Printable Flowers? Custom-tailored Photonic Cellulose Films with Engineered Surface Topography

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Printing Flowers? Custom-tailored Photonic Cellulose Films with Engineered Surface Topography

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ABSTRACT: Wrought by nature’s wondrous hand, surface topographies are discovered on all length scales in living creatures with variety of functions. Inspired by the floral striations, here we developed a scalable means of fabricating custom-tailored photonic cellulose films that contained
cholesteric organization and microscopic wrinkly surface topography. The freestanding films were prepared by moulding cellulose nanocrystal ink onto an oriented wrinkle template through evaporation-assisted nanoimprinting lithography, yielding morphology-induced light scattering at short wavelength as well as optically tuneable structural colour that derived from helical cellulose matrix. Moreover, this wrinkled surface relief on cholesteric cellulose films could be precisely controlled, enabling engineered printing of microscopic patterned images. These bio-inspired films offer a convenient opportunity for the production of coupled photonic crystals which may be of value in advanced optical devices.

INTRODUCTION

Structural coloration is widely existed in nature which performs signalling functions within or between species.\textsuperscript{1, 2} Diverse forms of photonic architectures exhibit striking structural colours that derive from the interference of light, have been reported in a range of creatures such as insects, birds, fish and plants.\textsuperscript{3-6} Some flowering plants display bright colours to distinguish themselves from the environment and attract pollinators which due to the combination of wavelength-selective absorbing pigments in petal cells and floral striations (approximate to diffraction grating) of the cuticle on the petal epidermis.\textsuperscript{7, 8} For example in tulip \textit{Queen of the night} (Figure 1a, b), the dark purple colour arises from the angle-independent anthocyanin pigment and the strong rainbow-like iridescent appearance is a result of angle-dependent light scattering effect that generated by its long-range periodic surface striations.\textsuperscript{9} However, in other cases (\textit{e.g.}, beetles and butterflies), mixing of different structural colours can lead to single iridescent colour which are associated with their hierarchically ordered structures.\textsuperscript{10} These natural photonic structures are inspiring researchers
to develop novel materials with controllable coupled structural colour for applications in sensors and optoelectronic devices.

As the major constituent of plants, cellulose is one of the most abundant biopolymers on earth. Cellulose nanocrystals (CNCs), which are produced by acid hydrolysis of bulk cellulose, have gained increasing attention for their unique chemistry and self-assembly capabilities.\textsuperscript{11, 12} In water, colloidal CNC can self-organize into a cholesteric liquid crystal phase above critical concentration and dry into solid state upon slow evaporation, thereby resulting in vivid iridescent films with helical organization.\textsuperscript{13, 14} Although CNC liquid crystals have been extensively studied from the perspective of templating, particle assembling, photonic sensing and non-equilibrium assembly,\textsuperscript{15-21} to the best of our knowledge, no attempt has yet been made, to develop a custom-tailored photonic structure that mimics the surface morphology in flowers. Mihi and Godinho et al. recently created some iridescent films from hydroxypropyl cellulose liquid crystals through shear casting and nanoimprinting lithography,\textsuperscript{22-24} however, the structural colours originated purely from the light diffractions on patterned surface topography and no cholesteric ordering was retained after film processing. Furthermore, previous studies indicate that periodic surface wrinkles can only be generated on top of cholesteric liquid crystal under harsh conditions.\textsuperscript{25, 26} Thus, it will be attractive to develop an easy way to prepare wrinkly cholesteric CNC film with controllable photonic properties.

Herein we report on a series of floral-mimetic cholesteric CNC films that exhibit long-range ordered surface wrinkles and bistructural iridescence (Figure 1c, d). CNC was used as photonic ink and cast onto a wrinkled poly (dimethyl siloxane) (PDMS) mould. After evaporation, CNCs self-assembled into vivid cholesteric films with subtle surface patterns that imprinted from the template. Notice that the helical pitch of CNC matrix and its corresponding surface relief were
highly editable, generating an iridescent film with tuneable structural colour that varied from blue, green, red and transparent. Optical analysis of this hierarchically ordered cholesteric film demonstrated angle-dependent UV-blue scattering as well as selective reflection and diffraction of left-handed circularly polarized (LCP) light, acting as special polarization gratings. Hence, both the cholesteric ordering in bulk phase and diffraction gratings on film surface can be termed as photonic crystal, yielded a hierarchical photonic architecture.

Figure 1. Comparison of natural flower and custom-tailored photonic cellulose film.

(a), (b) Photograph and scanning electron microscopy (SEM) image of tulipa *Queen of the night*, displaying floral iridescence and parallel cuticular striations on flat cells (adopted with permission from reference [2]). (c), (d) Photograph and SEM image of the photonic cellulose film, showing bistructural colour and periodic surface wrinkles that similar to floral petals.
RESULTS AND DISCUSSION

The approach to produce cholesteric wrinkled films (denoted as CWFs) through evaporation-assisted soft nanoimprinting lithography is illustrated in Figure 2a. An aqueous CNC dispersion (5.0 wt%, zeta potential -53 mV) was mixed with varying amounts of polyvinyl alcohol (PVA, ranging from 0.5 to 6.0 wt%, CWF1-4, Supporting Information) as initial ink and poured on top of a pre-prepared wrinkled PDMS mould. Wrinkled PDMS was obtained by oxygen plasma treatment along with mechanical stretching and releasing. Plasma oxidation converted the topmost of PDMS into a hydrophilic silica layer, with wrinkled surface relief tuneable by plasma treatment duration (Supporting Information, Figure S1 and Table S1), owning to the increased thickness and Young’s modulus of the silica layer. Compared with a pure CNC dispersion, CNC-PVA ink had several advantages such as adjustable helical pitch in cholesteric phase and excellent wettability on PDMS due to the reduced surface tension. After drying under ambient conditions, colourful cholesteric composite films were obtained and peeled off, resulting in freestanding iridescent CWFs (Figure S2). Moreover, when viewing normal to film upper surface, the CWFs presented a tuneable structural colour with the photonic band-gaps varying from UV, visible to NIR region, which derived from the increasing of helical pitch, typical of cholesteric organization (Figure 2b, c). Apart from the cholesteric photonic band-gap for CWF2-4, we observed a double-peak structure (245 and 300 nm, see magnified spectra in Figure S3) in the UV-blue spectral range which resulted from wrinkle-induced light diffraction (confirmed by wrinkle-free reference sample, Figure S4), analogous to the spectral structure of natural flower Mentzelia lindleyi. This feature was strongly suppressed when the wrinkle orientation was changed by rotating the sample, while the photonic band-gap remained the same (Figure S5). For CWF1 whose photonic band-gap was located in the same spectra range, we observed an intense peak at 297 nm
with the strongest iridescence among all the tested samples (Figure S6). This observation
suggested the photonic coupling effect in surface topography derived light scattering and inherent
helical ordering. Due to the microscopic anisotropy of the oriented surface wrinkles, the circular
dichroism signals for CWFs demonstrated slightly linear dichroism and linear birefringence at the
UV-blue range (Figure S7). Another attractive feature of CWF was its flexibility. While pure
cholesteric CNC films were brittle, they became ductile and highly flexible after the addition of
polymer. Tensile stress-strain curve of CWF3 showed the tensile strength of approximately 10.5
MPa and elongation of 84% at break (Figure 2d), similar to previous reported wrinkle-free
cholesteric CNC-PVA composite.28

Figure 2. Preparation, optical and mechanical properties for CWF composite.
(a) Schematic of fabrication method to generate freestanding CWF. (b) Photographs of CWF1-CWF4 exhibit varying structural colours. (c) UV-Vis-NIR spectra of CWFs show varied photonic band-gap and wrinkle-induced diffraction peaks at UV-blue range. Inset shows the photonic band-gap of CWF4 at IR region. (d) Stress-strain curve for CWF3. The sample is flexible and can be bent without visible damage (inset).

To characterize the surface morphology of the composite, CWF samples were analysed by polarized optical microscopy (POM), SEM and atomic force microscopy (AFM), respectively. POM images of CWF2 showed distinct birefringence colour and long-range ordered parallel striations that were similar to the fingerprint texture for cholesteric organization (Figure 3a and Figure S8). Tuning the focal plane of CWF2 from its upper surface to bottom side uncovered a transition of the texture from parallel striations to relatively smooth, indicative of Janus surface (Figure 3b and Figure S9). Further confirmation of the hierarchical structure of CWF by a series of SEM tests, showed that the CWFs had a periodic wrinkled surface that was imprinted from the PDMS mould, with a repeating waved morphology at 2.5 µm intervals (Figure 3c). High-magnification image exhibited glossy microscopic surface along the wrinkles, implying the planar anchoring of CNC at the PDMS interface during evaporation (Figure 3c, inset). At fractures perpendicular to the CWF surface, we observed a porous twisted layered structure with CNC director rotated in a counter-clockwise direction (Figure 3d, e and Figure S10), which gave rise to the cholesteric structure responsible for the selective reflection of light. Focusing on cross-sections, periodic layered structure was presented near the wrinkle surface with a degree of distortions (Figure 3f and Figure S11), while the helix axis remained parallel to the waved surface and pitch length kept constant (320 nm). Figure 3g shows the 3D reconstructed AFM image and its numerical analysis. The surface geometry exhibited a periodic wavelength and amplitude of 2.5
μm and 270 nm, respectively, consistent with its PDMS template (Figure S12). It should be noted that wrinkled PDMS moulds with varying parameters can be used to fabricate the composites with coincide surface morphology, leading to a highly editable surface relief on CWF (Table S2).

Based on the above, Figure 3h is sketched to illustrate the hierarchical structure of CWF composite. During evaporation, CNCs are self-assembled into cholesteric ordering that divided into two parts along the film thickness. One part is the bulk region in which CNCs are close to the air-water interface and free-assembled into helical organization, the other part is the cholesteric wrinkled surface region, i.e., the PDMS-CNC interface where the CNCs are confined and distorted. In order to reach the minimum energy state at PDMS surface, the alignment of CNC director is planar anchored along its wrinkled surface with the orientation of helix axis remained perpendicular to the waved surface, showing bend-splay orientation distortions with constant pitch. The wavelength and amplitude of these cholesteric wrinkles are determined and imprinted by the PDMS mould which can be easily tuned on demand. In contrast, the director field of cholesteric CNC in bulk region is continuous and remains undistorted without any topological defect, in agreement with our SEM observations (Figure S13).
Figure 3. Morphology characterization for CWF composite.

POM images of CWF2 that focus on the upper (a) and bottom (b) surface of the film. (c) Top view of the upper surface for CWF2 with low and high (inset) magnifications. (d) Top view of a cracked film shows porous layered structure under the wrinkles. (e) Side view at high magnification of the porous structure reveals a left-handed helical organization. (f) Side view of the interface between wrinkles and bulk phase showing distorted structure. (g) AFM image and numerical analysis of the CWF composite. (h) Illustration of the hierarchical structure of CWF composite.

Chirality is ubiquitous in nature. Cholesteric assembly of CNCs allows for controlling chiral light-matter interactions in photonic structure that is not only relevant for fundamental aspects but also for practical interests.\textsuperscript{32-34} In order to highlight the wrinkle-induced iridescence,
we chose CWF4 as an ideal example due to its cholesteric photonic band-gap was far away from the visible range. When a collimated white light beam impinged on the film surface and aligned with surface wrinkle perpendicular to the plane of light incidence, it exhibited a striking rainbow-like appearance that derived from the grating-induced light interference (Figure 4a). Rotating the sample led to variation in its structural colour which finally vanished and became transparent when the wrinkle orientation lying parallel to the plane of incidence (Figure 4b). Interestingly, vivid iridescent colours were observed only in LCP light, while the photograph taken under right-handed circularly polarized (RCP) light was totally colourless (Figure 4c). As comparison, the iridescent signal for a cholesteric-free wrinkled CNC-PVA reference sample remain unchanged when viewed under LCP/RCP light, which implied the coupling effect between cholesteric matrix and surface wrinkles (Figure S14). Based on above, we inferred that only LCP light was selectively reflected and scattered in CWF, generating an intense visible angle-dependent polarized iridescent signal.

A sketch of the proposed mechanism for polarized light diffraction is shown in Figure 4d. The structural colours in CWFs arise from two parts: the helical organization of CNC matrix and the periodic surface wrinkles that termed as diffraction grating. Diffraction grating is an array of diffractive elements which periodically modulate the phase and amplitude of incident light, dispersing monochromatic incident light wave into different angular directions, named orders.9 According to the diffraction grating equation \[d (\sin \theta_i - \sin \theta_d) = m \lambda,\] where \(\theta_i\) and \(\theta_d\) are the incidence and diffraction angles, respectively, \(d\) is the distance between wrinkles, \(\lambda\) is the diffracted incident light wavelength and \(m\) is the diffraction order), for any incident light at given value of \(\theta_i\) with wavelength of \(\lambda\), the reflected light scatters into different angular directions with constructive interference, i.e., the optical path difference between two beams must be an integral multiple of the wavelength \((m \lambda, m = 0, 1, 2 \ldots)\). On the other hand, when a beam of light is illuminated on the
surface of CWF, the reflected light is always in LCP state that matches the handedness of cholesteric CNC matrix while RCP light is fully transmitted.\textsuperscript{35,36} Therefore, the incident light is not only selectively reflected but also further scattered in the plane perpendicular to the wrinkle direction, leading to chiral light-matter interactions and serving as polarization-selective gratings.

This phenomenon was further quantified by angular-resolved spectroscopic scattering measurements that performed by shining either LCP or RCP light onto the film surface. For LCP illumination, the narrow scattering band at 0° was resulted from zero-order reflection with its intensity remained strong in the visible-NIR spectral range (450-900 nm) (Figure 4e). This zero-order reflection pattern was controlled by both the cholesteric photonic band-gap ($\lambda = n_{avg}P$, where $n_{avg}$ is the average refractive index, $P$ is the helical pitch and $\lambda$ is the reflected wavelength\textsuperscript{37}) and surface wrinkles. Particularly, we noted that some wavelength-dependent diffraction peaks were visible not only at around 0°, but also expanded between 20° and -40°, which could be ascribed to the first, second and third-order diffractions, characteristic of grating-derived iridescence. Besides, most of the diffraction intensities were above 450 nm, in agreement with its green iridescent appearance (Figure S15). However, the diffraction pattern illuminated with RCP light exhibited the highest zero-order reflection intensity only at around 500 nm, and then rapidly decreased by moving to other wavelength (Figure 4f). Comparing with the LCP illumination the secondary diffraction peaks with RCP illumination were much weaker, which correlated with decreased scattering of RCP light. Therefore, we concluded that the iridescence occurring in CWF could be kindled or extinguished by circularly polarized illumination.
Figure 4. Wrinkle-induced polarization sensitive photonic structure with strong anisotropy.

(a) Photograph of CWF4 taken with a beam of white light illuminated parallel to the wrinkle direction, showing rainbow-like surface iridescence. (b) Photograph of CWF4 with surface wrinkles perpendicular to the plane of incident light. The arrow shows the wrinkle direction. (c) Photographs of CWF4 viewed under a LCP filter (left) and RCP filter (right), respectively. (d) Schematic description of the polarization-selective diffraction grating in which the reflected LCP light shows constructive interference. Two-dimensional maps showing the angle-resolved
scattering spectra for CWF2 under LCP (e) and RCP (f) illumination. Bands contain zero-order reflections are marked by stars.

From the spectral analysis we confirmed that the optical signals in CWFs were not only affected by their interior helical ordering in CNC matrix but also by the long-range parallel surface wrinkles. However, floral surfaces in nature are not only limited to simple grating-like patterns, at times, they can be quite complex and vary from ordered, quasi-ordered and random striations in different species of flowering plants. Besides wrinkles, we also observed some subtle microscopic structures (e.g., defects and cracks) on CWFs that were exact duplicate of the PDMS mould (Figure S16), which inspired us to print designed patterns on CWF through engineering its template. Figure 5a-c are the optical images of zigzag patterned CWF composite in which the wrinkles are transformed into a controllable herringbone jog angle. A zigzag patterned PDMS mould was prepared by sequential release of the biaxial pre-strained PDMS sheet in one direction followed by release of the strain in the other direction after plasma oxidation (Supporting Information). This pattern can be transferred onto CWF surface through replica moulding with high fidelity and the jog angle can be tuned by changing the ratio of the biaxial strain state. It should be noted that zigzag ordered cholesteric structure was recently discovered in *Odontodactylus scyllarus* to improve the damage-tolerance and impact-resistance of its dactyl club. In addition to line structures, designed graphic wrinkle patterns were obtained by masking the stretched PDMS sheet for selective treatment of oxygen plasma (Supporting Information). Figure 5d-g exhibit a series of surface patterned CWF in which the wrinkles are formed into an array of squares. The wrinkles in square region were highly aligned into one direction with well-defined location and short-range order, while the wrinkle boundaries were totally smooth (Figure 5d, e). The distance between square regions was 28 µm with square area of 250 µm², comparable to the dimensions of mask
and mould (Figure S17, 18). In addition, both the pattern and orientation of these surface wrinkles on CWF could be further engineered, demonstrating an order-to-disorder transition, namely, the wrinkles in square regions transformed from oriented to random and square boundary was built of disordered wrinkles (Figure 5f, g and Figure S19, 20). Inspired by the success of editable printing of surface patterns, we employed a custom-made mask to print a microscopic-scale wrinkled Technion logo on CWF (Figure 5h and Figure S21), which underscored the general utility and accuracy of this printing technique.

Figure 5. Custom-tailored surface patterns with cholesteric ordering.

(a)-(c) POM and SEM images of zigzag patterned CWF at different magnifications. (d), (e) POM images of the square patterned CWF composite with smooth boundary. (f), (g) Optical images of
CWFs with order-to-disorder transited square patterns and disorder wrinkled boundary. (h) Optical image of a wrinkled Technion logo (highlighted in grey) on CWF.

CONCLUSION

In summary, we demonstrated a CNC-based CWF composite with tuneable bistructural colour that resulted from the cholesteric ordering in matrix and periodic wrinkles on surface. Both bottom-up and top-down approaches were involved in the preparation process, i.e., self-assembly of CNC into helical organization and imprint the microscopic surface wrinkles from PDMS template. The morphology, texture and optical signals of these CWFs were studied in detail, presenting iridescent photonic structures similar to the floral petals. Moreover, owing to the highly editable surface relief for PDMS mould, the resulting patterns on CWFs could be easily tuned on demand. We anticipate that this intriguing CWF concept could be extended to various arbitrarily patterned structures (for example, nanopillars, nanoholes or twisted grating lines) at different length scales, bearing great potential for future metamaterial design and fabrication.

ASSOCIATED CONTENT

Supporting Information

Additional experimental details and figures as well as tables are demonstrated in Supporting Information.

AUTHOR INFORMATION

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Author Contributions

G. C. prepared the CWF composite films and carried out the experimental measurement and data analysis. A. C. and D. P. carried out the light scattering measurement. G. C. and E. Z. designed and led the project. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

1. Whitney, H.M., Reed, A., Rands, S.A., Chittka, L., and Glover, B.J. (2016). Flower iridescence increases object detection in the insect visual system without compromising object identity. Curr. Biol. 26, 802-808.
2. Moyroud, E., Wenzel, T., Middleton, R., Rudall, P.J., Banks, H., Reed, A., Mellers, G., Killoran, P., Westwood, M.M., and Steiner, U. (2017). Disorder in convergent floral nanostructures enhances signalling to bees. Nature 550, 469-474.
3. Sharma, V., Crne, M., Park, J.O., and Srinivasarao, M. (2009). Structural origin of circularly polarized iridescence in jeweled beetles. Science 325, 449-451.
4. Noh, H., Liew, S.F., Saranathan, V., Mochrie, S.G., Prum, R.O., Dufresne, E.R., and Cao, H. (2010). How Noniridescent Colors Are Generated by Quasi-ordered Structures of Bird Feathers. Adv. Mater. 22, 2871-2880.
5. Jordan, T., Partridge, J., and Roberts N. (2012). Non-polarizing broadband multilayer reflectors in fish. Nat. Photonics 6, 759-763.
6. Thomas, K.R., Kolle, M., Whitney, H.M., Glover, B.J., and Steiner, U. (2010). Function of blue iridescence in tropical understorey plants. J. R. Soc. Interface 7, 1699-1707.
7. Kooi, C.J., Wilts, B.D., Leertouwer, H.L., Staal, M., Elzenga, J.T.M., and Stavenga, D.G. (2014). Iridescent flowers? Contribution of surface structures to optical signaling. New Phytol. 203, 667-673.
8. Wilts, B.D., Rudall, P.J., Moyroud, E., Gregory, T., Ogawa, Y., Vignolini, S., Steiner, U., and Glover, B.J. (2018). Ultrastructure and optics of the prism-like petal epidermal cells of Eschscholzia californica (California poppy). New Phytol. 219, 1124-1133.
9. Vignolini, S., Moyroud, E., Glover, B.J., and Steiner, U. (2013). Analysing photonic structures in plants. J. R. Soc. Interface 10, 20130394.
10. Seago, A.E., Brady, P., Vigneron, J.P., and Schultz, T.D. (2008). Gold bugs and beyond: a review of iridescence and structural colour mechanisms in beetles (Coleoptera). J. R. Soc. Interface 6, S165-S184.
11. Rånby, B.G. (1951). Fibrous macromolecular systems. Cellulose and muscle. The colloidal properties of cellulose micelles. Discuss. Faraday Soc. 11, 158-164.
12. Habibi, Y., Lucia, L.A., and Rojas, O.J. (2010). Cellulose nanocrystals: chemistry, self-assembly, and applications. Chem. Rev. 110, 3479-3500.
13. Revol, J.F., Bradford, H., Giasson, J., Marchessault, R., and Gray, D. (1992). Helicoidal self-ordering of cellulose microfibrils in aqueous suspension. Int. J. Biol. Macromol. 14, 170-172.
14. Mu, X., and Gray, D.G. (2014). Formation of chiral nematic films from cellulose nanocrystal suspensions is a two-stage process. Langmuir 30, 9256-9260.
15. Shopsowitz, K.E., Qi, H., Hamad, W.Y., and MacLachlan, M.J. (2010). Free-standing mesoporous silica films with tunable chiral nematic structures. Nature 468, 422-425.
16. Shopsowitz, K.E., Hamad, W.Y., and MacLachlan, M.J. (2011). Chiral nematic mesoporous carbon derived from nanocrystalline cellulose. Angew. Chem. Int. Ed. 50, 10991-10995.
17. Chu, G., Feng, J., Wang, Y., Zhang, X., Xu, Y., and Zhang, H. (2014). Chiral nematic mesoporous films of ZrO$_2$: Eu$^{3+}$: new luminescent materials. Dalton Trans. 43, 15321-15327.
18. Thérien-Aubin, H., Lukach, A., Pitch, N., and Kumacheva, E. (2015). Coassembly of nanorods and nanospheres in suspensions and in stratified films. Angew. Chem. Int. Ed. 54, 5618-5622.
19. Querejeta-Fernández, A., Chauve, G.G., Methot, M., Bouchard, J., and Kumacheva, E. (2014). Chiral plasmonic films formed by gold nanorods and cellulose nanocrystals. J. Am. Chem. Soc. 136, 4788-4793.
20. Khan, M.K., Giese, M., Yu, M., Kelly, J.A., Hamad, W.Y., and MacLachlan, M.J. (2013). Flexible mesoporous photonic resins with tunable chiral nematic structures. Angew. Chem. 125, 9089-9092.
21. Chu, G., Vilensky, R., Vasilyev, G., Martin, P., Zhang, R., and Zussman, E. (2018). Structure Evolution and Drying Dynamics in Sliding Cholesteric Cellulose Nanocrystals. J. Phys. Chem. Lett. 9, 1845-1851.
22. Fernandes, S.N., Geng, Y., Vignolini, S., Glover, B.J., Trindade, A.C., Canejo, J.P., Almeida, P.L., Brogueira, P., and Godinho, M.H. (2013). Structural color and iridescence in transparent sheared cellulose films. Macromol. Chem. Phys. 214, 25-32.
23. Godinho, M., Fonseca, J., Ribeiro, A., Melo, L., and Brogueira, P. (2002). Atomic force microscopy study of hydroxypropylecellulose films prepared from liquid crystalline aqueous solutions. Macromolecules 35, 5932-5936.
24. Espinha, A., Dore, C., Matricardi, C., Alonso, M.I., Goñi A.R., and Mihi, A. (2018). Hydroxypropyl cellulose photonic architectures by soft nanoimprinting lithography. Nat. Photonics 12, 343-348.
25. Rofouie, P., Pasini, D., and Rey, A. (2015). Tunable nano-wrinkling of chiral surfaces: Structure and diffraction optics. J. Chem. Phys. 143, 114701.
26. Nagai, H., Liang, X., Nishikawa, Y., Nakajima, K., and Urayama, K. (2016). Periodic surface undulation in cholesteric liquid crystal elastomers. Macromolecules 49, 9561-9567.
27. Genzer, J., and Groenewold, J. (2006). Soft matter with hard skin: From skin wrinkles to templating and material characterization. Soft Matter 2, 310-323.
28. Wang, B., and Walther, A. (2015). Self-assembled, iridescent, crustacean-mimetic nanocomposites with tailored periodicity and layered cuticular structure. ACS Nano 9, 10637-10646.
29. Chu, G., Vilensky, R., Vasilyev, G., Deng, S., Qu, D., Xu, Y., and Zussman, E. (2017). Structural Transition in Liquid Crystal Bubbles Generated from Fluidic Nanocellulose Colloids. Angew. Chem. Int. Ed. 56, 8751-8755.
30. Kolle, M. (2011) Photonic structures inspired by nature. Springer: New York.
31. Saha, P., and Davis, V.A. (2018). Photonic Properties and Applications of Cellulose Nanocrystal Films with Planar Anchoring. ACS Appl. Nano Mater. 1, 2175-2183.
32. Chu, G., Wang, X., Chen, T., Gao, J., Gai, F., Wang, Y., and Xu, Y. (2015). Optically Tunable Chiral Plasmonic Guest-Host Cellulose Films Weaved with Long-range Ordered Silver Nanowires. ACS Appl. Mater. Interfaces 7, 11863-11870.
33. Chu, G., Wang, X., Yin, H., Shi, Y., Jiang, H., Chen, T., Gao, J., Qu, D., Xu, Y., and Ding, D. (2015). Free-standing optically switchable chiral plasmonic photonic crystal based on self-assembled cellulose nanorods and gold nanoparticles. ACS Appl. Mater. Interfaces 7, 21797-21806.
34. Chu, G., Yin, H., Jiang, H., Qu, D., Shi, Y., Ding, D., and Xu, Y. (2016). Ultrafast Optical Modulation of Rationally Engineered Photonic-Plasmonic Coupling in Self-Assembled Nanocrystalline Cellulose/Silver Hybrid Material. J. Phys. Chem. C 120, 27541-27547.
35. Tamaoki, N. (2001). Cholesteric liquid crystals for color information technology. Adv. Mater. 13, 1135-1147.
36. Mitov, M. (2012). Cholesteric liquid crystals with a broad light reflection band. Adv. Mater. 24, 6260-6276.
37. De Vries, H. (1951). Rotatory power and other optical properties of certain liquid crystals. Acta Crystallogr. 4, 219-226.
38. Yaraghi, N.A., Guarín-Zapata, N., Grunenfelder, L.K., Hintsala, E., Bhowmick, S., Hiller, J.M., Betts, M., Principe, E.L., Jung, J.Y., and Sheppard, L. (2016). A sinusoidally architected helicoidal biocomposite. Adv. Mater. 28, 6835-6844.
Floral-mimetic films with bistructural colour were obtained from nanocellulose liquid crystal. This hierarchical structured composite contained both cholesteric organization and microscopic wrinkly surface topography, demonstrating chiral light-matter interactions in coupled photonic architecture.
Supporting Information

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1. Materials and Apparatus

All Chemicals were used as received without further purification. Poly (vinyl alcohol) (PVA, $M_w = 31000$, AR) and sulfuric acid ($H_2SO_4$, 98wt.%) were purchased from Sigma-Aldrich. Poly (dimethyl siloxane) (PDMS, Sylgard 184 Silicone Elastomer Kit) was obtained from Dow Corning. Cotton pulp board was purchased from Hebei Paper Group of China.

Polarized optical microscopy (POM) image was conducted on Olympus BX51-P microscope with images taken by polarizers in a perpendicular arrangement to verify to the anisotropy of the composite samples. Surface morphologies of the samples were characterized using a Zeiss Ultra Plus high-resolution scanning electron microscope (HR-SEM) at an accelerating voltage of 3 KV. AFM test was conducted on Dimension 3100 Atomic Force Microscope in tapping mode. The obtained images were analysed using non-commercial software NanoScope Analysis (version 1.50 R2Sr2.111746). Zeta potential was performed on Malvern Zetasizer Nano-ZS90. Tensile strength measurements were carried out on 25×5 mm strips using a Dynamic Mechanical Analysis Q800 (T.A. Instrument) at 50% relative humidity. UV-visible-NIR spectra were recorded on Cary 5000 UV-Vis/NIR spectrophotometer in reflection mode which coupled with integrating sphere and the surface of the samples was mounted perpendicular to the beam path. Circular dichroism (CD) spectra were recorded on a BioLogic MOS-450 spectropolarimeter with the samples were mounted normal to the beam. The optical set-up for angular-resolved scattering measurements was based on previous report,¹ which composed by a broadband Deuterium-Halogen light source.
(mod. DH-2000, Ocean Optics) coupled to a multimode optical fibre. The output beam is collimated by a quartz lens, providing a spot size on the sample of 3 mm (angle of incidence 35°). The polarization of the incident beam was controlled by a combination of a linear polarization and a quarter waveplate. The light diffused by the sample is collected by a second optical fibre coupled to a spectrometer (mod. Flame, Ocean Optics). The collection fibre is mounted on a micrometric rotation stage for measuring spectra at various angles. Measurements were taken under left-handed circularly polarized and right-handed circularly polarized light illumination, respectively. Spectra were acquired at detection angles between 0° and 70°.

2. Experimental Section

Preparation of PDMS Sheet

PDMS film was prepared by mixing silicone elastomer with curing agent at a weight ratio of 10:1. Then, 5.0 g of the mixture was poured into a Petri dish (diameter 60 mm) with the thickness of PDMS layer about 2 mm. After that the mixture was degased in vacuum oven at room temperature for 20 min and cross-linked in an oven at 70 °C for 3 hour. Finally, the resulting PDMS sheet was cut into a rectangle shape with 4 cm in length and 2 cm in width for further usage.

Preparation of uniaxial wrinkled PDMS mould

The wrinkled PDMS sheet were prepared by a thermal shrinkage process with plasma treatment that as previously reported. Typically, the PDMS sheet was mounted onto a home-made sample holder with a uniaxial pre-stretch of 10%. Then, the strained PDMS
sheet was placed into a plasma vacuum chamber (Harrick Plasma, PDC-32G) for an oxygen plasma treatment at a pressure of 250 mTorr with high power input for a certain time duration (t=10 min and 20 min, respectively). This treatment can convert the topmost layer of PDMS into a hydrophilic silica coating. Finally, the pre-strain was relieved slowly and periodic oriented wrinkles spontaneously formed on the surface of PDMS to resist thermal shrinkage upon cooling the PDMS to room temperature.

**Preparation of square patterned and Technion logo patterned surface wrinkles on PDMS mould**

The editable patterned surface wrinkles were prepared by a selective plasma treatment that reported by W. Ding et al.² Briefly, the prepared PDMS sheet was mounted on a home-made sample holder with designed uniaxial pre-stretch (ε = 10%). After that, a fresh copper grid (Agar Scientific, 300 Mesh without carbon) or an engineered Technion logo mask (STI Laser Industries Ltd.) was attached to its surface and partially obscured the upper surface of PDMS sheet. Then, the strained PDMS substrate was placed into the vacuum chamber and underwent a selective oxygen plasma treatment in the same situation as above. Finally, the copper grid or the engineered mask was taken away along with relieving the pre-strain slowly and selectively patterned wrinkles was formed on the surface of PDMS sheet.

**Preparation of square patterned PDMS mould with wrinkled boundary**

After we got the square patterned surface wrinkles, the PDMS sheet was further processed with gold coating. Gold film was sputtered onto the surface of the prepared PDMS sheet with an SC7620 sputter coater (Quorum Technologies Ltd.) at pressure of
6 × 10^{-2} \text{ mbar and current of 18 mA. After coating for varied duration times (15 and 90 s, respectively), the gold coated PDMS sheet was heated at 90 °C for 1 hour and cool down to room temperature. The PDMS sheet that coated for 15 s exhibited a mixed wrinkle pattern with ordered square regions and disordered boundary; the PDMS sheet coated for 90 s exhibited a surface pattern that all the wrinkles in square regions and boundaries are disordered.}

**Preparation of zigzag wrinkles on PDMS mould**

The preparation method is similar to uniaxial wrinkled PDMS mould, the PDMS sheet was applied a biaxial stretching ($\epsilon_x = 5\%$, $\epsilon_y = 10\%$). After the plasma treatment, the biaxial strain was released in sequence (first x direction for width and then y direction for length) and ordered zigzag wrinkle patterns was formed on the surface of PDMS sheet.\(^3\)

**Preparation of cellulose nanocrystals (CNCs)**

In a typical experiment, 50 g of bleached commercial cotton pulp was milled using a commercial pulper containing 1000 mL of deionized water, followed by oven-drying. Next, 20 g of milled pulp was hydrolysed in 200 mL of H\(_2\)SO\(_4\) (1g pulp / 10 ml H\(_2\)SO\(_4\)) aqueous solution (64 wt\%) under vigorous stirring at 45 °C for 60 min. The pulp slurry was diluted with cold deionized water (about ten times the volume of the acid solution used) to stop the hydrolysis, and allowed to subside overnight. The clear top layer was decanted and the remaining cloudy layer was centrifuged. The supernatant was decanted and the resulting thick white slurry was washed three times with deionized water. Finally, the white thick suspension was placed into a Millipore ultrafiltration cell
(model 8400) to wash the cellulose nanocrystals with deionized water until the pH of solution was stable at 3 (usually take 4-5 days). The thick pulp slurry from the Millipore cell was dispersed by subjecting it to ultrasound treatment for 5 min, subsequently diluted to desired concentration.\textsuperscript{4,5} The CNCs have an average diameter of 15 nm with length of 200-300 nm.

**Preparation of cholesteric wrinkled film (CWF)**

An aqueous CNC suspension (5 g, 5.0 wt\%) was mixed with varying amount of PVA powder (0.025 g, 0.102 g, 0.208 g and 0.319 g, respectively) and stirred at room temperature for 3 h to allow the formation of a homogeneous mixture, which used as CNC-PVA ink for soft lithography process. Then, the ink was transferred onto the surface of the prepared PDMS mould ($\varepsilon = 10\%$, $t=10$ min) with the mould embedded into a PDMS coated Petri dish (60 mm, plasma treated) and the ink was fully spread onto the surface of PDMS. This mixture was allowed to evaporate under ambient conditions until solid films had formed on the surface of PDMS (typically ca. 2 days), generating CNC-PVA composite with cholesteric ordering. Finally, the CNC-PVA films was carefully peeled off from the PDMS mould with wrinkles imprinted onto the bottom surface of the film, giving rise to free-standing cholesteric wrinkled films (CWFs). Depending on the CNC-to-PVA ratio, the resulting composites were donated as CWF1-4, respectively. The corresponding wrinkle-free composites were prepared in the same condition by casting the CNC-PVA ink onto plasma treated PDMS sheet with smooth surface.
As a comparison, the wrinkled CNC-PVA composite film without cholesteric ordering was prepared by casting CNC-PVA-NaCl ink onto wrinkled PDMS mould in a similar process as above described. Typically, the ink was prepared by mixing PVA (0.319 g) with aqueous CNC suspension (5 g, 5.0 wt%) through vigorous stirring for 1 hour, and then NaCl was added into the mixture with the final concentration of 5 mM. After that, this CNC-PVA-NaCl ink was casted onto PDMS sheet for two days to generate a cholesteric-free wrinkled composite film.

The preparation process of surface patterned CWF was similar to regular uniaxial CWF. Typically, the CNC-PVA ink (CNC 5 g, 5.0 wt%; PVA 0.102 g) was casted onto the surface engineered PDMS mould with different kinds of patterns (zigzag, square patterns, etc.). After the CNC-PVA composites were dried, peeling off the film could imprint the surface patterns from the mould, leading to a free-standing engineered CWF.
3. Supporting Figures and Tables

![Figure S1](image.png)

**Figure S1** Optical images of the uniaxial wrinkled PDMS mould with the plasma treatment for 10 min (a) and 20 min (b), respectively.

**Table S1** Wavelength and amplitude of the wrinkled PDMS mould with varying plasma treatment time.

| Time   | Wavelength | Amplitude |
|--------|------------|-----------|
| 10 min | 2.3 µm     | 265 nm    |
| 20 min | 3.2 µm     | 290 nm    |
Figure S2 (a)-(d) Photographs of CWF1-4 showing photonic structural colour varied from blue, green, red and transparent as well as rainbow-like diffraction colour.

Figure S3 UV spectra of CWF1-4 in short wavelength which highlight the double peaks structure at 245 and 300 nm.
**Figure S4** UV-Vis spectra of wrinkle-free reference samples (REF1-3 corresponding to CWF1-3) exhibit only photonic band-gaps that derive from the helical organization of CNC.

**Figure S5** UV-Vis spectra of sample CWF3 rotated at varying angles 0°, 45° and 90°, respectively.
Figure S6 Photographs of a piece of CWF1 taken under different orientations showing strong angle-resolved iridescence.

Figure S7 CD spectra of sample CWF3. (a), (b) The comparison of CD signals for CWF3 and wrinkle-free REF3 at different spectra range. (c), (d) CD spectra of CWF3
rotated at different angles normal to the beam path, implying slightly linear dichroism at UV-blue range. (e), (f) The “front-and-back” CD measurements for CWF3 at different spectra range. The CD signal at UV-blue range changed as we flipped the sample, indicating the existent of linear birefringence for the wrinkle derived signal. Noted that the strong positive CD signal at 700-800 nm is due to the helical organization in CNC matrix.
Figure S8 (a1)-(a4) POM images of CWF1-4 at low magnifications. (b1)-(b4) POM images of CWF1-4 at high magnifications.
Figure S9 SEM image of the bottom surface of CWF2, showing smooth surface of the film.

Figure S10 POM (a) and SEM (b)-(d) images of CWF2 that focus on the cross sections of the film with different magnifications.
Figure S11 (a)-(d) Side view SEM images of cracked CWF2 composite with different magnifications, revealing the distortion of helical structure at the interface between bulk phase and wrinkles.
Figure S12 Two dimensional AFM image of PDMS mould and its corresponding numerical analysis (plasma treatment for 10 min, $\varepsilon = 10\%$).

Table S2 Comparison of PDMS mould and CWF2 for their wavelength and amplitude.

| Sample     | Wavelength | Amplitude |
|------------|------------|-----------|
| PDMS mould | 2.3 $\mu$m | 265 nm    |
| CWF2       | 2.5 $\mu$m | 270 nm    |
**Figure S13** Side view SEM images of the bulk phase in CWF with different magnifications.

**Figure S14** Photograph of a CNC-PVA composite film only with wrinkles (without cholesteric ordering) taken under left-handed and right-handed circular polarizer shows strong iridescence that due to the wrinkle-induced light diffraction.
**Figure S15** Photograph of CWF2 taken under left-handed and right-handed circular polarizer. It appears strong iridescence under a left-handed polarizer while its colour disappears under a right-handed polarizer.

**Figure S16** (a) Optical image of a wrinkled PDMS mould with cracks and defects. (b) POM image of CWF2 shows obvious cracks (highlight by arrow) and defects (highlight by ellipse) that imprinted from PDMS mould. (c), (d) SEM images of CWF2 that highlight the crack and defect, respectively.
Figure S17 Photograph of the square patterned PDMS mould which shows strong iridescent structural colour at the mask-free area.

Figure S18 (a) Optical image of the Cu-grid which used as mask for preparing square patterned wrinkles. (b) Optical image of the square patterned PDMS mould. (c) POM
image of the square patterned CWF composite. (d) Optical image of the square patterned CWF composite without polarizer.

**Figure S19** (a), (b) Optical images of the wrinkled PDMS mould with ordered wrinkles in square region and disordered wrinkles in boundary. (c), (d) Optical images of the wrinkled PDMS mould with disordered wrinkles in square region and boundary.
Figure S20 (a)-(d) POM images of a CWF composite with order-to-disorder transited square patterns and disorder wrinkled boundary. (a), (c) were regular POM images and (b), (d) were obtained with a full-wavelength (530 nm) retardation plate.
Figure S21 (a) Optical image of a hollowed-out mask with Technion logo. (b) Optical image of wrinkled PDMS mould with Technion logo. POM images of a CWF composite with Technion logo obtained without (c) and with (d) a 530 nm retardation plate.

REFERENCE:

1. Vignolini, S., Moyroud, E., Glover, B.J., and Steiner, U. (2013). Analysing photonic structures in plants. J. R. Soc. Interface 10, 20130394.
2. Ding, W., Yang, Y., Zhao, Y., Jiang, S., Cao, Y., and Lu, C. (2013). Well-defined orthogonal surface wrinkles directed by the wrinkled boundary. Soft Matter 9, 3720-3726.
3. Yin, J., Yagüe, J.L., Eggenspieler, D., Gleason, K.K., and Boyce, M.C. (2012). Deterministic order in surface micro-topologies through sequential wrinkling. Adv. Mater. 24, 5441-5446.
4. Chu, G., Wang, X., Yin, H., Shi, Y., Jiang, H., Chen, T., Gao, J., Qu, D., Xu, Y., and Ding, D. (2015). Free-standing optically switchable chiral plasmonic photonic crystal based on self-assembled cellulose nanorods and gold nanoparticles. ACS Appl. Mater. Interfaces 7, 21797-21806.
5. Chu, G., Feng, J., Wang, Y., Zhang, X., Xu, Y., and Zhang, H. (2014). Chiral nematic mesoporous films of ZrO$_2$: Eu$^{3+}$: new luminescent materials. Dalton Trans. 43, 15321-15327.