Extremal stiffness of crustacean cuticle through hierarchical optimization: Experiments and modeling from ab initio to macroscale

H. Fabritius[4], A. Ziegler[1], S. Hild[2], S. Nikolov[3], M. Petrov[4],
C. Sachs[5], L. Lymperakis[4] , M. Friák[4], J. Neugebauer[4] , D. Raabe[3]

1) University of Ulm, Central Facility for Electron Microscopy. Germany
2) Johannes Kepler University Linz (JKU), Department of Polymer Science, Austria
3) Max-Planck-Institut für Eisenforschung GmbH, Department Microstructure Physics, Germany
4) Max-Planck-Institut für Eisenforschung GmbH, Department of Computational Materials Design, Germany
5) Department for Materials Science, MIT, USA

d.raabe@mpie.de

Max-Planck-Institut für Eisenforschung GmbH

Institute for Polymer Science
Johannes Kepler University Linz

ulm university universität ulm

January 08th, 2009; PLASTICITY 2009, St Thomas, Virgin Islands, USA

Overview

- **Introduction to mineralized composite materials based on <u>chitin</u> and proteins**
- **Hierarchical <u>structure</u>**
- **Hierarchical <u>mechanical</u> properties**
- **<u>Theoretical</u> understanding through multiscale modeling (ab-initio, coarse graining, continuum)**

Overview

- **Introduction to mineralized composite materials based on chitin and proteins**
- **Hierarchical structure**
- **Hierarchical mechanical properties**
- **Theoretical understanding through multiscale modeling (ab-initio, coarse graining, continuum)**

Introduction - Arthropod cuticle

Main exoskeleton component of more than 90% of all animal species …

adaptive material → candidate for bio-inspired material

Crustacean cuticle (subgroup of arthropods)

- cuticle surrounds the whole animal
- forms different skeletal elements
- cover a vast variety of physical properties
- adapted to:
  - the specific function of the skeletal element
  - ecophysiological strains of the animal

Birgus latro

Porcellio scaber

Armadillidium vulgare

Horseshoe crab

Homarus americanus

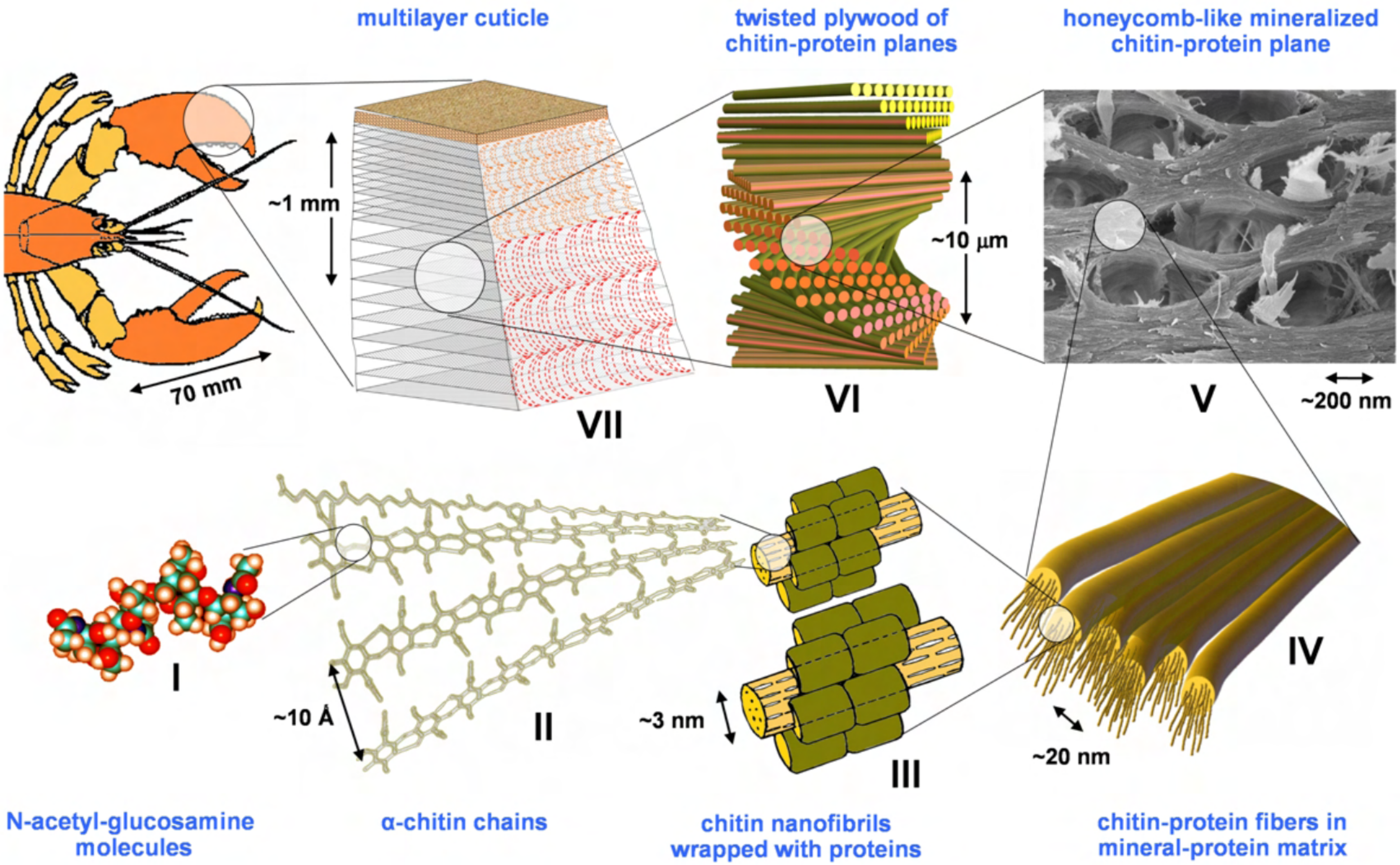
- hierarchical structure follows the same principle regardless of the specific properties of the cuticle

- Homarus americanus

- Carabus auronitens

- Chrysophanes virgaurea

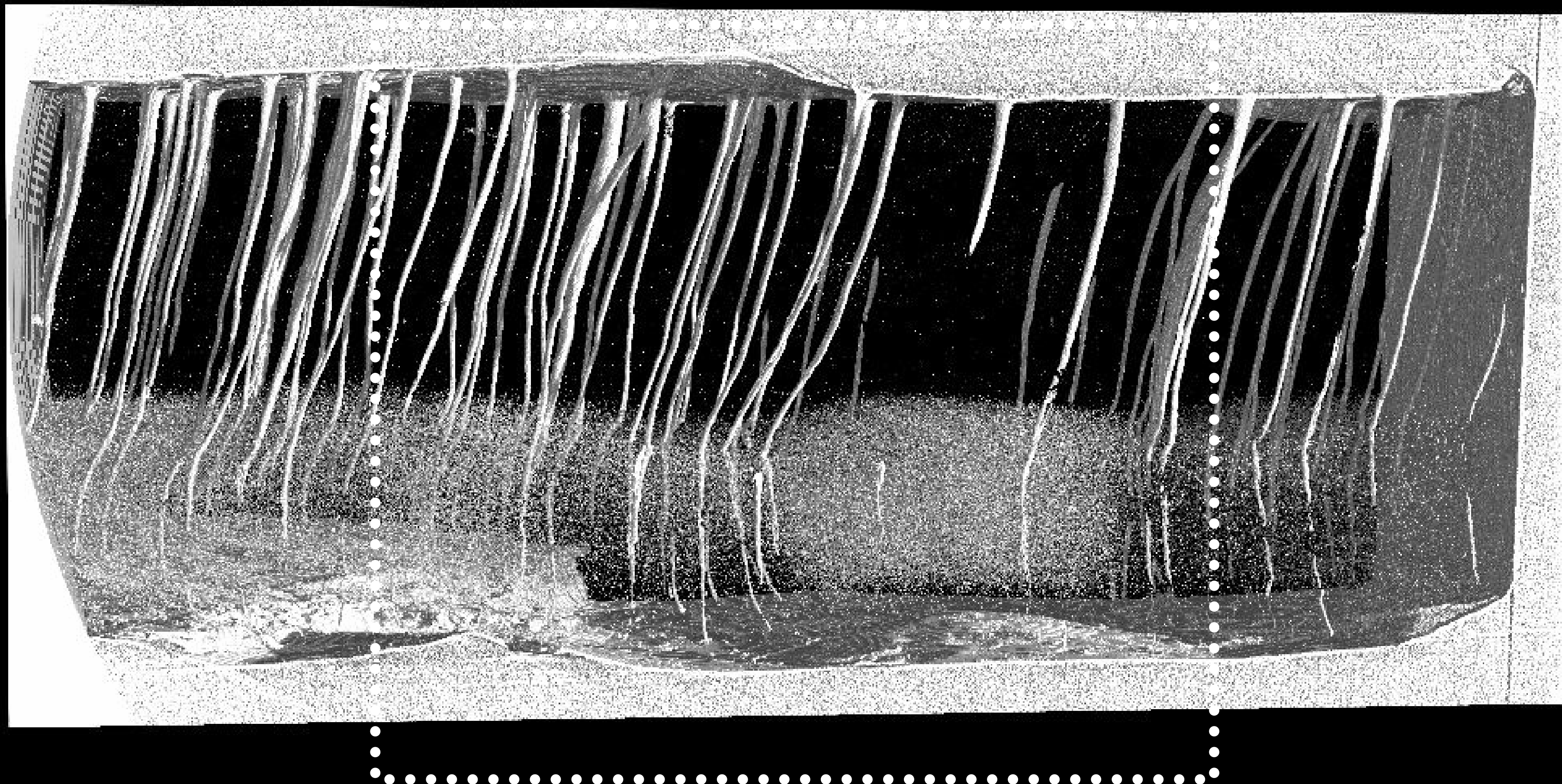
Introduction - Hierarchical organization



Overview

- Introduction to mineralized composite materials based on chitin and proteins
- **Hierarchical structure**
- Hierarchical mechanical properties
- Theoretical understanding through multiscale modeling (ab-initio, coarse graining, continuum)

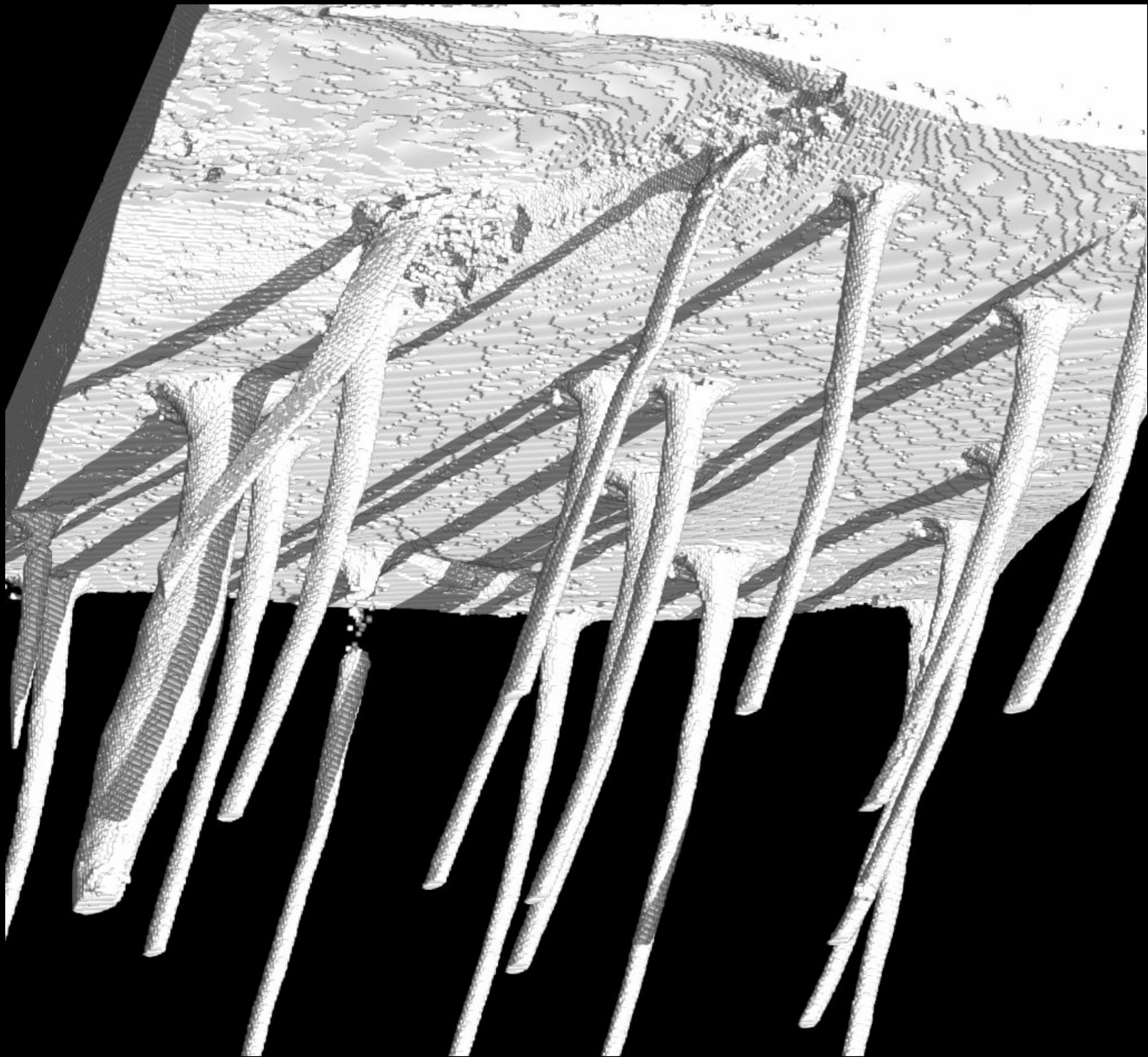
X-ray tomography, cuticle, horseshoe crab

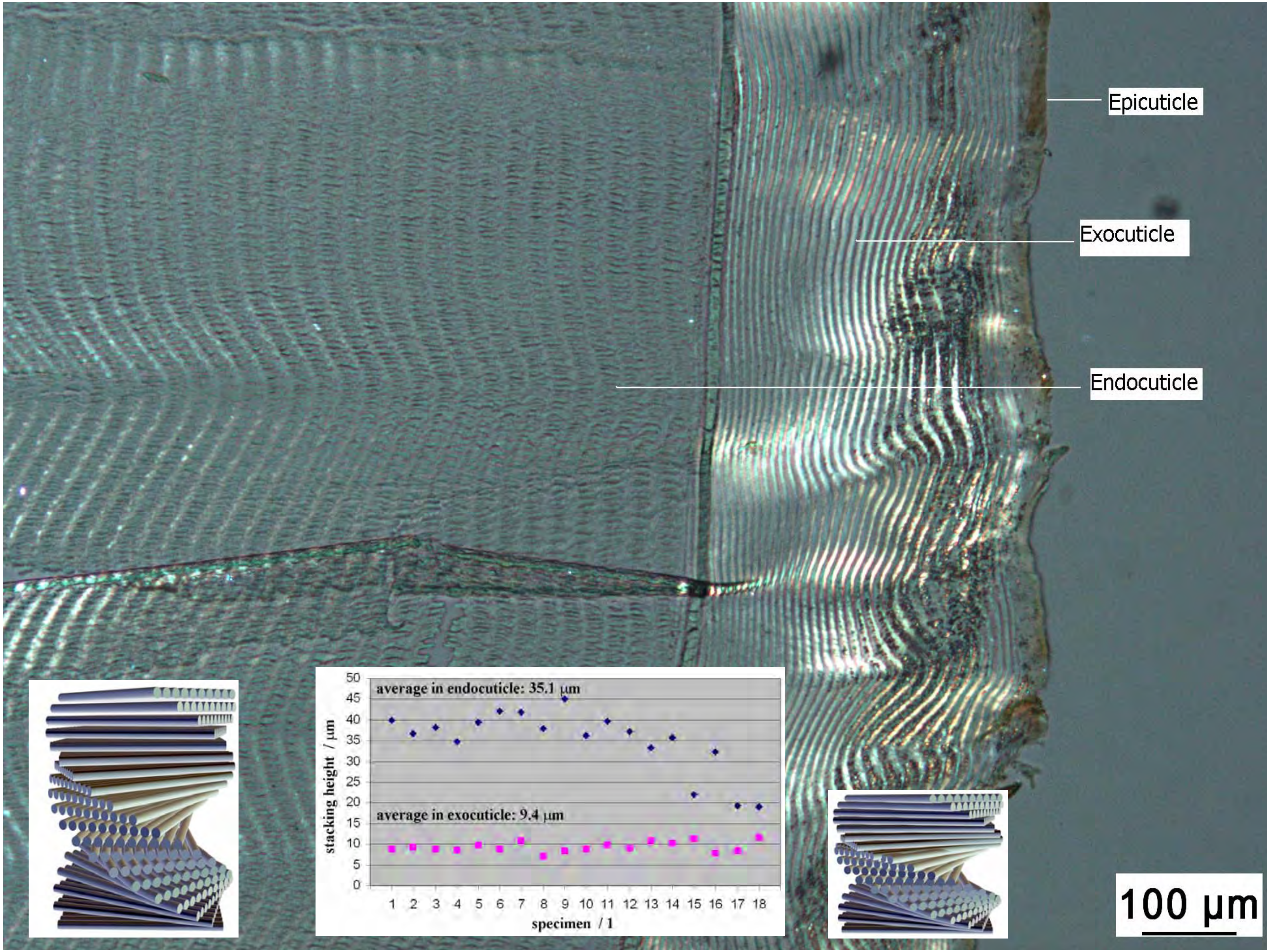


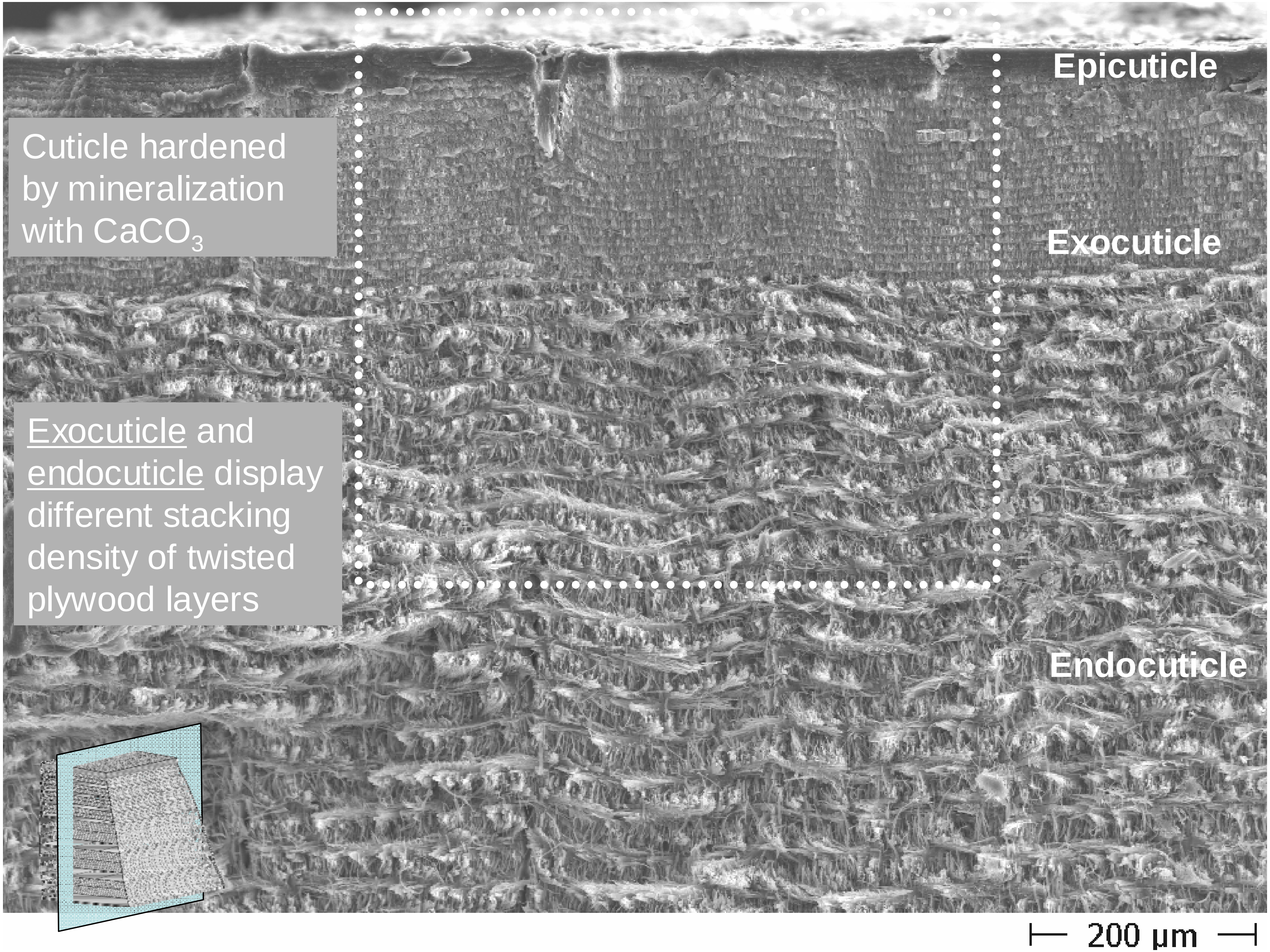
measurement by Astrid Haibel, BESSY, GKSS

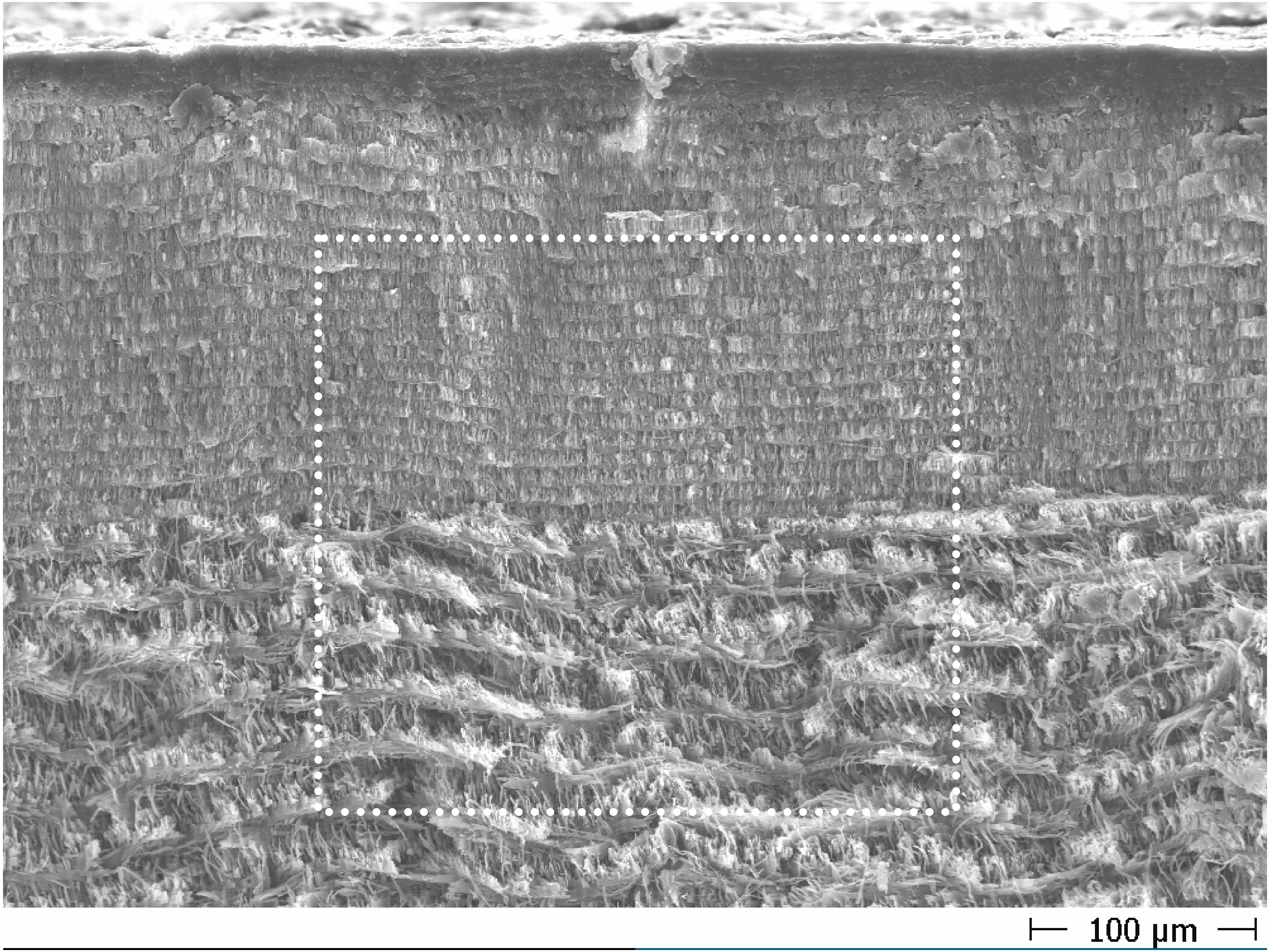
X-ray tomography, cuticle, horseshoe crab

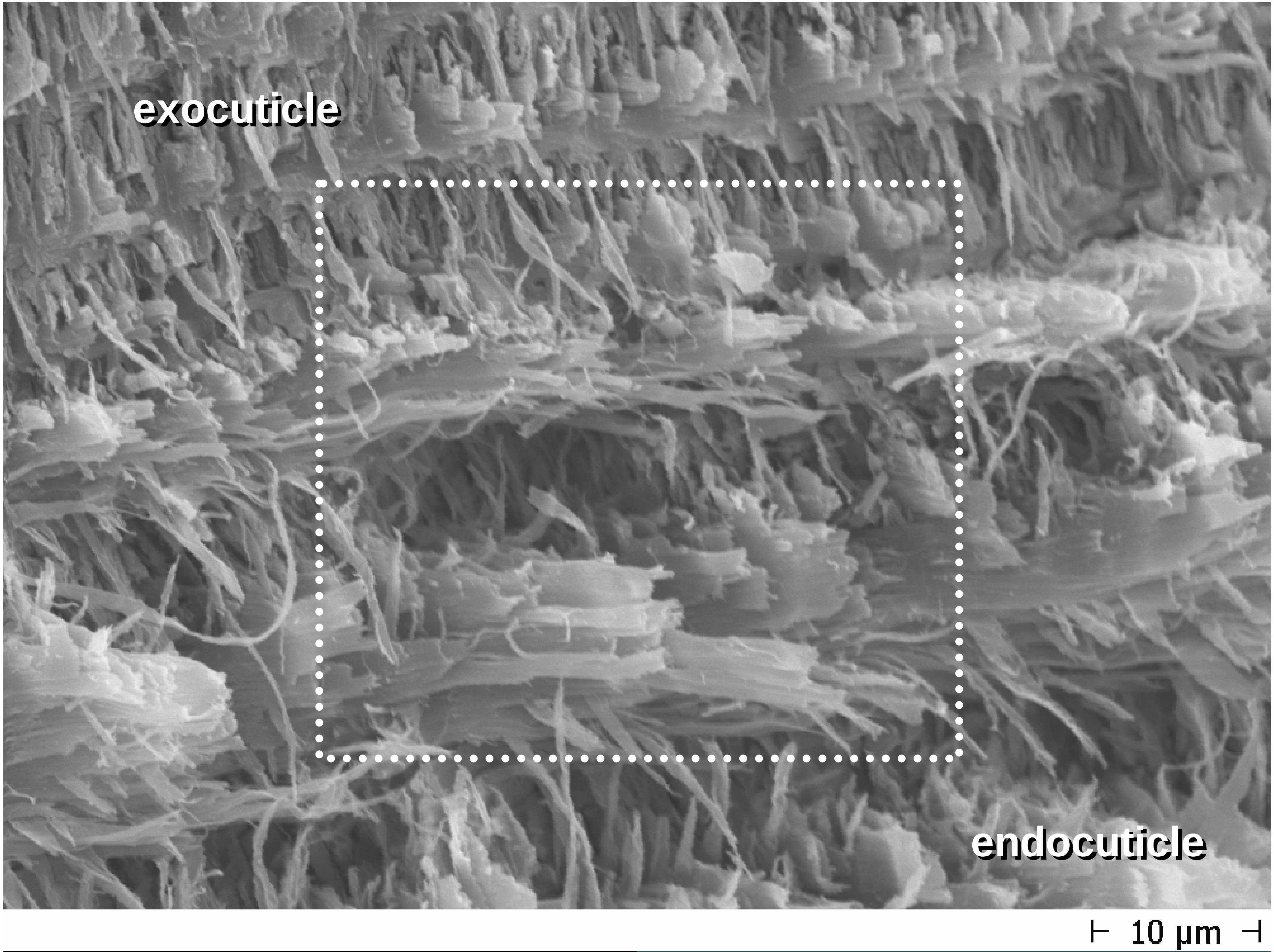
X-ray tomography, cuticle, horseshoe crab

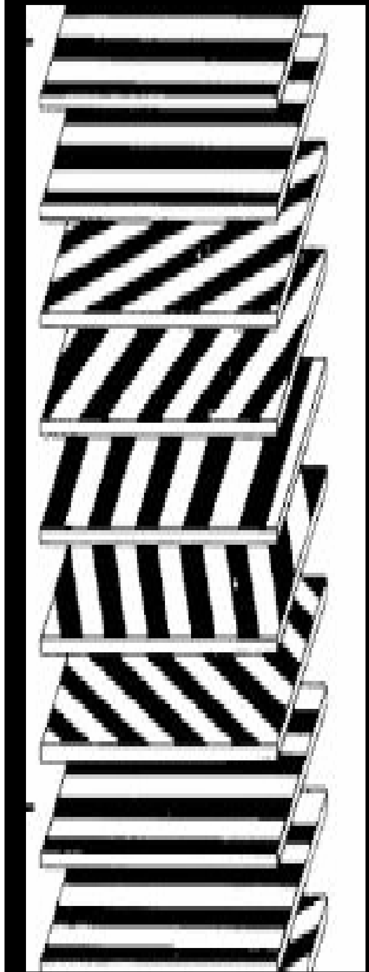


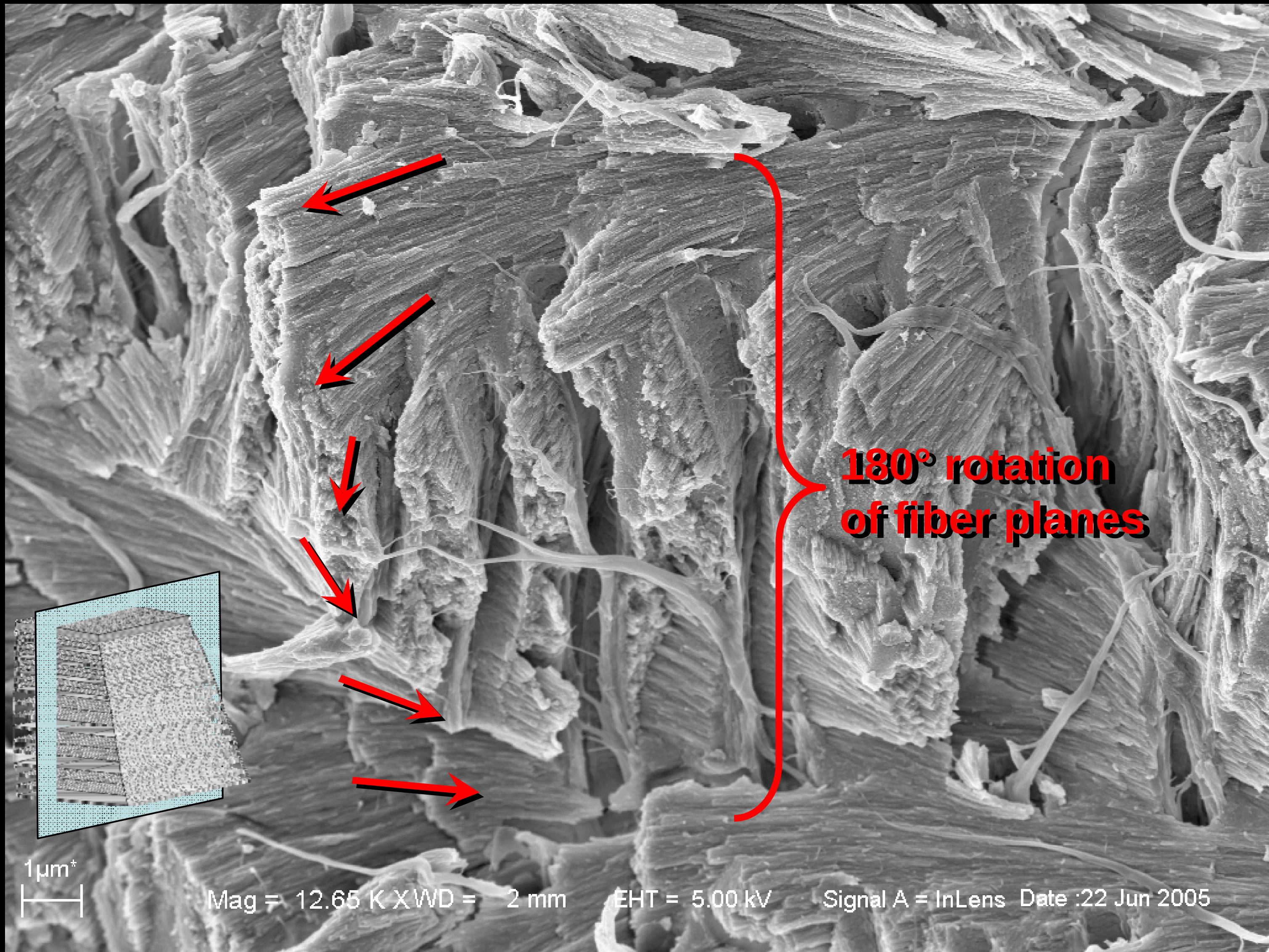

Epicuticle
Exocuticle
Endocuticle
average in endocuticle: 35.1 µm
average in exocuticle: 9.4 µm
stacking height / µm
specimen / 1
0
5
10
15
20
25
30
35
40
45
50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
100 µm

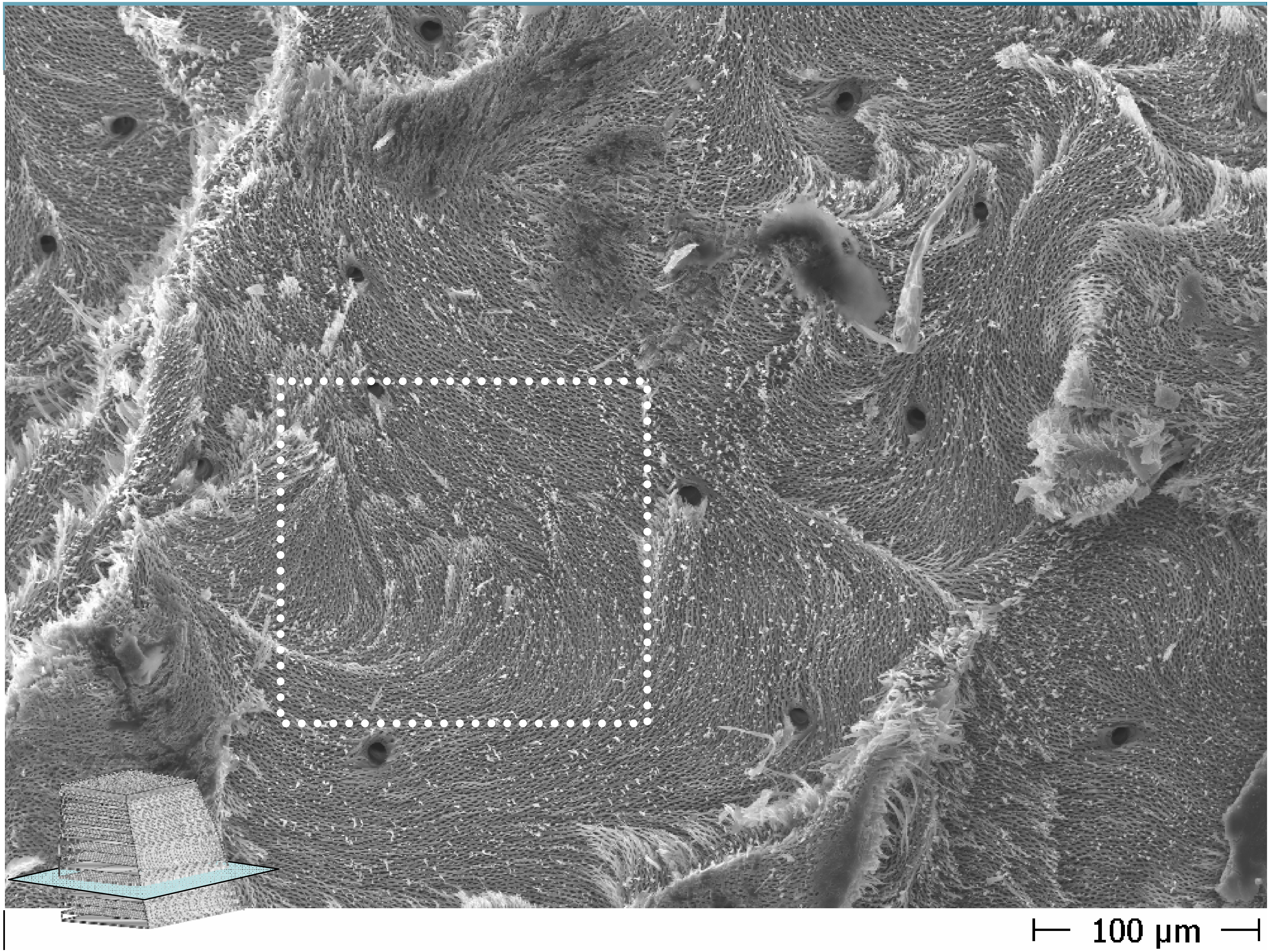

Epicuticle
Cuticle hardened by mineralization with $CaCO_3$
Exocuticle
Exocuticle and endocuticle display different stacking density of twisted plywood layers
Endocuticle
200 µm

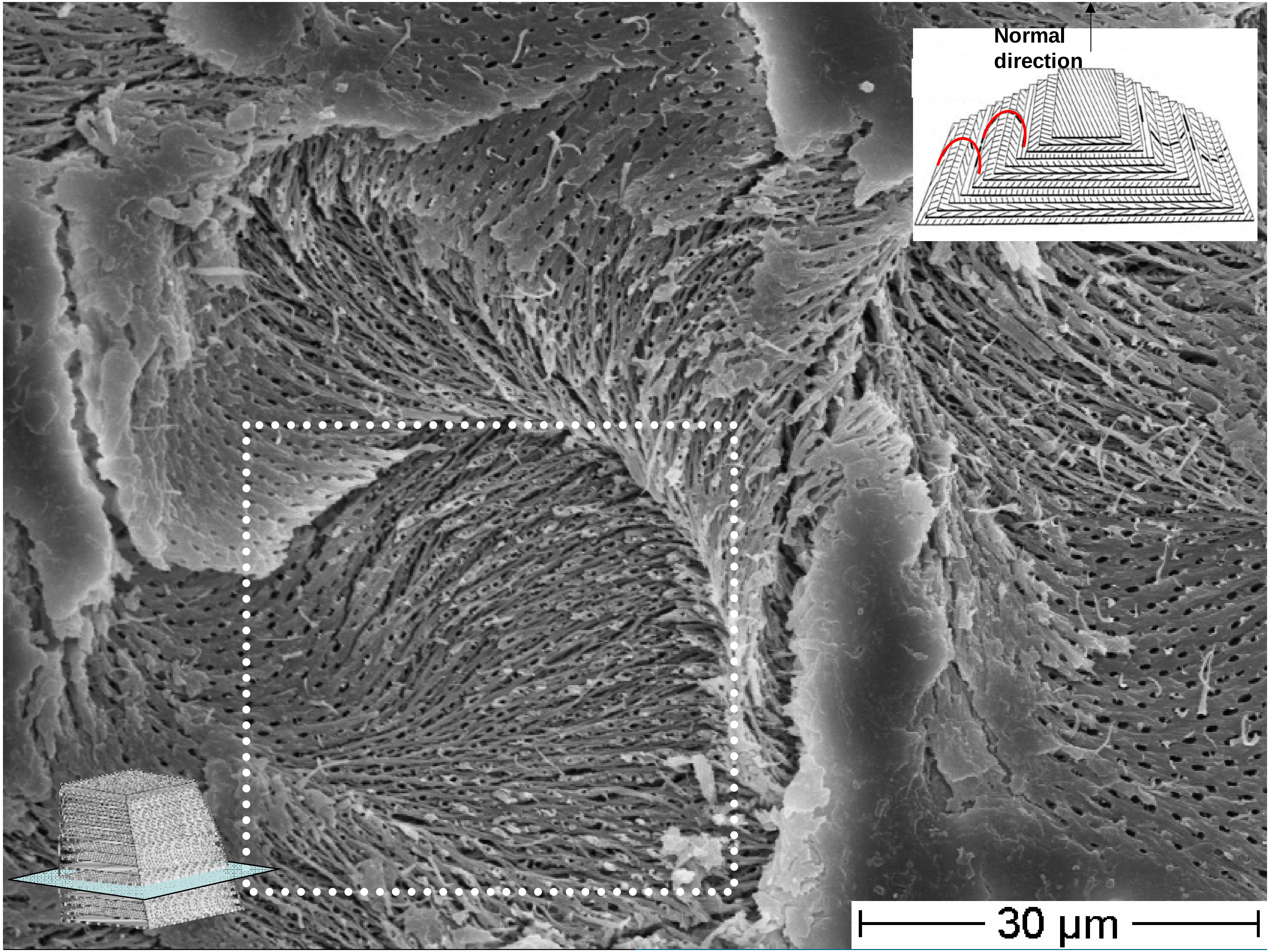

100 µm

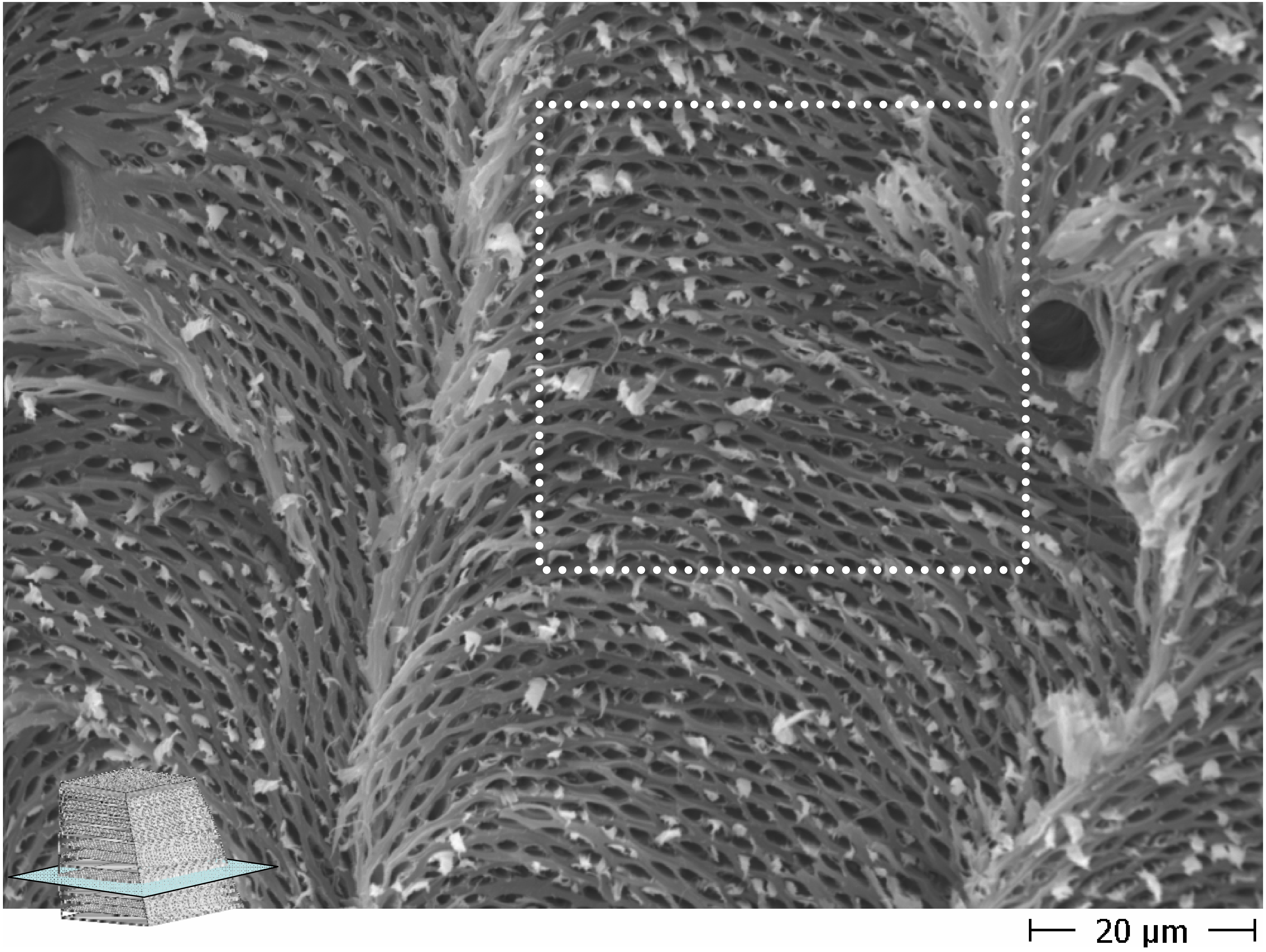

exocuticle
endocuticle
10 µm

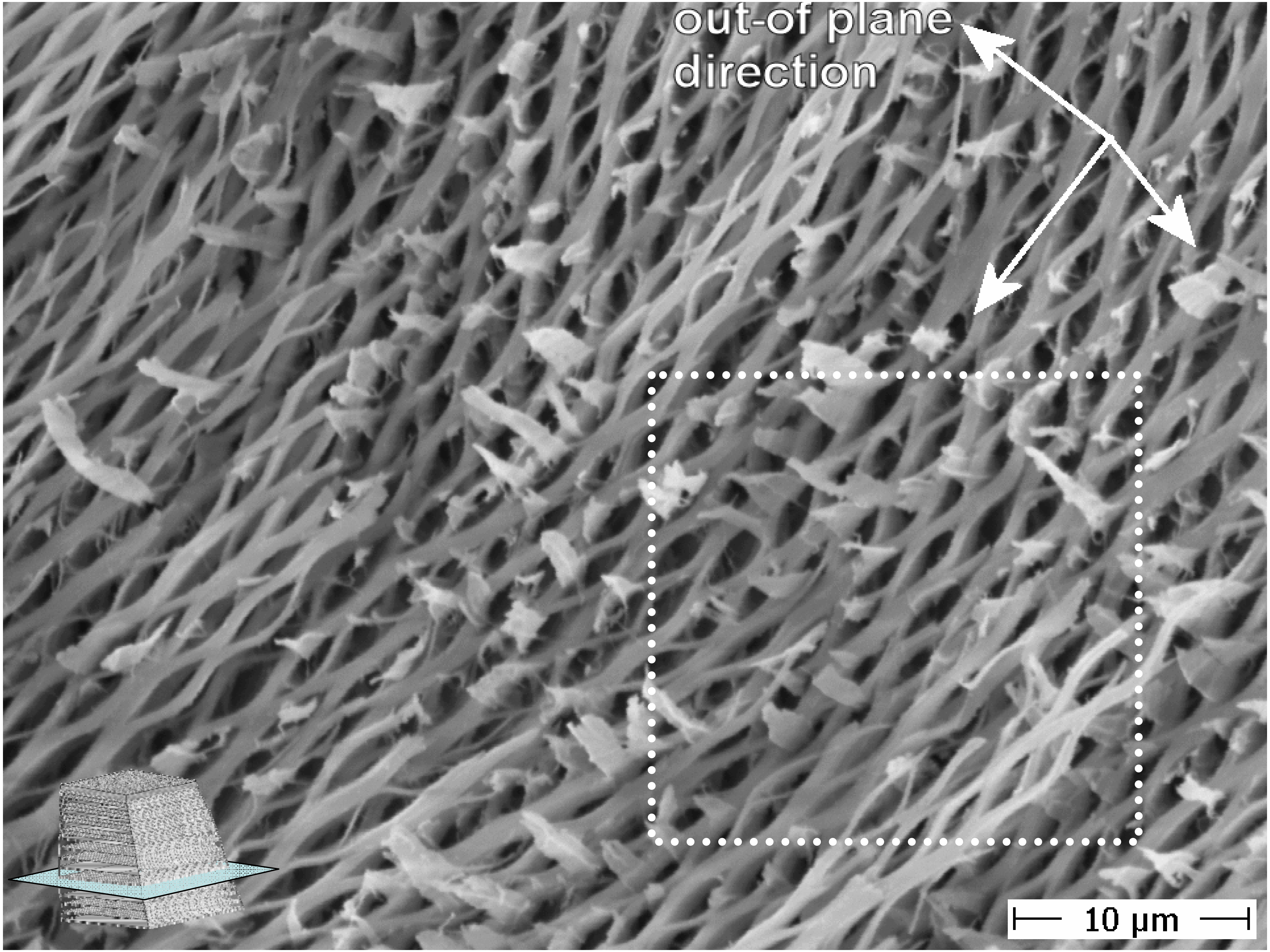


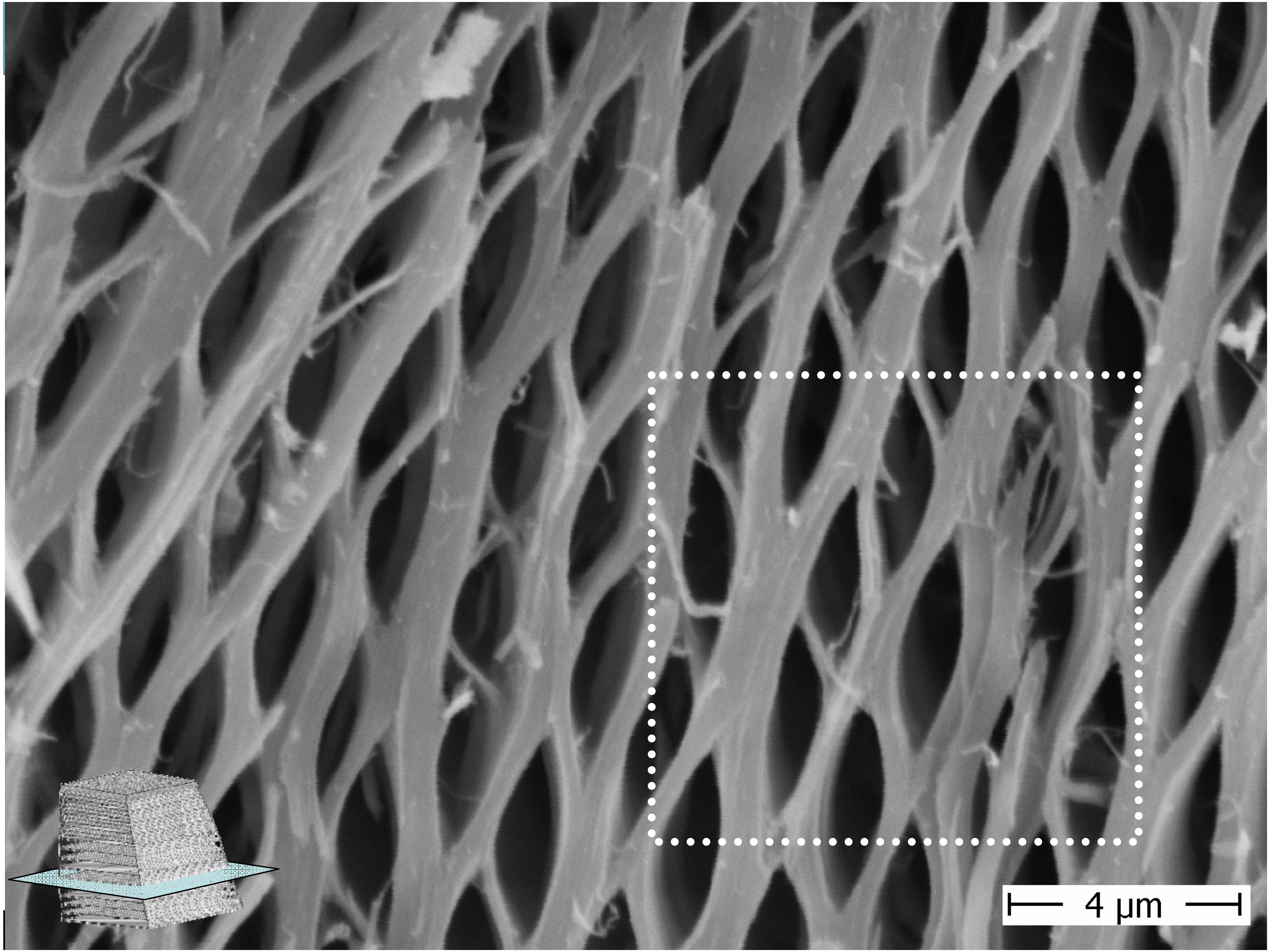

180° rotation
of fiber planes
1µm*
Mag = 12.65 K X WD = 2 mm EHT = 5.00 kV Signal A = InLens Date :22 Jun 2005

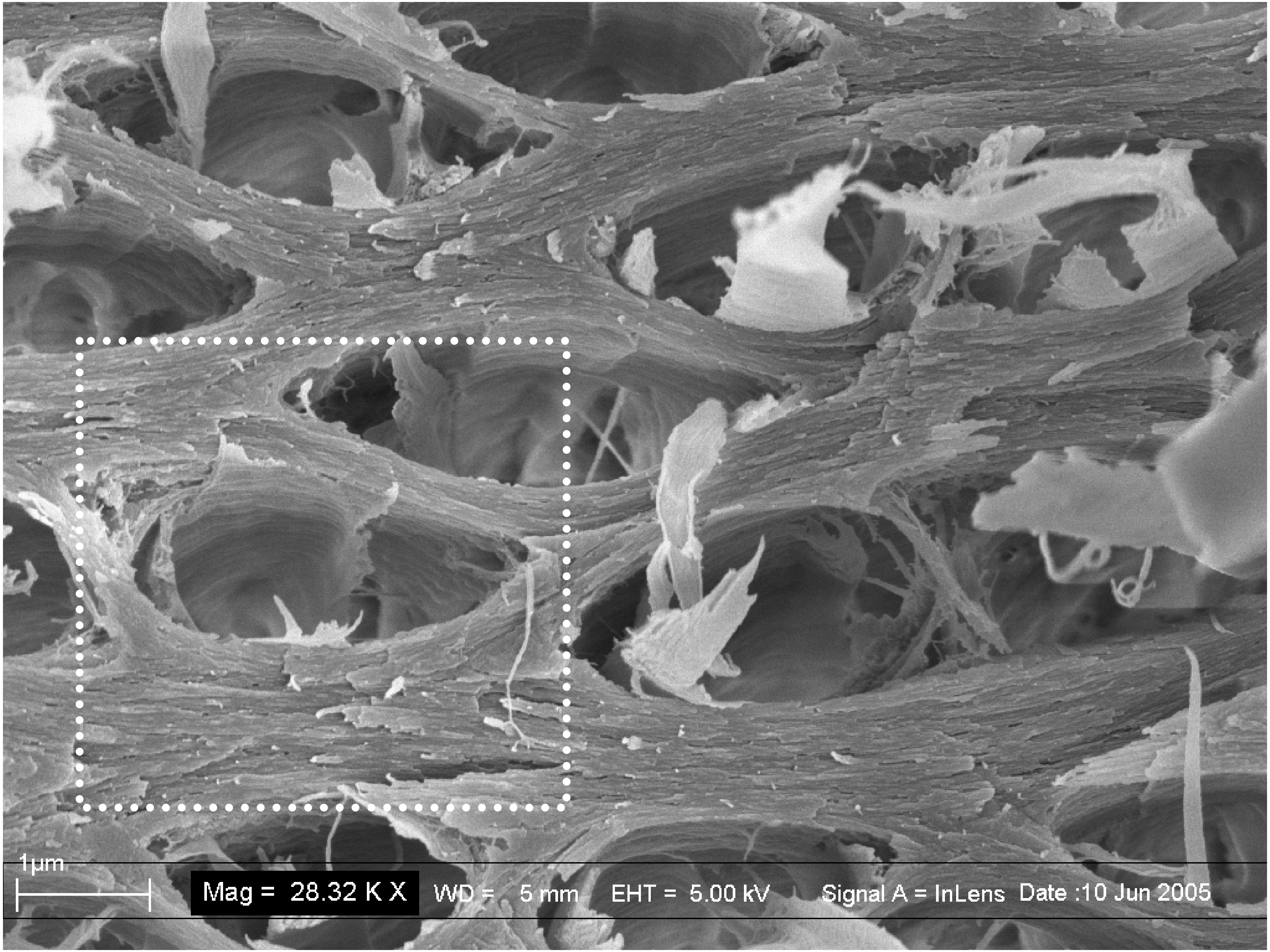

100 µm

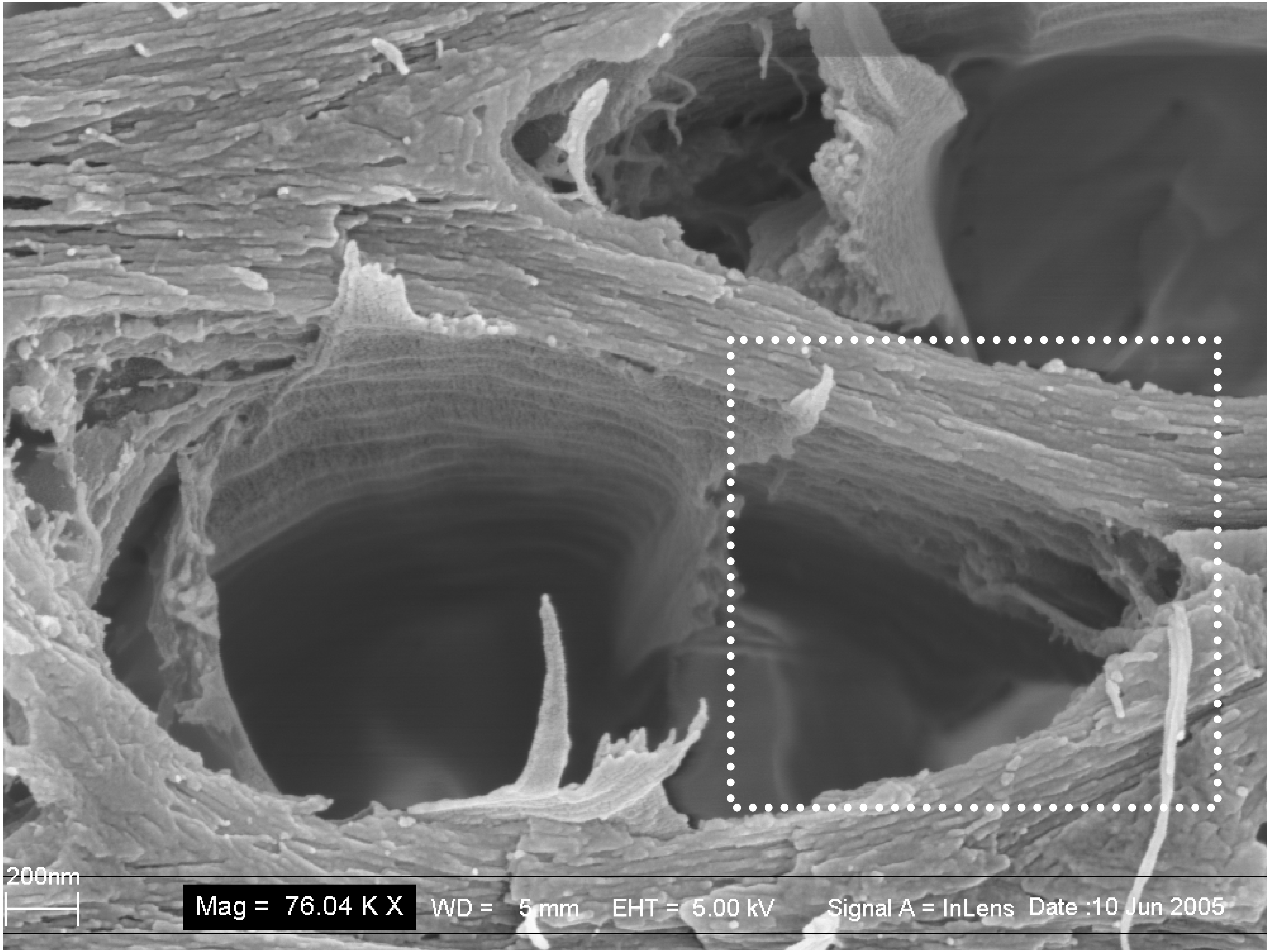

Normal direction
30 µm


20 µm

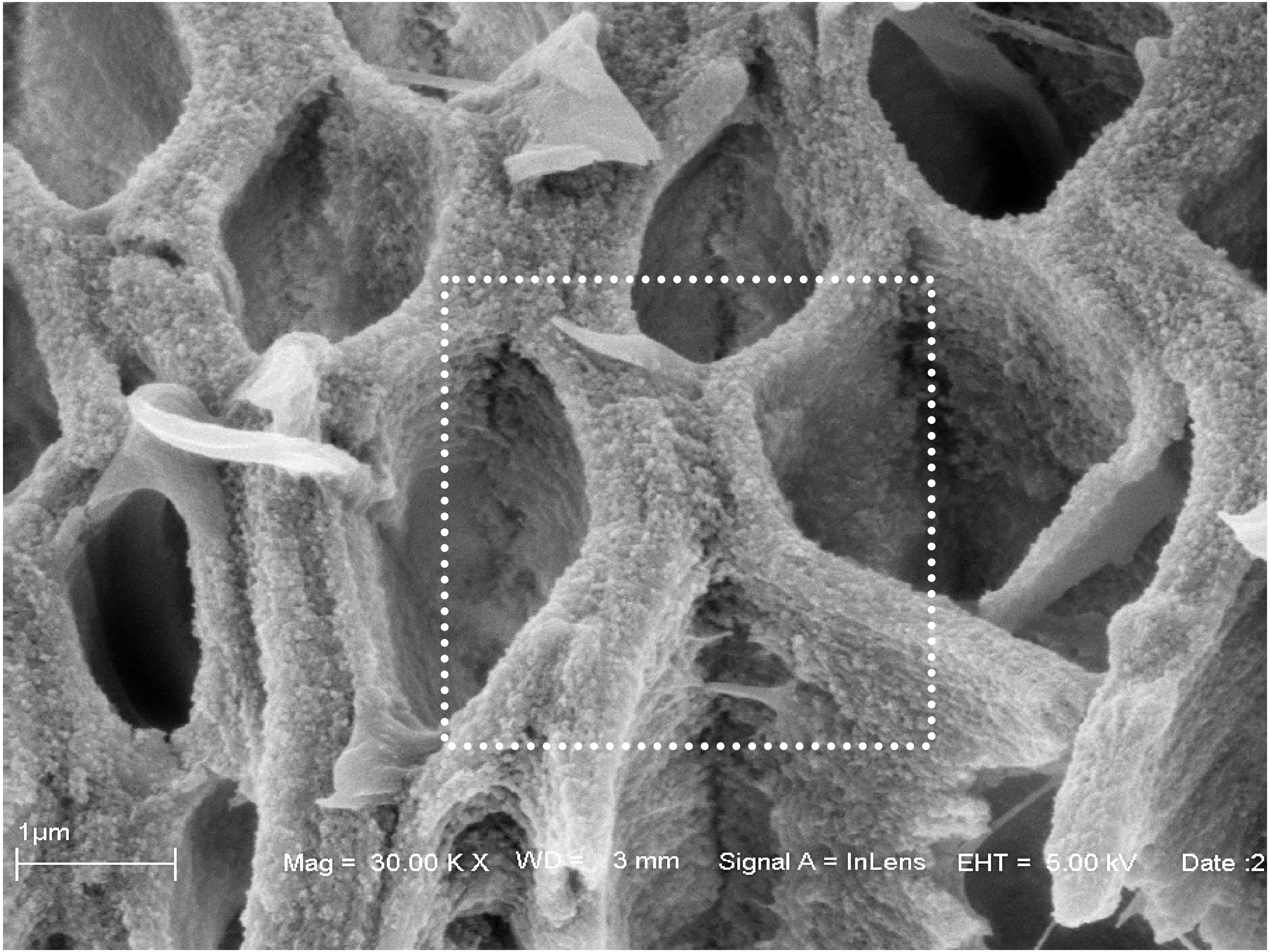

out-of plane
direction
10 µm

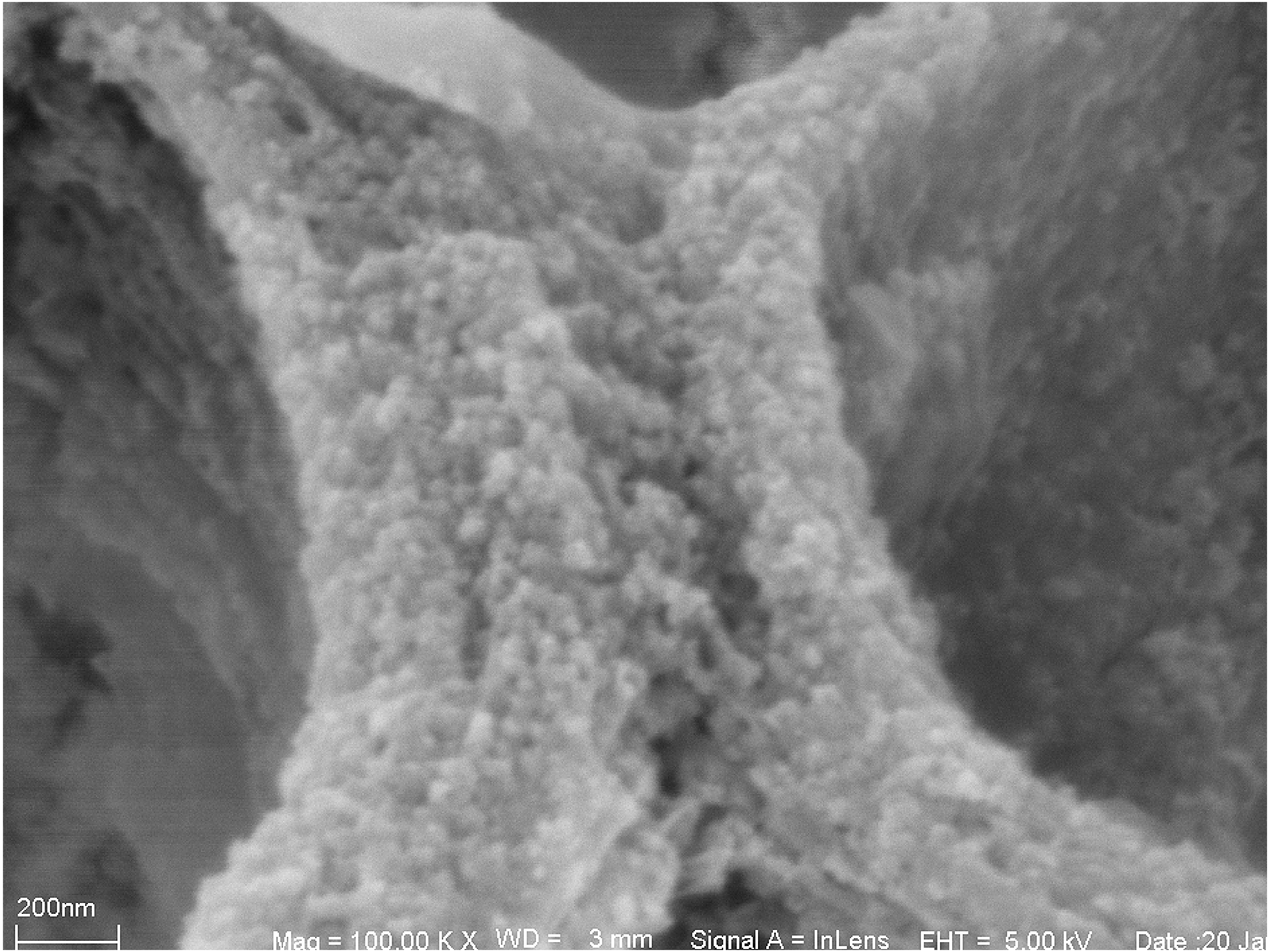

4 µm

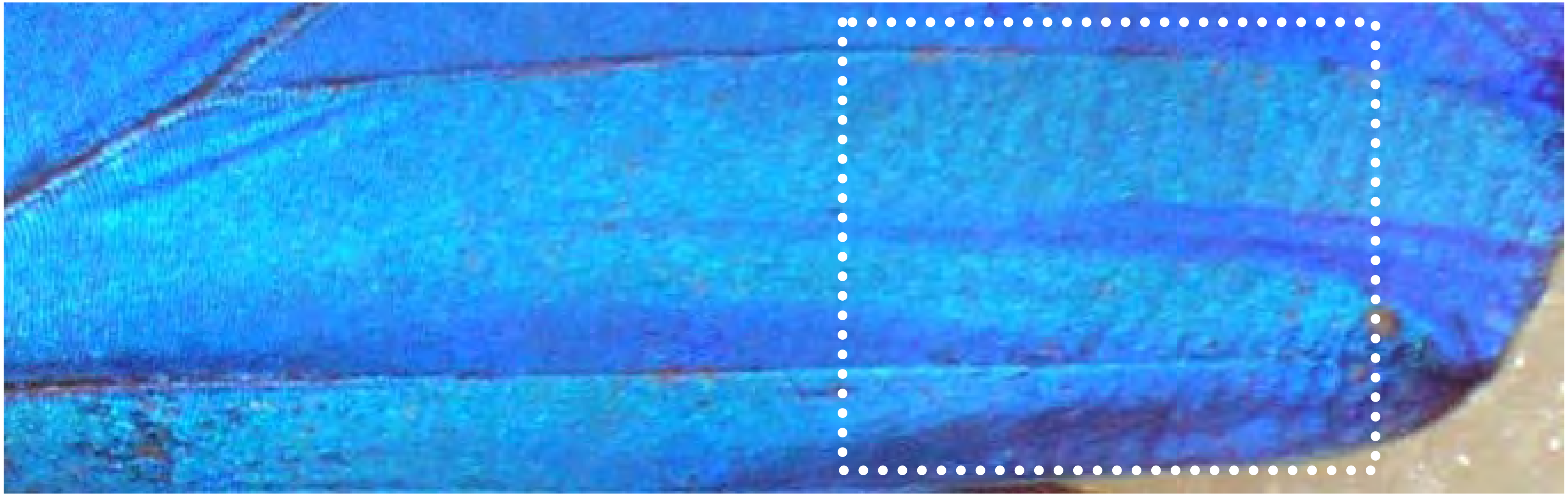

1µm
Mag = 28.32 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005

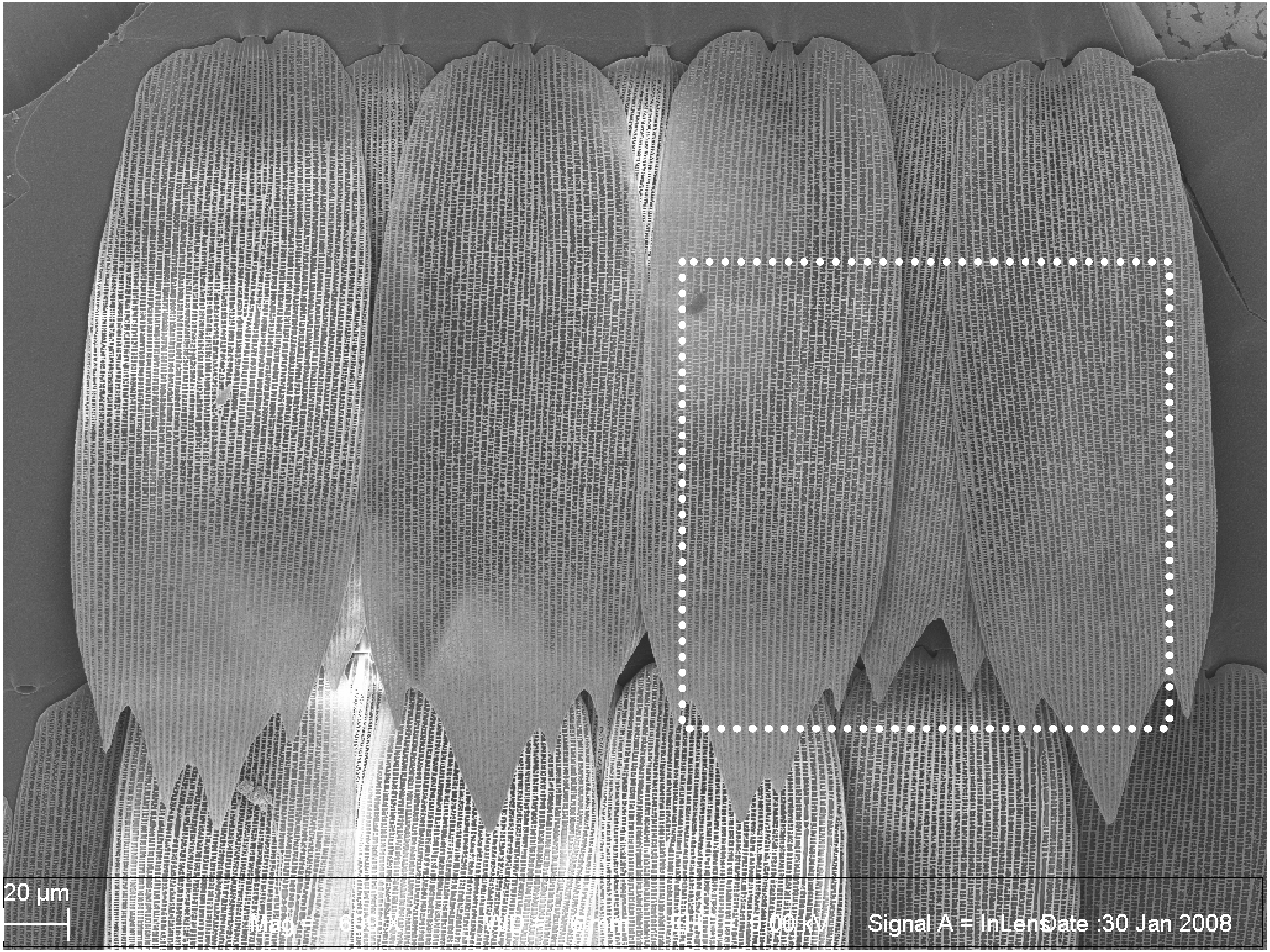

200nm
Mag = 76.04 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005

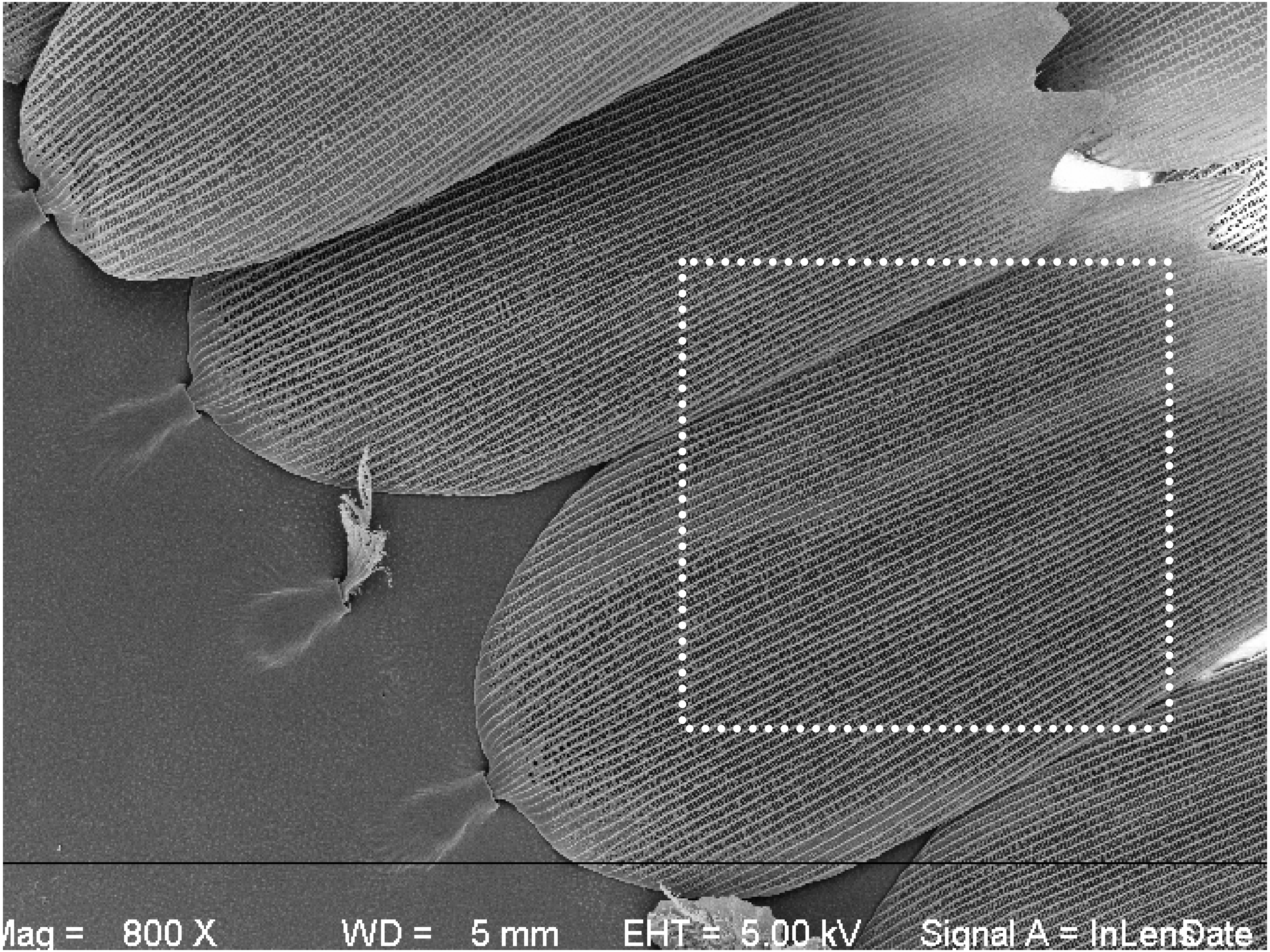

100nm
Mag = 133.31 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :9 Jun 2005

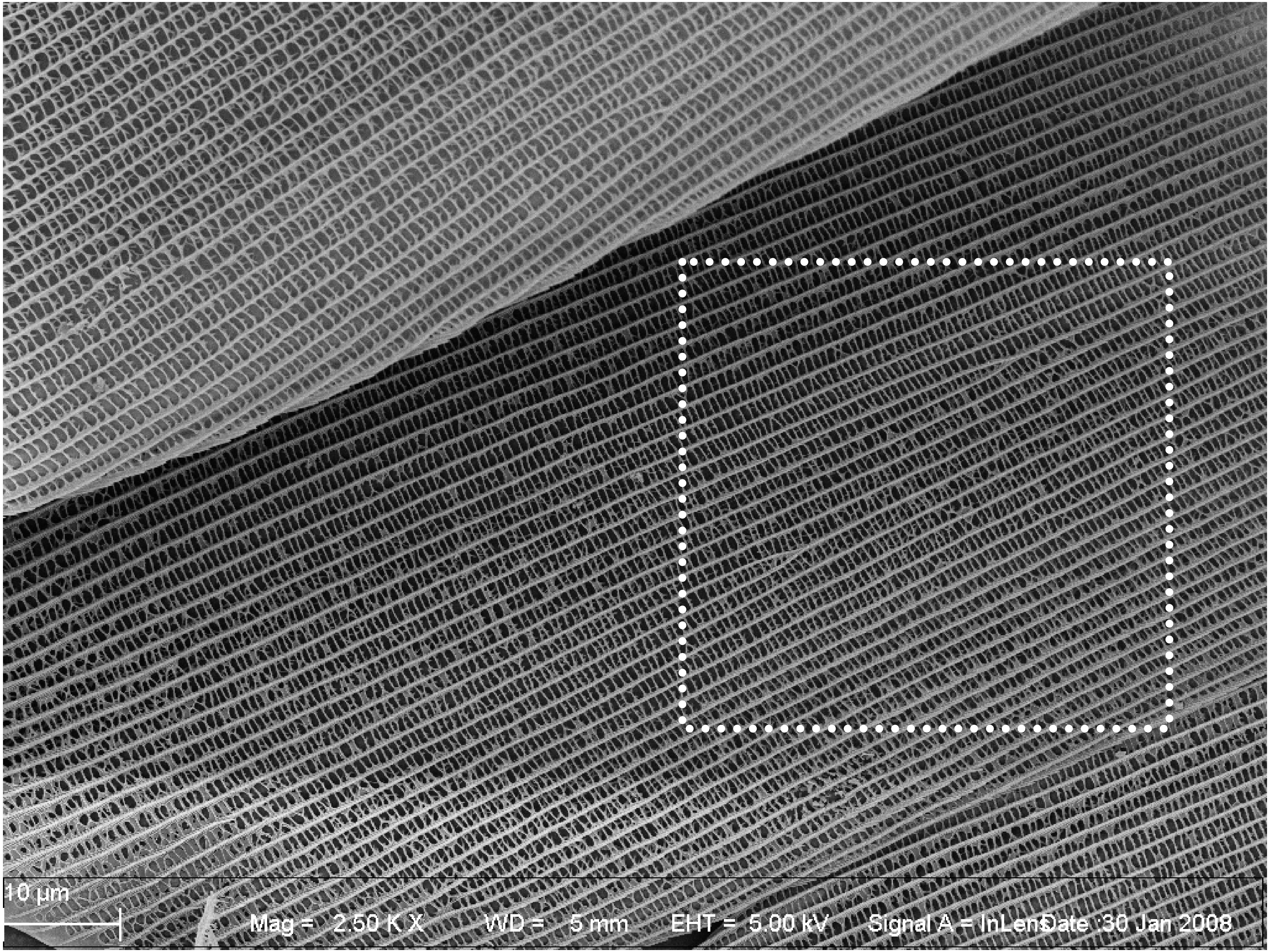

1μm
Mag = 30.00 K X
WD = 3 mm
Signal A = InLens
EHT = 5.00 kV
Date :2

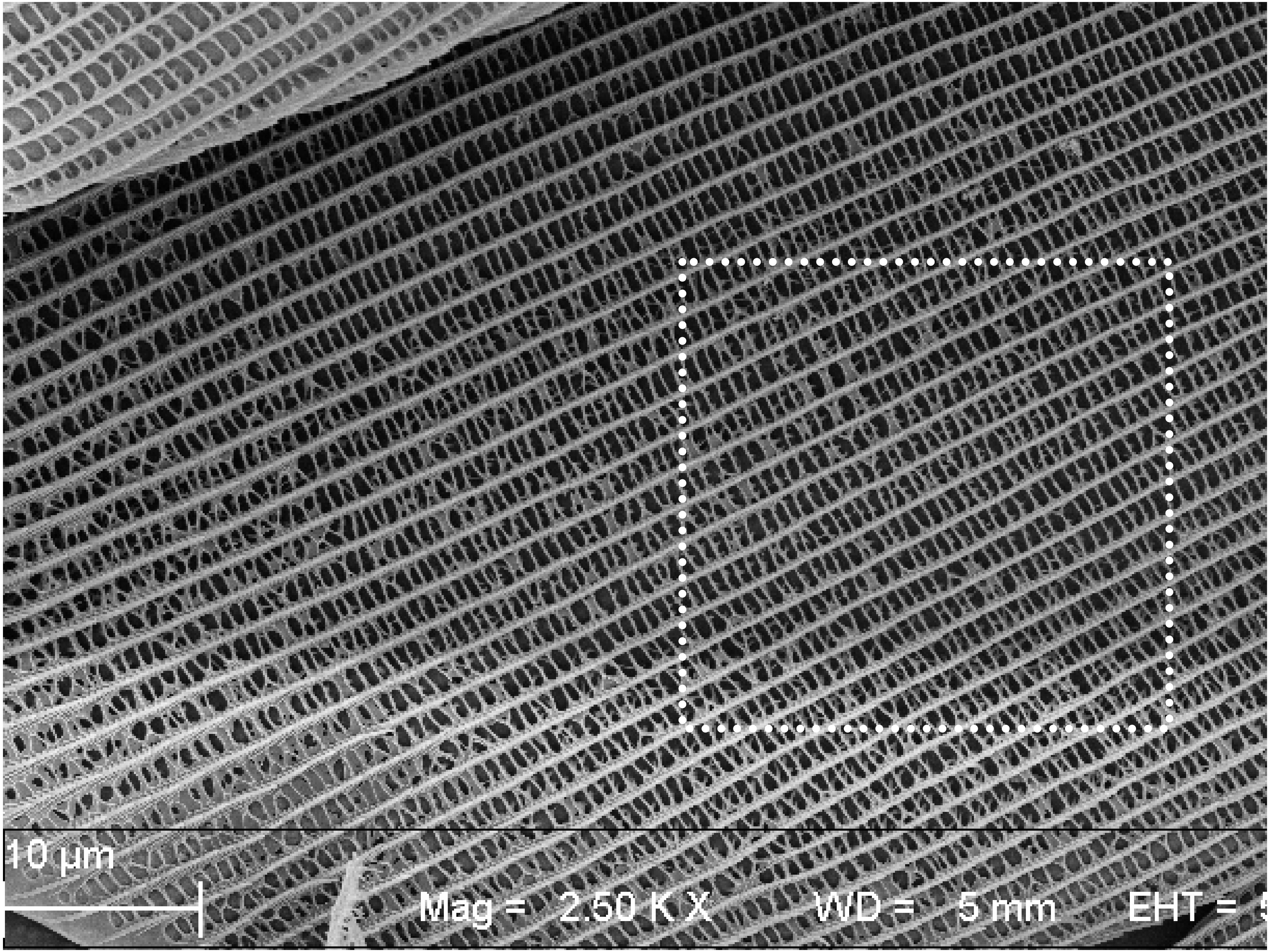

200nm
Mag = 100.00 K X
WD = 3 mm
Signal A = InLens
EHT = 5.00 kV
Date :20 Ja

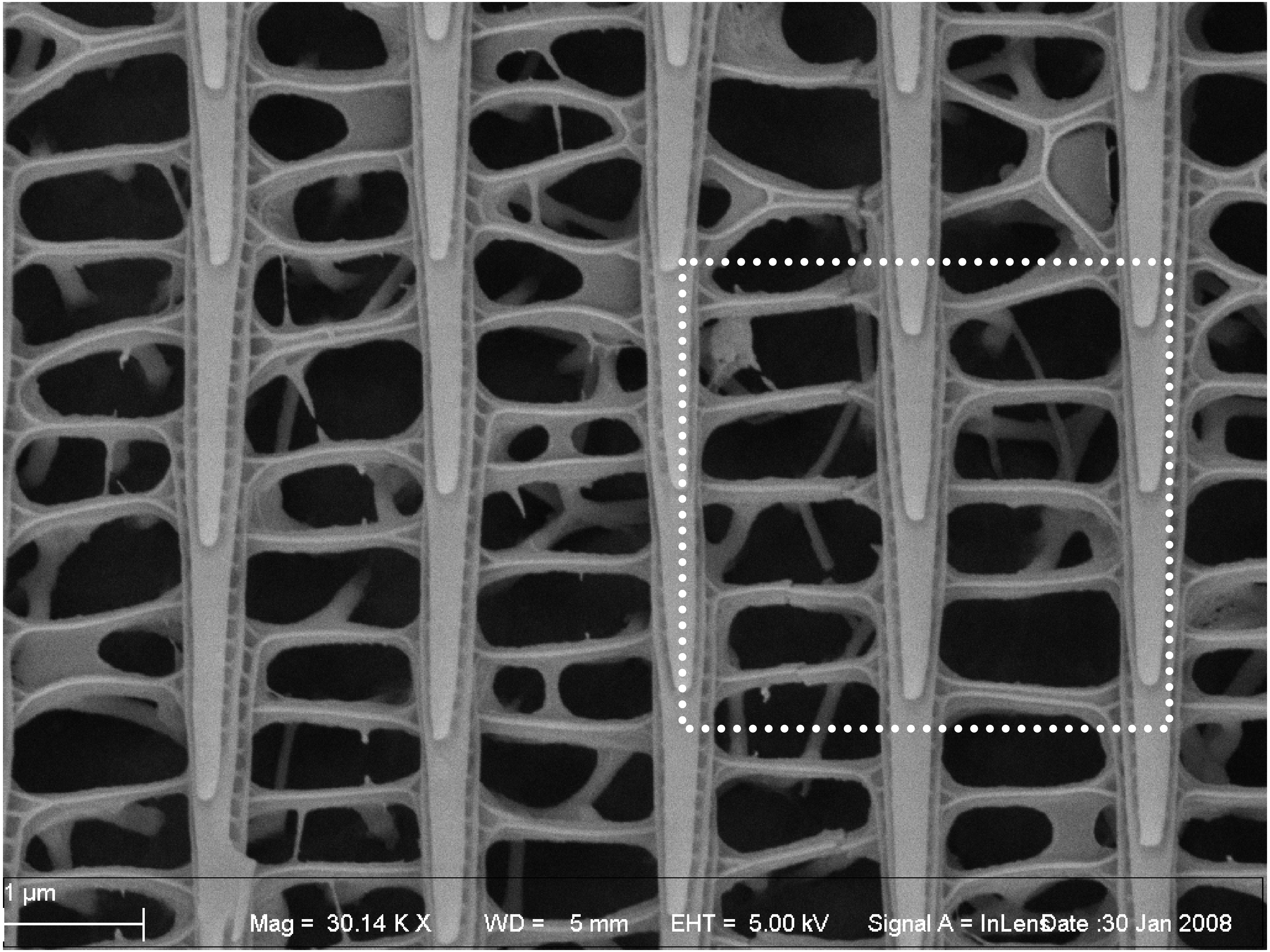


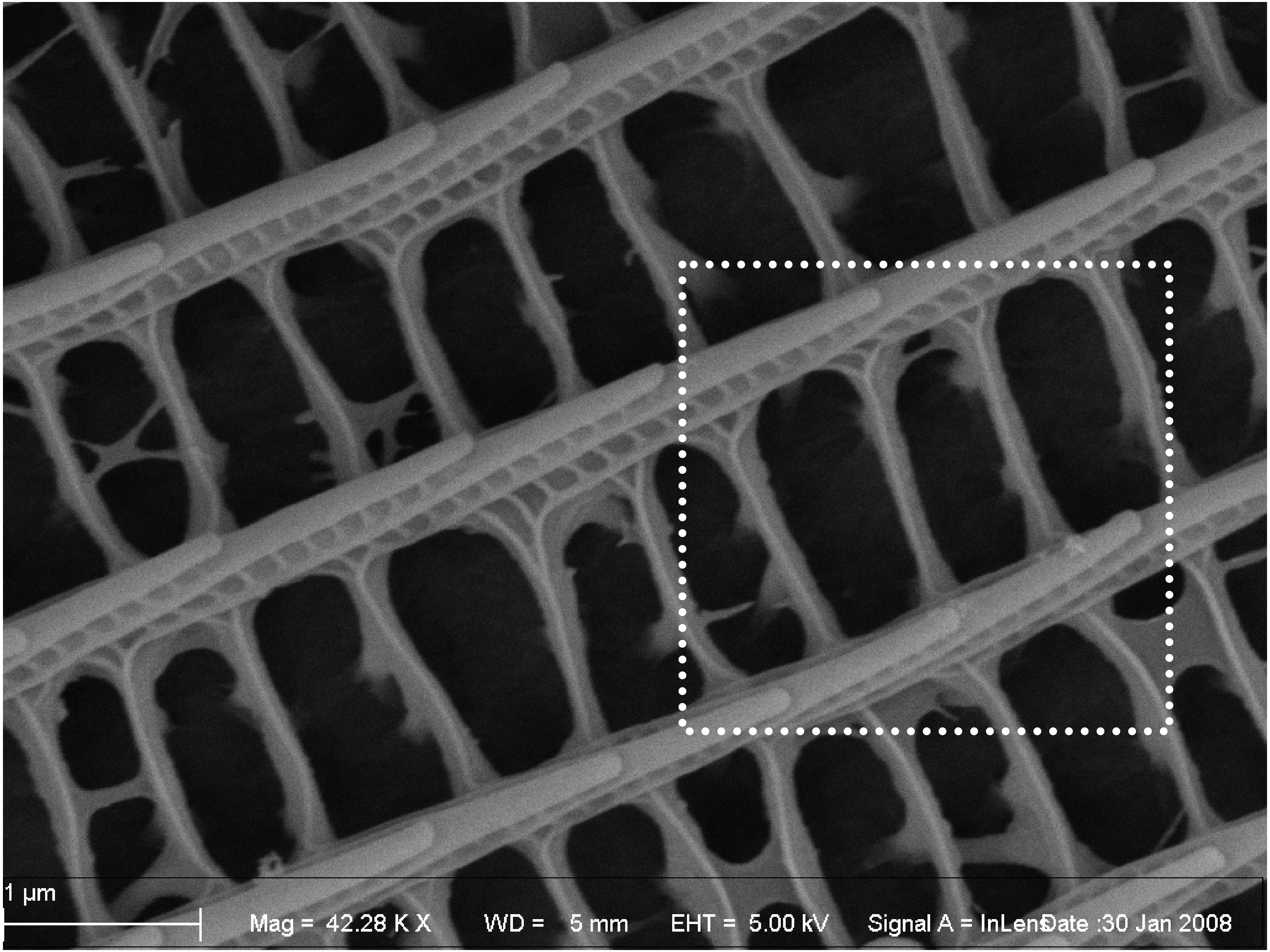

20 µm
Signal A = InLens
Date :30 Jan 2008

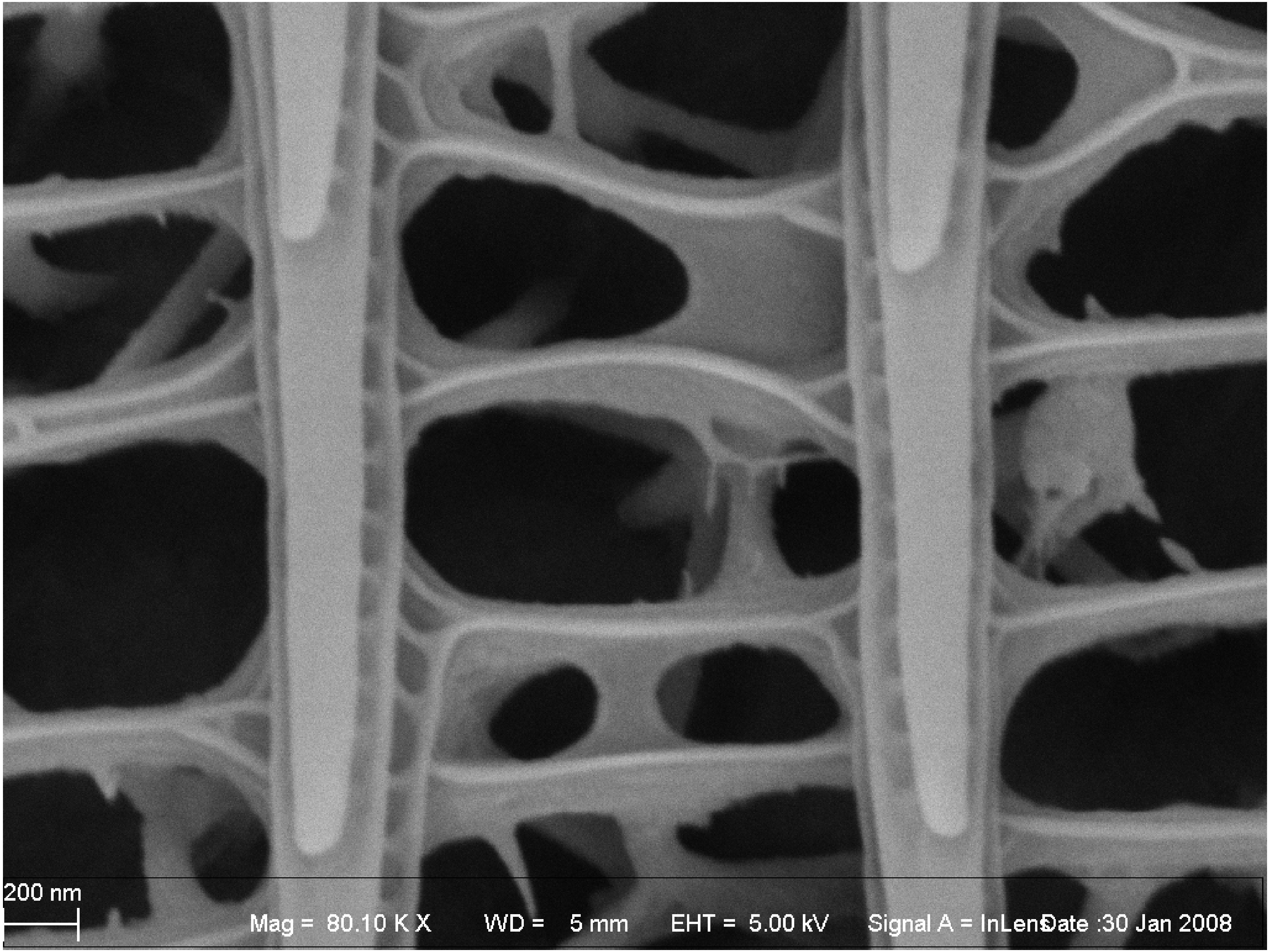

Mag = 800 X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date


10 µm
Mag = 2.50 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008


10 µm
Mag = 2.50 K X
WD = 5 mm
EHT = 5


1 μm
Mag = 30.14 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008

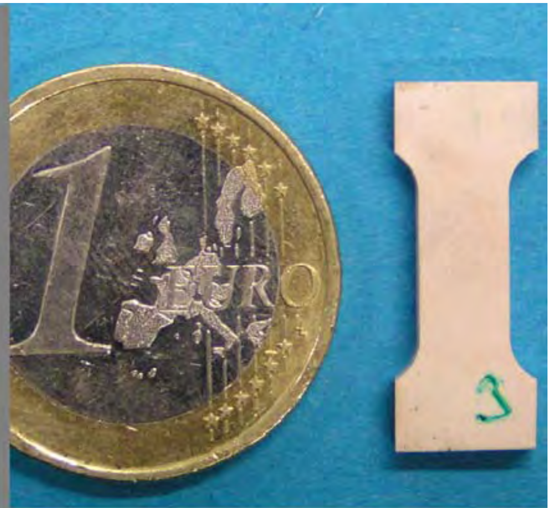

1 µm
Mag = 42.28 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008

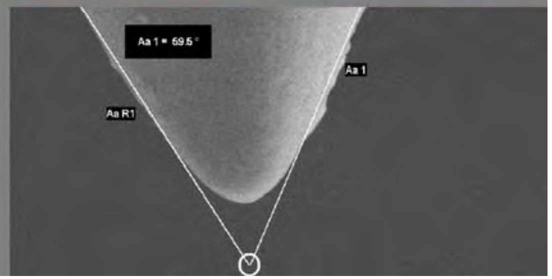

200 nm
Mag = 80.10 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :30 Jan 2008

Overview

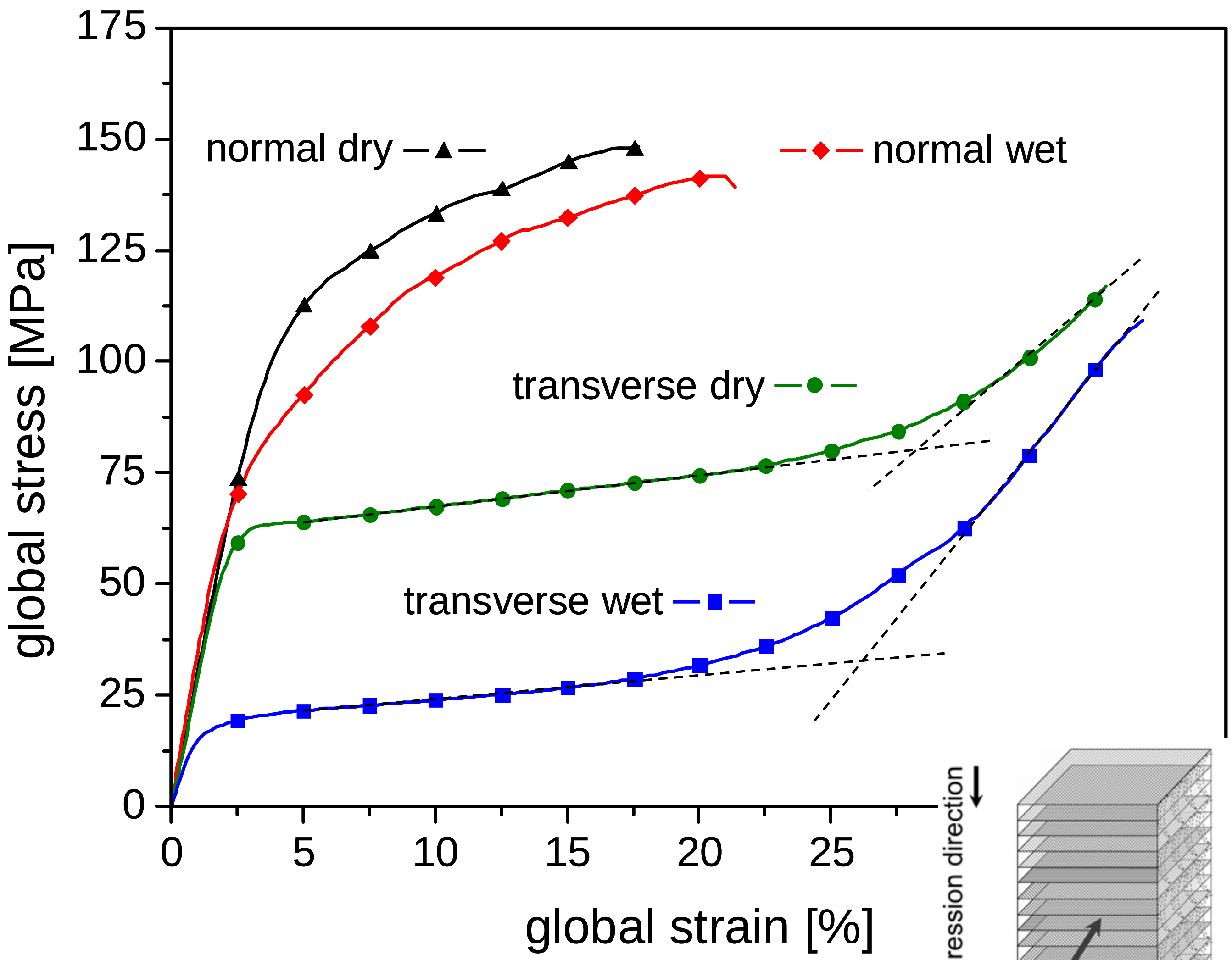
- Introduction to mineralized composite materials based on chitin and proteins
- Hierarchical structure
- **Hierarchical mechanical properties**
- Theoretical understanding through multiscale modeling (ab-initio, coarse graining, continuum)

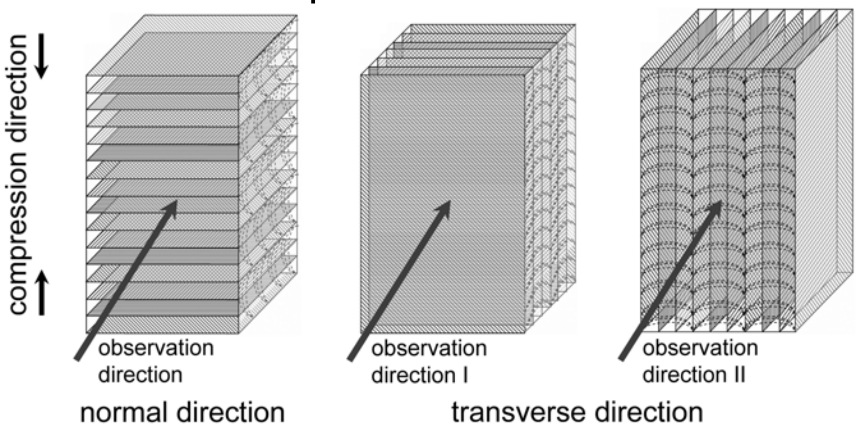
Hierarchical mechanics of decapoda



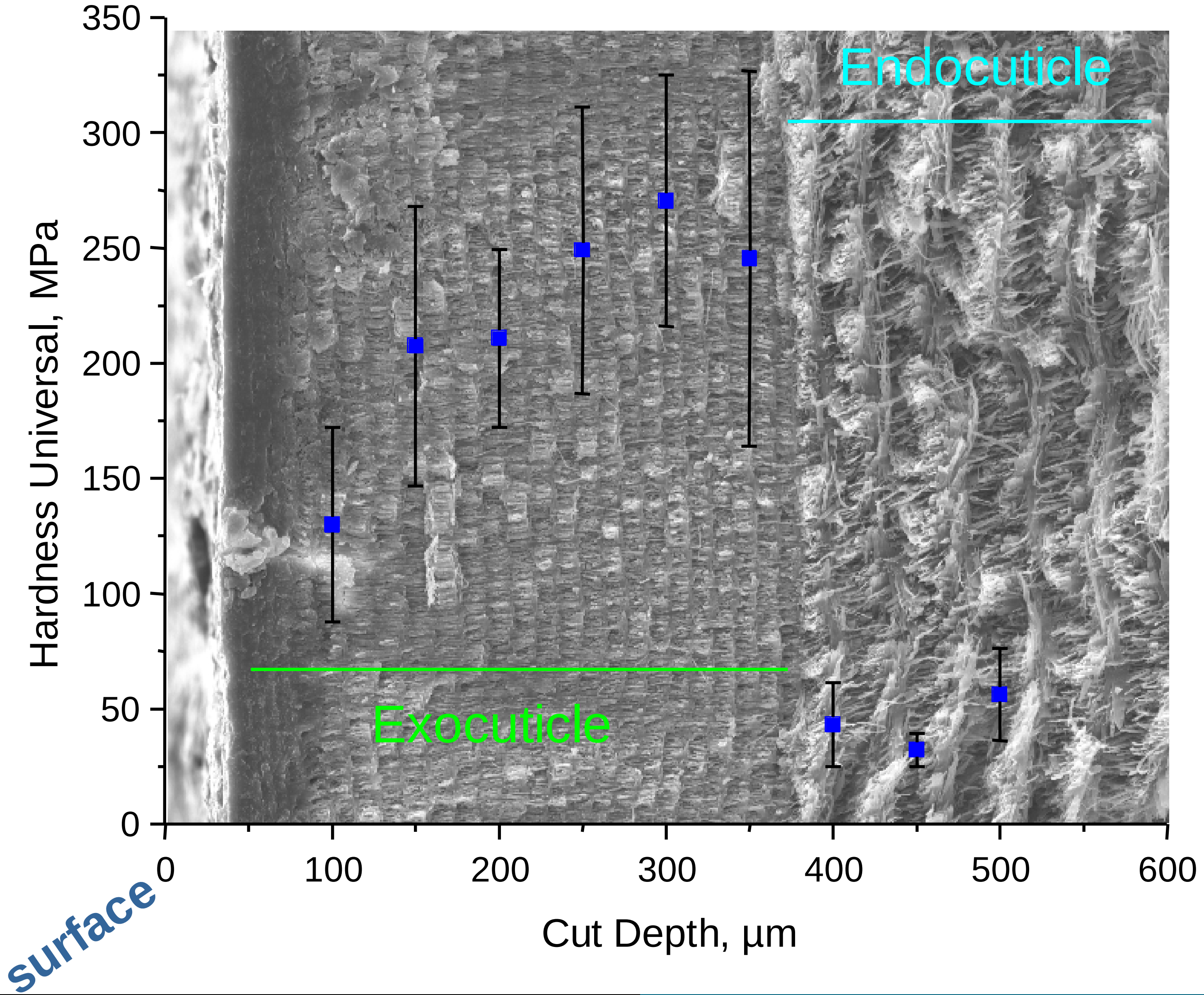


Compression tests (macroscopic), lobster



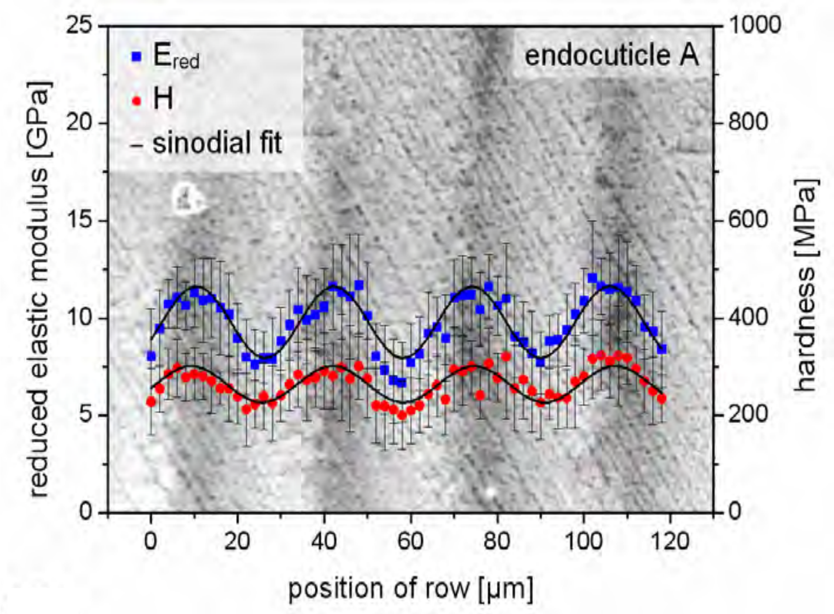


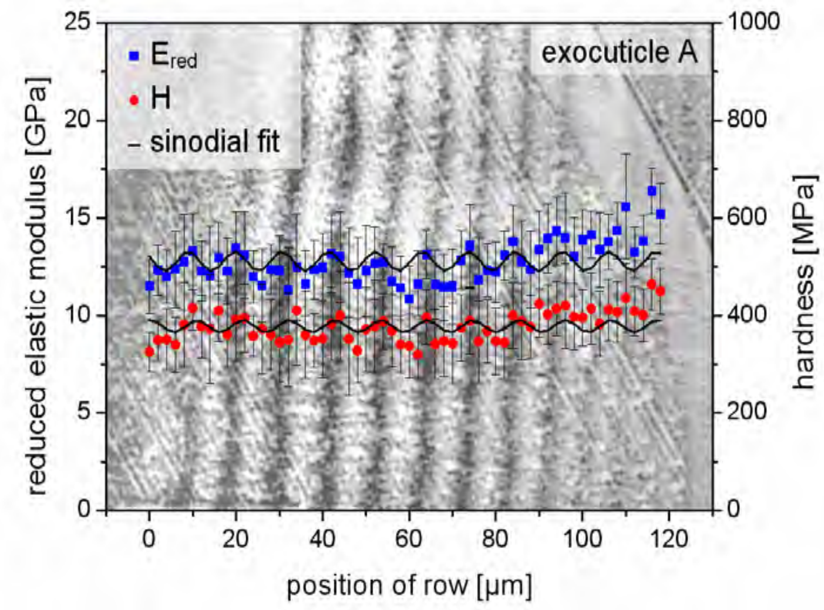
Hardness (mesoscopic)



Mechanical properties (micoscopic)

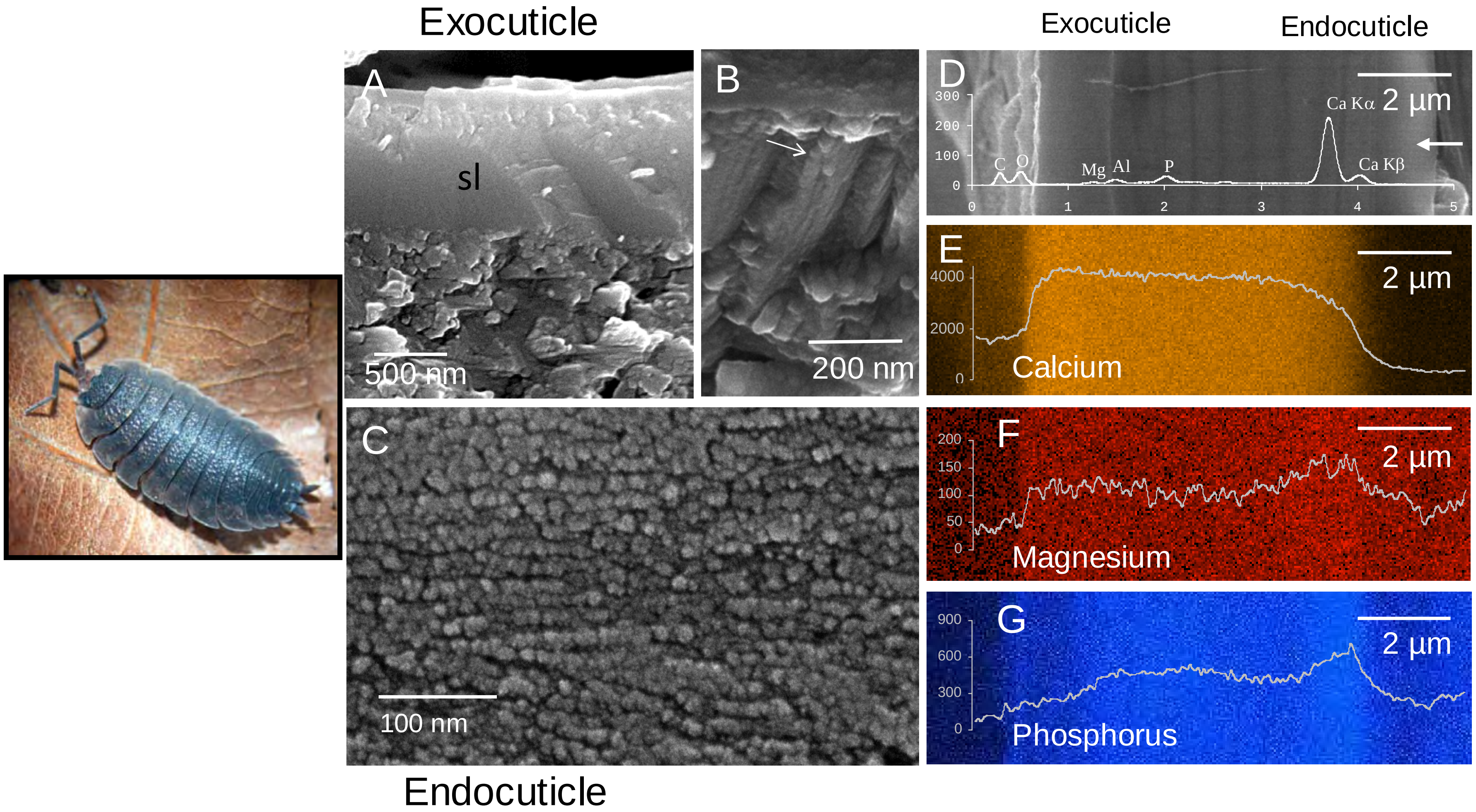
nanoindentation



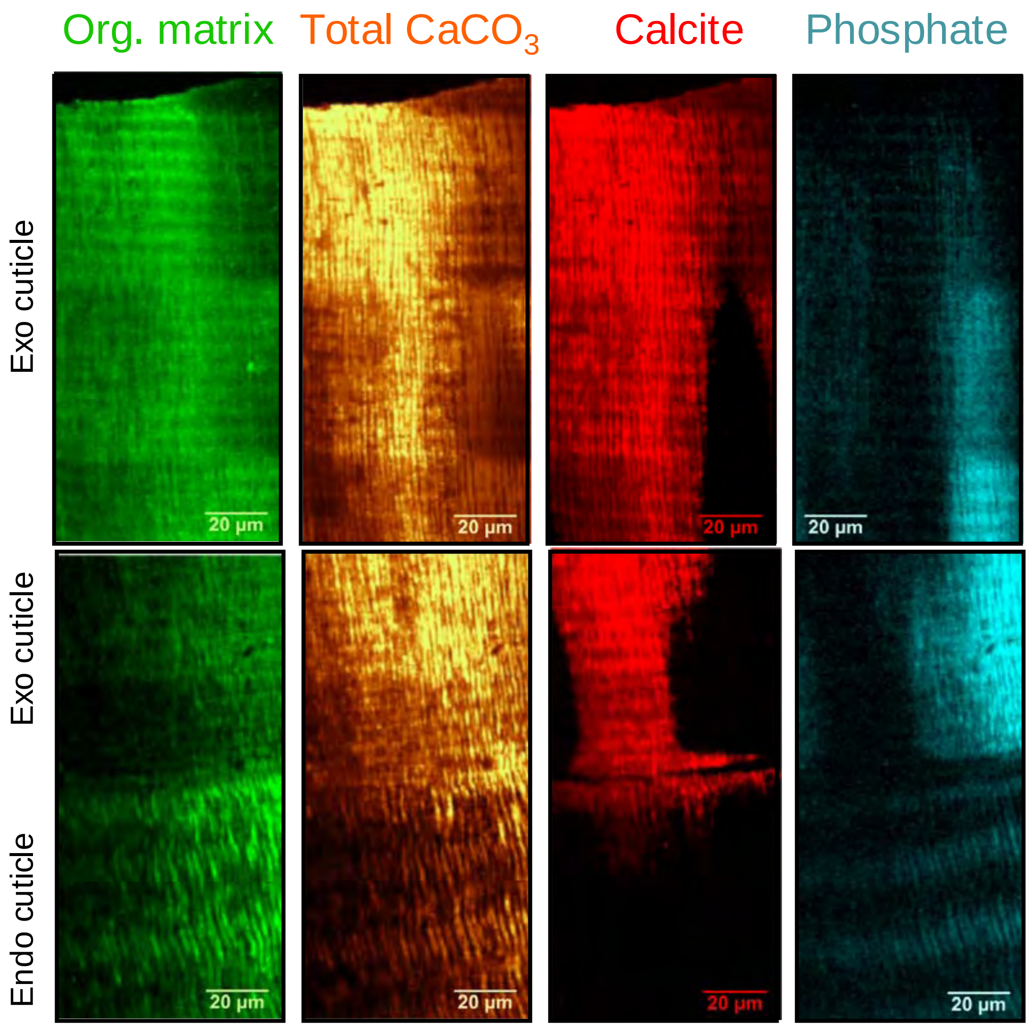


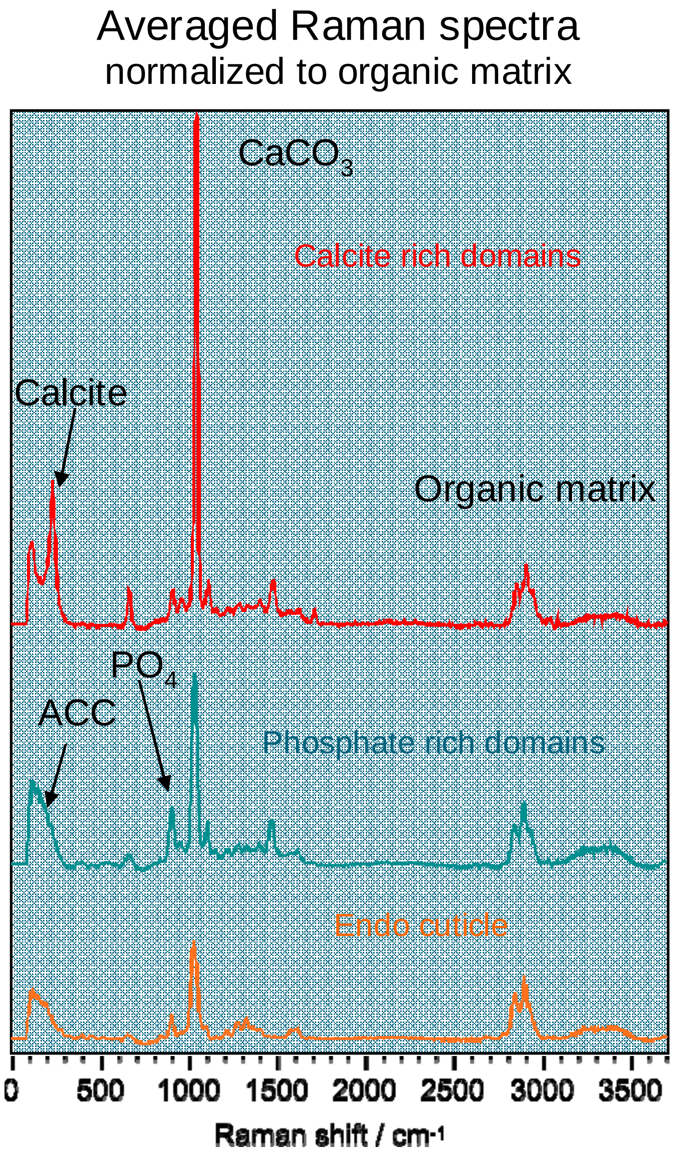
Variations in mechanical properties are the result of structural and chemical variations within the hierarchical level rather than by changes in the overal structural organisation

Structure and elemental distribution of porcellio scaber



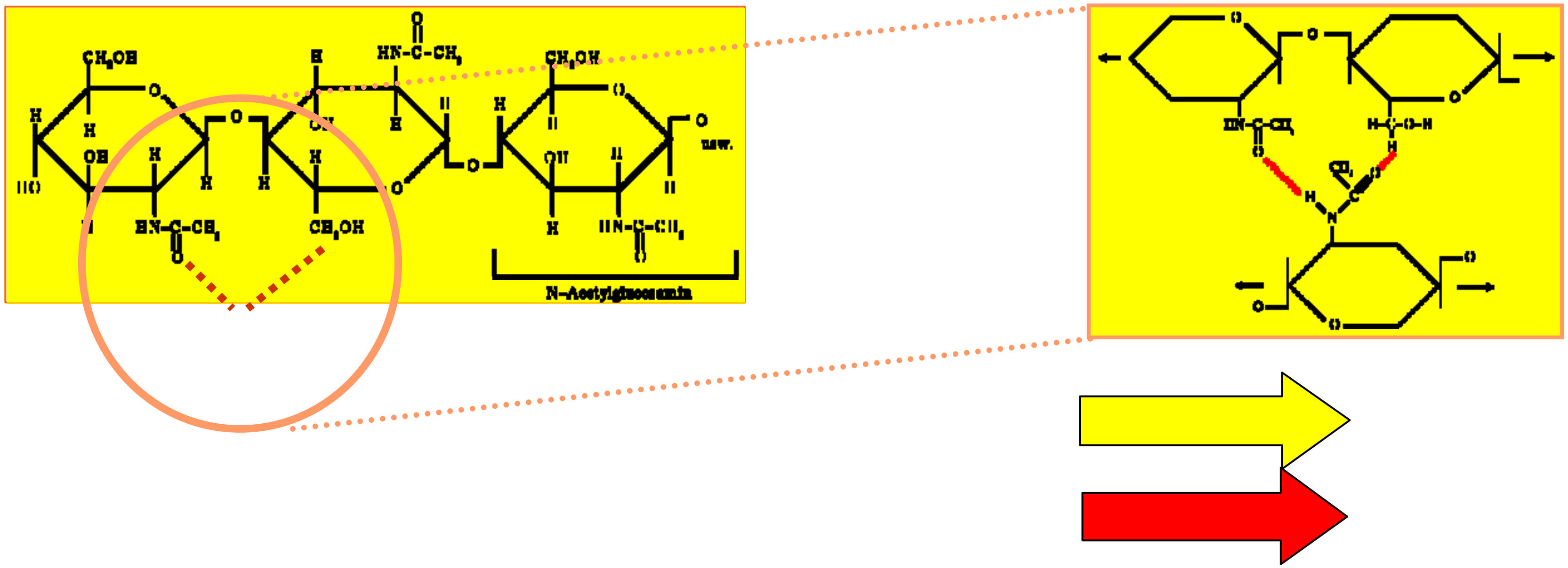
Raman imaging of the claw cuticle of H. americanus





Overview

- Introduction to mineralized composite materials based on chitin and proteins
- Hierarchical structure
- Hierarchical mechanical properties
- **Theoretical understanding through multiscale modeling (ab-initio, coarse graining, continuum)**



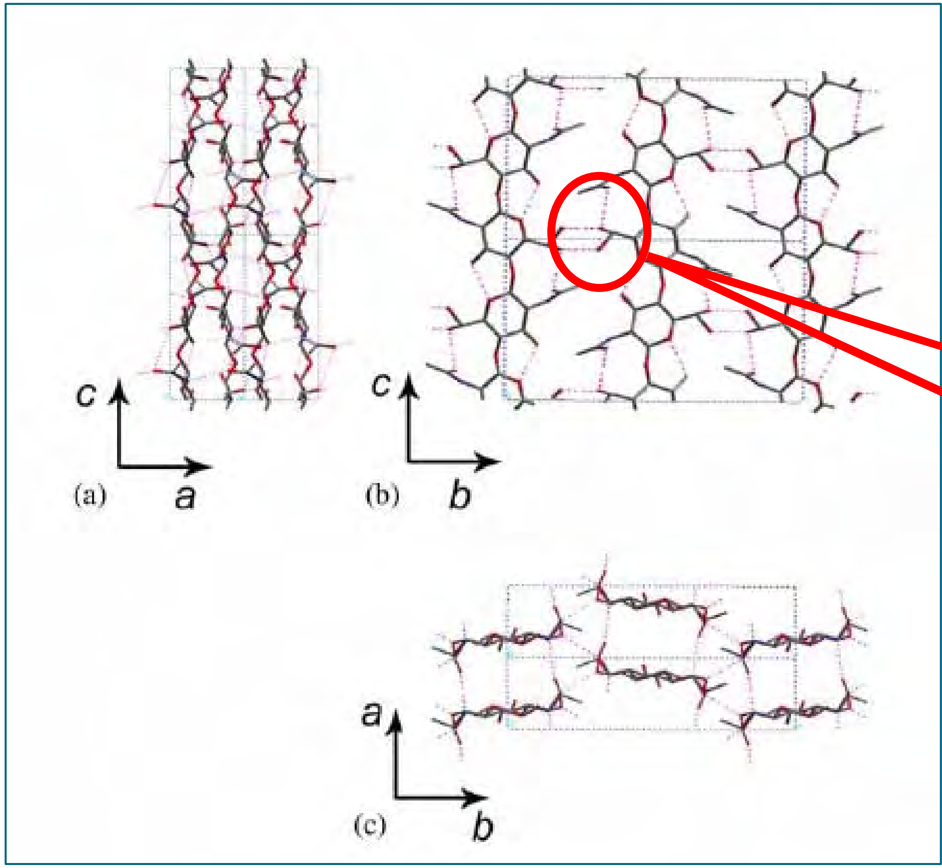
J. Biochem Biophys. Cytol., 1957, ***3****, 669 - 683.*

The crystal structure of α -chitin

Carlstrom, D.

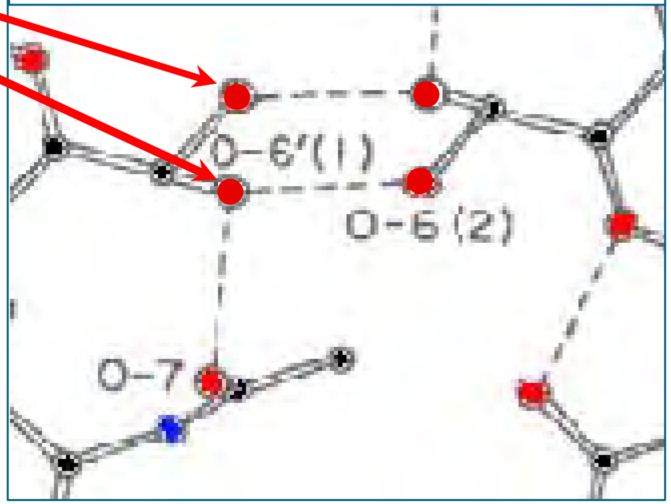
Polymer	Unit cell dimensions (Bohrradius)				Space group
	a	b	c	γ	
α-Chitin	8.96	35.64	19.50	90˚	P21

108 atoms / 52 unknown H-positions



Hydrogen positions?
H-bonding pattern ?

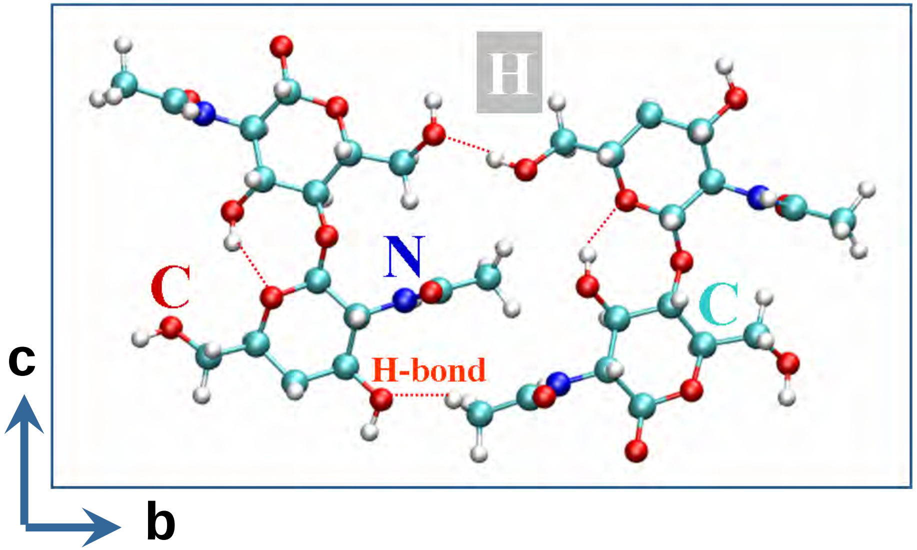
two conformations
of α-chitin

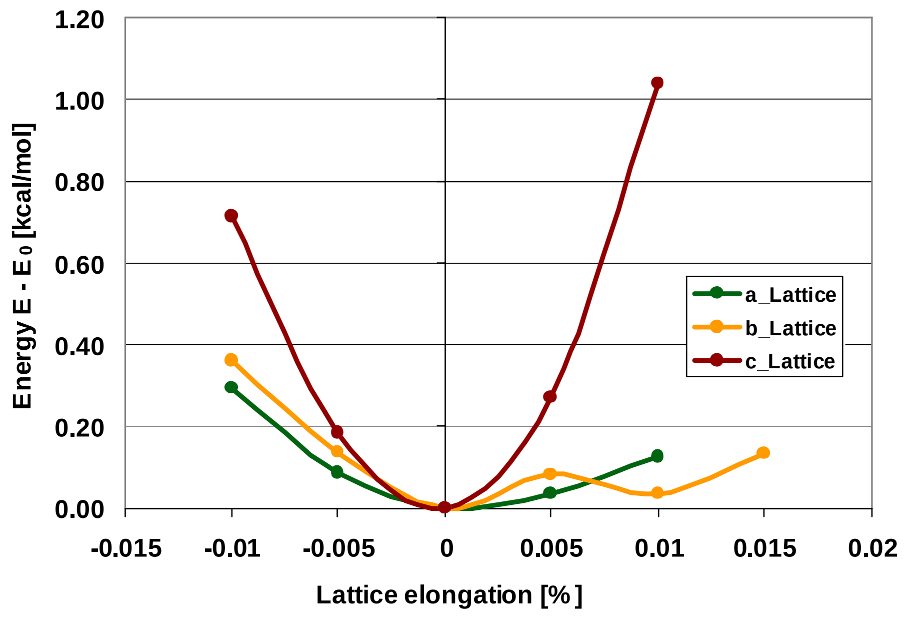


[1] R. Minke and J. Blackwell, J. Mol. Biol. **120**, (1978).

	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)	~500 min	Medium	**~10^2**
• **DFT** (PWs, PBE-GGA) Geometry Optimization (SPHIngX)	~10000 min	High	**~10^1**

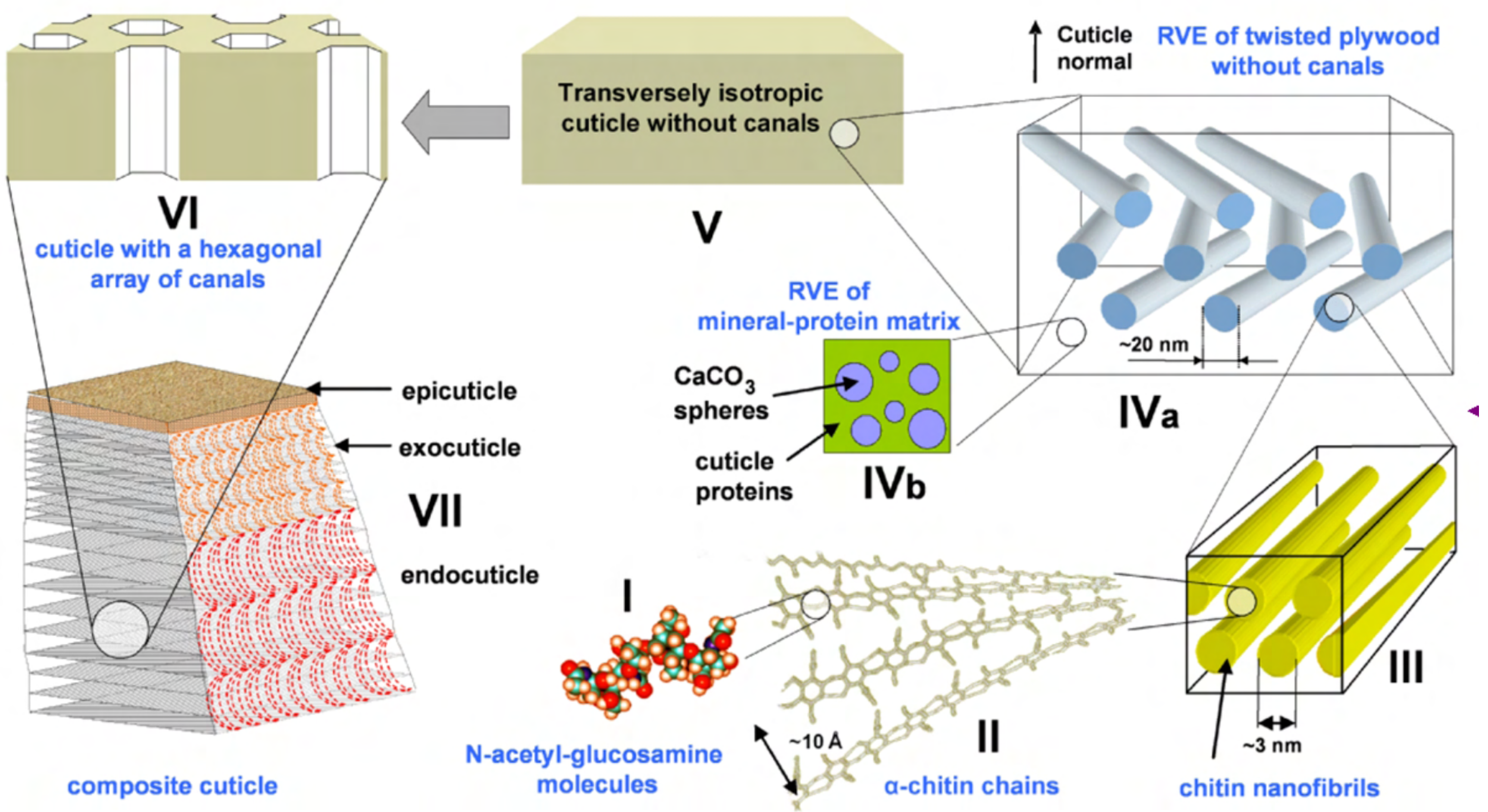
Ab initio prediction of α-chitin elastic properties





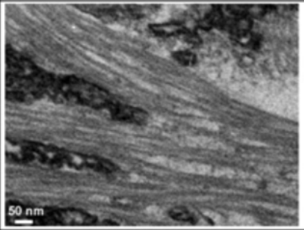
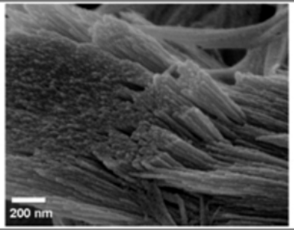
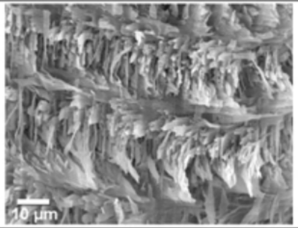
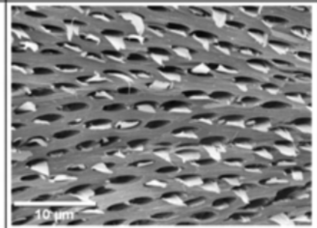
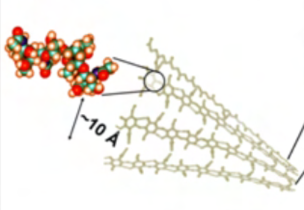
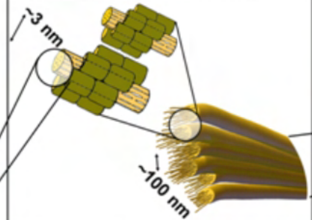
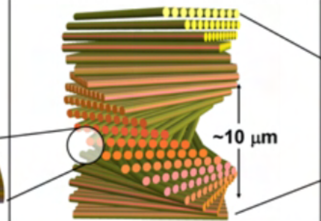
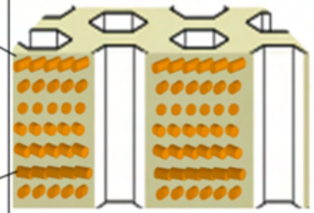
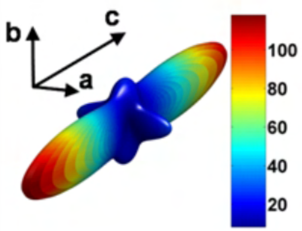
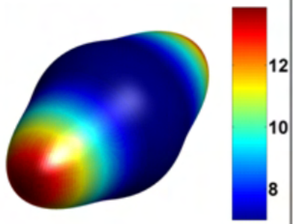
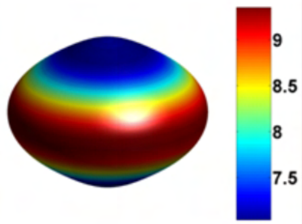
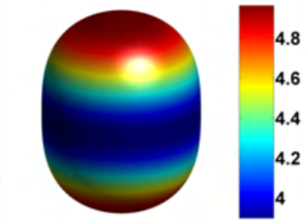
$$\underline{\underline{C_{CH}}} = \begin{bmatrix} 119 & 0.1 & 1.1 & 0 & 0 & 0 \\ 0.1 & 28 & 2 & 0 & 0 & 0 \\ 1.1 & 2 & 24 & 0 & 0 & 0 \\ 0 & 0 & 0 & 5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{bmatrix} \quad GPa$$

Hierarchical coarse graining

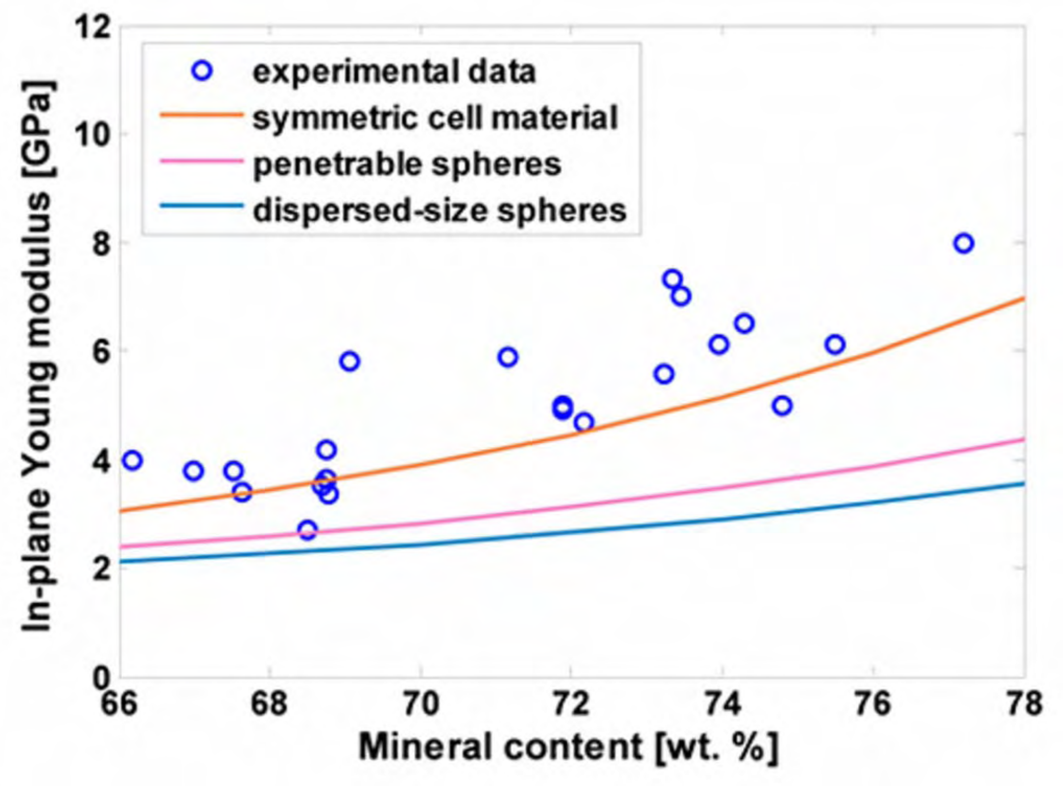


Hierarchical modelling of the lobster cuticle: (I), (II) α-chitin properties via *ab initio* calculations; (III) representative volume element (RVE) for a single chitin-protein fibre; (IV a) RVE for chitin-protein fibres arranged in twisted plywood and embedded in mineral-protein matrix; (IV b) RVE for the mineral-protein matrix. Level (V): homogenized twisted plywood without canals; (VI) homogenized plywood pierced with hexagonal array of canals; (VII) 3-layer cuticle.

Hierarchical stiffness modeling

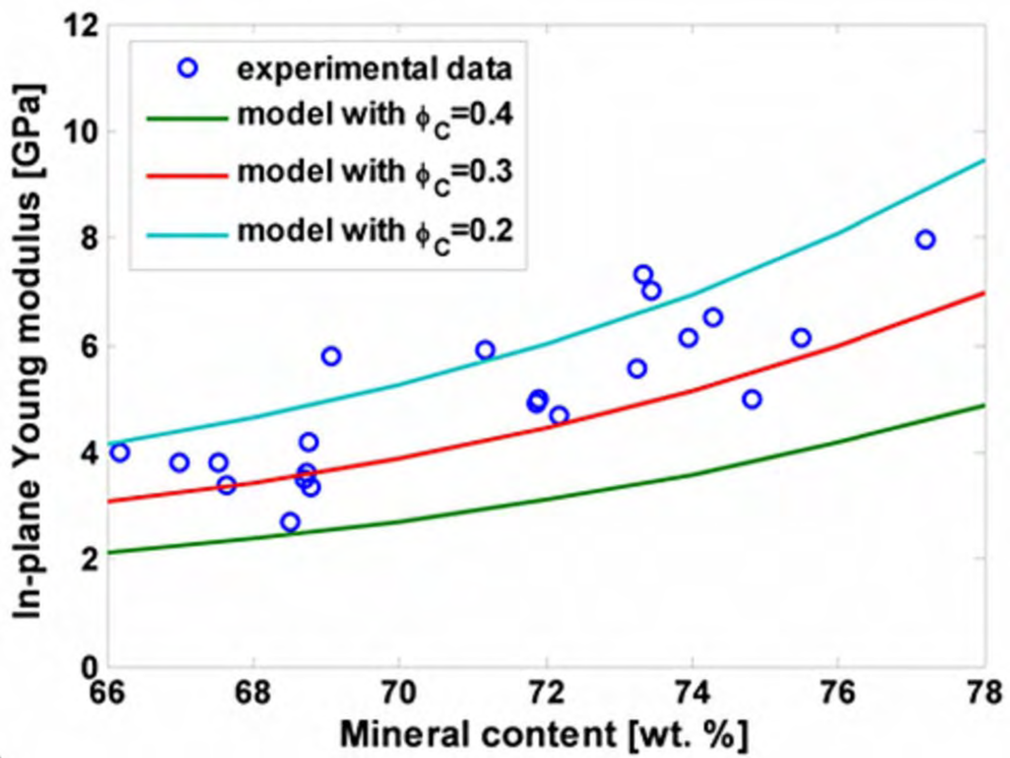
Scale	0.1 nm – 10 nm	10 nm – 100 nm	100 nm – 10 µm	10 µm – 1 mm
Hierarchical structure unit	α-chitin (H-bonded anti-parallel N-acetyl-glucosamine molecular chains)	Mineralized chitin-protein nanofibrils in a planar array	Twisted plywood stack of mineralized chitin-protein planes without pore canals	Twisted 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**				

Results and comparison with experiments



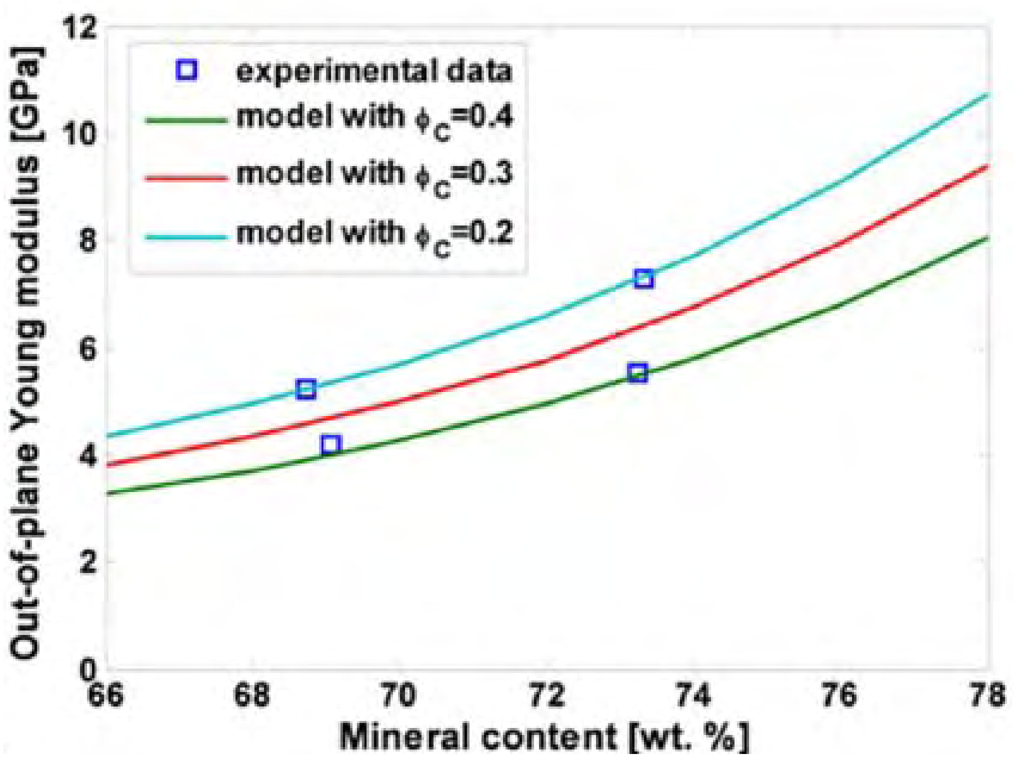
In-plane Young's modulus as a function of the mineral-protein matrix microstructure and the mineral content for 0.3 fraction of the pore canals.

Results and comparison with experiments



In-plane Young's modulus as a function of the mineral content for different in-plane area fractions of the pore canals.

Results and comparison with experiments



Out-of-plane Young's modulus for different canal pores area fractions vs. mineral content.

Conclusions

- **Hierarchical structure of mineralized chitin-protein nano-composites**

- **Hierarchical characterization of mechanical properties is required**

- **Multiscale modeling through repeated coarse graining: hierarchical modeling (here: ab-initio, multiple RVE, homogenization)**

Some references

- D. Raabe, C. Sachs, P. Romano: Acta Mater. 53 (2005) 4281-4292, The crustacean exoskeleton as an example of a structurally and mechanically graded biological nanocomposite material
- D. Raabe, P. Romano, C. Sachs, H. Fabritius, A. Al-Sawalmih, S.-B. Yi, G. Servos, H.G. Hartwig, Mater. Sc. Engin. A 421 (2006) 143–153, Microstructure and crystallographic texture of the chitin-protein network in the biological composite material of the exoskeleton of the lobster *Homarus americanus*
- D. Raabe, P. Romano, A. Al-Sawalmih, C. Sachs, G. Servos, H.G. Hartwig: Mesostructure of the Exoskeleton of the Lobster *Homarus Americanus*, Mater. Res. Soc. Sympos. Proc. Vol. 874 (2005) L.5.2; pages: 155-160.
- D. Raabe, C. Sachs: Mechanical Properties of the Lobster Cuticle, Mater. Res. Soc. Sympos. Proc. Vol. 874 (2005) L.5.3; pages: 161-166.
- C. Sachs, H. Fabritius, D. Raabe: Journal of Structural Biology 155 (2006) 409–425, Experimental investigation of the elastic-plastic deformation of mineralized lobster cuticle by digital image correlation
- C. Sachs, H. Fabritius, D. Raabe: Journal of Material Research 21 (2006) 1987-1995, Hardness and elastic properties of dehydrated cuticle from the lobster *Homarus americanus* obtained by nanoindentation
- P. Romano, H. Fabritius, D. Raabe: Acta Biomaterialia. 3 (2007) 301-309, The exoskeleton of the lobster Homarus americanus as an example of a smart anisotropic biological material
- D. Raabe, A. Al-Sawalmih, S. B. Yi, H. Fabritius: Acta Biomaterialia 3 (2007) 882-895, Preferred crystallographic texture of α-chitin as a microscopic and macroscopic design principle of the exoskeleton of the lobster Homarus americanus
- F. Boßelmann, P.Romano, H. Fabritius, D. Raabe, M. Epple: Thermochimica Acta 463 (2007) 65-68, The composition of the exoskeleton of two crustacea: The American lobster Homarus americanus and the edible crab Cancer pagurus
- C. Sachs, H. Fabritius, D. Raabe: Journal of Structural Biology 161 (2008) 120-132, Influence of microstructure on deformation anisotropy of mineralized cuticle from the lobster Homarus americanus
- A. Al-Sawalmih, C. Li, S. Siegel, H. Fabritius, S.B. Yi, D. Raabe, P. Fratzl, O. Paris: Advanced functional materials Vol. 18 (2008) pages: 3307-3314, Microtexture and Chitin/Calcite Orientation Relationship in the Mineralized Exoskeleton of the American Lobster