Nanostructures in 1 Billon Tons: Interface Engineering in Complex Steels and Biological Nanocomposites

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SFB 986 M3

TUHH Technische Universität Hamburg-Harburg | Universität Hamburg DER FORSCHUNG | DER LEHRE | DER BILDUNG | Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung

SFB 986: Maßgeschneiderte Multiskalige Materialsysteme – M3

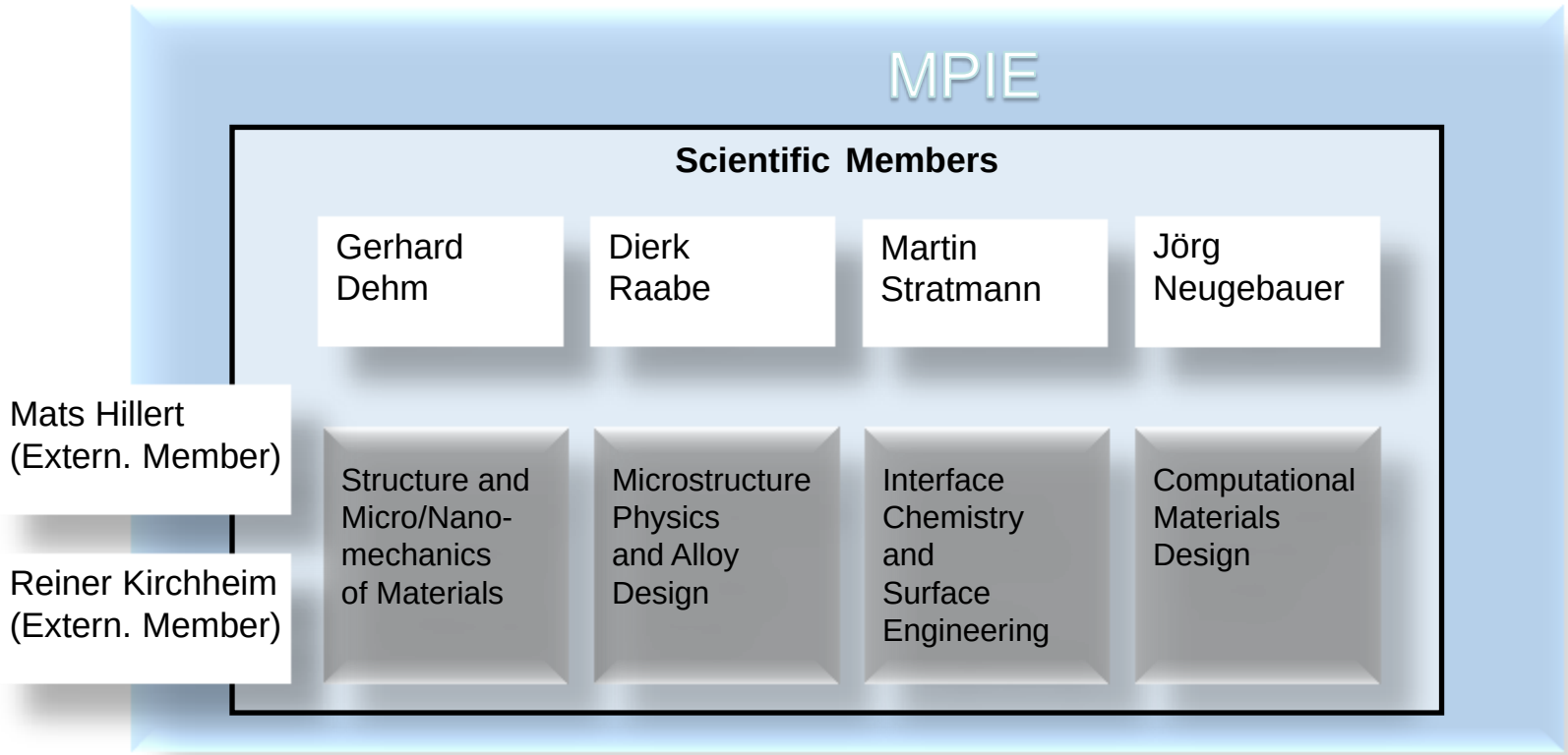
Max-Planck Institut für Eisenforschung GmbH, Düsseldorf

Foundation: 1917 as Kaiser-Wilhelm-Institut für Eisenforschung

Since 1971: Basic corporate budget financed by Max-Planck-Society (50%) and VDEh (50%)

Personnel: 250

100 years public-private partnership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Structure and Micro/Nano-mechanics of Materials
Microstructure Physics and Alloy Design
Interface Chemistry and Surface Engineering
Computational Materials Design

Answering societies' grand challenges with complex alloys

70% of all **industrial innovations** are associated with progress in **materials science and engineering**

Metallic Materials occupy key roles
(energy, transportation, health, safety, infrastructure)

Metals-related industries account for 46% of all EU manufacturing value and 11% of the EU's total domestic product

3.5 billion € per day in the EU
World Trade Organisation

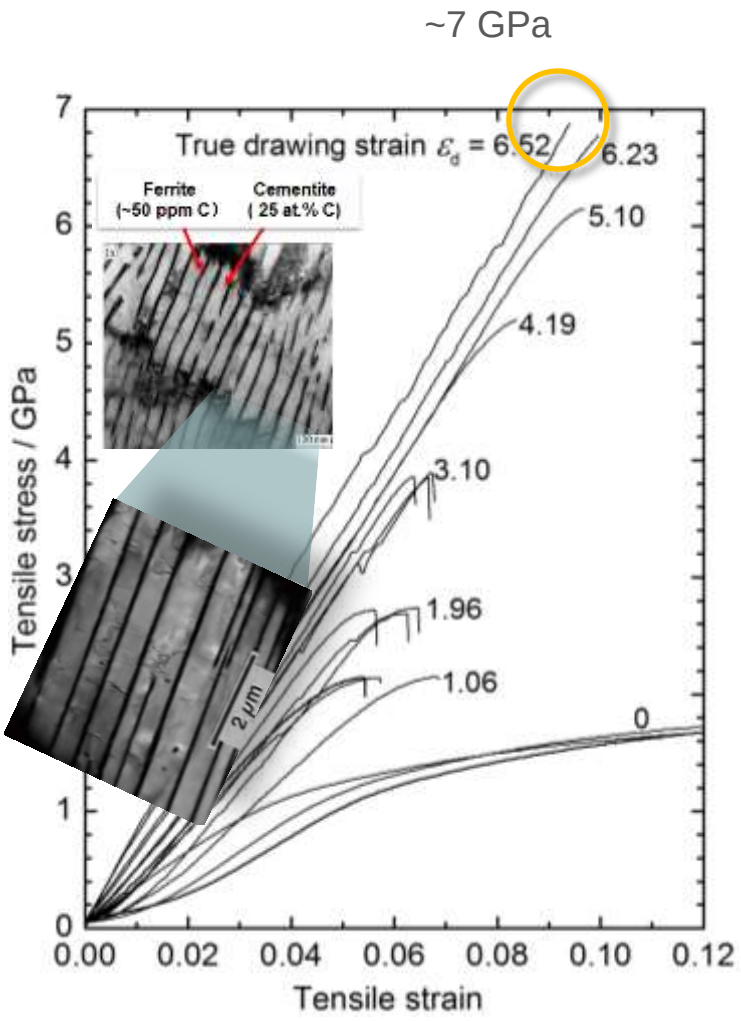
steels: 1.4 billion tons / year

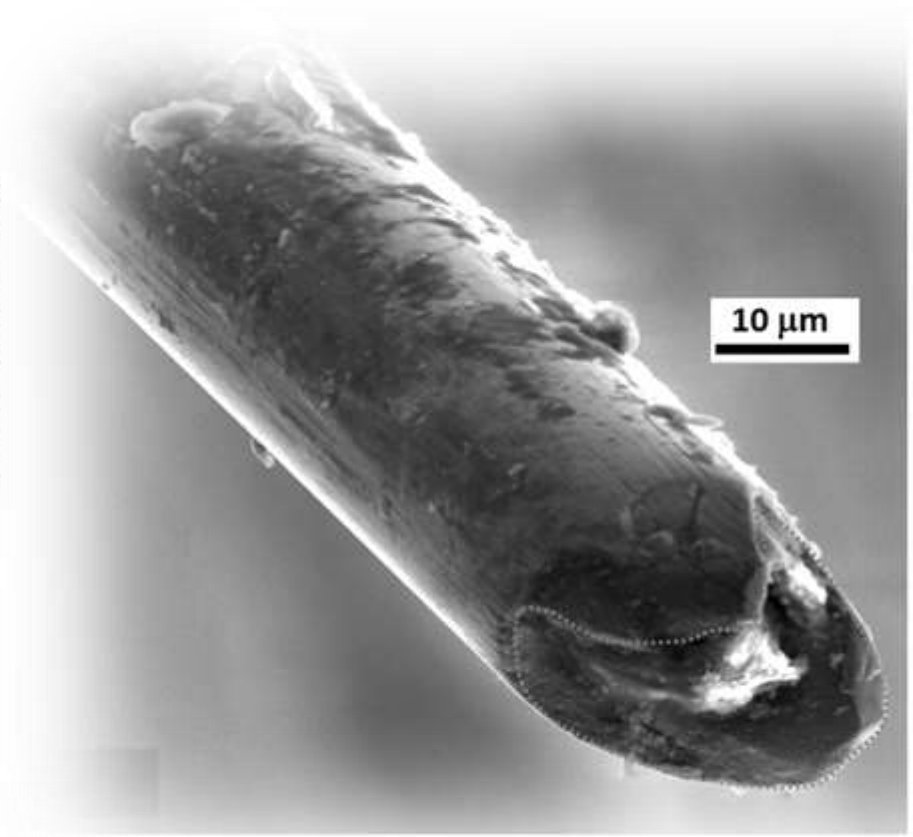
Pearlite: the limits of strength

Chitin-based biological nanocomposites

chitin: several billion tons / year
(ca. 300 thousand tons commercial)

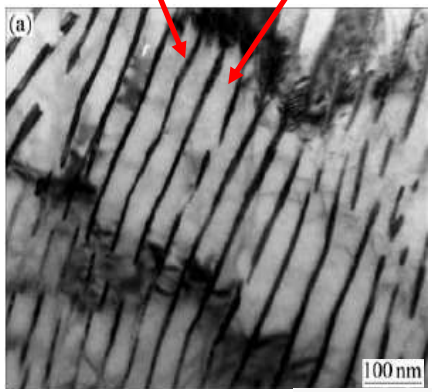
Towards the limits of strength and strain hardening





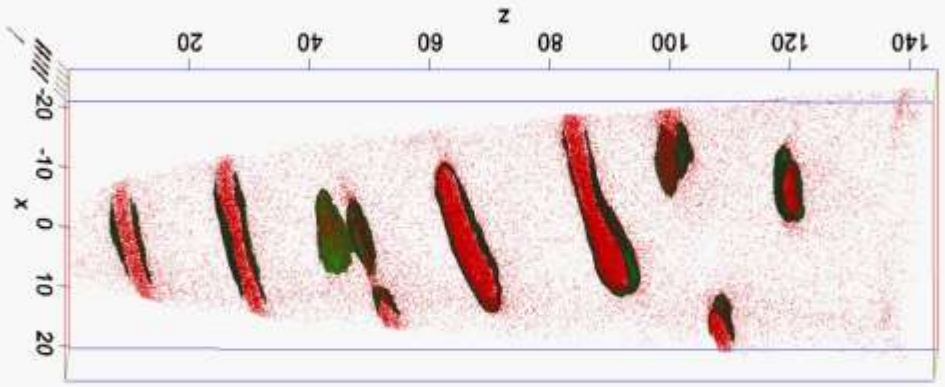
Towards the limits of strength: cold-drawn pearlitic steel

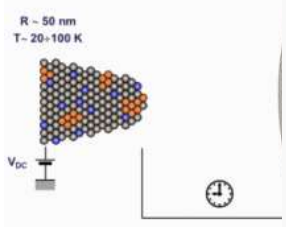
Ferrite (~50 ppm C) **Cementite (25 at.% C)**

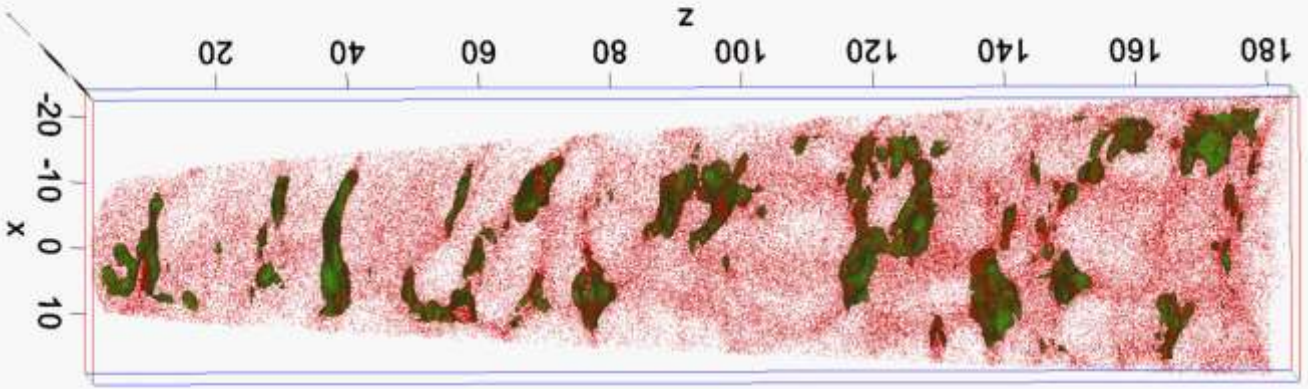


(ε = 2)

Scale: nm







(ε = 6.5)

C iso-concentration (7 at.%)

● C

Deformation-driven cementite dissolution - oversaturated ferrite

Towards the limits of strength: cold-drawn pearlitic steel

- Why does carbide dissolve?
- Where is the C?
- How stable is C in ferrite?
- What does that mean for the flow stress and strain hardening ?

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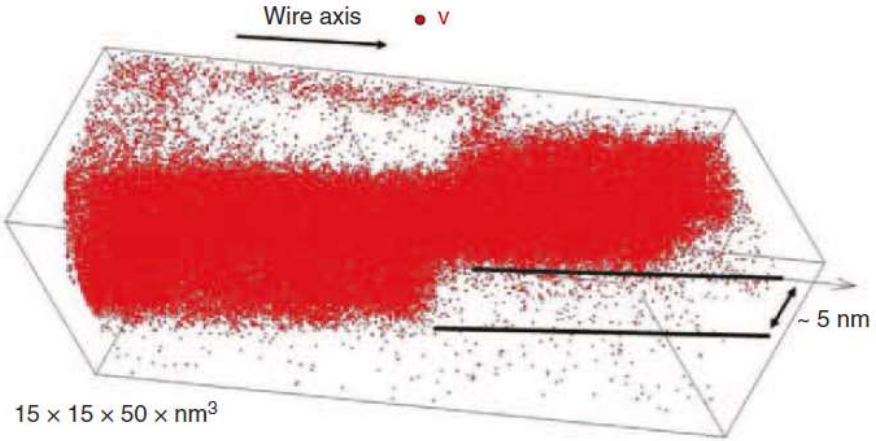
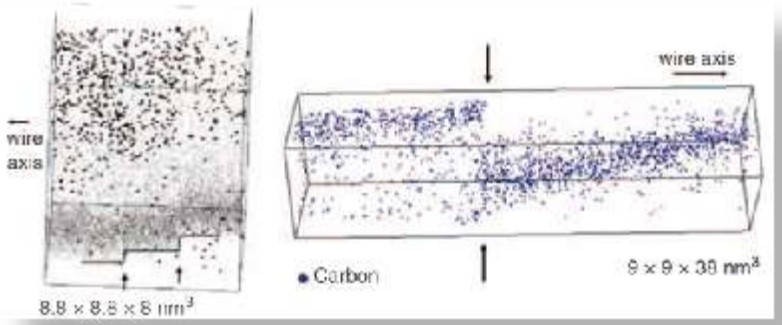
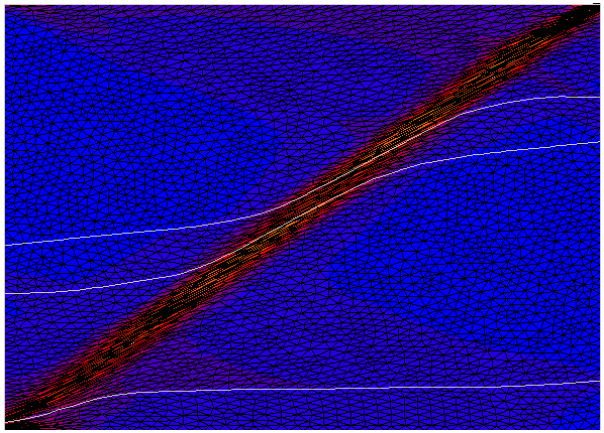


dataset by Xavier Sauvage





Characterization of GB segregation by correlative TEM / APT

ε=6.02 true strain, annealed for 2 min at 400ºC, ~ 6 GPa

- Why does carbide dissolve?
- Where is the C?
- How stable is C in ferrite?
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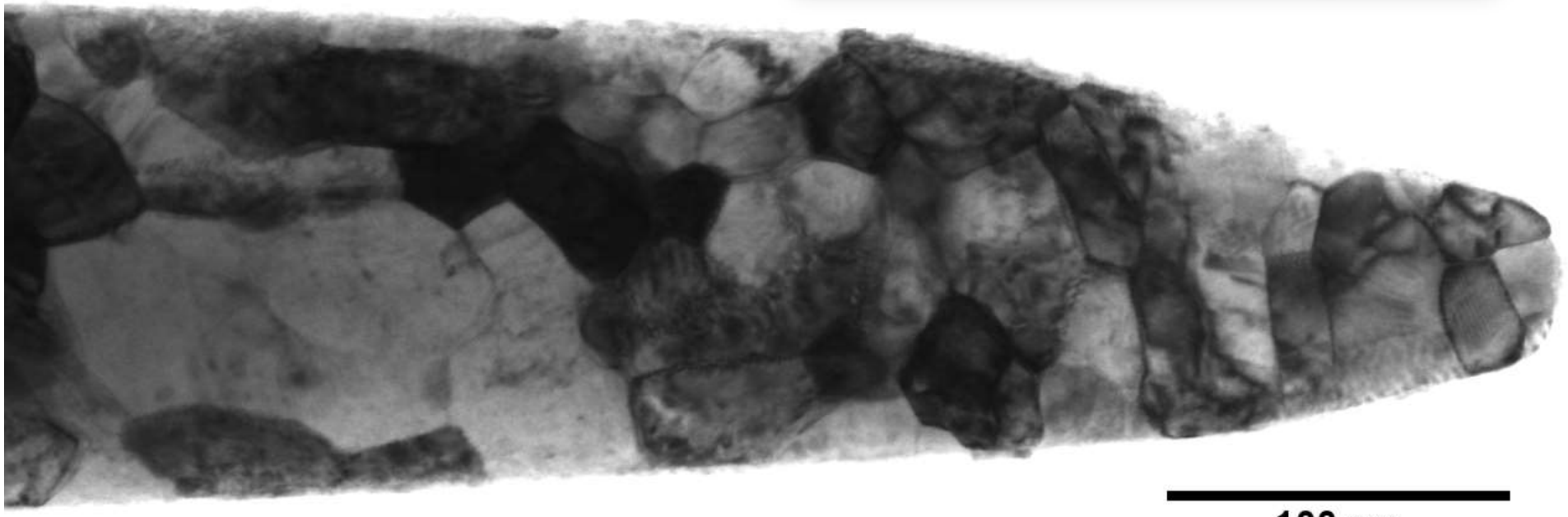
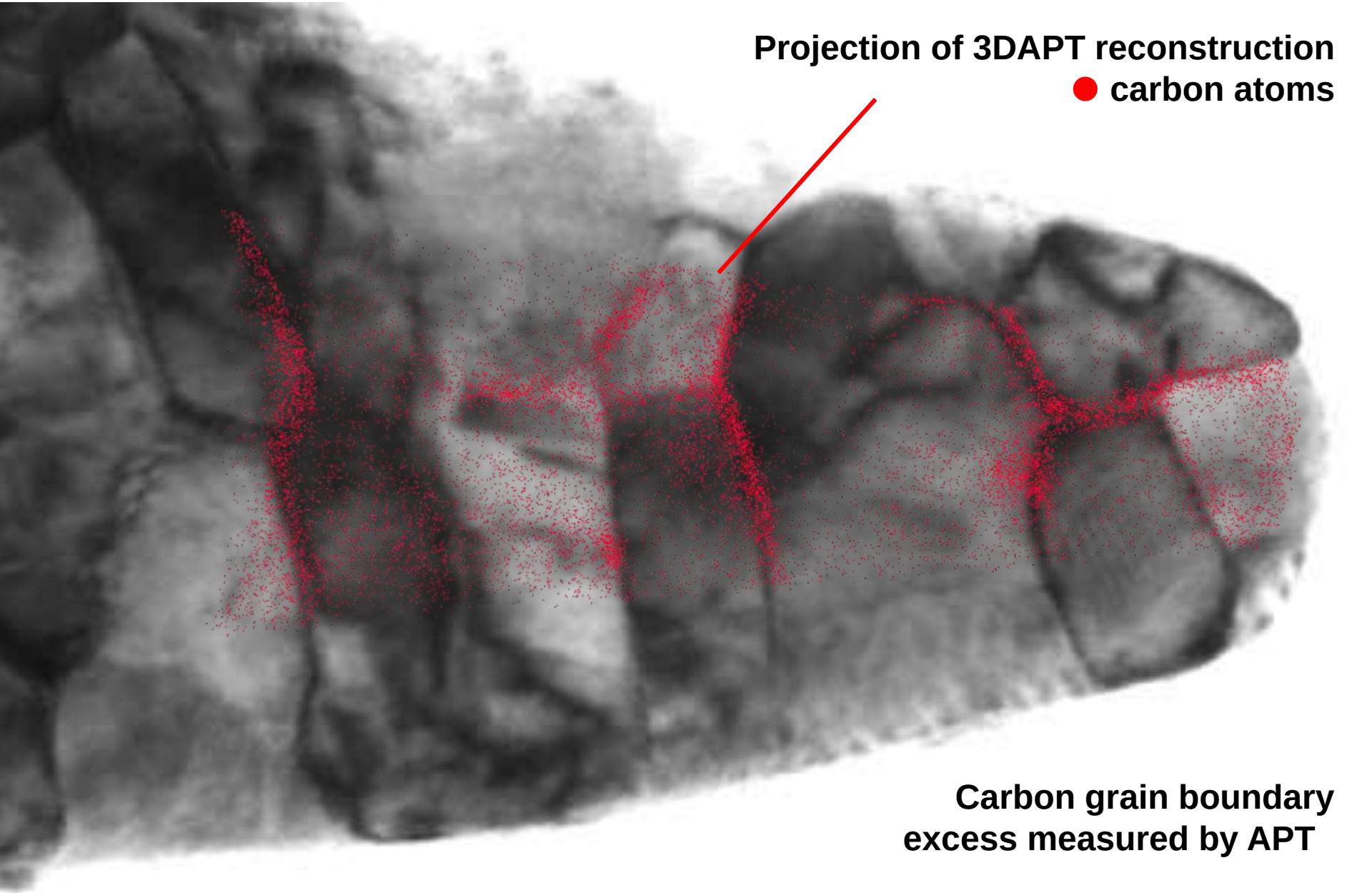


BF-STEM image of pearlitic atom probe tip, view along axis of columnar grains

Acta Mater: 59 (2011) 3965; 60 (2012) 4005

Characterization of GB segregation by correlative TEM / APT



Acta Mater: 59 (2011) 3965; 60 (2012) 4005

Towards the limits of strength: cold-drawn pearlitic steel

- Why does carbide dissolve?
- Where is the C?
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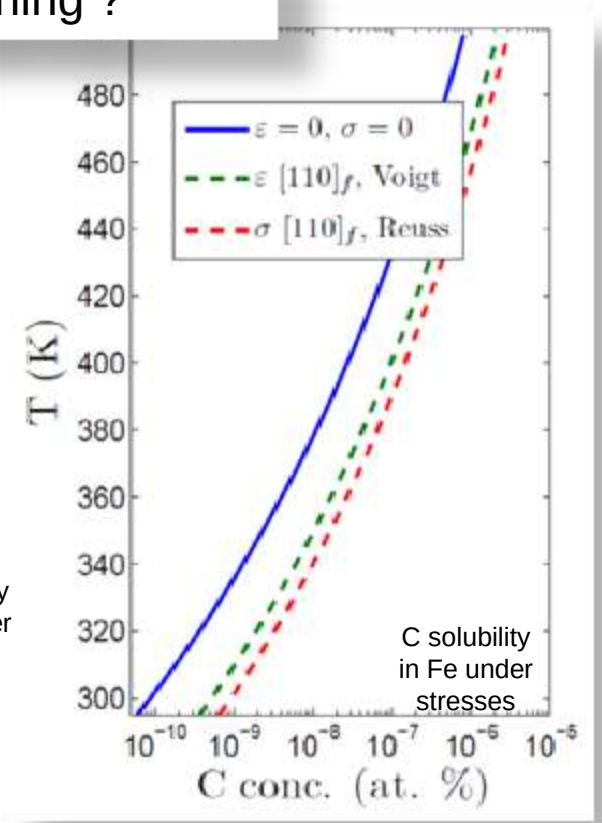
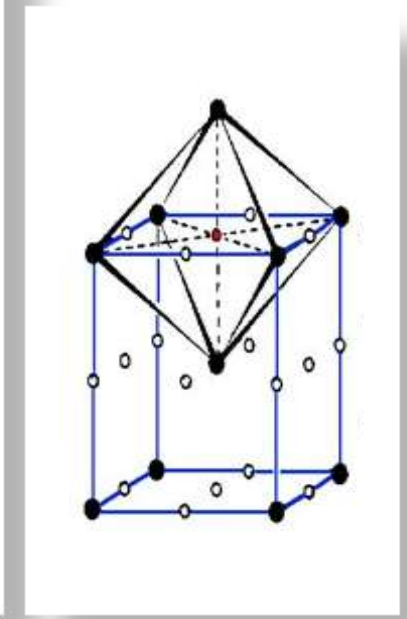
C solubility in Fe under stresses



C solubility in Fe under stresses



Pearlite: the limits of strength

Chitin-based biological nanocomposites

Chitin: Exoskeleton component of >90% of all animals on earth:

Arthropods: insects; crustaceans (lobsters, crabs, shrimp); chelicerates (spiders, scorpions)














The materials science of chitin composites: motivation

Arthropods have adapted to every habitat on earth: adaptive material → candidate for bio-inspired material

Chitin basics unknown → ab initio

Common feature: hierarchical cuticle → composite design

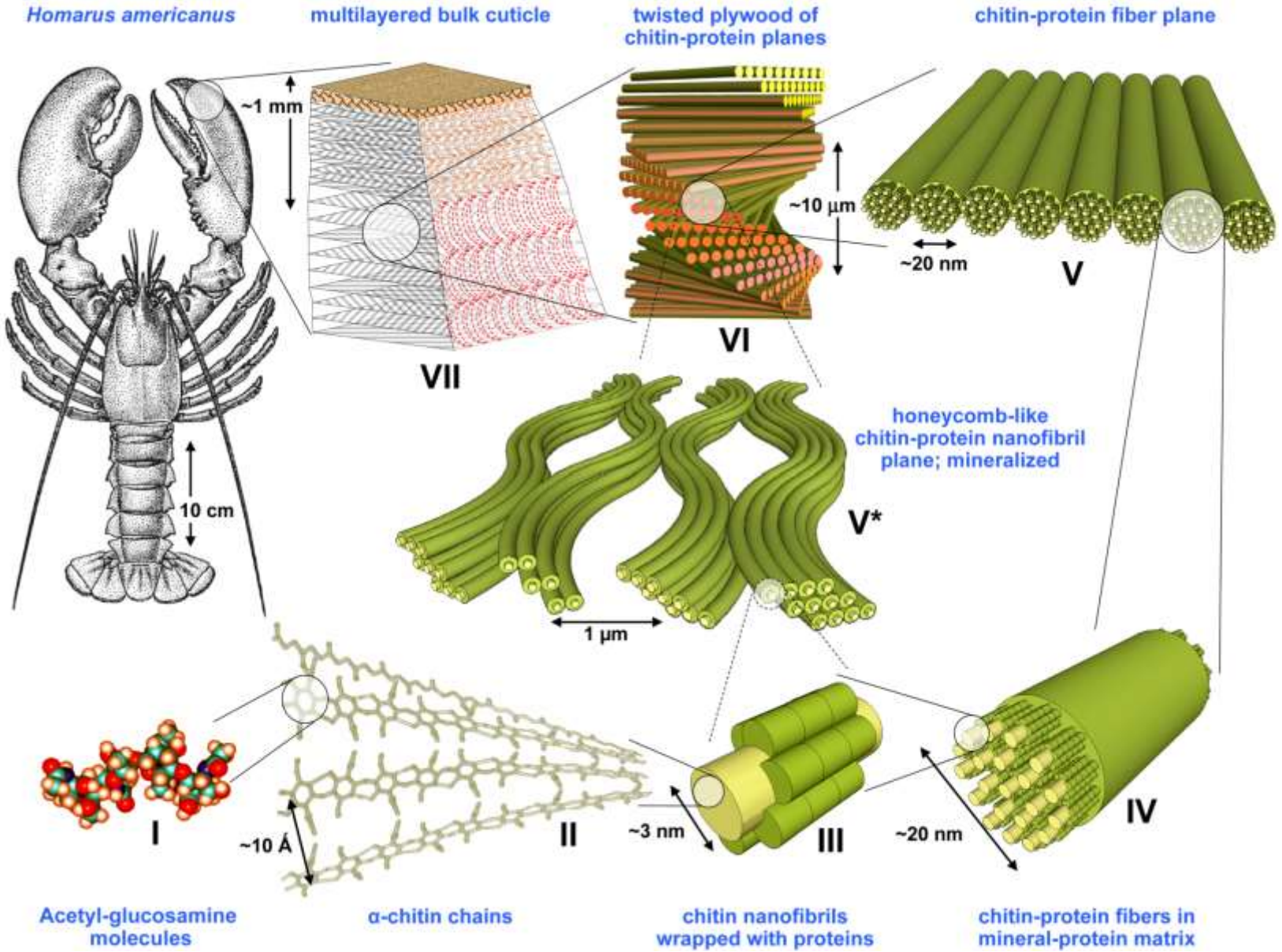
Good mechanical properties → multiscale modeling and bioinspired carbon-based compounds

Building units

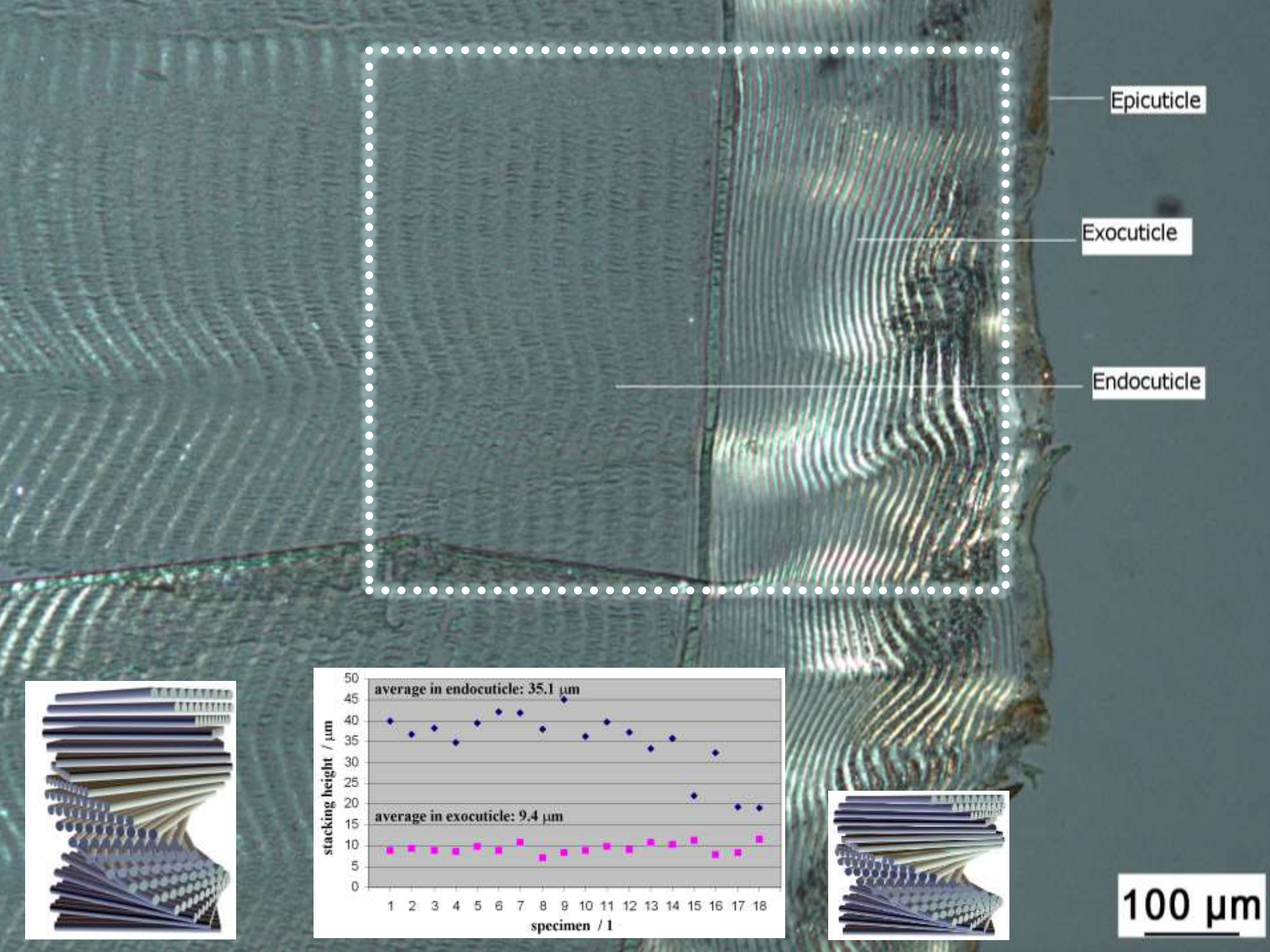
- Organic matrix in most parts of the cuticle
  - the organic material (chitin, proteins) is combined with inorganic nano-particles

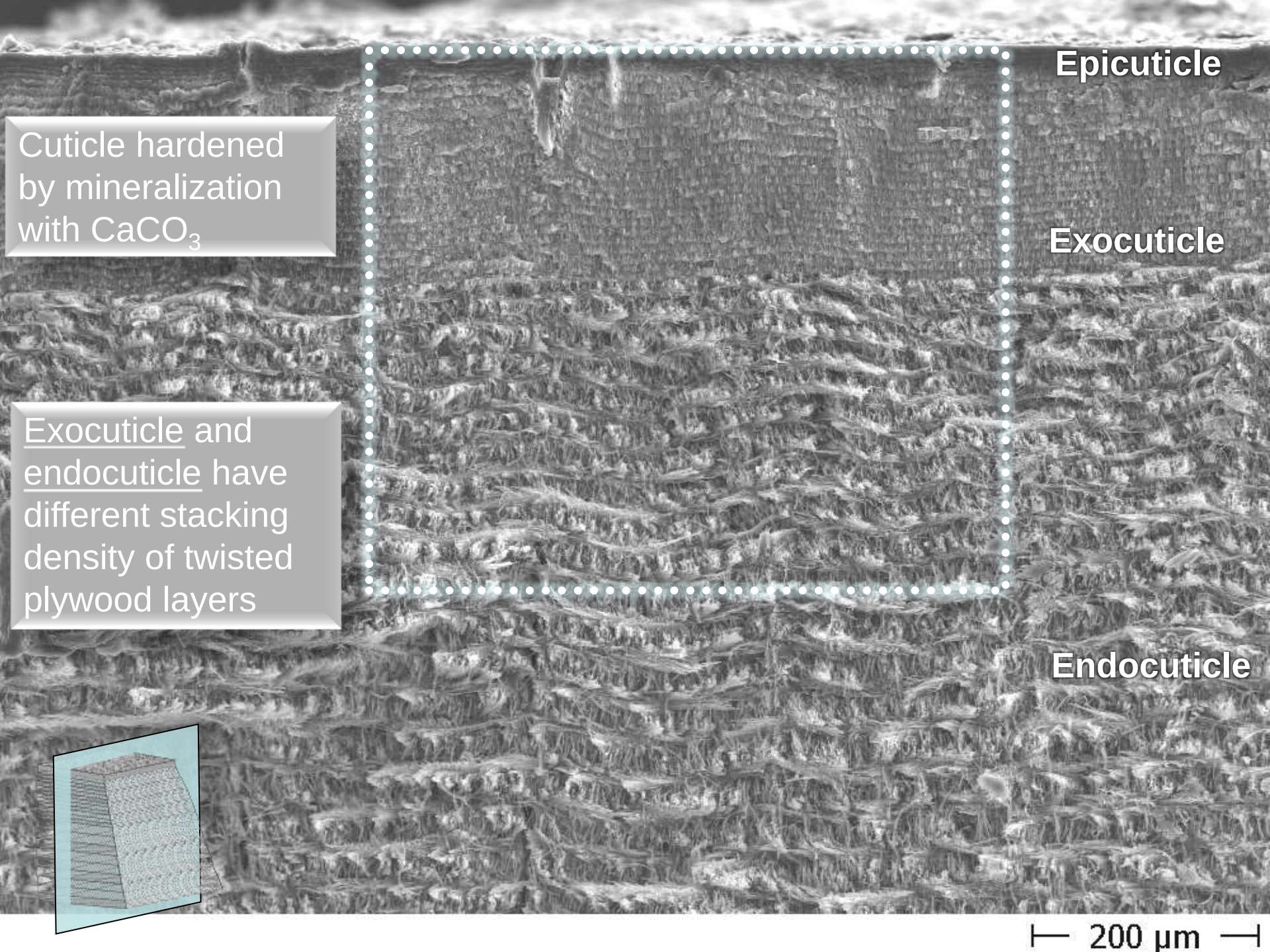
- Inorganic nano-particles
  - consists of amorphous or crystalline (calcite) $CaCO_3$
  - $CaCO_3$ doped by Mg

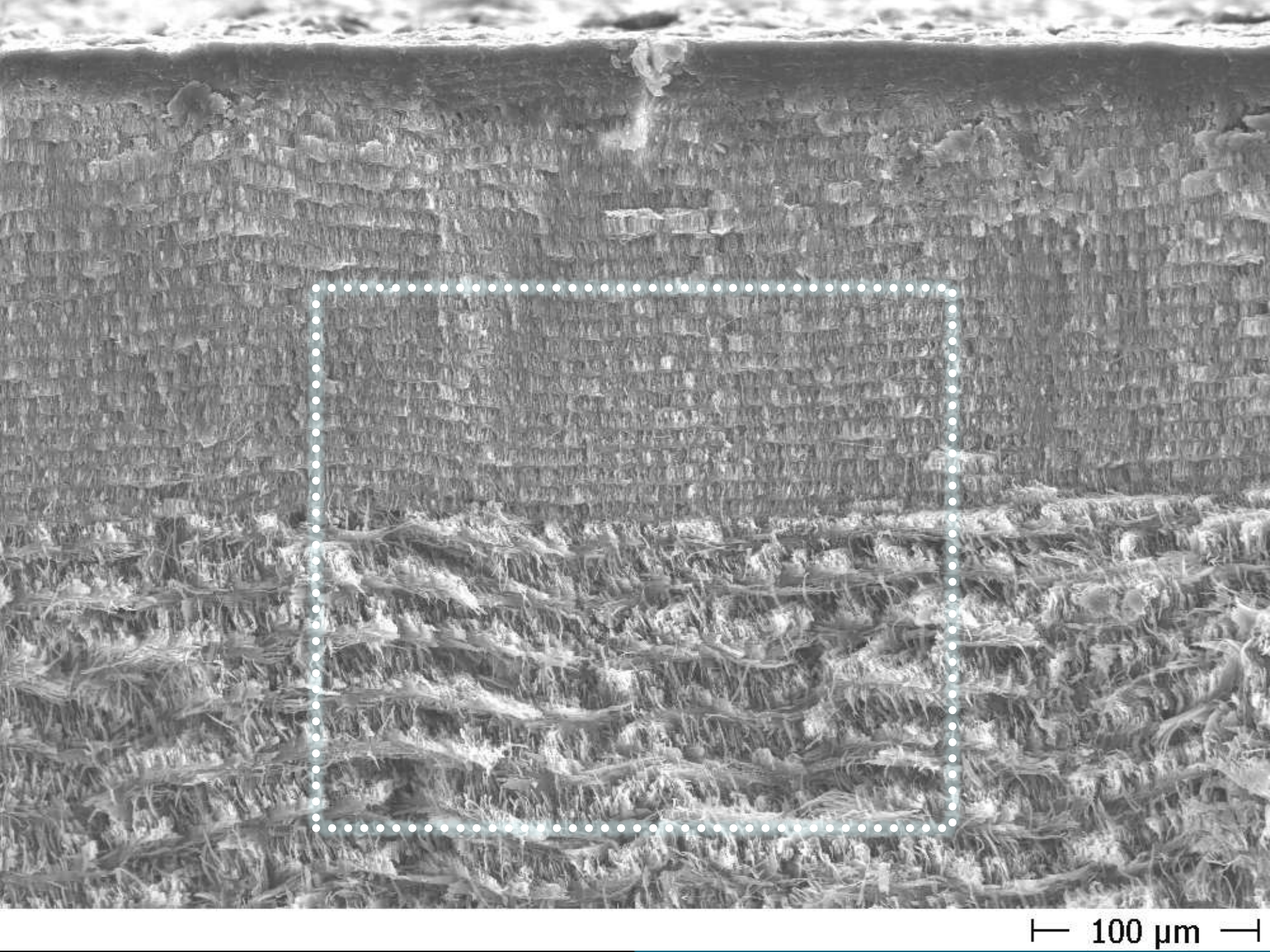
Structure hierarchy of chitin-compounds

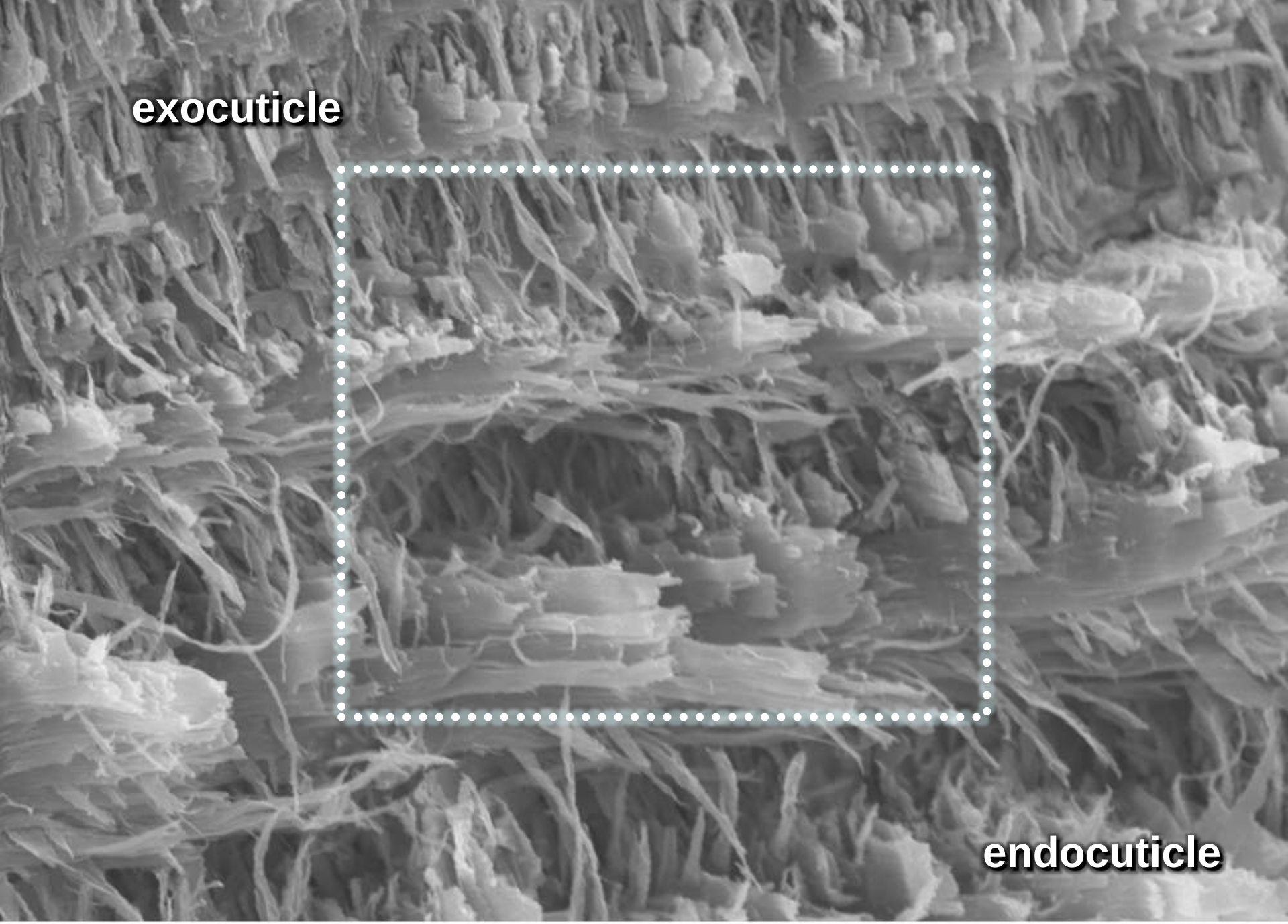


Nikolov et al.: Adv. Mater. 22 (2010) p. 519; Al-Sawalmih et al.: Adv. Funct. Mater. 18 (2008) 3307

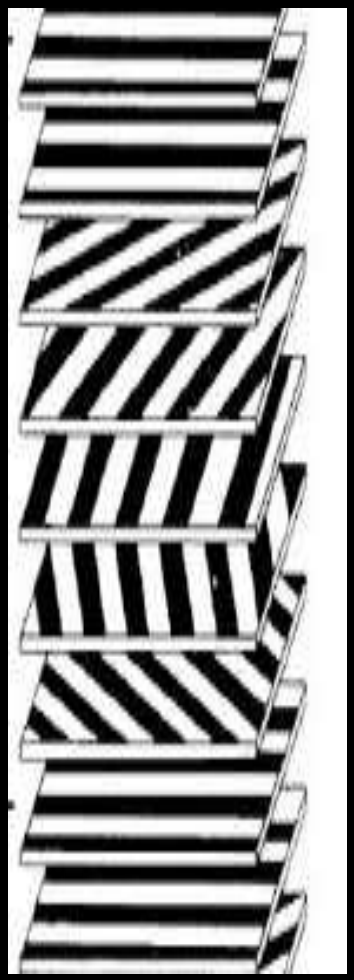

Epicuticle
Exocuticle
Endocuticle
average in endocuticle: 35.1 µm
average in exocuticle: 9.4 µm
stacking height / µm
specimen / 1
0
5
10
15
20
25
30
35
40
45
50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
100 µm

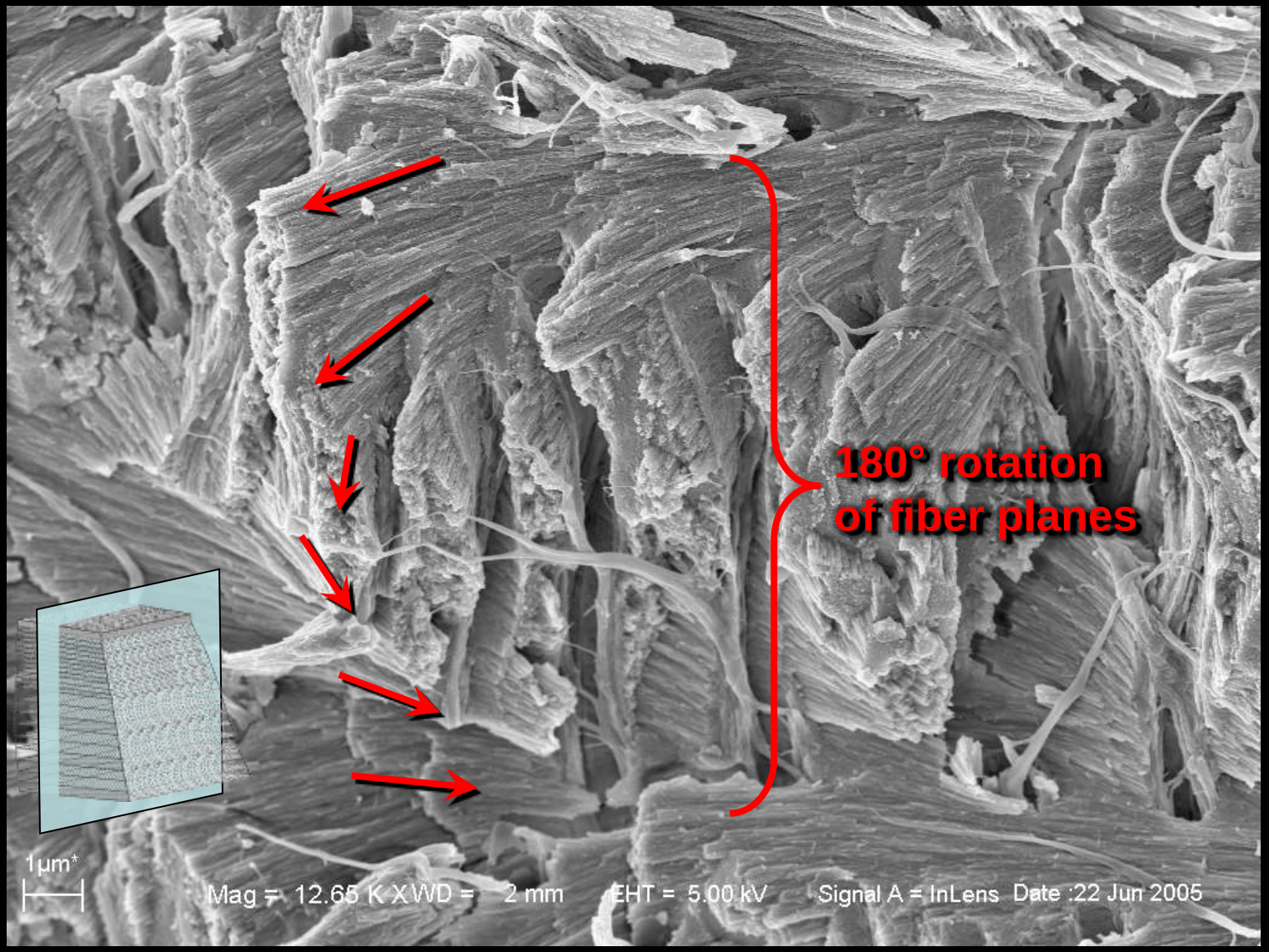

Epicuticle
Exocuticle
Endocuticle
Cuticle hardened by mineralization with $CaCO_3$
Exocuticle and endocuticle have different stacking density of twisted plywood layers
200 µm

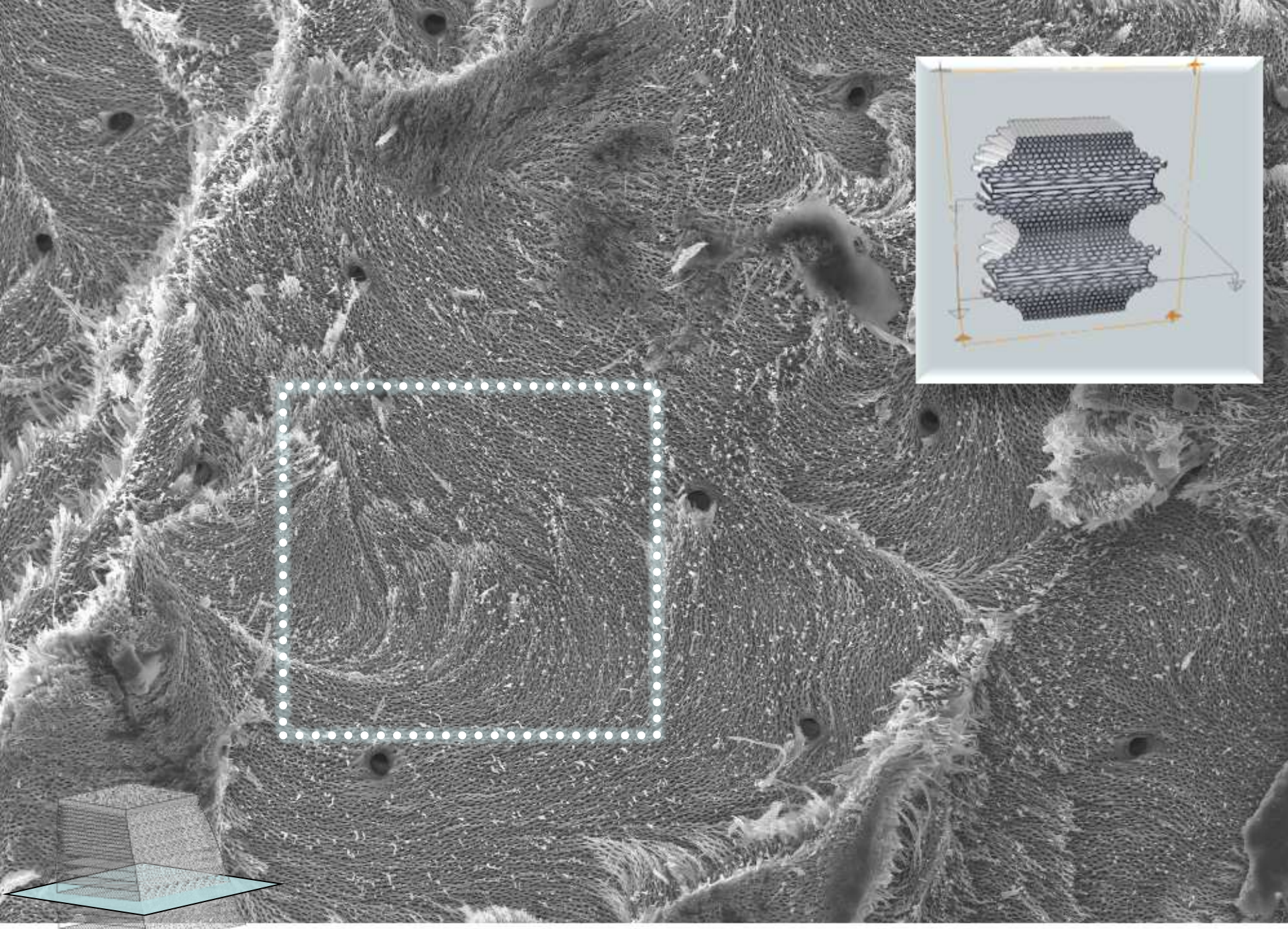

100 µm

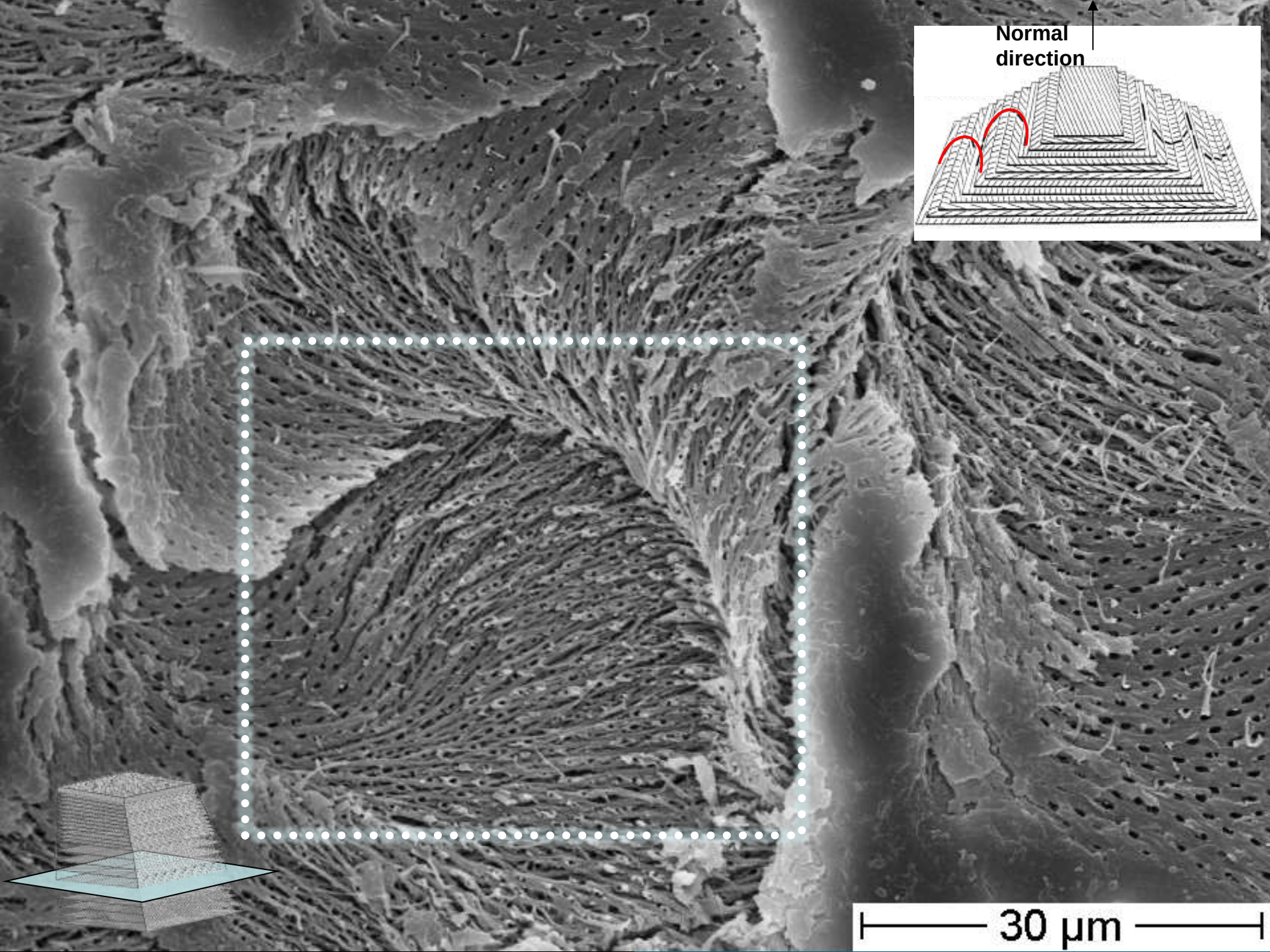


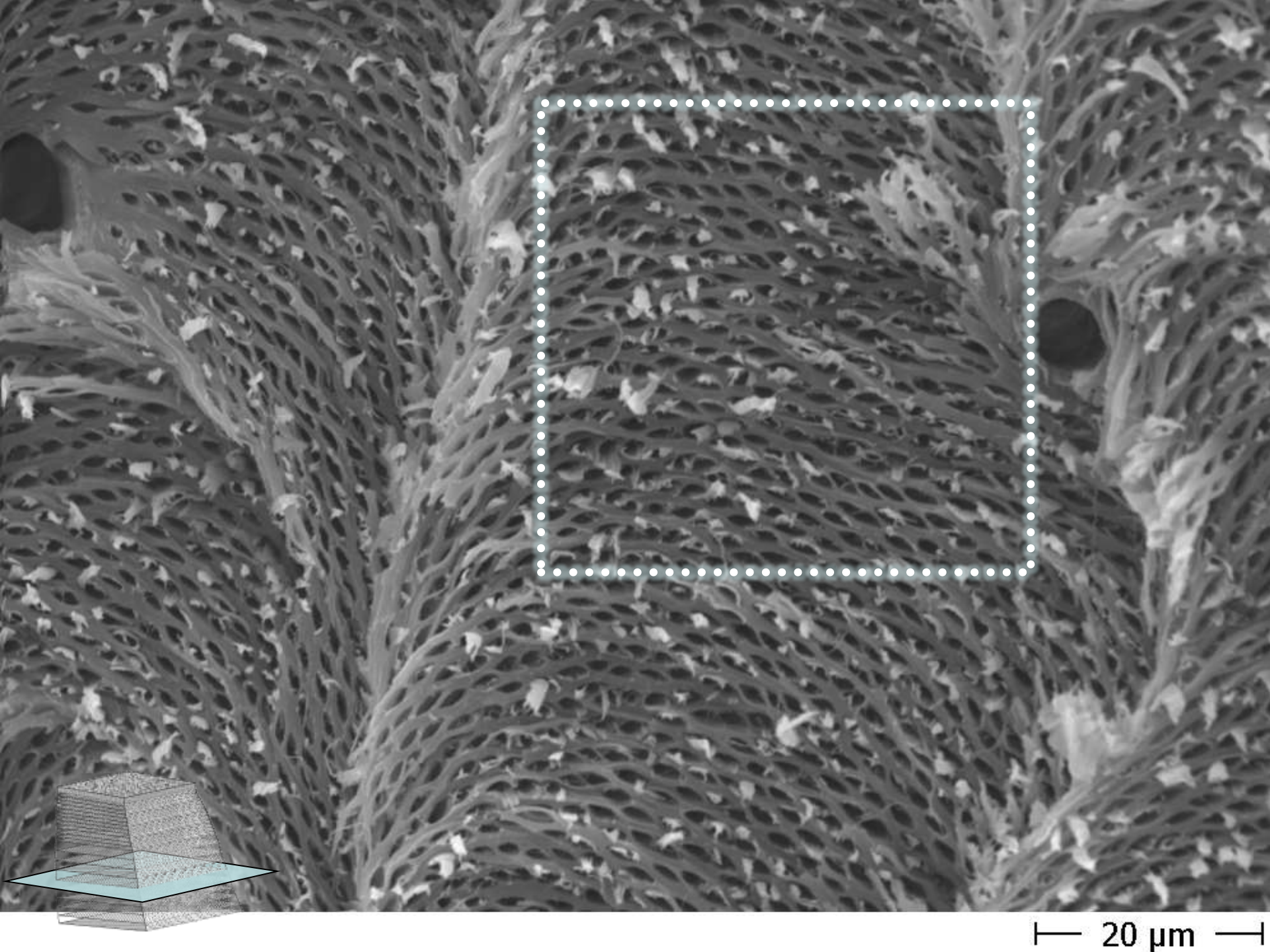
Nikolov et al.: Adv. Mater. 22 (2010) p. 519; Al-Sawalmih et al.: Adv. Funct. Mater. 18 (2008) 3307

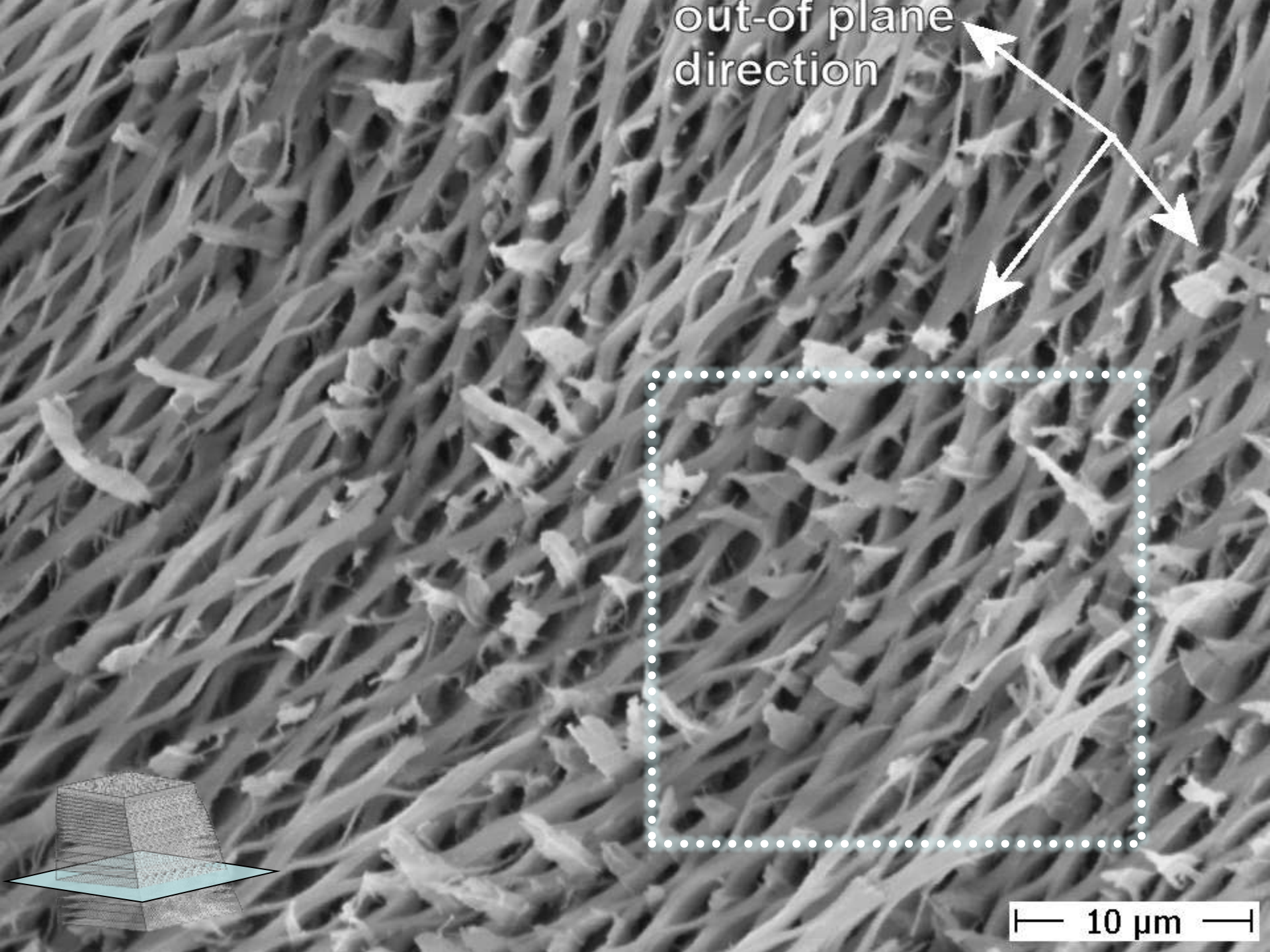


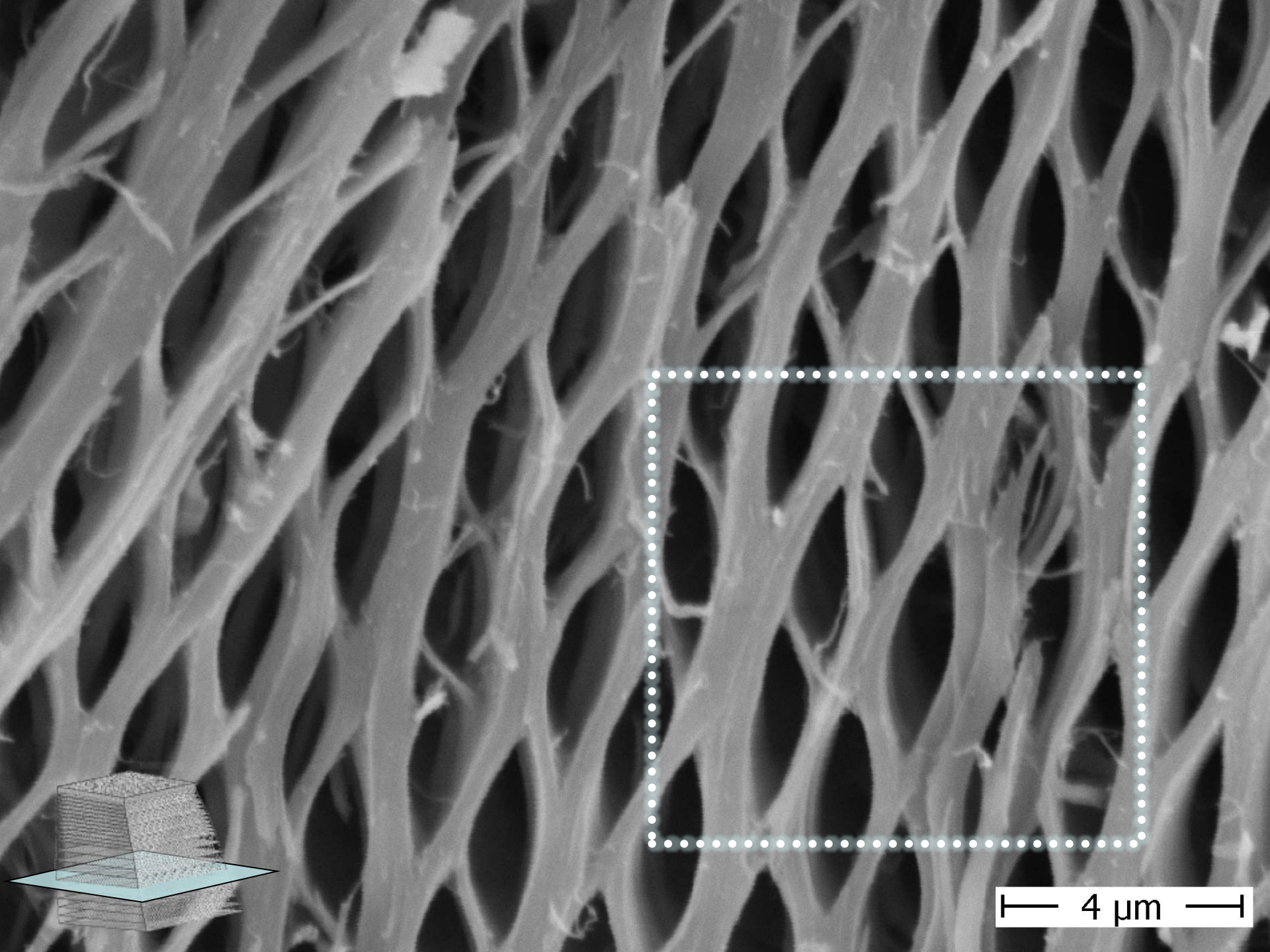

180° rotation
of fiber planes
1µm*
Mag = 12.66 K X WD = 2 mm EHT = 5.00 kV Signal A = InLens Date :22 Jun 2005

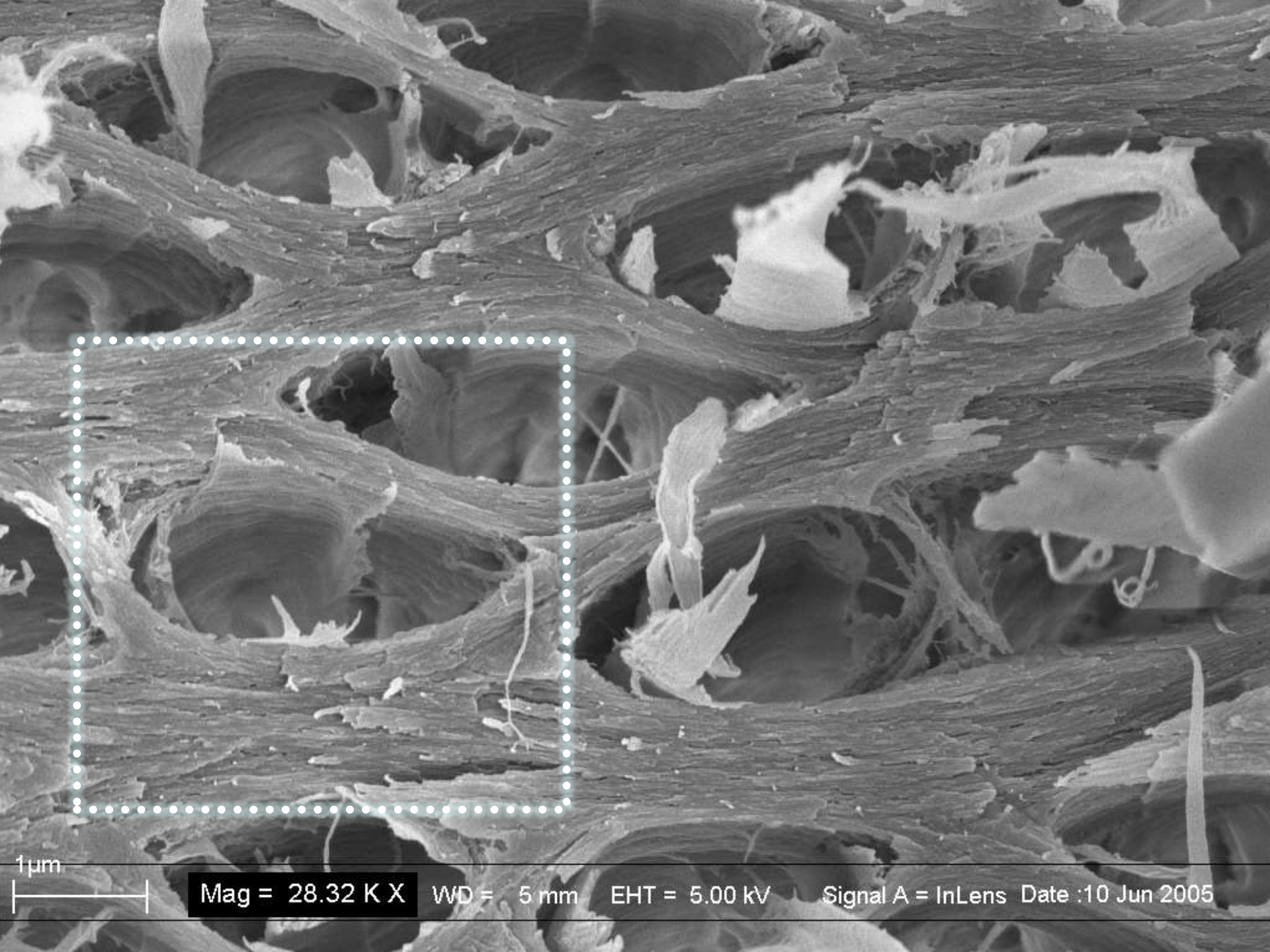

100 µm

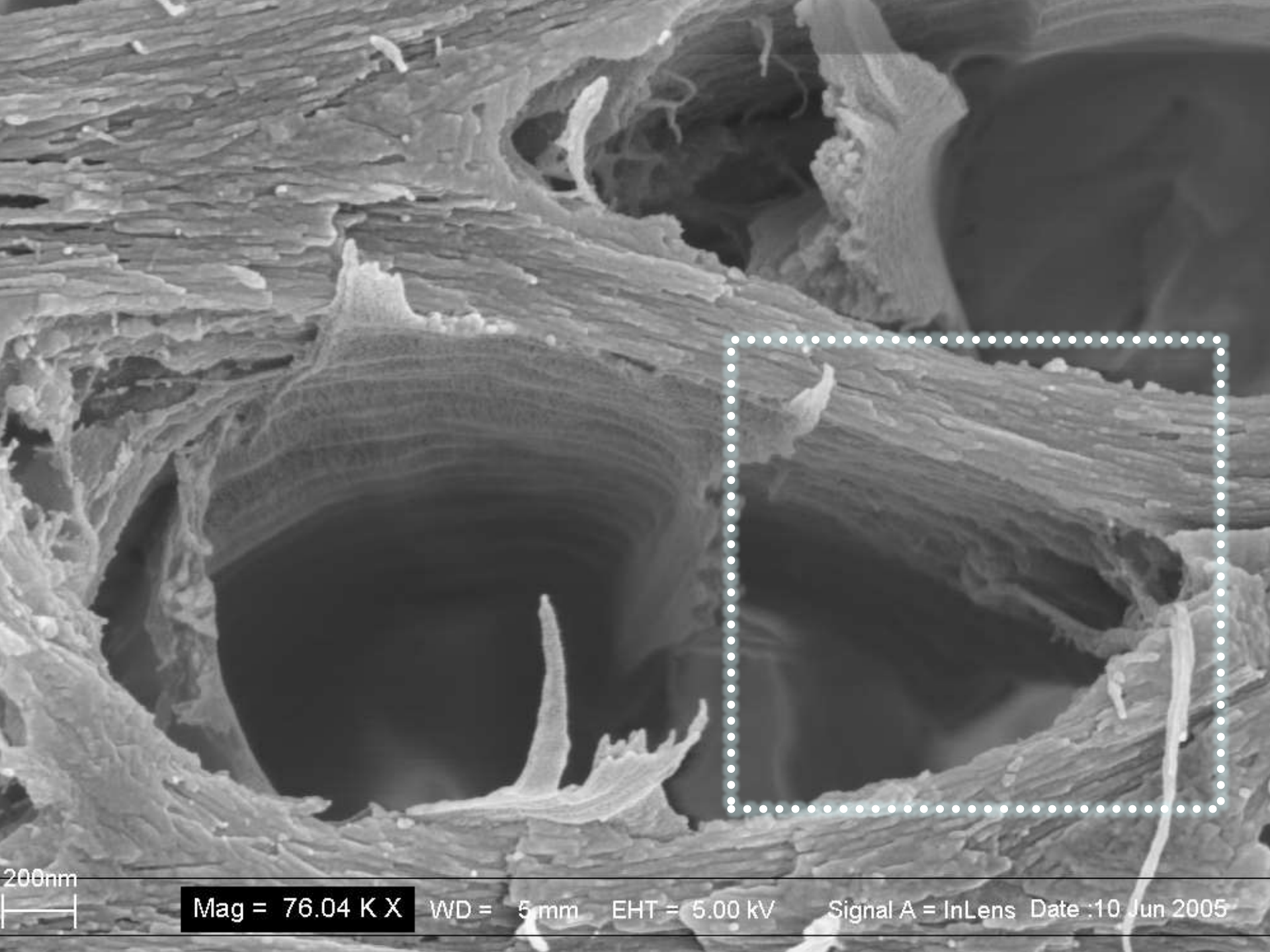

Normal
direction
30 µm


20 µm


out-of plane
direction
10 µm

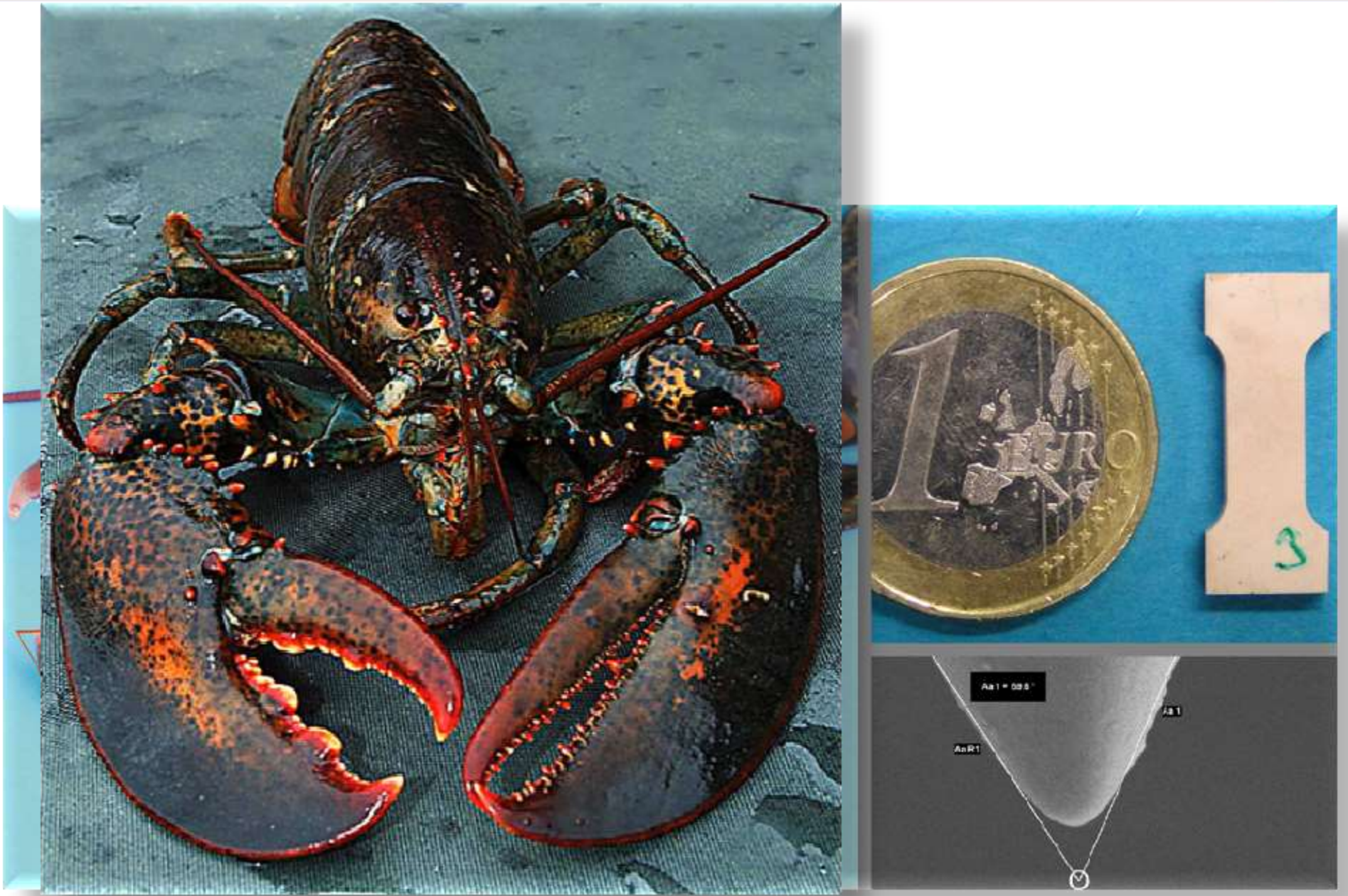

4 µm


1µm
Mag = 28.32 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005


200nm
Mag = 76.04 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005

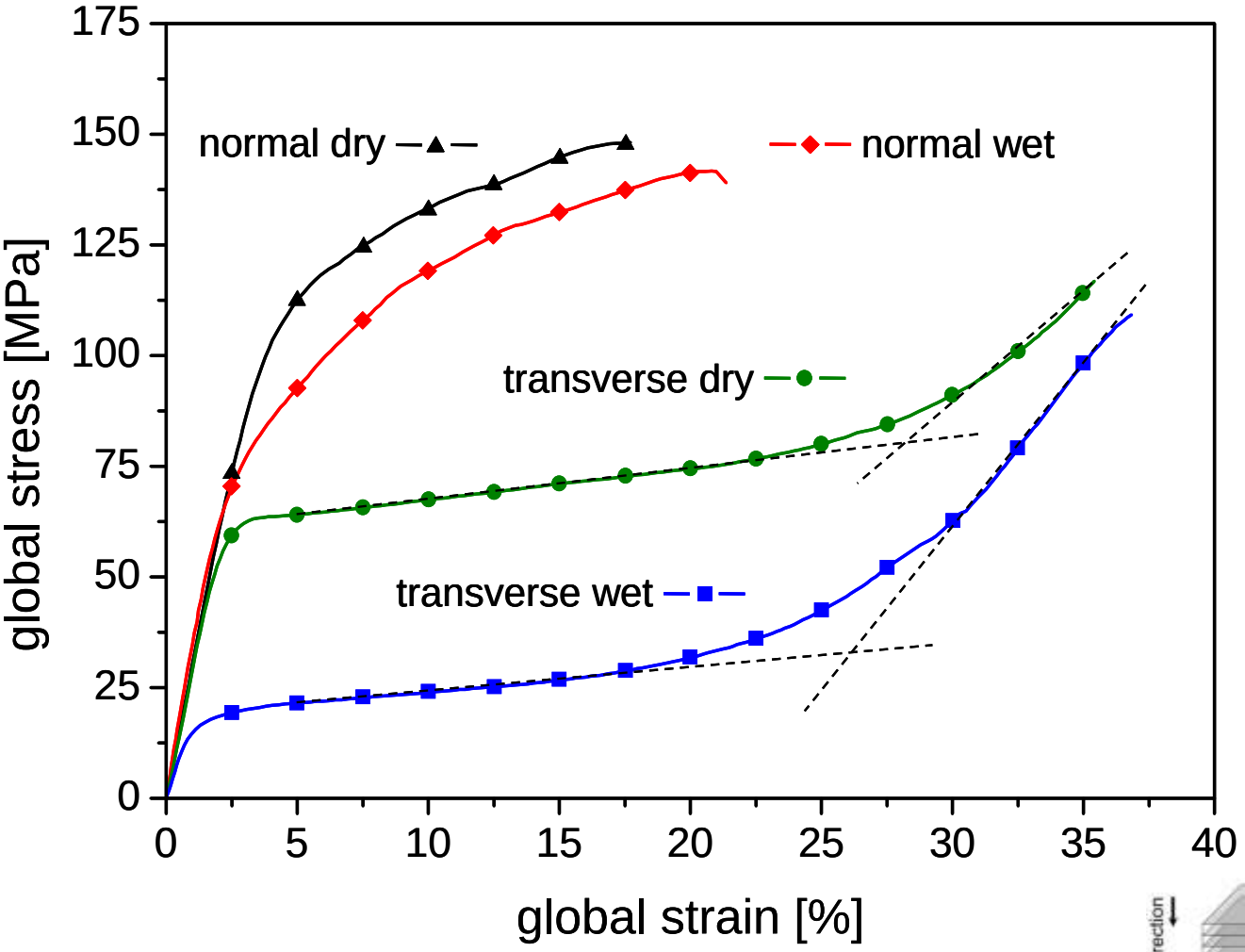

100nm
Mag = 133.31 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :9 Jun 2005

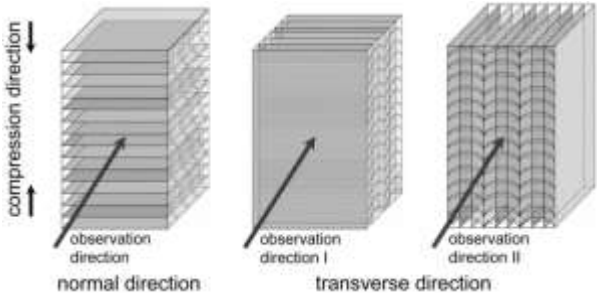
The materials science of chitin composites



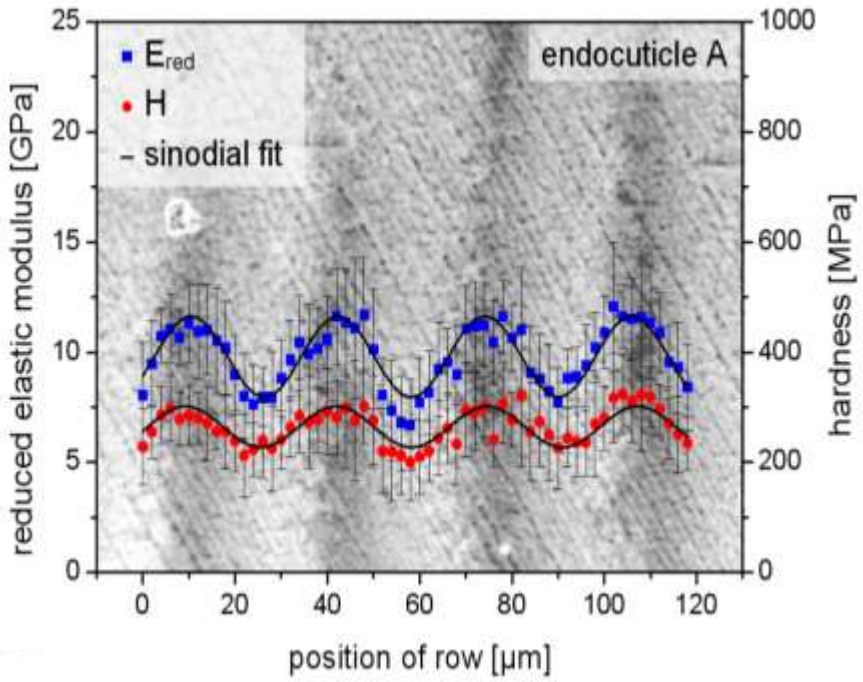
Fabritius, Sachs, Romano, Raabe : Adv. Mater. 21 (2009) 391

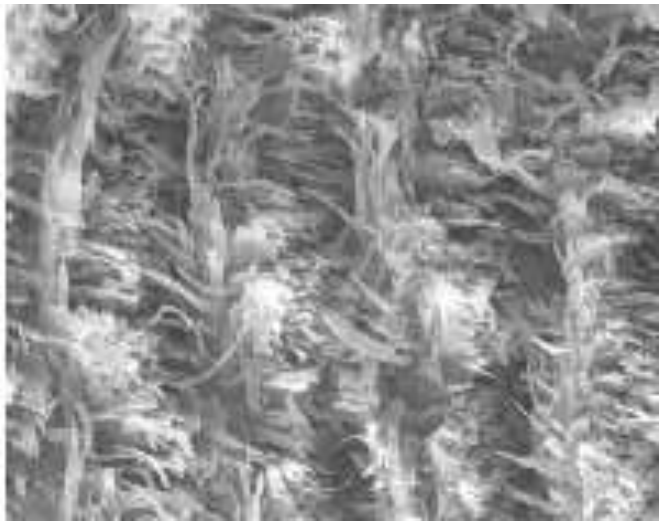
Compression tests (macroscopic), lobster

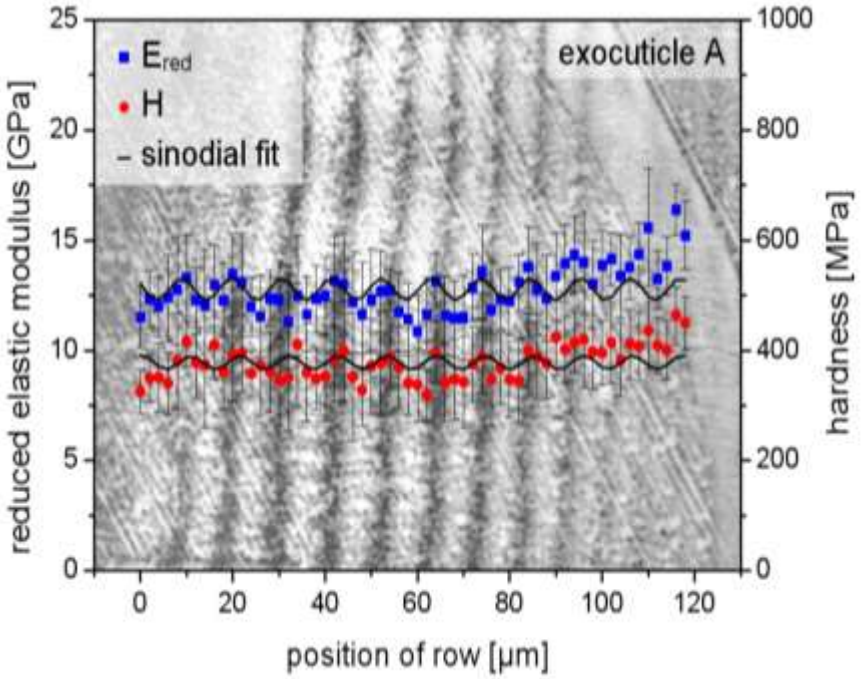


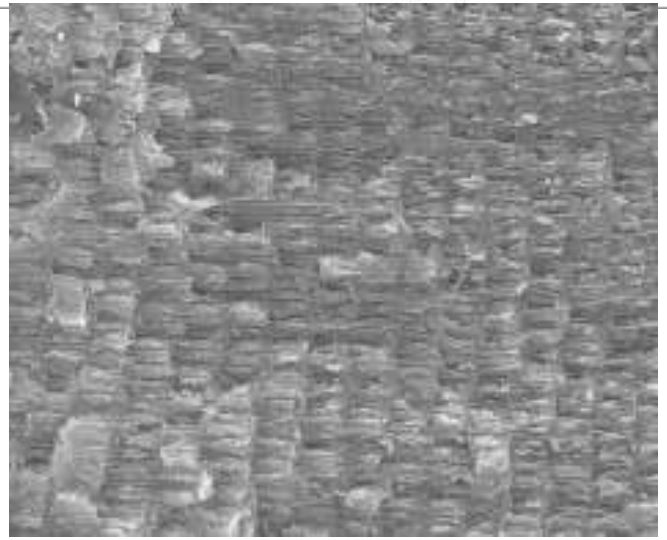


Mechanical properties (microscopic, nanoindentation)



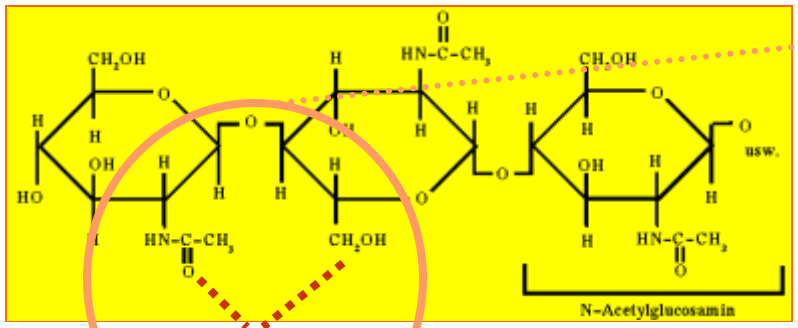


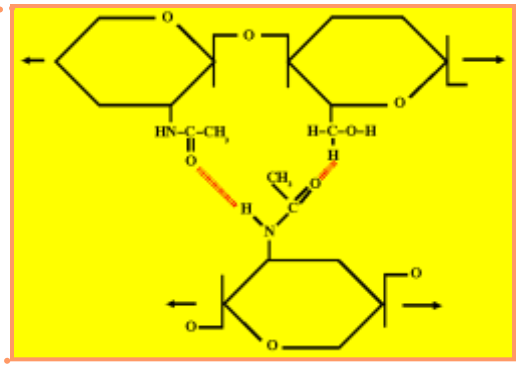




Sachs, Fabritius, Raabe: J Material Research 21 (2006) 1987

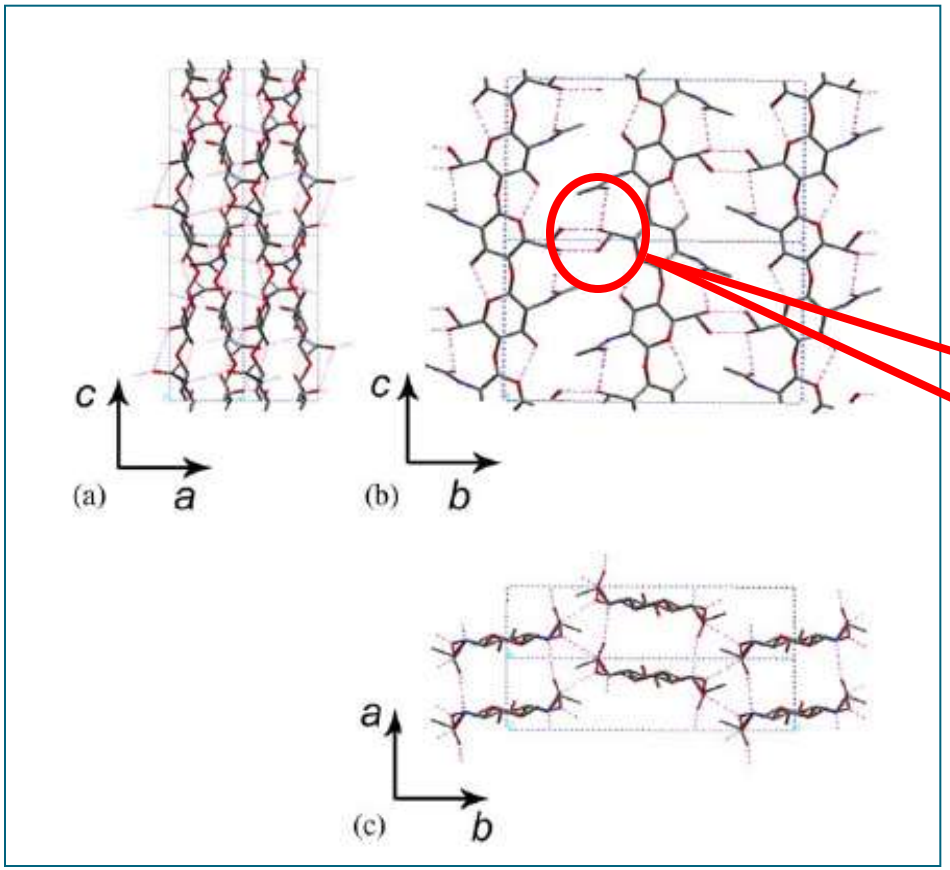
What is α-chitin?





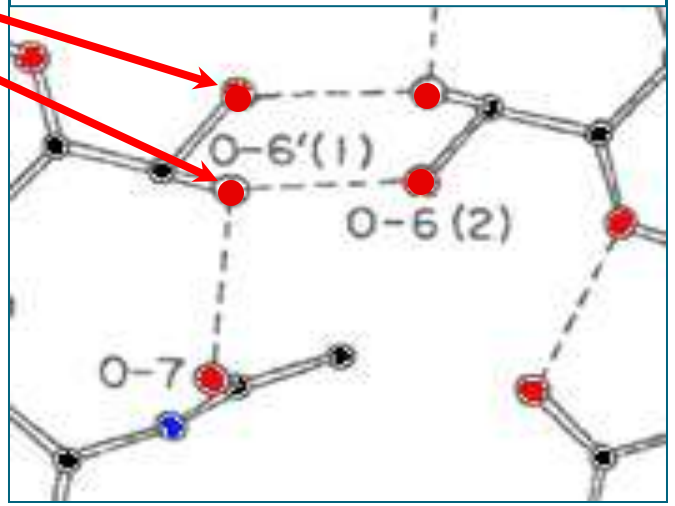
*J. Biochem Biophys. Cytol., 1957, **3**, 669 - 683.* **The crystal structure of α -chitin** **Carlstrom, D.**					
Polymer	**Unit cell dimensions (Bohrradius)**				**Space group**
	a	**b**	**c**	**γ**	
α-Chitin	**8.96**	**35.64**	**19.50**	**90˚**	**P21**

108 atoms / 52 unknown H-positions



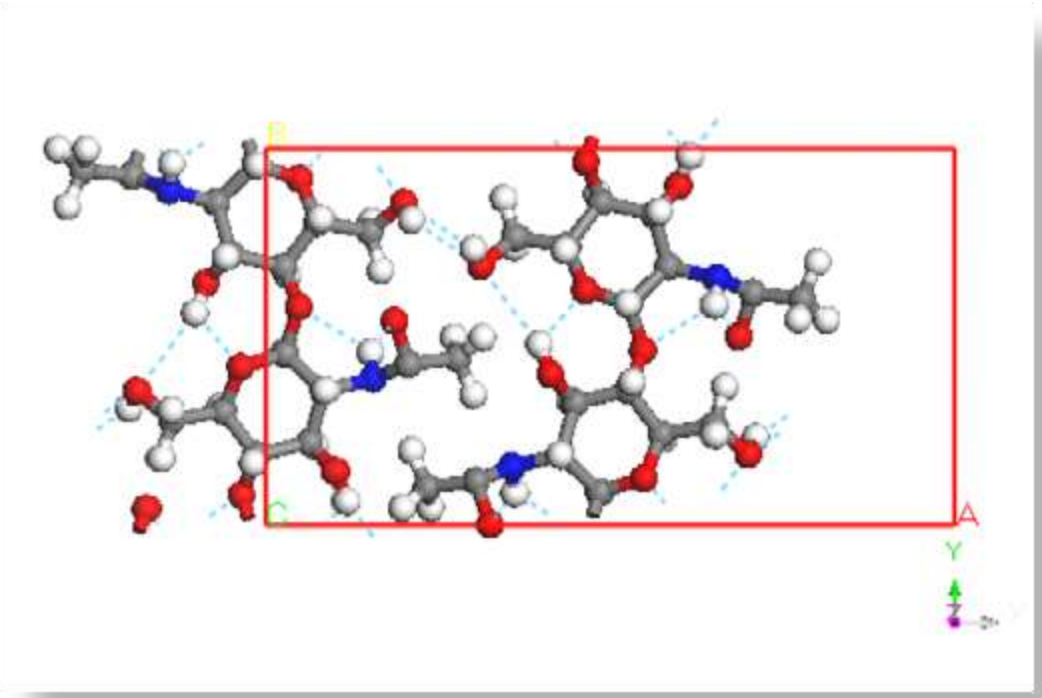
Hydrogen positions?
H-bonding pattern ?

two conformations
of α-chitin



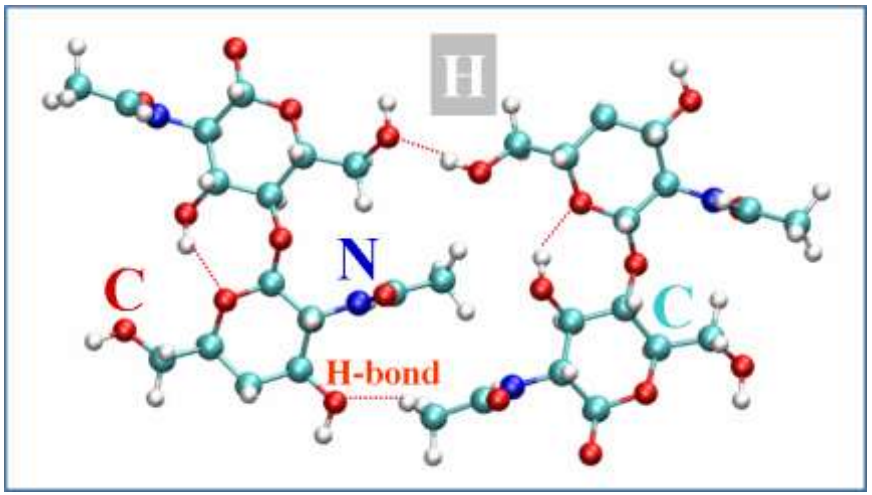
Minke and Blackwell, J. Mol. Biol. 120, (1978)

	CPU time	Accuracy	Resulting structures
•**Empirical Potentials** Geometry optimization Molecular Dynamics (universal force field)	~10 min	Low	**~10^3**
•**Tight Binding** (SCC-DFTB) Geometry optimization (SPHIngX)			
•**DFT** (PWs, PBE-GGA) Geometry Optimization (SPHIngX)			



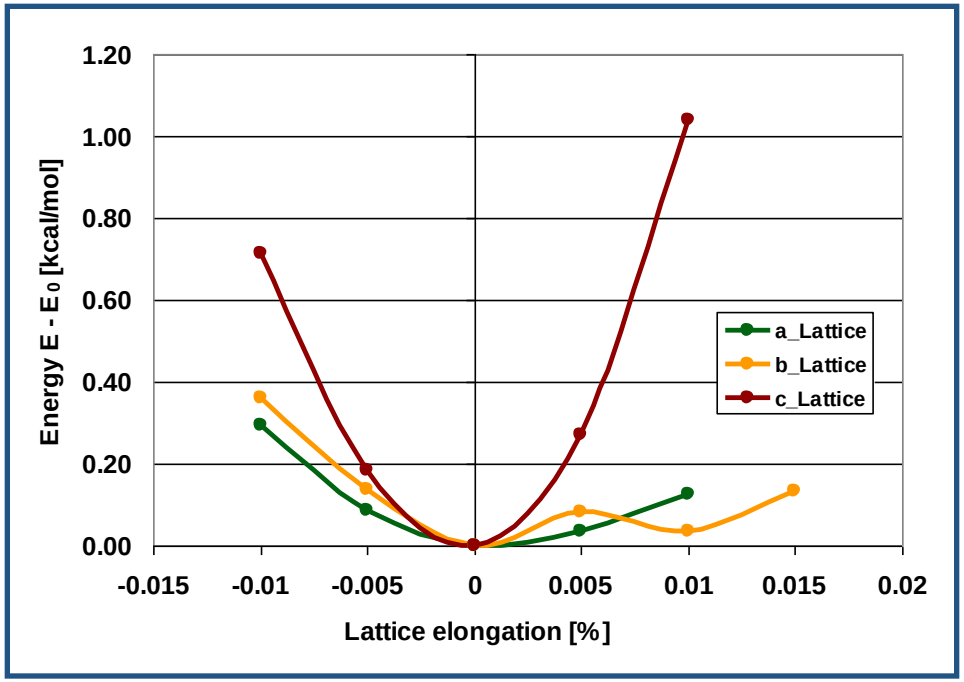
Nikolov et al. Advanced Materials 22 (2010), 519

Ab initio prediction of α-chitin elastic properties



Ab initio calculations:
a = 4.98 Å; *b* = 19.32 Å; *c* = 10.45 Å
(this study)

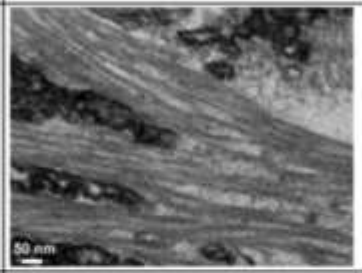
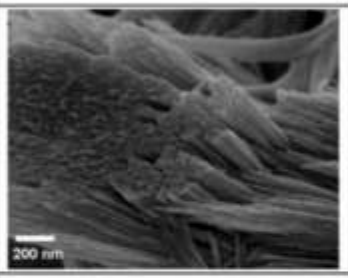
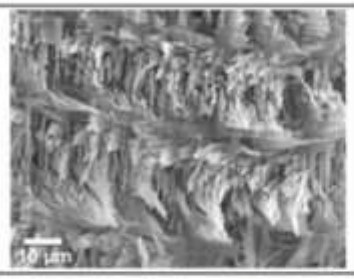
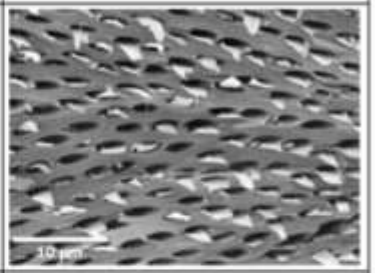
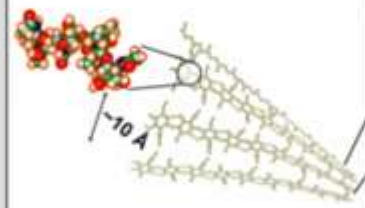
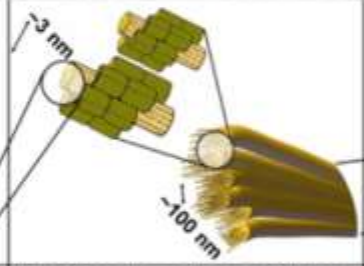
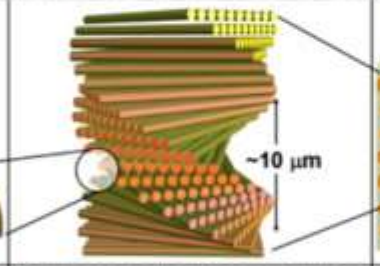
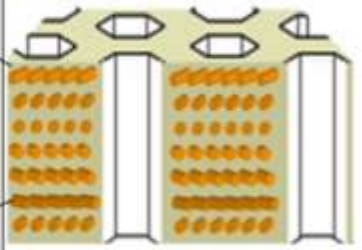
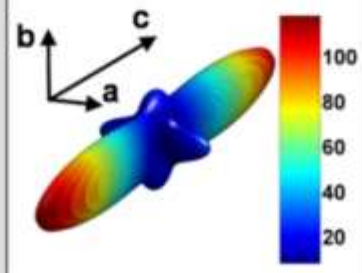
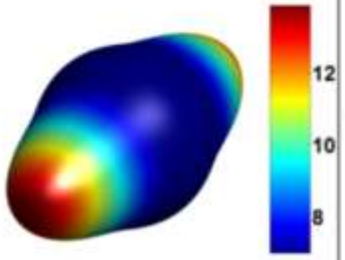
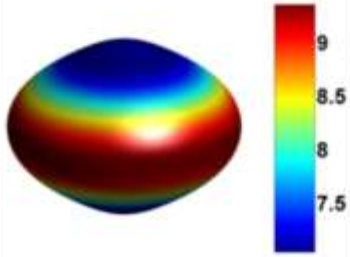
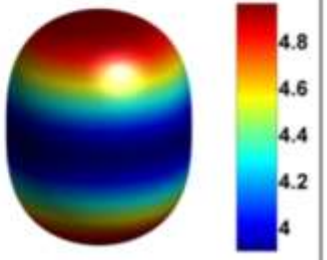
Exp. measured
a = 4.74 Å; *b* = 18.86 Å; *c* = 10.32 Å
(Minke & Blackwell J. Mol. Biol. 1978)



$$\underline{\underline{C}}_{CH} = \begin{bmatrix} 119 & 0.1 & 1.1 & 0 & 0 & 0 \\ 0.1 & 28 & 2 & 0 & 0 & 0 \\ 1.1 & 2 & 24 & 0 & 0 & 0 \\ 0 & 0 & 0 & 5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{bmatrix} GPa$$

Nikolov et al. Advanced Materials 22 (2010), 519

Hierarchical modeling of stiffness starting from ab initio

Scale	0.1 nm – 10 nm	10 nm – 100 nm	100 nm – 10 μm	10 μm – 1 mm
Hierarchical structure unit	α-chitin (H-bonded anti-parallel N-acetyl-glucosamine molecular chains)	Mineralized chitin-protein nanofibrils in a planar array	Twisted plywood stack of mineralized chitin-protein planes without pore canals	Twisted plywood stack of mineralized chitin-protein planes with pore canals
Experimental method	Transmission electron microscope	Field emission scanning electron microscope	Field emission scanning electron microscope	Field emission scanning electron microscope
Microstructure				
Schematic				
Simulation method	Ab initio; density functional theory	Mori-Tanaka scheme (chitin-protein fiber); Torquato 3-point scheme (mineral-protein matrix)	Voigt estimate, tensor rotation	Torquato 3-point homogenization
Elastic behavior, 3D map of Young's modulus [GPa] a,b-axis: basal directions of chitin cell c-axis: longitudinal axis of molecule				

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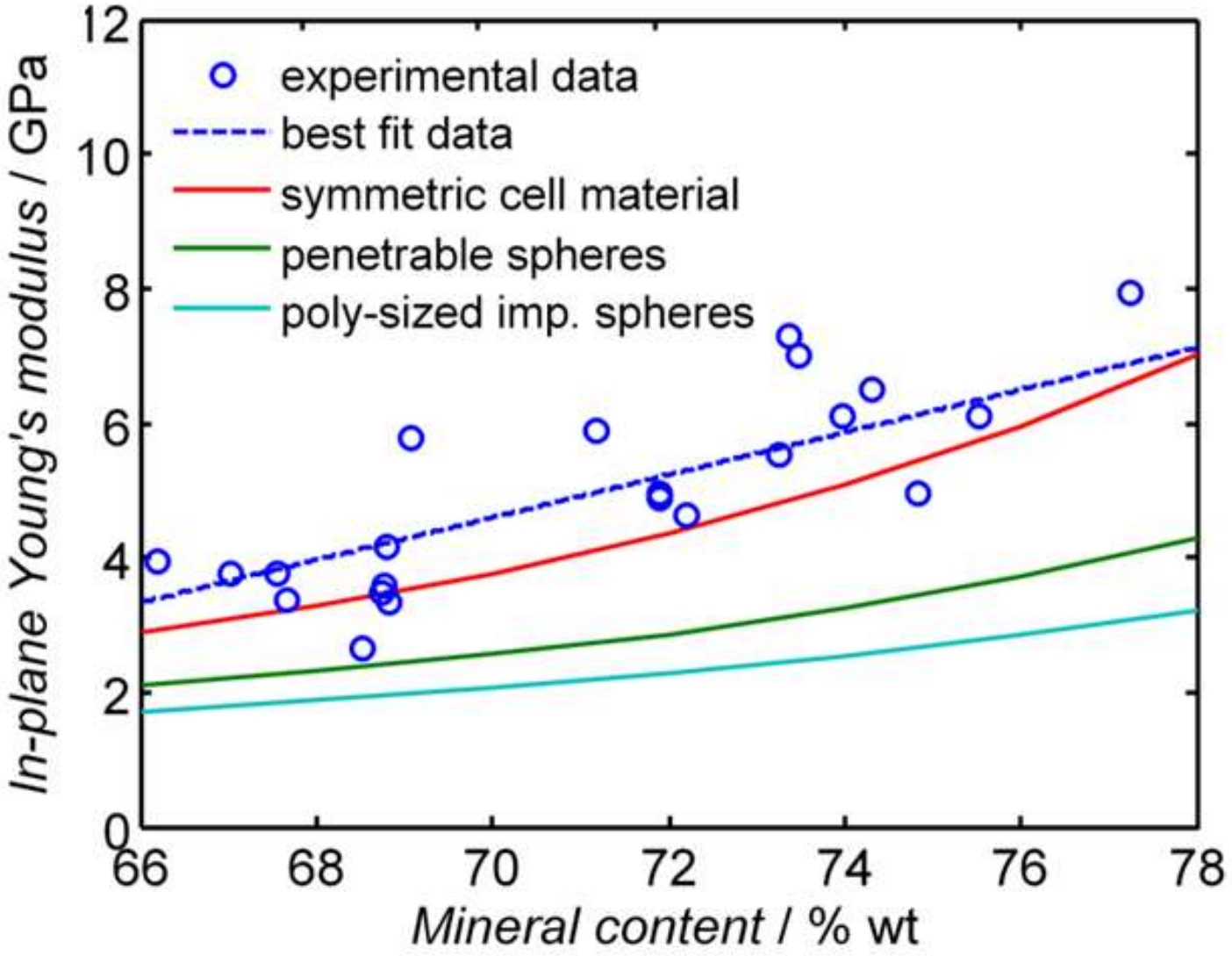
Predictions and comparison to experiments



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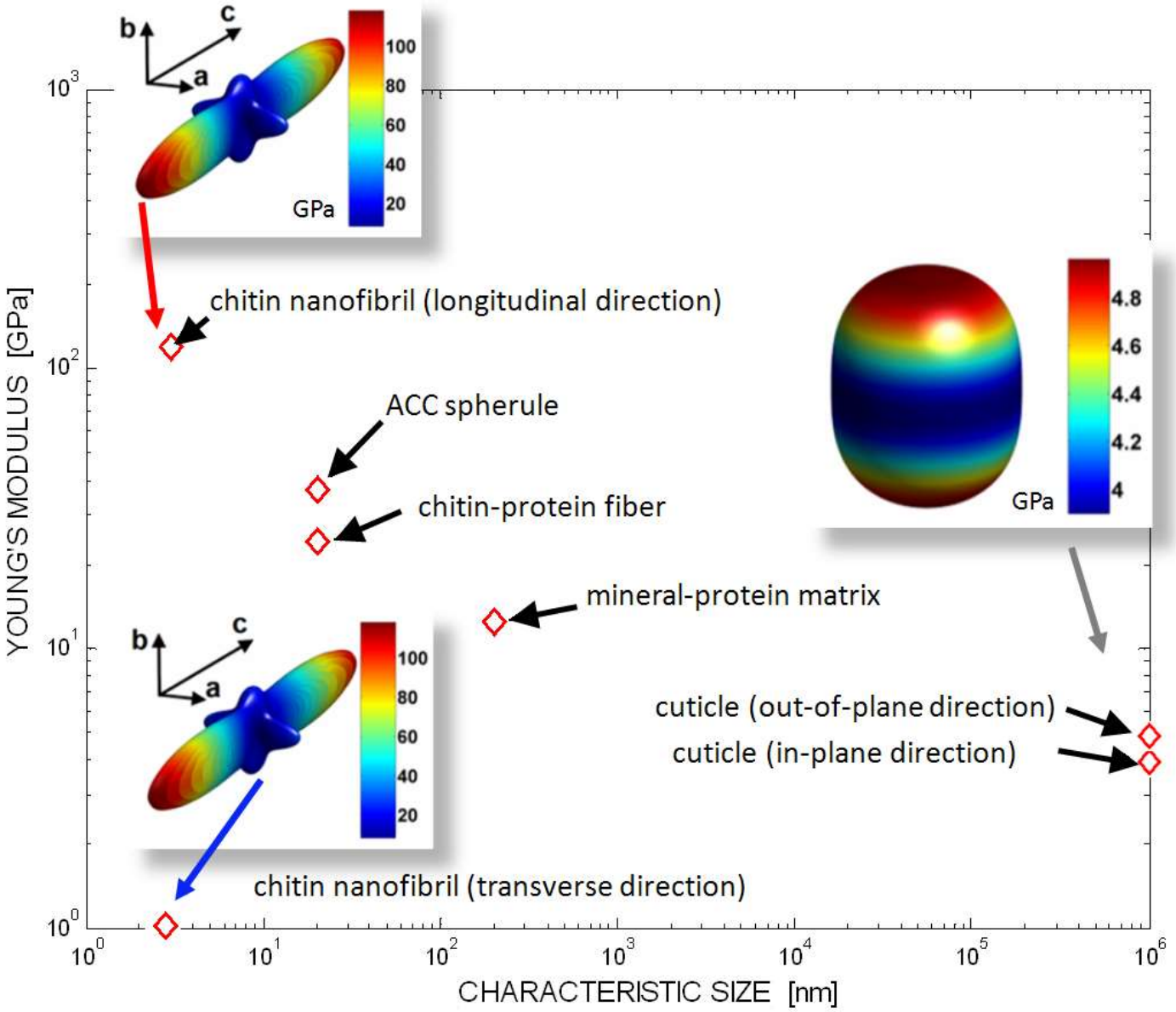
Hierarchical modeling of stiffness starting from ab initio



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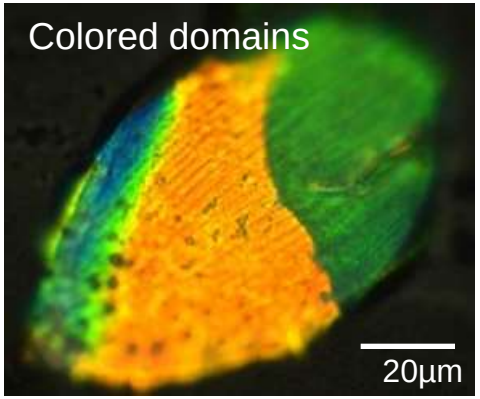
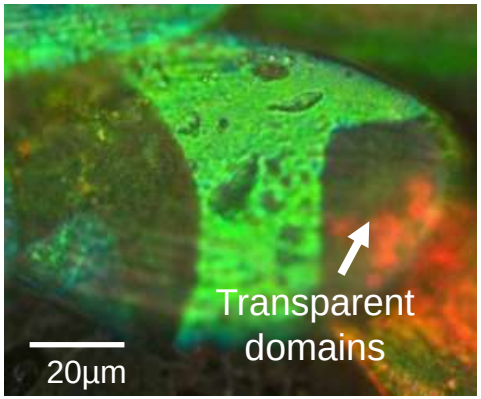
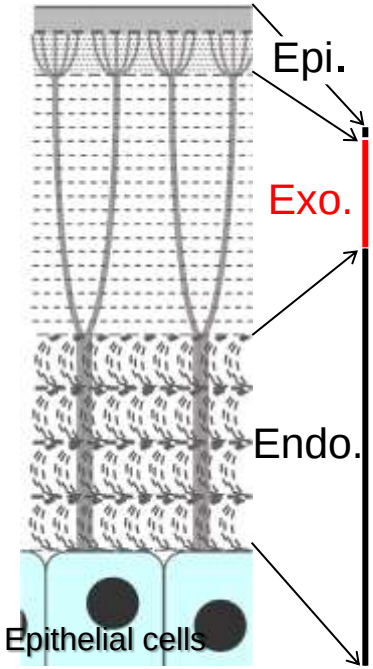
Model system: cuticular scales of Entimus imperialis

Entimus imperialis

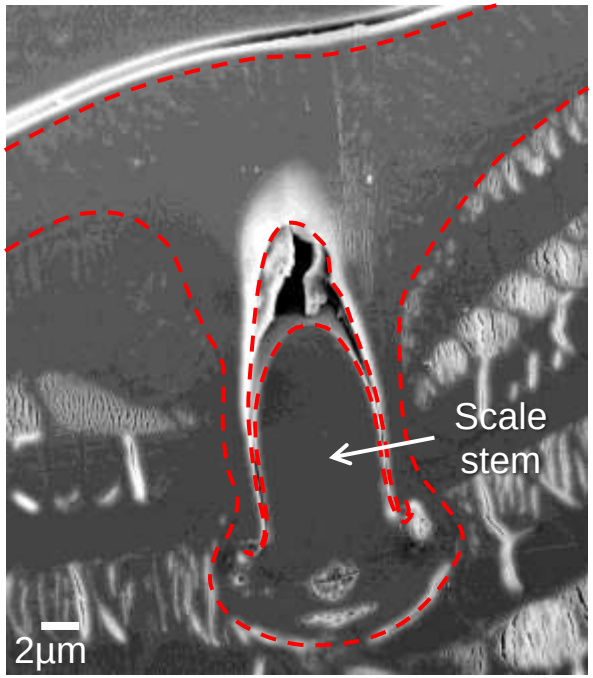




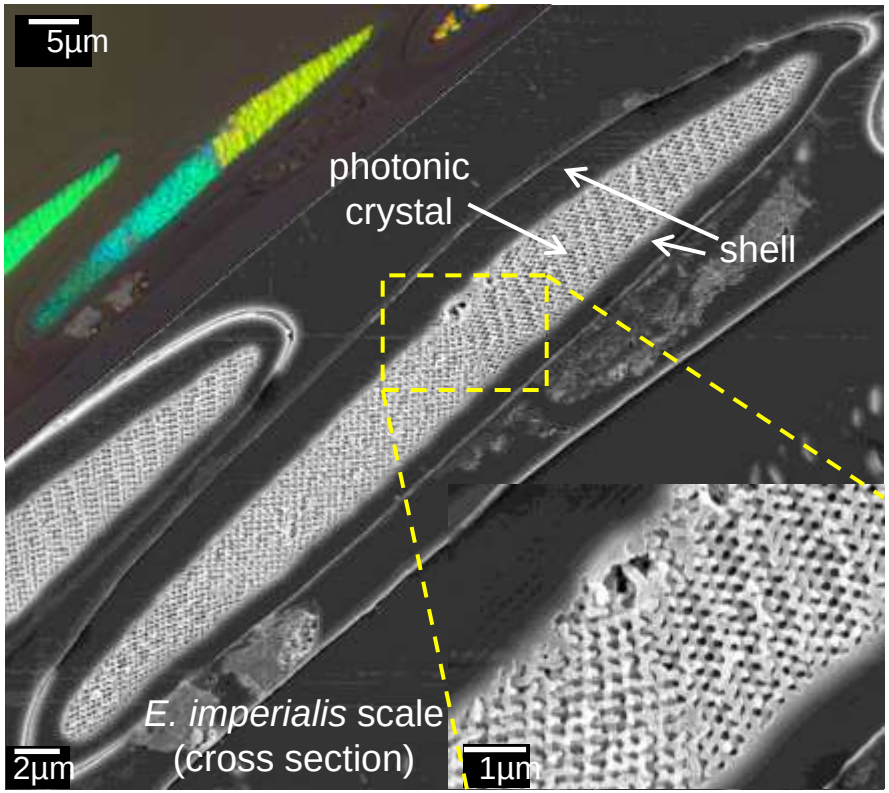
cuticular scales of *E. imperialis*



Insect cuticle (cross section)

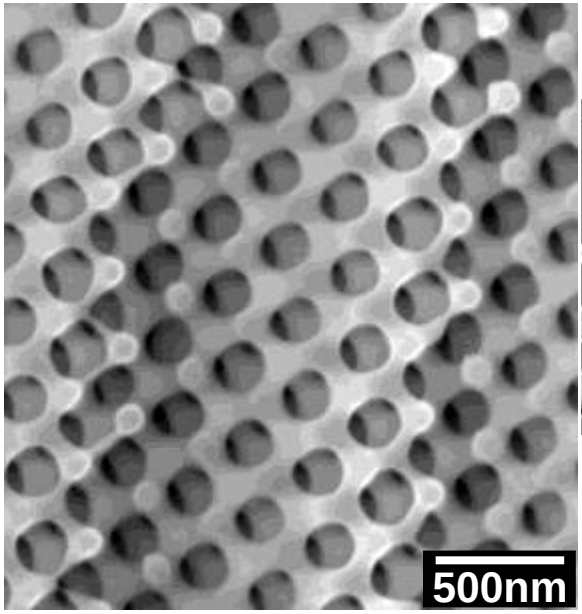


E. imperialis cuticle (cross section)

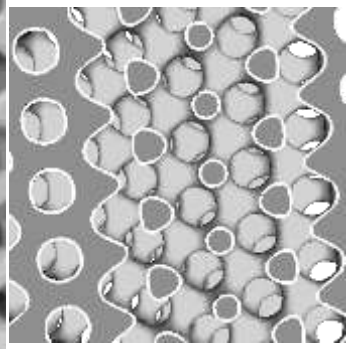


E. imperialis scale (cross section)

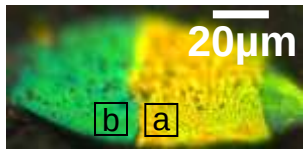
Structure-property relations of the *Entimus* photonic crystals

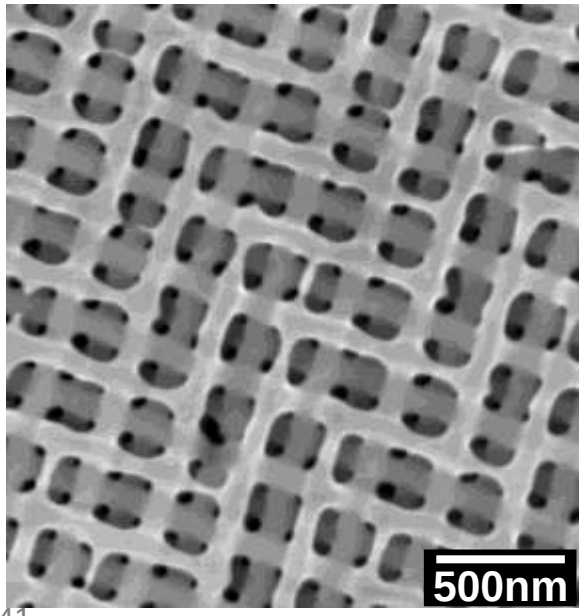


Yellow domain



~ (1 1 1) Γ-L





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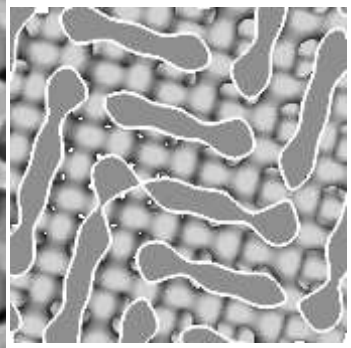

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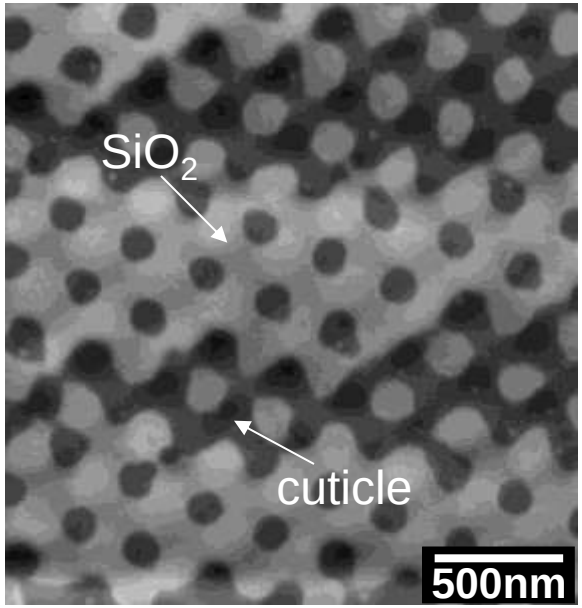

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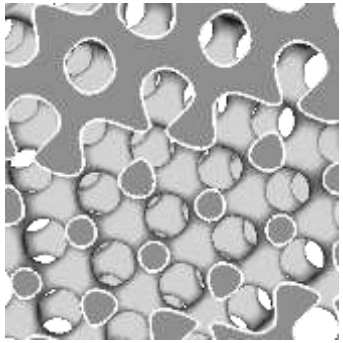

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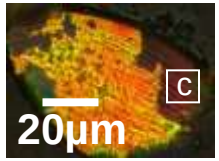

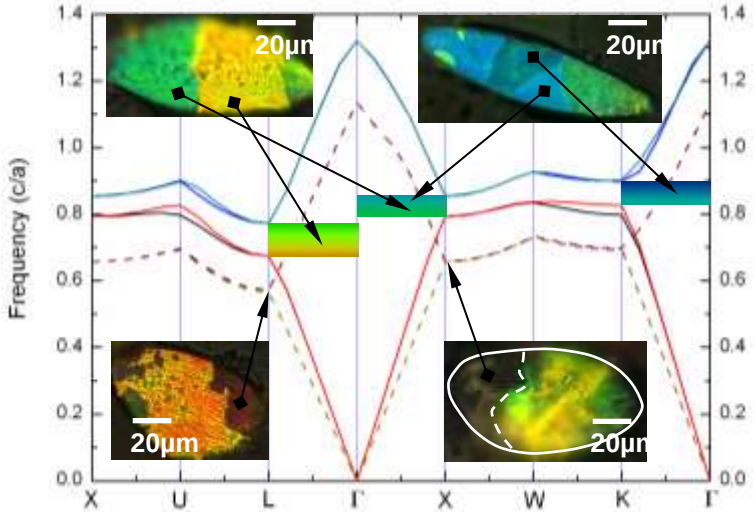

Naturally optimized optical properties:

Largest band gaps at 35% vol.fraction cuticular material

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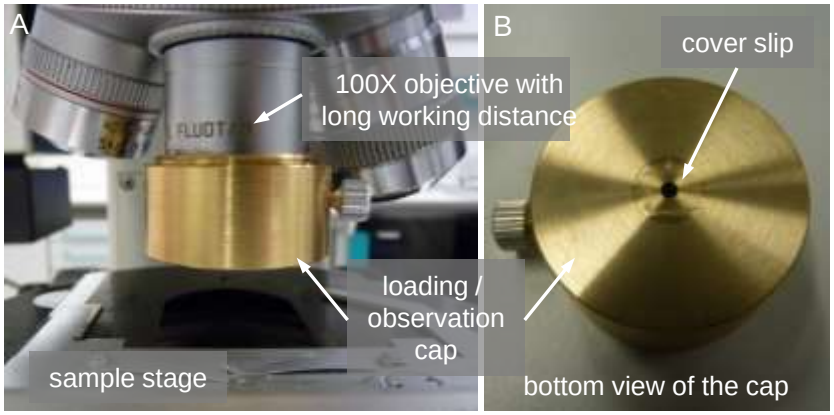
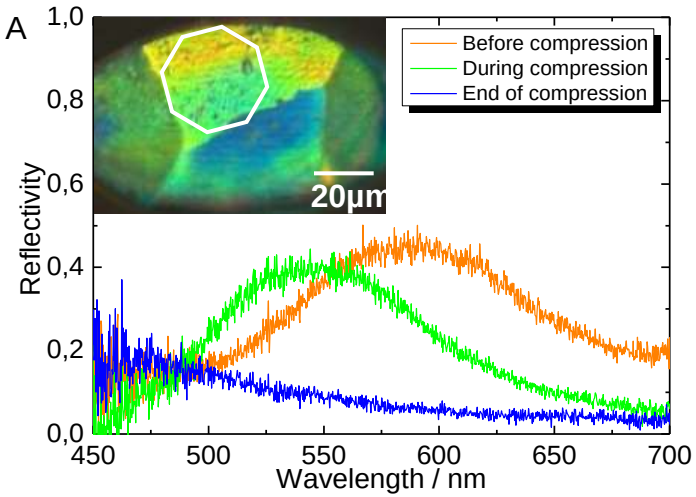
Mechanochromic performance of native scales (I)

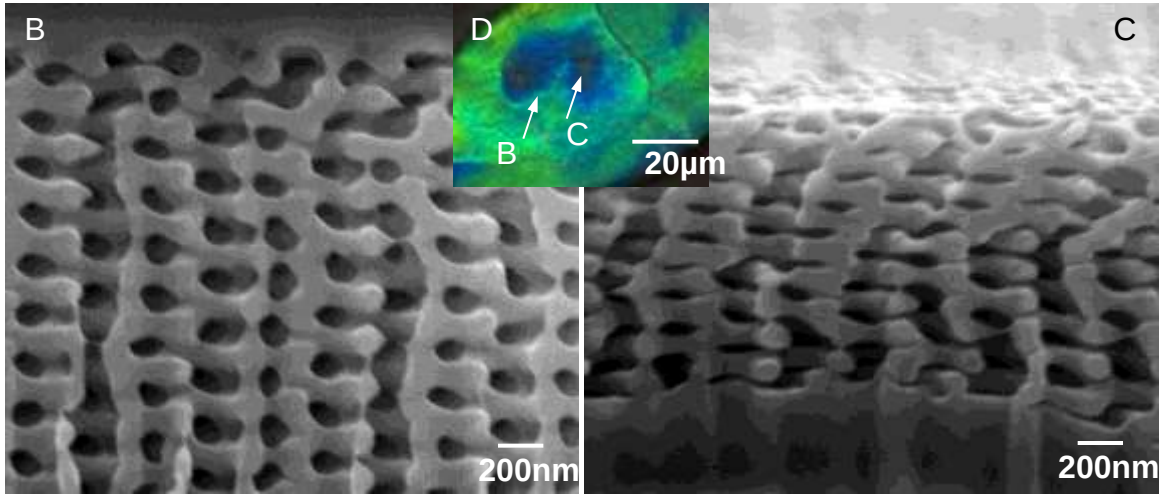


custom-built compression unit
attached to the objective of a light microscope

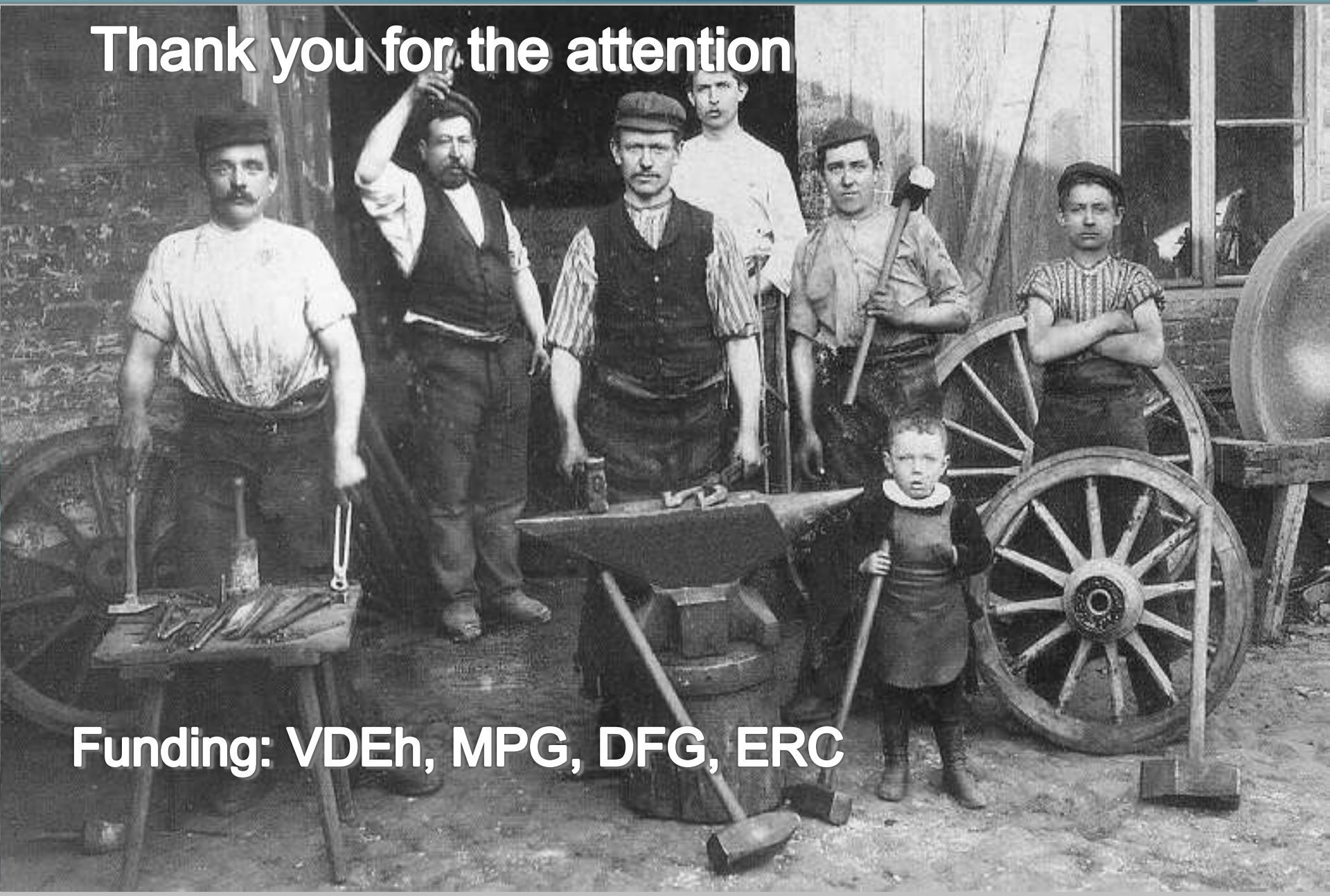
- measure the optical response during compression of native scales
- correlate the structural change with the optical response



Spectral shift of scales after compression



Deformation of the photonic crystals in scales after compression


Thank you for the attention
Funding: VDEh, MPG, DFG, ERC