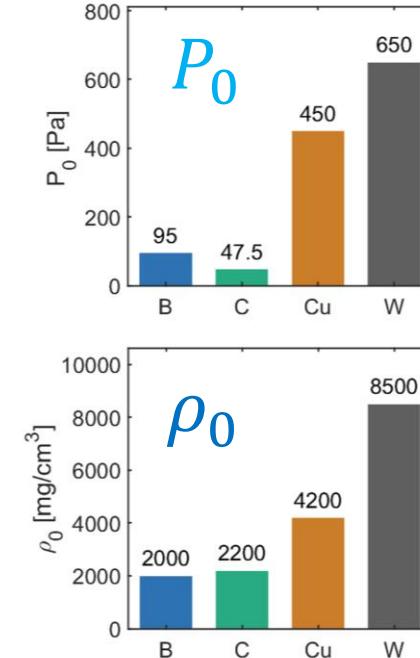
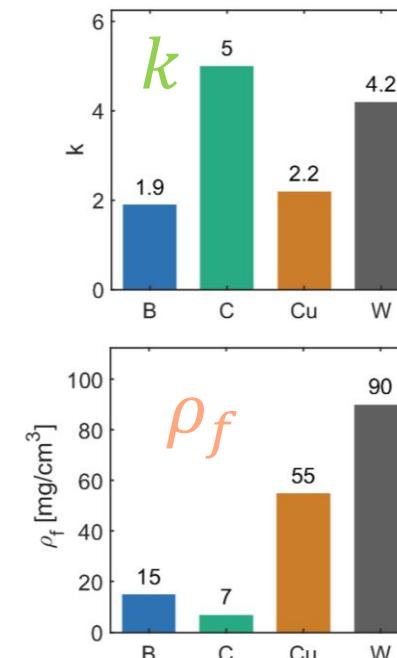
$$\rho(P) = \rho_0 \left( \frac{\rho_f}{\rho_0} \right)^k \left[ \frac{P^k}{P_0^k + P_0^k} \right]$$



$$\gamma \propto \frac{P}{R\rho v_t}$$

$$\dot{v} = -\gamma v$$

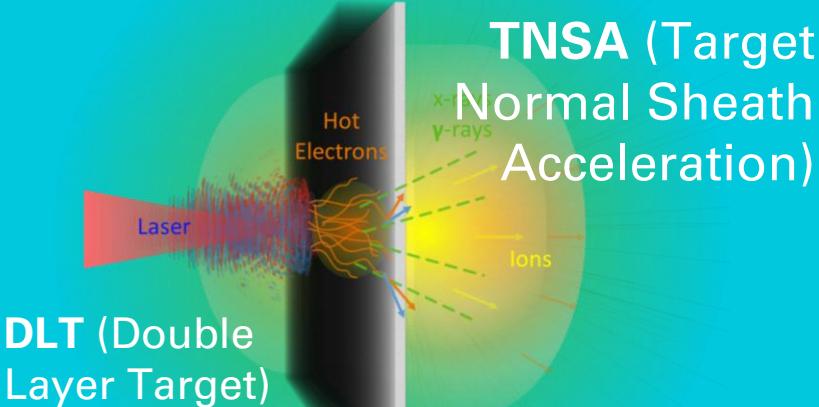
Dimension, energetics  
and density of ablated  
nanoparticles



Relative slowing efficiency of the background gas

Nanofoam average density and morphology

# Laser-driven particle acceleration



DLT (Double Layer Target)

Near-critical  
carbon  
nanofoam

- $\sim 6 \text{ mg/cm}^3$
- $9 - 54 \mu\text{m}$

Micrometric  
solid Al  
substrate

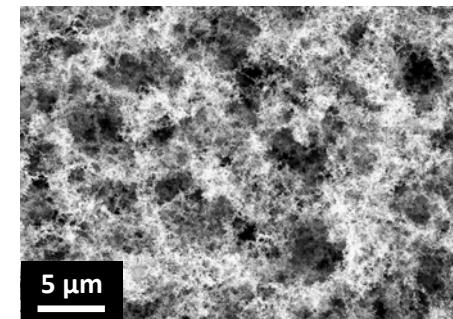
- solid density
- $0.75 - 13 \mu\text{m}$



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## VEGA 3

- **20 J**
- **30 fs**
- $\lambda = 800 \text{ nm}$
- $12 \mu\text{m}$  spot size
- **$10^{20} \text{ W/cm}^2$**
- $5 \times 10^{-12}$  contrast

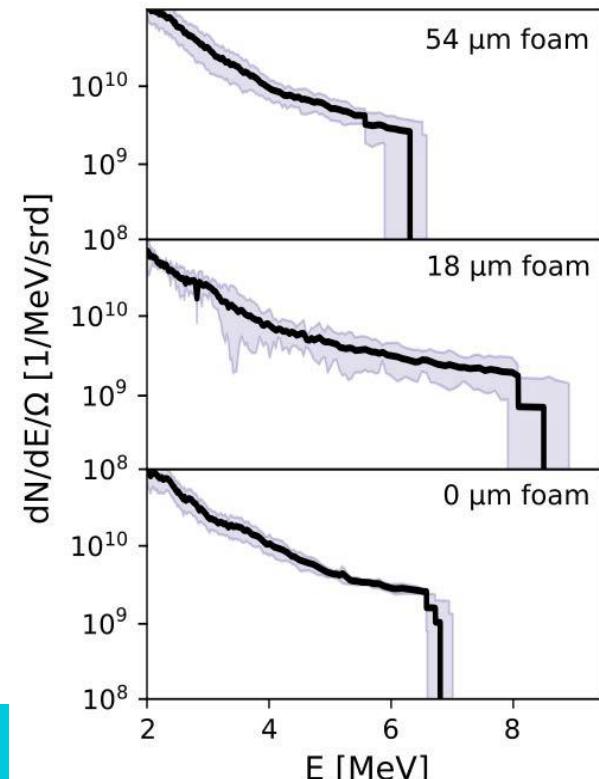


Low-density  
carbon  
nanofoam

Proton energy  
enhancement in DLTs



## Proton spectrum

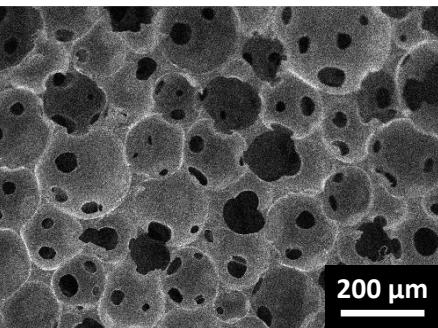
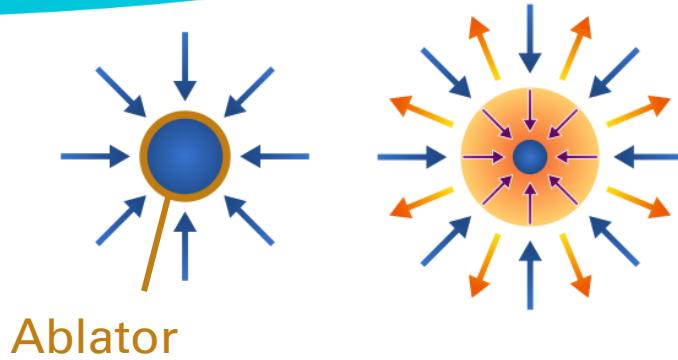


High-intensity  
laser applications

# Carbon nanofoams as inertial confinement fusion ablator

ABC

ENEA



1

Laser **absorption** enhancement

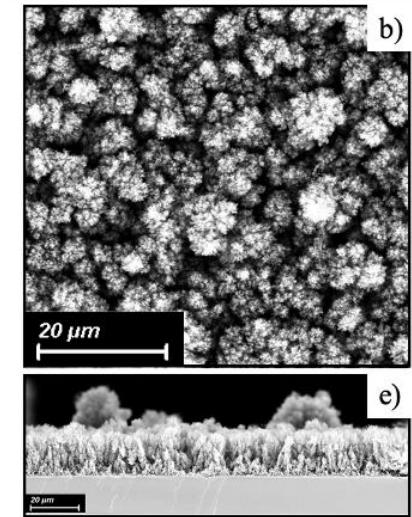
2

Laser **inhomogeneity** smoothing

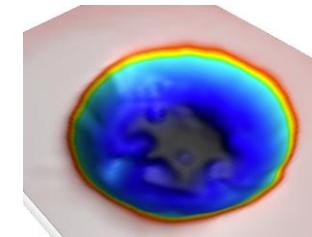
- 40 J
- 3 ns
- $\lambda = 1054 \text{ nm}$
- 100  $\mu\text{m}$  spot size
- $10^{14}\text{-}10^{15} \text{ W/cm}^2$



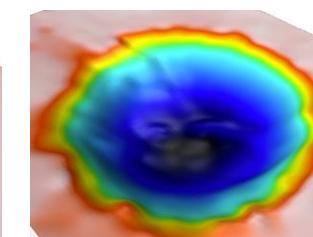
Significant **ablation loading** increase in **tree-like** films



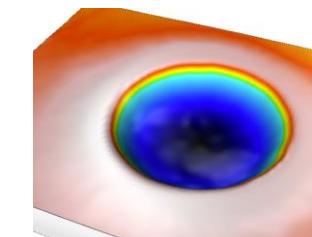
Foam on Al



Treelike on Al



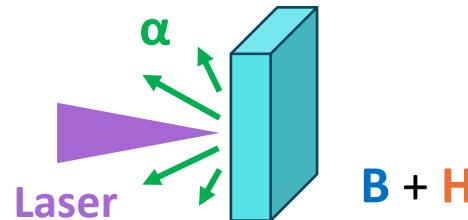
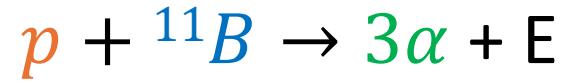
Bare Al



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# Boron nanofoams for proton-boron fusion



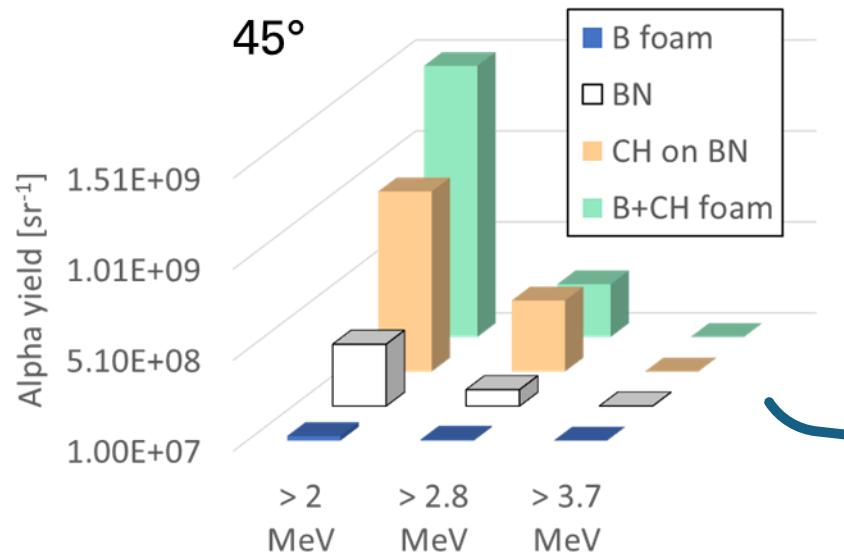
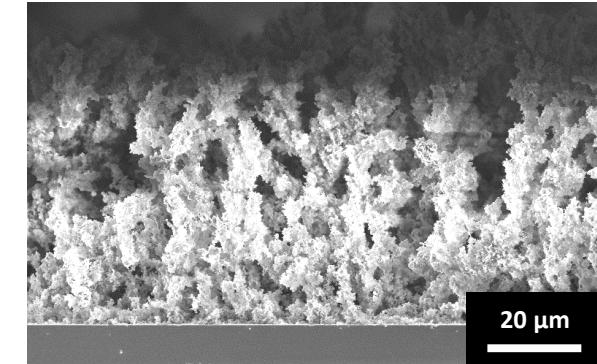
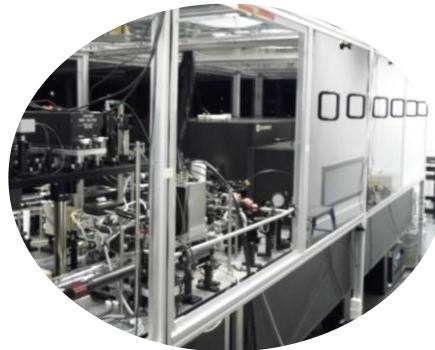
Hydrogen-enriched  
boron nanofoams



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## TARANIS

- 10 J
- 800 fs
- $\lambda = 1053 \text{ nm}$
- 5.5  $\mu\text{m}$  spot size
- $10^{19} \text{ W/cm}^2$
- $5 \times 10^{-7}$  contrast



fs-PLD codeposition with  
a boron/HDPE target

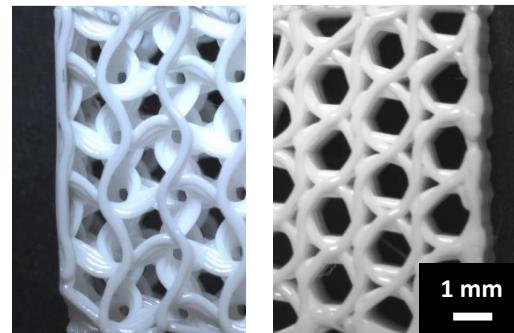
H/B ratio of 1.5  
20% C, 10% O

Substantial alpha  
yield enhancement

High-intensity  
laser applications

# Nanostructured hydroxyapatite coating for BTE

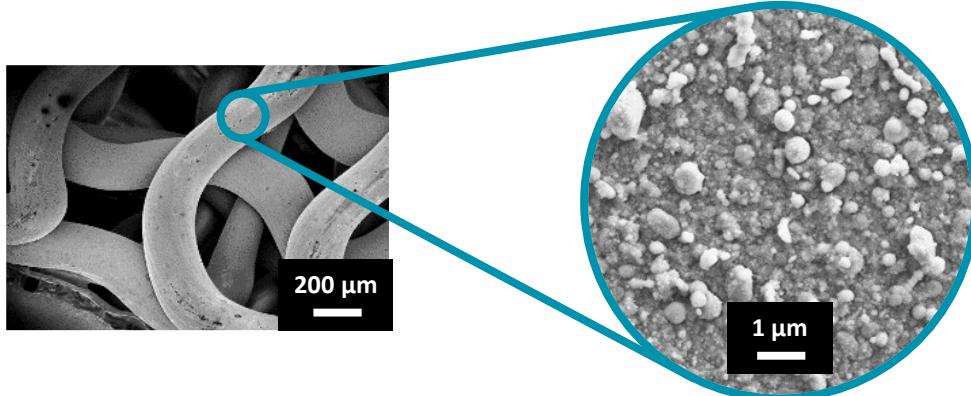
➤ **Mimic** different bone tissues



**3D** printed  
PLA **scaffold**

(Bone Tissue Engineering)

**Roughness, morphology**  
and chemical  
**composition** control



fs-PLD of **bovine**  
**bone** target

**Biogenic**  
hydroxyapatite  
**nanostructured**  
coating

**Stoichiometric** transfer  
*+ trace elements*

**Promising** 10 days  
**stability** in phosphate  
buffered saline solution



**Bone cells** growth  
investigation **planned**

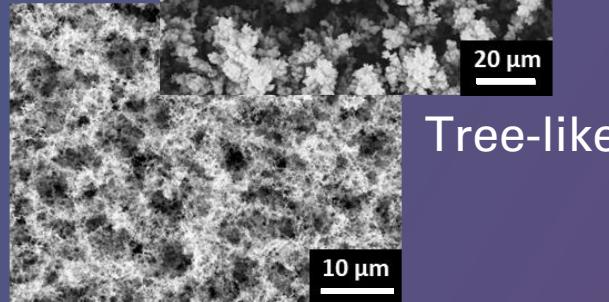
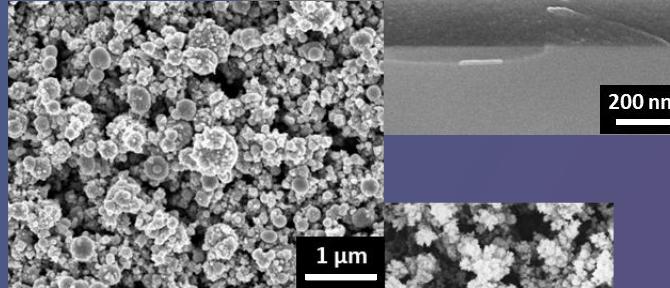


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# Conclusions

Nanoparticle-assembled



Nanofoam



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H	C	N	O	F	Ne
Li	Si	P	S	Cl	Ar
Be	Al	As	Se	Br	Kr
B	Si	Ge	Te	I	Xe
Na	Ca	Sc	V	Cr	Mn
Mg	Fe	Ti	Ru	Rh	Pd
Al	Co	Ni	Cu	Zn	Ga
Si	Fe	Cr	Fe	As	Se
P	Co	Mo	Fe	Se	Br
S	Ni	Tc	Fe	Br	Kr
Cl	Fe	W	Re	Os	Ir
Ar	Fe	Re	Os	Au	Hg
Kr	Fe	Ir	Pt	Pt	Pt
Xe	Fe	Os	Pd	Pd	Pd
Ca	Fe	Pd	Pd	Pd	Pd
Sr	Fe	Pd	Pd	Pd	Pd
Y	Fe	Pd	Pd	Pd	Pd
Zr	Fe	Pd	Pd	Pd	Pd
Nb	Fe	Pd	Pd	Pd	Pd
Mo	Fe	Pd	Pd	Pd	Pd
Tc	Fe	Pd	Pd	Pd	Pd
Ru	Fe	Pd	Pd	Pd	Pd
Rh	Fe	Pd	Pd	Pd	Pd
Pd	Fe	Pd	Pd	Pd	Pd
Ag	Fe	Pd	Pd	Pd	Pd
Cd	Fe	Pd	Pd	Pd	Pd
In	Fe	Pd	Pd	Pd	Pd
Sn	Fe	Pd	Pd	Pd	Pd
Sb	Fe	Pd	Pd	Pd	Pd
Te	Fe	Pd	Pd	Pd	Pd
I	Fe	Pd	Pd	Pd	Pd
Xe	Fe	Pd	Pd	Pd	Pd
La	Fe	Pd	Pd	Pd	Pd
Ce	Fe	Pd	Pd	Pd	Pd
Pr	Fe	Pd	Pd	Pd	Pd
Nd	Fe	Pd	Pd	Pd	Pd
Pm	Fe	Pd	Pd	Pd	Pd
Eu	Fe	Pd	Pd	Pd	Pd
Gd	Fe	Pd	Pd	Pd	Pd
Tb	Fe	Pd	Pd	Pd	Pd
Dy	Fe	Pd	Pd	Pd	Pd
Ho	Fe	Pd	Pd	Pd	Pd
Er	Fe	Pd	Pd	Pd	Pd
Tm	Fe	Pd	Pd	Pd	Pd
Yb	Fe	Pd	Pd	Pd	Pd
Lu	Fe	Pd	Pd	Pd	Pd
Ac	Fe	Pd	Pd	Pd	Pd
Th	Fe	Pd	Pd	Pd	Pd
Pa	Fe	Pd	Pd	Pd	Pd
U	Fe	Pd	Pd	Pd	Pd
Np	Fe	Pd	Pd	Pd	Pd
Pu	Fe	Pd	Pd	Pd	Pd
Am	Fe	Pd	Pd	Pd	Pd
Cm	Fe	Pd	Pd	Pd	Pd
Mc	Fe	Pd	Pd	Pd	Pd
Lv	Fe	Pd	Pd	Pd	Pd
Dy	Fe	Pd	Pd	Pd	Pd

Dimension, energetics  
and density of ablated  
nanoparticles

ns-PLD and fs-PLD are  
complementary and  
versatile techniques

Material properties

Laser coupling  
enhancement

Application  
requirements



Relative slowing  
efficiency of the  
background gas

{ Laser-driven particle energy  
ICF ablation loading  
Proton-boron fusion yield

Promising  
nanostructured  
coating for BTE

Conclusions



Thank you for  
your attention!

