**Supporting Information for "Formation of chiral nematic films from cellulose nanocrystal suspensions is a two-stage process." by Xiaoyue Mu and Derek G. Gray***

## Experimental details

CNC suspensions were prepared from dried Whatman cotton powder (40 g.) by treatment with a preheated sulfuric acid solution (64% w/w, 700 mL) at 45°C for 45 min, after which the reaction was quenched by 5L of deionized water. The suspension was washed by repeated centrifugation and re-dilution before extensive dialysis against deionized water until the effluent remained at neutral pH. The suspensions were dispersed by sonication, mixed-bed ion-exchange resin was added and stirred for 24 h to complex any stray ions and the suspension was filtered through glass microfibre filters (0.45 μm pore size) to remove particulate impurities introduced by the sonicator tip. The concentration of the acid ($H^+$) form suspensions was determined gravimetrically as 5.2% w/w. CNC-glucose suspensions were prepared by adding solid D-(+)-glucose (anhydrous, Sigma-Aldrich) to known volumes of the 5.2% w/w CNC suspension to give samples with glucose concentrations of 1%, 3%, 5%, 7% and 10% w/v. The colloidal CNC-glucose samples were briefly sonicated for 1min or until all glucose had dissolved, and stirred for 24h. For polarized light microscopy, small amounts of each sample were transferred to 1.0 x 10 mm rectangular cross-section glass micro-slides (VitroCom, Mountain Lakes, NJ), sealed with Parafilm® and allowed to stand vertically for 2-3 days until phase separation occurred. Replicate pitch measurements were made at different locations of individual suspensions prepared from a single CNC sample. Droplets of the suspensions were deposited on glass or black acrylic substrates and allowed to evaporate under ambient conditions. Images of the liquid crystalline suspensions in glass microslides were taken in transmission with a Nikon Eclipse LV100POL optical microscope equipped with a camera and a 530 nm wave plate. The images were used to estimate the chiral nematic pitch, *P*, for the suspensions, where the pitch is twice the line spacing of the fingerprint regions of the image. Photographs of the iridescent films against a black background were taken with a Canon EOS T3i camera.

Reflection spectra of selected films were measured with a confocal microscope attached to a UV-visible spectrometer (Horiba-Jobin). An example is shown below; the broad bands result from the range of reflection colors displayed by the films.

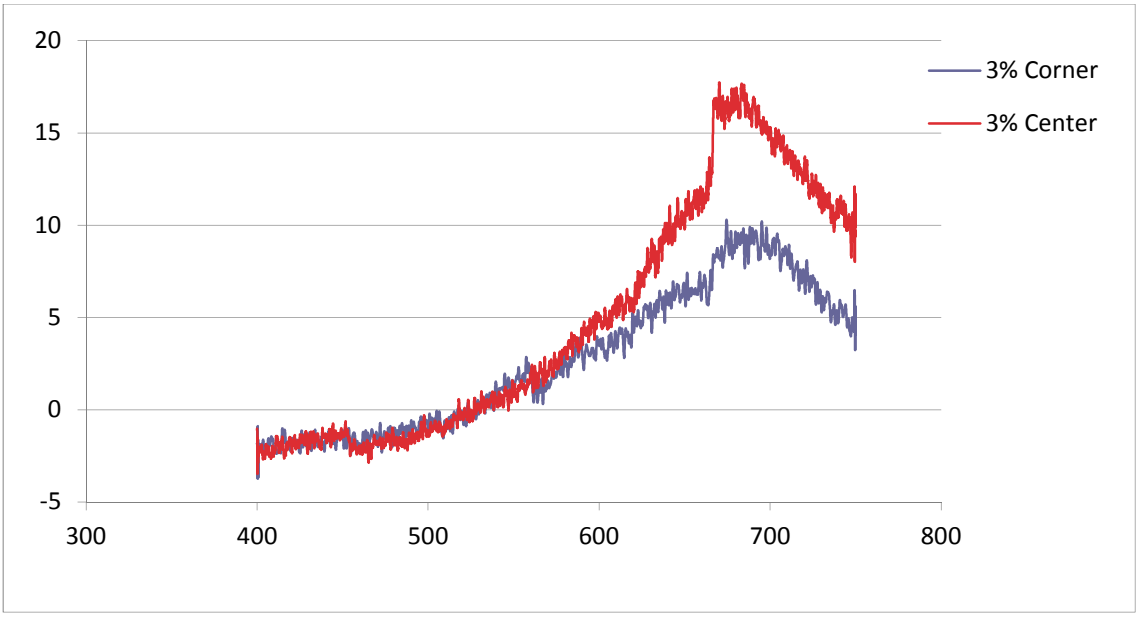


Fig. S1. Reflection spectra of films containing 5.2% CNC and 3% glucose, measured at different locations on the film.

**Topography of dried films**

When placed on acrylic and glass surfaces, the suspensions formed sessile droplets with a finite contact angle. For the evaporation of pure water droplets on a glass surface,[1] the contact line remains pinned at the droplet edge, and the apparent contact angle decreases during evaporation. As shown by Deegan et al.[2] in describing the "coffee-stain effect", solids dispersed in a drying drop migrate to the edge of the drop to form a solid ring, where the migration is caused by the evaporation-driven outward flow of liquid in the droplet. In the case of the rod-like cellulose nanocrystals, the droplet suspension is already in the ordered state, and the increase in CNC concentration at the edge of the evaporating droplet is sufficient for gel formation, which tends to fix the chiral nematic pitch. Thus, there is a buildup of chiral nematic

gel at the edge, whereas the lower concentration suspension is found in the middle. This was demonstrated by measuring the height of the film with a surface profilometer (Ambios XP200) and 2.5 μm stylus at a scan speed of 0.2 mm/s (Fig.S2).

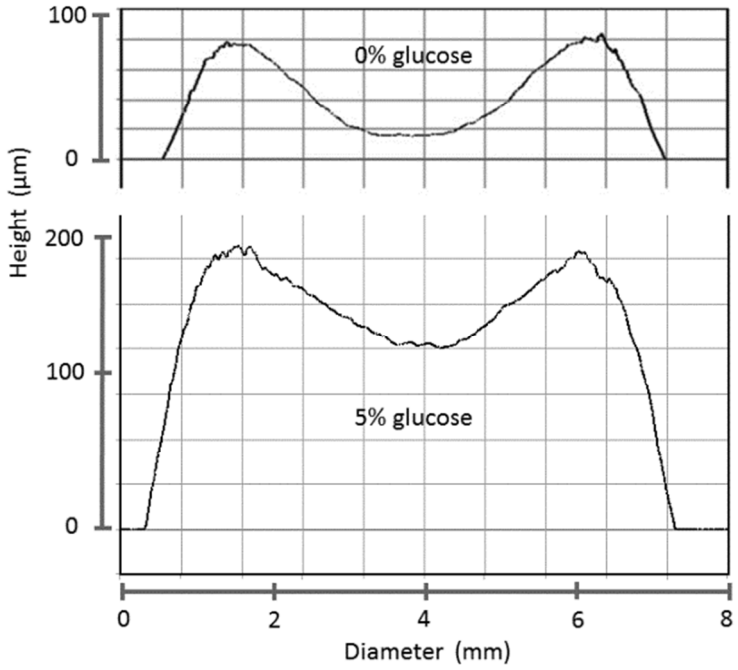


**Figure S2.** Profilometer scans across diameter of dry films cast from CNC suspensions containing 0 and 5% glucose.

Without glucose, the evaporation-driven mass transfer of CNC to the edge of the drop produces a high concentration of CNC relative to the center, leading to gel formation, starting at the perimeter of the drying drop, and trapping the chiral nematic pitch at the red end of the spectrum. The residual more dilute suspension has more time to attain its equilibrium (shorter pitch) helicoidal arrangement before being trapped in a gel or glassy state. The general shape of the cross-section is maintained on addition of glucose (Fig.S2) but the 5% glucose sample contains as much glucose as CNC, which adds to the bulk of the film and shifts the reflection band to longer wavelengths, since glucose itself forms a glass and acts as a diluent, preventing the CNC from attaining shorter-pitch values.

ACKNOWLEDGMENT

We thank Dr. H.P.T. Nguyen, Department of Electrical and Computer Engineering, McGill University for the profilometry measurements, and Drs. M. Andrews, A. Hill and F. Hajiaboli for the reflectance spectra.

REFERENCES

(1) Birdi, K. S.; Vu, D. T.; Winter, A. A Study of the Evaporation Rates of Small Water Drops Placed on a Solid Surface. *J. Phys. Chem.* **1989**, *93*, 3702-3703

(2) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **1997**, *389,* 827–829.