BIO-BASED OPTICAL AND PHOTONIC MATERIALS:

TOWARDS NATURE-BASED PRODUCTION METHODS FOR PHOTONICS

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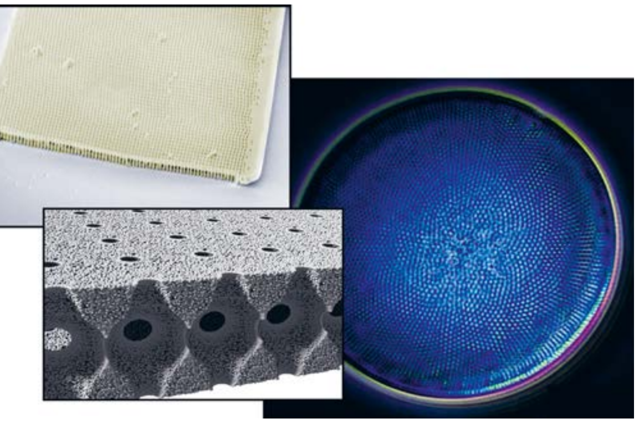

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Nature has been a source of inspiration for the fabrication of new optical materials for centuries. During the last decades, the rapid developments in nanofabrication allowed mimicking the photonic properties of living organisms towards more efficient functional devices. But nanophotonics still relies on nanofabrication techniques and materials not compatible with the current environmental challenges. Bio-based optical materials have emerged as a sustainable alternative combining the best of both worlds: precise nanostructuring and unique optical properties with environmentally friendly natural production protocols.

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PHOTONIC NATURAL SYSTEMS BEYOND BIOINSPIRATION

The very urgent climate emergency demands advanced materials sustainable both in their properties and their fabrication procedures. Reducing carbon footprint is a top priority worldwide. Under this scenario, making the properties of photonic materials more efficient for a particular application is not enough. The fabrication and manipulation of those materials should be sustainable and with the smallest carbon footprint possible. In this context, Bio-based Optical Materials (BOMs), advanced optical materials produced by living organisms, have been raised as a sustainable alternative for future photonic technologies.

Indeed, natural systems can overcome man-made optical technologies [1]. And although BOMS can show extraordinary anisotropies or narrow absorptions due to their material composition, they usually present low refractive indexes reducing their possibilities as bulk photonic materials. Interestingly, natural systems can produce very complex structurations at all scales providing BOMs with advanced photonic properties. The most studied case of BOM optical nanostructures are the scales of insects and feathers of birds, responsible for bright and resilient structural colours. But in recent years, a large family of BOMs with functionalities beyond colour display such as enhanced sensitivity in vision or thermal protection have been discovered.

These discoveries triggered at first biomimetic implementations which consisted mainly of top-down approaches where, to solve a specific technological need, researchers seek into nature a "blueprint" that fulfils the device requirements. But this approach suffers from the same limitations and large carbon footprint as non-biomimetic technologies. To solve this, a new family of BOMs are being developed in which living systems are not just an inspiration but the actual source of functional photonic nanomaterials. BOMs such as silk, lignin or bacteria are already showing interesting possibilities. In the following, we discuss the three main types of photonic BOMs depending on their optical properties and their level of technology implementation.

BIOPOLYMERS IN NANOPHOTONICS

Biopolymers are natural polymers produced or derived from cells of a living organism. In a biopolymer, the monomer unit is replicated to form a larger molecule and render some of the most important molecules for life such as DNA or cellulose. Although biopolymers can vary widely in composition, their material properties have been extensively studied and exploited at both research and industrial scales. However, their use in photonic technologies has been very limited. In recent years, developments in nano and biotechnology have opened the possibility to use biopolymers as actual photonic devices in a wide set of applications, particularly for biopolymers based on proteins and polysaccharides.

One of the most studied cases of photonic biopolymers in nature is chitin. Chitin is a polysaccharide present in the exoskeletons, wings and cell walls of many organisms (Fig.1). Optically, chitin presents a homogenous refractive index (approx 1.55) with neglectable absorption in the VIS. A couple of decades from now, the seminal works in the field showed that chitin forms complex nanostructures such as 3D photonic crystals [2] which promoted the developments of biomimetic devices based on these structures (Fig.1) [3]. However, the growth of chitin photonic nanostructures in the laboratory has not yet been achieved.

Despite chitin's interesting properties, probably the most studied

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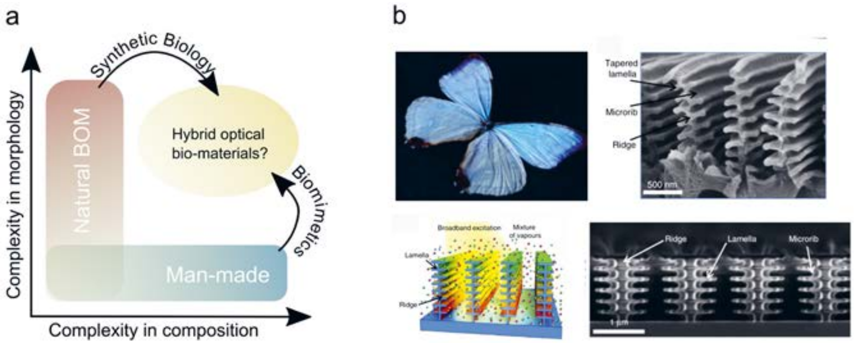

Figure 1. a) Man-made photonic nanostructures benefit from material complexity. Natural photonic materials on the other hand are often simple in composition but they can present complex morphologies with diffrent levels of structuration. While biomimetic approaches might allow to reach higher degrees of morphological complexity, the use of synthetic biology methodologies might enable similar performance with greener implementations. Figure adapted from [1]. b) Example of bioinspired photonic nanostructures. The strong blue color of the wings of a *Morpho* butterfly (left) is produced by interference at the 3D chitin nanostructures (top right). Bottom right shows the biomimetic counterpart produced by patterning PMMA polymer using e-beam lithography. The PMMA has a refractive index n=1.49 across the visible and negligible extinction coefficient (extracted from Ref. [3]). In a gas sensor implementation, different vapours fill the nanopores inducing a local refractive index change detectable as variation in the reflected color (bottom left).

example of photonic biopolymers in the last years is cellulose. Cellulose is a polysaccharide biopolymer present in plants and is also the most abundant biopolymer on earth. From an optical perspective, cellulose is a homogenous material with a relatively low refractive index (n≈1.53). However, it can arrange to form chiral structures in cell walls. The formation of such chiral photonic crystals provides these cell walls with some of the brightest colours in nature [4] (Fig.2b). In recent breakthroughs, these structures were replicated in the laboratory by inducing the self-assembly of cellulose nanofibers and nanocrystals which lead to the fabrication of large-scale, cost-less and sustainable cellulose-based photonic devices [5] (Fig.2c).

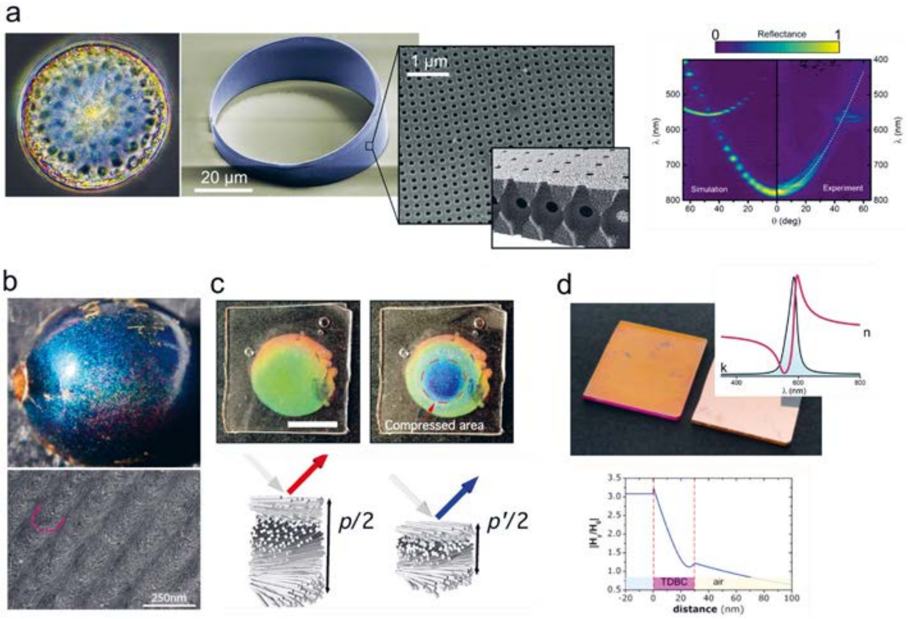

Figure 2. a) Biomineralization in diatom microalgue can produce high quality slab photonic crystals. The image shows a specimen of species *C.granii* (left), a biosilica membrane (known as girdle band) after separation from the organic material and a close up of the natural slab photonic crystal. The biosilica membrane is approximately 1 um thick and it is perforated by a square lattice of period a≈300nm well preserved among individuals of the same species. Angle resolved spectroscopy (right) shows the dispersion corresponding to a low contrast slab photonic crystal structure. Data extracted from [8]. b) In some organism (in the image fruit of *Pollia condensata*) cellulose can form Bragg-like stacks with a chiral twist as shown in the electron micrograph (images extracted from [4]). c) Encapsulation of hydroxipropil cellulose in PDMS polymer can be controlled in the laboratory to obtain chiral Bragg-like reflectors tunable through pitch selection. The central wavelength changes upon compression of the cellulose multilayer (image extrated from [5]). d) Organic excitonic dyes found in nature can show narrowband highly resonant dielectric constants (inset) allowing strong reflectance and surface polariton propagation. In the image, photograh of a thin film of gold (right) and J-agregate TDBC molecule (left) embedded in a Poly(vinyl alcohol) (PVA) matrix. Note the metallic narrowband strong reflection of the organic film. Surface polariton modes are supported at both interfaces of the J-aggregate film as shown in the magnetic field calculation. Images extracted from [7].

NATURAL PIGMENTS FOR RESONANT PHOTONICS

Many organisms showing advanced optical properties present a combination of biopolymers and organic pigmentations within the same nanostructure. Interestingly, the organic dye can induce a strong resonance in the dielectric constant hence adding an extra parameter in the "design" of the natural photonic structure. Probably the most interesting case of natural pigment-protein systems is the molecular complexes responsible for photosynthesis. In these complexes, the chromophores are compactly arranged within a protein scaffold. The proximity of the chromophores in the nanostructure allows the delocalisation of excitons among them, rendering an almost unity efficiency of energy transport [6].

Interestingly, the exciton delocalisation of photosynthetic complexes can be mimicked by bio-supramolecular assemblies known as J-aggregates which are present in some molluscs, plants or fruits. The delocalisation of the exciton within the monomers forming the supramolecule provides them with narrow and strong resonances bringing up shinning colours. Noteworthy, J-aggregates can be embedded in polymer matrix allowing their incorporation into photonic nanostructures. The final composite is a strong dispersive material [7] with a resonant dielectric constant which provides these materials with metal-like optical properties and support for surface exciton-polaritons (Fig 2d). Moreover, they can be incorporated as sharp absorbers into photonic cavities for strong coupling polaritonics. These properties could open the door for the development of metal-free resonant nanophotonics and metamaterials fully based on naturally produced organic matter.

PHOTONIC MATERIALS THROUGH BIOMINERALIZATION

Biomineralization is the process by which many endos- and exoskeletons in living systems as algae, clams or plants are formed. The outcome of biomineralization is organic-inorganic composites that can show intricated hierarchical nanostructures often providing the living organism with stiffer and harder properties than biopolymers. As with biopolymers, the interest in these BOMs has drastically increased during the last few years. Firstly, the composition of biomineralized BOMs is often based on calcium salts (calcification) or silicon oxides (silicification), both compatible with current photonic technologies. In addition, they present multidimensional photonic-scale structuring with features at least as precisely defined as those obtained with complex etching and patterning techniques in the cleanroom (see Fig.2a).

In this context, diatom microalgae are one of the most interesting BOMs. They are unicellular organisms whose most characteristic feature is a silica-rich exoskeleton, known as frustule, which size can range from tenths to hundreds of microns per cell. Their photonic properties were debated for decades but it was recently demonstrated that the frustule can show slab photonic crystal features comparable to those produced with man-made nanofabrication [8]. Moreover, diatoms photonic biosilica structures can be doped during cell growth by adding organic dyes or plasmonic nanoparticles paving the way to *in-vivo* production of ad-hoc hierarchical nanostructures with specific photonic functionalities. Yet, the appropriate tailoring of the photonic properties will need a better understanding of the biomineralization processes during the morphogenesis of the diatom exoskeleton.

Interestingly, the nanostructures produced by biomineralization can be isolated from other bio-products with relatively simple procedures. In the case of diatoms, these products could be biosilica, pigments and oils. Whilst biosilica and pigments can be desirable for optical applications, the oils can be used as biofuel and/or feedstock. Therefore, photonic structures resulting from biomineralization in plants or algae might allow for circular economy approaches where all bio-products, photonic or not, could find a use enabling a zero-waste technology.

CONCLUSIONS AND FUTURE OPPORTUNITIES

The field of natural photonics was originally fuelled by human curiosity for understanding how living organisms play with light. More recently, biomimetic photonics was propelled by the search to replicate the extraordinary natural structures in the laboratory towards technological applications. Now, the rapid advances in synthetic biology [9] anticipate a completely new era for photonics where it will be possible to manipulate the biochemical processes behind the BOM formation at the cellular level enabling the production of ad-hoc hierarchical natural photonic nanostructures. This will change drastically how we design and produce photonic devices making the collaboration between synthetic biologists, chemists, engineers and physicists essential to push forward this new generation of clean photonic technologies. ●

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