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Invited Article: Chiral optics of helicoidal cellulose nanocrystal films

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Cellulose nanocrystals in water suspensions behave as lyotropic liquid crystals forming a chiral nematic phase above a critical concentration. Such an organization can be retained in solid films and give rise to an intense colored appearance. Here, we characterize their optical response by applying optical and scanning electron microscopy, imaging scatterometry, and angle-resolved reflectance measurements. We show that the experimental results are well explained by computational modeling using the finite-difference time-domain method, but slightly less well by Berreman’s analytical model. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/; [http://dx.doi.org/10.1063/1.4978387]

I. INTRODUCTION

Pathways to the successful fabrication of photonic crystals using biopolymeric materials have been recently demonstrated.1–7 Within the plethora of architectures and materials that have been explored, cellulose-based chiral reflectors have been intensively studied, principally because it is possible to design the optical response of the deposited or fabricated films a priori by controlling the characteristic of the cellulose building blocks.8–10 Natural cellulose consists of hierarchically structured nanofibrils, which comprise localized crystalline domains separated by spaces of an amorphous structure. By strong acid hydrolysis, it is possible to extract rod-like, crystalline particles with dimensions that are strongly characteristic of the source of the cellulose.9,11 The production of these cellulose nanocrystals (CNCs) has been undertaken with the aim of producing bio-compatible composite materials with optimized mechanical properties.12

In colloidal suspensions, cellulosic nanorods spontaneously display a nematic liquid crystalline behavior at a critical concentration13,14 by forming a helicoidal nanostructure, which can be retained in a solid form.15–17 The optical response primarily relies on the properties of the nanoscale building blocks, i.e., the size distribution of the CNCs and the CNC density, but other important factors are the nature of the surface chemistry of the nanocrystals,16 the substrate material,18 and the temperature.19

The production of cellulosic photonic structures with chiral nematic ultrastructure and the parameters that affect their self-assembly have been amply investigated in the past but a complete optical characterization of the structures in terms of their optical response is absent. Here we combine different techniques to measure the angular- and polarization-dependent reflection properties of cellulose-based chiral films, and we compare the experimentally collected optical data with analytical and finite-difference time-domain (FDTD) calculations of detailed analogous models. Our results

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will contribute to better understand the advantages and limitations of using cellulose-based chiral films for structural color applications. The iridescent effect (i.e., the change of color as a function of the observation and/or illumination direction), the hallmark of structural coloration from ordered photonic structures, provides a vivid and metallic appearance to the films. This effect can be highly desirable for effect paints, but might be equally problematic for applications where color purity is required. Similarly, it is important to consider that CNC films can be used as efficient color-selective polarization filters, however only for small range of incidence angles. We here further show that their efficiency as polarization filters is, in fact, limited to angles smaller than 50°.

II. MATERIALS AND METHODS

A. Sample preparation

CNC films were produced from wood pulp using acid hydrolysis. This is described in Ref. 2 and comprises a modified form of the method of Revol et al. 22 Briefly, the wood pulp was dissolved in 64 w/w% sulfuric acid at 45 °C under continuous stirring for 1 h (ratio of cellulose to acid is kept at 1:9). The cellulose–sulfuric acid solution was diluted 10 times with cold deionized (DI) water, to stop the hydrolysis reaction, and then allowed to settle overnight. The resulting clear top layer was discarded, and after centrifugation of the remaining white suspension, the supernatant was removed. The remaining suspension was first diluted with DI water, re-concentrated by three more times centrifugation, to abolish all soluble cellulosic materials, and then dialyzed in dialysis membrane tubes with a 12 000–14 000 molecular weight cutoff (Spectrumlabs/Spectrapor membranes) against slow running pure water over 2–4 weeks or until the CNC suspension reached a pH of 6. The suspension was then concentrated to 35% using centrifugation and redispersed in deionized water to a final concentration of 1.1 w/w%.

In order to produce a homogeneously colored film and minimize defects and multi-domain formation, a custom-built stainless steel chamber was used for the self-assembly through slow evaporation. The relative humidity inside this chamber was adjusted to 50% using a solvent vapor annealing arrangement comprising two independent gas lines with computer-controlled nitrogen flow. 23 In one of the lines, the nitrogen was bubbled through DI water in a wash bottle, the temperature of which was thermostatically kept at 21 °C, before it was combined with the dry nitrogen of the other line (the relative flow rates in the two lines were adjusted to maintain 50% relative humidity in the output flow).

B. Optical microscopy

The reflectance spectra of the cellulose film were measured with a microspectrophotometer, an Olympus BX51 microscope with an Olympus MPLFLN 50x/NA 0.8 objective, connected to an Ocean Optics QE6500 spectrometer (Ocean Optics, Ltd., UK). The white balance of the digital camera (Lumenera Infinity 2-2; Lumenera, Inc., Ottawa, CA) was calibrated with a reflectance standard (Spectralon, Labsphere, North Sutton, NH, USA). Circular polarization was measured by inserting into the detection beam path a custom-built circular polarization filter, comprising an achromatic quarter-wave plate (Bernhard Halle Nachfl. GmbH, Berlin, Germany) and a linear polarizer (Thorlabs, UK). A silver mirror was used as a reference. Each polarization channel is normalized to the reflection of the mirror collected in the same polarization channel. The diameter of the measurement area was approximately 20 µm.

C. Angle-dependent spectroscopy

Angle-resolved spectroscopy was conducted using a home-built goniometer featuring two optical fibers. 24,25 The light source, a xenon lamp (HPX-2000, Ocean Optics), supplied a collimated beam onto the sample via a reflective collimator (RC08SMA-F01, Thorlabs) attached to an optic fiber. The sample is positioned axially in the goniometric system, mounted on a motorized rotation stage. The spot size on the sample had a diameter of approximately 2 mm. The light reflected by the sample was channeled by a reflective collimator into an optic fiber mounted on a moveable supporting arm, and subsequently to a photodiode spectrometer (AvaSpec-HS2048, Avantes, the Netherlands) that
was used to measure the spectral composition of the reflected light. The light intensity reflected by the sample was normalized with respect to that of a Lambertian diffuser. Edmund Optics stock nos. 88-098 and 88-101 circular polarizers were put 1 cm in front of the detector when measuring the left- and right-circular polarization (LCP and RCP), respectively. The polarizers’ characteristics limited the detectable wavelength range to $>410\,\text{nm}$. A series of measurements were taken by changing the angle of incidence on the sample and the detection arm so that the specular reflection from the sample was collected by the detector (i.e., in a symmetric $\theta$-$2\theta$-fashion).

**D. Scanning electron microscopy**

The ultrastructure of fractured samples was analyzed using a LEO GEMINI 1530 VP FEG-SEM electron microscope. To prevent charging effects, prior to imaging the samples were coated with a thin layer of Au/Pd (80:20) using an Emitech K550 sputter coater at a current of 55 mA for 6 s and an Au/Pd target.

**E. Imaging scatterometry**

The hemispherical far-field light scattering pattern of a single flake of cellulose was visualized with an imaging scatterometer. The scatterometer is built around an ellipsoidal mirror, which collects light from the full hemisphere around its first focal point, where the sample is positioned. A white light source (a xenon lamp) delivered either a narrow aperture ($\sim5^\circ$) or a full aperture (180$^\circ$) beam. For circular-polarization-dependent measurements, a circular sheet polarizer (Knight Optical) was added to the detection path. A small piece of magnesium oxide served as a white diffuse reference object. Images were acquired with an Olympus DP-70 camera and were subsequently corrected for geometrical distortions using a MATLAB routine.

**F. Finite-difference time-domain simulations**

We performed three-dimensional finite-difference time-domain (FDTD) calculations, using Lumerical FDTD Solutions 8.16, a commercial-grade Maxwell equation solver, to simulate the polarization-dependent light scattering from a liquid-crystalline, helicoidal stack of cellulose in the wavelength range 350-700 nm. A stack with a fixed thickness of 3 $\mu$m and varying pitch length $p$, defined here as the periodicity of the helicoidal structure after a 180$^\circ$ rotation, was placed in a three-dimensional simulation volume of $2 \times 2 \times 4\,\mu\text{m}^3$. Within the finite-differences approach, the governing differential equations (i.e., the real-space time-domain Maxwell equations) are discretized onto a regular lattice in time (equidistant time steps) and space (cubic voxels on the Yee grid). Propagation of electromagnetic fields is simulated by time step-wise forward integration. The refractive index of cellulose was assumed to be anisotropic with a refractive index 1.53/1.58, i.e., a birefringence of 0.05$^2,28$ with a variation of the director of the pitch perpendicular to the film surface.

**III. RESULTS AND DISCUSSION**

**A. Optical response and ultrastructure of the cellulose film**

Cellulose chiral reflectors were produced by the evaporation-induced self-assembly of a 3 ml CNC suspension into a polystyrene Petri dish (see Section II). Figure 1(a) shows a macroscopic picture of a typical cellulose film. All the measurements reported were obtained in the central, homogeneously colored area of the film; this avoided the additional linear dichroism induced at the film’s edge by water meniscus effects.$^2,29$ Polarization microscopy showed strong circular-polarization dichroism of the film (Figs. 1(b) and 1(c)). An intense blue color appearance was clearly observed in the Left Circularly Polarized (LCP) channel (Fig. 1(b)), but the sample channel featured only a very minor reflection in the Right Circularly Polarized (RCP, Fig. 1(c)) channel. This demonstrates that the film is an efficient chiral reflector. Reflectance spectrophotometry (Fig. 1(f)) on the same area confirmed that the structure reflects LCP light preferentially, with a peak reflectance wavelength at approximately 450 nm.

To reveal the physical origin of the color and correlate it with the chiral nematic pitch, we studied cross sections of the film by scanning electron microscopy (SEM). The low-magnification
SEM image of Figure 1(d) shows a homogeneous layering across a large area, with the chiral nematic director clearly oriented perpendicularly to the sample surface. The high-magnification SEM image of Figure 1(e) reveals a pseudo-layered helical structure, characteristic for a system with a left-hand twisted alignment of the nanocrystals, archetypal of helicoidal Bouligand structures.\textsuperscript{2,9,30} The chiral nematic order of the studied samples appeared to be quite uniform along the entire fracture edge, with an average periodicity (i.e., defined here as the pitch $p$) being about 145 ± 10 nm.

### B. Angle- and polarization-dependent reflectance

To investigate the angle-dependent reflectance of the CNC film, we investigated its circular polarization response with imaging scatterometry and angle-dependent goniometry (Fig. 2). Imaging scatterometry confirmed the different response of LCP and RCP light: it shows that incident, narrow-aperture light is reflected in a mirror-like fashion (insets of Figs. 2(a) and 2(c)). Illuminating the sample with a wide-aperture beam covering the entire hemisphere images the angle-dependent iridescence of the film in a single scatterogram.\textsuperscript{27} Figures 2(a) and 2(c) show the resulting scatterograms for both LCP and RCP states. With increasing scattering angles, the color of the reflected light shifts hypsochromically, from blue to violet, becoming whitish at scattering angles $>60^\circ$. LCP light is strongly reflected (Fig. 2(a)) and shows strong blue coloration in the central area (associated with polar angles below 30$^\circ$) and pronounced color shifting to violet (typical of iridescent systems) and to white for large scattering angles. In contrast to this, brightly scattered RCP light only becomes significant for large scattering angles ($>60^\circ$). At smaller scattering angles, RCP reflection is comparatively low.

To characterize the optics of the CNC films quantitatively further, we measured the reflectance spectra of a free-standing cellulose film at different angles of incidence (Figs. 2(b) and 2(d)). The sample was illuminated with unpolarized light, while a circular polarizer was inserted into the detection path. This enabled measurement of the polarization-dependent optical response of the film. A clear reflection band centered around 450 nm with a FWHM of ~60 nm is observed for the LCP
FIG. 2. Circular polarization-dependent reflectance of a cellulose film. ((a) and (c)) Wide-aperture scatterograms and ((b) and (d)) angle-dependent reflectance spectra. ((a) and (b)) LCP and ((c) and (d)) RCP light. Insets in (a) and (c): imaging scatterograms with narrow-aperture illumination. The red circles in the scatterograms indicate scattering angles of 5°, 30°, 60°, and 90°, from the center outwards, respectively; the black bar at 9 o’clock is due to the glass micropipette holding the sample.

channel, but no spectral features were obtained in the RCP channel. This corresponds to the data presented in Figure 1(f). For increasing angles of incidence, the LCP reflectance is severely blue-shifted, subsequently moving below 410 nm at ~50°.

C. Optical modelling

To quantitatively understand the angle-dependence of the chiro-optical reflectance, we performed finite-difference time-domain (FDTD) modeling,31,32 as well as calculations based on Berreman’s 4 × 4 matrix formalism.33,34 For the FDTD calculations, the cellulose helicoid was placed at the center of the simulation box with absorbing boundary layers above and below the structure and periodic boundary conditions in the plane. The reflectance was then calculated for incidence angles of light from 0° (normal incidence) to 70° in steps of 10°, for both the LCP and RCP states (see Section II). Figure 3(a) shows the effect of the pitch length on the optical response. Not surprisingly, the peak reflectance wavelength shifts bathochromically, i.e., to longer (red) wavelengths, as the layer pitch increases. A cellulose film with a pitch of 125 nm yields a peak reflectance at ~380 nm, whereas a pitch of 200 nm results in a peak reflectance at ~630 nm. Furthermore, the FWHM of the peak increases with increasing pitch length. This confirms that thin films of cellulose nanocrystals are highly tunable photonic structures. The FDTD-modelled results are in very good agreement with data obtained employing Berreman’s method with the same parameters of pitch, refractive index, and film thickness (Fig. 3(a)). We ascribe the 4 nm mismatch in the two methods’ peak reflectance wavelength positions to numerical differences between FDTD and Berreman calculations, while the lack of an angular independent reflectance (of about 4%–5% in each polarization channel) is due to the fact that Berreman’s method treats the CNC film as a homogenous medium and therefore does not account for the air-CNC film interface. This is instead considered in the full FDTD simulations and is observed in the experimental measurements.

Finally, the angle-dependent reflectance calculated for the two polarization states is shown in Figures 3(b) and 3(c). The peak reflectance for LCP light is at 460 nm, with a FWHM of 30 nm. With an angle of incidence increasing to 70°, the reflectance peak shifts to ~370 nm. However, as also
FIG. 3. Optical simulations of the circular polarization-dependent reflectance of a chiral cellulose stack. (a) Reflectance spectra for pitch values $p$ ranging between 125 and 200 nm. Solid lines: finite-difference time-domain simulations; dashed lines: analytical modelling data following from Berremann’s formalism. (b) and (c) FDTD simulations of the polarization-dependent reflectance for (b) LCP and (c) RCP light for a chiral cellulose stack with a pitch of ~147 nm showing clear iridescence.

observed experimentally, the peak prominence (defined as the ratio between the reflected intensity at the peak wavelength with respect to the background) decreases. In contrast, the reflectance in the RCP channel does not display a clear peak through the entire wavelength range for all angles of incidence. For both polarization channels, the reflectance significantly increases for angles of light incidence above 50°. By comparing the experimental results of Figure 2 with the FDTD calculations, we conclude that the modelling captures the angular- and polarization-dependent response very well. The narrower FWHM of the calculated reflectance peak indicates the presence of a relative disorder in the value of the pitch of the cellulose layers.

IV. CONCLUSION

We have investigated the angle-dependent reflectance of a self-assembled cellulose film, and we have shown that the strong difference in circular polarization is maintained over a large angular range of light incidence. This reflectance can be well understood by employing finite-difference time-domain modelling. Earlier studies have shown that the color appearance of the films can be controlled by changing the self-assembly conditions for CNCs. Together, these studies provide a more complete
understanding of the angle-dependent color appearance of helicoidal layers that might be ultimately employed to create sustainable colored materials, e.g., responsive dyes or food colorants.

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