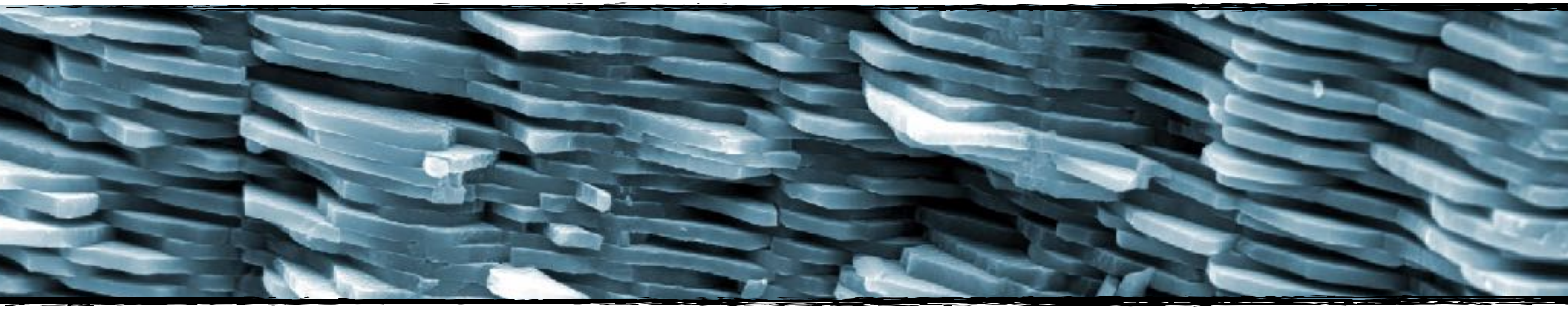
Structural biological and bioinspired materials: The case of nacre



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@DevilleSy

MECAMAT 2019, Aussois

MECAMAT 2019


MECAMAT 2020

Propriétés mécaniques des matériaux céramiques mis en forme en congelant des petites suspensions avec des particules anisotropes et d’autres sphériques mais plus petites et en congelant le tout, ou bien sinon en pressant les poudres sèches, et puis en pressant le tout à haute température pour avoir des matériaux bien denses ou sinon je peux aussi faire un poster sur la congélation des émulsions, c’est un chouette sujet aussi, et puis il fait froid à Aussois alors y’a plein de glace alors ca fait une bonne thématique et ca changerait un peu de la mécanique parce que là je comprends pas grand chose. Enfin bref, je reviendrais bien volontiers c’est sympa ici. Non mais vous avez vraiment eu le temps de lire jusqu’ici ? Vous êtes vraiment rapides et en plus c’est écrit tout petit vous avez de sacrément bons yeux

Natural materials

Process

Composition

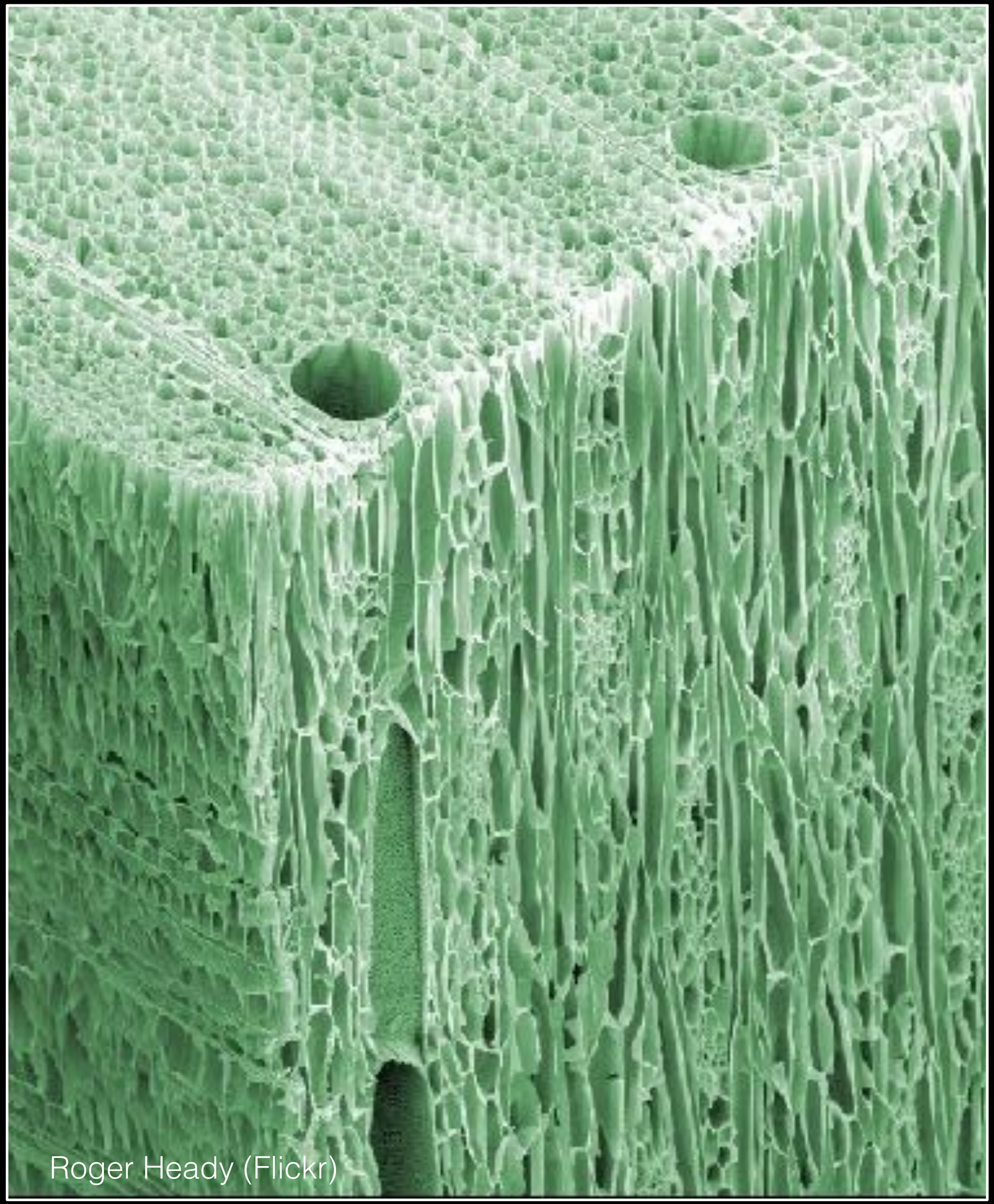
Structure

Self-healing

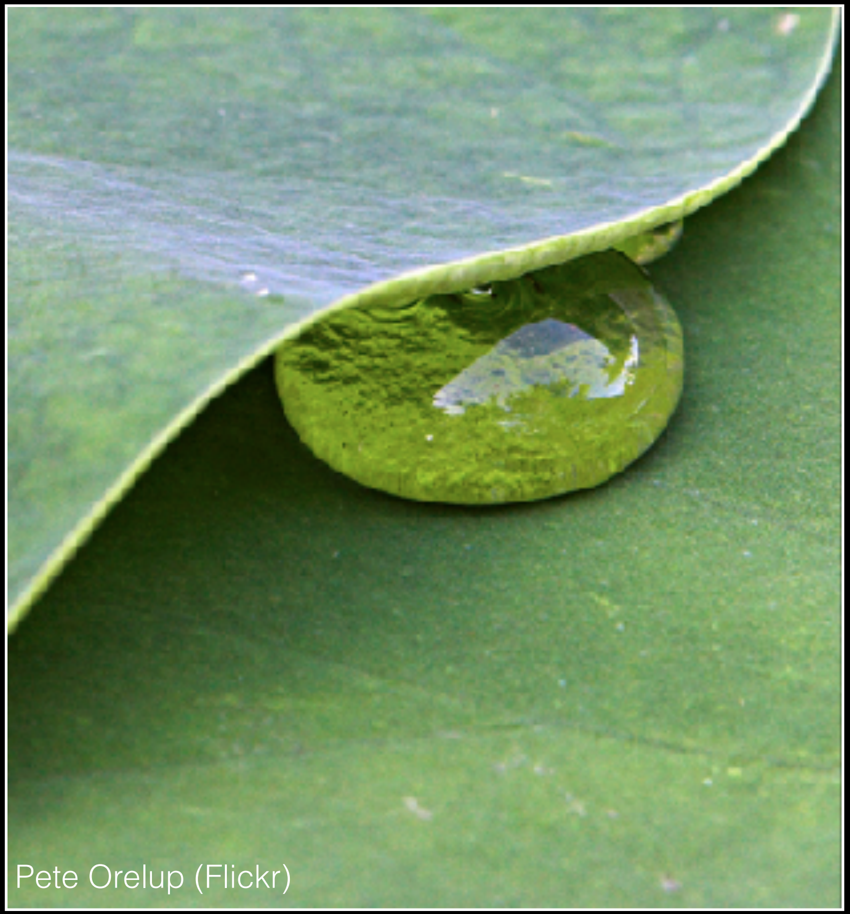
Biomaterials and bioinspiration

Process

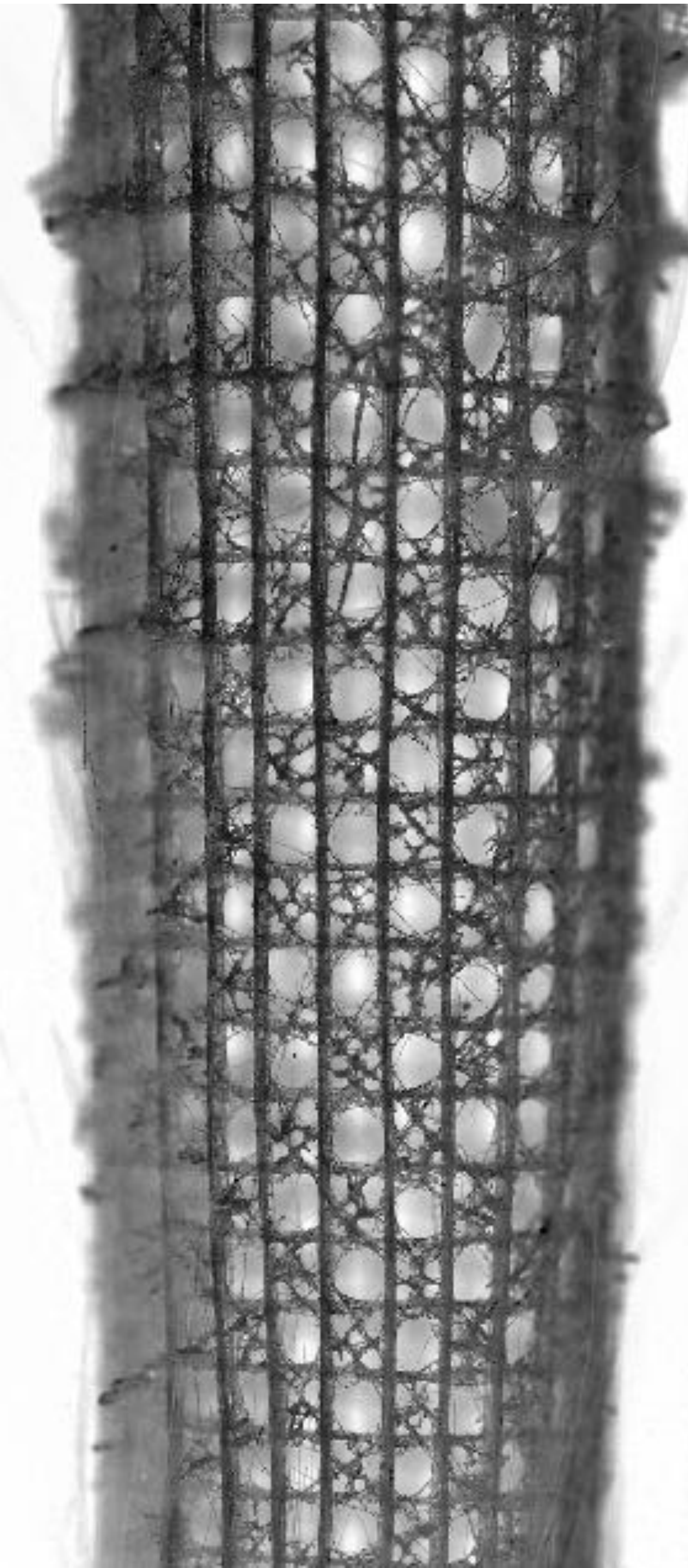
Functions



Structure

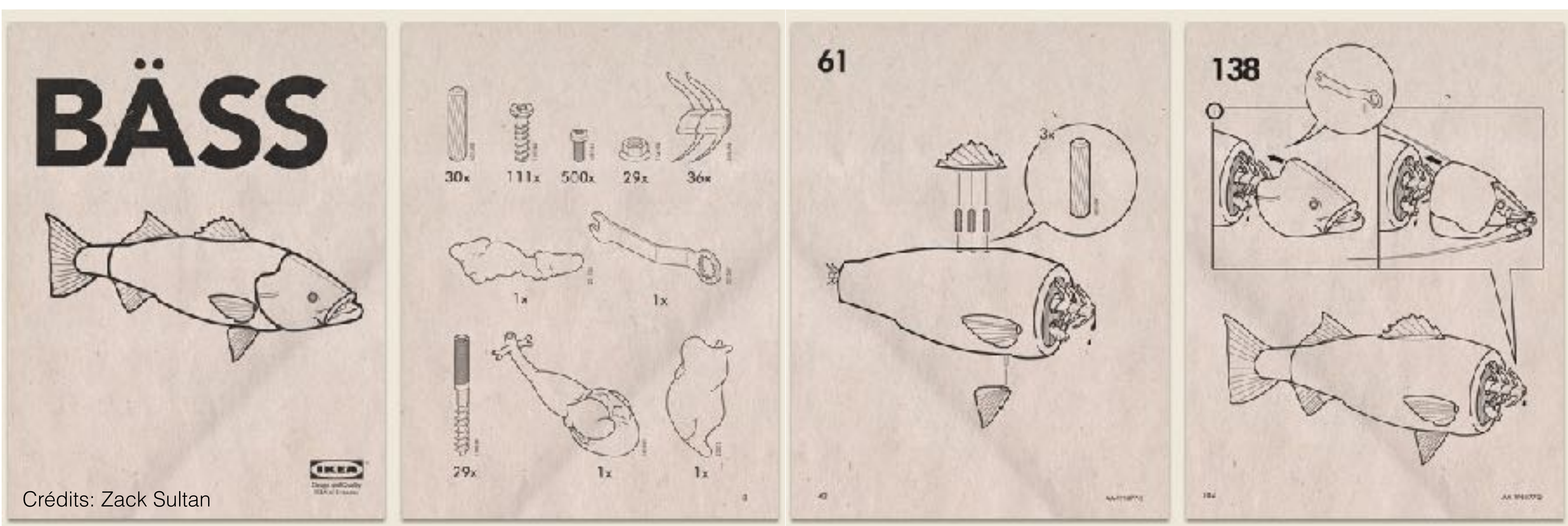


Biomaterials are (almost) always multifunctional



Strategy

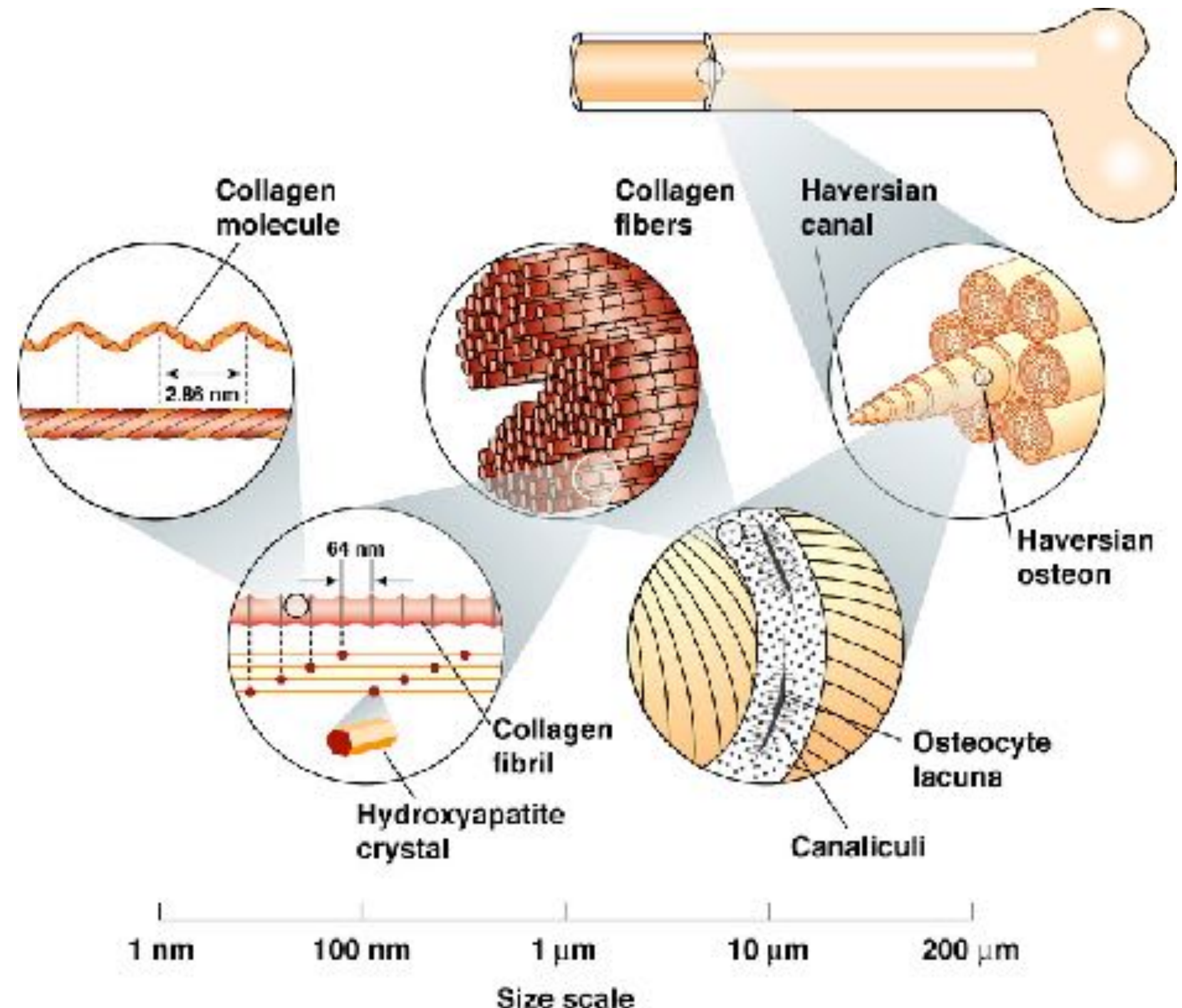
- Find structural biomaterials
- Understand structure/properties relationships in structural biomaterials
- ~~Reprocess natural materials with a synthetic approach~~
- Get ideas to implement in synthetic materials
- Find a way to do it



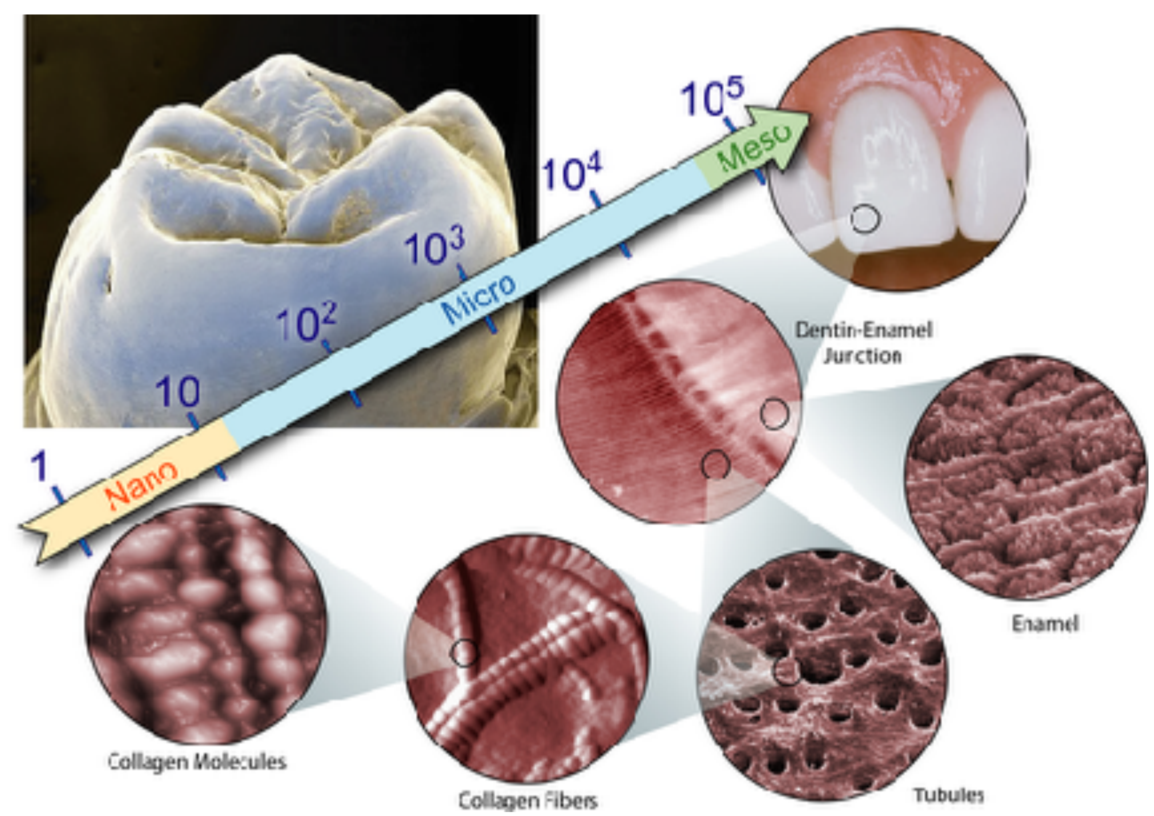
Crédits: Zack Sultan

Structural biomaterials: any one will do

- Wood
- Bone
- Dentin
- Nacre
- Silk
- anything, really

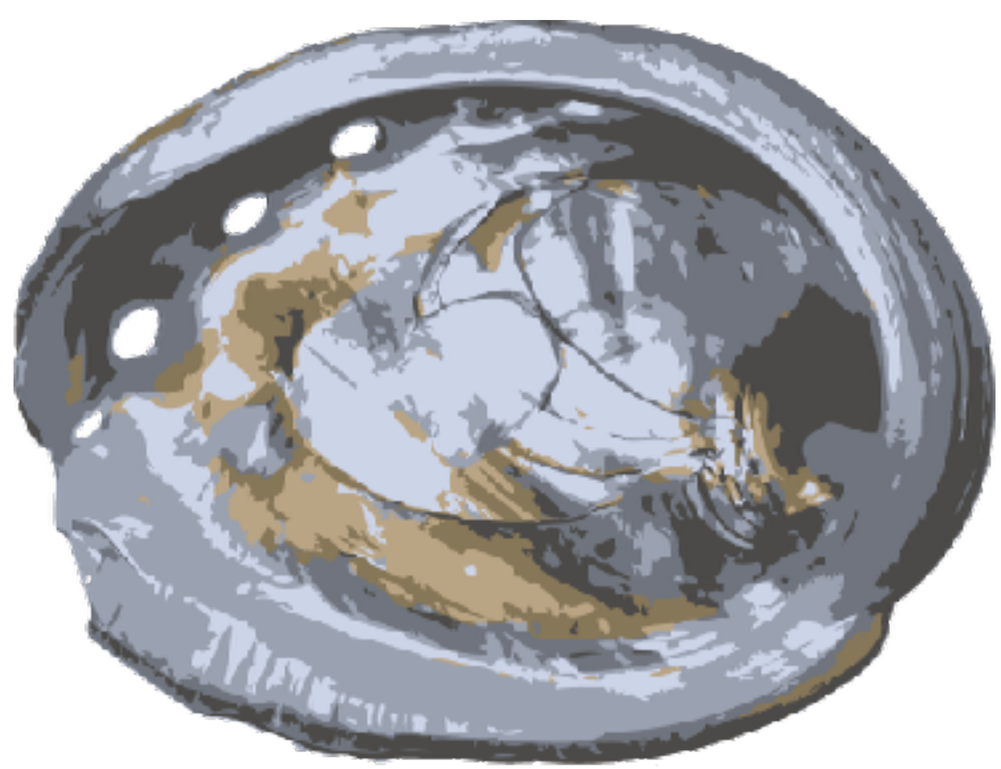


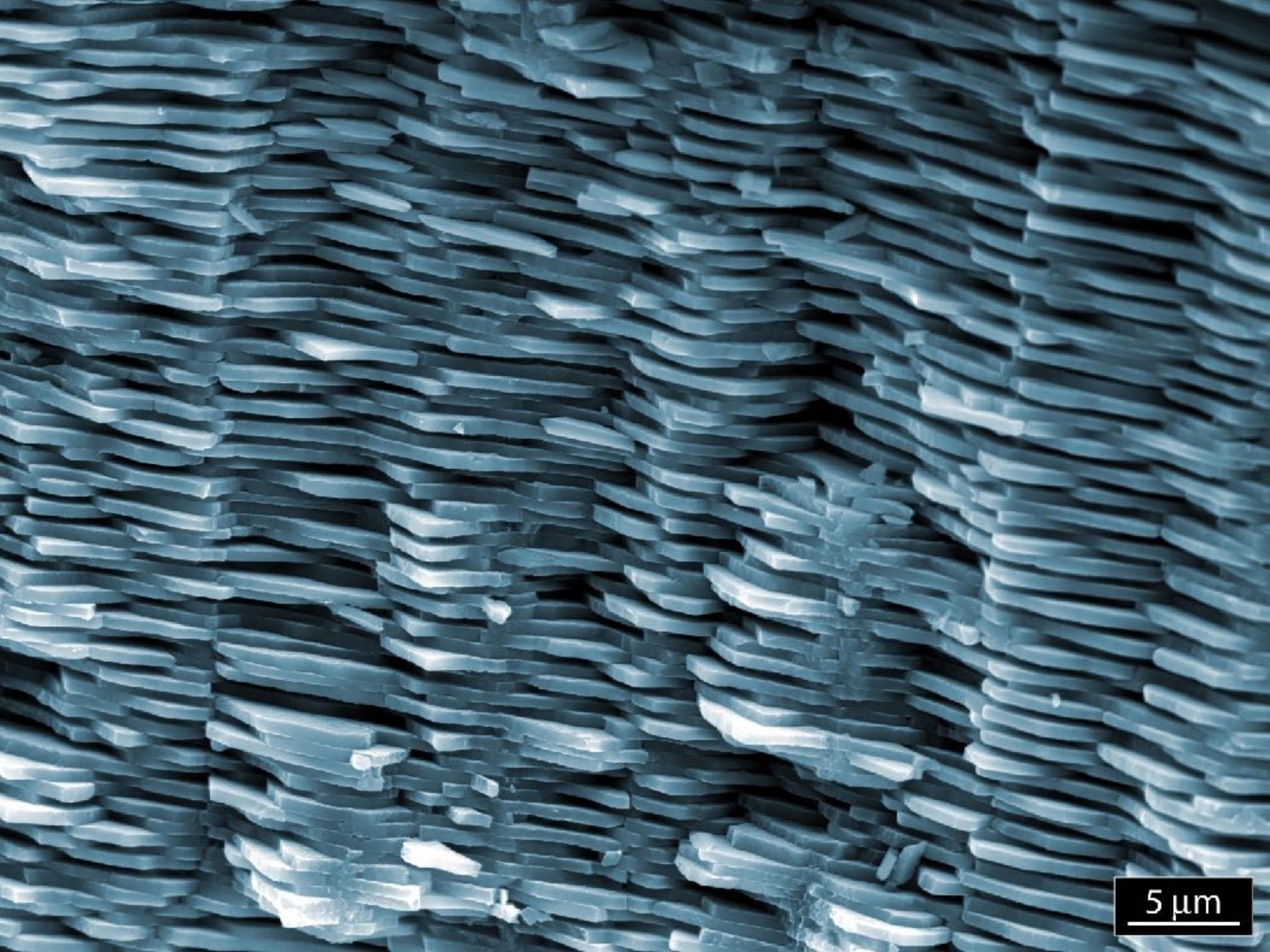
Courtesy AP Tomsia, LBNL



Chen, P.-Y. et al. Structure and mechanical properties of selected biological materials. *J. Mech. Behav. Biomed. Mater.* (2008).

Nacre: architecture and mechanics




5 µm

A 220M years old (at least) structure

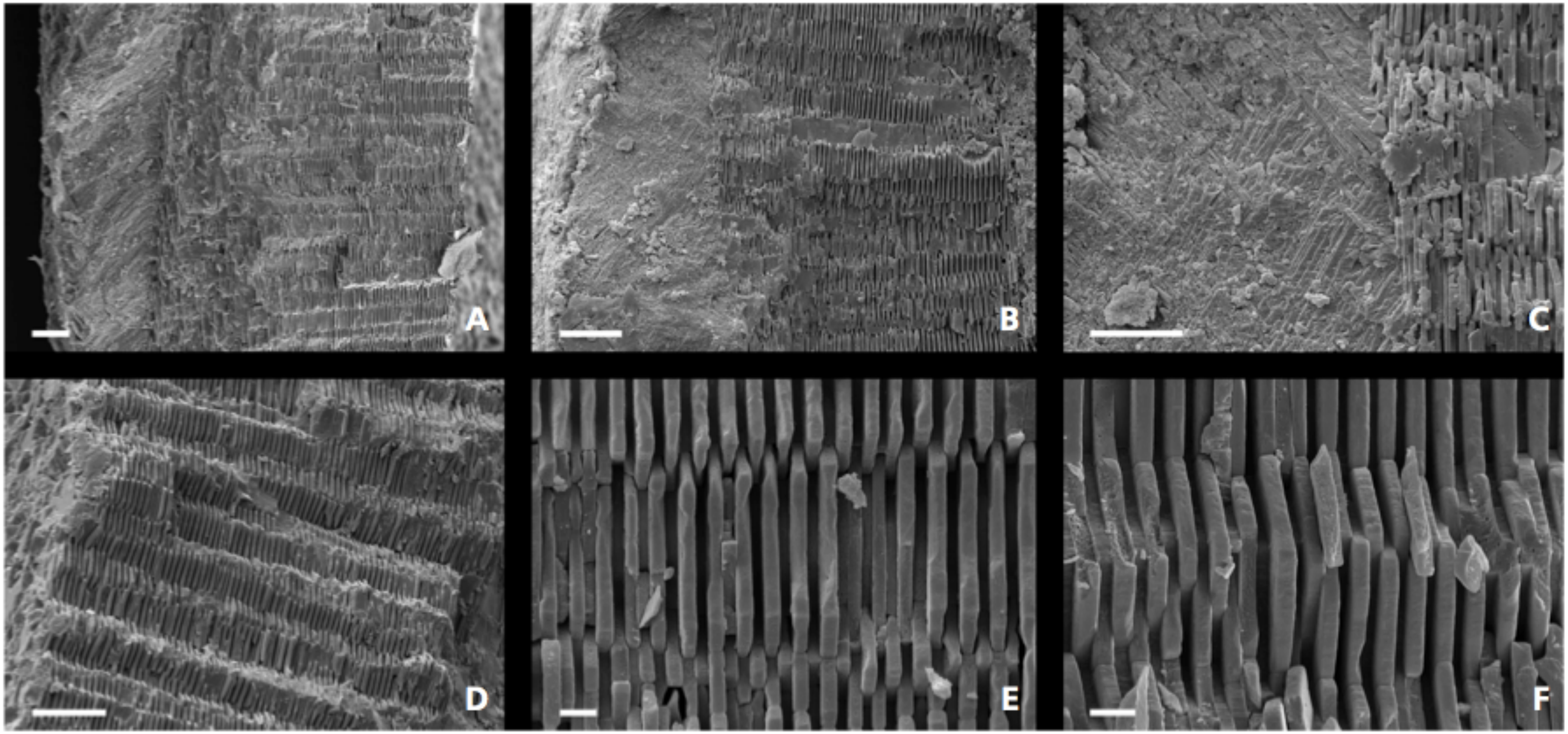


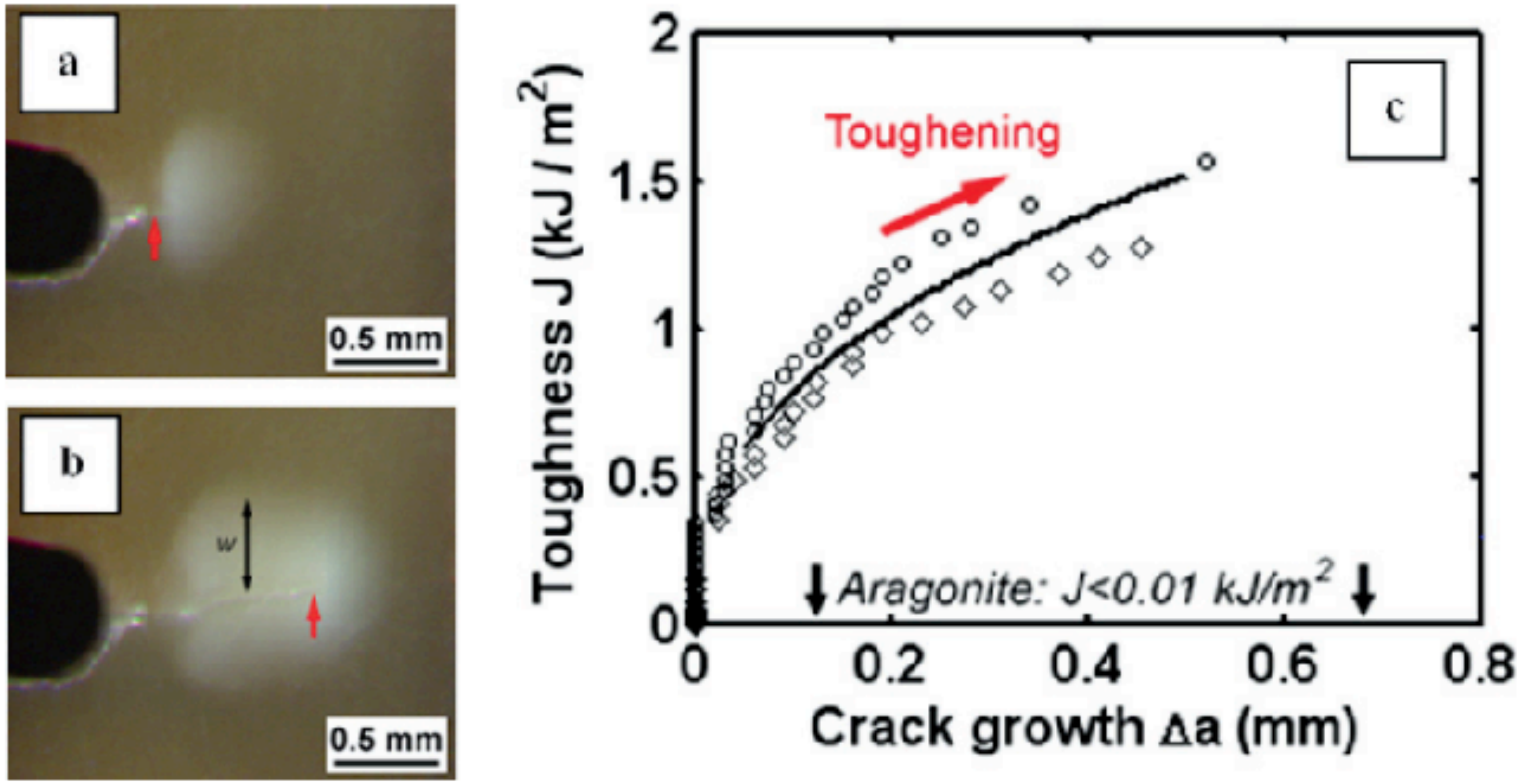
Figure 1. Secondary electron images of shell fragments of the Late Triassic *Wortheniella coralliophila* Kittl, 1891, from the St. Cassian Formation. • A, B – overall views of broken shell showing its outer layer (left) composed of spherulite sectors and inner nacreous layer (right). • C – detailed view of the boundary between spherulitic and nacreous layers. • D – view of the inner layer showing the columnar arrangement of nacreous platelets. • E, F – detailed views of nacreous platelets. Localities: A, D and F – Campo, B, C and E – Misurina; both localities near the Cortina d'Ampezzo, Dolomites. Scale bars: A, B, D – 20 μm; C – 10 μm; E, F – 2 μm.

Frýda, J.,Crystallographic texture of Late Triassic gastropod nacre: evidence of long-term stability of the mechanism controlling its formation. *Bull. Geosci.* 747–756 (2009)

Table 1 Classification of some mollusk shells that consist of nacre

Class	Family	Genus	Species	References
Bivalves	Meretricinae	*Meretrix*	*Meretrix lusoria*	Fleischli *et al.*[10]
	Mytilidae	*Bathymodiolus*	*Bathymodiolus azoricus*	Machado *et al.*[114]
		Perna	*Perna canaliculus* (green mussel)	Leung and Sinha;[106] Pokroy *et al.*;[115] Moshe-Drezner *et al.*[110]
		Modiolus	*Modiolus modiolus*	Currey[45]
	Nuculidae	*Nucula*	*Nucula nitidosa*	Cartwright and Checa;[9] Checa *et al.*[37,94]
	Pinnidae (pen shell)	*Atrina*	*Atrina pectinata*	Cartwright and Checa[9]
			Atrina rigida	Nudelman *et al.*[88]
			Atrina vexillum	Currey[45]
	Pteriidae	*Pteria*	*Pteria avicula*	Cartwright and Checa;[9] Cartwright *et al.*[3] Fig. 1
			Pteria hirundo	Cartwright and Checa;[9] Cartwright *et al.*[3]
			Pteria penguin	Fleischli *et al.*[10]
		Pinctada (pearl oysters)	*Pinctada maxima*	Stempflé and Brendlé;[107] Stempflé *et al.*;[116] Wang *et al.*[5]
			Pinctada margaritifera	Chateigner *et al.*;[83] Checa *et al.*;[94] Currey;[45] Currey *et al.*;[117] Jackson *et al.*;[13] Rousseau *et al.*[101]
			Pinctada sp.	Currey[45]
	Tellinidae	*Tellinella*	*Tellinella asperrima*	Ren *et al.*[118]
	Unionidae	*Anodonta*	*Anodonta cygnea* (swan mussel)	Cartwright and Checa;[9] Currey;[45] Machado *et al.*[114]
		Hyriopsis	*Hyriopsis schlegeli*	Song *et al.*[119]
		Lamprotula	*Lamprotuda fibrosa*	Sun and Tong[17]
Gastropods	Calliostomatidae	*Calliostoma*	*C. zizyphinum*	Cartwright and Checa[9]
	Haliotidae	*Haliotis* (abalone)	*Haliotis asinina*	Cartwright and Checa[9]
			Haliotis fulgens (green abalone)	Lin and Meyers;[91] Meyers *et al.*[25,86]
			Haliotis genus	Heinemann *et al.*[43]
			Haliotis iris	Song *et al.*[35,36]
			Haliotis laevigata (greenlip abalone)	Blank *et al.*;[84] Heinemann *et al.*[43]
			Haliotis rufescens (red abalone)	Barthelat *et al.*;[31,48] Bezares *et al.*;[109,120] Fleischli *et al.*;[10] Fritz *et al.*;[87] Li *et al.*;[38,54] Lin *et al.*[68] Fig. 3, Fig. 8; Lin and Meyers;[91,121] Katti *et al.*;[41,50] Menig *et al.*;[46] Meyers *et al.*;[32,26,86] Mohanty *et al.*;[51] Schäffer *et al.*;[33] Verma *et al.*;[95] Wang *et al.*;[5] Yao *et al.*;[102] Yourdkhani *et al.*;[8] Zaremba *et al.*[2]
			unkonwn	Meyers and Chawla[97]
	Pleurotomariidae	*Perotrochus*	*Perotrochus caledonicus*	Checa *et al.*[94]
	Strombidae	*Strombus*	*Strombus gigas*	Menig *et al.*[122]
	Trochidae	*Gibbula*	*Gibbula pennanti*	Cartwright and Checa[9]
			Gibbula umbilicalis	Cartwright and Checa[9]
		Trochus	*Trochus niloticus* (top shell)	Bruet *et al.*;[49] Currey[45]
	Turbinidae	*Bolma*	*Bolma rugosa*	Cartwright and Checa[9]
		Turbo	*Turbo marmoratus*	Chateigner *et al.*;[83] Currey[45]
Cephalopods	Nautilidae	*Nautilus*	*Nautilus pompilius*	Currey[45]
Monoplacophora	Neopilinidae	*Veleropilina*	*Veleropilina zografi*	Checa *et al.*[94]

Nacre is tough



Crédit: Alfredo Mendez

Barthelat, F., A Review on the Structure and Mechanical Properties of Mollusk Shells – *Perspectives on Synthetic Biomimetic Materials*

Why is nacre tough? Survival !

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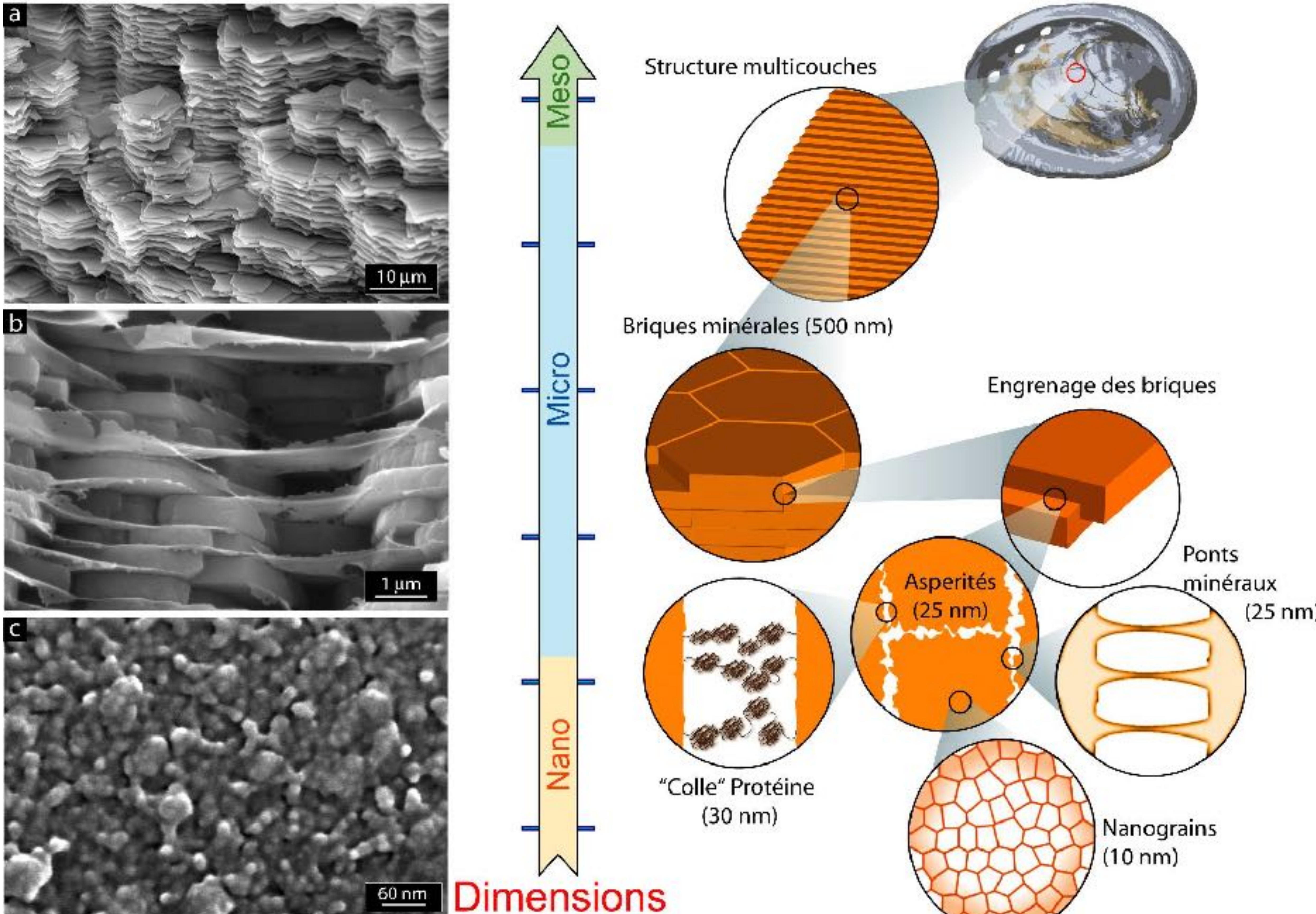
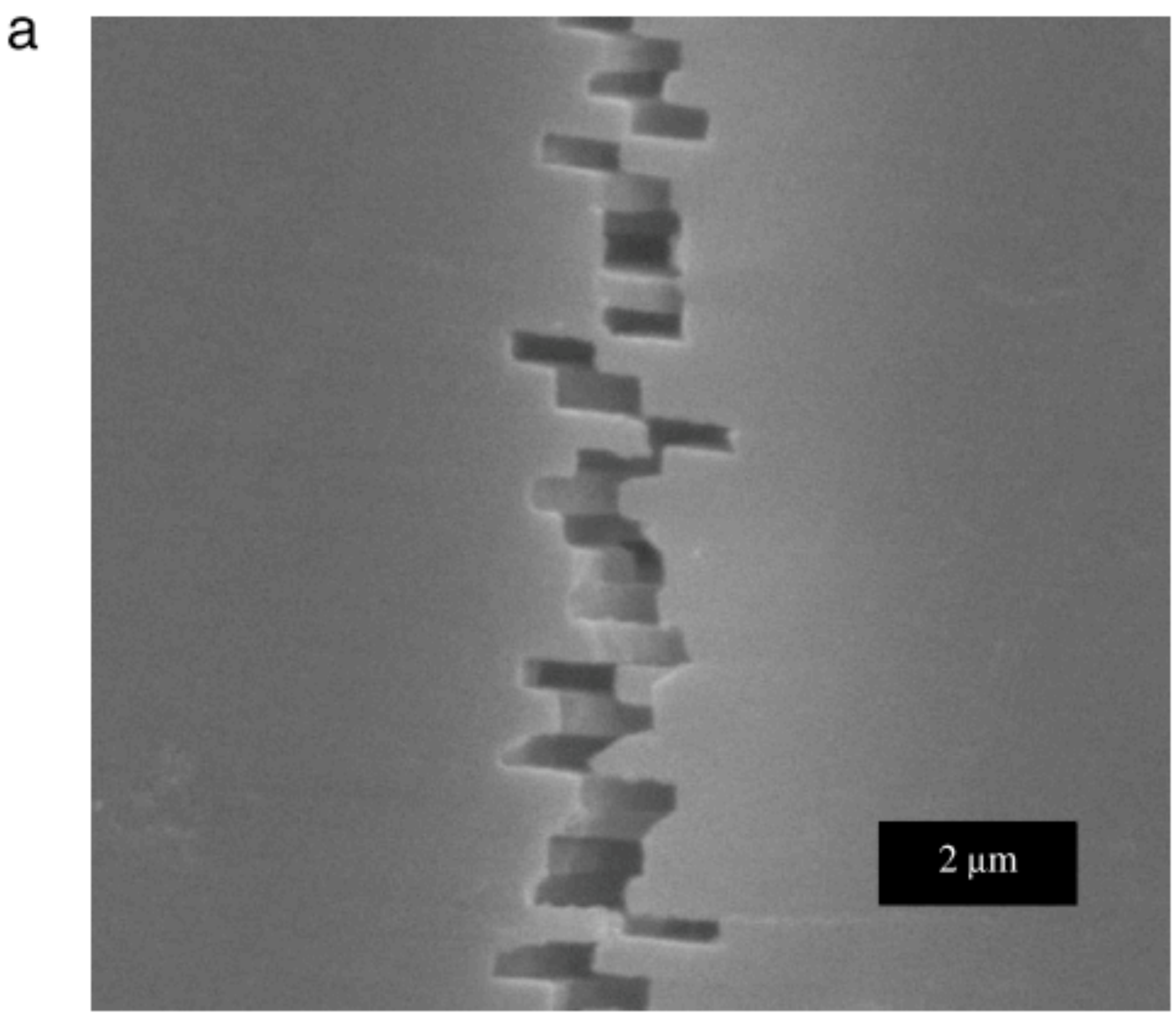
A hierarchical material



A brick and mortar structure

Crack deflection and platelets pull-out



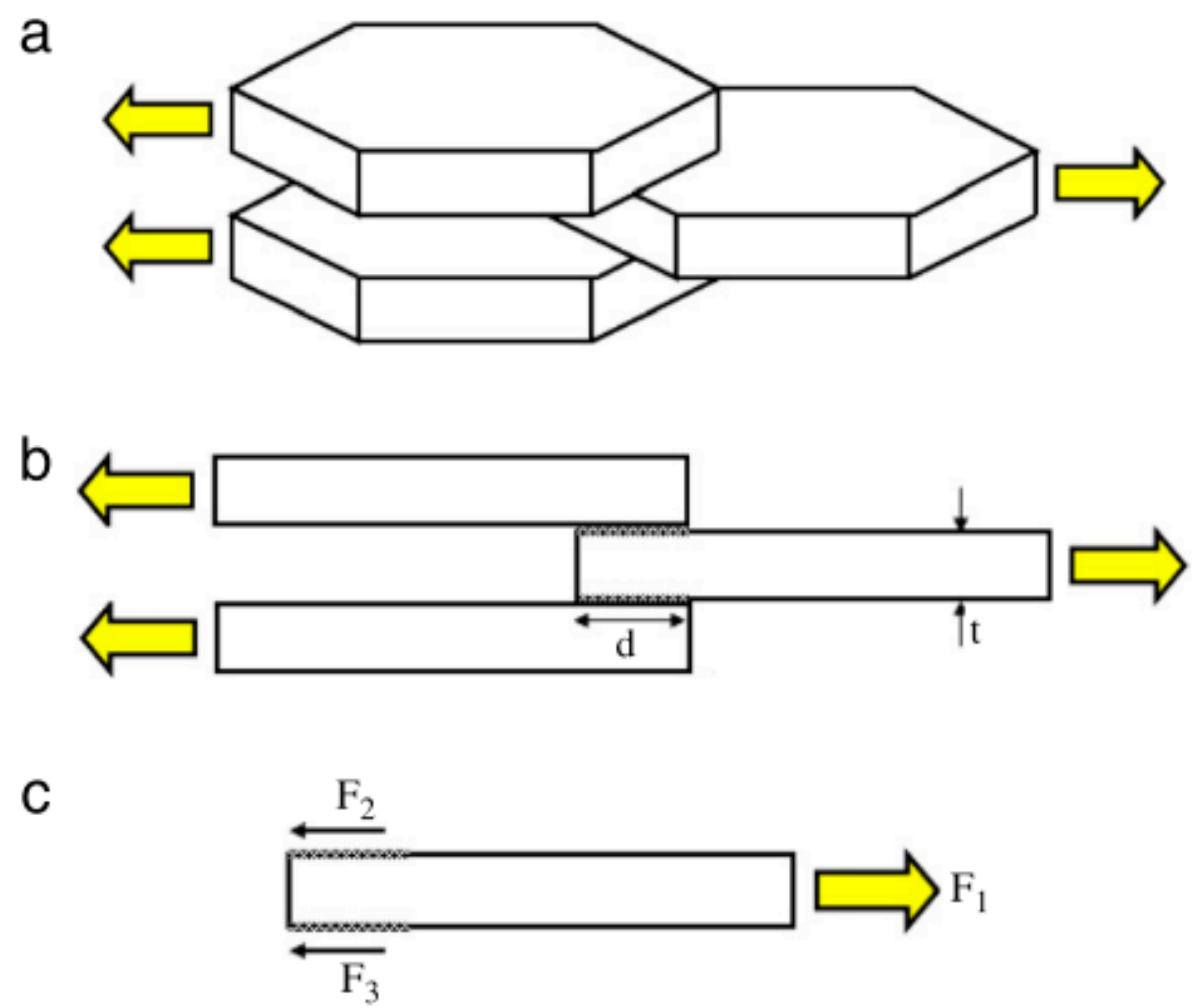
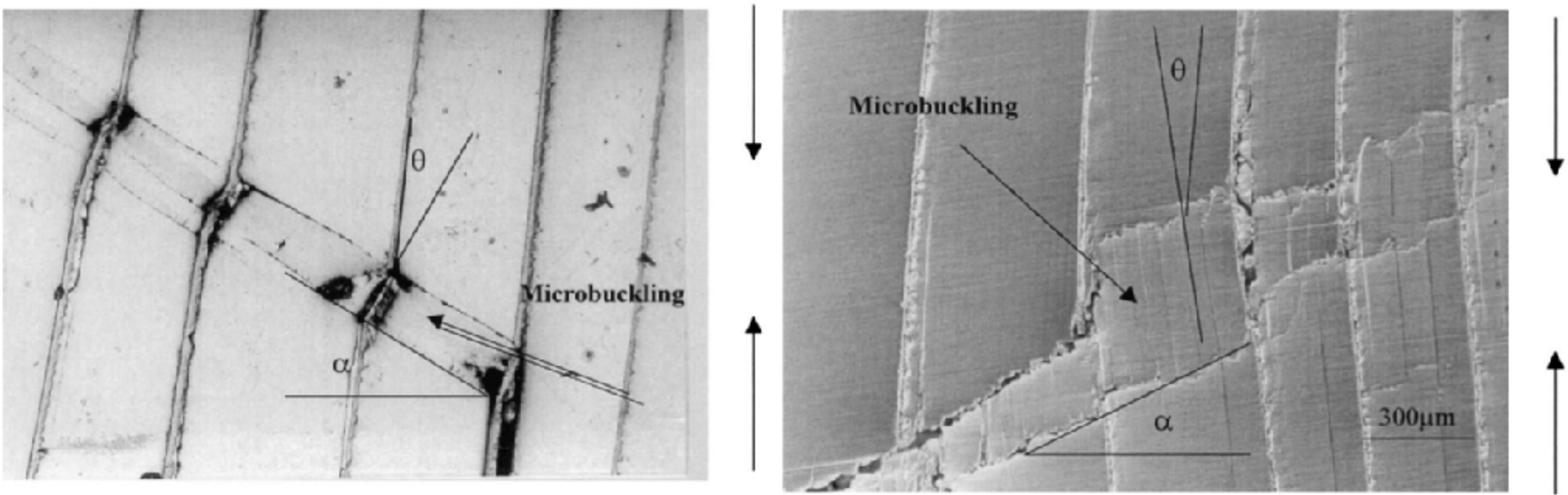


Fig. 7 – Schematic diagram showing pull-out of overlapping tile layers.

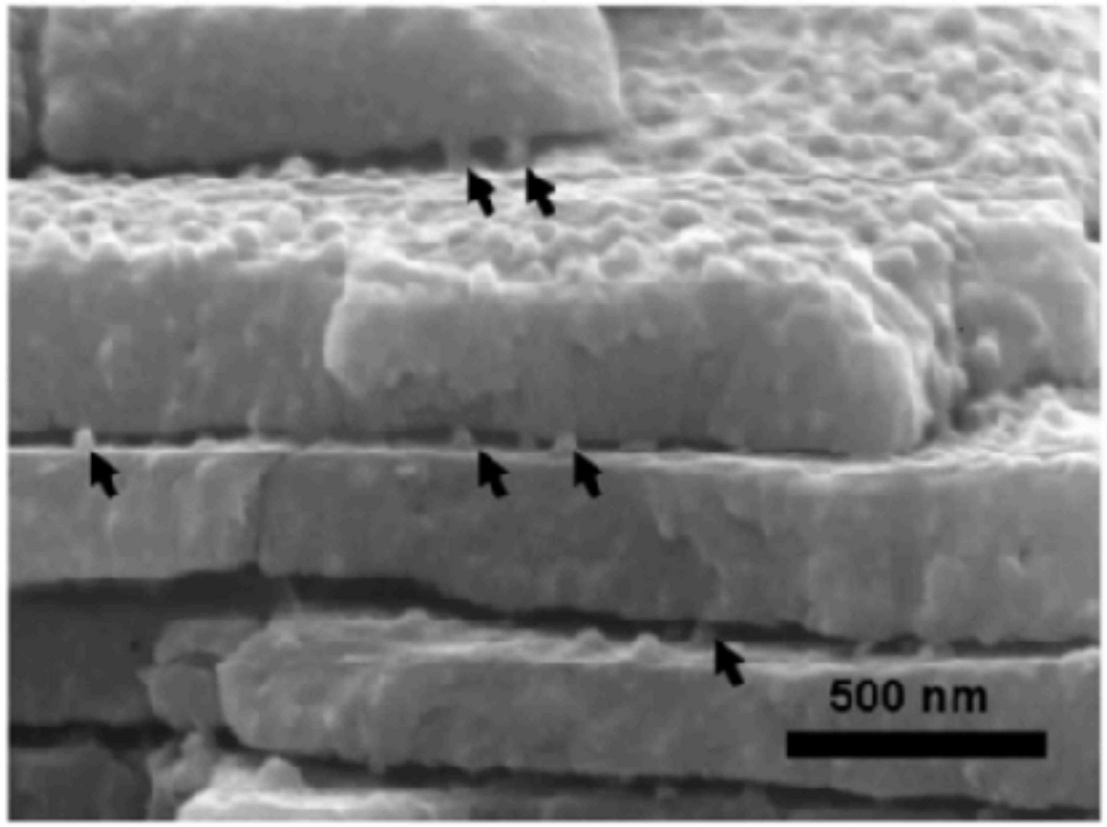
Lin, A.Y. M., Interfacial shear strength in abalone nacre. *J. Mech. Behav. Biomed. Mater.* (2009).

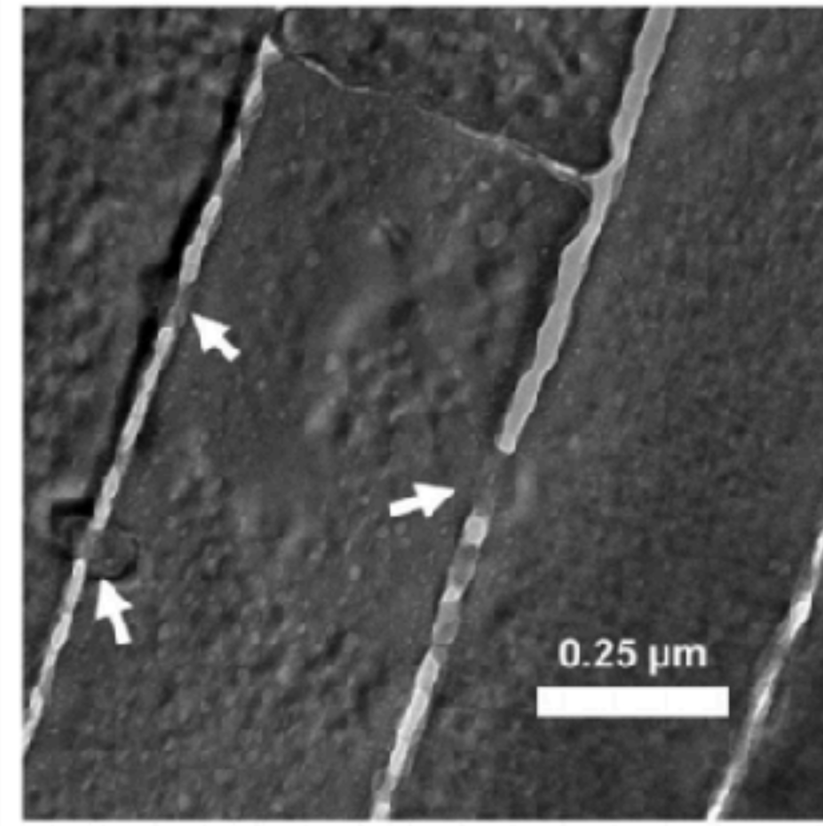
Microbuckling of platelets

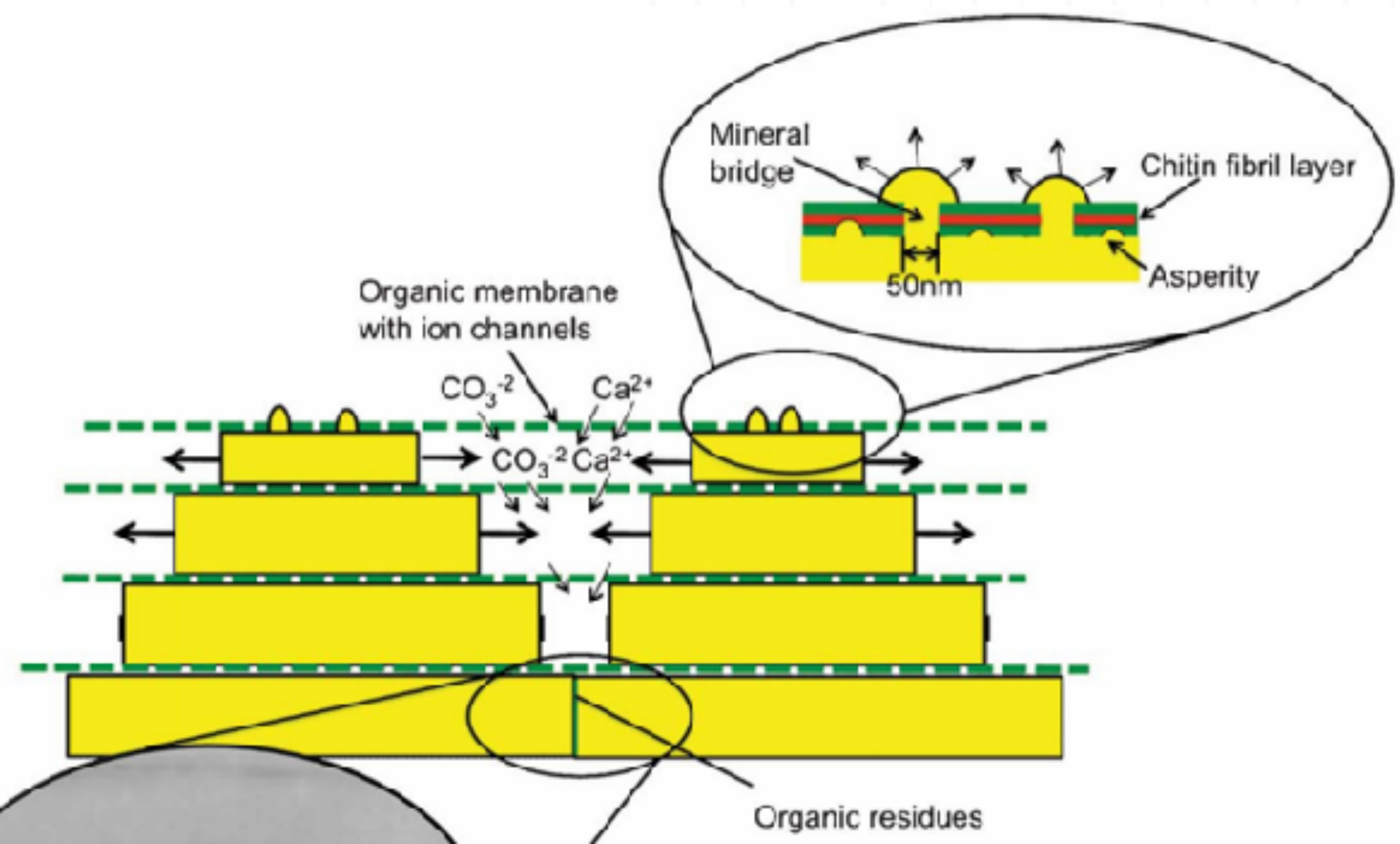


Menig, R., Quasi-static and dynamic mechanical response of Strombus gigas (conch) shells.
Mater. Sci. Eng. A 297, 203–211 (2001).

Inorganic bridges

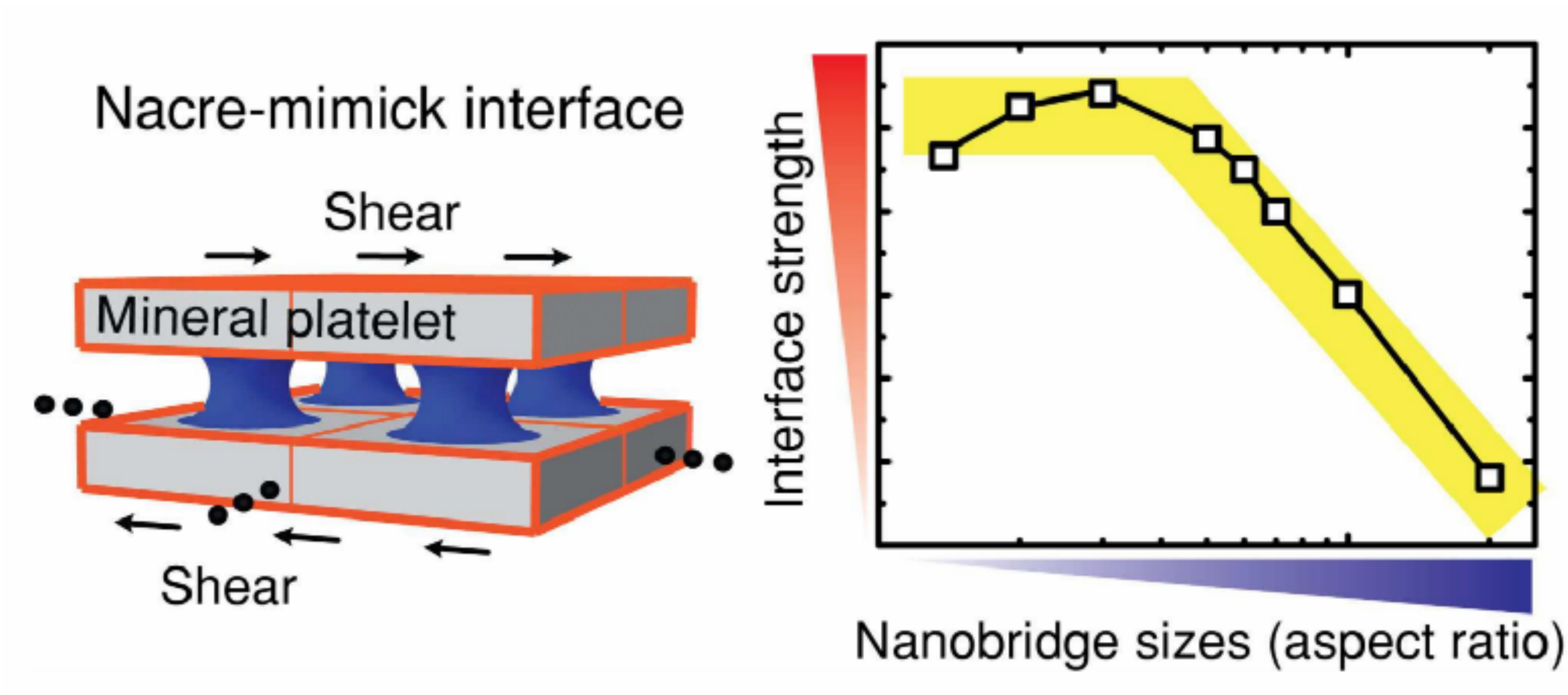






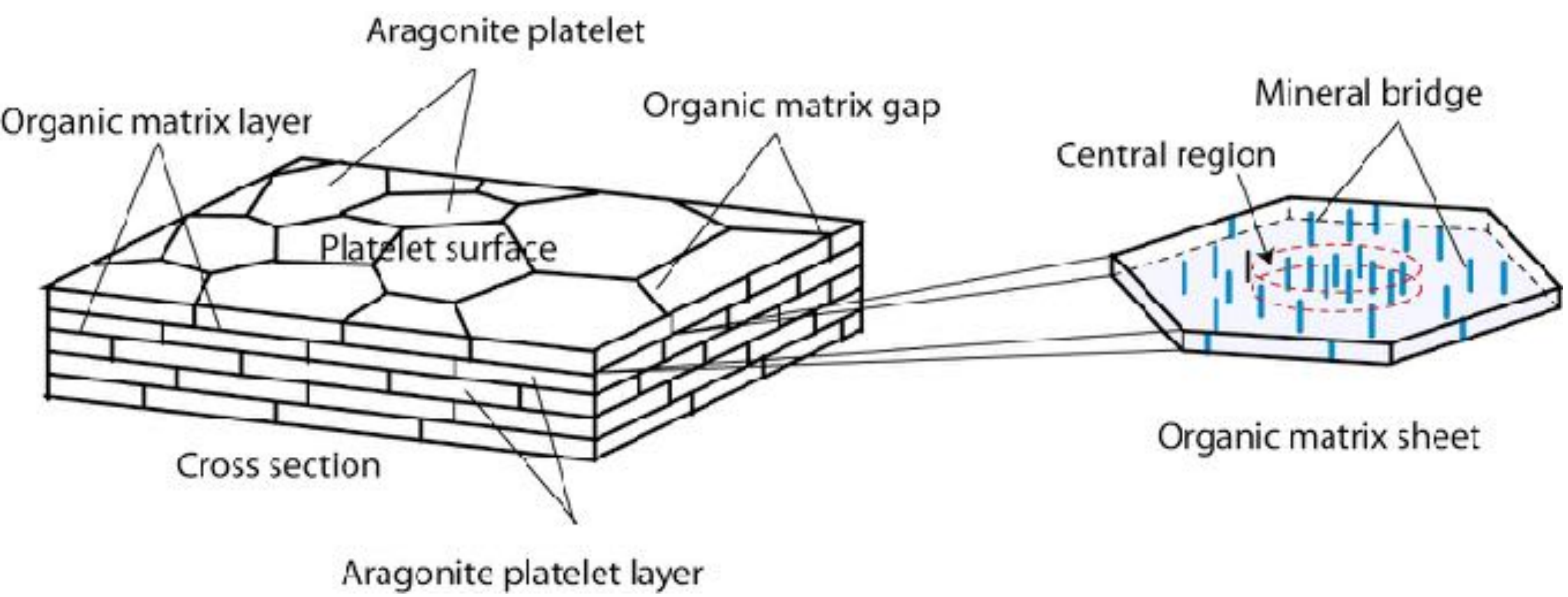
1. Sun, J. & Bhushan, B. Hierarchical structure and mechanical properties of nacre: A review. *RSC Adv.* 2, 7617–7632 (2012).

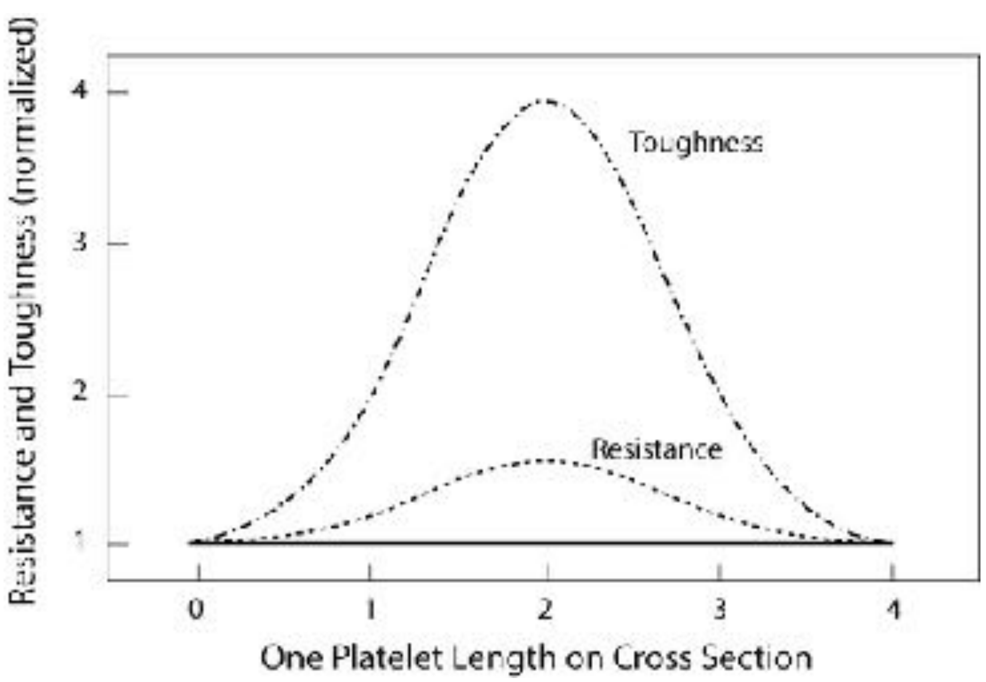
Inorganic bridges

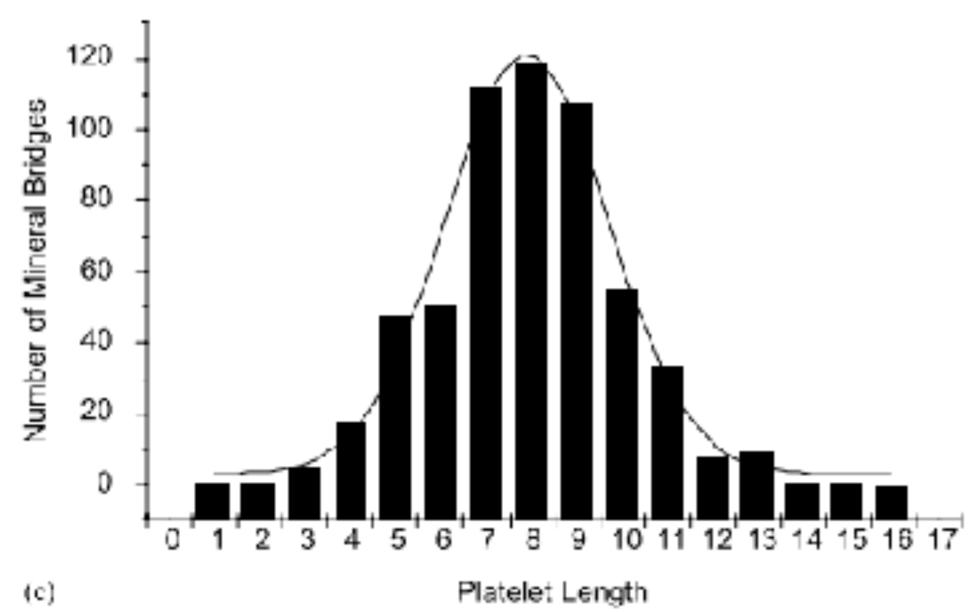


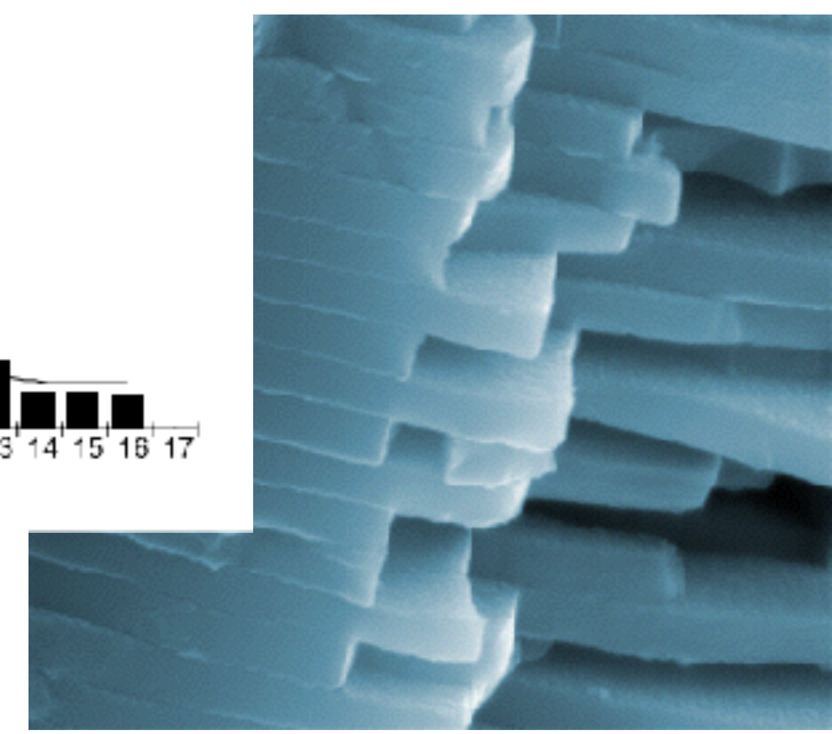
Shao, Y., Zhao, H.-P. & Feng, X.-Q. Optimal characteristic nanosizes of mineral bridges in mollusk nacre. *RSC Adv.* 4, 32451 (2014).

Inorganic bridges distribution



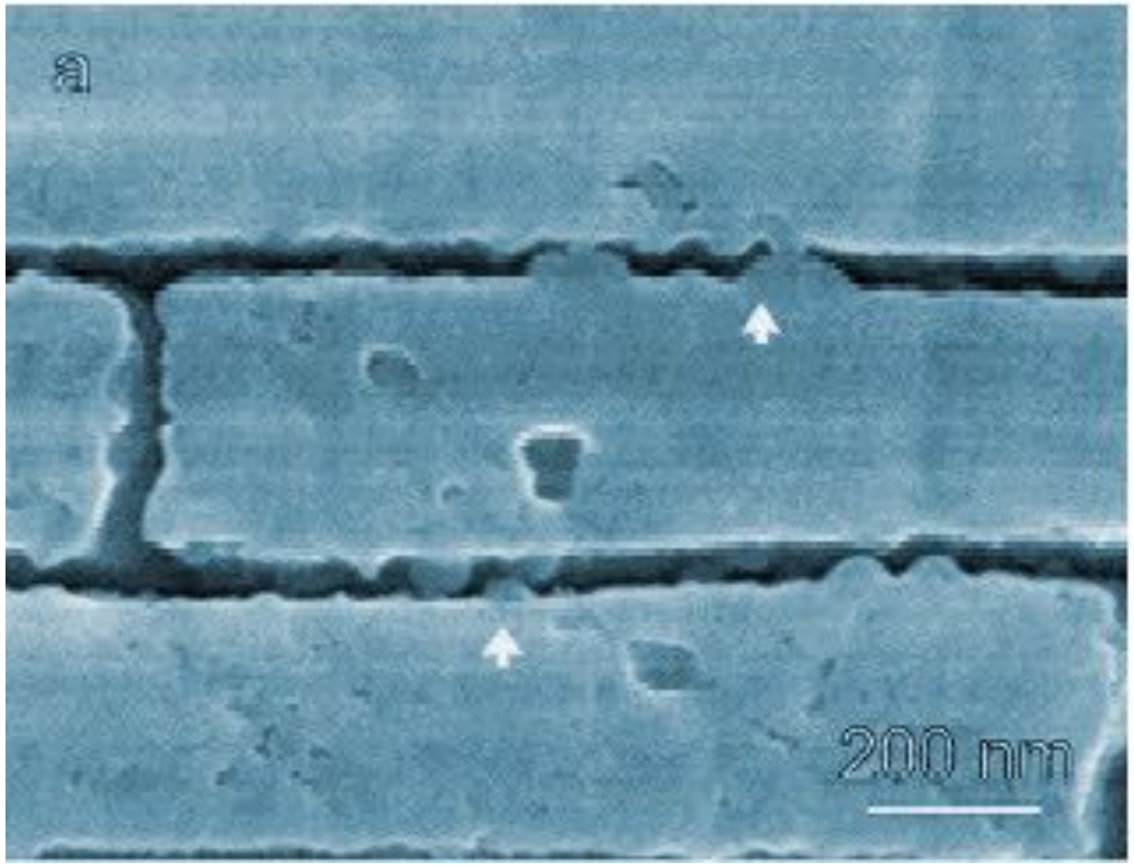


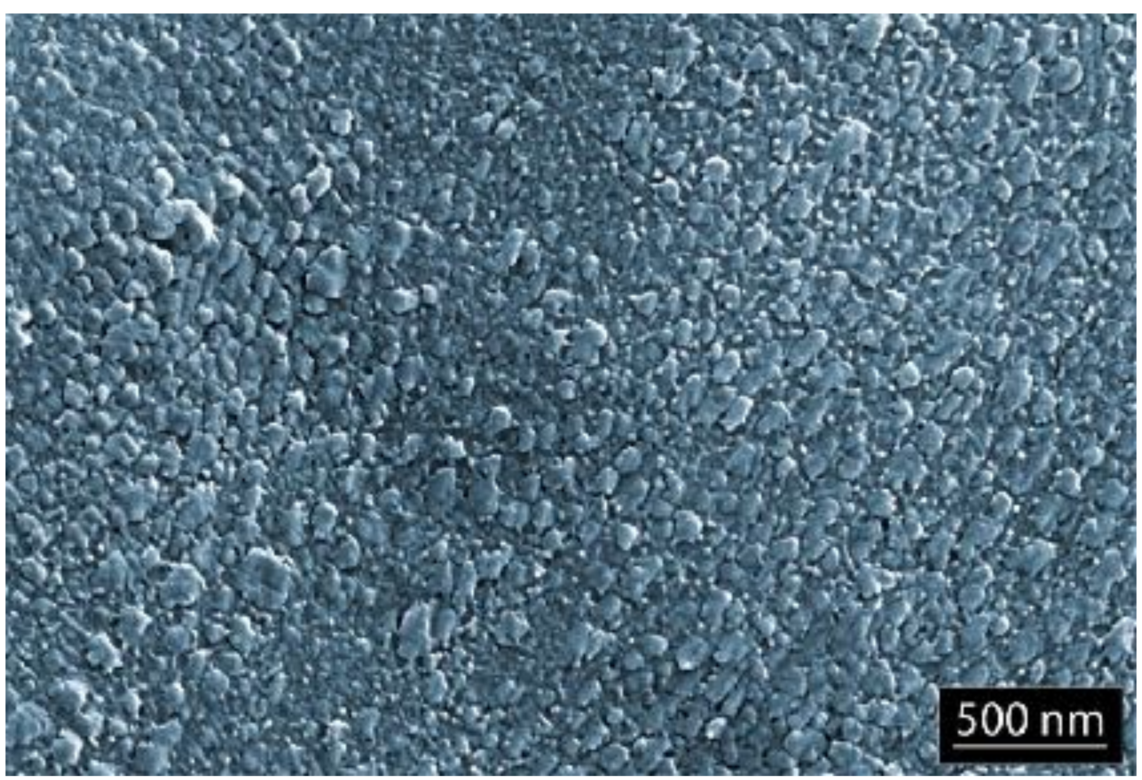


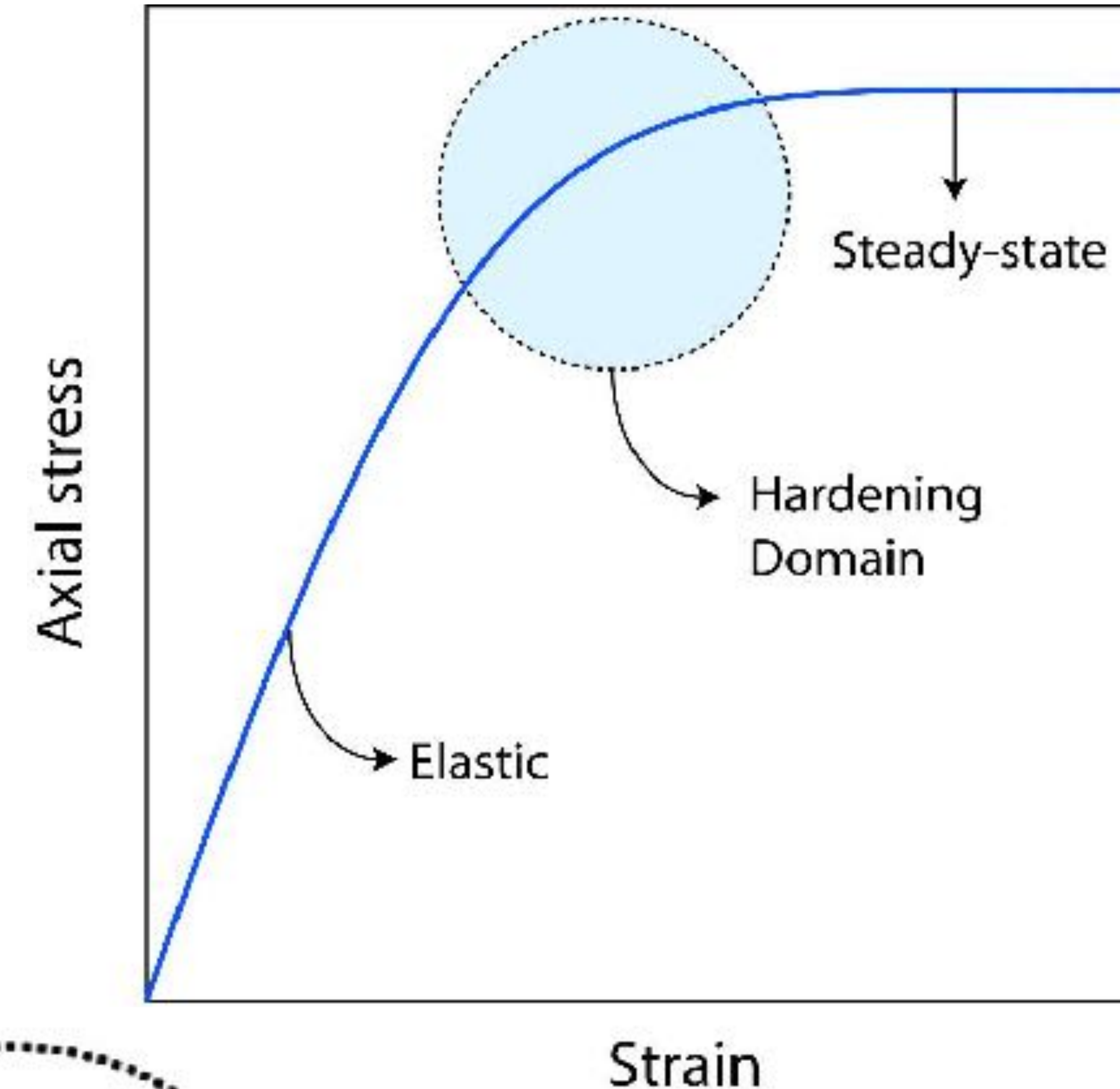


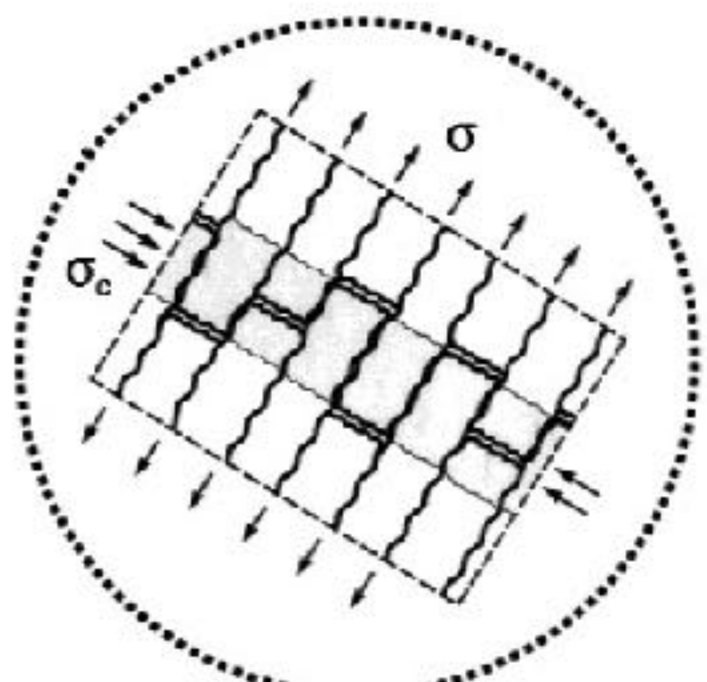
Song, F., Structural and mechanical properties of the organic matrix layers of nacre. *Biomaterials* 24, 3623–3631 (2003).

Surface roughness of bricks









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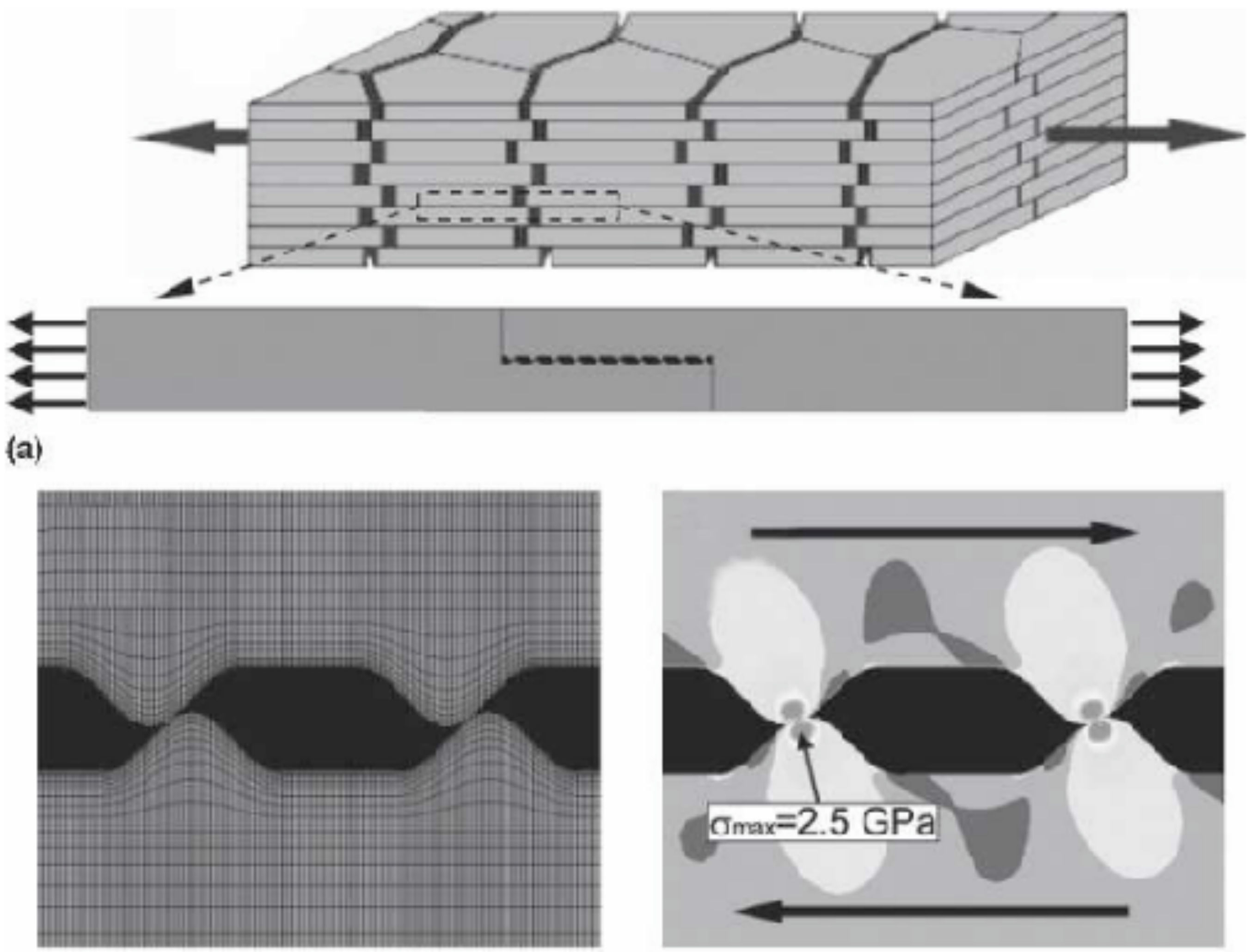
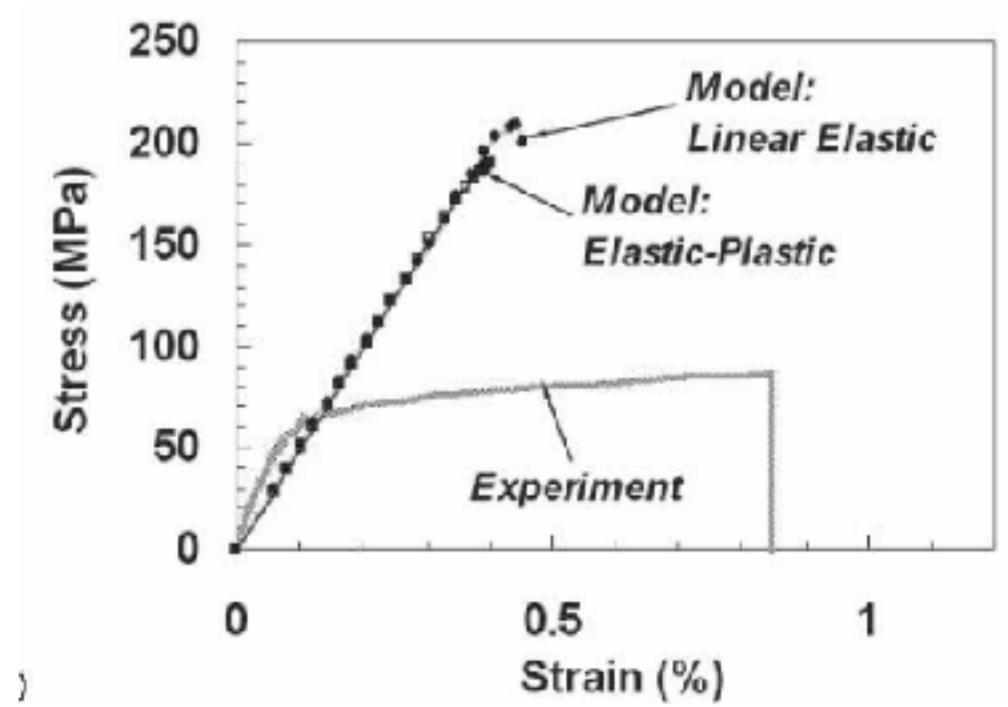
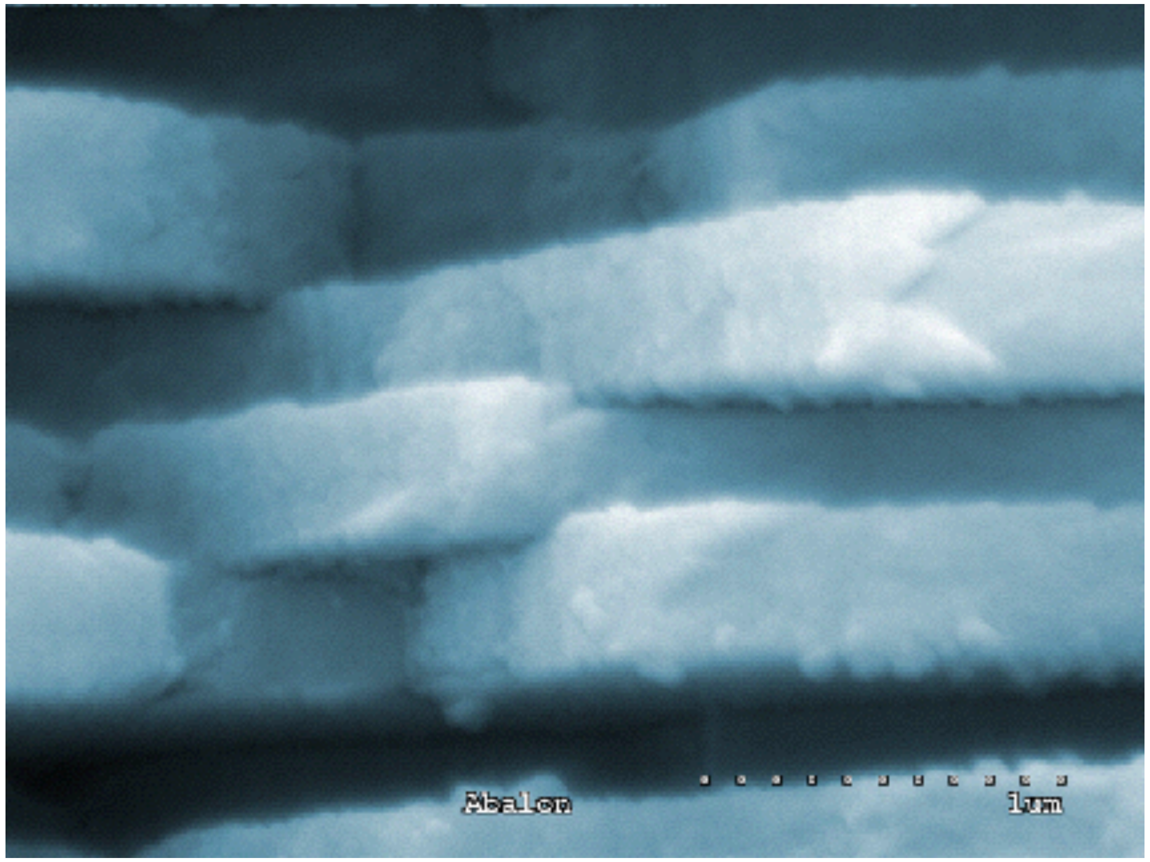
Surface roughness of bricks

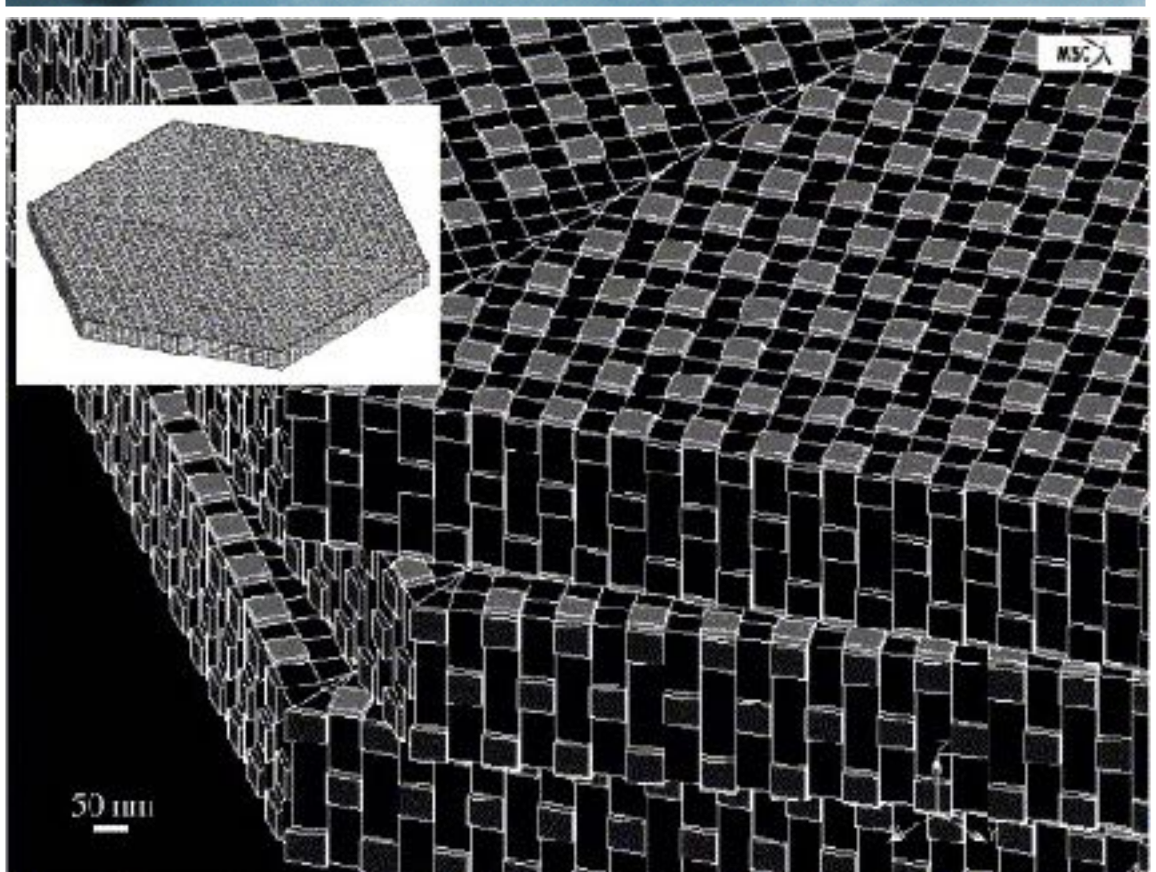


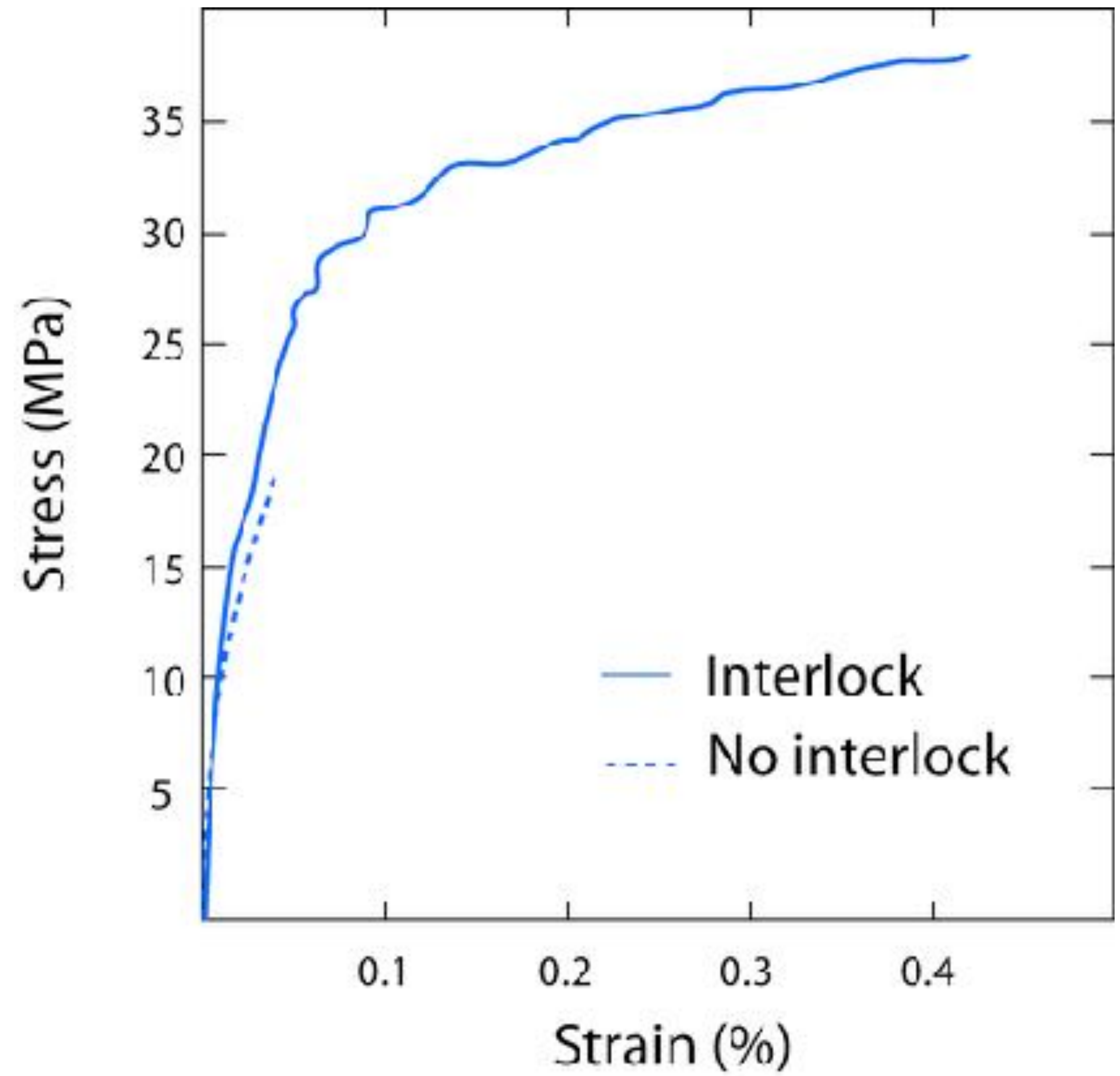


Barthelat, F., Mechanical properties of nacre constituents and their impact on mechanical performance. *J. Mater. Res.* 21, 1977–1986 (2011).

An interlocked structure

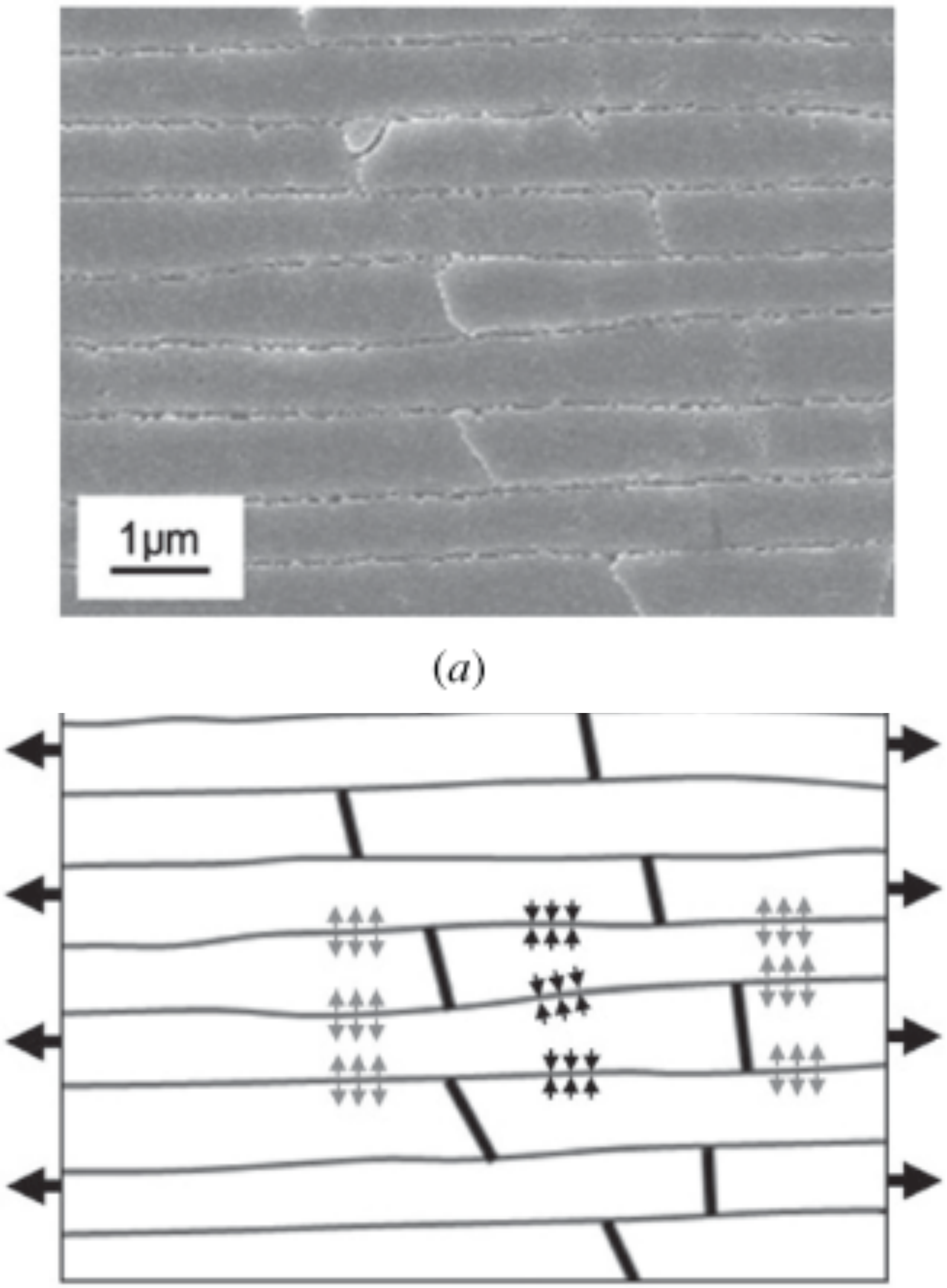






Katti, K. S., Platelet interlocks are the key to toughness and strength in nacre. *J. Mater. Res.* 20, 1097–1100 (2005).

An interlocked structure



(a)

(b)

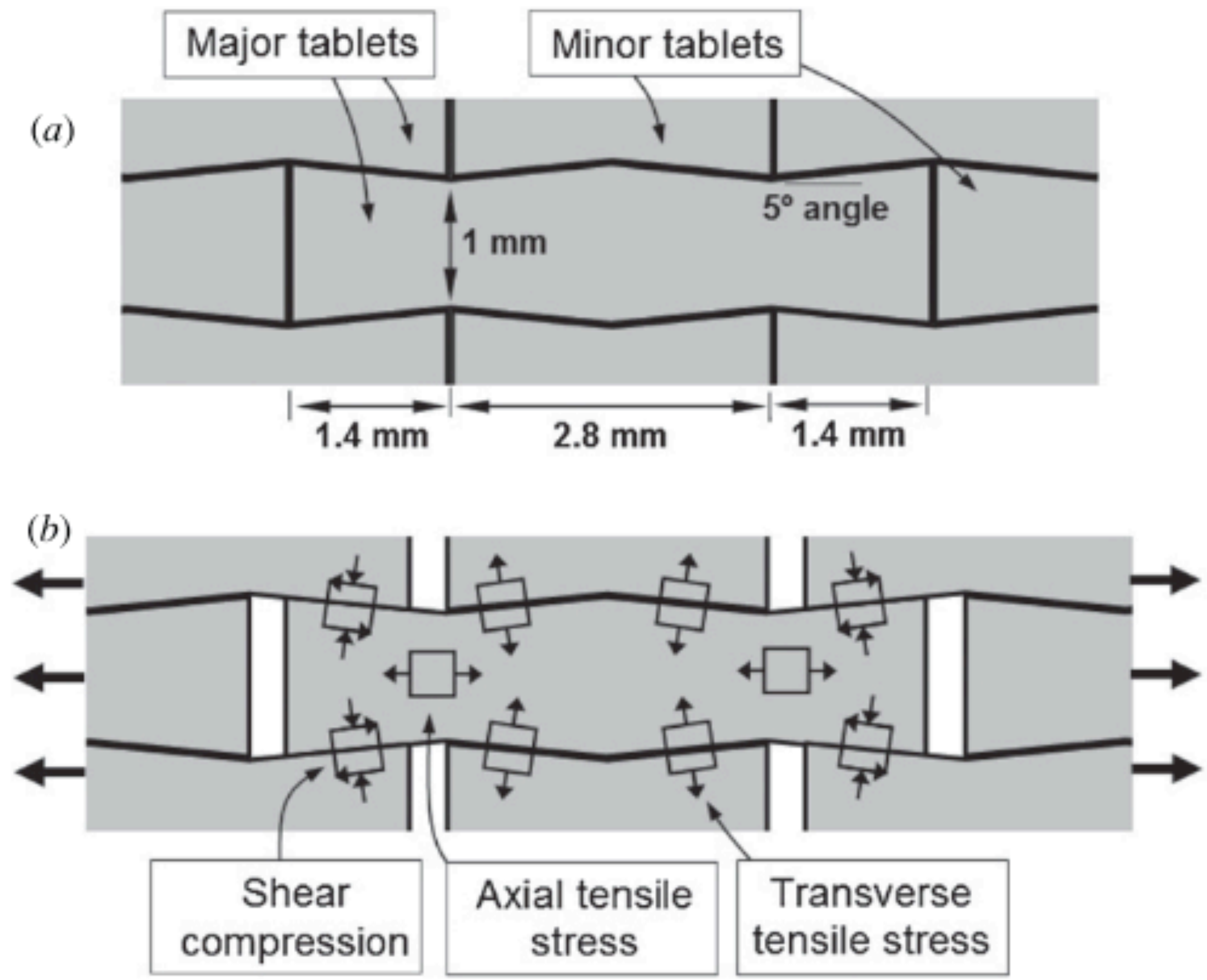
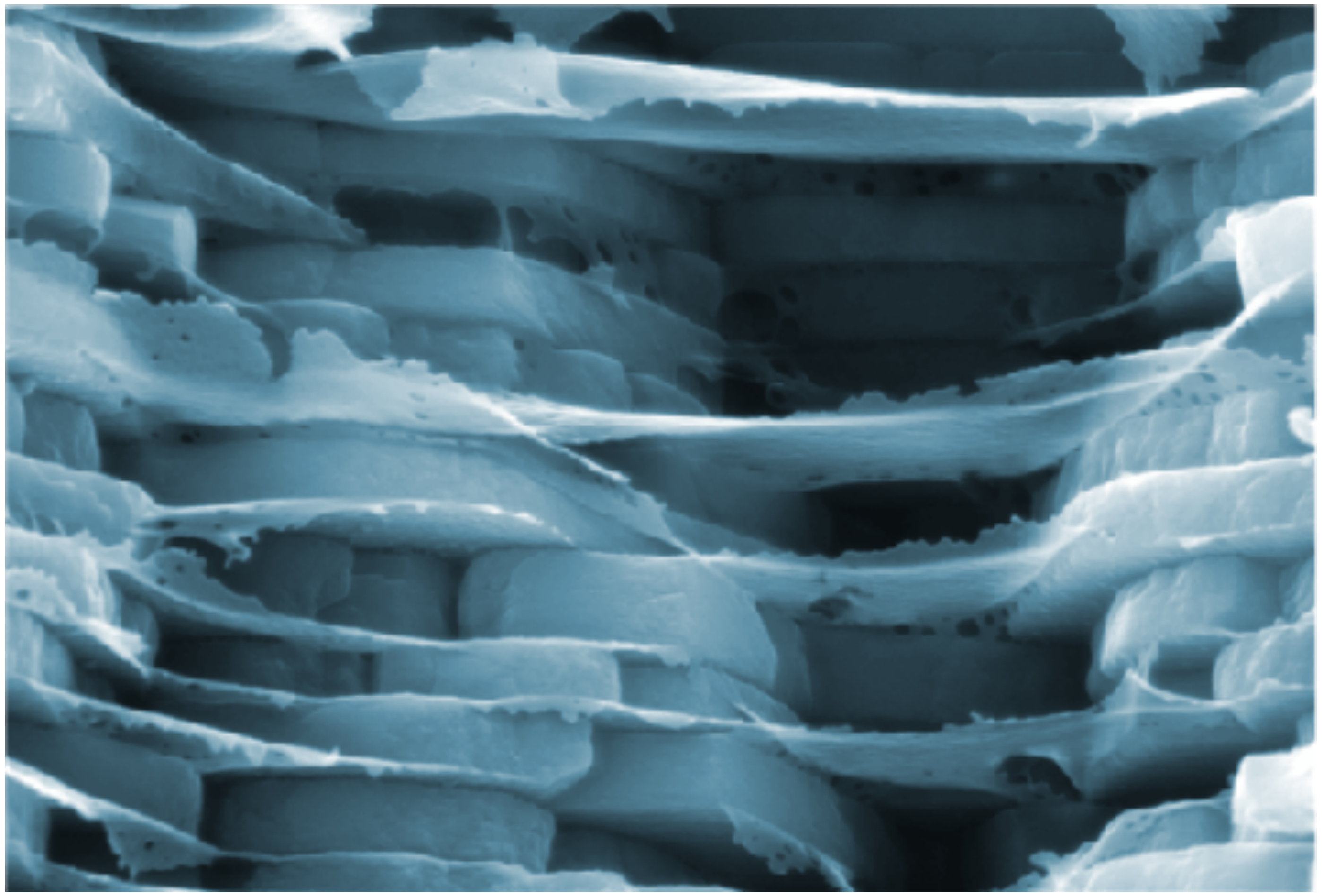
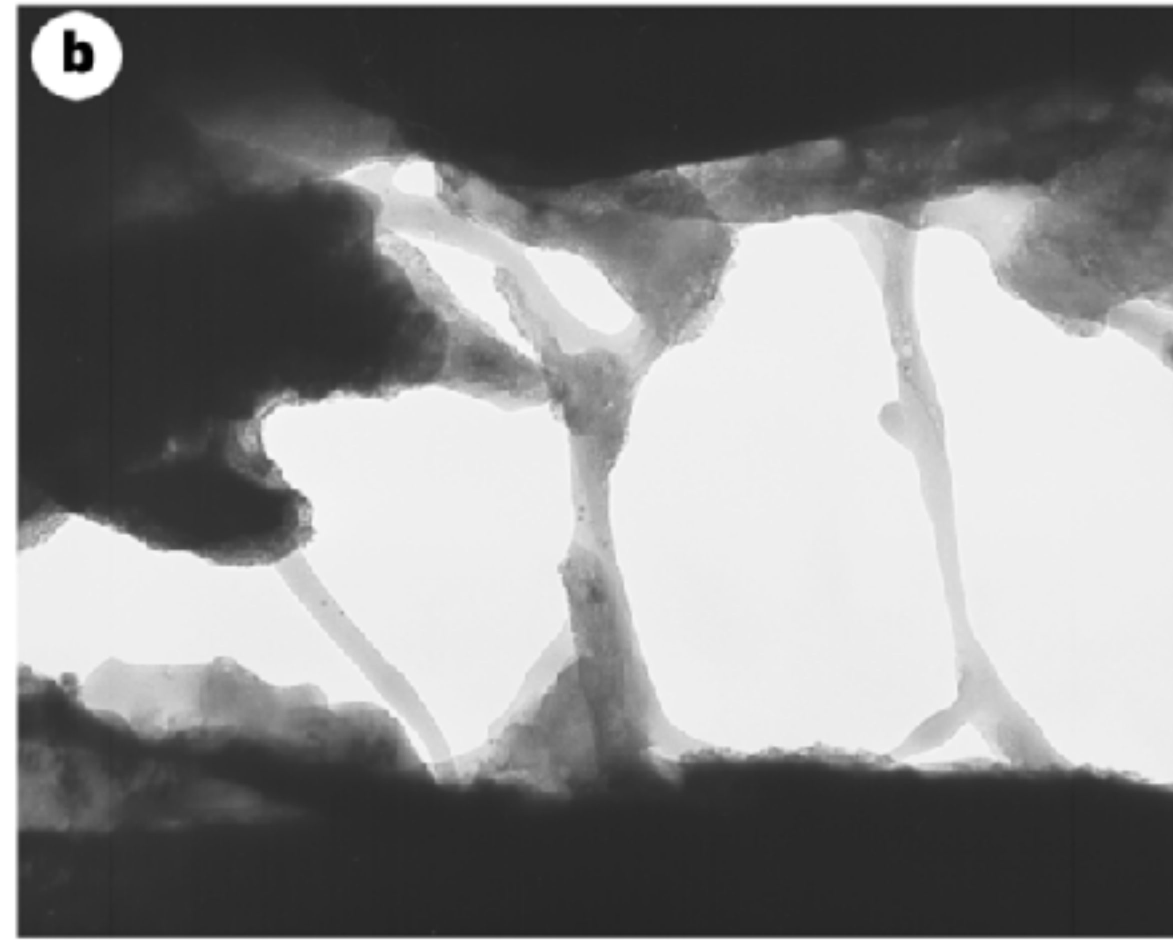


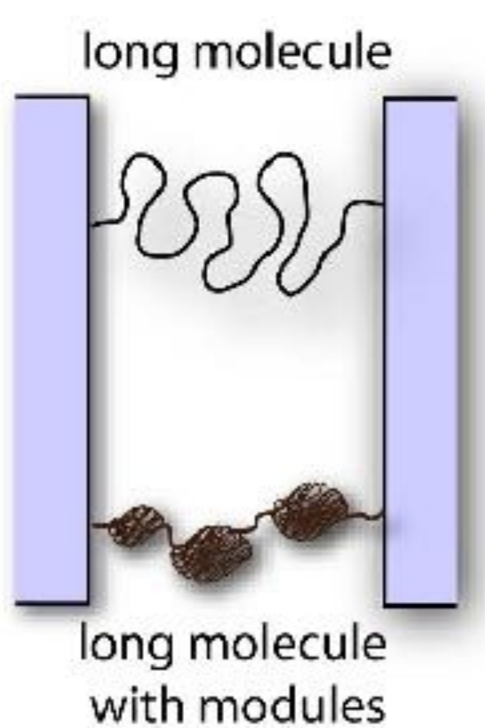
Figure 6. (*a*) Artificial nacre geometry with dimensions; (*b*) main stresses involved when the material is loaded in tension

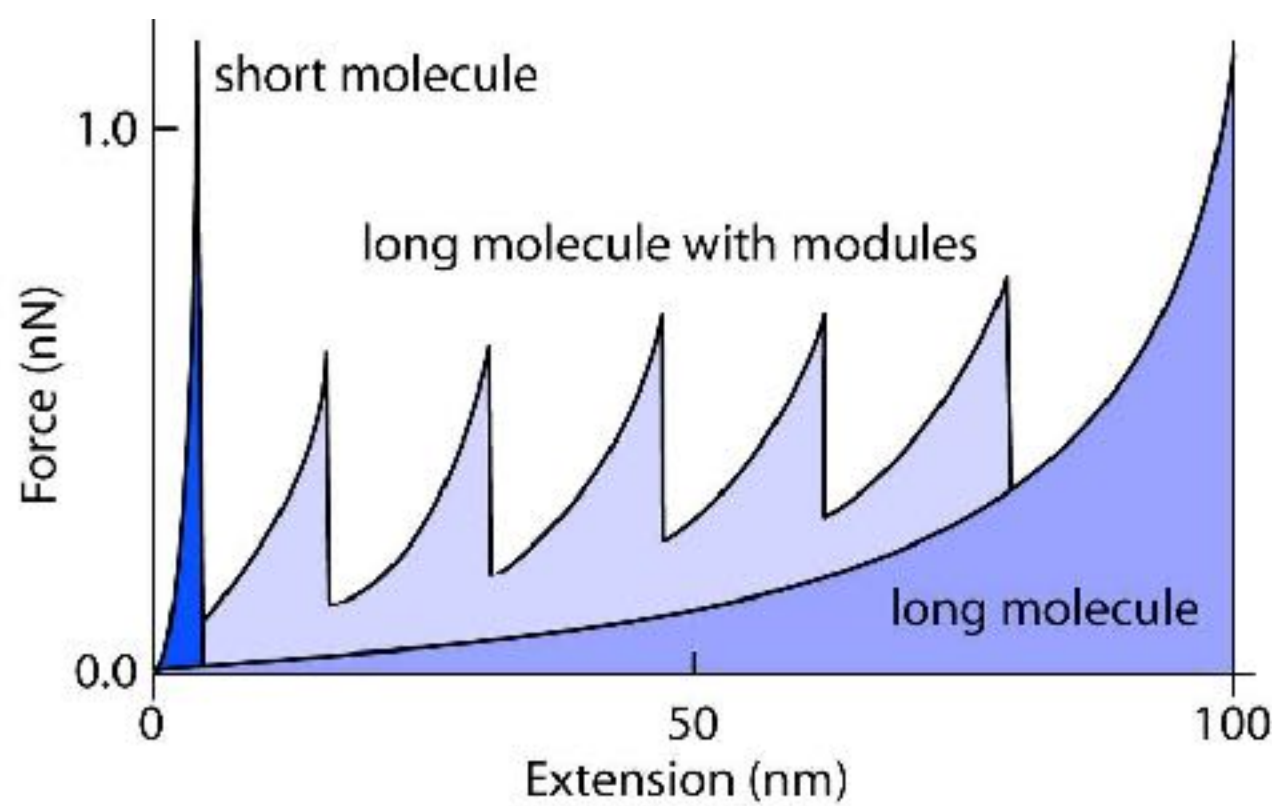
Barthelat, F. Nacre from mollusk shells: a model for high-performance structural materials. *Bioinspir. Biomim*. 5, 035001 (2010).

Protein glue









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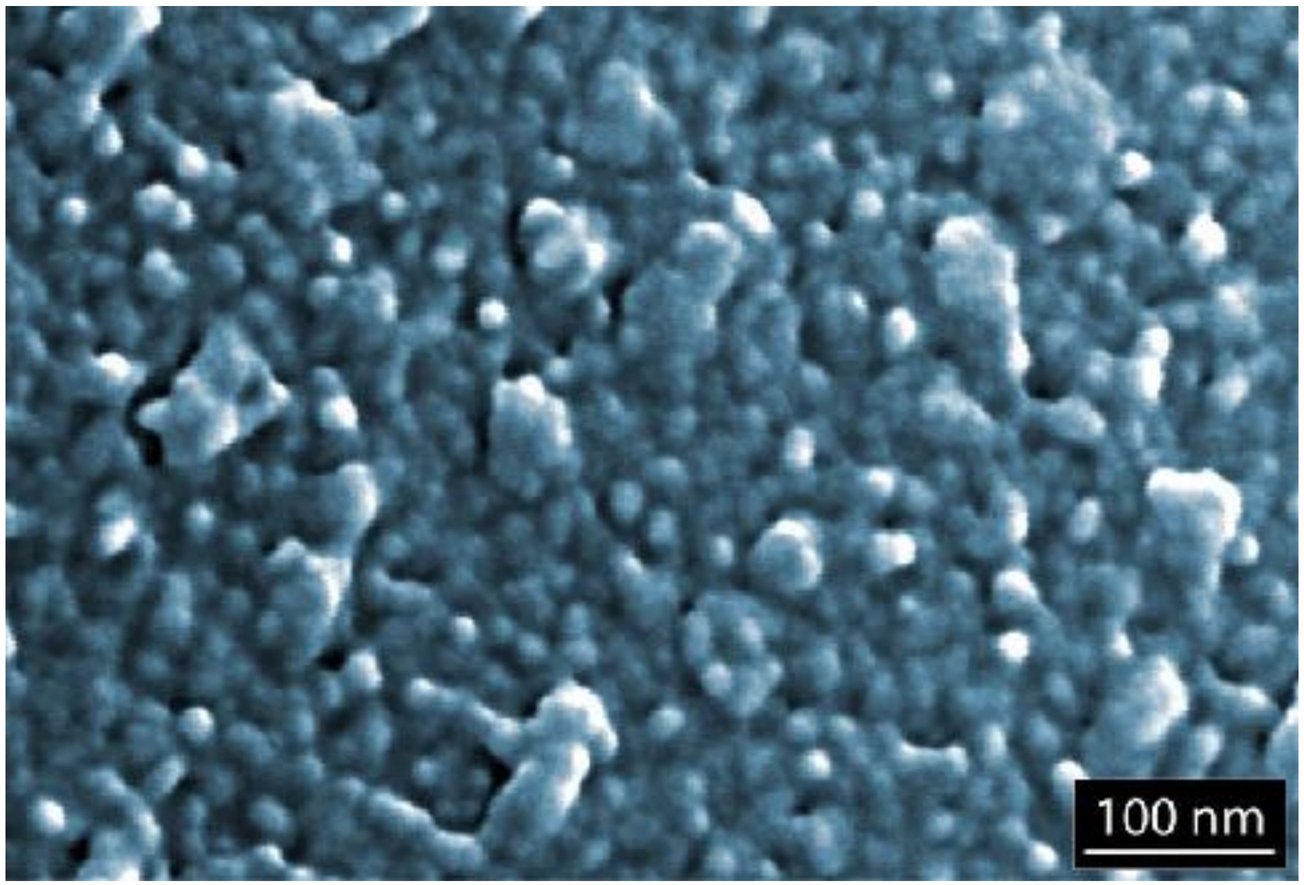
Nanograins



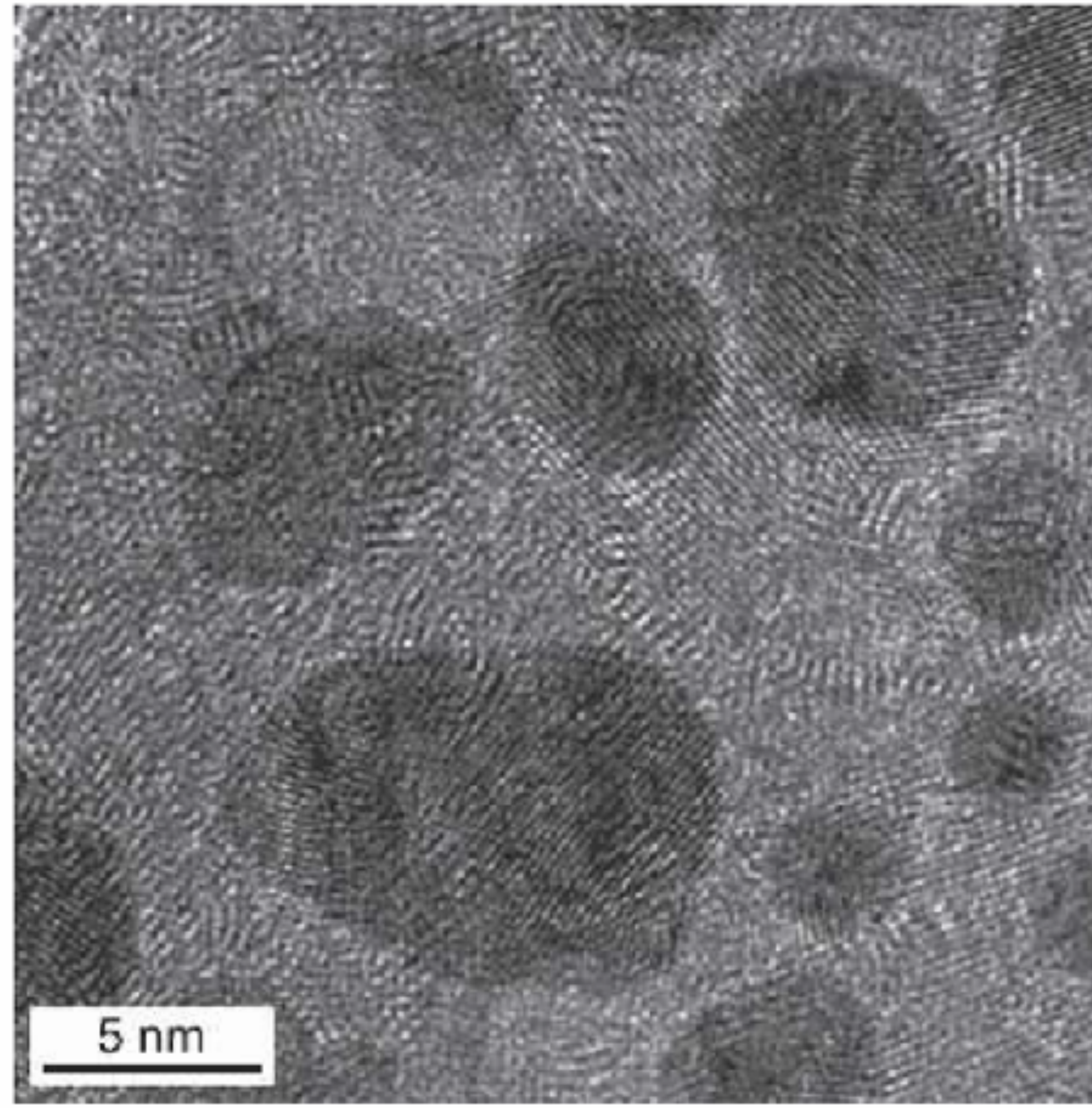


FIG. 3. High-resolution TEM (face-on view) of a tablet showing nanograins about 3–10 nm in size.

Barthelat, F., Mechanical properties of nacre constituents and their impact on mechanical performance. *J. Mater. Res.* 21, 1977–1986 (2011).

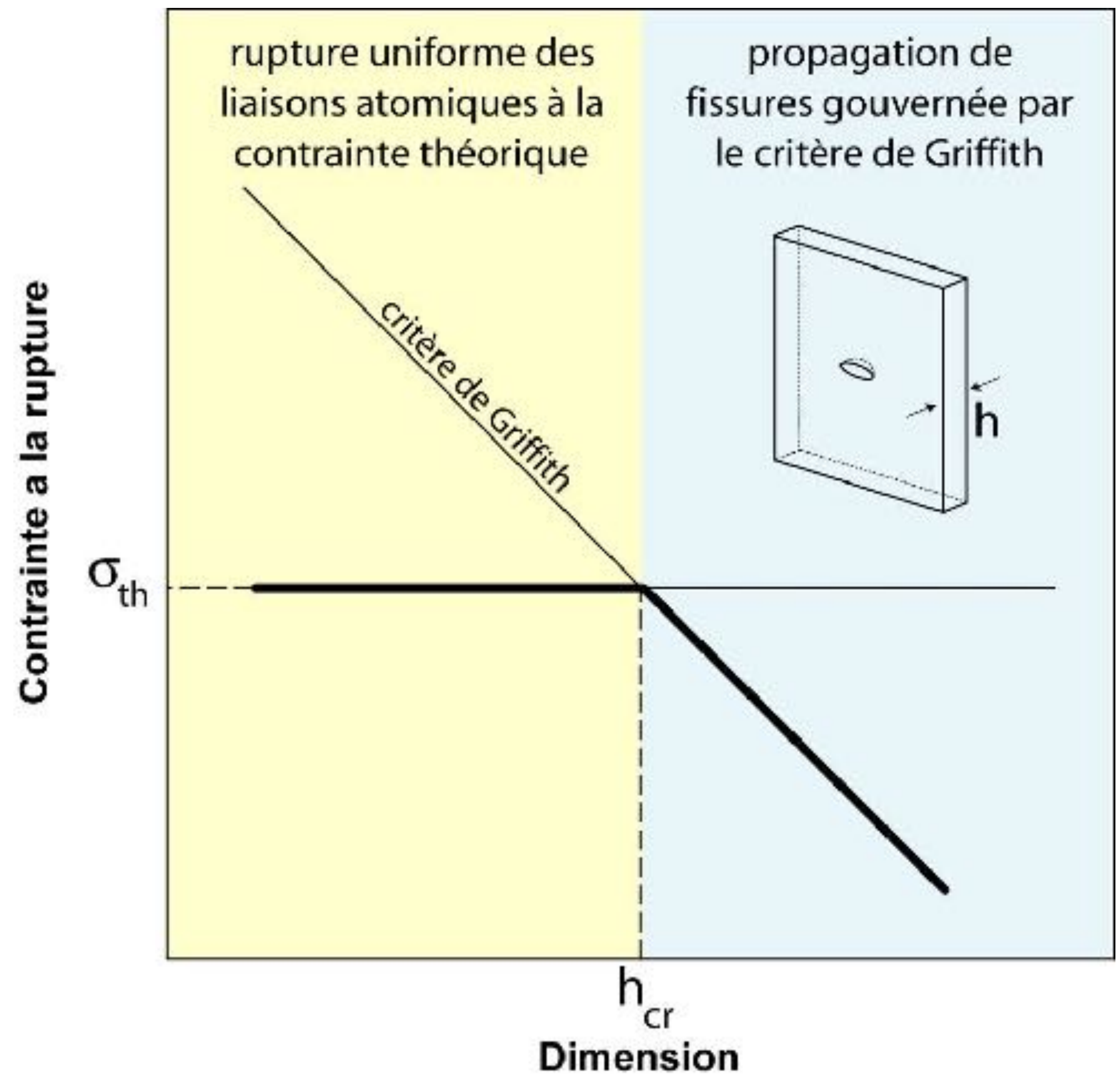
Nanograins

Critère de Griffith

$$\sigma_m^f = \alpha E_m \sqrt{\frac{\gamma}{E_m h}}$$

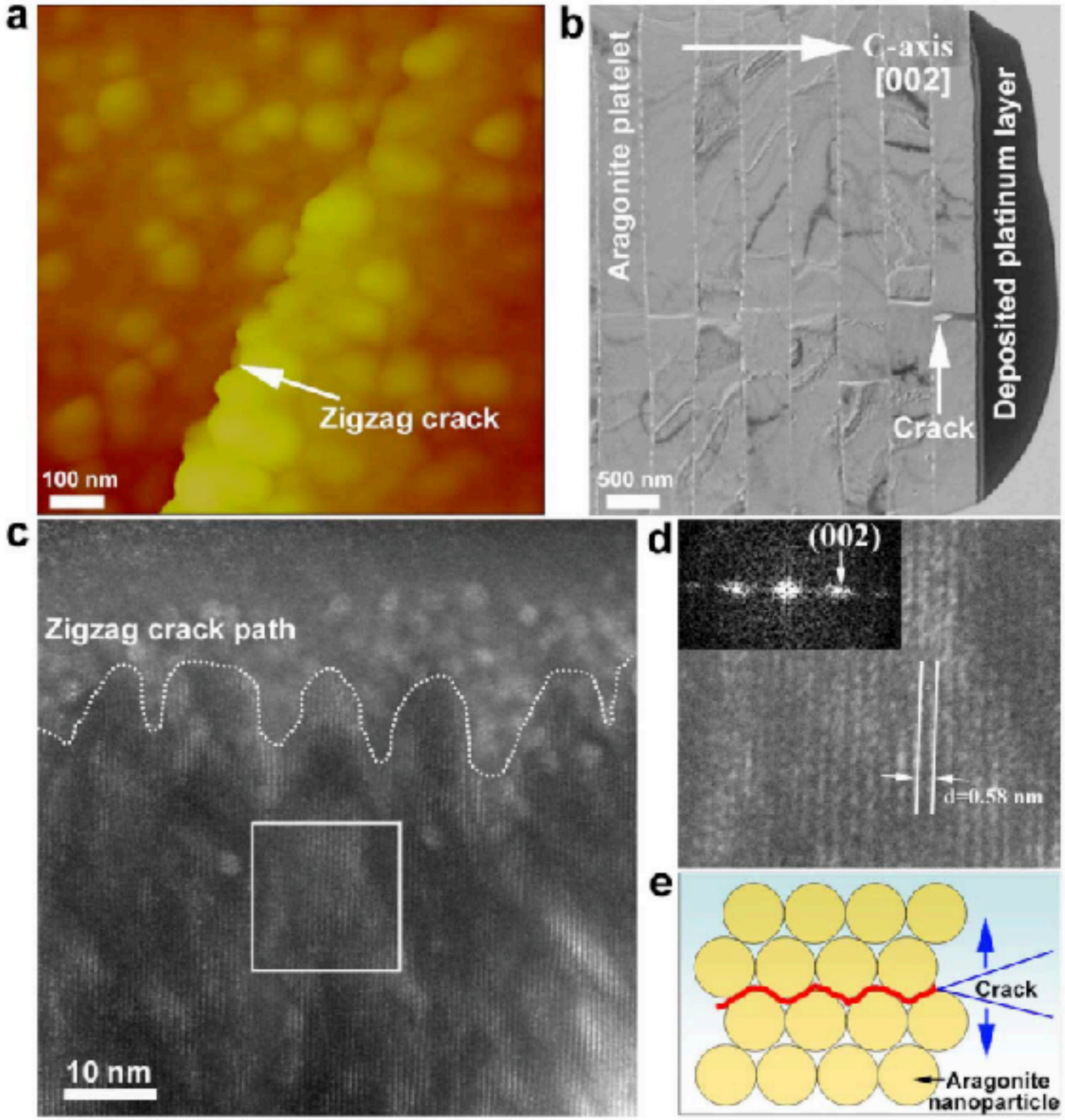
Longueur critique

$$h_{cr} \approx \alpha^2 \frac{\gamma E_m}{\sigma_{th}^2} \approx 30\, nm$$



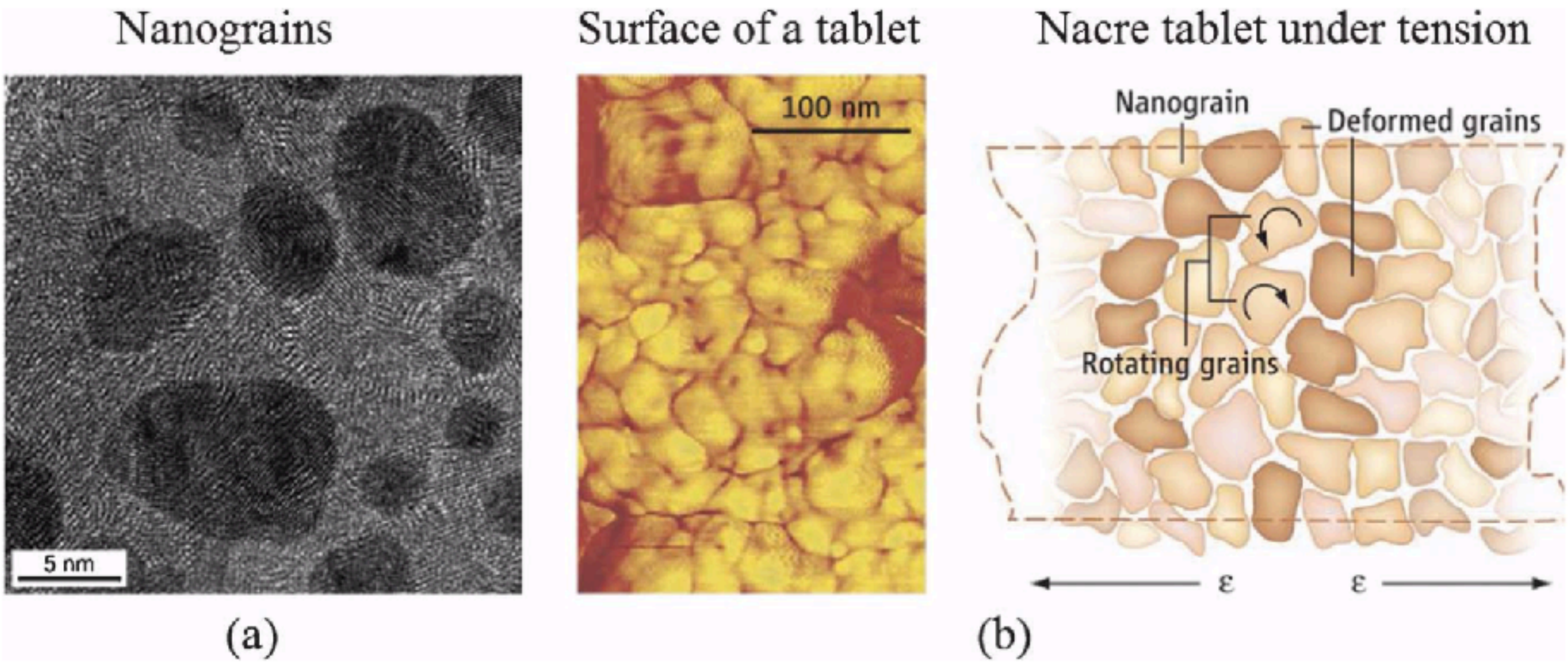
Gao, H., Materials become insensitive to flaws at nanoscale: lessons from nature. *Proc. Natl. Acad. Sci. U. S. A.* 100, 5597–600 (2003).

Intergranular crack propagation



Huang, Z. & Li, X. Origin of flaw-tolerance in nacre. *Sci. Rep.* 3, 1693 (2013).

Nanograins rotation



Li, X., In situ observation of nanograin rotation and deformation in nacre. *Nano Lett.* (2006).

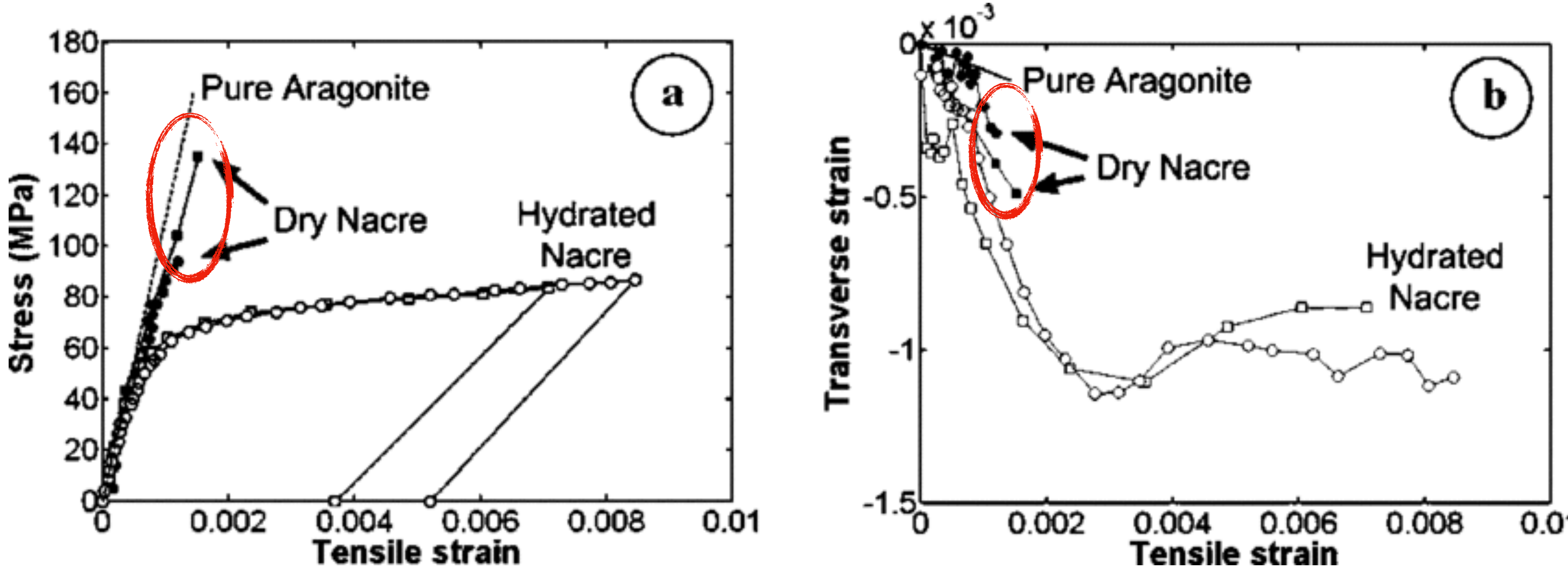
But…

Performances

J. Bizzie (Flickr)

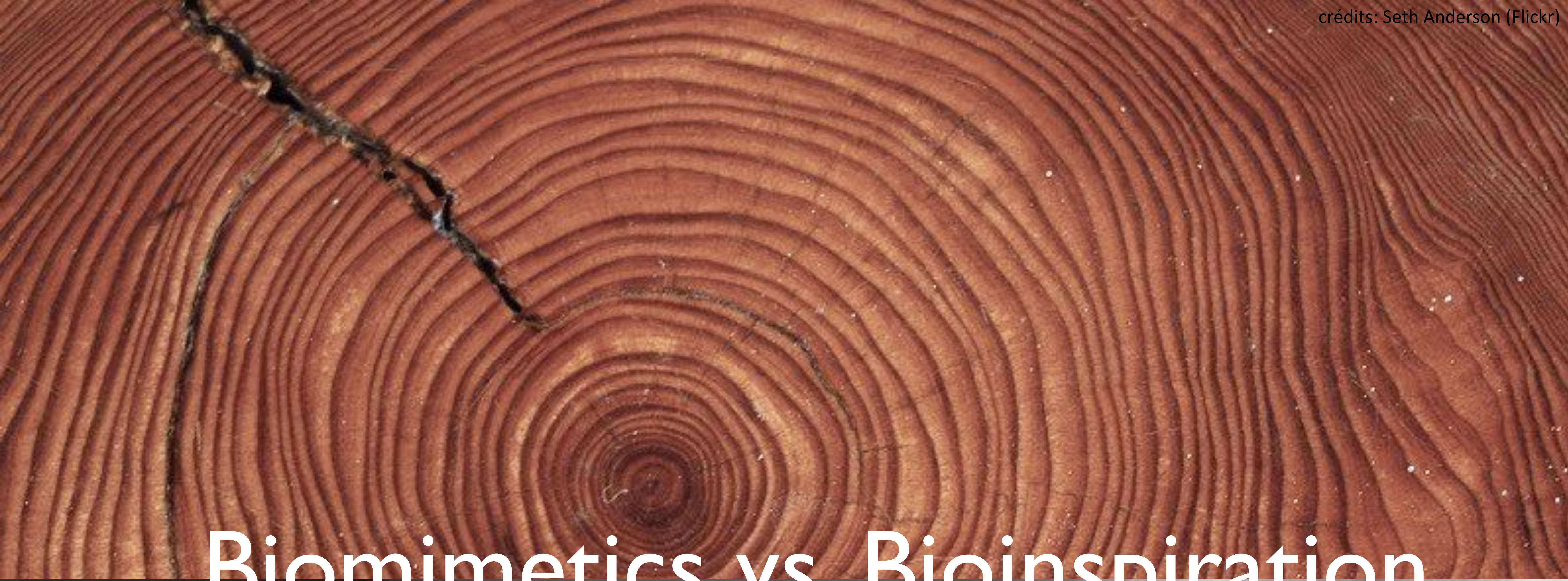
Brian Hefele (Flickr)

Properties of dry nacre



Barthelat, F., An experimental investigation of deformation and fracture of nacre–mother of pearl. *Experimental mechanics*, (2007) 2-4 mm/month

Vince42 (Flickr)



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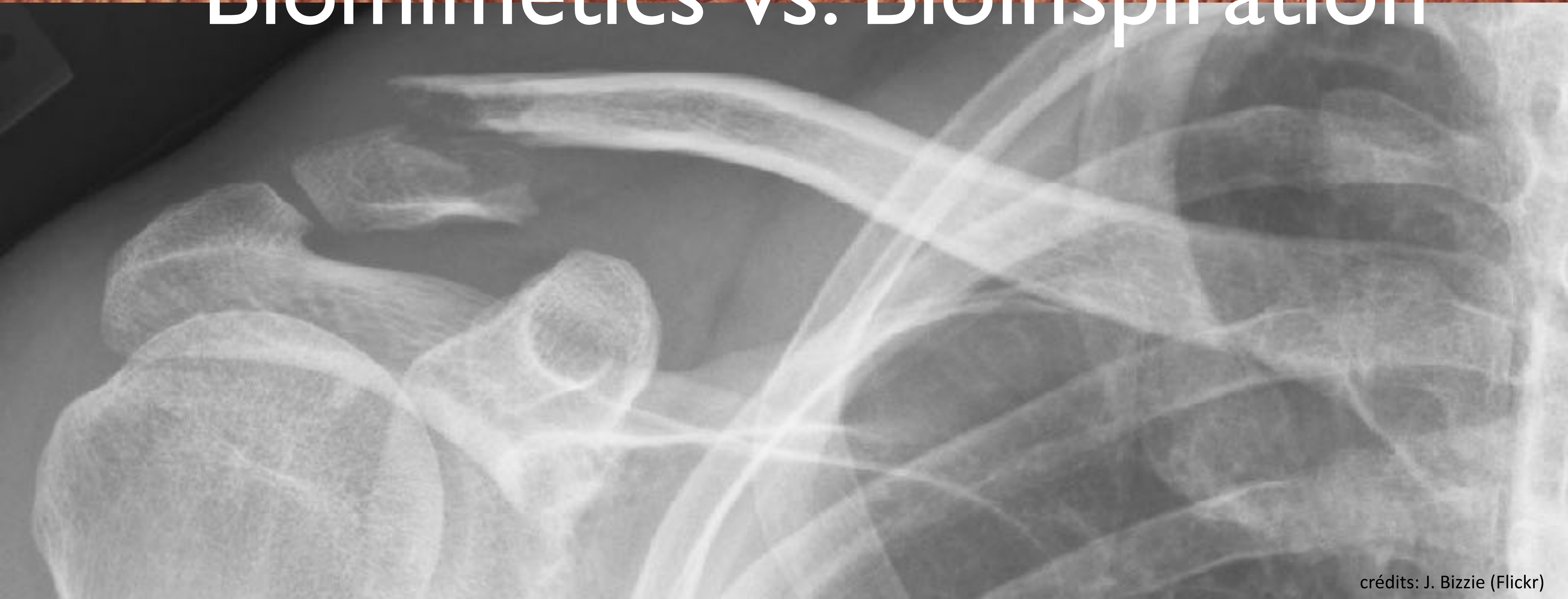
Biomimetics vs. Bioinspiration



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Models without materials

Triangular spring-bead lattice

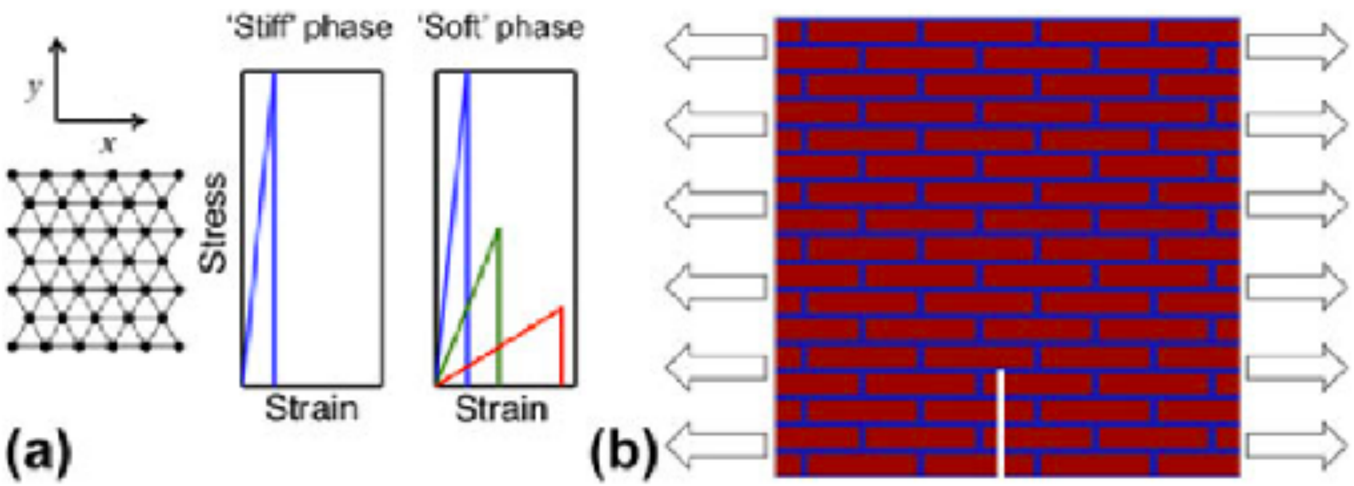


FIG. 1. (a) Triangular lattice spring-bead material representation to describe a coarse-grained model of the material. All lines are of identical length. We present the constitutive relations for stiff phase as well as

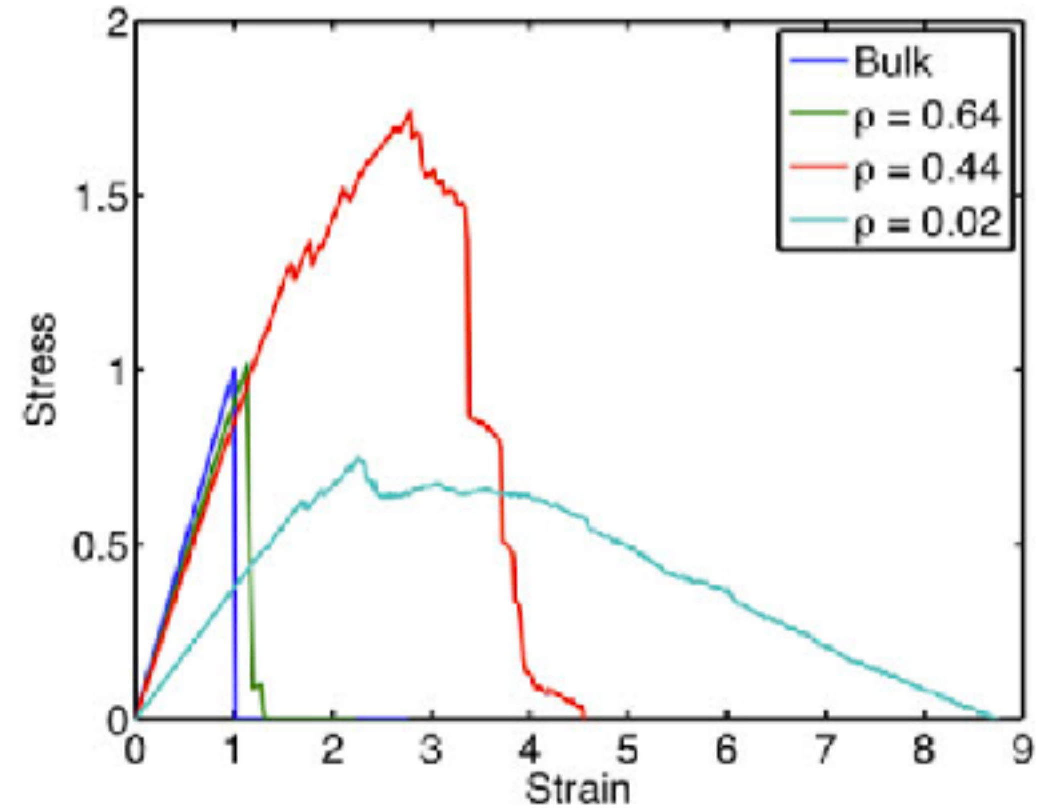
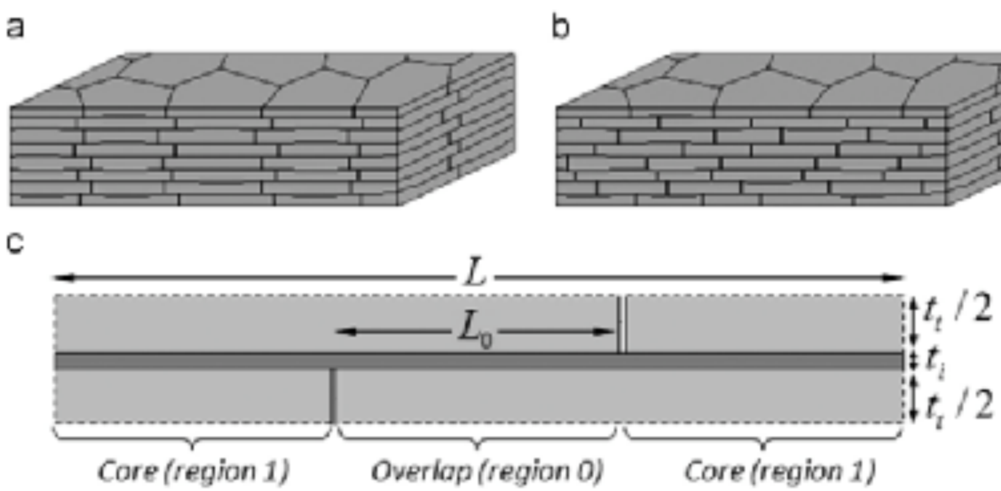


FIG. 2. Stress-strain responses for the bulk system and three composite structures, $\rho = 0.64$, 0.44, and 0.02 (recall that $\rho = E_{soft}/E_{stiff}$). The strain and the stress are normalized by the maximum strain and stress of the brittle bulk system. Graphs indicate the rapid change in composite behavior as the stiffness ratio is varied.

- triangular spring-bead lattice
- interactions between beads are governed by springs following a linear- Hookean force extension law

Dimas, L. S.. Tough and stiff composites with simple building blocks. *J. Mater. Res*. 28, 1295–1303 (2013).

Analytical models



- tablets: linear elastic and brittle material
- interfaces : linear elastic-perfectly plastic

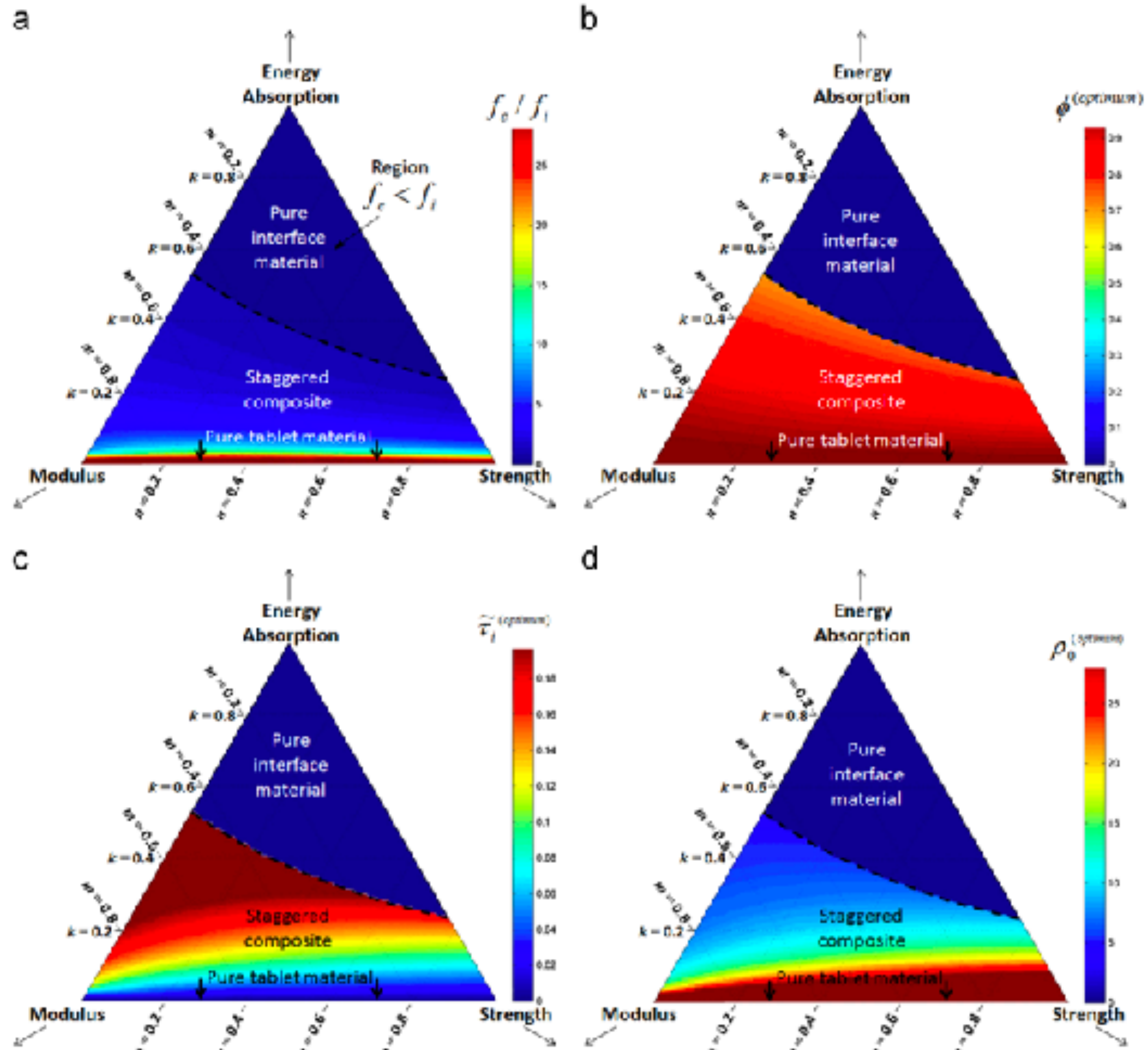


Fig. 8. Ternary diagrams showing optimum materials, composition and microstructure for all combinations (m,n,k), $a/t_t = 0.1$ and $\bar{E}_i = \tau_i$. The optimum failure criterion was used. (a) fitness of the composite normalized by the fitness of the pure interface material; (b) optimum tablet concentration; (c) optimum interface strength and (d) optimum overlap length.

Barthelat, F., Designing nacre-like materials for simultaneous stiffness, strength and toughness: Optimum materials, composition, microstructure and size. *J. Mech. Phys. Solids* 73, 22–37 (2014).

Discrete Elements

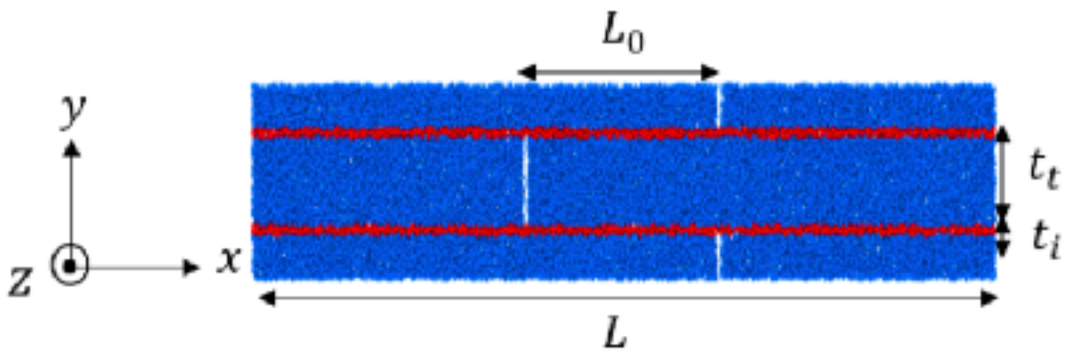


FIGURE 5: Representative Volume Element generated with discrete particles. Red particles mesh interface and blue particles mesh tablets. L, L_0, t and t_i are geometrical parameters characterizing the RVE.

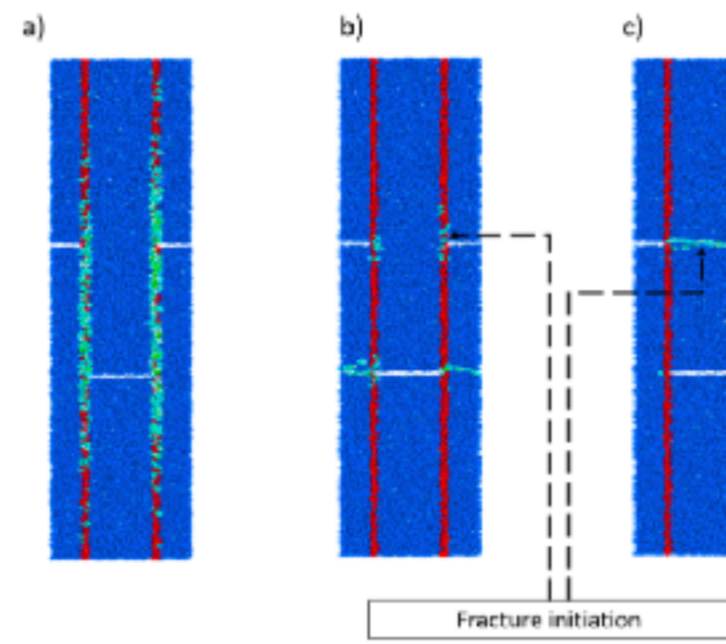


FIGURE 14: The corresponding illustrations of number of broken bonds per particle for the three cases of crack initiation and propagation. (a) Interface fracture initiation and propagation (b) Interface fracture initiation and tablet fracture propagation (c) Tablet fracture initiation and propagation.

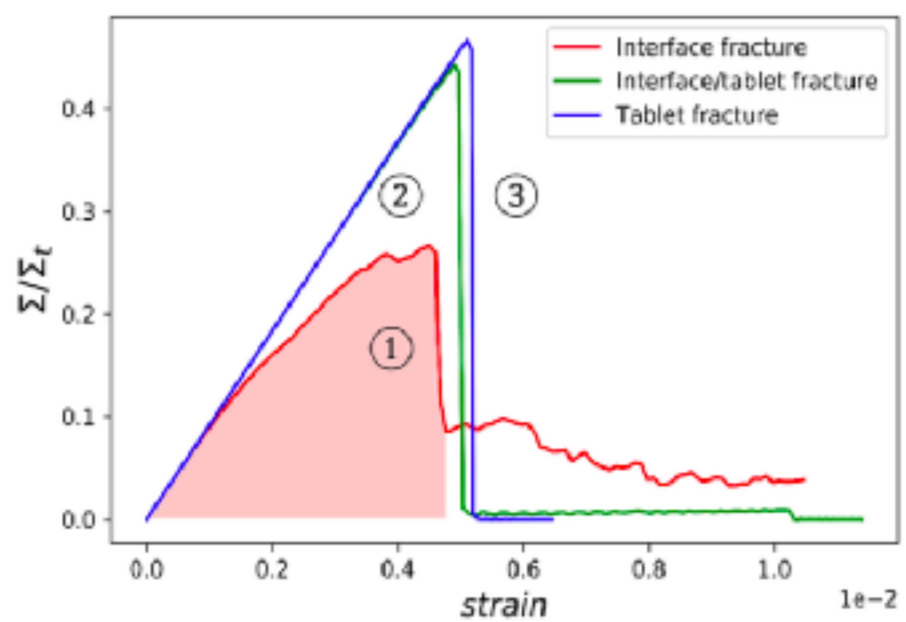


FIGURE 12: Typical stress-strain curves for Σ_i = 200 MPa ,1 200 MPa and 4 000 MPa. Three fracture regimes can be identified with increasing interface strengths Σ_i : (1) Interface fracture, (2) Interface/tablet fracture and (3) Tablet fracture.

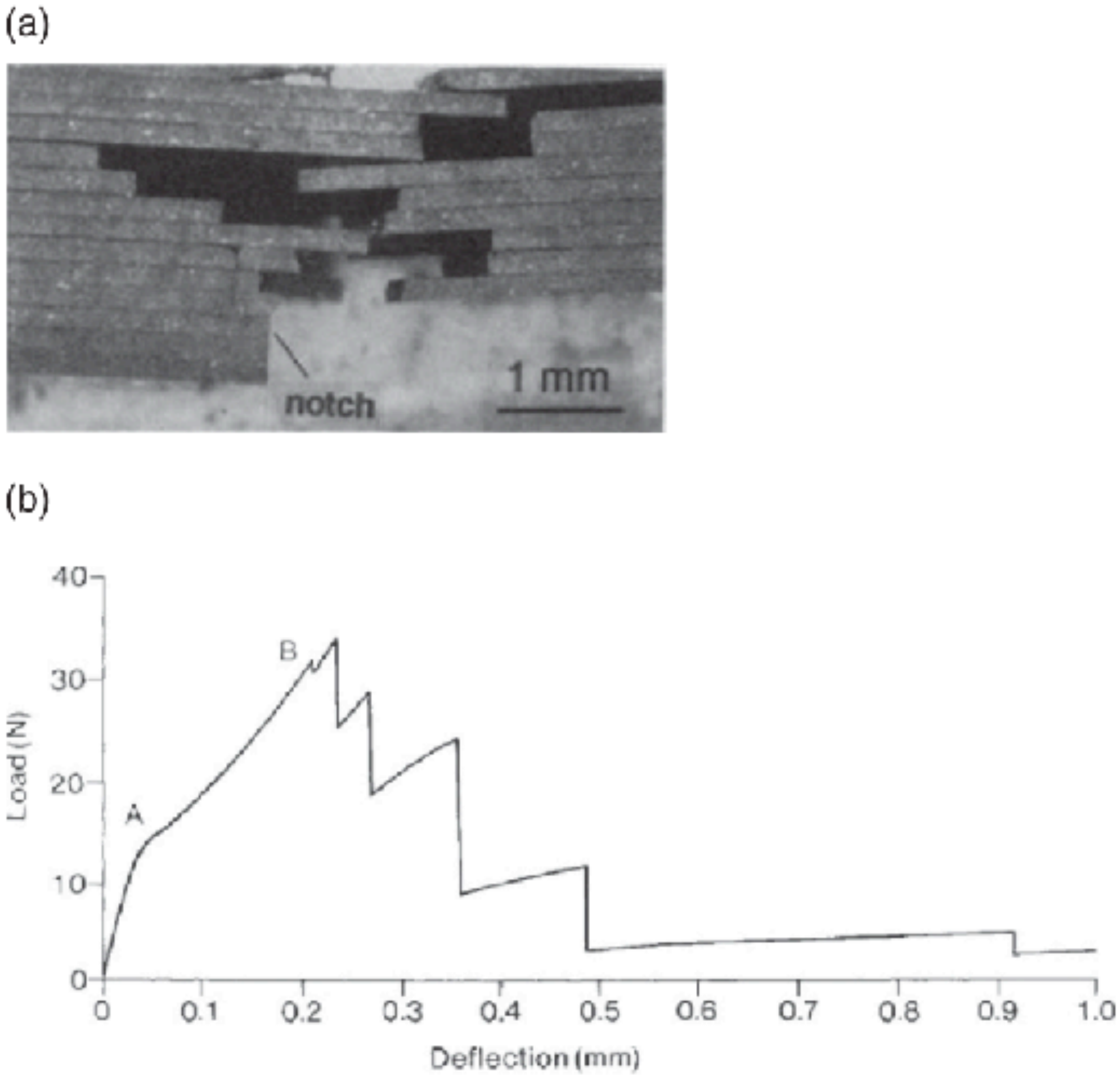
✅ Crack initiation

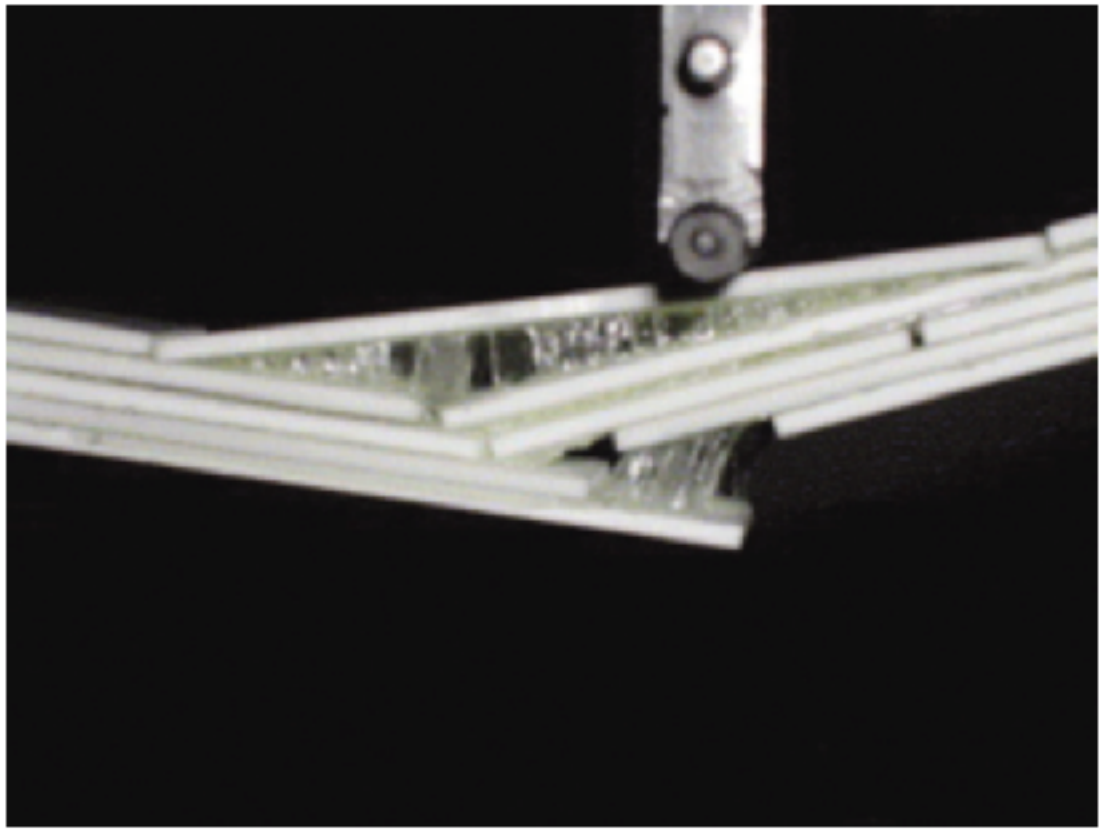
✅ Crack propagation

K. Radi, Elasticity and fracture of brick and mortar materials with discrete elements simulations (coming soon)

Model materials to understand nacre's properties

Laminates

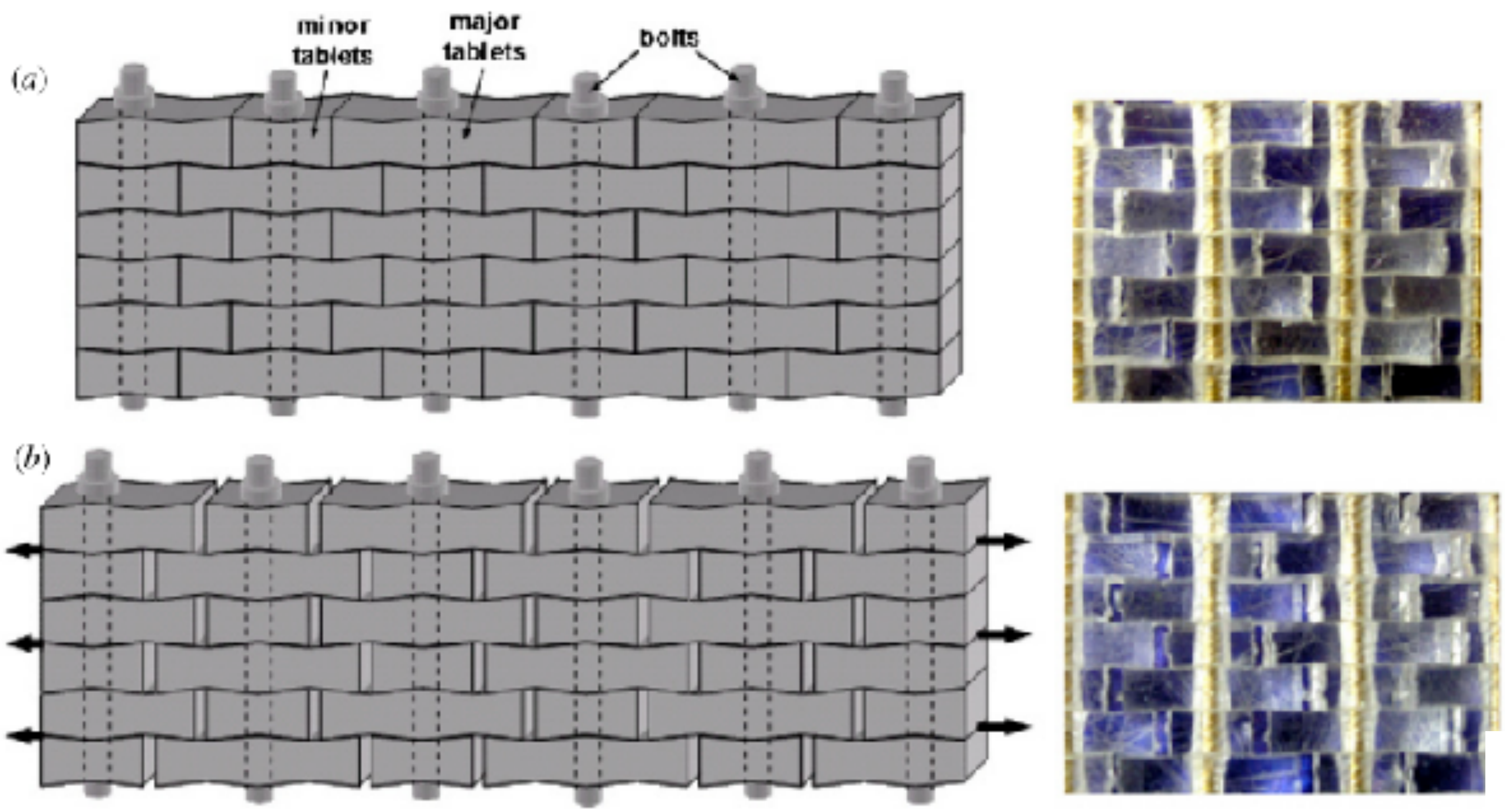




Clegg WJ, A simple way to make tough ceramics. *Nature* (1990)

Mayer G (2006) New classes of tough composite materials – lessons from natural rigid biological systems. *Mater Sci Eng C Biomimetic Supramol Syst*

Synthetic interlocked structure



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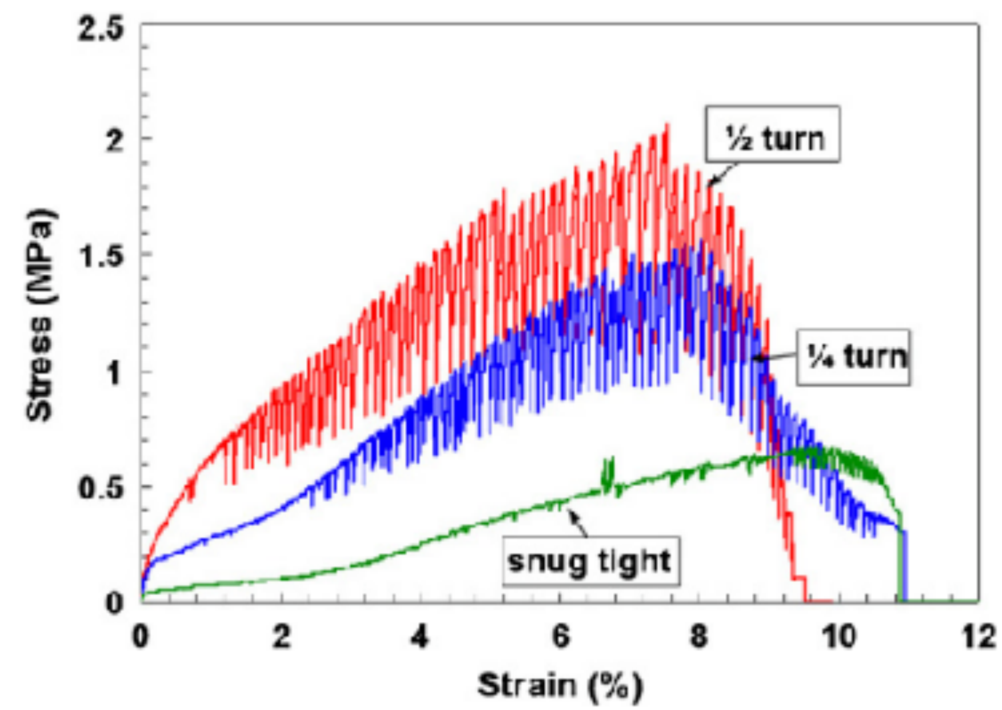
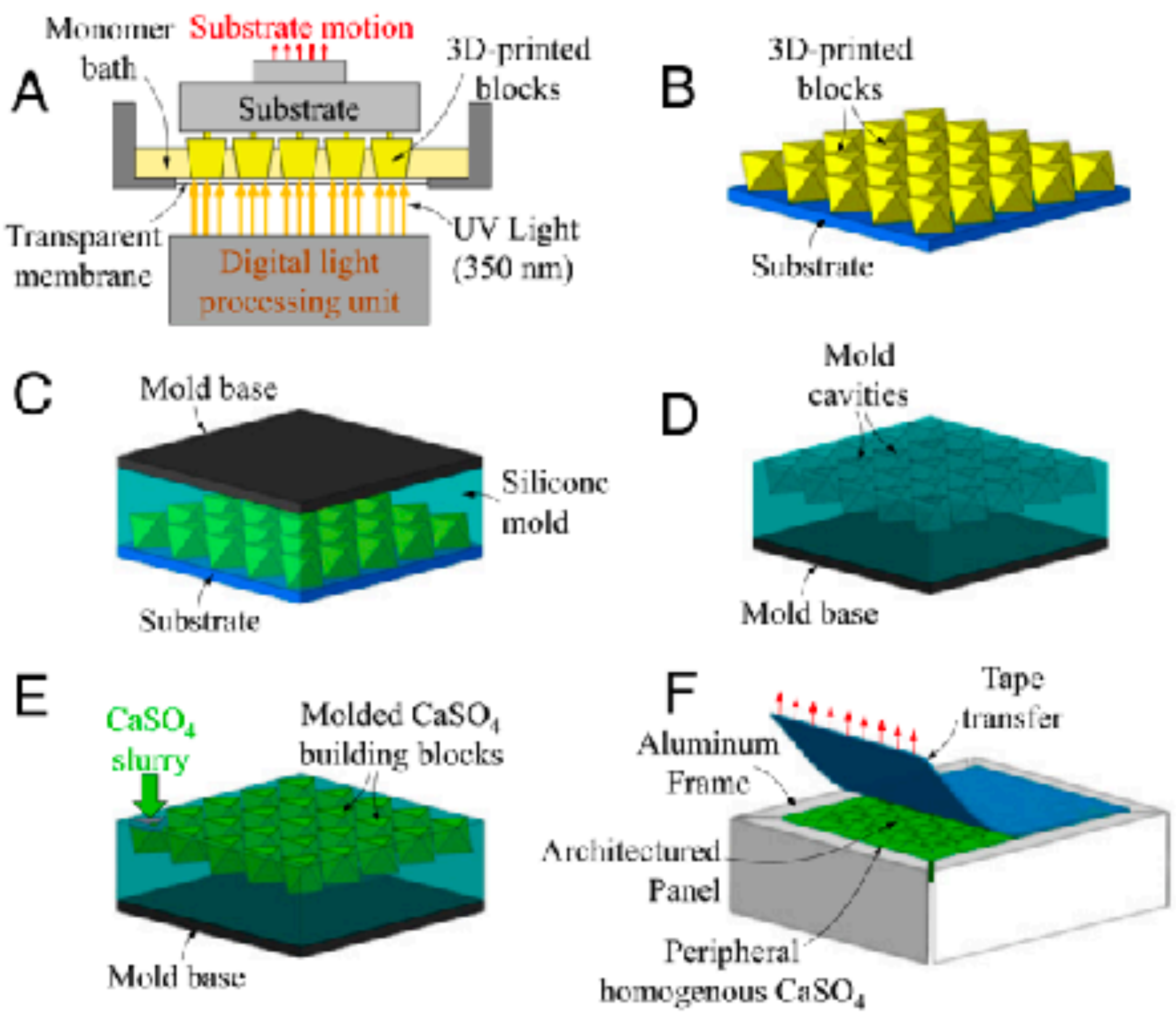
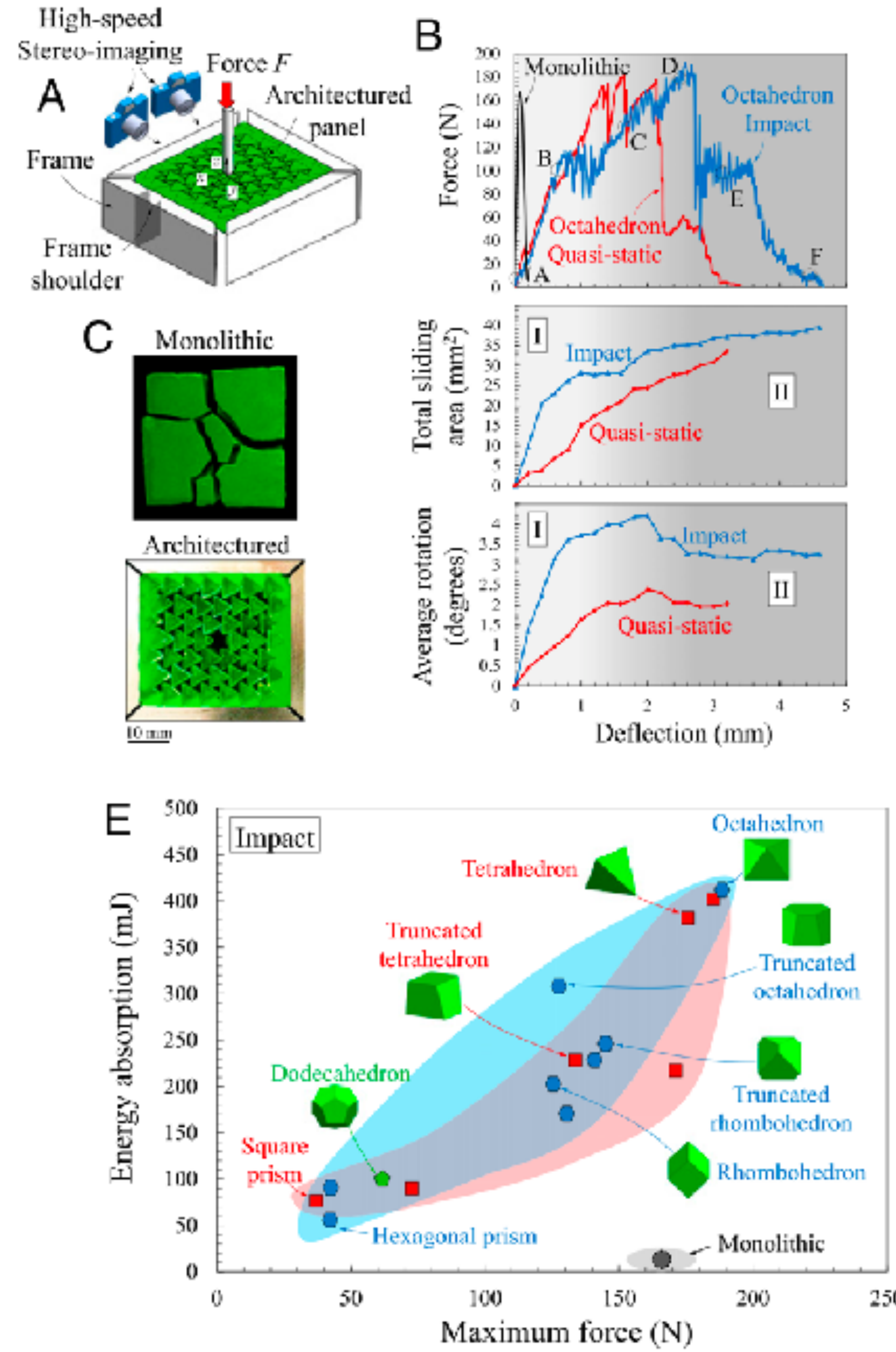


Figure 8. Tensile stress strain curves for artificial nacre for different levels of bolt tightening.

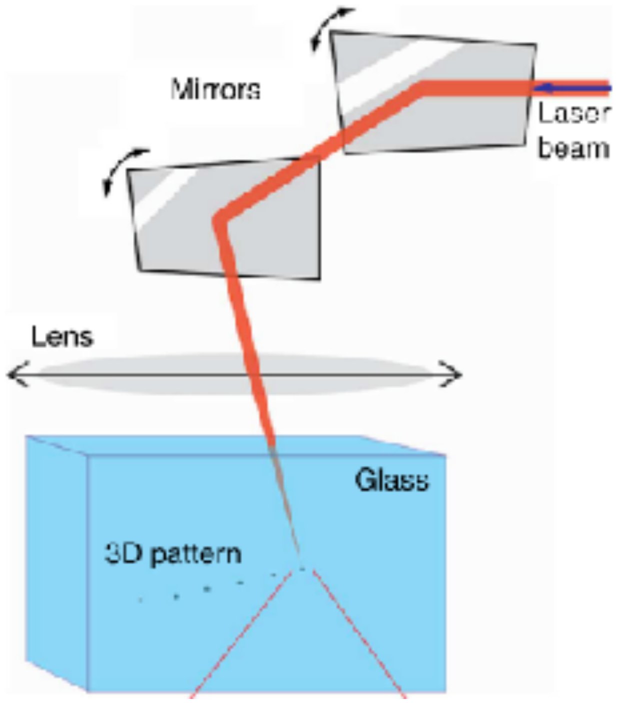
Synthetic interlocked structure

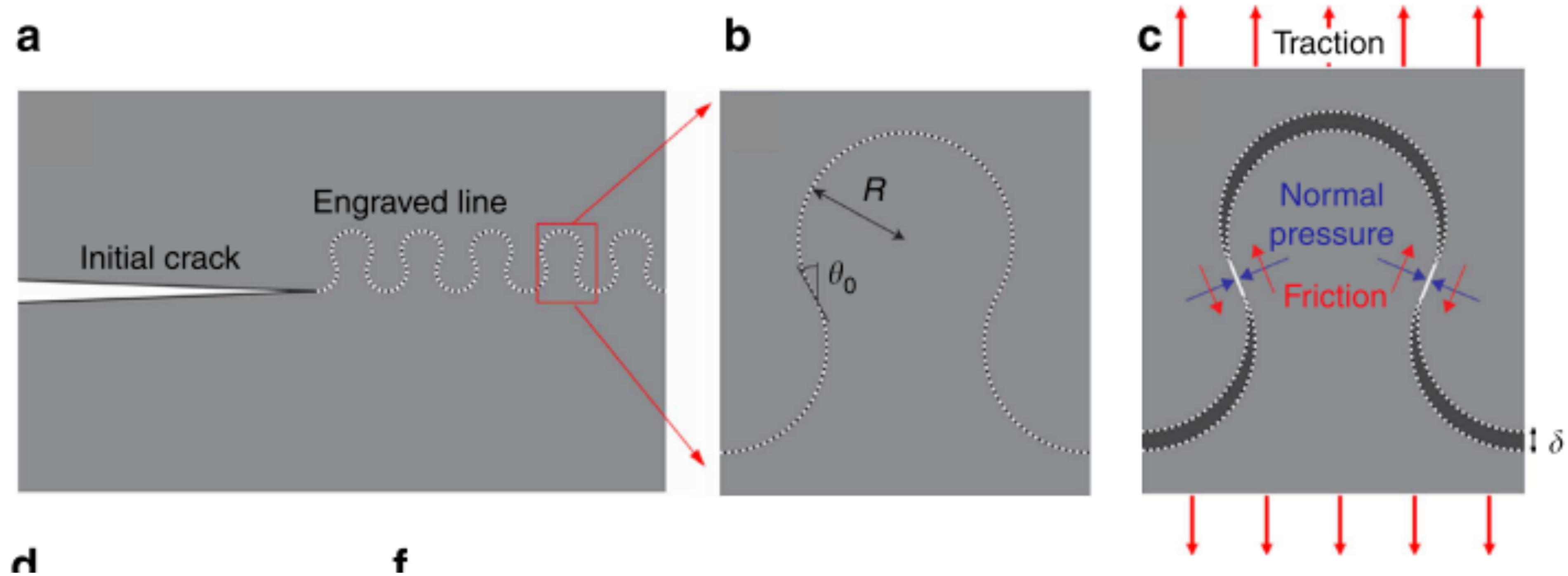


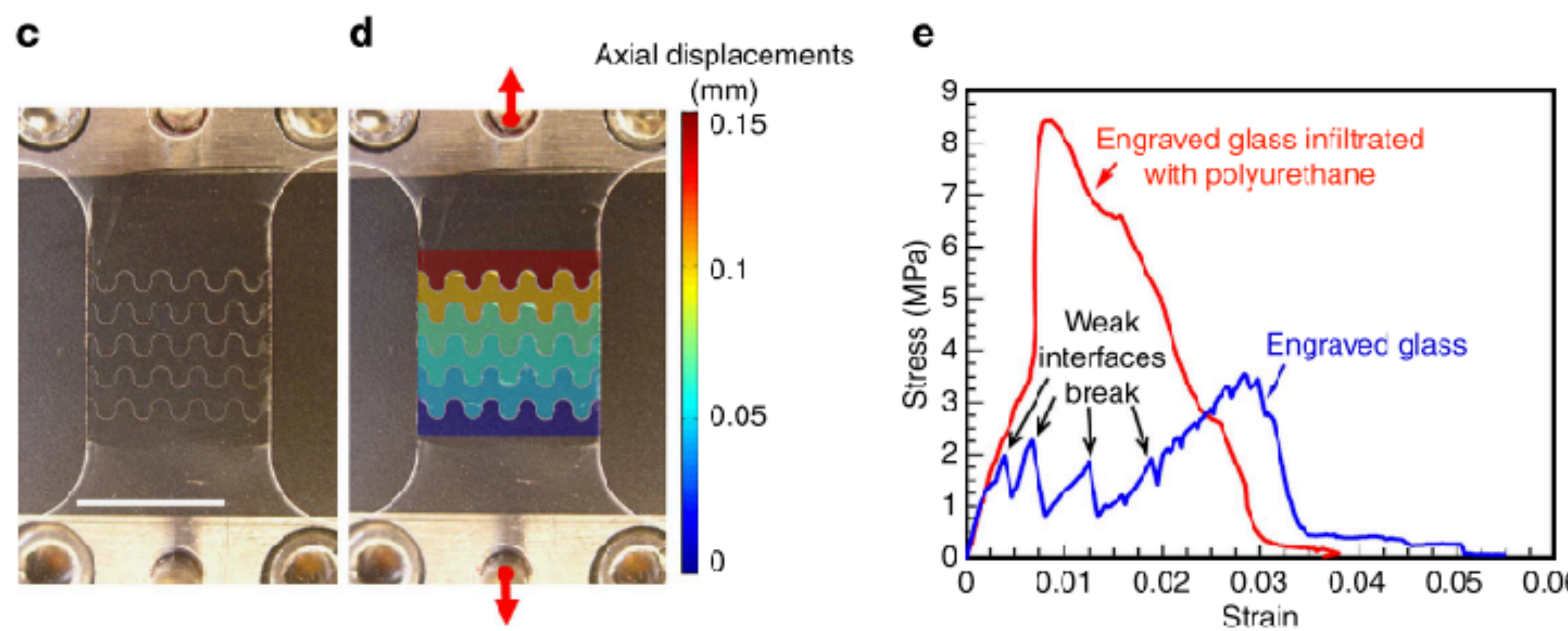


Mirkhalaf, M., Simultaneous improvements of strength and toughness in topologically interlocked ceramics. Proc. Natl. Acad. Sci. 201807272 (2018)

Crack deflection in brittle materials







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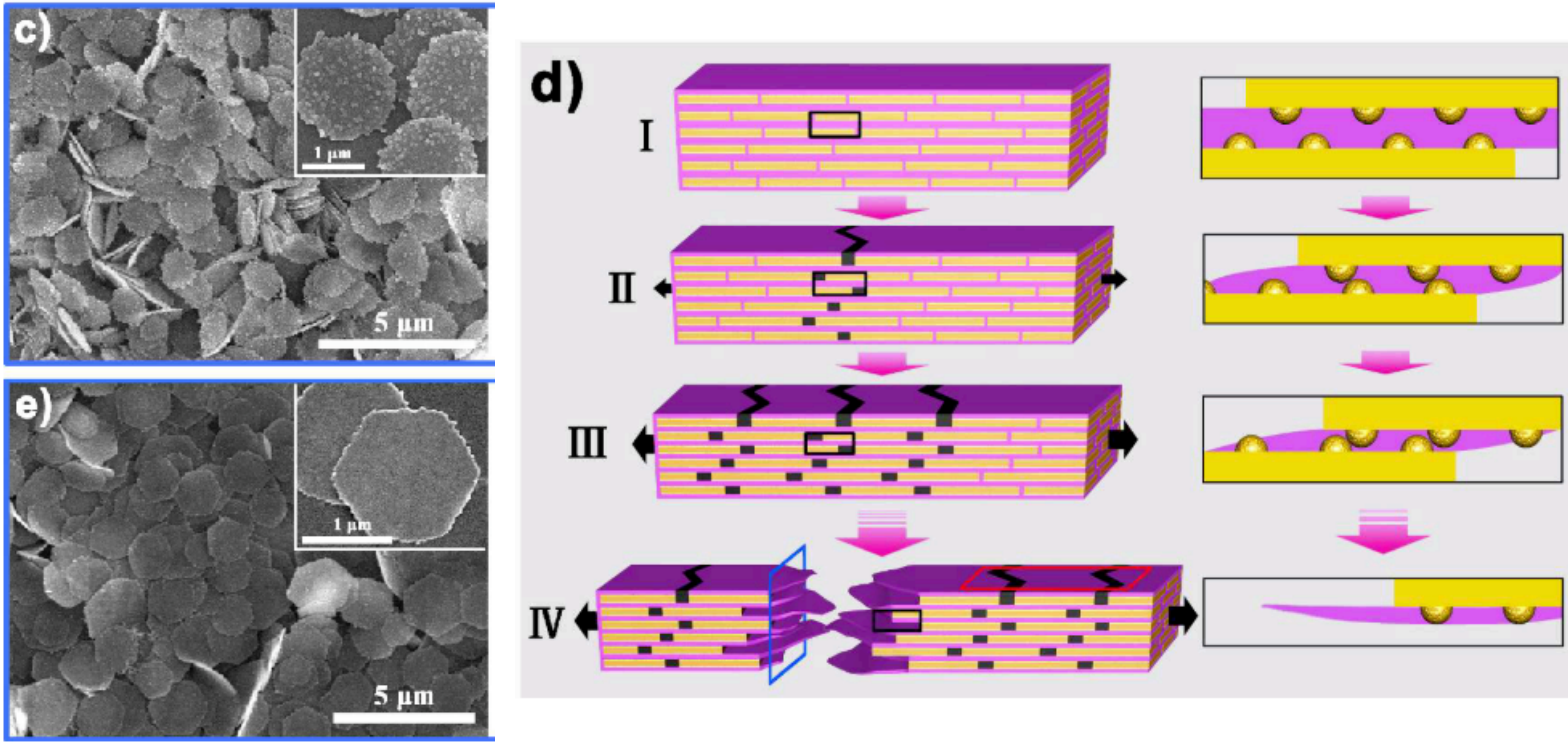
Role of surface roughness



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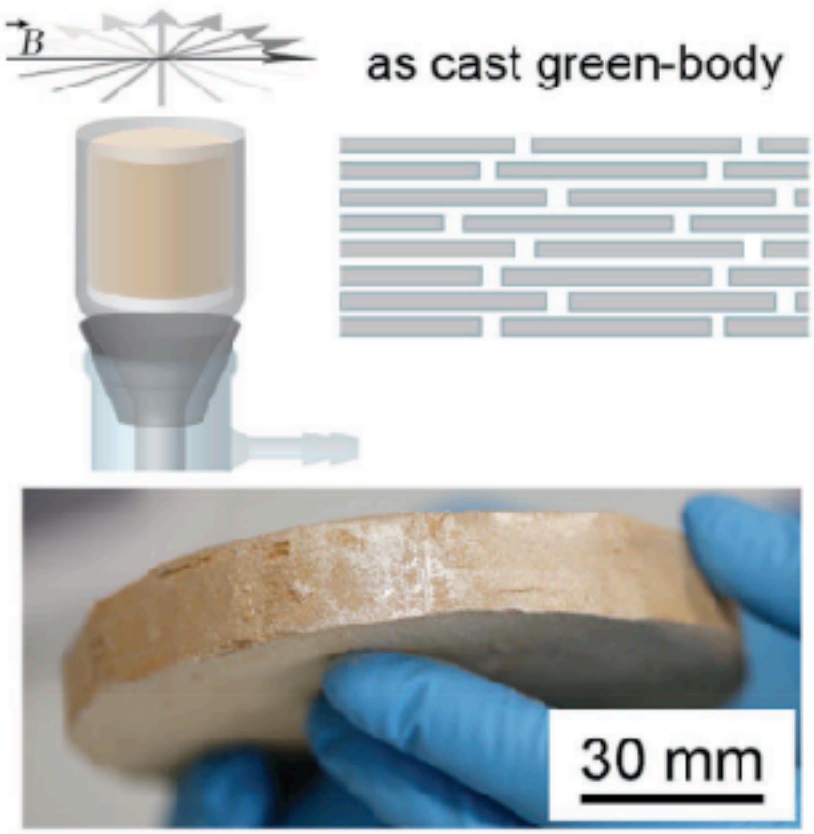
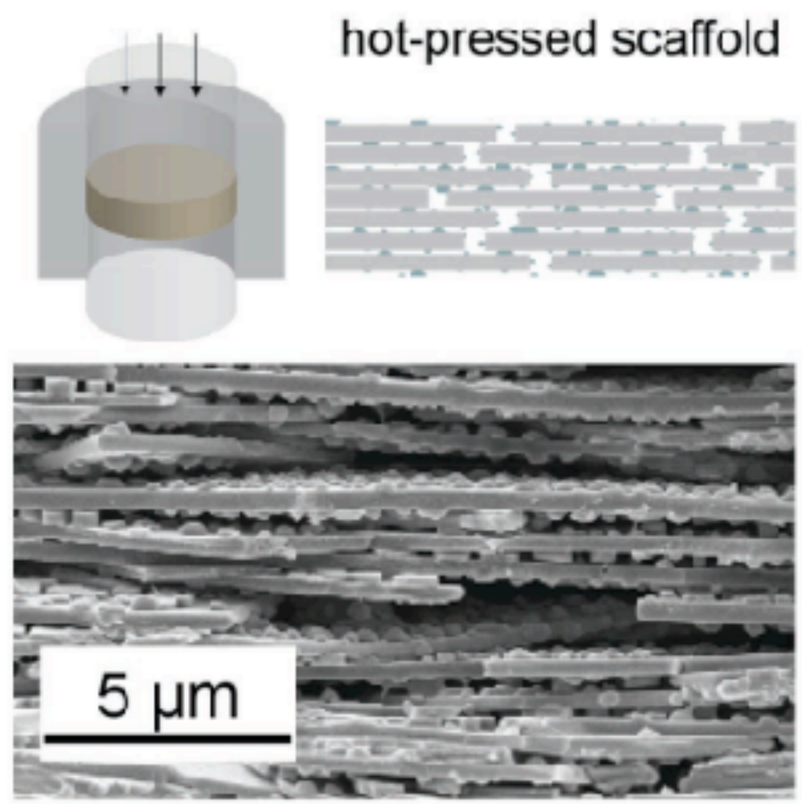
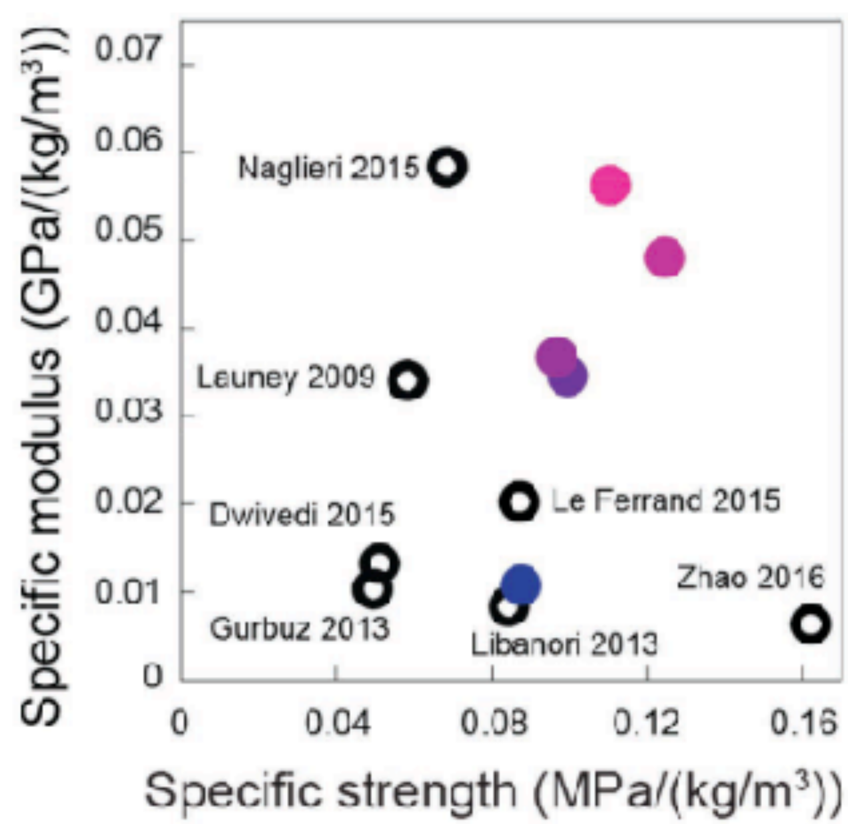
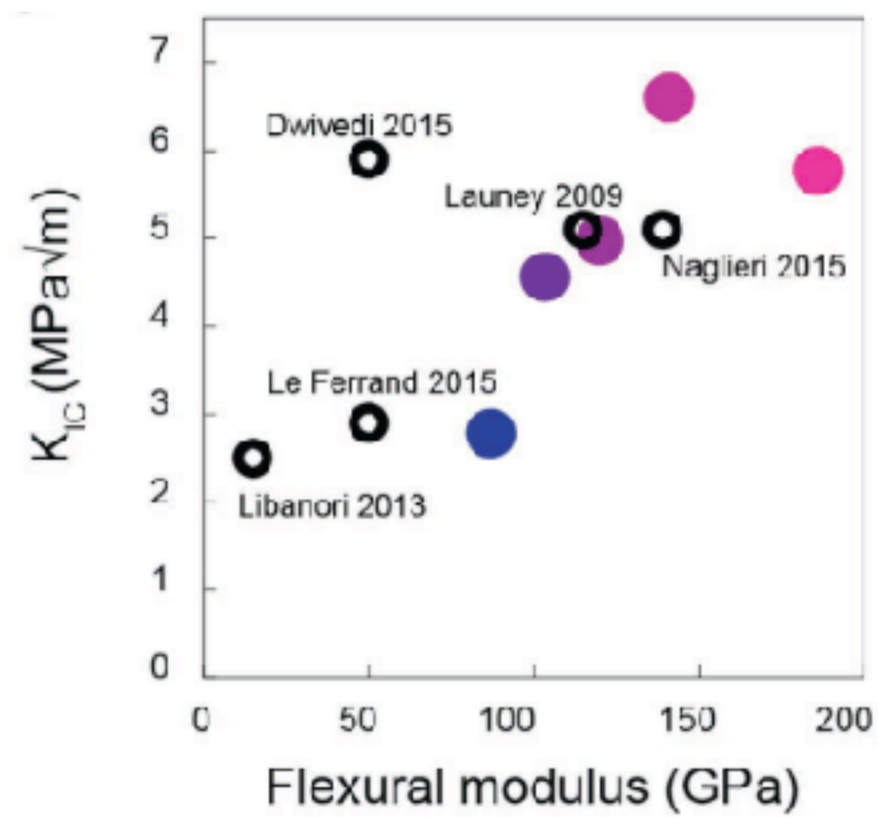
Role of mineral bridges



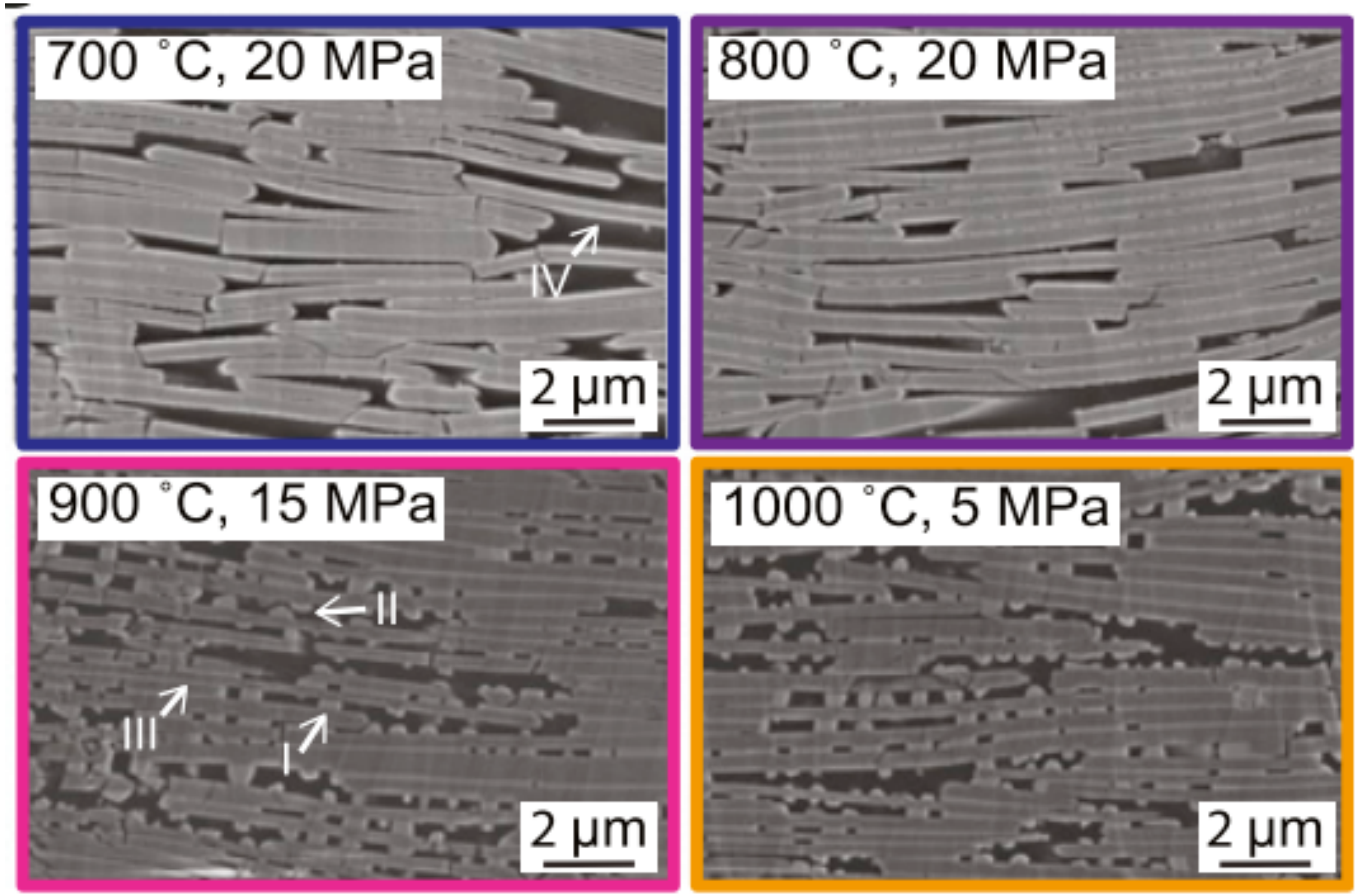


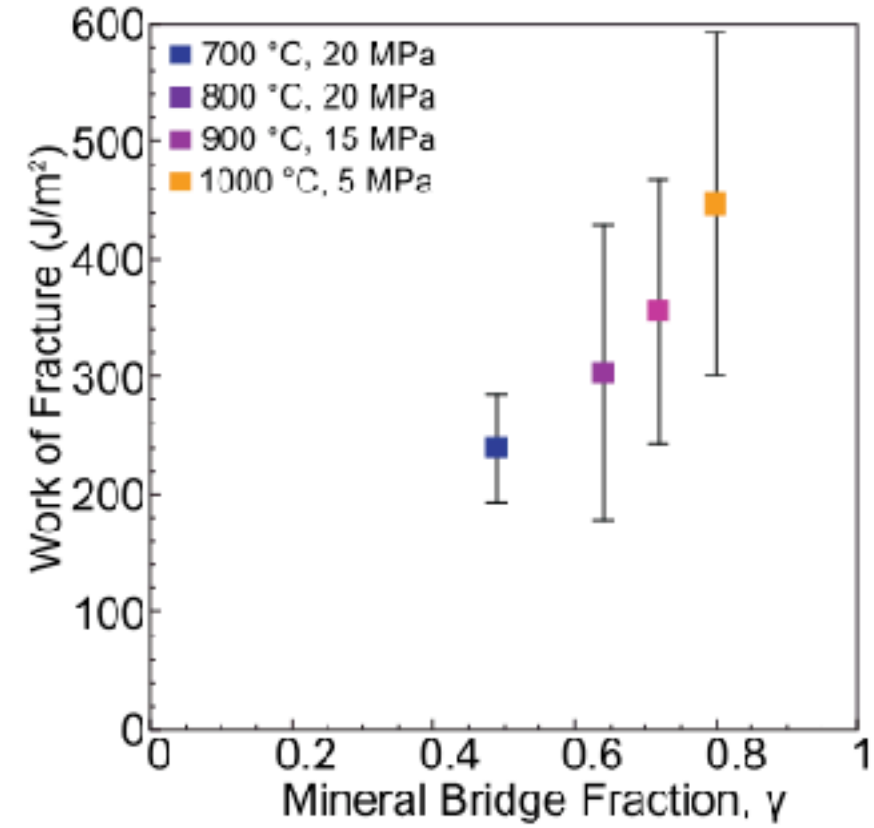
Grossman, M. et al. Mineral Nano-Interconnectivity Stiffens and Toughens Nacre-like Composite Materials. *Adv. Mater.* (2017).

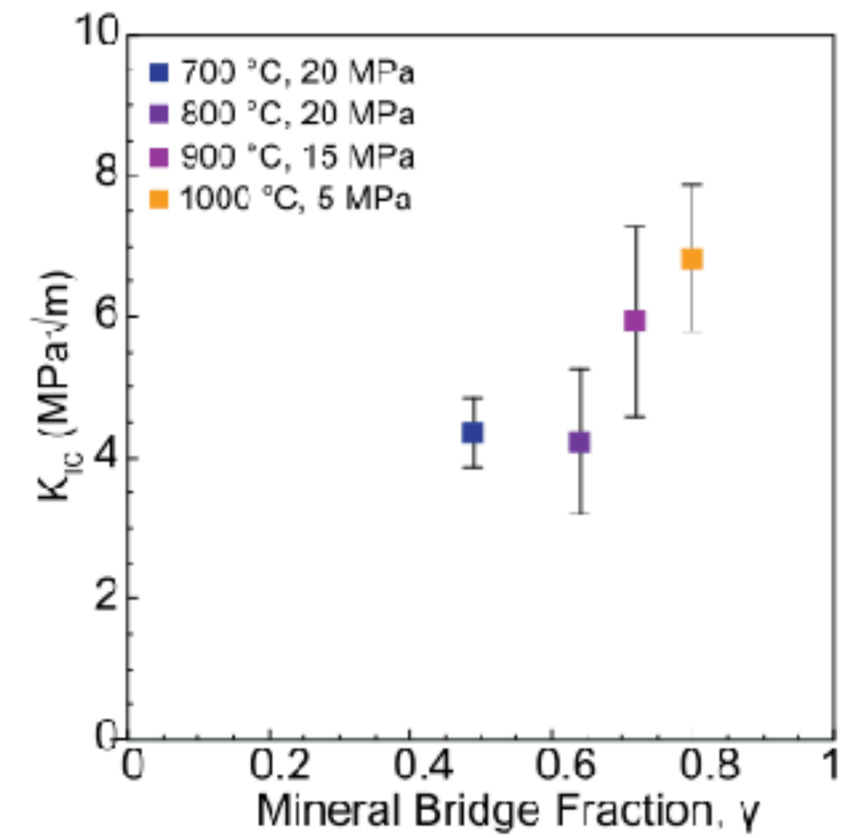




Role of mineral bridges

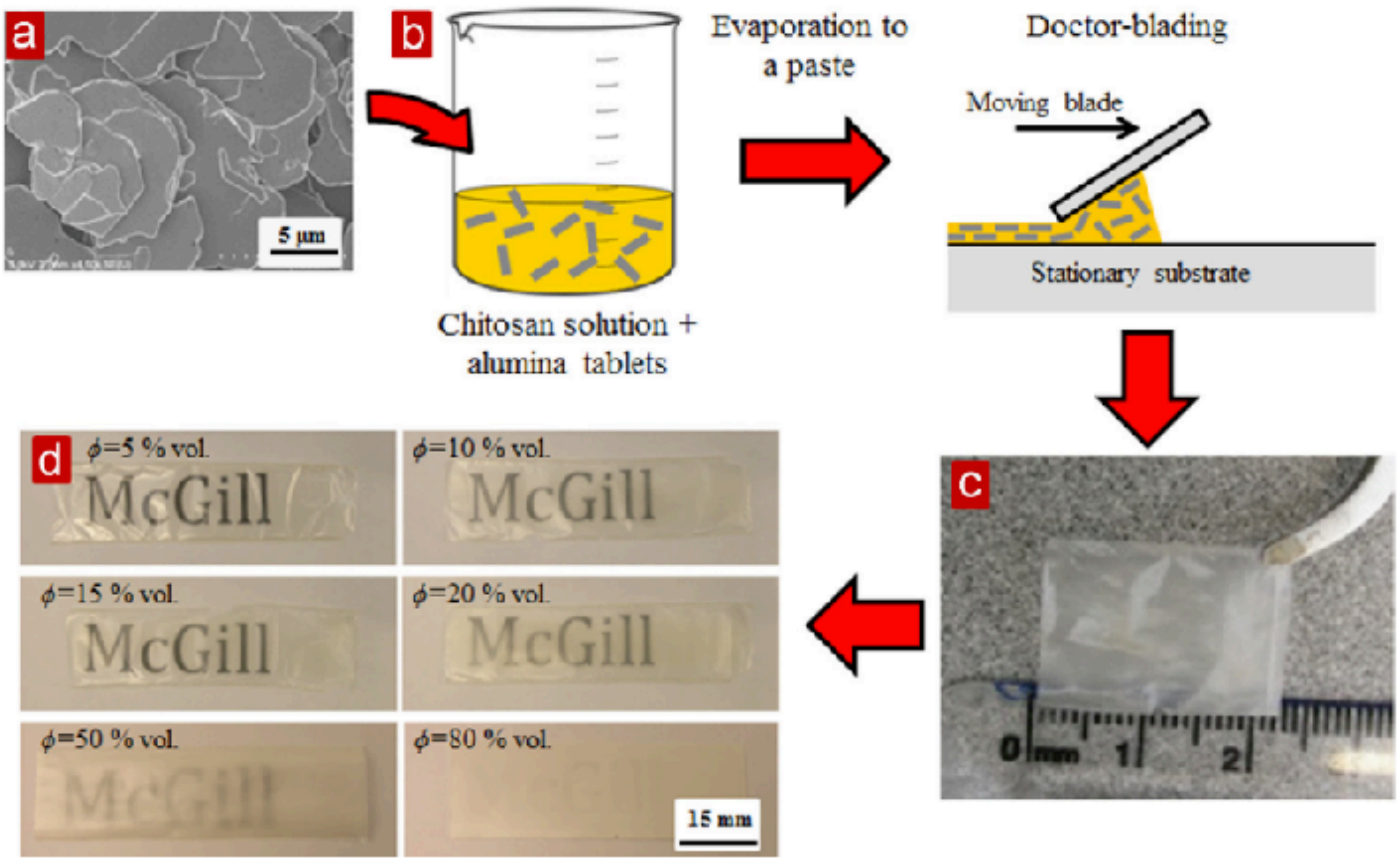






Grossman, M. et al. , Quantifying the role of mineral bridges on the fracture resistance of nacre-like composites. *Proc. Natl. Acad. Sci.* (2018)

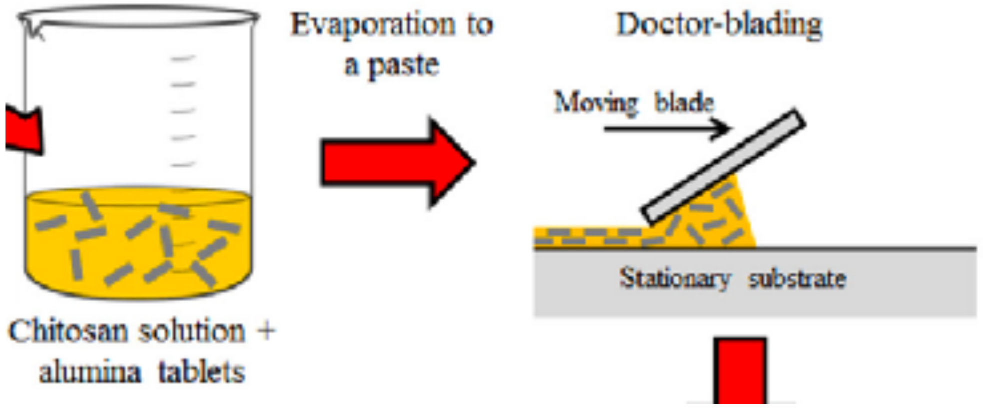
Platelets alignement

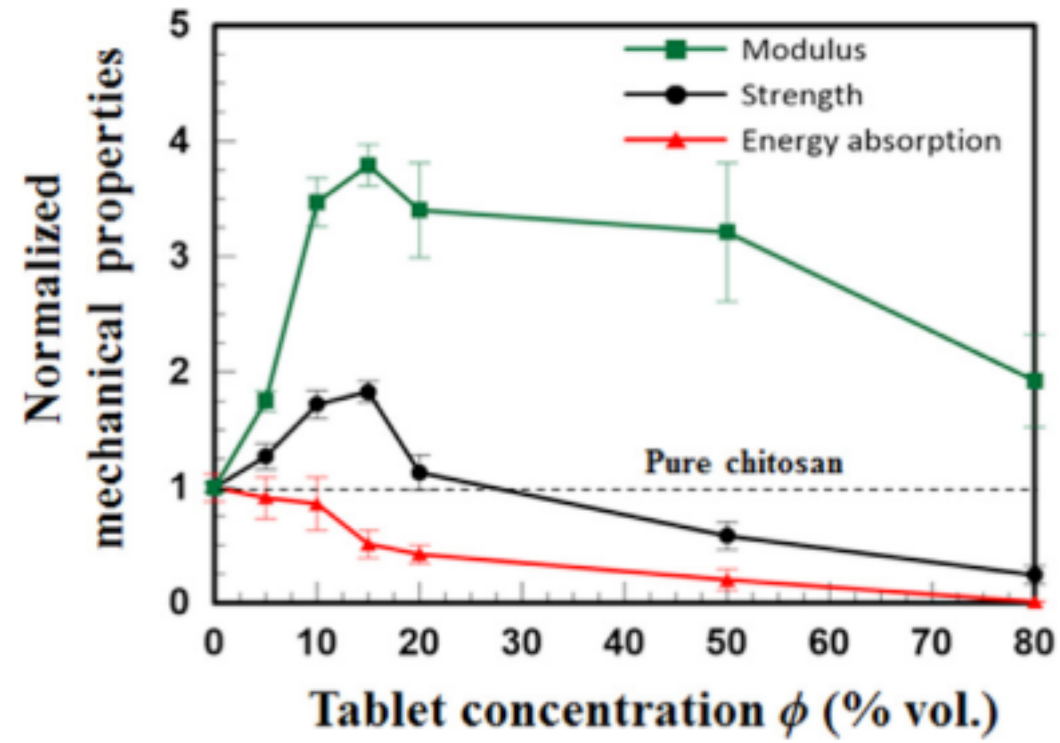


Mirkhalaf, M. Nacre-like materials using a simple doctor blading technique: Fabrication, testing and modeling. *J. Mech. Behav. Biomed. Mater.* 56, 23–33 (2016).

Platelets alignement

Mirkhalaf, M., Nacre-like materials using a simple doctor blading technique: Fabrication, testing and modeling. *J. Mech. Behav. Biomed. Mater.* (2016).





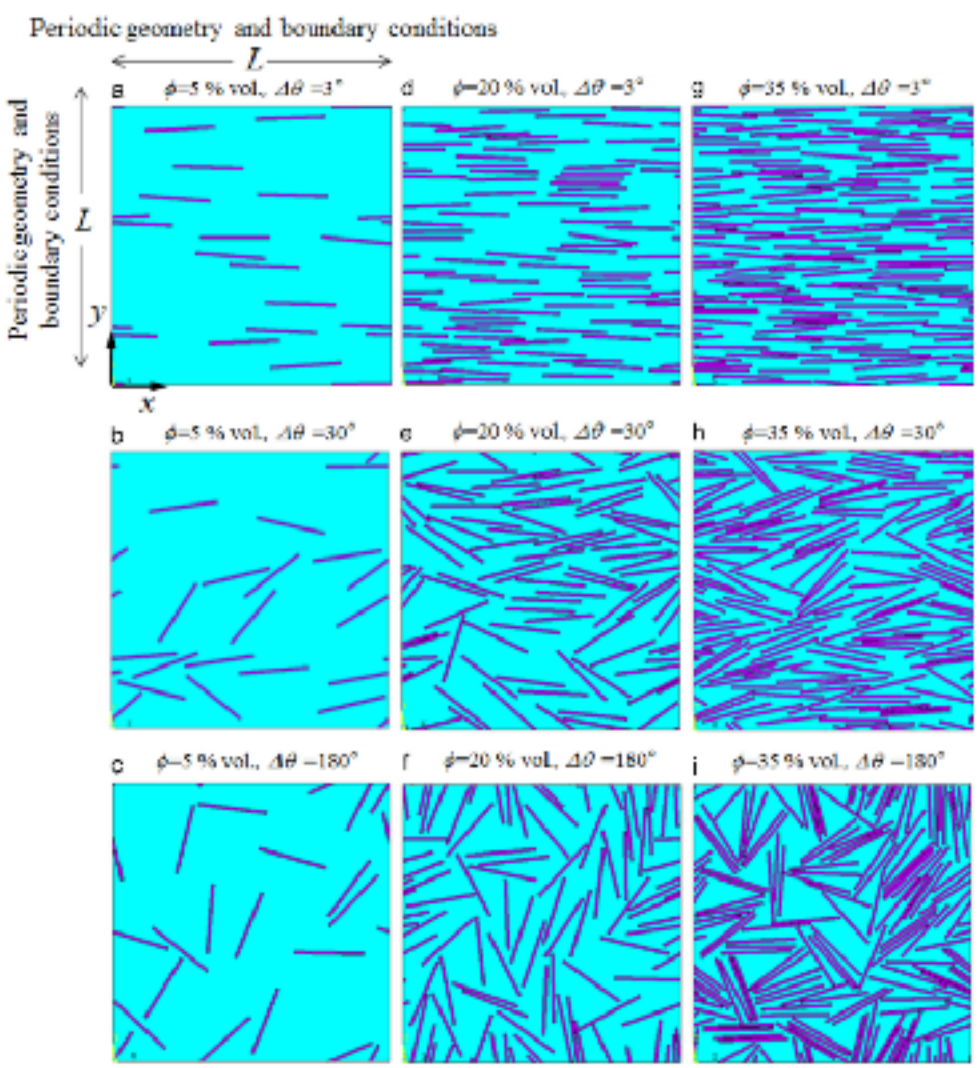
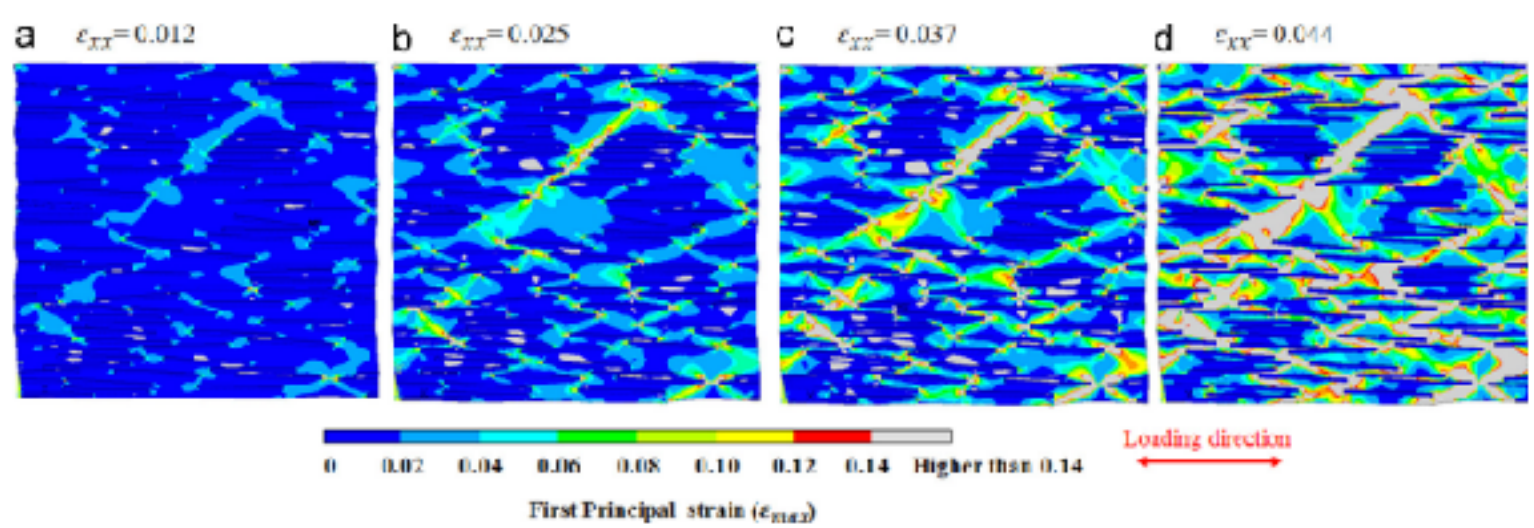
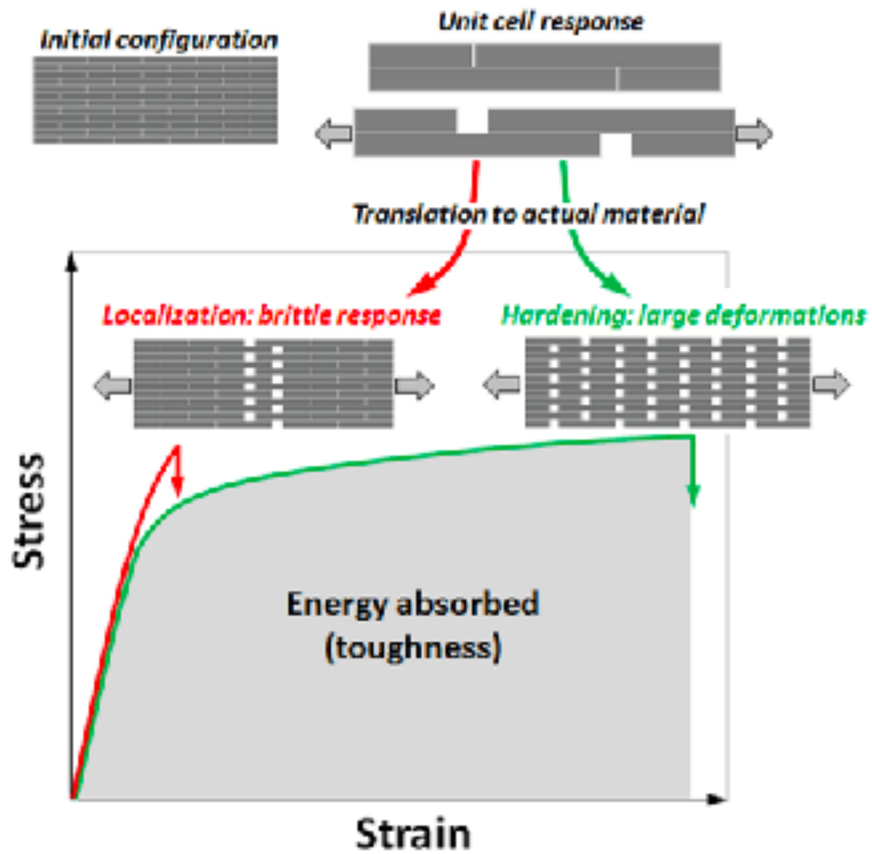
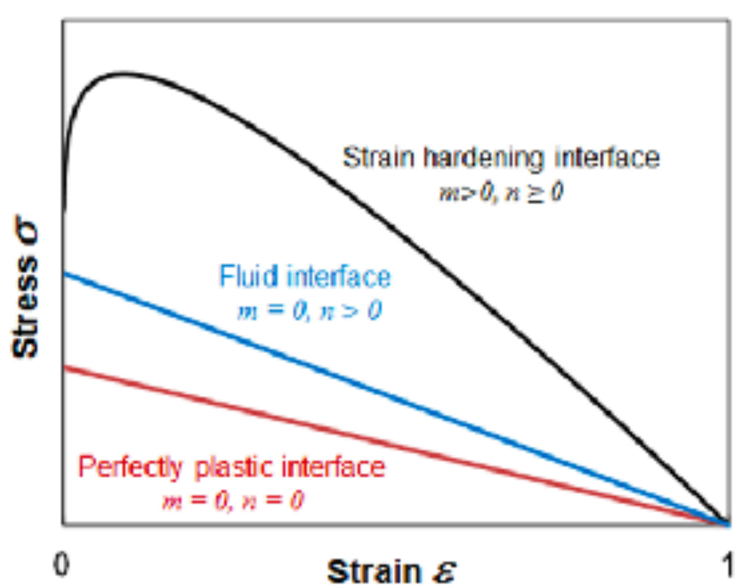


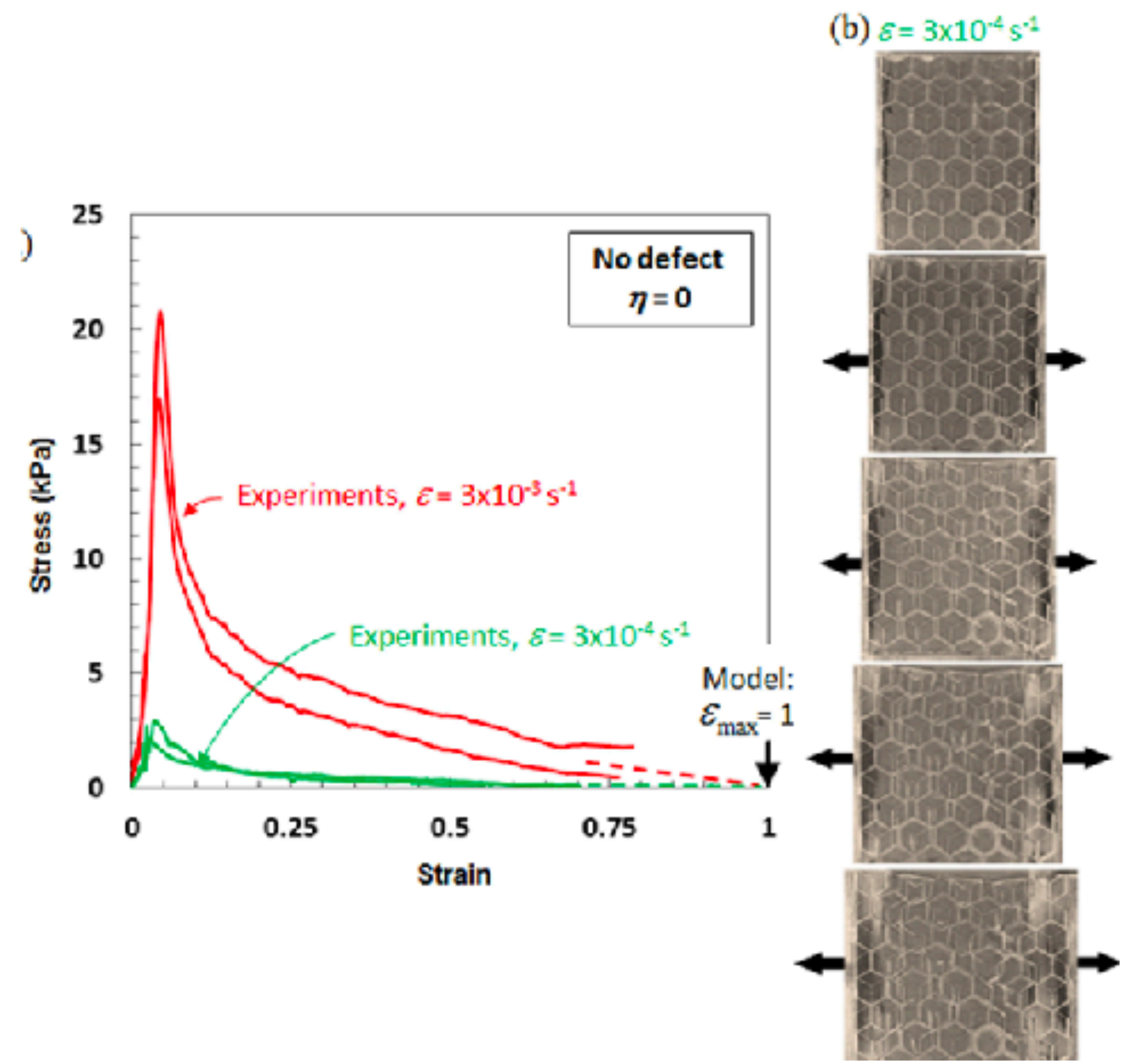
Fig. 7 – RVEs for materials with a range of tablet contents and orientations: (a, b, and c) ϕ = 5 vol%, and $\Delta\theta$ = 3°, 30°, and 180°, respectively, (d, e, and f) ϕ = 20 vol%, and $\Delta\theta$ = 3°, 30°, and 180° respectively (g, h, and i) ϕ = 35 vol%, and $\Delta\theta$ = 3°, 30°, and 180° respectively.



Strain rate hardening?

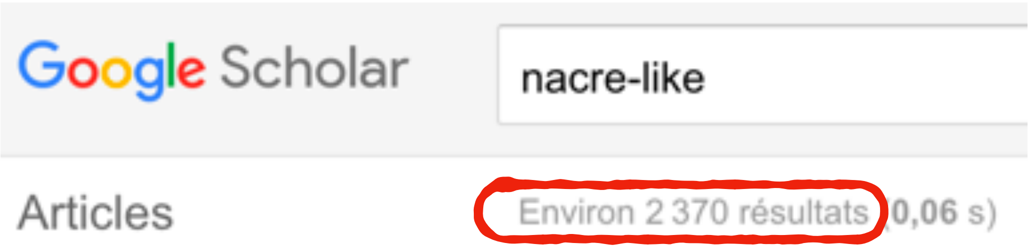


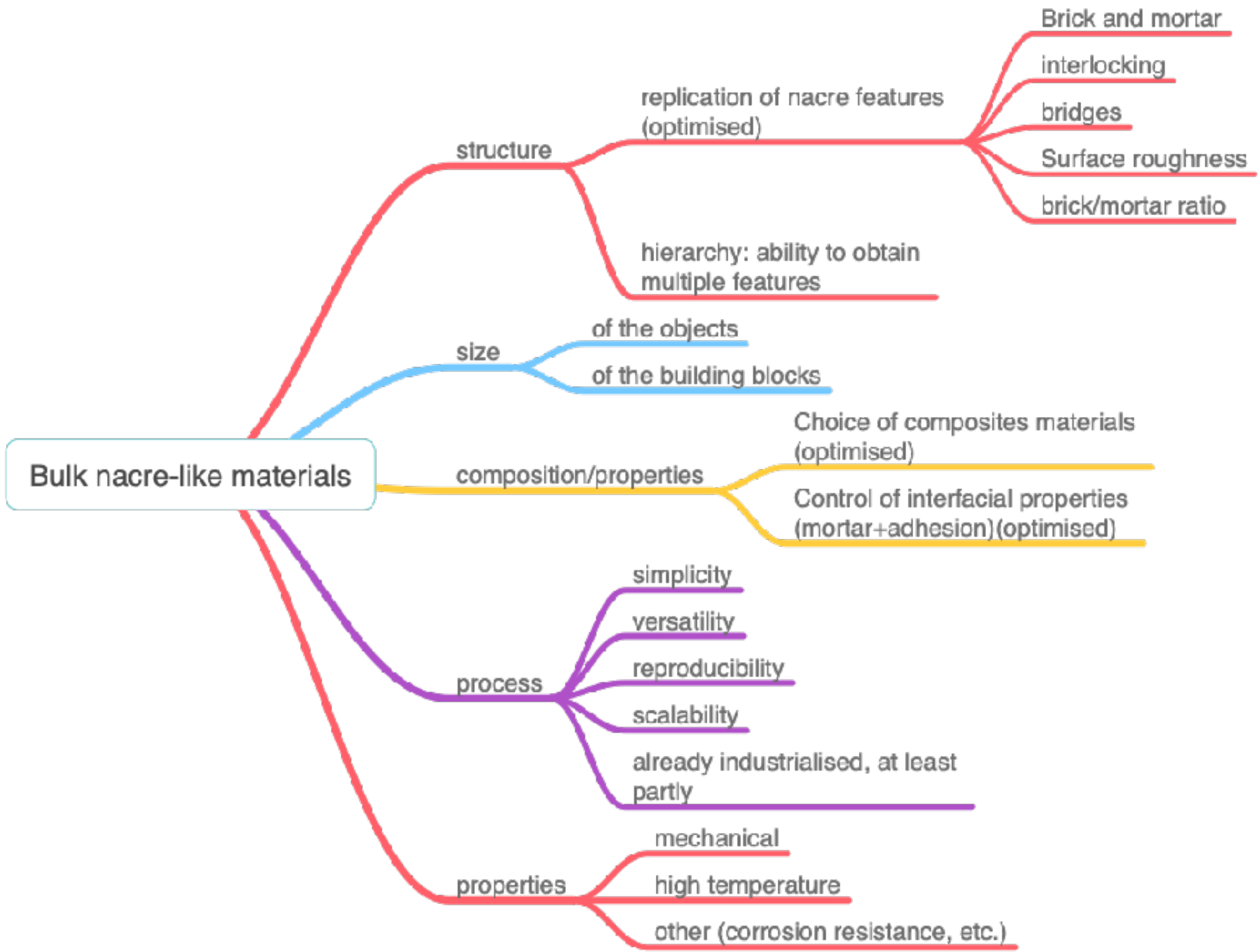




Chintapalli, R. K., Strain rate hardening: a hidden but critical mechanism for biological composites? Acta Biomater. 10, 5064–73 (2014).

Nacre-like materials

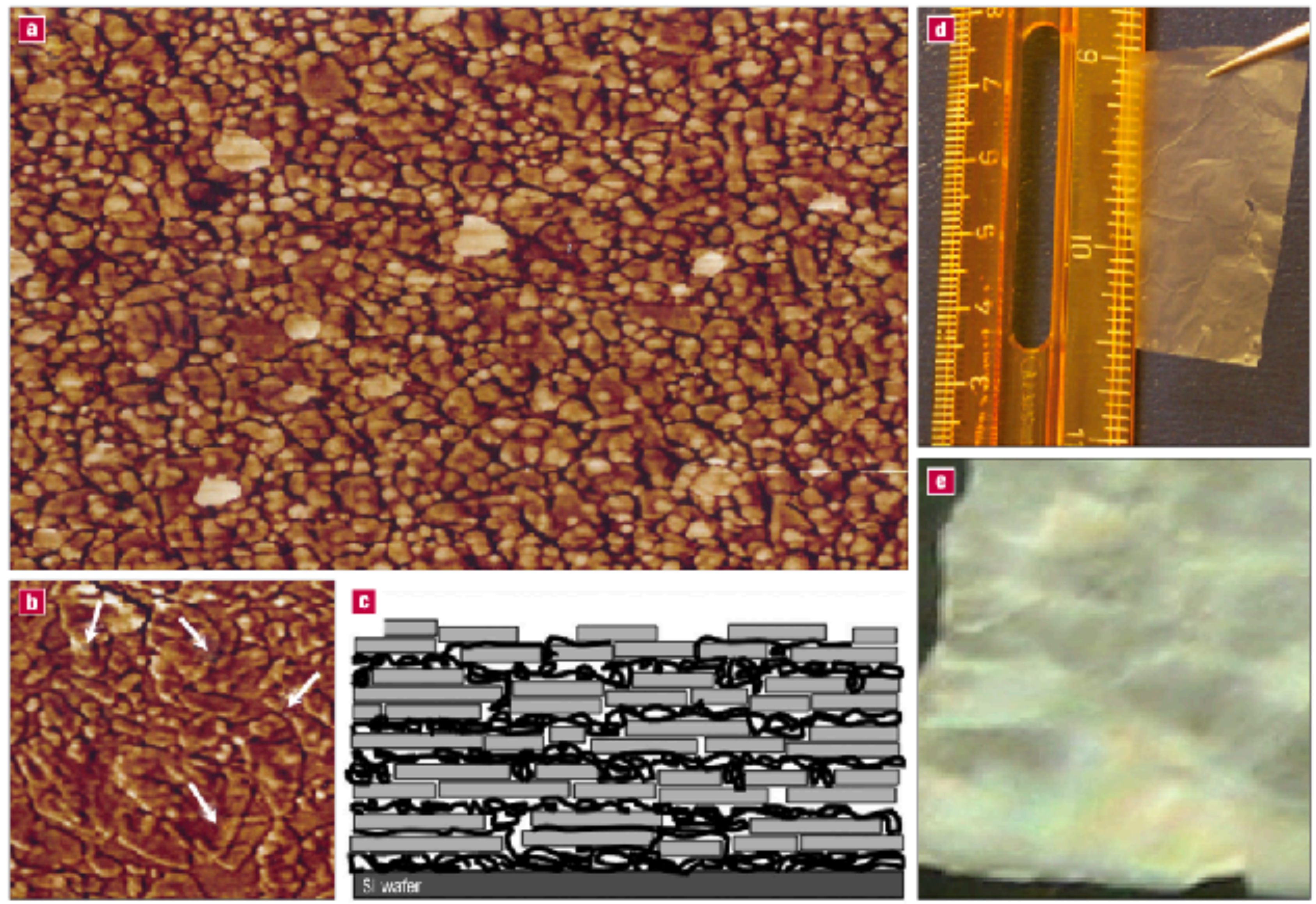




Bulk nacre-like materials
structure
replication of nacre features (optimised)
Brick and mortar
interlocking
bridges
Surface roughness
brick/mortar ratio
hierarchy: ability to obtain multiple features
size
of the objects
of the building blocks
composition/properties
Choice of composites materials (optimised)
Control of interfacial properties (mortar+adhesion)(optimised)
process
simplicity
versatility
reproducibility
scalability
already industrialised, at least partly
properties
mechanical
high temperature
other (corrosion resistance, etc.)

Films and coatings

- Self-assembly
- Biomineralization
- Evaporation
- EPD



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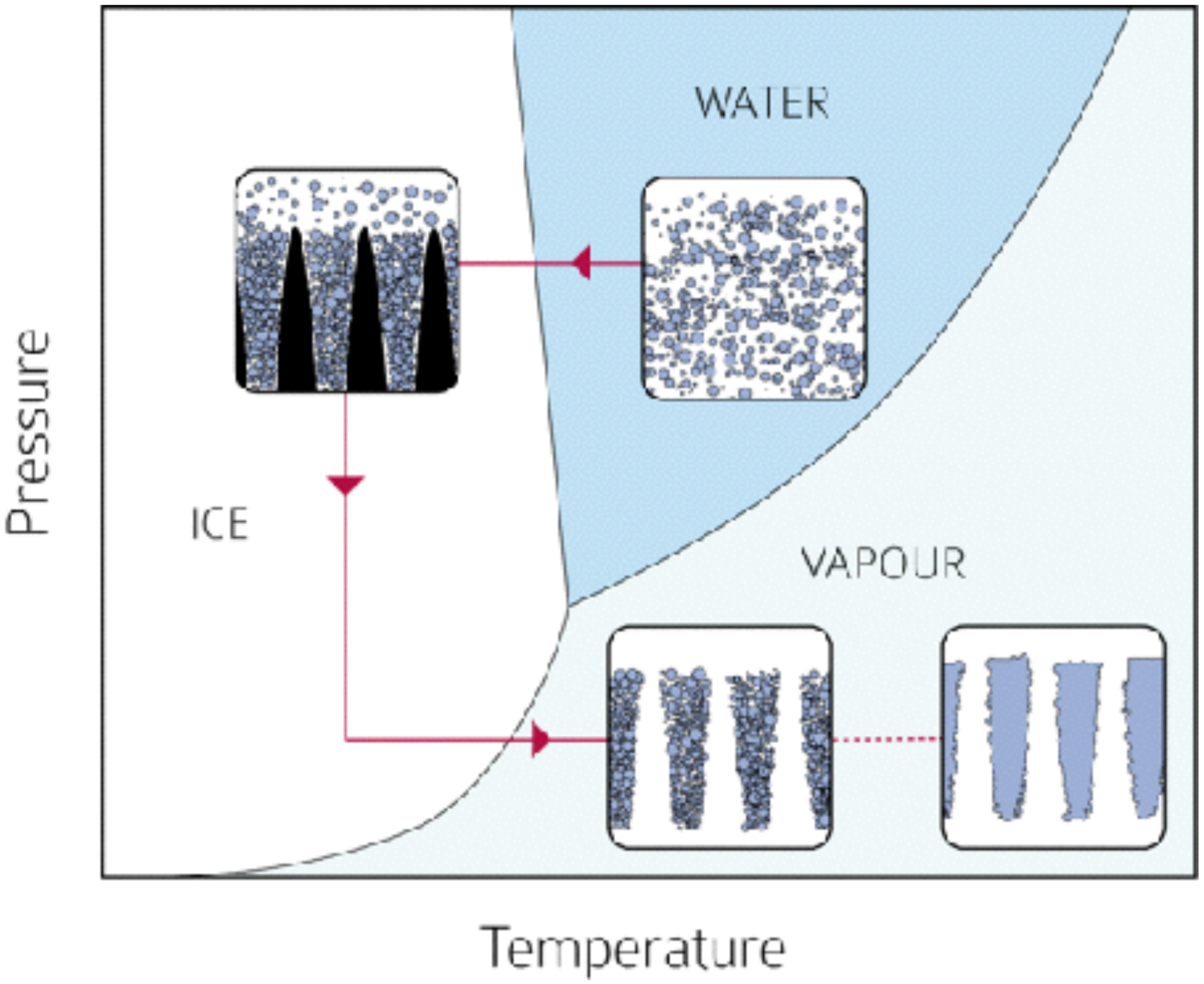
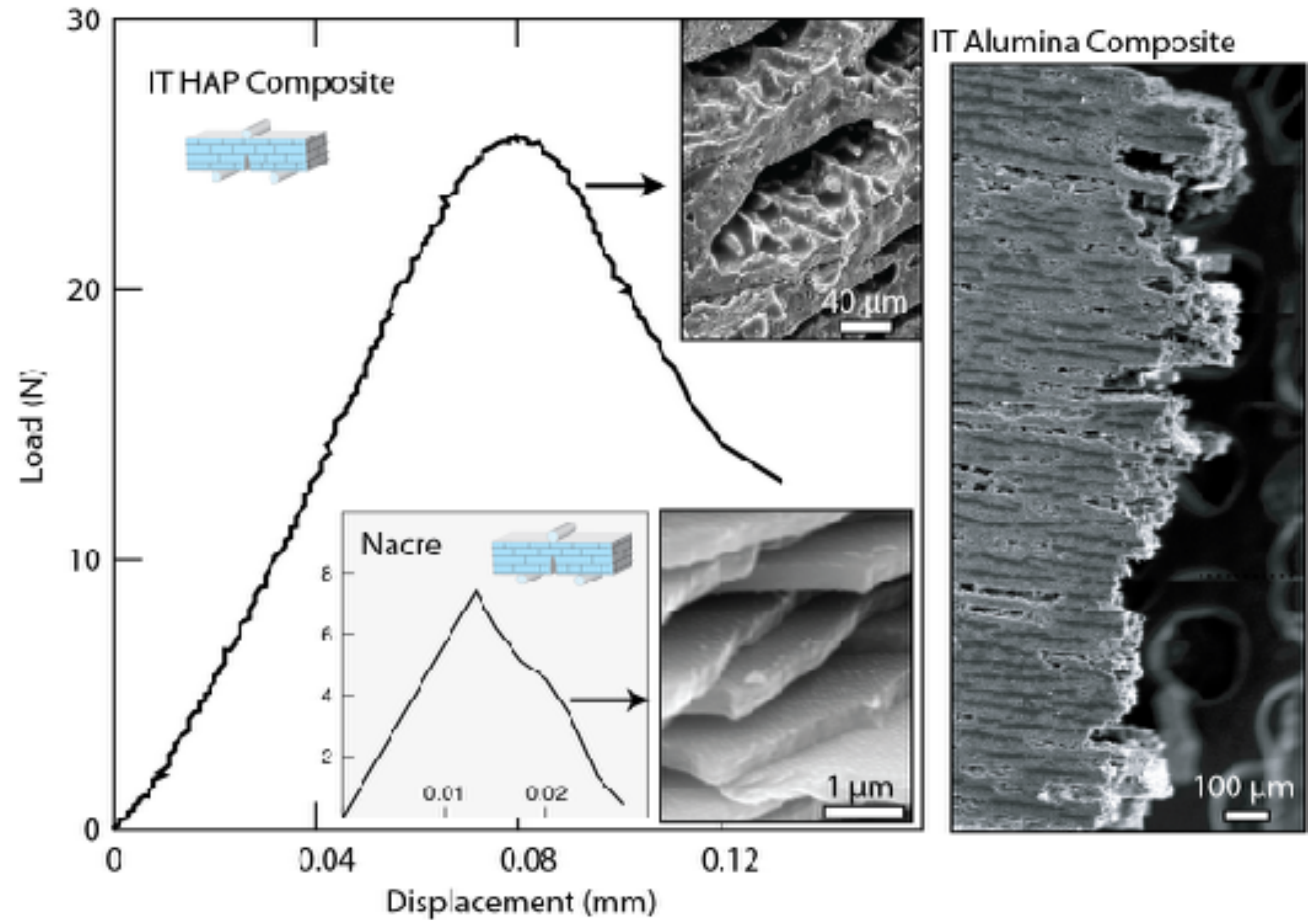
Ice-templating to create bricks





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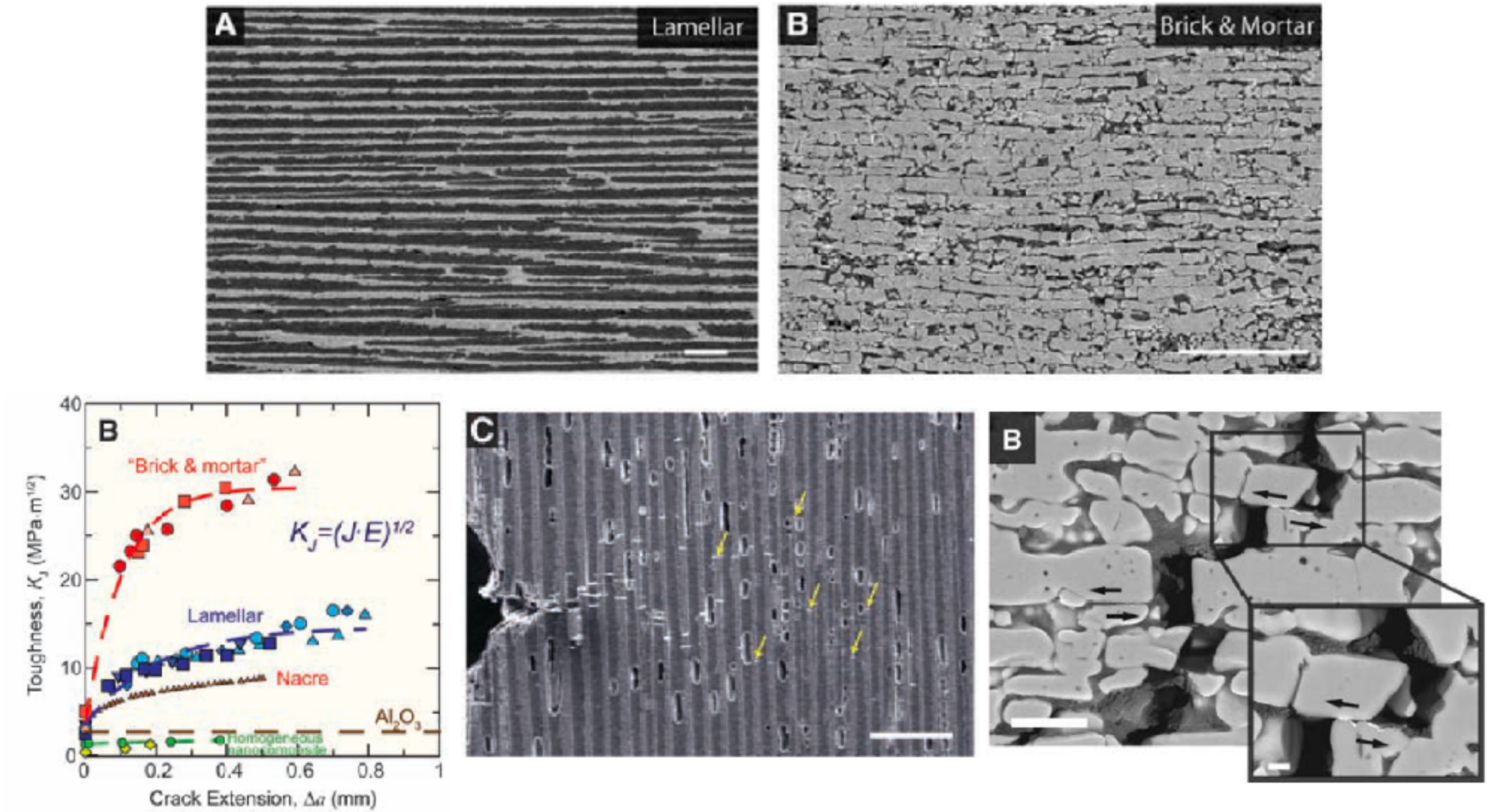
Ice-templating to create bricks



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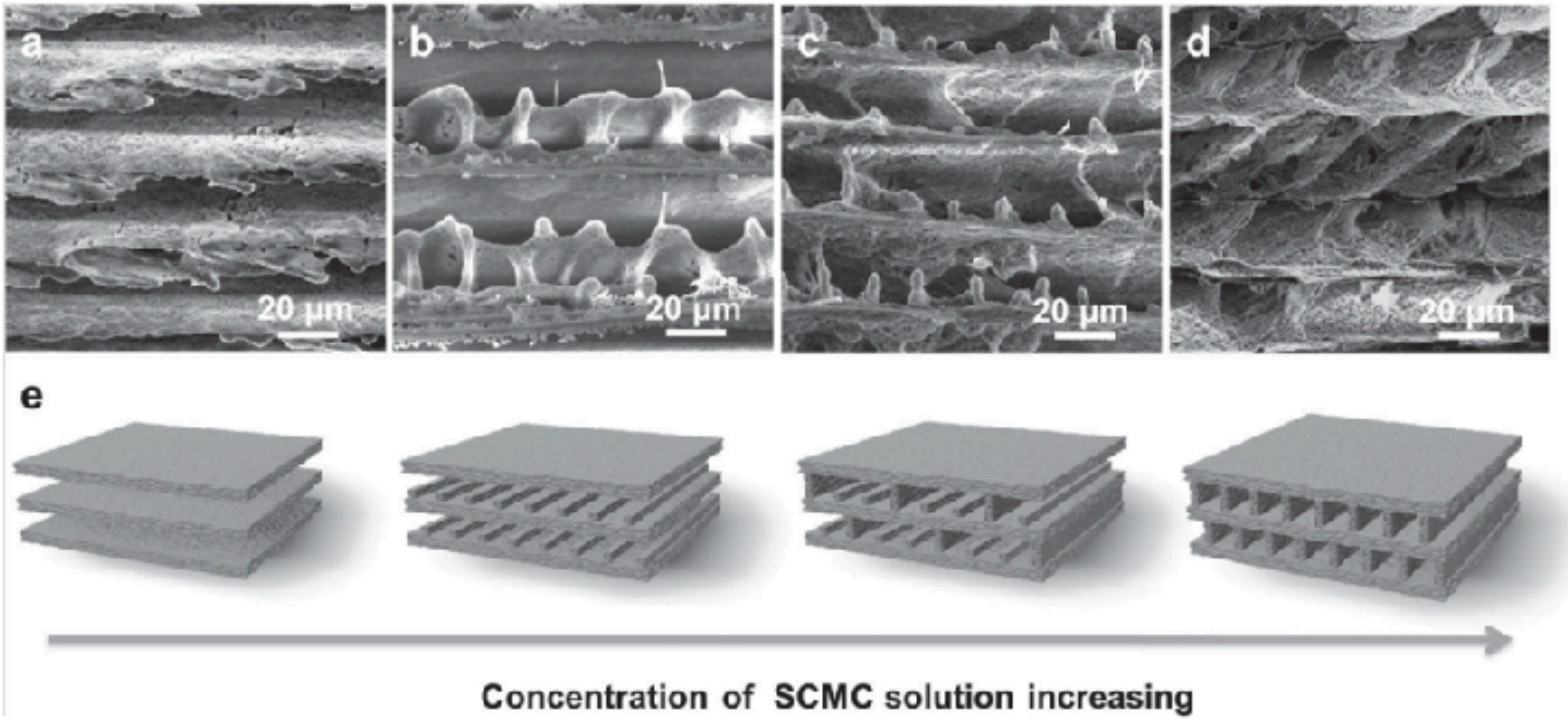
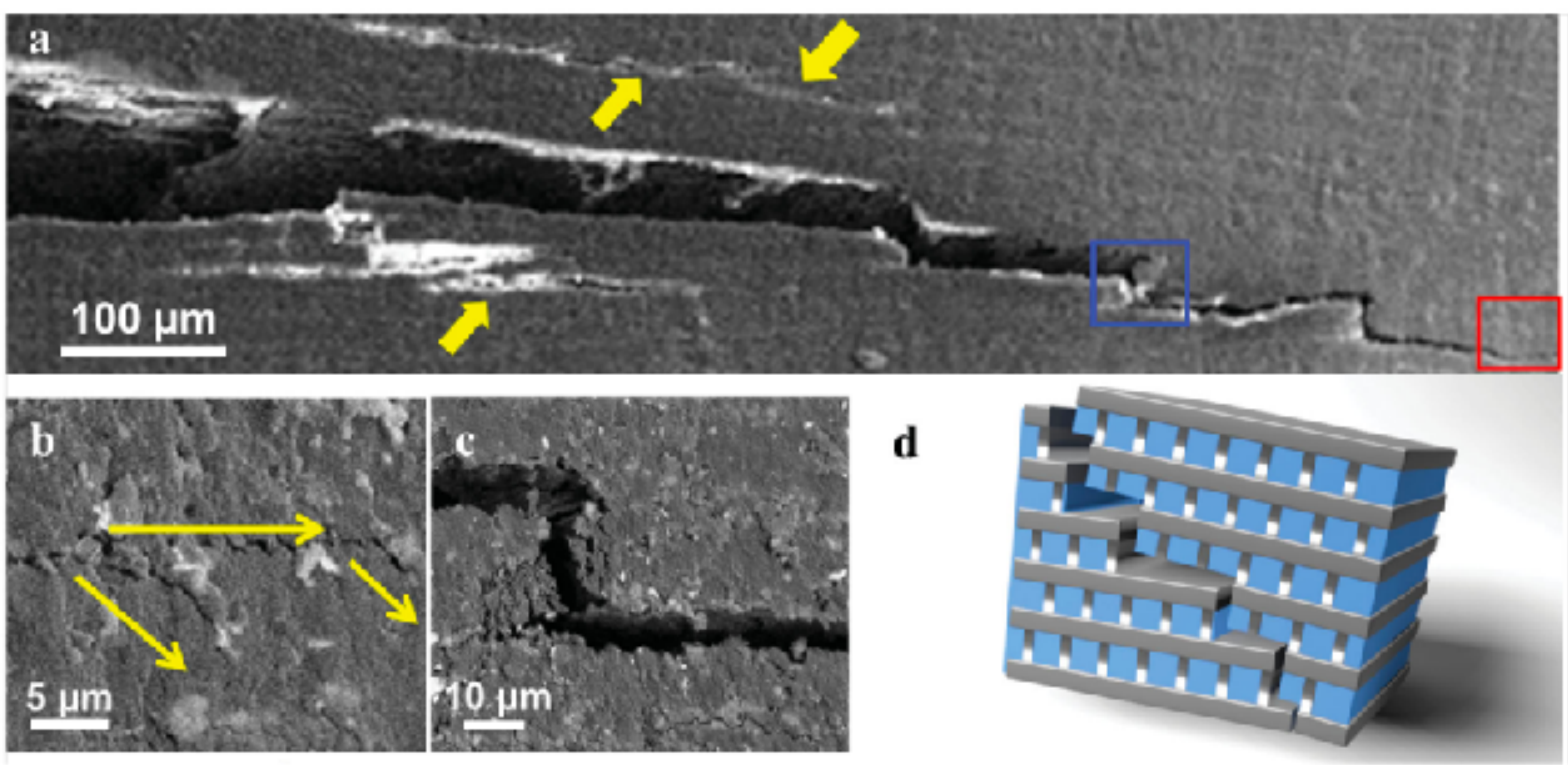
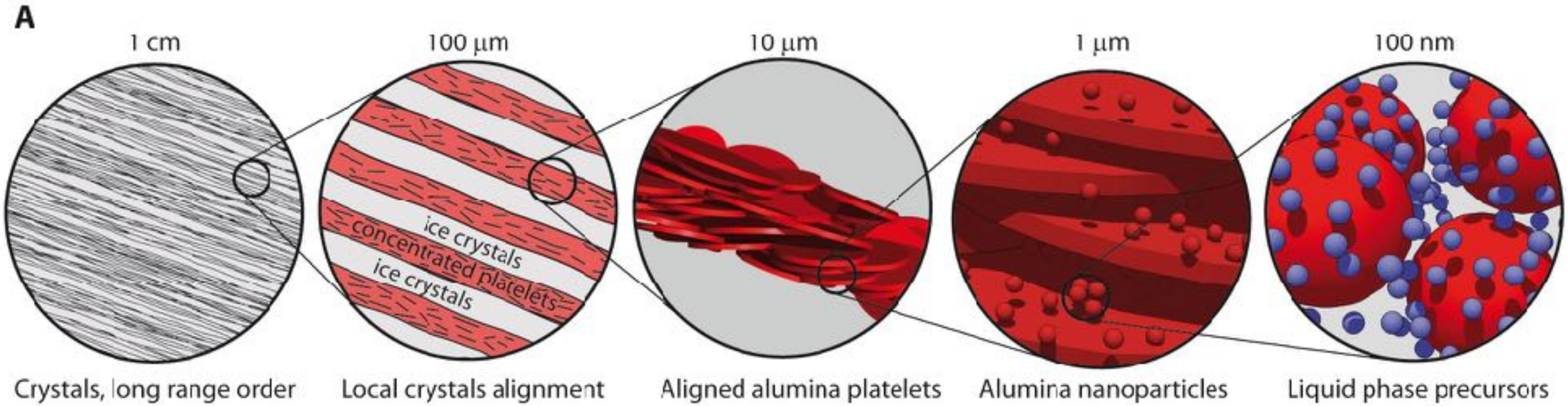
Ice-templating and bridges

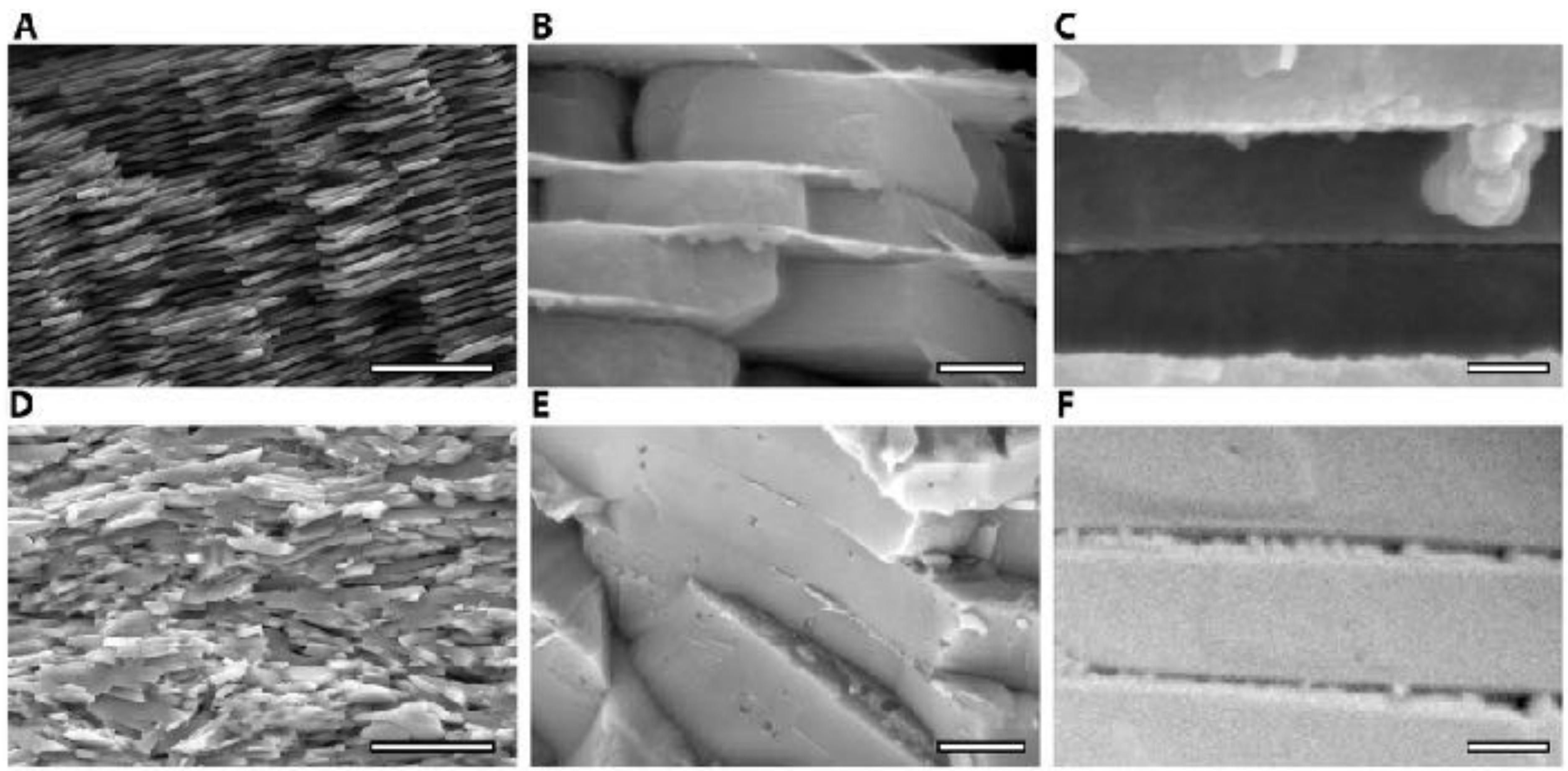




Zhao, H. et al. Cloning Nacre's 3D Interlocking Skeleton in Engineering Composites to Achieve Exceptional Mechanical Properties. *Adv. Mater.* 28, 5099–5105 (2016).

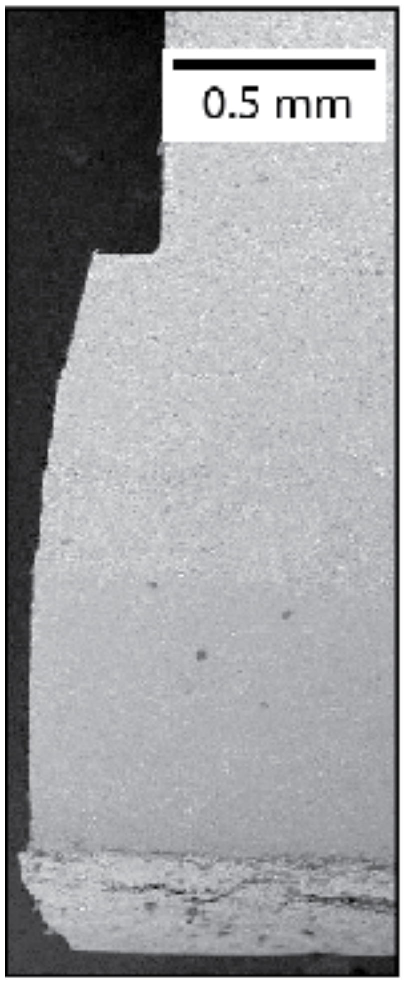
Ice-templating to align bricks

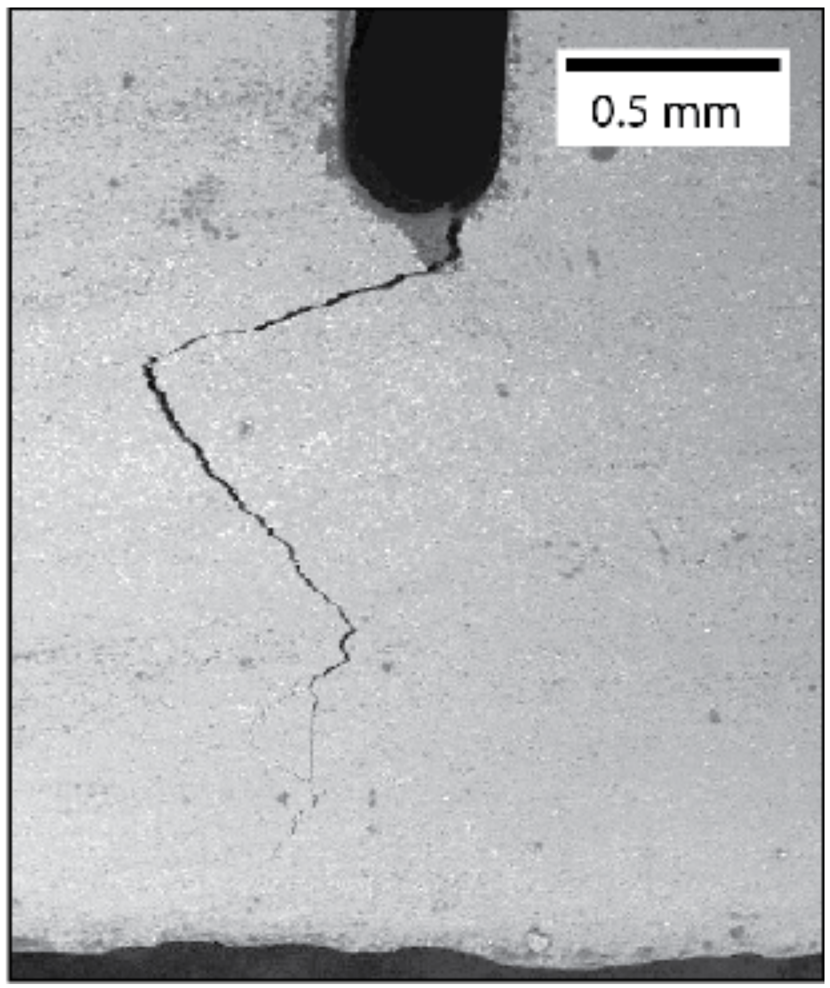


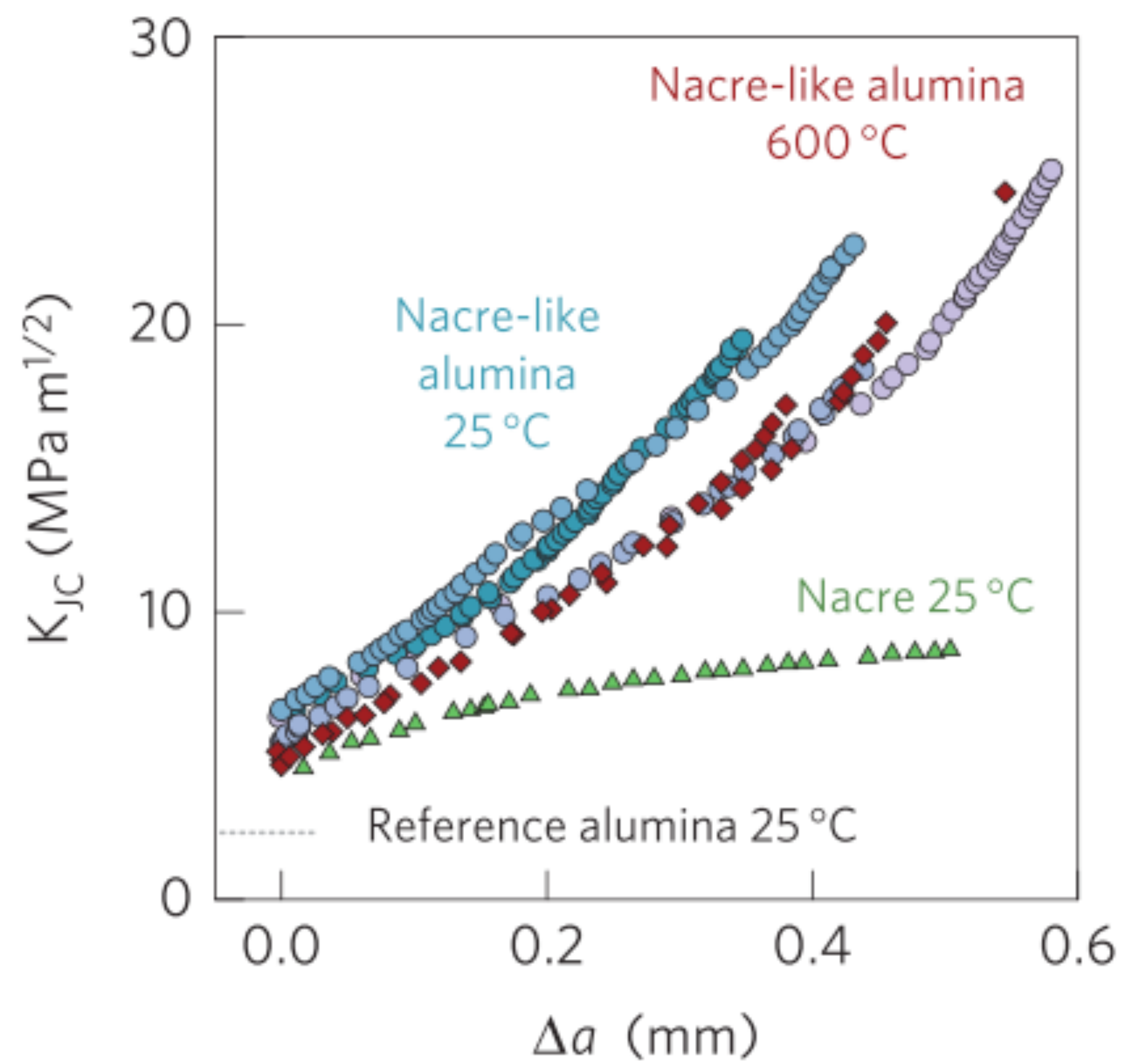


Bouville, F. , Strong, tough and stiff bioinspired ceramics from brittle constituents. *Nat. Mater.* (2014).

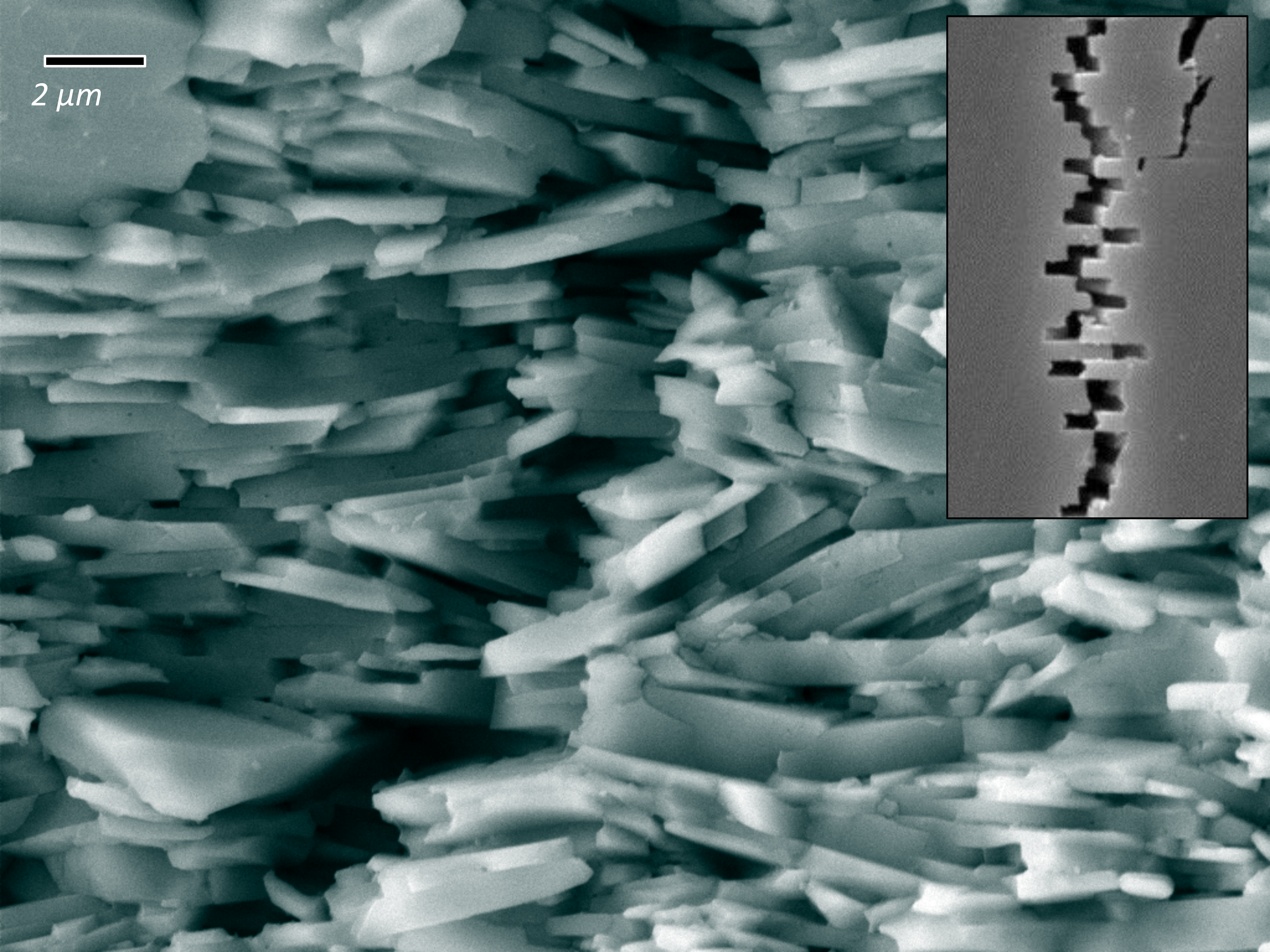
Ice-templating to align bricks



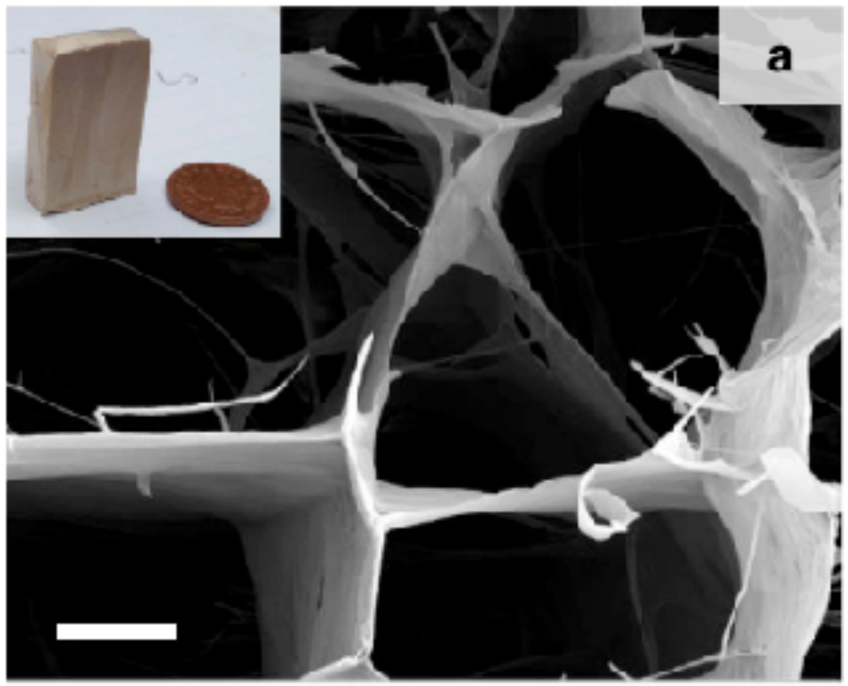


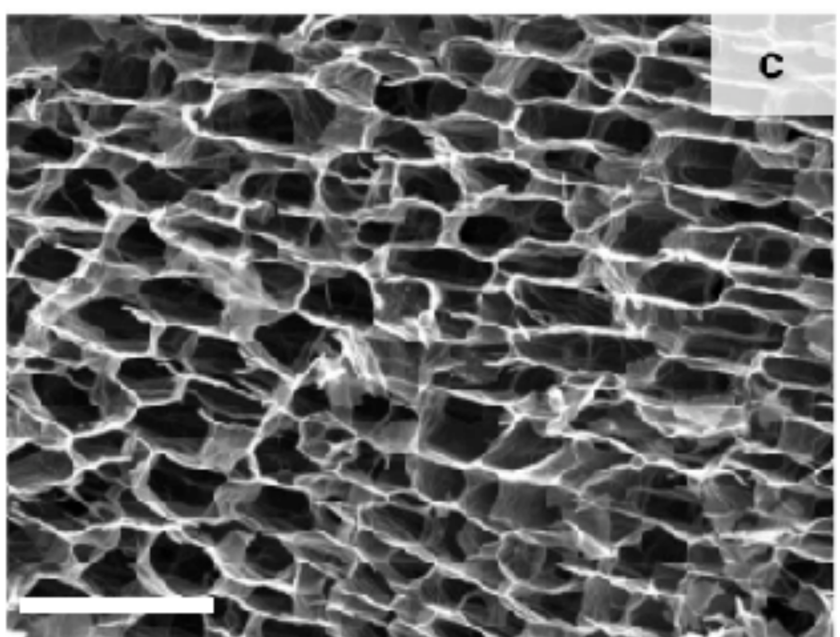


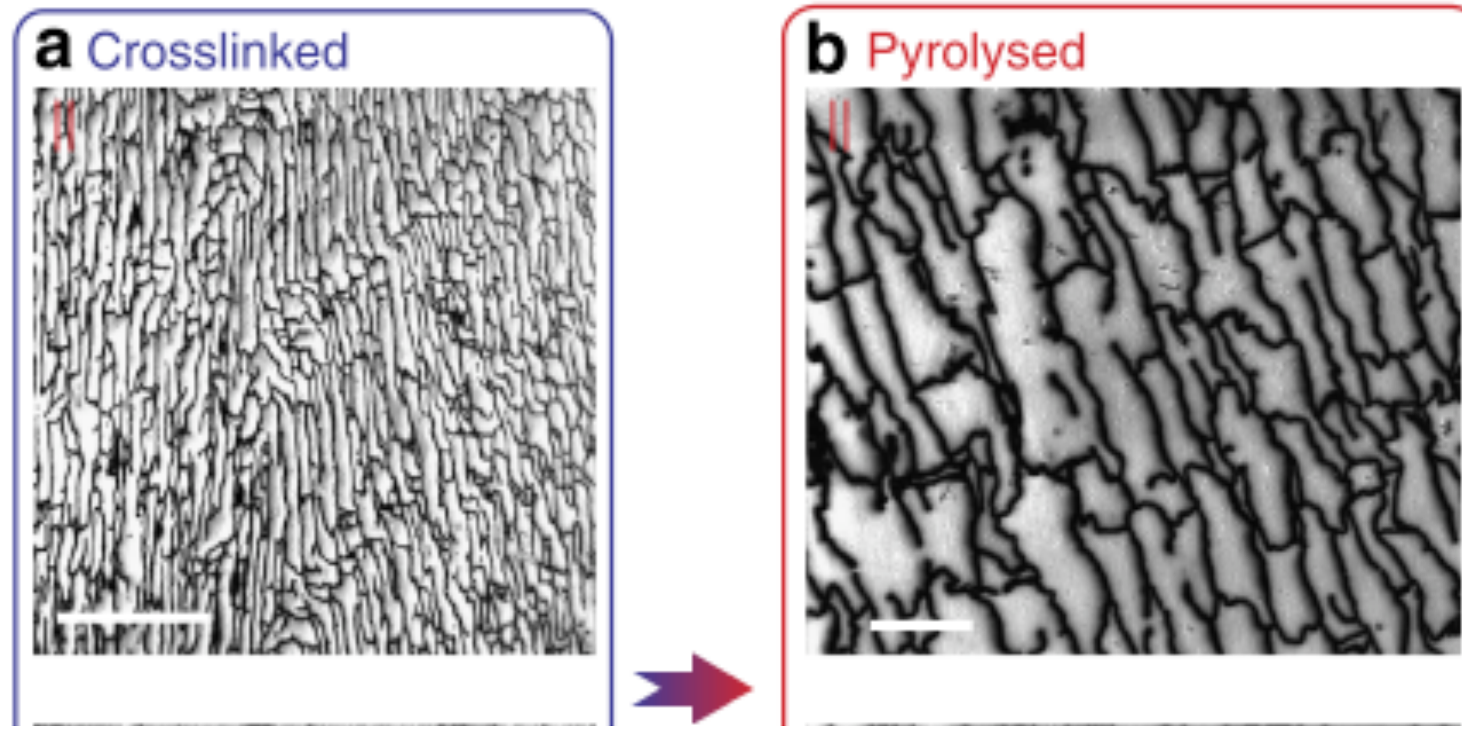
Bouville, F., Strong, tough and stiff bioinspired ceramics from brittle constituents. *Nat. Mater*. (2014).

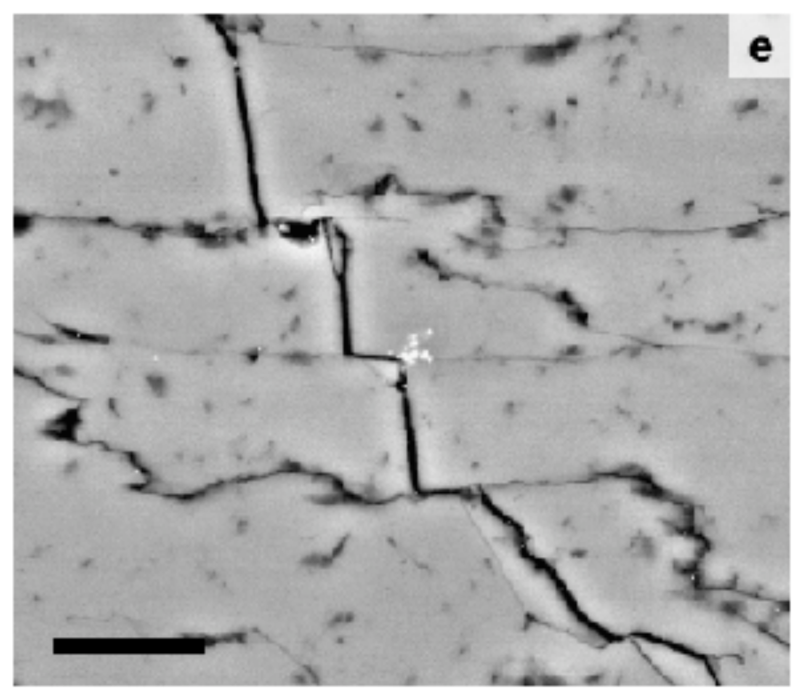

2 μm

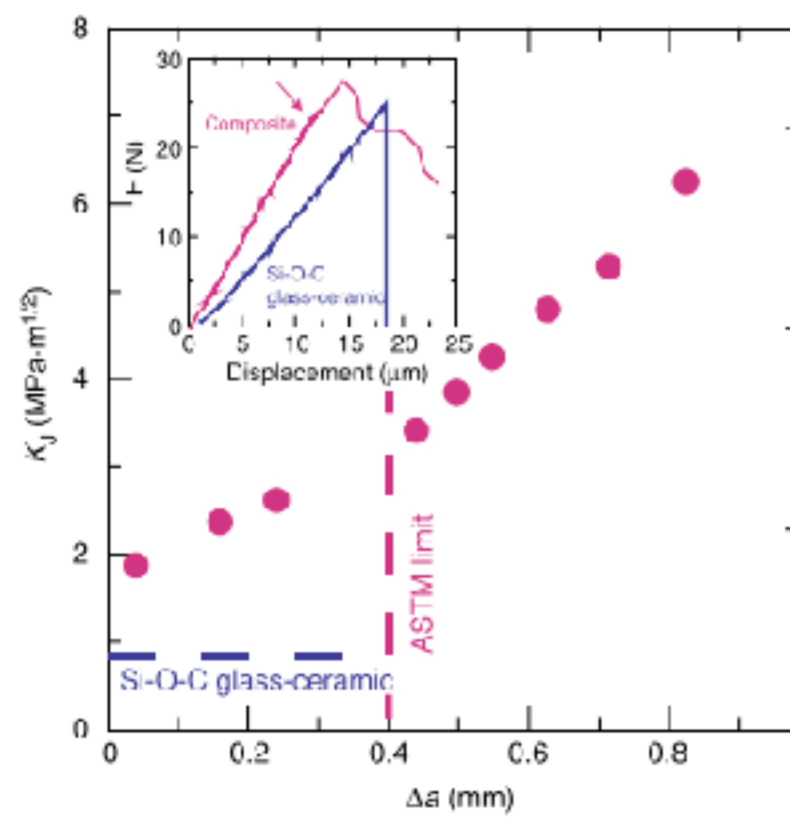
Ice-templating to create the interface first





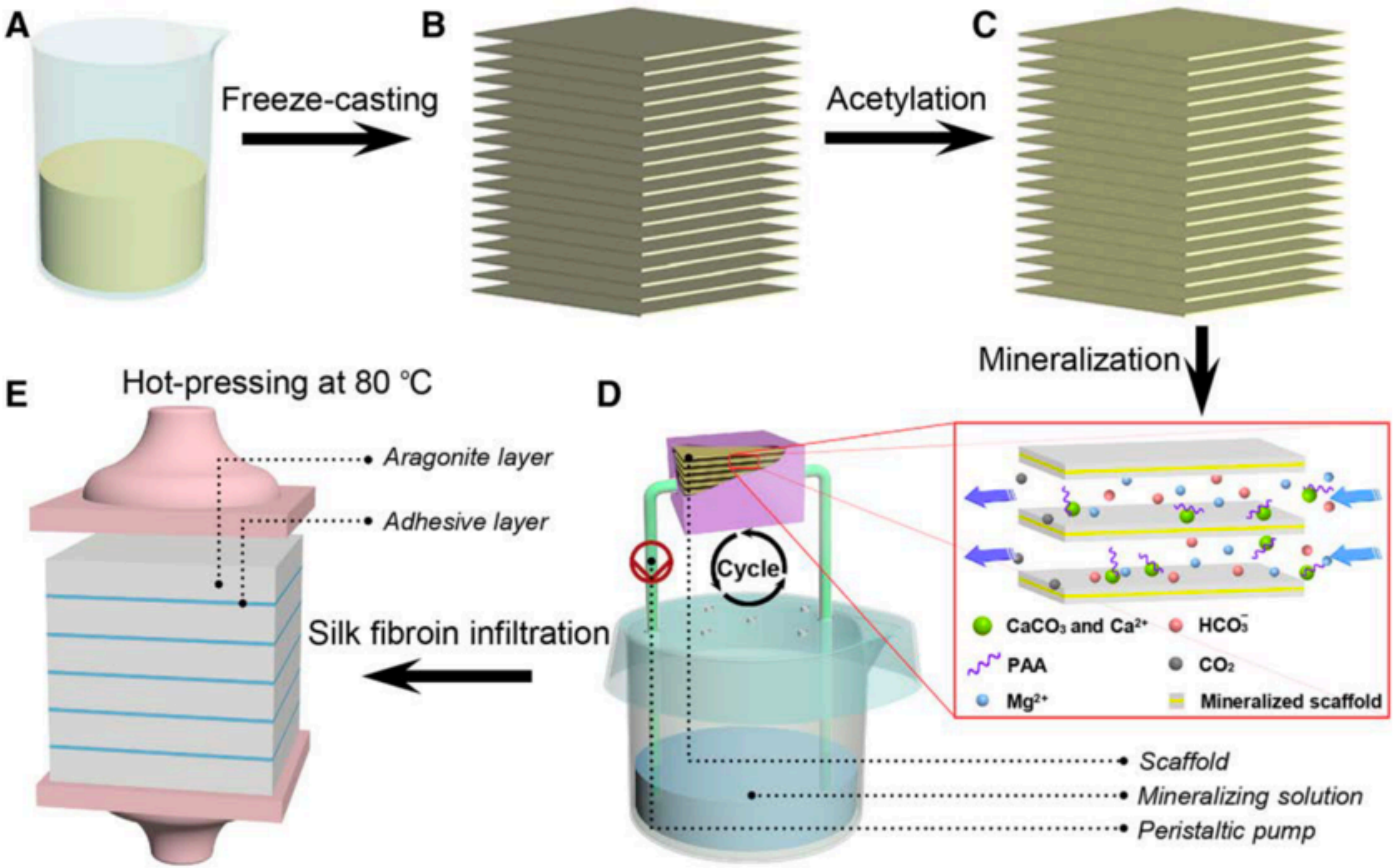






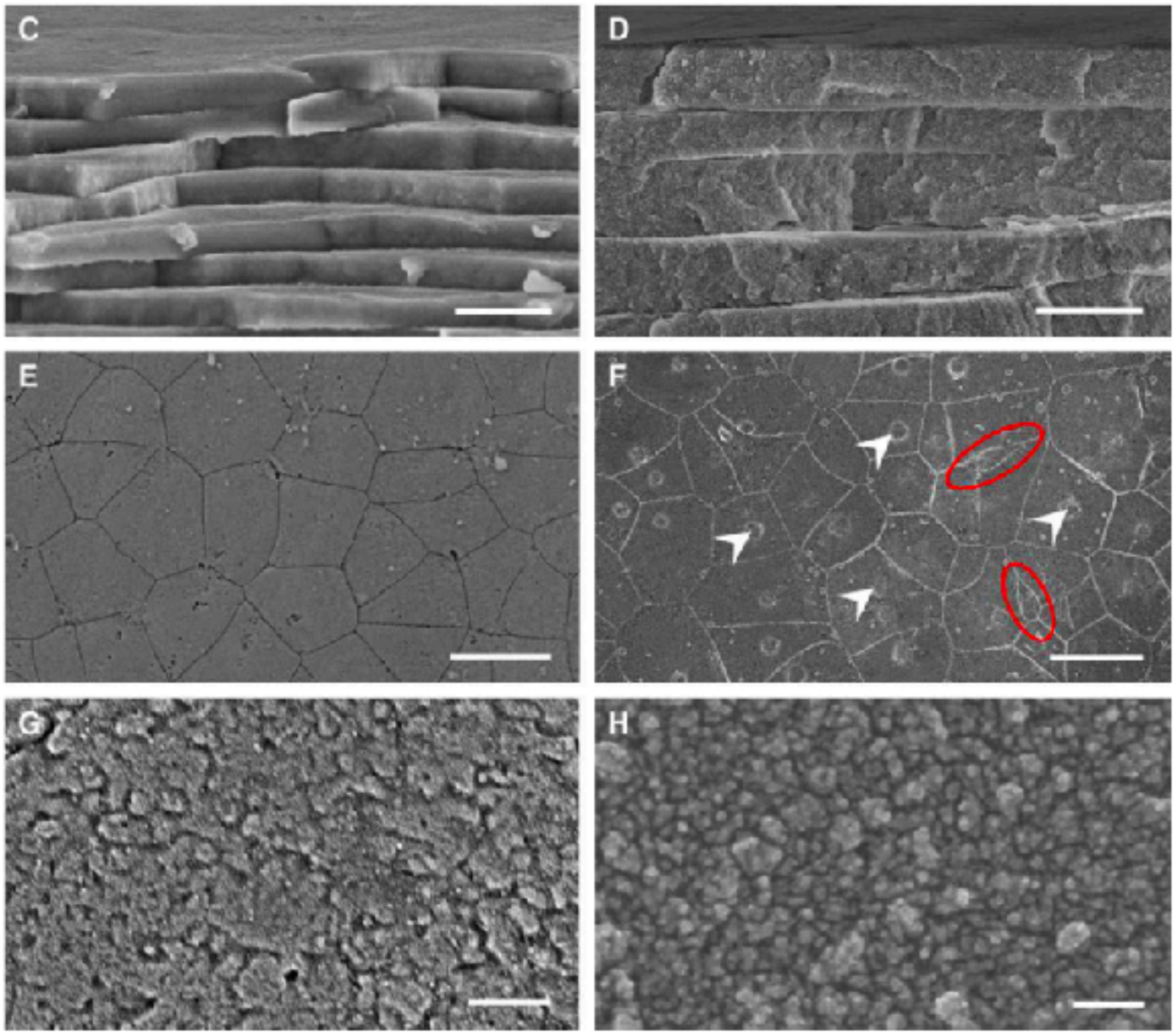
Picot, O.T. et al. Using graphene networks to build bioinspired self-monitoring ceramics. *Nat. Commun.*(2017).

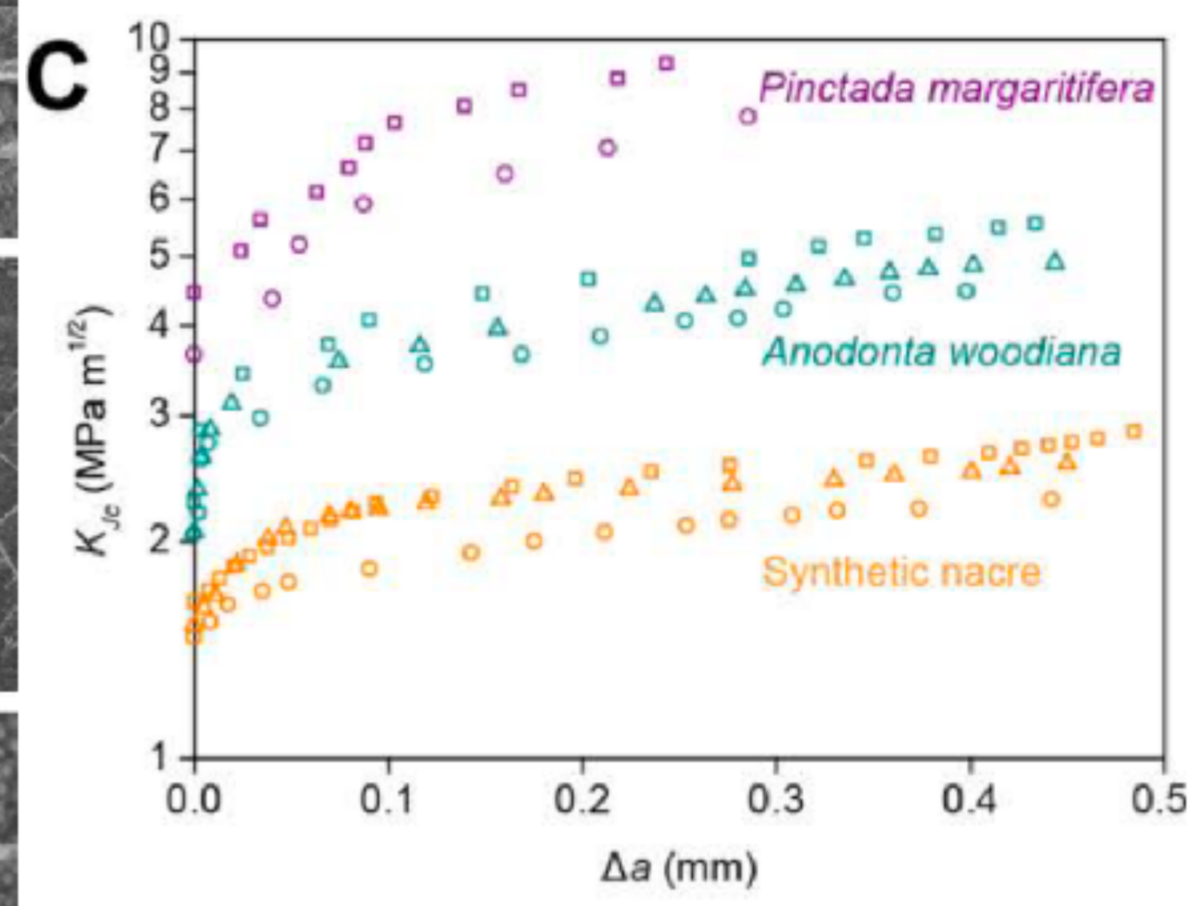
Ice-templating to create the interface first



Mao, L.-B. et al. Synthetic nacre by predesigned matrix-directed mineralization. *Science*. 354, 107–110 (2016).

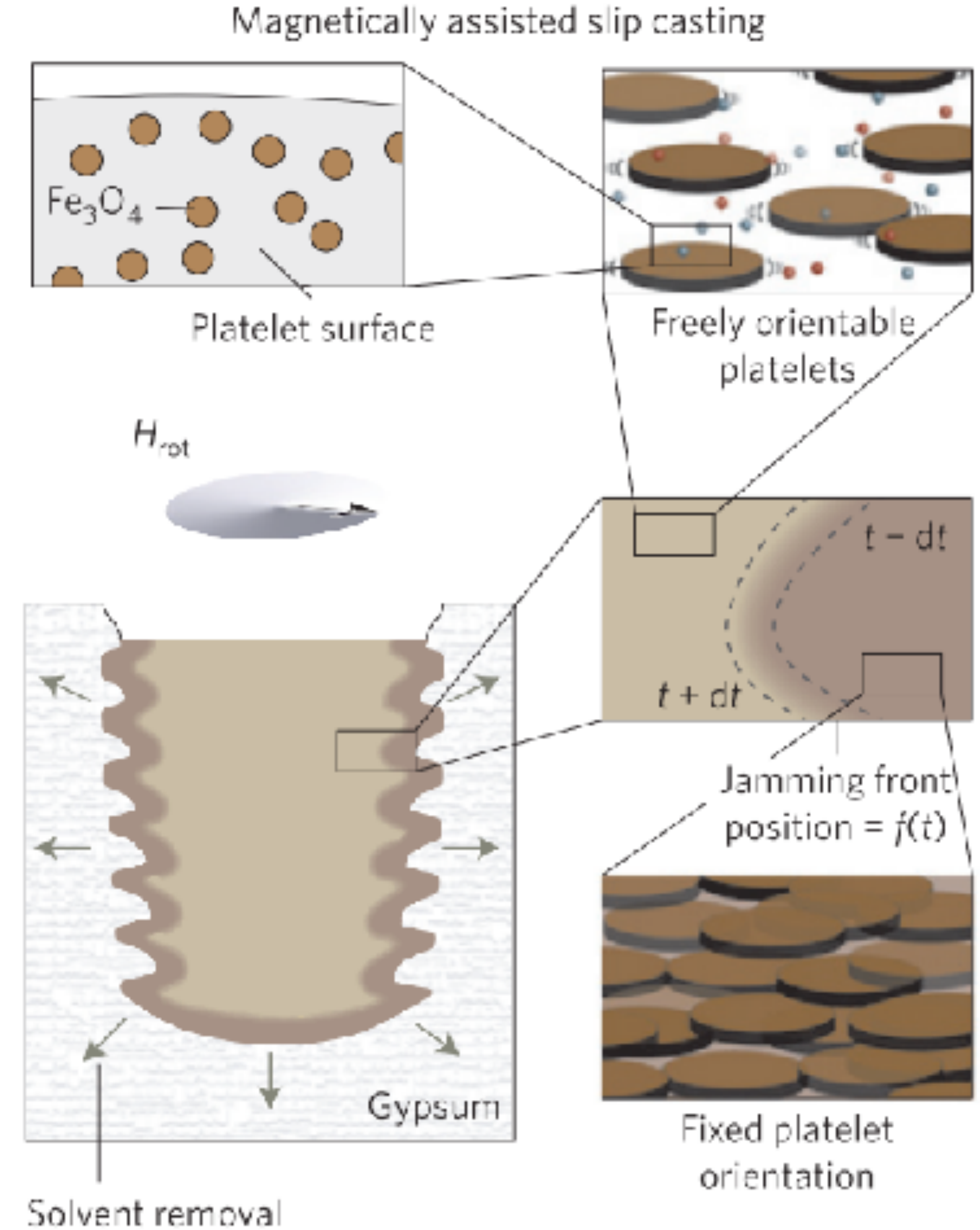
Ice-templating to create the interface first



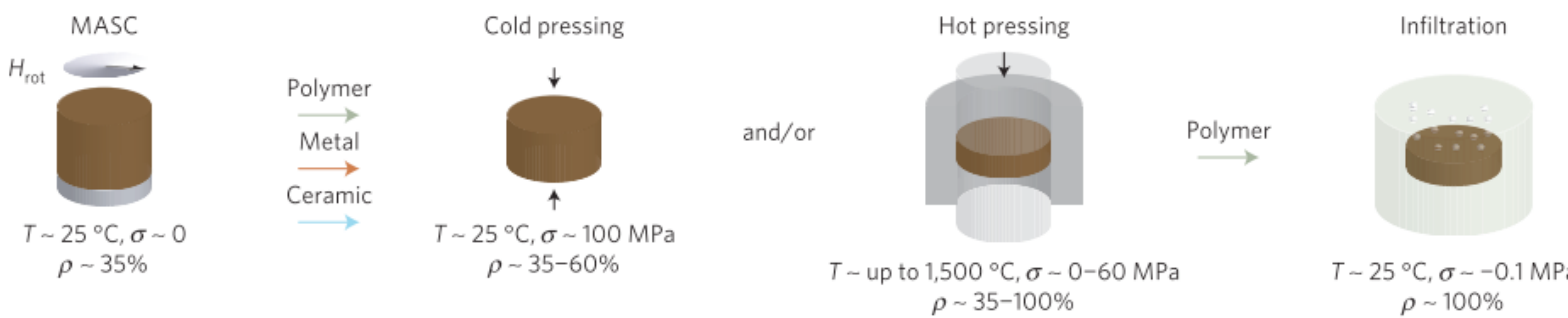


Mao, L.-B. et al. Synthetic nacre by predesigned matrix-directed mineralization. *Science*. 354, 107–110 (2016).

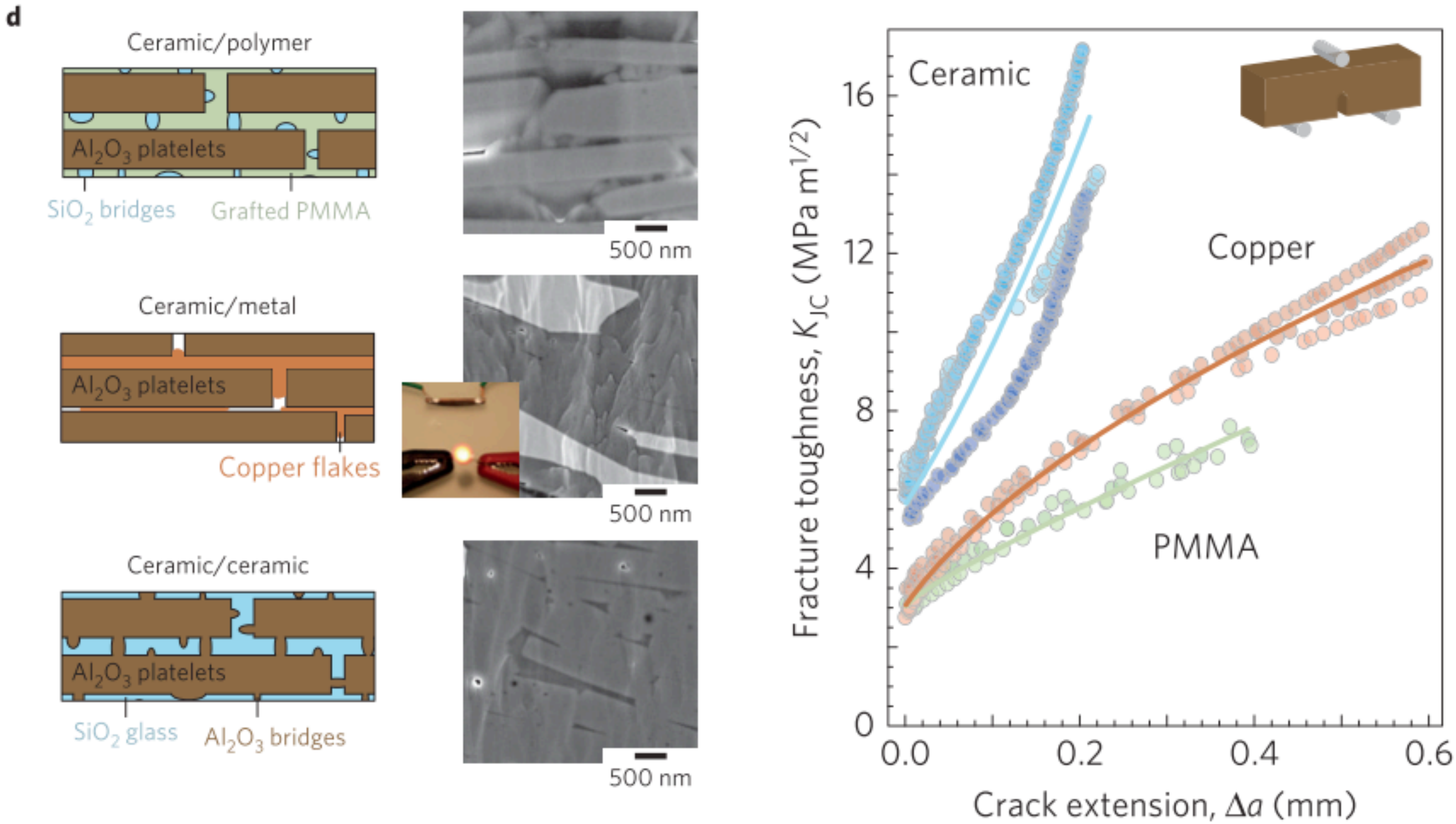
Slip casting



Le Ferrand, H., Magnetically assisted slip casting of bioinspired heterogeneous composites. *Nat. Mater.* (2015).

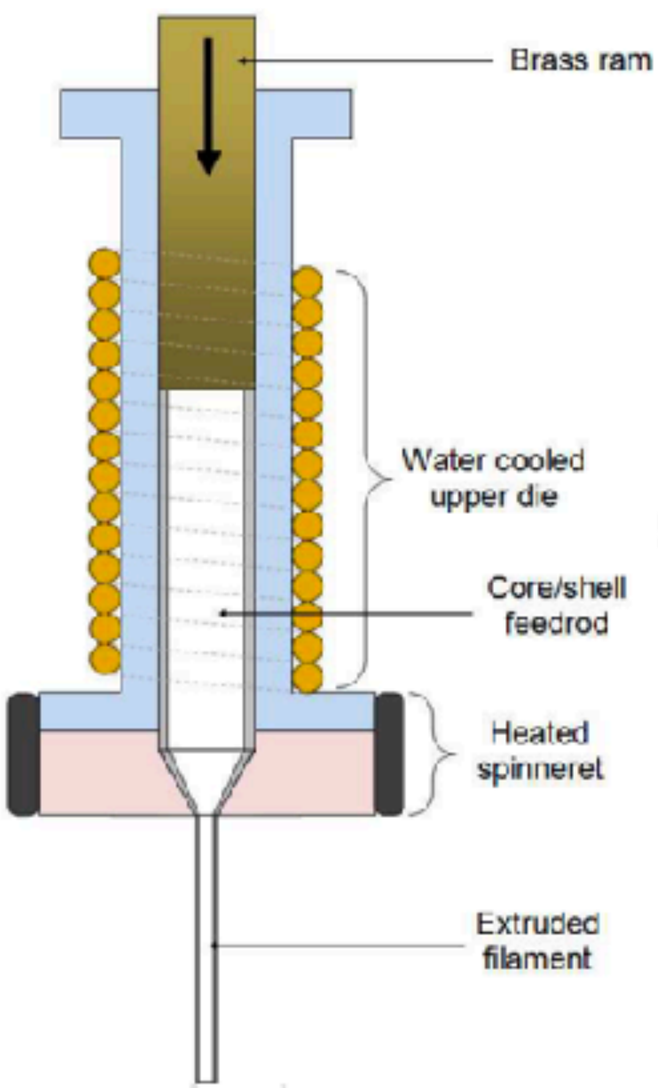


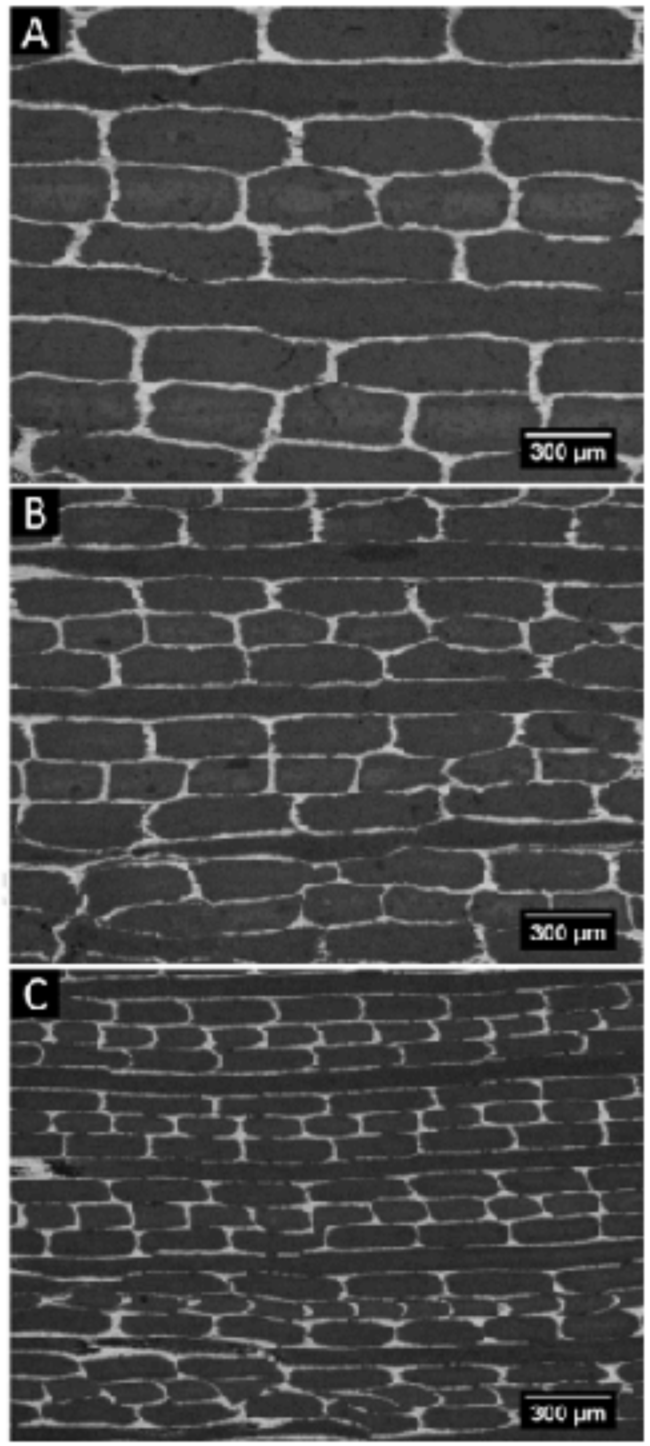
Slip casting

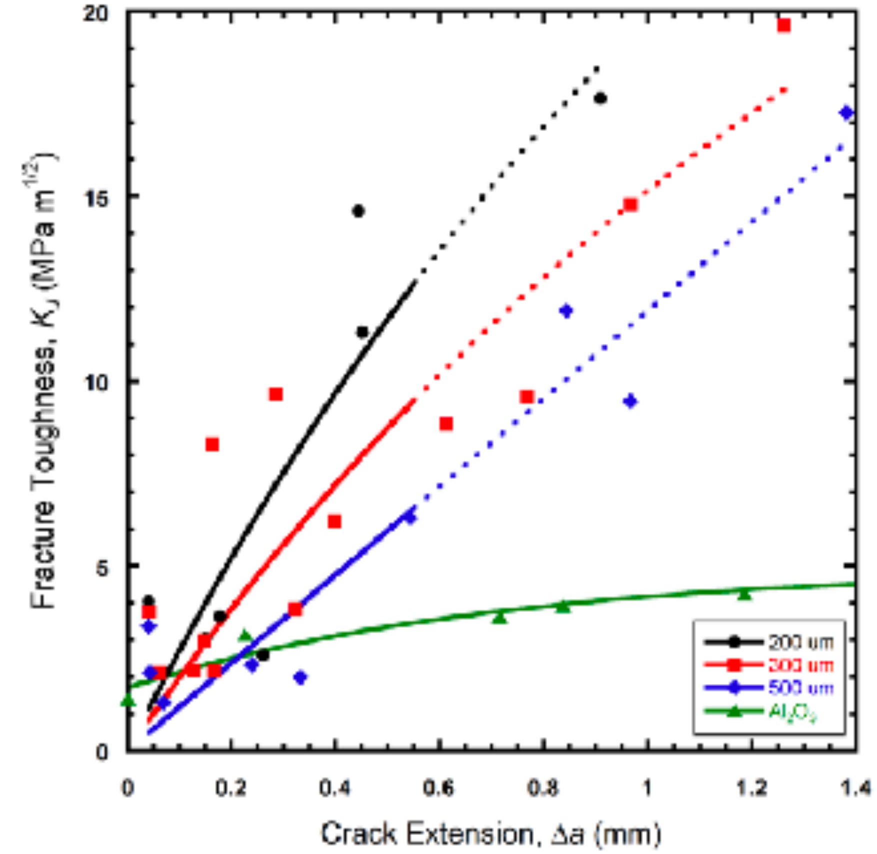


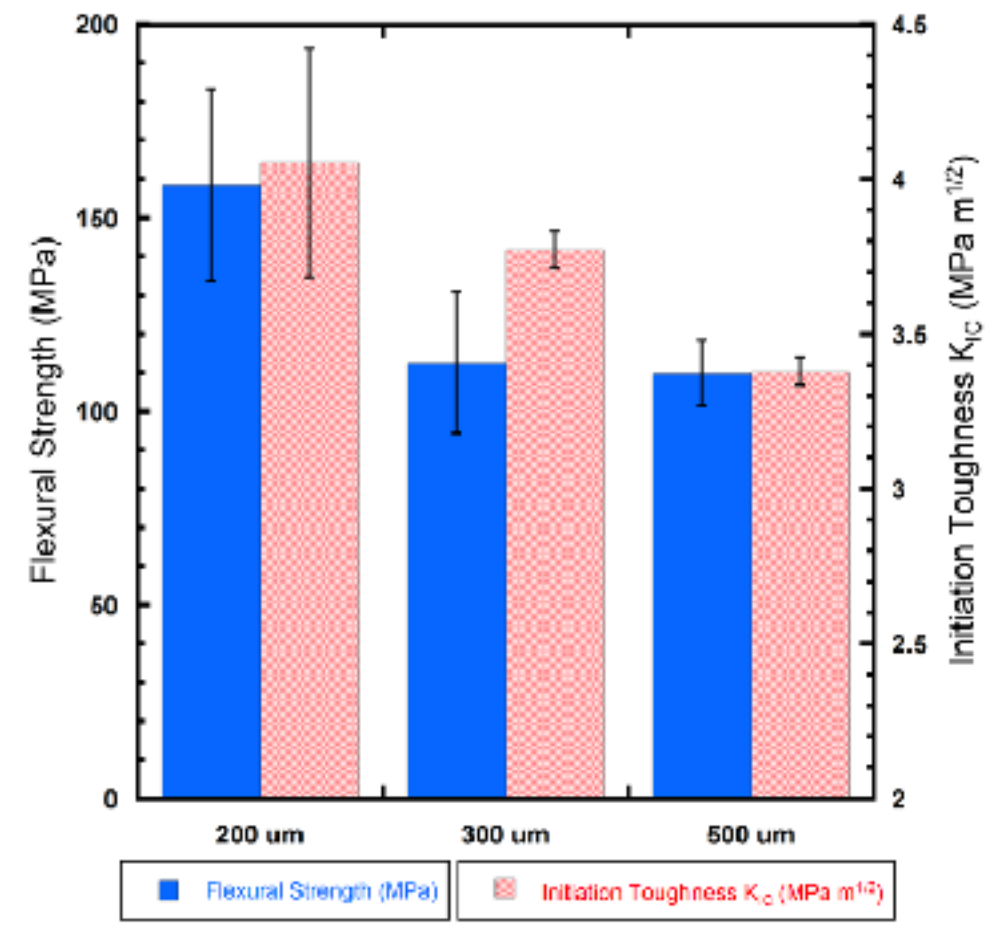
Le Ferrand, H., Magnetically assisted slip casting of bioinspired heterogeneous composites. *Nat. Mater.* 14, 1–17 (2015).

Co-extrusion









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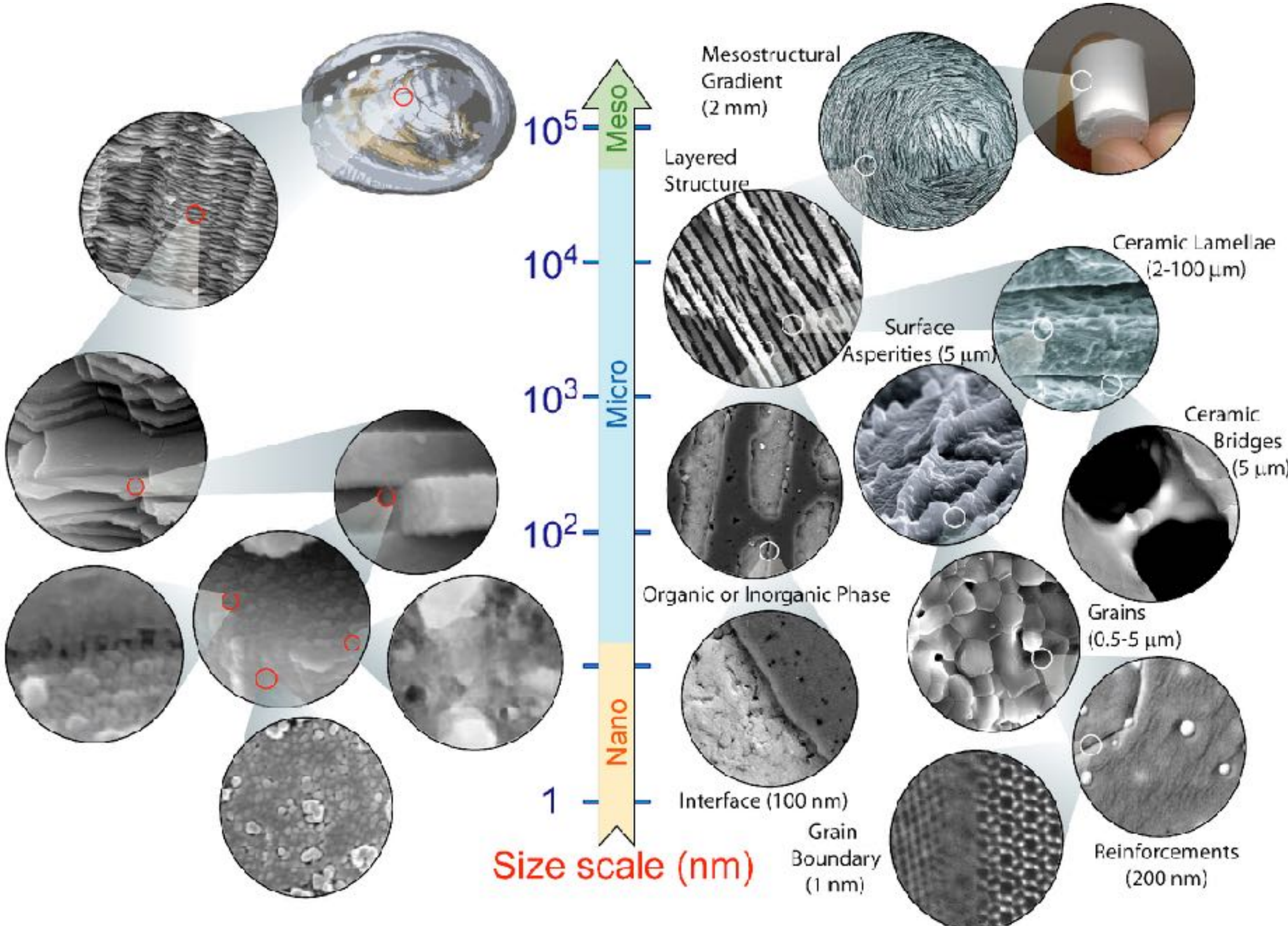
Remaining challenges

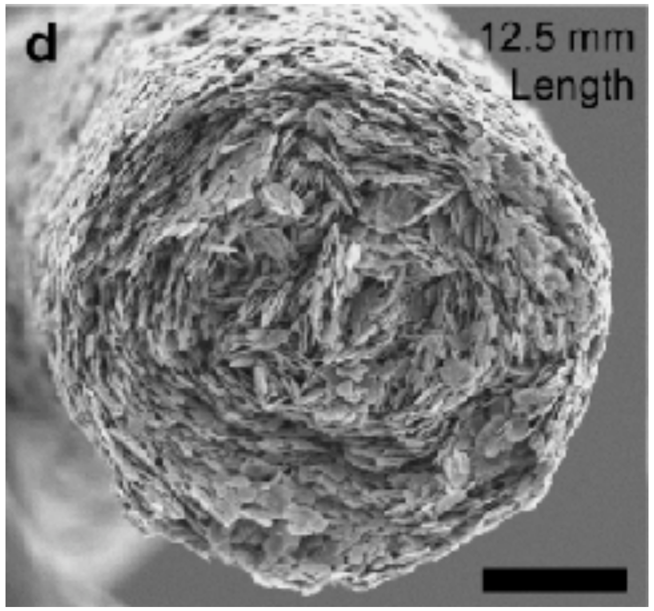
Remaining challenges

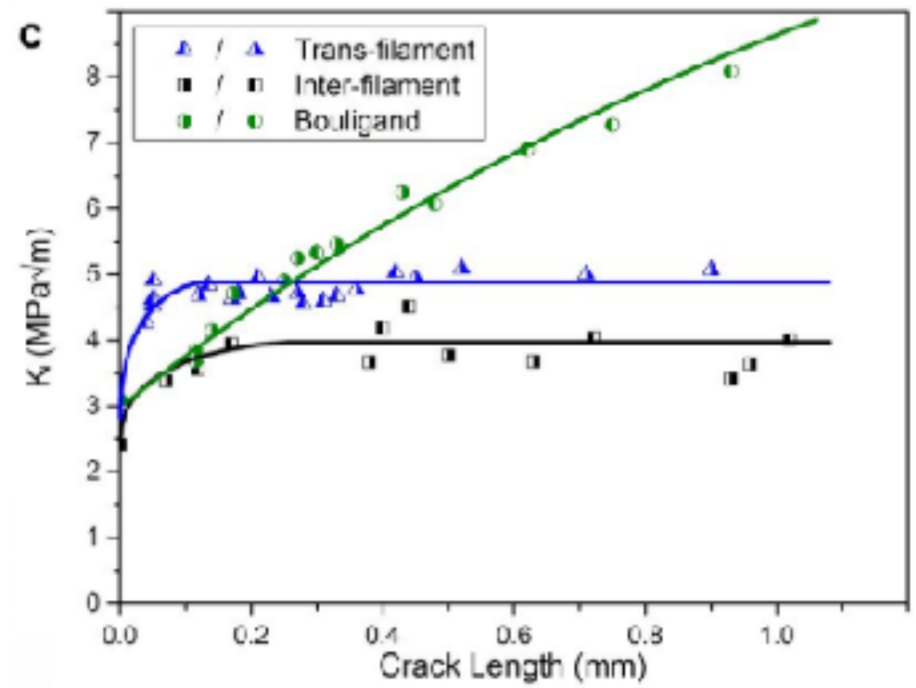
- Materials
  - Materials for harsh conditions (corrosion/high temperature)
  - Ballistics
  - Rational control of interfacial properties
  - Hierarchy
  - Scale up
- Processing
  - Reproducibility
  - Scale-up
  - Transfer to industry
- Models
  - Statistical description of the microstructure
  - Assess relative importance of toughening mechanisms
  - Crack initiation / crack propagation

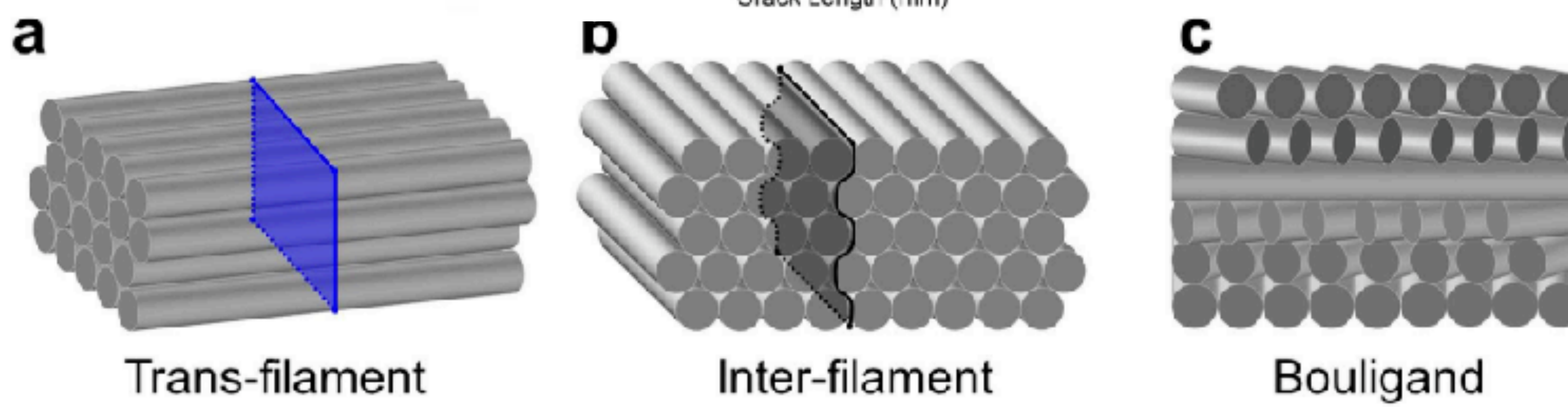
Remaining challenges: control of hierarchy

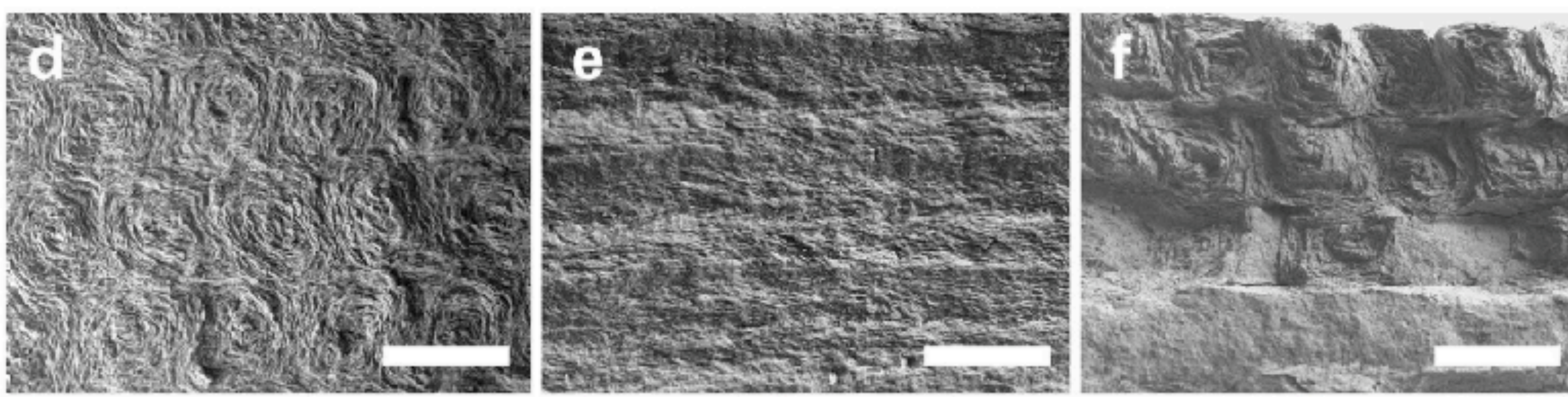


Remaining challenges: control of hierarchy









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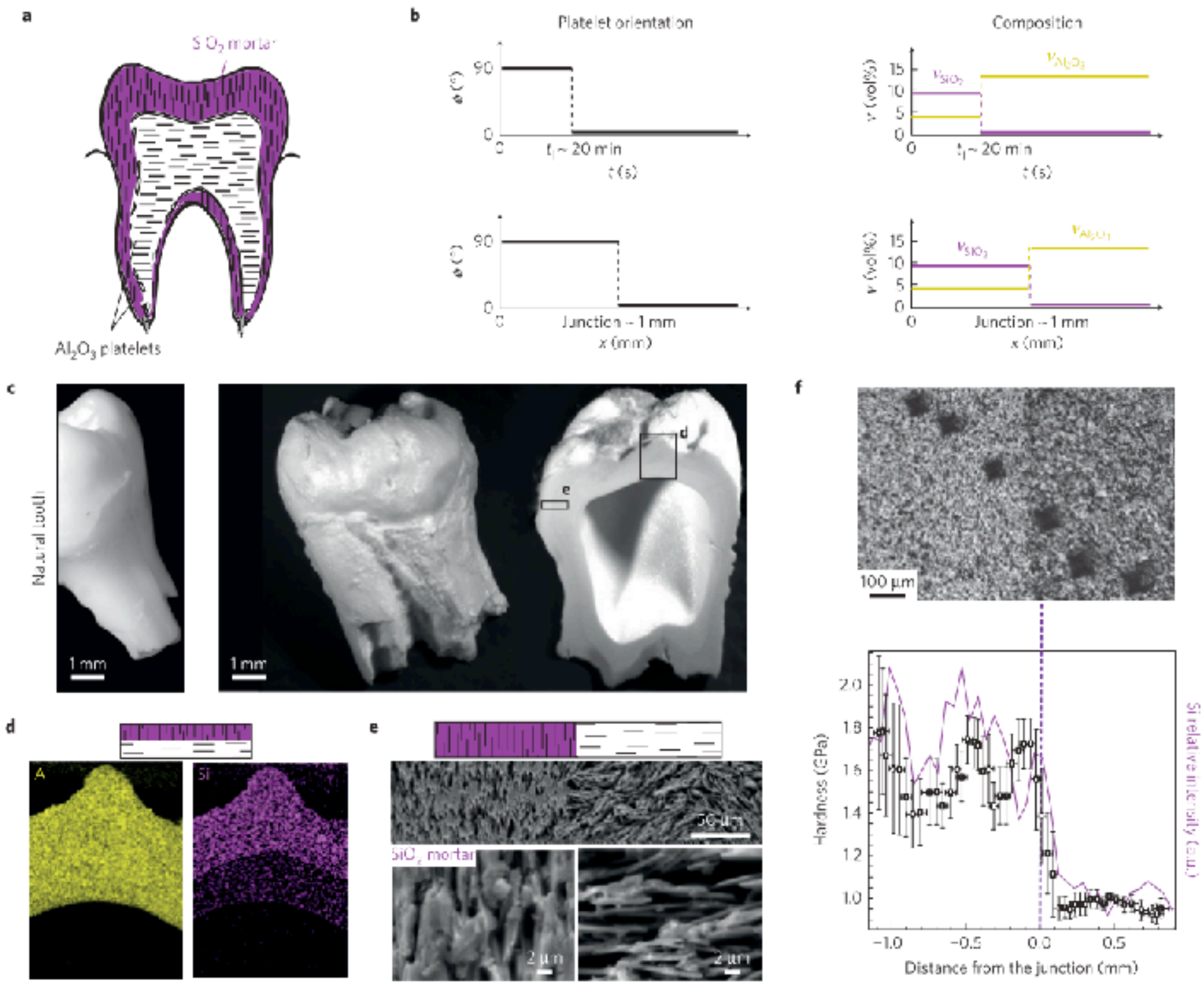
Remaining challenges: control of hierarchy



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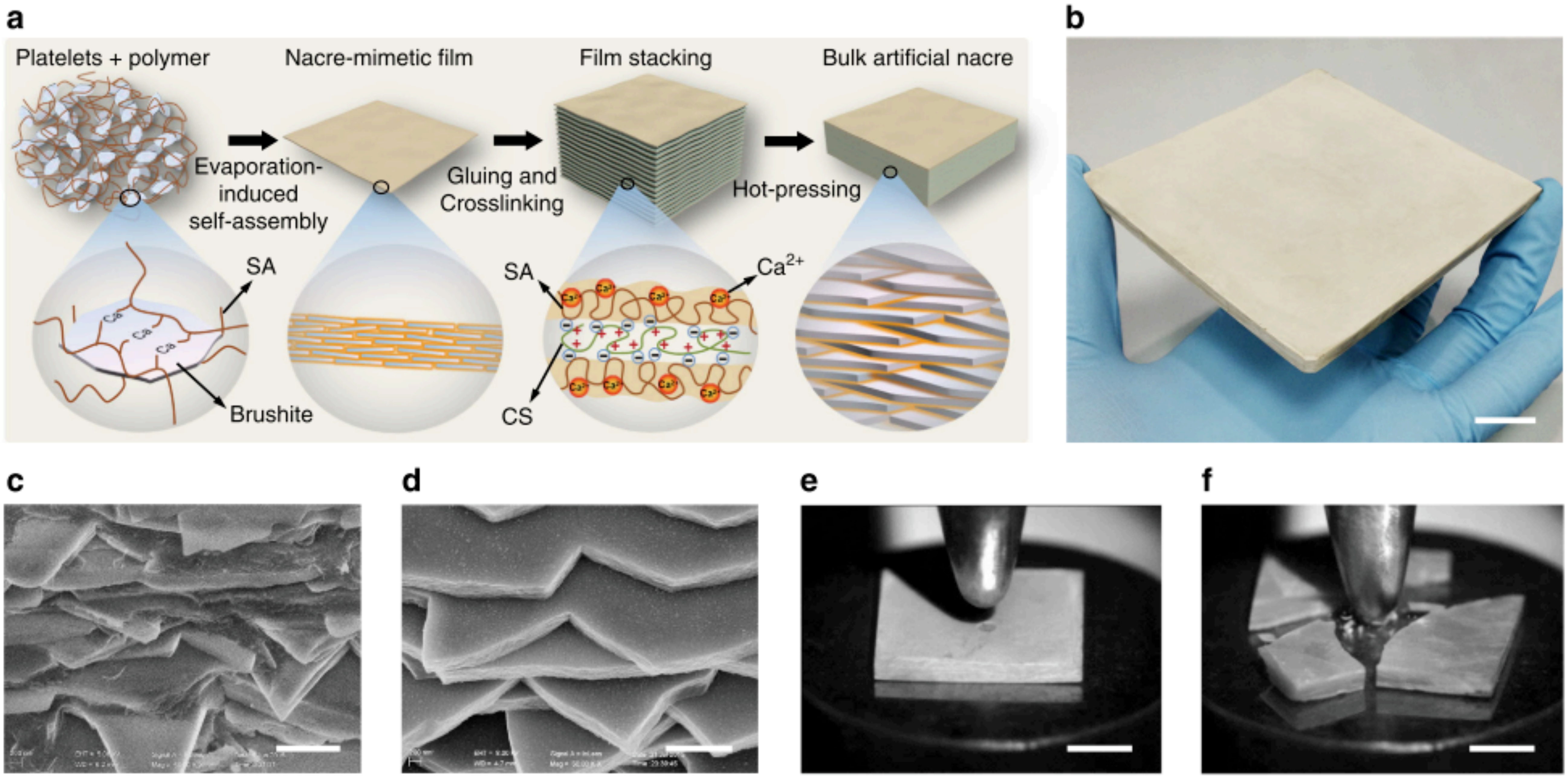
Remaining challenges: scale up



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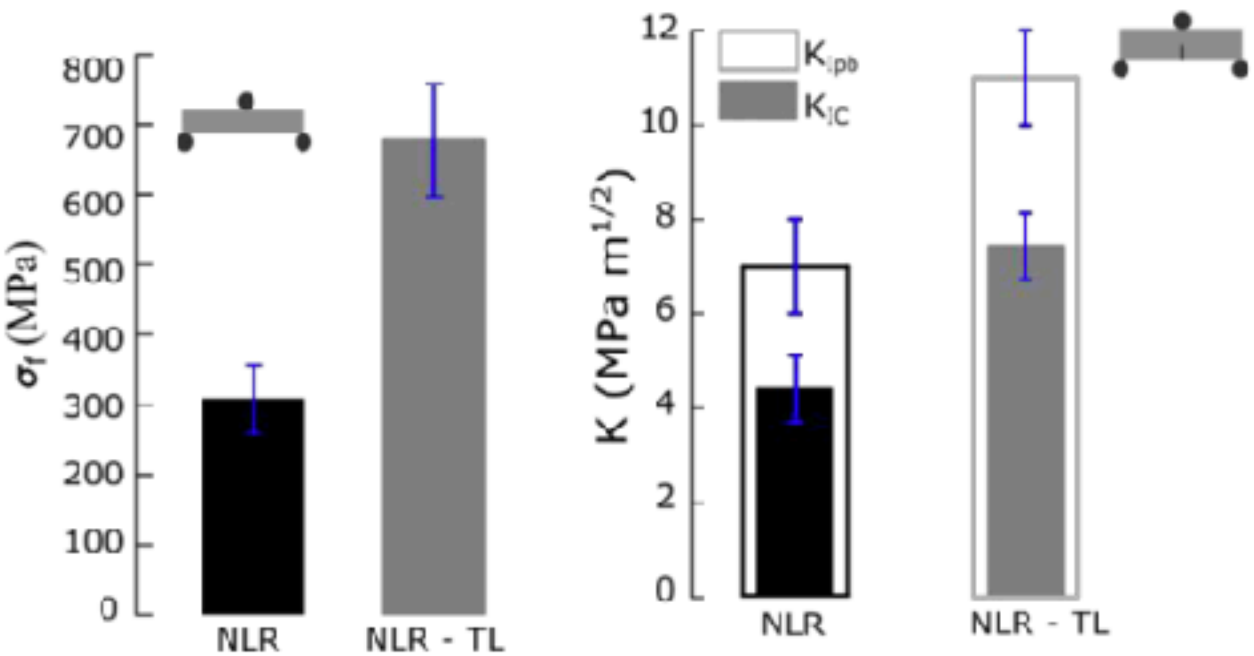
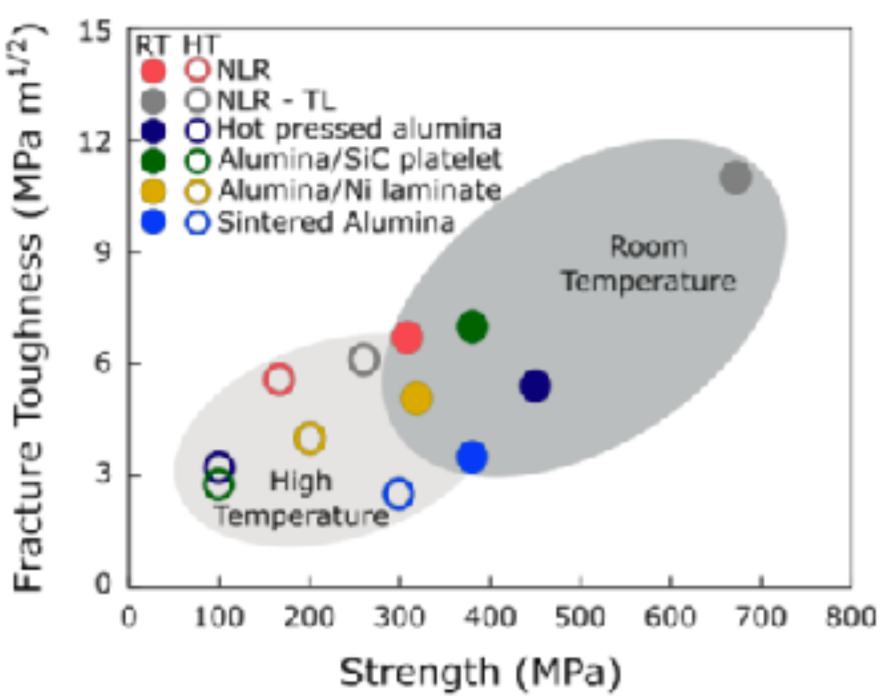
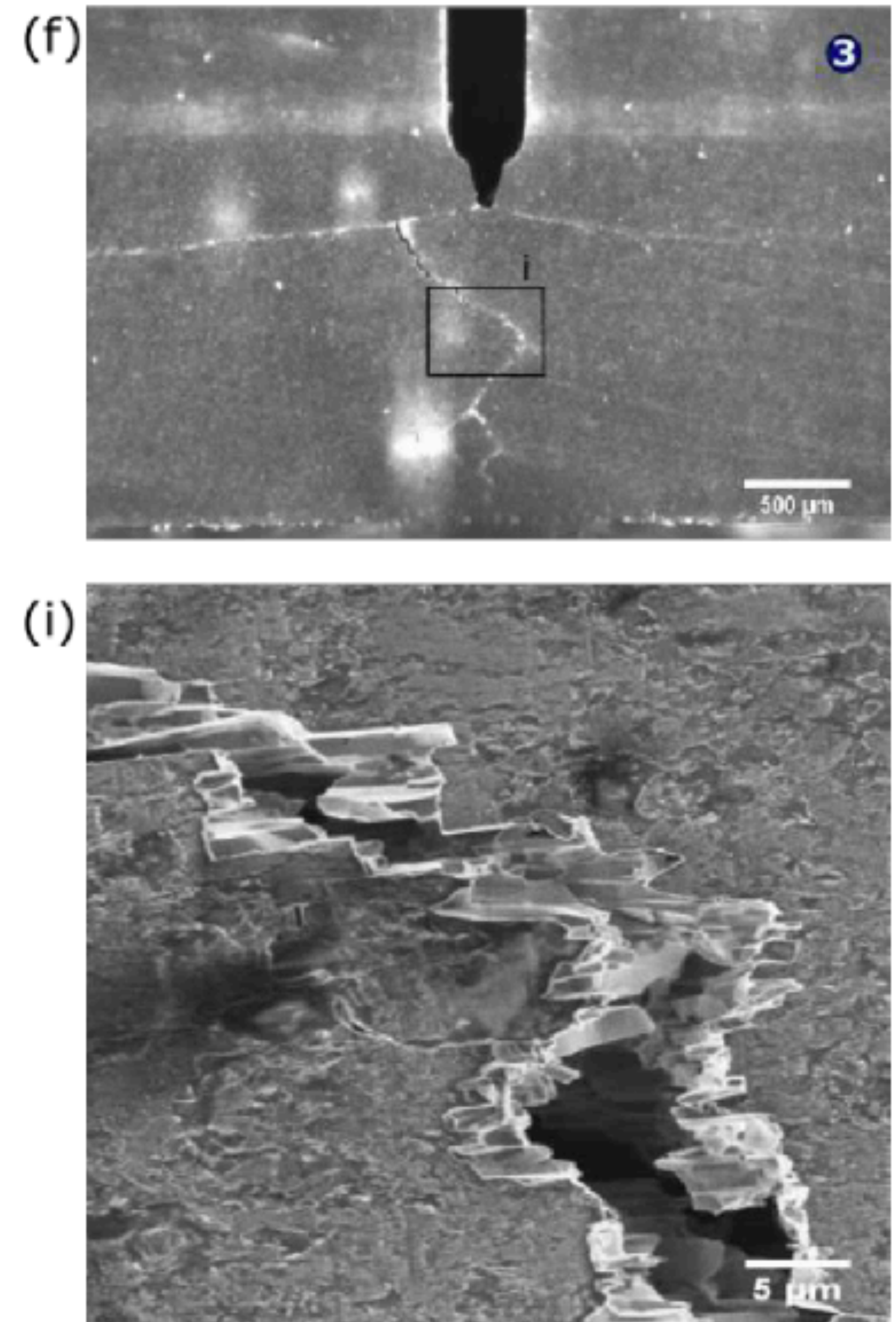
Control of the interface properties

borate interphase instead of aluminosilicate glass







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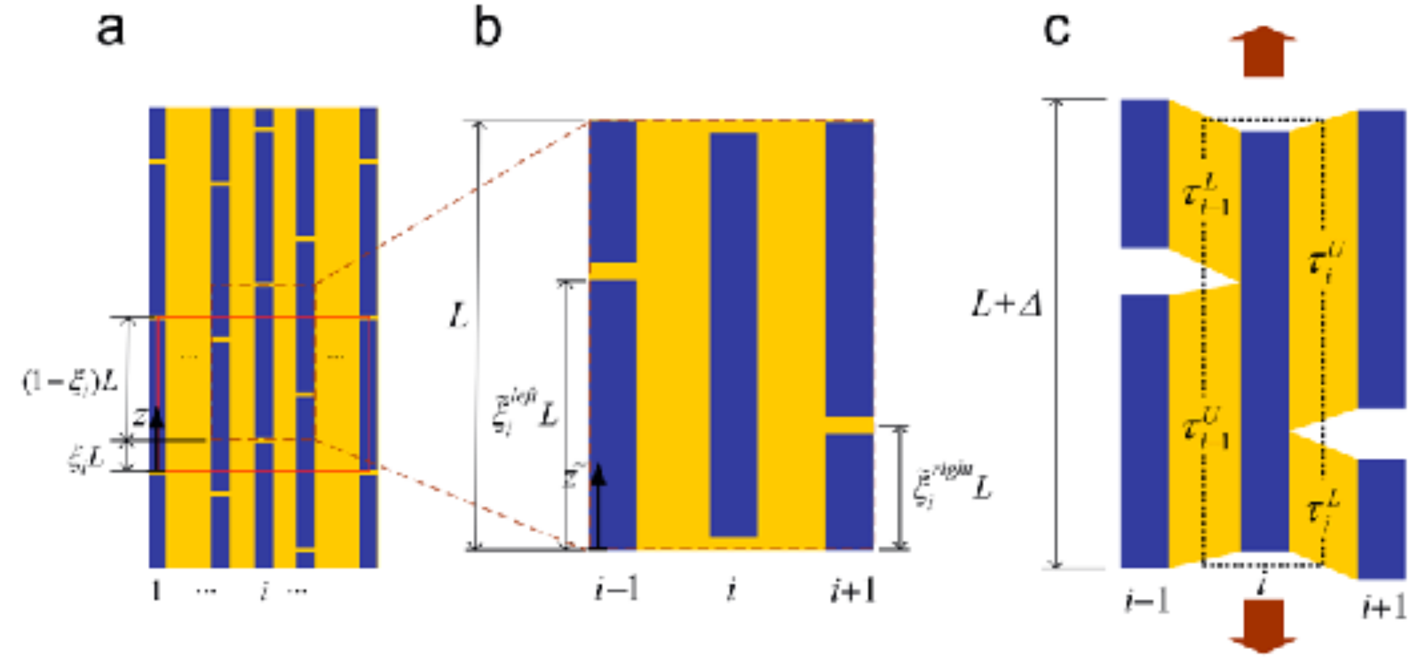
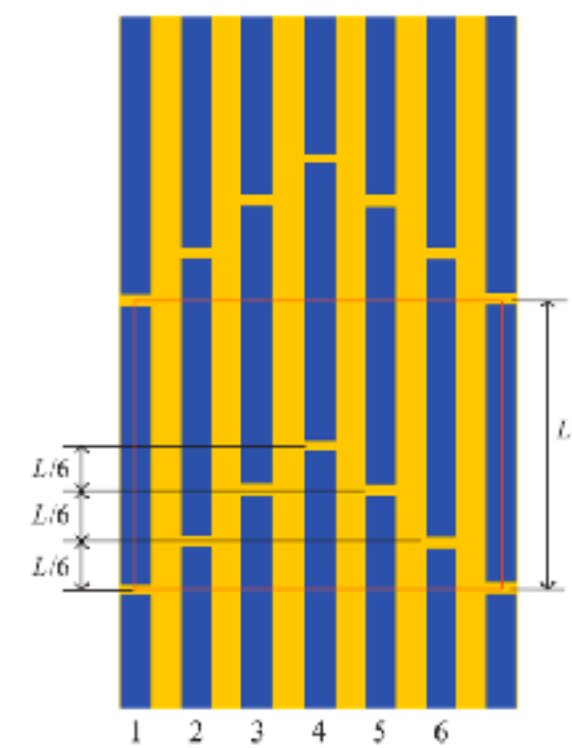
Towards more realistic models?

- How realistic do we need to be?
- Statistical description of the microstructure
  - Platelets orientation
  - Platelets size
  - Bridges distribution

Towards more realistic models?

- Statistical description of the microstructure
  - Platelets orientation
  - Platelets size
  - Bridges distribution
- How realistic do we need to be?
- Synergy between reinforcement mechanism?





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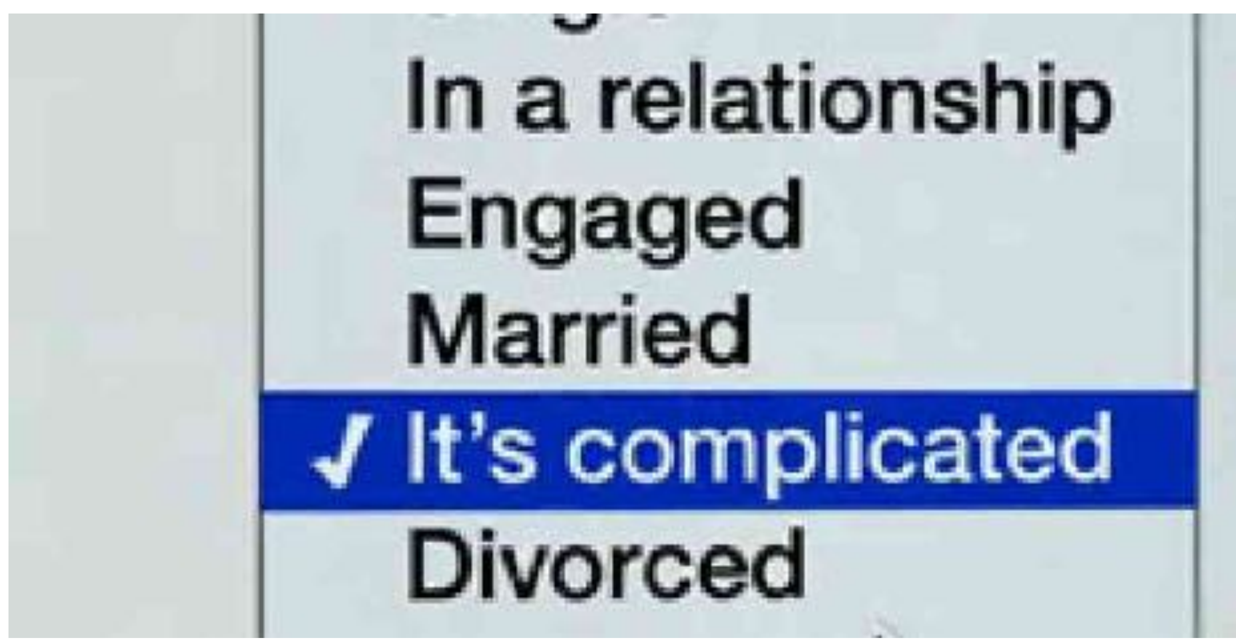
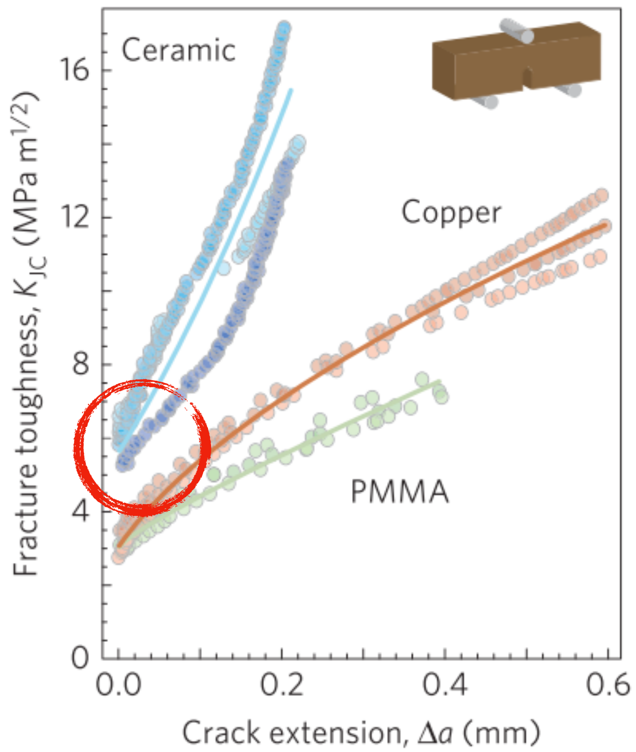
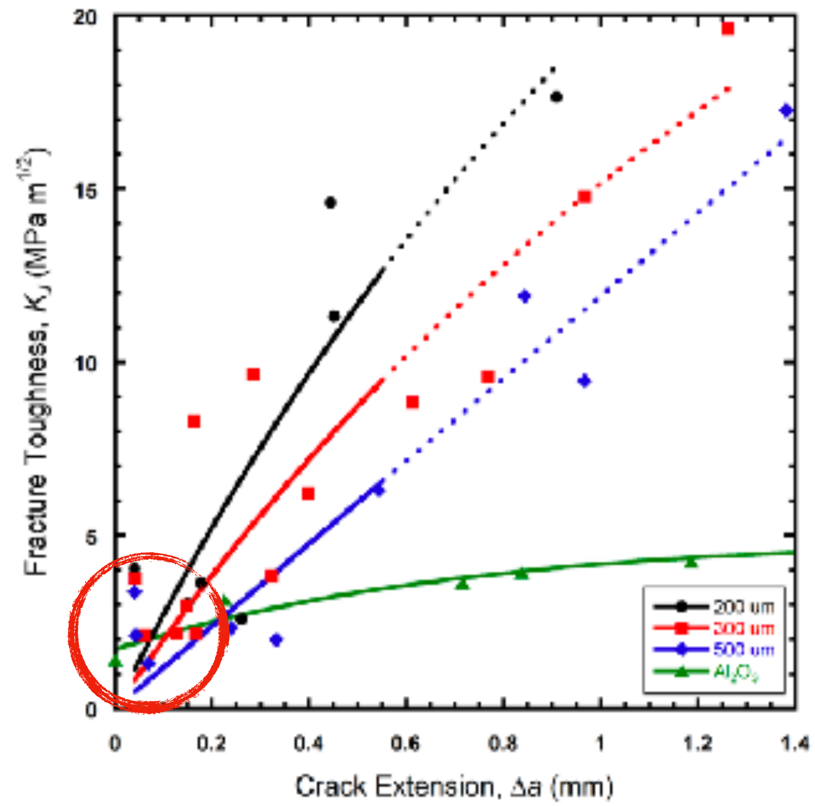
Relative importance of toughening mechanisms?

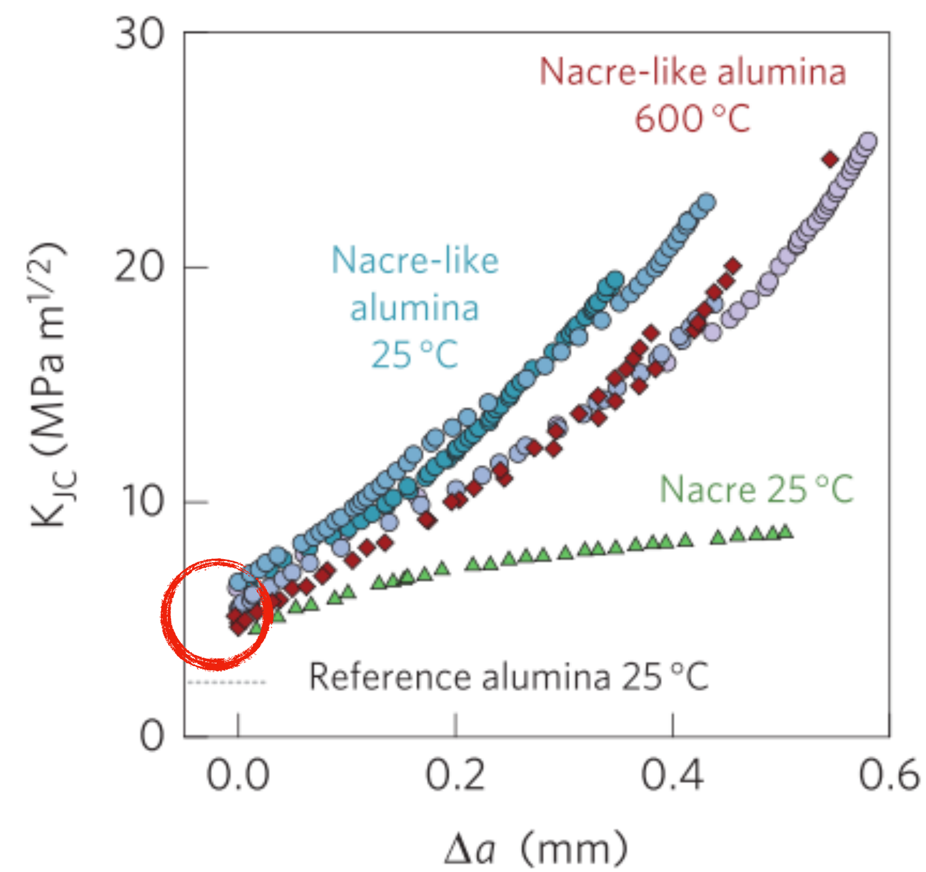
Do we need to replicate every single feature of nacre?

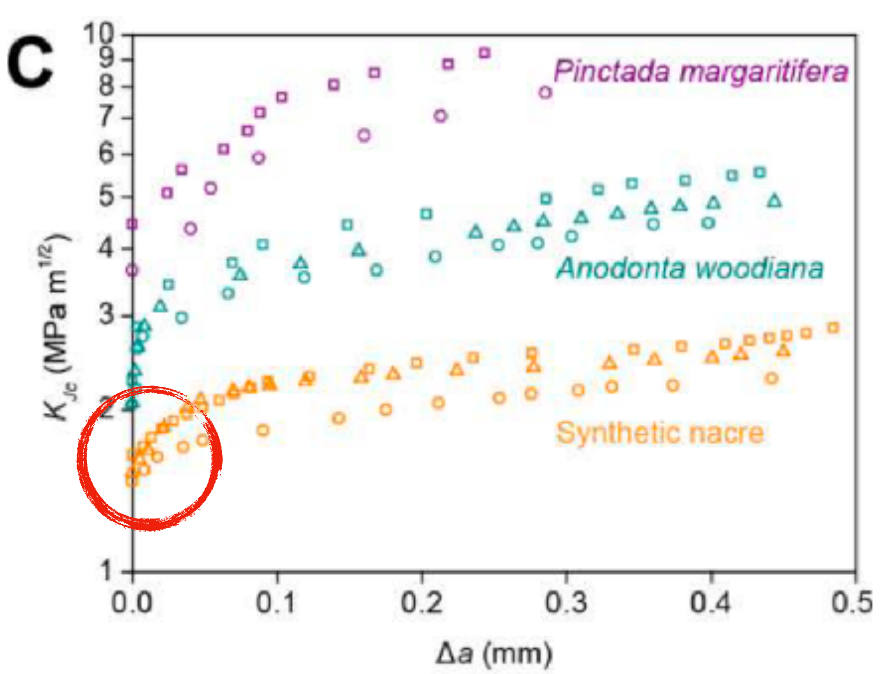


+30 years later, still waiting for applications









Easier to get R-curves than increase initiation toughness

In natural materials, R-curves come with self-repair capacities

Conclusions

- Nacre: a very nice model system (could have chosen among thousands others)
- Mechanics is just one constraint of the problem
- Self-repair would be nice
- Do we focus on the most important problem?