# SUPPORTING INFORMATION

## Tuning the Iridescence of Chiral Nematic Cellulose Nanocrystals and Mesoporous Silica Films by Substrate Variation

### Thanh-Dinh Nguyen,<sup>a</sup> Wadood Y. Hamad,<sup>b</sup> and Mark J. MacLachlan<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, University of British Columbia,
2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada
<sup>b</sup>CelluForce, Inc., 3800 Wesbrook Mall, Vancouver, British Columbia, V6S 2L9, Canada
\*E-mail: mmaclach@chem.ubc.ca

#### **1. Experimental Section**

**Starting Materials**: Tetramethyl orthosilicate (TMOS, Si(OCH<sub>3</sub>)<sub>4</sub>,  $\geq$ 99%, Acros-Organic), polydimethylsiloxane (PDMS, 99%, Acros-Organic), hydrogen peroxide, sulfuric acid, and nitromethane were purchased and used as received. Teflon (Nalgene company), paraffin (parafilm roll, Neenah), polyethylene (ziplock bag), aluminum foil (Alcan), alloy steel sheet, cellulose membrane of dialysis tubing (Aldrich), silicon wafer (University Wafer), slide glass plate (Fisher Scientific), mica (Chhaperia mica product), cellulose acetate (Xerox transparencies), and polystyrene (polystyrene Petri dish, Fisherbrand) were purchased and designed as supported substrates. Cellulose nanocrystals (CNCs) were prepared as previously described from sulfuric acid hydrolysis of fully-bleached, commercial kraft softwood pulp.<sup>[1]</sup> CNCs prepared by this method contain strongly acidic surface sulfate groups (ca. 1 per 20 glucose units) that provide CNCs with a negative surface charge when suspended in water.

**Preparation of substrates**: The substrate films of teflon, paraffin, polyethylene, cellulose membrane of dialysis tubing, aluminum foil, nitrocellulose, and cellulose acetate were cut to 10 cm x 10 cm pieces and adhered to a glass plate using double-sided tape. The silicon wafer and slide glass plate substrates were washed by soaking in a Piranha solution (20 mL 30%  $H_2O_2/100$  mL 98%  $H_2SO_4$ ) for 45 min followed by rinsing with copious distilled water.

**Preparation of polydimethylsiloxane (PDMS)-coated glass plate**: The glass slide after washing by the Piranha solution was dried with nitrogen. The clean glass slide was coated with a thin layer of PDMS by dipping the plate into a PDMS solution (0.1 vol.% in hexane). The PDMS layer was cured at 80 °C for 1 h with blowing air to form a PDMS-coated glass plate with highly hydrophilic surface.

**Preparation of nitrocellulose films**: A concentrated HNO<sub>3</sub> (63%) and H<sub>2</sub>SO<sub>4</sub> (98%) solution with HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> volume ratio of 1:2 was prepared in a round-bottomed flask. The acid mixture was chilled on an ice bath followed by slowly adding cellulose (filter paper) with cellulose:HNO<sub>3</sub> weight ratio of 1:50. The reaction mixture was stirred for 2 h until no clumps formed, then the reaction was quenched with ice water and filtered to collect white-colored nitrocellulose powders. A homogeneous dispersion of nitrocellulose was prepared by dissolving 200 mg nitrocellulose in 4 mL nitromethane under stirring overnight. Nitrocellulose films were cast on a 60 mm diameter glass Petri dish and left to dry in the fumehood for 24 h.

**Preparation of chiral nematic mesoporous silica (CNMS) films.** An aqueous CNC dispersion (60 mL, 3.0 wt.% CNC, pH 2.4) was sonicated for 10 min and then mixed with 2.8 mL Si(OCH<sub>3</sub>)<sub>4</sub> under stirring for 60 min at room temperature to form a homogeneous silica-CNC composite mixture. A silica:CNC ratio of 39:61 wt.% was used to obtain red-shifted composite samples prepared on highly hydrophilic substrates (e.g., aluminum, PDMS-coated glass plate) that allowed us to generate visible photonic silica structures after calcination (i.e., this ratio gave the best range). Portions (5.0 mL) were drop-cast on the clean surface of the different substrates at the same conditions (ambient conditions for 48 h) to give silica-CNC composite films (see Table S1). To adjust the evaporation rate of water in the dispersion on the substrates inside a working fumehood (faster evaporation than ambient) and in a desiccator with a partially opened lid (slower evaporation than ambient). To remove the CNC template, the silica-CNC composites were heated to 540 °C at a heating rate of 2 °C min<sup>-1</sup> under air and held at that temperature for6 h.

**Characterization:** Ultraviolet-visible/near-infrared spectroscopy was conducted on a Cary 5000 UV-Vis/NIR spectrophotometer. Circular dichroism (CD) experiments were recorded using a JASCO J-710 spectropolarimeter. In both cases, quartz slides were used and small pieces of the films were mounted perpendicular to the beam path. For the CD spectroscopy, the dried silica films usually show very intense CD signals so it is necessary to only partially cover the aperture. The signals were all normalized to 1000 mdeg. Note that the position of the reflectance peak of the silica films templated by CNCs has slightly shifted from our previous results owing to different batches of CNCs and small changes in the preparative conditions. In the current work, the same CNC dispersion (3

wt.%, pH 2.4) was used throughout and the reflectance peak was consistent. The thickness of the films was determined with an electronic digital micrometer (Marathon). Scanning electron microscopy (SEM) images of the samples were obtained on a Hitachi S4700 electron microscope. The samples were prepared by breaking the films into small pieces and attaching them to aluminum stubs using double-sided adhesive tape and then sputter-coated with gold (5 nm). Transmission electron microscope (TEM) images of the samples were obtained on a Hitachi H7600 electron microscope. The silica film samples were gently ground to a fine powder, suspended in ethanol, and then deposited onto TEM grids. Polarized optical microscopy (POM) was performed on an Olympus BX41 microscope. Nitrogen adsorption/desorption isotherms were obtained on a Micromeritics Accelerated Surface Area & Porosity (ASAP) 2000 system; before measurements, the film samples (~120 mg) were degassed at 150 °C in vacuum for 4 h. Static contact angle measurement of the aqueous CNC dispersion droplets on the different substrates was obtained on a contact angle instrument (ASTM standard D 724-99). The droplets with appropriate volumes (3  $\mu$ L) of the aqueous CNC dispersion were released from a syringe on the substrates for measurement.

Sample <sup>a</sup>	Substrate	Composites	Iridescence	Thickness [µm]	Reflectance peak [nm]	Pitch [nm] <sup>b</sup>		
Pure CNC films								
N1	aluminum		blue	100	340			
N2	cellulose acetate		yellow-red	130	630			
N3	teflon		nacre-like	380	740			
Silica-CNC composites and CNMS films								
<b>S1</b>	aluminum	C1	blue		370	~400		
S2	alloy steel sheet	C2	blue		600			
<b>S</b> 3	acid-treated silicon wafer	C3	blue-yellow		590			
<b>S4</b>	mica	C4	yellow		712			
<b>S</b> 5	cellulose acetate	C5	yellow-red		710			
<b>S6</b>	polystyrene	C6	red		850	~800		
<b>S7</b>	teflon	C7	nacre-like		550	~250		
<b>S8</b>	paraffin	<b>C8</b>	nacre-like		520			
<b>S9</b>	polyethylene	С9	nacre-like		530			
S10	nitrocellulose	C10	violet-blue		440	~400		
S11	PDMS-coated glass plate	C11	blue		380			

### Table S1. Different preparation conditions of the chiral nematic films of pure CNCs and CNMS.

[*a*] Evaporation-induced self-assembly of the aqueous dispersions was carried out at ambient conditions. [*b*] The helical pitches were estimated by observing fracture cross-sections of the CNMS films using SEM image. The ratio of silica to CNC in the composites was fixed at 39:61 wt.% (assuming complete condensation) in all of the preparations of the CNMS films.



Pure CNC films

Figure S1. SEM images viewed along fracture edges of the chiral nematic films of pure CNC and silica-CNC composites prepared on the different substrates: (a,b) aluminum foil; (c,d) cellulose acetate; (e,f) teflon; (g,h) nitrocellulose.



**Figure S2.** POM images of the pure CNC films prepared on the different substrates (all scale bars =  $100 \ \mu m$ ).



Figure S3. POM images of (a) the silica-CNC composites prepared on aluminum and (b) corresponding silica films after calcination (scale bars = 100  $\mu$ m). (c) UV-vis-NIR transmission spectra of the composites prepared on aluminum (C1), acid-treated silicon wafer (C3), cellulose acetate (C5), nitrocellulose (C10), and polystyrene (C6). (d) CD spectrum of the composites prepared on aluminum (C1).



Figure S4. POM images of the CNMS films prepared on the different substrates (all scale bars =  $100 \mu m$ ).



**Figure S5.** Optical characterization of the chiral nematic films prepared on the hydrophilic substrates. (a) UV-vis-NIR transmission spectra of the silica-CNC composites prepared on PDMS-coated glass plate (C11), alloy steel sheet (C2), mica (C4), and acid-treated glass plate. (b) UV-vis transmission spectra, (c) photograph, (d) normalized CD spectra of the CNMS films prepared on PDMS-coated glass plate (S11), alloy steel sheet (S2), mica (S4), and acid-treated glass plate.



**Figure S6.** Optical characterization of the chiral nematic films prepared on the hydrophobic substrates. (a) UV-vis-NIR transmission spectra of the silica-CNC composites prepared on teflon (C7), paraffin (C8), polyethylene (C9). (b) UV-vis-NIR transmission spectra of the corresponding calcined silica films S7, S8, S9. (c) CD spectrum of the CNMS films prepared on teflon (S7).

Sample	$\frac{\mathbf{S}_{BET}}{[\mathrm{m}^2  \mathrm{g}^{-1}]}$	$\frac{V_{pore}}{[cm^{3}g^{-1}]}$	d <sub>pore diameter</sub> [nm]
S1	617	0.50	3.7
<b>S</b> 3	587	0.40	3.6
<b>S5</b>	590	0.46	3.9
<b>S6</b>	600	0.47	3.8
S7	619	0.52	3.8
<b>S8</b>	594	0.46	3.9
<b>S10</b>	620	0.55	4.0

Table S2. Surface areas, pore volumes, and pore diameters of typical CNMS films.



**Figure S7.** Porosity of the CNMS films. (a) Nitrogen adsorption/desorption isotherms, (b) BJH pore size distribution, (c) Cross-sectional SEM image viewed at a high magnification and (d) TEM image of the CNMS films prepared on aluminum (**S1**).



Figure S8. SEM images viewed along fracture edges of the CNMS films prepared on (a) nitrocellulose (S10) and (b) teflon (S7).



**Figure S9.** SEM images viewed along edges (between top surface and cross-section) and flat surfaces at both under and upper sides of the CNMS films prepared on teflon (**S7**). The edge side of the air-exposed surface (a) and the substrate-contacted surface (b) of the films. The top surface of the films exposed to air (c) and contacted with the supported substrate (d) during self-assembly. SEM images of the different sides of the films show similar morphologies of the chiral nematic textures.



**Figure S10.** SEM image of the mesoporous silica films prepared on cellulose membrane of dialysis tubing. We observed that a highly wet impregnation of the composite dispersion with the highly hydrophilic cellulose membrane substrate gave thin composite films. Calcination of the thin composites recovered very thin mesoporous silica films showing no iridescence as presented in the photograph (inset), while retaining the chiral nematic order as observed by SEM. This observation reveals that increasing the affinity of the substrate surface for the dispersion resulted in a dramatic decrease of the helical pitch of the composite films. The iridescence of the silica films disappeared due to the shift in reflected wavelength to the UV region. This result further confirms the blue-shifted iridescence of the CNMS films prepared on the highly hydrophilic surface (e.g., aluminum) whereas the use of the less hydrophilic surface (e.g., polystyrene) generally gave the red-shifted CNMS films.



**Figure S11.** Controlling the evaporation rate of the aqueous composite dispersions on the substrates allowed for tuning the iridescence of CNMS films.

(A) UV-vis-NIR spectra of CNMS films prepared at ambient conditions on (a) polystyrene and (b) cellulose acetate and CNMS films prepared in a desiccator with a partially opened lid on (c) polystyrene and (d) cellulose acetate. The CNMS films prepared in the container where the water evaporation was slower was blue-shifted relative to the samples prepared under ambient conditions. In the container, slower water evaporation than ambient could result in slowly self-assembly rate of CNCs in favor of the formation of packed arrays in the composites, probably resulting in a decrease of the helical pitch.

(**B**) UV-vis-NIR spectra of CNMS films prepared at ambient conditions on (a) aluminum and (b) nitrocellulose and CNMS films prepared in a working fumehood on (c) aluminum and (d) nitrocellulose. Under the fumehood, the films prepared were red-shifted arising from faster water evaporation that could accelerate the self-assembly of CNCs to induce an increase in the helical pitch.

Note that CNMS films prepared on the hydrophobic substrates (e.g., teflon) show no tunable iridescence when adjusting the evaporation rate of the dispersion. This is assumed that the dispersion dispensed on the highly hydrophobic surface has a high surface tension inducing close-packed twisted arrays of CNCs that may be only weakly sensitive to the water evaporation rate.

#### References

[1] (a) K. E. Shopsowitz, H. Qi, W. Y. Hamad, M. J. MacLachlan, *Nature*, 2010, **468**, 422. (b) K. E. Shopsowitz, W. Y. Hamad, M. J. MacLachlan, *J. Am. Chem. Soc.*, 2012, **134**, 867.