

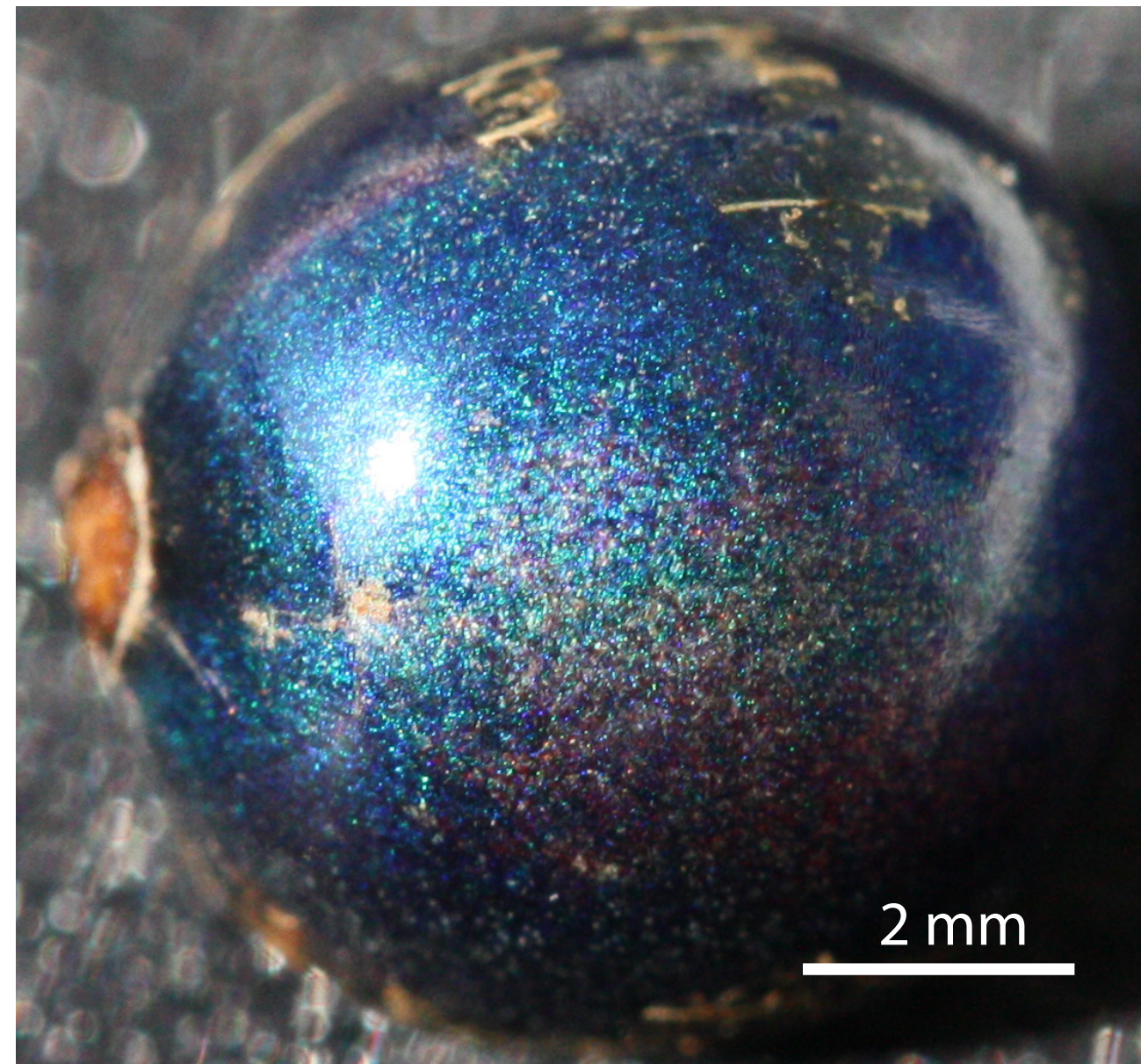
Natural and bio-inspired photonic materials

S. Vignolini

University of Cambridge, Department of Chemistry - Melville Laboratory for Polymer Synthesis - Lensfield Road Cambridge CB2 1EW United Kingdom

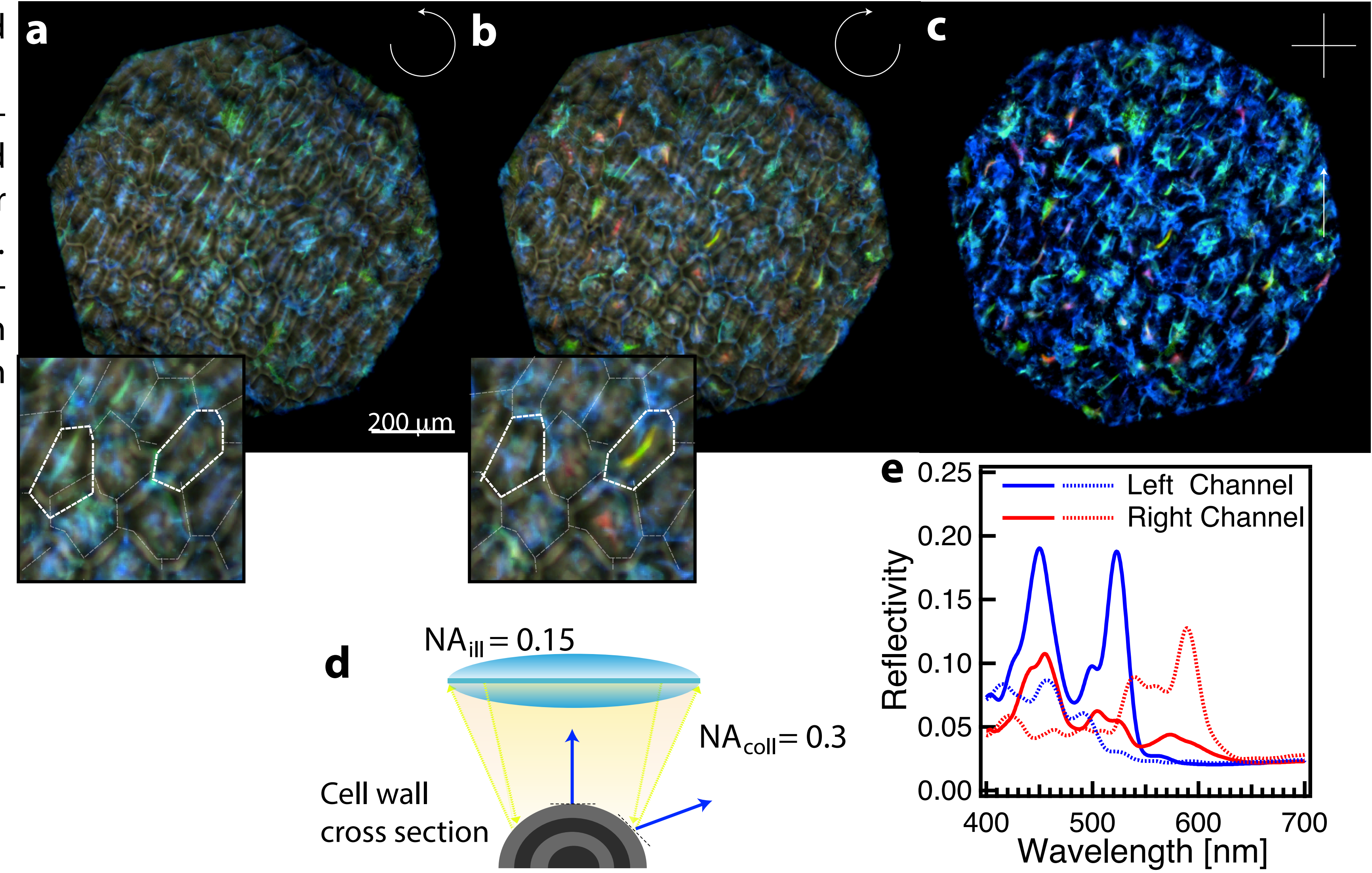
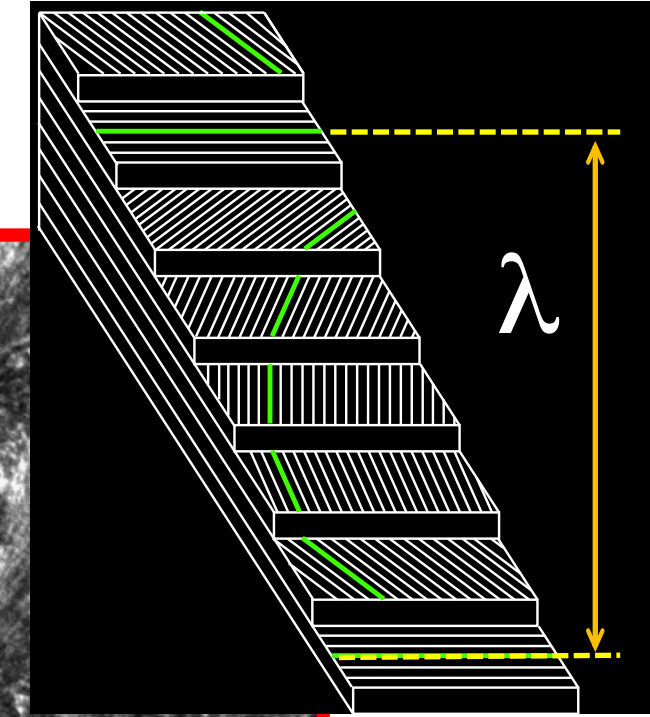
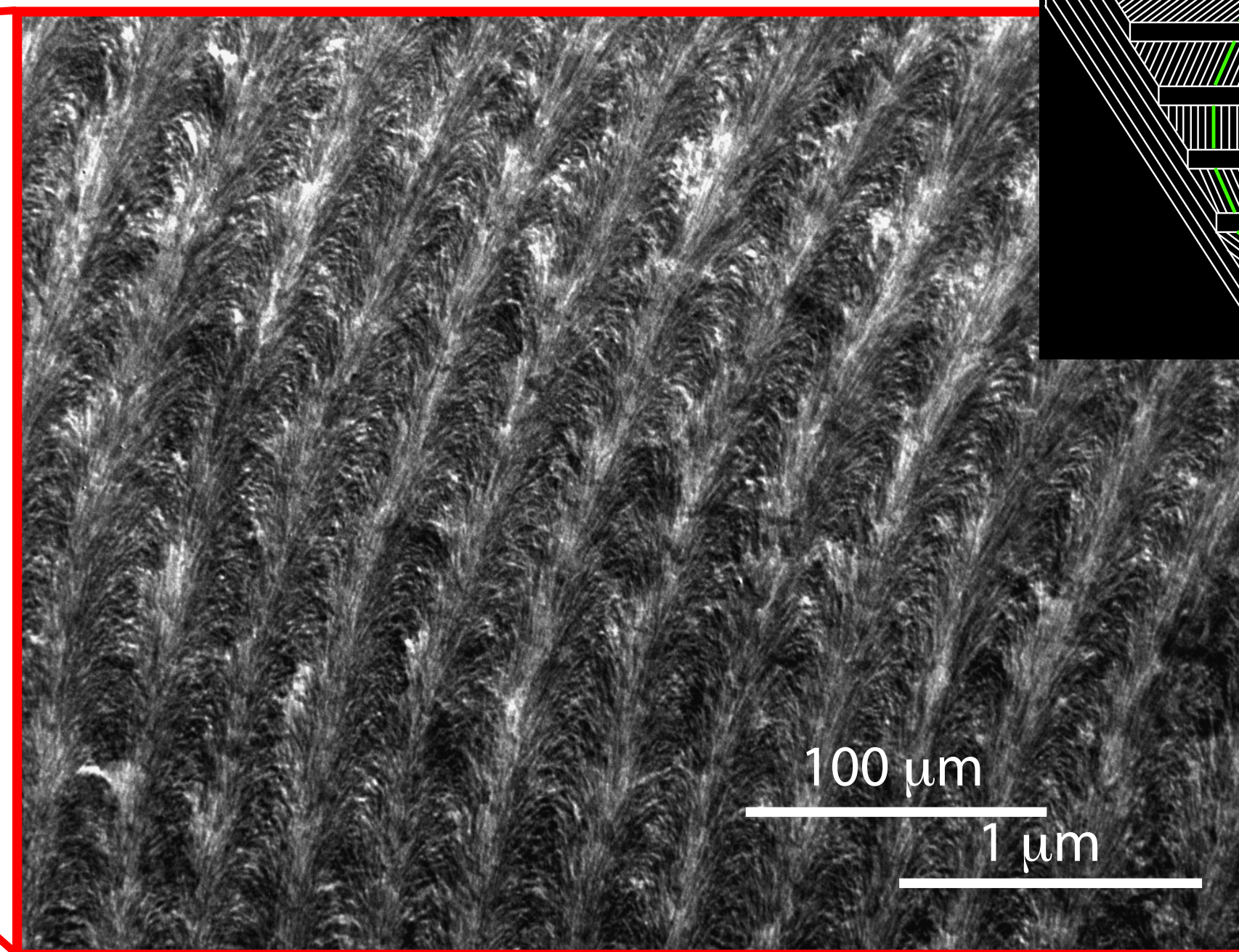
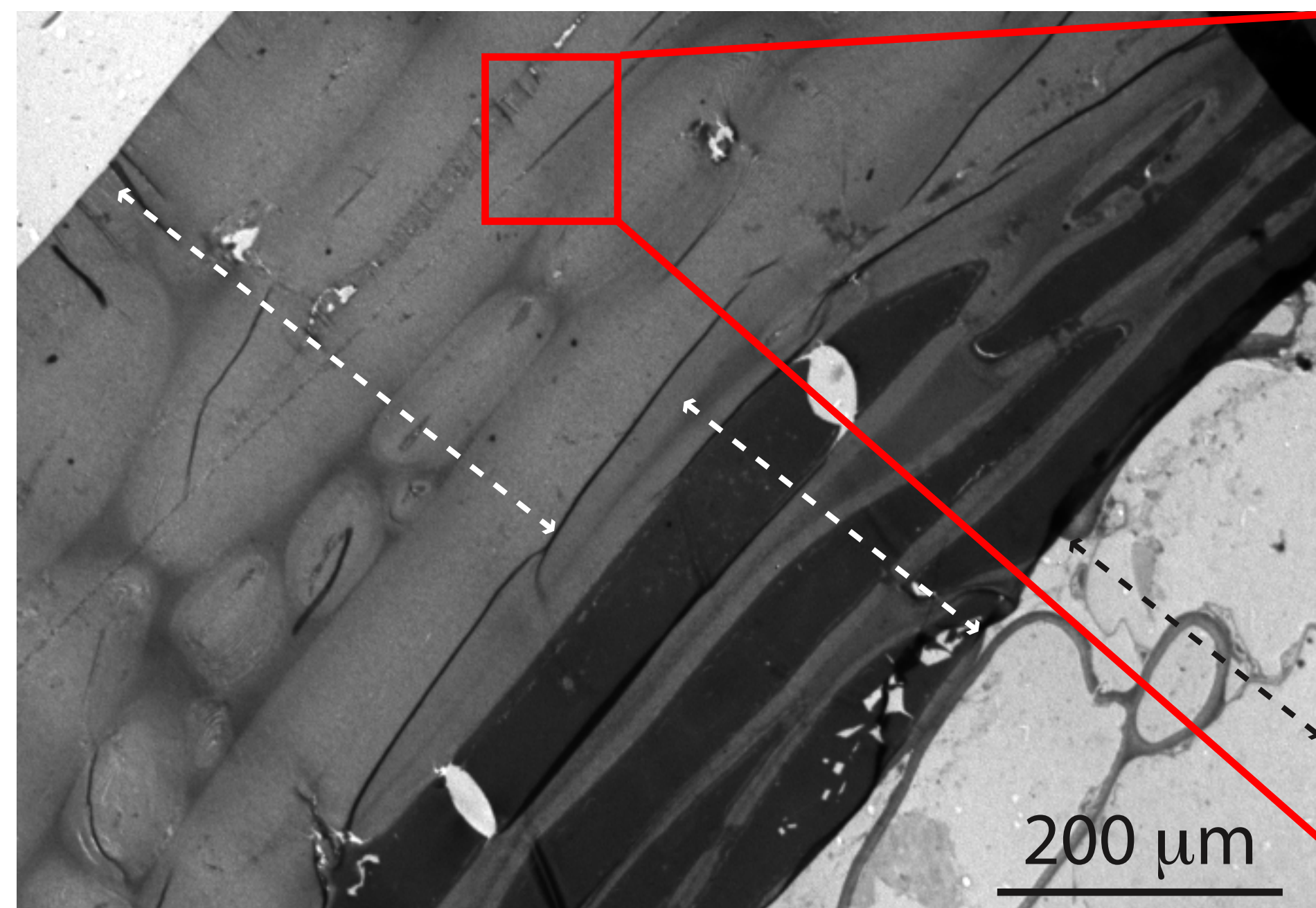
This project will open a new interdisciplinary field of research: natural photonics. The project combines different disciplines and techniques in order to obtain from one side low cost, edible, sustainable photonic materials and on the other to answer fundamental questions about the biological significance, the assembly and the role of disorder in cellulose-based natural photonic structures. Although structural colour in the animal kingdom has been studied and mimicked previously, only very recently plants have also been shown to develop intense and strong structural colours. They achieve this using a simple and very interesting material: cellulose. Cellulose micro-fibrils, found in several types of cells and in a wide variety of plants, form a chiral multilayer structure, which provides a strong and colour-selective reflection of light. The mechanism by which these structures are naturally formed in plant cell walls remains an unresolved problem in developmental biology. Biomimetics with cellulose-based architectures is key to understand biological processes at work during the growth of these structures in cell walls. Importantly it also enables us to fabricate novel photonic structures using low cost materials in ambient conditions since cellulose is the most abundant polymer available on the planet.

Inspiration from nature



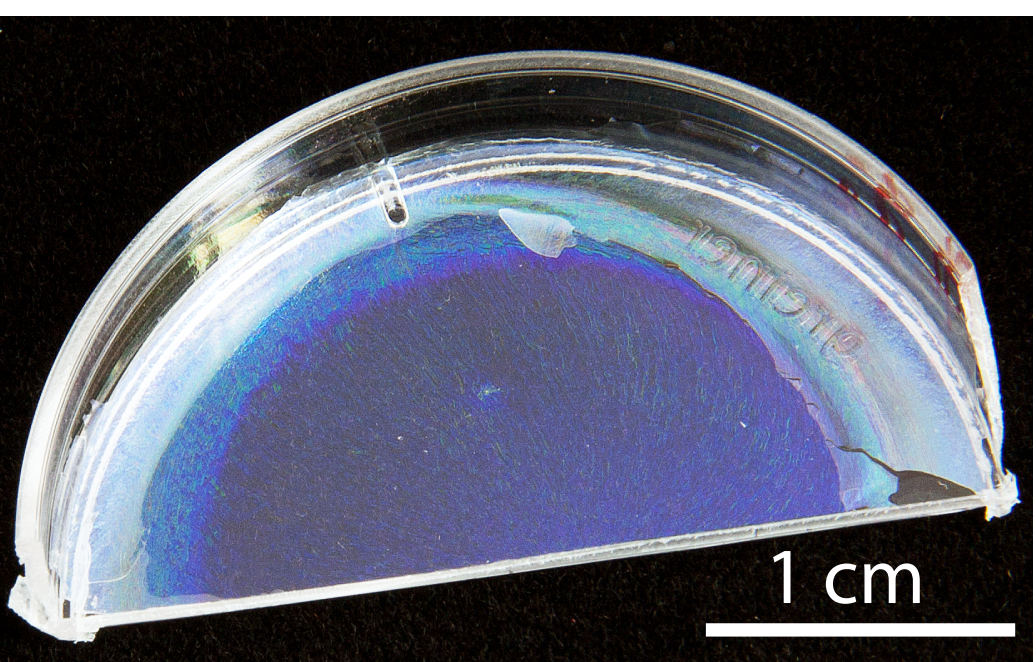
Polia condensata fruits reveal the first example of multilayer-based strong iridescent colouration in plants. The colour is caused by Bragg-reflection of helicoidally stacked cellulose microfibrils, which form multilayers in the cell walls of the epicarp. Uniquely in nature, the reflected colour differs from cell to cell, as the layer thicknesses in the multilayer stack vary, giving the fruit a striking pixelated or 'pointillist' appearance. Because the multilayers form with both helicoidities, optical characterisation reveals that the reflected light from every epidermal cell can be polarised either circularly left or right, never previously observed in the same tissue.

TEM transverse section of the fruit epidermal layer



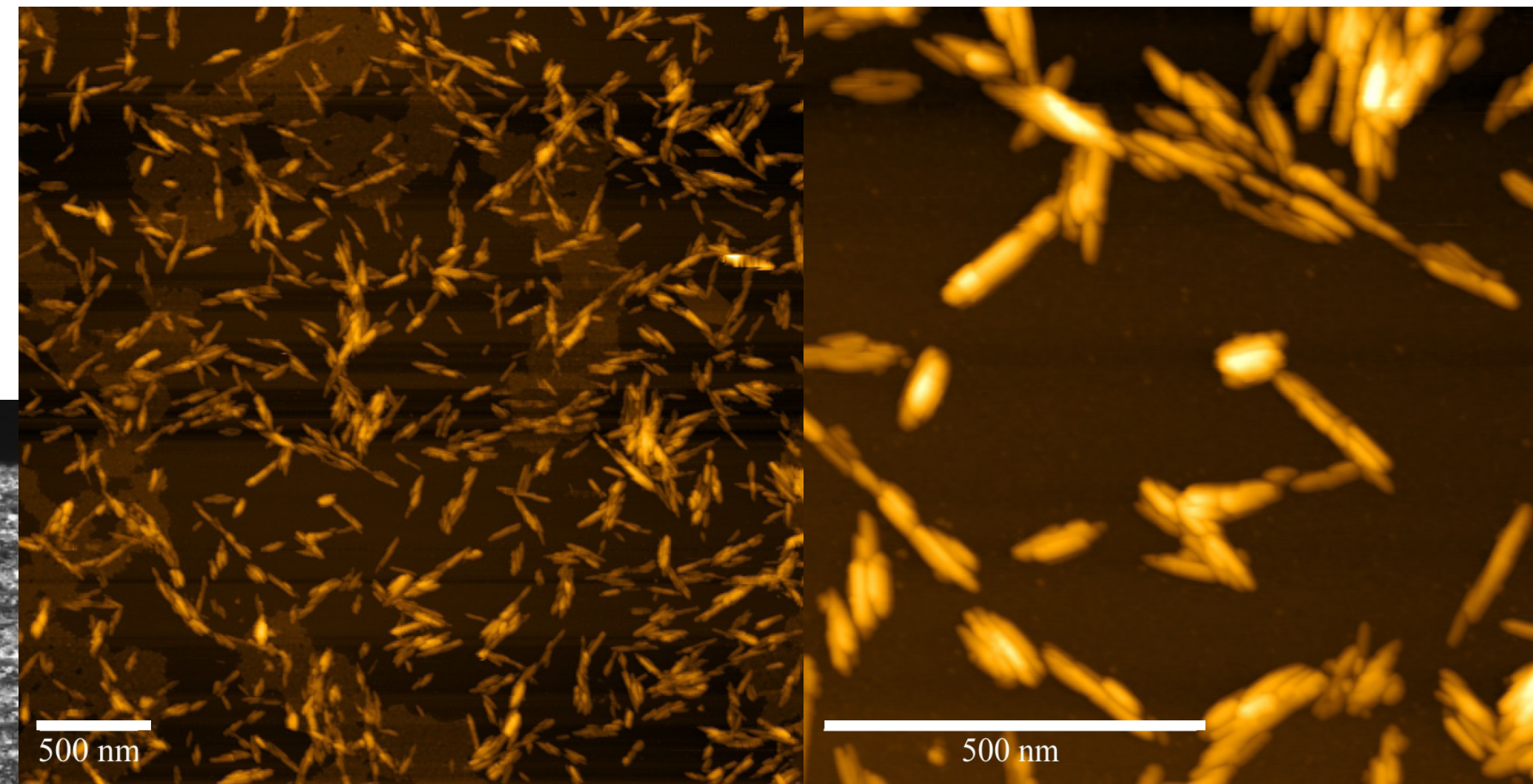
Polarised reflection of Pollia fruit. (a) Left Handed and (a) Right Handed optical micrographs of the same area of the fruit under epi-illumination. The insets show a zoom of the central areas, with white lines delimiting the cells. (c) The same area of the fruit surface was also imaged between crossed polarisers. (d) Schematic representation of light reflection from a curved multilayer, representing the ellipsoidal shape of the epicarp cells. Only light reflected from the central part of the cell is reflected into the numerical aperture of the objective ($NA = 0.3$). This results in a colour stripe in the centre of the cell, as seen in a,b. (e) Spectra from two different cells.

Biomimetic structures: cellulose photonics



SEM transverse section of biomimetic film

AFM of Cellulose nanocrystals



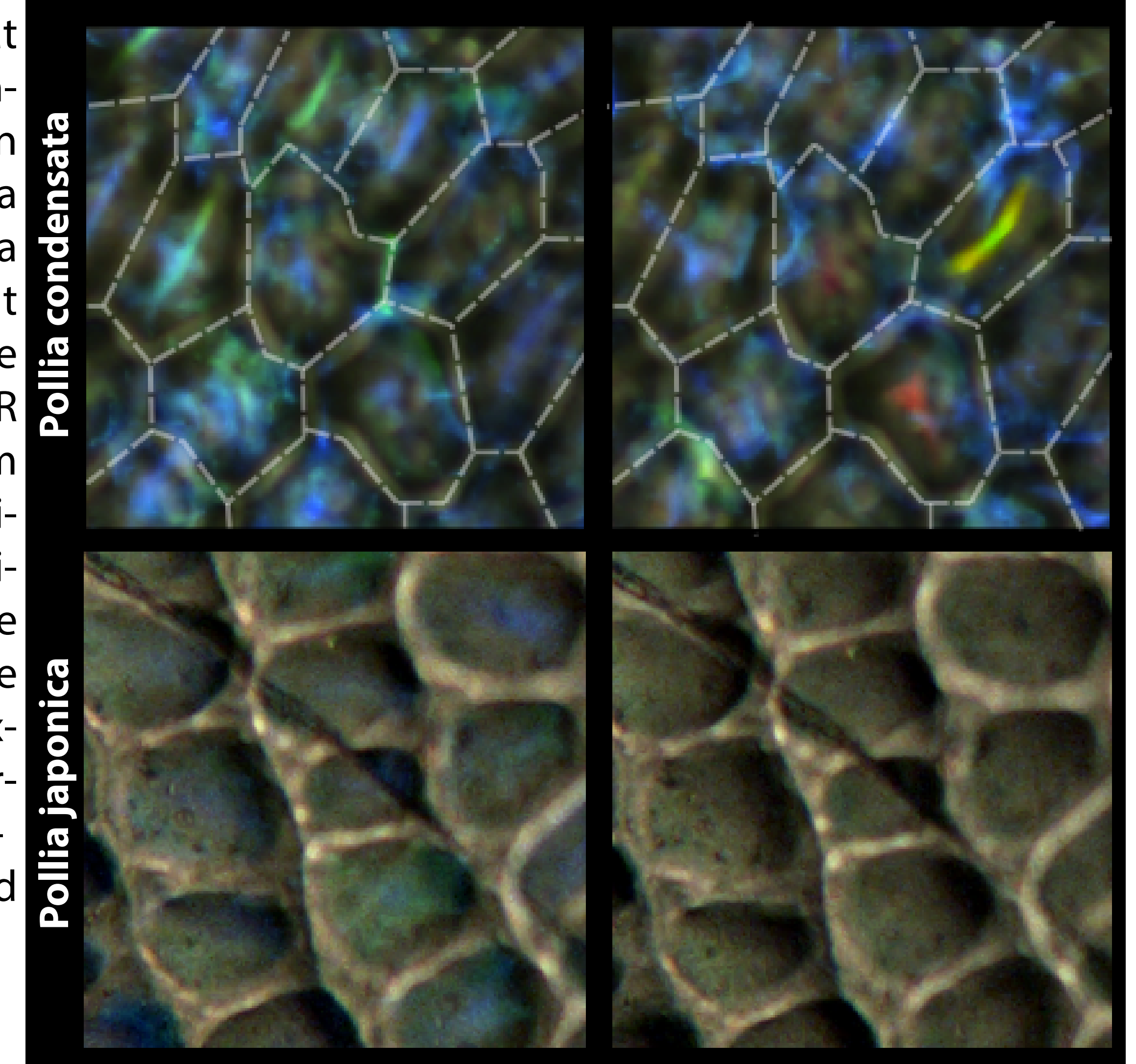
Cellulose nanocrystals can spontaneously assemble in a chiral nematic liquid crystalline phase in water, that can be retained in dry conditions, giving rise to strongly coloured films.

Digital Color in Cellulose Nanocrystal Films, ACS Appl. Mater. Interfaces 6 (15), pp 12302–12306 (2014)
Controlled bio-inspired self-assembly of cellulose-based chiral reflectors, Adv. Opt. Mat. 2, 646-650 (2014)

Cellulose assembly in plants

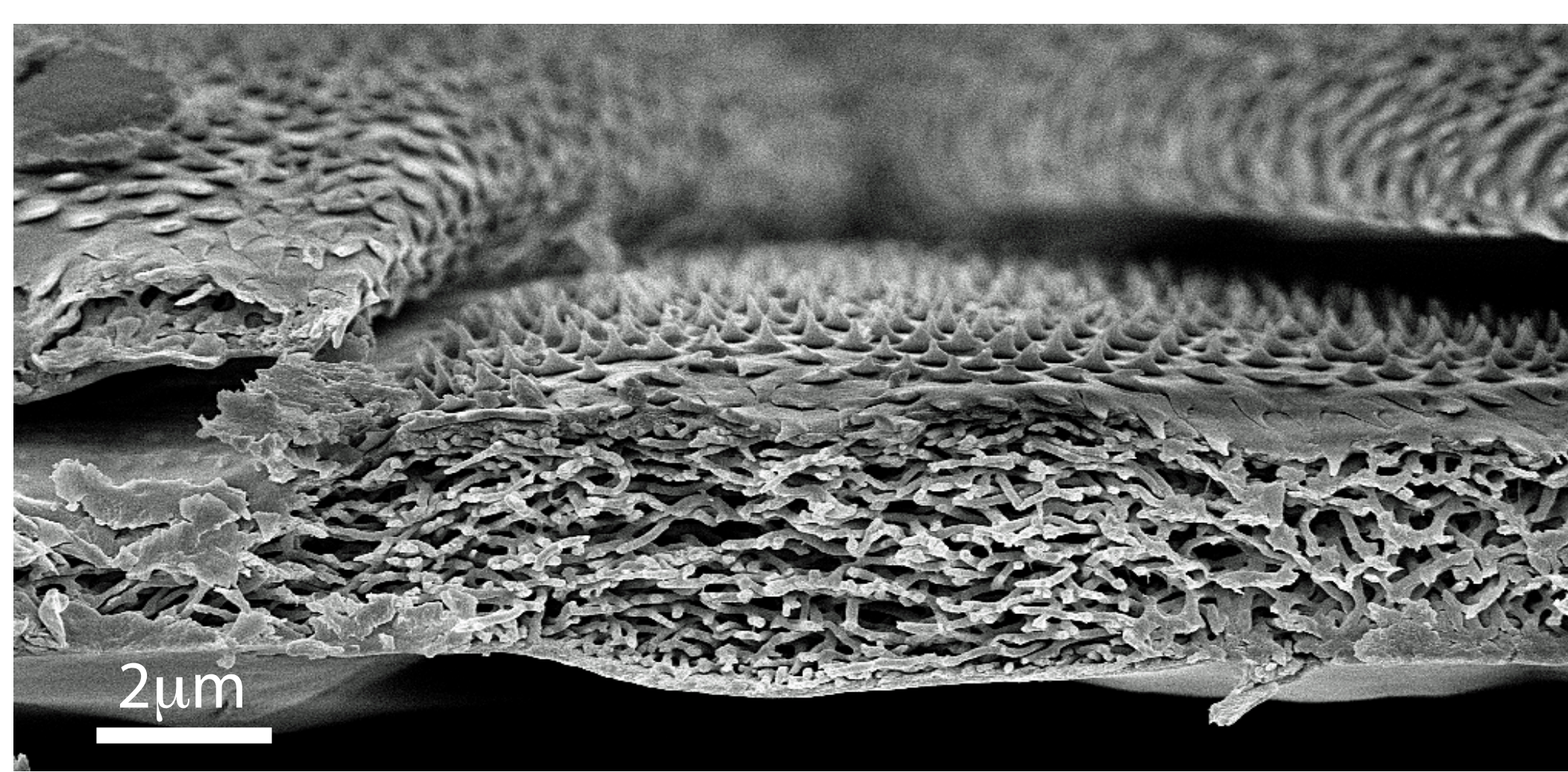
Cellulose from different species of plants, (that show different assemblies of cellulose), in the same genus (*Polia japonica* and *Polia condensata*) at different stages of growth will be extracted. X-ray NMR and Fourier Transform Spectroscopy will indicate the exact composition of the cellulose micro-fibrils. Once the cellulose fibrils are extracted from the different fruits the self-assembly will be tested in water.

Polarisation sensitive microscopy



Disorder in Nature

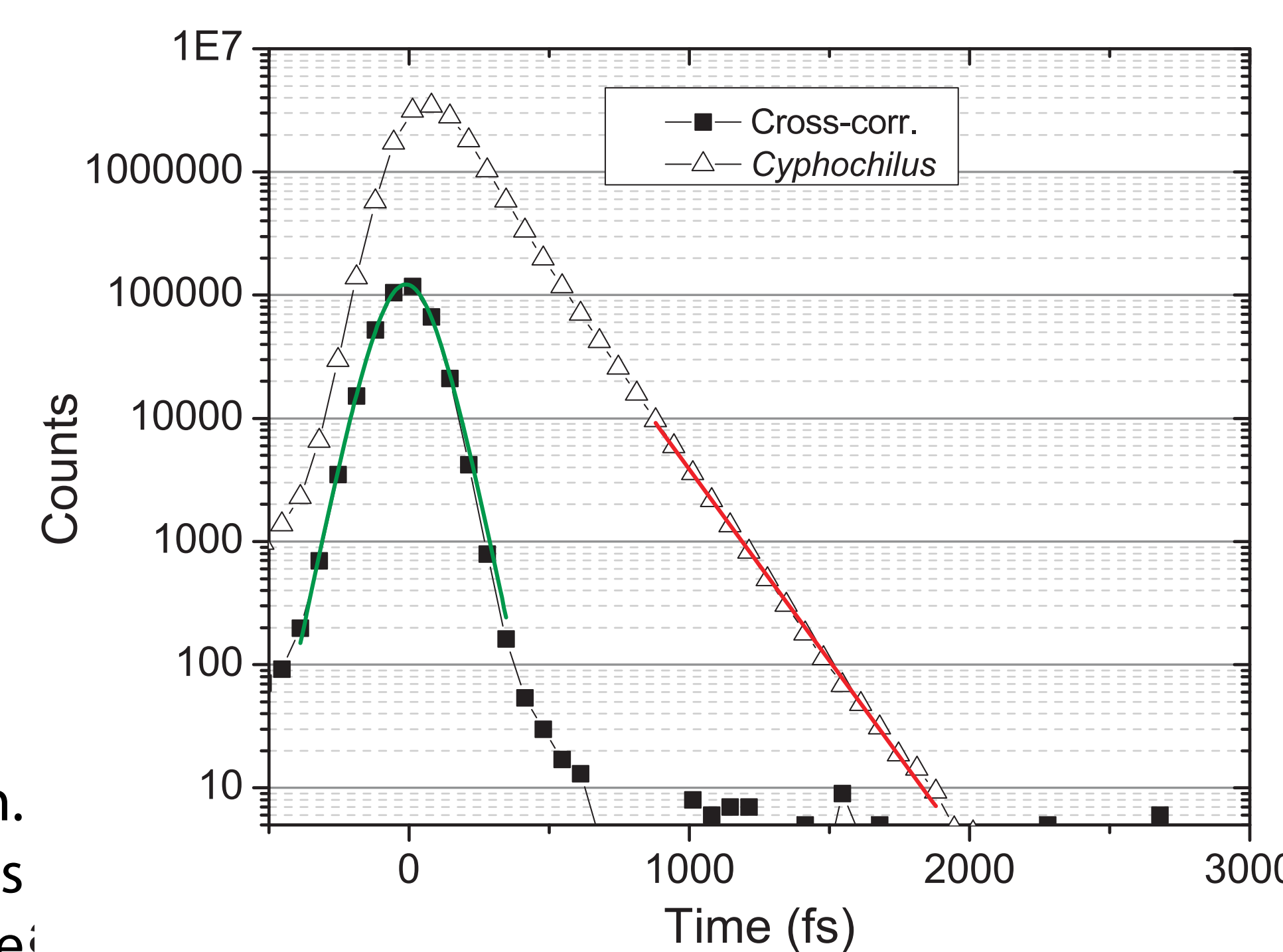
Another aspect I worked on in collaboration with LENS and University of Florence is the optical response of white beetles. We investigated the optical properties of these scales, which have shown that they are able to scatter light more efficiently than any other biological tissue known, which is how they are able to achieve such a bright whiteness. Animals produce colours for several purposes, from camouflage to communication, to mating and thermoregulation. Bright colours are usually produced using pigments, which absorb certain wavelengths of light and reflect others, which our eyes then perceive as colour.



SEM image of Cyphochilus scales in cross section

The ultra-white *Cyphochilus* produces this colouration by exploiting the geometry of a dense complex network of chitin. The nano-structured chitin network have optimised in order to produce maximum white with minimum material. This efficiency is particularly important for insects that fly, as it makes them lighter. Over millions of years of evolution the beetles have developed a compressed network of chitin filaments. This network is directionally-dependent, or anisotropic, which allows high intensities of reflected light for all colours at the same time, resulting in a very intense white with very little material.

COLLABORATION with Prof. D. WIERSMA University of Florence Italy



Bright-White Beetle scales Optimise Multiple Scattering of Light, Sci. Rep. 4, 6075 (2014)

Time-of-flight of light transmitted through the scale of *Cyphochilus* (open triangles). The reference measurement (cross-correlation) of the probe pulse is shown as black squares. The fit of the pulse transmitted through the scales exhibits an exponential tail with lifetimes of $\tau \approx 140$ fs corresponding to a scattering mean free path of less than $2 \mu\text{m}$, value still impossible to achieve with man-made materials with the same refractive index.