Biomimicry of multifunctional nanostructures in the neck feathers of mallard (Anas platyrhynchos L.) drakes

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Biological systems serve as fundamental sources of inspiration for the development of artificially colored devices, and their investigation provides a great number of photonic design opportunities. While several successful biomimetic designs have been detailed in the literature, conventional fabrication techniques nonetheless remain inferior to their natural counterparts in complexity, ease of production and material economy. Here, we investigate the iridescent neck feathers of Anas platyrhynchos drakes, show that they feature an unusual arrangement of two-dimensional (2D) photonic crystals and further exhibit a superhydrophobic surface, and mimic this multifunctional structure using a nanostructure composite fabricated by a recently developed top-down iterative size reduction method, which avoids the above-mentioned fabrication challenges, provides macroscale control and enhances hydrophobicity through the surface structure. Our 2D solid core photonic crystal fibres strongly resemble drake neck plumage in structure and fully polymeric material composition, and can be produced in wide array of colors by minor alterations during the size reduction process.

Nature offers a great diversity of well-optimized photonic engineering designs, which often represent a compromise between several potentially conflicting purposes and can maintain such a diverse array of functions as mate attraction, UV protection, water repulsion, camouflage and sensory enhancement¹². During the last decade, advancements in nanoscience and modern fabrication methods have enabled the detailed investigation and functional mimicry of these natural designs, especially with regards to the structural coloration effects found in biological systems³–⁷. The physical phenomena responsible for structural coloration have also received considerable attention⁶, as these structures derive their colors from a number of optical effects, such as interference, scattering, photonic crystal effects, or a combination thereof⁶. Photonic crystals in living systems are especially notable for their iridescence and exceptionally bright coloration⁸, which may assist in camouflage¹⁰,¹¹, communication¹², sensing¹³–¹⁵ and other purposes that still remain largely unexplored. The imitation of these nanostructures represents significant advances¹⁶ in the area of nano-optics, and promotes the design of novel photonic configurations¹⁷,¹⁸. However, current fabrication methods cannot satisfactorily mimic the architectural complexity¹⁹ found in natural systems without greatly compromising control capacity, ease of fabrication and/or production costs. In particular, while nature-inspired 1D and 3D photonic crystals can be fabricated²⁰,²¹ by self-assembly or deposition techniques, functional imitations of 2D photonic crystals observed in nature²²–²⁴ are yet to be produced.

Here we investigate and successfully imitate a peculiar 2D photonic scheme observed on the neck feathers of mallard drakes. Our bioinspired 2D photonic crystals successfully replicate not only the optical properties, but also the material features and the architectural complexity of the original structure. A novel top-down approach, called iterative size reduction (ISR)²⁵–²⁷, is used to avoid potential issues associated with the fabrication of solid core 2D photonic crystals and to produce a biomimetic design that displays the same structural complexity and functionality as mallard feather barbules with low fabrication costs, short processing times and minimal labor intensity. In addition to its optical properties, the barbule surface is also shown to be strongly hydrophobic, and this property is also successfully replicated in our bio-inspired 2D photonic crystals. The present work represents the first successful fabrication of an all-polymer 2D solid-core photonic crystal capable of functioning at optical frequencies. We further demonstrate that biomimetic fiber arrays displaying a great range of colors can be obtained by minor alterations in a single fabrication step, without necessitating individual process optimization procedures for each desired color.
Neck feathers of mallard (*A. platyrhynchos*) drakes (Figure 1a) are investigated to determine the phenomena responsible for their bright green coloration. Optical microscopy characterization suggests that neck feathers are strongly iridescent, as the green hue observed under a low angle of incidence (x20 magnification, Figure 1b) changes into a distinctive blue color when the angle of illumination is increased (x50 magnification, Figure 1c). The barbule morphology possesses a non-circular cross-section, which may serve to maximize the functional surface areas of the barbule elements responsible for iridescent coloration (Figure 1d). Well-aligned, hexagonally distributed rods are observed to occur on barbule edges in five- or six-layer arrays (Figure 1e, Figure S1) and represent an unusual form of 2D photonic crystal. Barbules are primarily composed of melanin pigments (rods) embedded in a keratin matrix (filling material), and display real refractive indices of 2.00 and 1.56, values of which fluctuate slightly over the visible spectrum. Complex refractive index values of these materials play a minor role in coloration by the 2D photonic crystal effect, as they mainly alter the reflected intensity. These fluctuations assumed to be negligible in our calculations.

A moderate refractive index contrast, such as that found in mallard feathers, allows the reflection of a narrow band of wavelengths, the position of which shifts depending on the viewing angle. Consequently, optical simulation techniques were utilized to determine the location and properties of the reflection band associated with barbule elements. Design parameters (Figure 1f) obtained from SEM images of neck feather barbules are used in FDTD and MPB simulations, and the resulting directional band-gap diagram and reflectance spectrum are both found to overlap in the green and ultraviolet regions of the electromagnetic spectrum (Figure 1g–h). The consistency of our simulation and measurement results (Figure S2) further support the notion that the presence of 2D photonic crystals is responsible for the green color displayed by feather barbules (Figure 1i).

The structural orientation of the barbule elements is then utilized in the fabrication of a novel material for use in 2D photonic crystal based devices. Iterative size reduction is utilized in order to mimic the structural properties observed in mallard feathers, and the size and material data taken from feather barbules are used to simplify the design process. Polycarbonate (PC) and polyvinylidifluoride (PVDF) are selected as the material components due to their thermal compatibility, which is required for the thermal drawing process, and low refractive index contrast (n\textsubscript{PC} = 1.58 and n\textsubscript{PVDF} = 1.41), which closely approximates the original configuration (Figure S3). The first step macroscopic preform (Figure 2a, Figure S4a, b) is prepared by successively wrapping PVDF and PC polymers around a PC rod, which is then thermally consolidated in a furnace (see Methods). The final macrostructure measures several centimeters in diameter, and is thermally drawn in a custom-built fibre tower system to effect the iterative reduction of structure dimensions (see Ref. 25 for details). Fabricated step I fibres (Figure 2b) possess an excellent cross-sectional regularity that is preserved along the length of the fibre. Microstructures obtained after step I are cut and prepared for the second step of the fabrication (Figure 2b).

Composite fibres with outer diameters of several hundred microns are embedded in a polymer sheath (i.e. a rectangular hollow preform prepared for the insertion of first step microfibres) (Figure S4c, d) in self-arranged hexagonal arrays and redrawn to produce indefinitely long 2D photonic crystal microstructures. Microwire arrays present within the PVDF matrix of step II fibres preserve their initial structure profile, as can be observed from their cross-section images (Figure 2e). A third step, similar in procedure to step II but utilizing only one step II fibre, can then be performed to produce step III fibres with nano- to microscale lattice constants (Figure 2c). Microstructures with rectangular cross-sections composed of hexagonal arrays of nanorods are obtained after three consecutive drawing steps, and bear a great resemblance to the fine structure of mallard feathers. 2D photonic crystal structures obtained as a result of step II and step III fabrications span a wide range of lattice sizes (50 µm–100 nm).

SEM images of step III fibres are relatively low-quality due to the low contrast between the photonic crystal components (Figure 2f).
Minor deformations observed in rod structures may slightly alter the local hue, but do not significantly change the overall color.

Our multiple size reduction process can therefore be utilized to convert the white-colored macro-prototype into structurally colored photonic crystal fibres (Figure 3a). The green hue observed in optical microscope images of 2D all-polymer photonic crystal structures (Figure 3b) shifts into blue under higher magnifications as a result of its iridescence (Figure 3c). Longitudinal SEM images reveal that the PVDF shell acts as an embedding matrix for PC nanorods (Figure 3d). Roughnesses are observed to exist on the photonic crystal surface, but are too small to display Mie scattering or thin film interference, and are therefore expected to play an insignificant role in coloration.26,31. Lattice constants and rod diameters are measured to be around 200 nm and 175 nm for green-colored 2D photonic crystal fibres. The reflection spectra and band structure behavior of produced fibres can be simulated accurately by using these values (Figure 3f, g). Our measurement and unpolarized light simulation data are also in good agreement for green-colored fibres (Figure 3h).

Our bioinspired solid-core 2D photonic crystal fibres are also used for the production of a diverse array of colored fibres spanning the visible spectrum. Decreasing lattice constants and rod diameters gradually change the hues observed on a tapered part of photonic crystal fibre (Figure 4a). A 3D map of the photonic crystal effect clearly demonstrates band-gap positions associated with specific lattice constants, and can assist in the design of colored photonic crystal fibres (Figure 4b). Narrow reflection bands allow the clear observation of each color. The reduction factor can be altered during the third step of the drawing process to modify the lattice constant of the final product and to facilitate the single-step fabrication of arbitrarily long, structurally colored photonic crystal fibres (Figure 4c).

Mallard neck feathers (unlike flight feathers32) and our bio-inspired photonic 2D crystal fibres are both found to be strongly hydrophobic due to their similar surface architectures, though different effects are responsible for their enhanced hydrophobicities (Figure 5). SEM images of feather barbules suggest hat three surface effects contribute to feather hydrophobicity (CA > 152° ± 2°): (1) The gaps present within the barbule arrays, (2) the interlocking steps between each barbule cluster and (3) the nanoscale roughness of each barbule surface (Figure 5a,b)33. Similarly, the surface nanopattern and arrangement of our photonic crystal fibres, as well as the intrinsically hydrophobic nature of the PVDF polymer shell, contribute to the superhydrophobicity of our bio-inspired photonic crystals (Figure 5c,d). PVDF is a fluoride-containing polymer, and fluorinated residues are well-known to promote hydrophobicity34 (Figure S5a). However, our all-polymer step III photonic crystal structures (CA > 160° ± 5°) are more hydrophobic than PVDF polymer films (CA > 91°), suggesting that, in addition to material composition, surface hierarchy also contributes significantly to the superhydrophobicity of the fibrous photonic crystal surfaces (Figure 5e). Higher hydrophobicities are also observed for step II fibres (CA > 124°), which possess microscale surface patterns, as opposed to the nanoscale features of step III fibres (Figure S5b).

The polymeric composition of our 2D photonic crystal design also confers additional features such as biocompatibility, elasticity and...
pliability to structurally colored fibres. These fibres can also be produced in millimeter to nanometer scales, and can therefore be utilized on different operation wavelengths (i.e., UV, visible and IR). In addition, our fabrication method allows the precise control of the fibre production process, and therefore can effectively facilitate the fabrication of a broad range of complex nanoarchitectures. The fabrication of hard-to-produce 2D photonic crystal structures with distinct material compositions can also be accomplished by choosing thermally compatible raw materials. Such photonic crystal fibers are promising for use in applications relating to filtering, colored fabric woven and their superhydrophobic character is particularly useful in anisotropic wettable fibers.

Figure 3 | Characterization of biomimetic all-polymer photonic crystal structures. (a), A diverse array of 2D photonic crystal nanostructures can be engineered from a unique macroscale preform. (b), The vivid green hue observed under light microscopy confirms the presence of photonic crystal effects. (c), Biomimetic photonic crystal fibres appear iridescent as the magnification of light microscope is increased. The green color is transformed into blue as a result of the photonic crystal effect. (d–e), SEM images reveal the ribbonlike photonic crystal formation and hexagonal distribution of PC rods inside the PVDF matrix, with lattice constants around 200 nm. (f), Reflection and (g), bandstructure calculations are performed using the optical and size parameters of the material components. (h), Reflection measurements from green colored photonic crystal structures are consistent with FDTD modelling results.

Figure 4 | Band-gap tunable all-polymer colorful photonic crystal structures. (a), A tapered photonic crystal structure exhibits lattice constant-dependent changes in color along 200 μm of its length. Measurements are taken from each hue observed on the tapered photonic crystal (inset). (b), A map of bandstructure calculations can be used in the design of any desired color. (c), A large array of colors can also be obtained during the third fabrication step by altering the reduction factor. Millimeter-scale structures displaying seven distinct colors are shown as a proof-of-concept.
Arrays. Alignment of the fiber arrays both contribute to surface superhydrophobicity. The water contact angle is measured to exceed 165°.

Methods

Macroscopic composite preparation, consolidation and thermal size reduction.

Photonic crystals are produced using three iterative fabrication steps. A single step I preform is utilized throughout the fabrication process, and uses a PC rod as a core component, which in turn is prepared using a hollow PC preform with an initial diameter of 30 mm. Briefly, the PC preform is cut into four equal pieces, and a turning machine is used to shape a single quadrant into a cylindrical rod with a diameter of 10 mm. A PVDF polymer film is then wrapped around this rod until a total diameter of 12 mm is reached, and a PC film is wrapped around the PC/PVDF core until the total diameter exceeds 20 mm (the complete preform therefore has a diameter ratio of 10:2:8 for PC:PVDF:PC).

The macroscopic preform is then consolidated above the glass transition temperature of its components (185°C for 10 minutes, under a 10⁻⁵ Torr vacuum), and thermally drawn in a custom-built fibre tower, specifications of which can be found in Ref 25. Briefly, the macroscopic structure is heated and drawn into step I microwires in a vertical two-zone furnace, with a top zone temperature of 224°C. Drawing parameters, such as drawing speed, down feed speed and temperature, are controlled throughout the fabrication process. Fibres with outside diameters of 400 μm are obtained as a result of step I fabrication, and the outer coat of PC is stripped prior to the subsequent steps (the non-adhesive layer between PVDF and PC facilitates the convenient removal of PC).

Functional biomimicry of the rectangular photonic crystal structures observed in mallard feathers is accomplished using a rectangular step II preform (step II preforms are hollow PC structures into which step I fibres are inserted). The rectangular step II preform is prepared by wrapping PC film around a bare glass substrate with the dimensions of 20 mm × 1.5 mm × 7 cm, to a final thickness of 35 mm × 15 mm × 7 cm. This preform is then thermally consolidated in a consolidation furnace, with an extended heating time (>2 h) to ensure that the outer PC layer conforms fully to the shape of the glass rod. The glass rod is then dissolved using 48% HF, leaving behind the rectangular preform. A 4cm-long array of 500 step I fibres is inserted into this step II preform and thermally drawn at a temperature of 230°C in our custom fibre tower system (see also Ref. 25 for other parameters used in the fibre drawing process, such as capstan and down-feed speed). Fibres with outside diameters of 1.5 mm are obtained at the end of the second step. Step III is identical to step II, except that step III preforms are filled with a single step I fibre. Arbitrarily long photonic crystals can be produced with a broad crystal parameter range (including lattice constant > 100 nm) after step III, and the process can be repeated to obtain smaller structure diameters. The overall reduction factor at the end of step III is 10⁻³.

Sample preparation and imaging. Dichloromethane (DCM) (Carlo Erba) is utilized to etch the PC sheath covering the photonic crystal structures, exposing the latter for longitudinal imaging by electron and optical microscopy. Exposed nanostructures are rinsed gently with DCM for the removal of residual polymer. PVDF shells of photonic crystal structures are highly resistant to DCM etching, and are not damaged during the nanostucture extraction process. Cross-sectional images of mallard barbules and bio-inspired photonic fibres were obtained by embedding both structures in epoxy resin and sectioning them by ultramicrotome prior to imaging. Cross-sectional images are difficult to obtain due to the low contrast between the material components of both feather barbules and our bio-inspired fibres. SEM imaging is performed under both high pressure and low pressure modes to minimize this problem.

FDTD simulations and MPB calculations. FDTD simulations are performed by using commercial finite-difference time-domain software (Lumerical Solutions Inc.). A plane wave source is used for illumination. FDTD simulations are calculated in two dimensional simulation regions. Frequency-domain power monitors are used to collect reflected light from periodic layers of rods embedded in host material. Reflective indices of PC and PVDF are assumed to be constant in the visible spectrum, and taken as 1.58 and 1.41 (see Figure S3).
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