



Structured color humidity indicator from reversible pitch tuning in self-assembled nanocrystalline cellulose films

Yu Ping Zhang^a, Vamsy P. Chodavarapu^a, Andrew G. Kirk^a, Mark P. Andrews^{b,*}

^a Department of Electrical and Computer Engineering, McGill University, Montreal, QC H3A2A7, Canada

^b Department of Chemistry, McGill University, 801 Sherbrooke St West, Montreal, QC H3A 0B8, Canada

ARTICLE INFO

Article history:

Received 16 July 2012

Received in revised form

27 September 2012

Accepted 28 September 2012

Available online 6 October 2012

Keywords:

Iridescence

Humidity indicator

Colorimetric indicator

Helical tuning

Nanocrystalline cellulose

Chiral nematic film

Cholesteric film

Bragg reflector

ABSTRACT

Iridescence is an example of structured color that is widespread in the biosphere, exhibited by multilayer inorganic thin films for optical filters, photonic crystals and other materials in which the periodic patterning of matter interacts with an electromagnetic field. Nanocrystalline cellulose (NCC) can be cast in the form of thick iridescent films whose color originates in the multi-domain chiral nematic texture created by self-assembly of the rigid rod crystallites. Scanning electron microscopy confirms the periodic layer structure that arises from the helical twist axis of the chiral nematic mesophase film. In effect, the film comprises multi-domain Bragg reflectors. On exposure to liquid water, and high relative humidity (RH), a reversible shift in the film iridescence from dry state blue-green to wet state red-orange is observed. This color change, which requires no pigment, is quantified by reflectance spectroscopy. The color transition is attributed to sorption of water that causes the pitch of the Bragg reflector to enlarge, and this leads to a red shift in the iridescence. The subsequent expansion of the film thickness was observed using polarized optical microscopy. The effect resembles molecular dopant and electric field induced pitch tuning along the helicoid axis in one-dimensional photonic crystal-like chiral nematic molecular systems. The color shift for a 40 μm thick NCC film is slow, occurring on timescale of 1–3 min. Thinner films change color in less than 2 s.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Color indicators have broad appeal for monitoring the quality, freshness and shelf life of packaged foods, pharmaceuticals and chemicals. In particular, disposable indicators offer ease of visual readout with no need for electronic circuitry. Moreover, advances in flexographic and gravure tools to print functional inks create opportunities for both the print and packaging industries to create what can be viewed as one of the simplest of “indicator displays” – a symbol, a surface area or a design that changes color on exposure to an analyte. Humidity sensors are desirable in the food industry, which makes conflicting demands with respect to moisture content [1]. Thus while excess moisture can accelerate decomposition of meats, most water laden fruits and vegetables are best stored under 95% relative humidity (RH) at near 0°C; but sugar and salt lose texture and desirable flow characteristics if the moisture content is too high. Grains can become rancid when the RH is too low. Archival materials like books and paintings require careful monitoring to prevent mold and bacterial decomposition. For some

technological hardware, the functionality of electronic components can be compromised if the RH is too high.

Conventionally, humidity sensors are made from electronic hygrometers based on capacitive or resistive systems that measure the change in conductivity of a polymer or ceramic film as a function of relative humidity [2]. Such devices have limitations in their operating conditions and can be expensive and bulky to use [3]. Colorimetric humidity indicators are advantageous because color change is easily detected visually, obviating the use of any electronics or instruments. There has been a number of proposed colorimetric relative humidity indicators, the majority of which are based on the use of inorganic salts such as cobalt(II)chloride. A typical commercial form of the latter is the Humitector[®] Humidity Indicator Card (Chemie Inc., USA). Hybrid polymer/CoCl₂ nanocomposites have been used in combination with lithographically prepared diffraction gratings for humidity sensing [4]. Despite the simplicity of the CoCl₂ indicator, cobalt-free humidity cards have been advocated as replacements to satisfy the European Chemical Bureau REACH directive [5]. Elsewhere, polymer-based colorimetric inks have been suggested as potential low cost alternatives [6]. Some of these are based on chromogenic dyes [7], while others offer polymer-based photonic crystals [8]. The latter are interesting in view of the ways that ordered materials can interact with light to produce a variety of optical effects

* Corresponding author. Tel.: +1 514 398 4459.

E-mail address: mark.andrews@mcgill.ca (M.P. Andrews).

collectively known as structured color. Structured color is caused by scattering that arises from spectral reflection due to the physical interaction between light and the geometric patterning of matter over different length scales. Changes in structured color can be used for a variety of sensing applications, though the underlying mechanisms by which the color changes evolve can differ. In the biosphere, the longhorn insect species, *Tmesisternus isabellae*, constructs its own colorimetric humidity indicator from periodic alternating layers of dense melanoprotein and inhomogeneous layers of melanoprotein nanoparticles and air voids [9]. Constructive multilayer interference gives rise to a gold iridescence in the dry state. Water sorption and infiltration swell the multilayers and alter the refractive index and layer spacing. Simultaneously, the reflectance exhibits changes in iridescence from gold at low RH to red in the wet state. Photonic crystals belong to the category of structured color materials as well. Indeed, recent research [10] has shown that oblique vapor phase deposition produces mesoporous TiO₂ films suitable for photonic crystal humidity sensing. Shi et al. [8] developed a nanoporous one-dimensional polymer photonic crystal colorimetric sensor based on holographic interference patterning of a polymer dispersed liquid crystal. Changes in RH altered the refractive index contrast between nonporous and nanoporous regions, and thus the transmittance and bandgap position. Liquid crystal (LC) materials are of interest because their optical response is controlled by self-assembly, ie, a nonlocal response to a perturbation which might be in the form of electric, optical, or mechanical field forces. The combination of self-assembly with colorimetric sensing is attractive because it can reduce sensor cost and sensor assembly complexity. Chiral nematic (CN) liquid crystals are candidates for colorimetric sensing because they can exhibit brilliant colors without the use of absorbing or emitting chromophores. A planar, uniformly textured CN material behaves as one-dimensional self-organized chiral photonic crystal. In the CN phase, the long axis of the LC-forming species rotates in a plane about a perpendicular helix. The CN phase shows a periodic variation in refractive index, allowing it to be used to filter circularly polarized incident light of the same handedness as its helix. A single-pitch (single domain planar texture) CN material will selectively reflect light at the Bragg wavelength centered at $\lambda_0 = n_{\text{ave}} P$, where n_{ave} is the average refractive index of the CN material and P is the pitch. CN films having non-uniform pitch distribution, where the pitch lengths and helicoid tilt axes are different in different regions, will reflect light with much wider bandwidth than single-pitch CN films. The pitch length P of the helix corresponding to a 2π molecular rotation is determined by several factors that can include concentration, helical twisting power and even charge in the case of ions. For colorimetric sensing, if analyte binding changes the pitch (expands or contracts the helix), there should be a corresponding change in the reflectance. In this context, Saha et al. [11] constructed a colorimeter humidity-sensing device based on doping an high helical twisting power binaphthyl moiety, bis-[binaphthyl-(2,2')-dioxo]-silan, into a nematic liquid crystal phase. Colored films of the composite behaved as slowly responsive irreversible integrating sensors since the pitch, hence the color, changed irreversibly on hydrolysis of the binaphthylene silicon alkoxide linkages.

Nanocrystalline cellulose derived from forest resources is well known to form a chiral nematic liquid crystal phase [12]. Maclachlan and co-workers [13] have used nanocrystalline cellulose as a lyotropic template to control polycondensation of bridged alkoxy silanes to prepare flexible chiral nematic mesoporous silica films. The visible reflection spectral response (iridescence) of these films is reversibly lost due to close matching of the refractive index of the organosilica walls by vapors that invade the lacunae. But if nanocrystalline cellulose can be a template for a periodic mesoporous silica humidity indicator, then perhaps a

simpler construct is the bio-resource NCC itself, when cast as a broad band non-uniform pitch film. The concept is appealing because the colorimetric indicator is derived solely from insoluble cellulose nanocrystallites, which are nonetheless hydrophilic. The rod-like crystallites can undergo an Onsager-type phase transition in fluid medium yielding an iridescent chiral nematic texture. Films cast from CN NCC suspensions exhibit planar texture when aligned in a magnetic field [12], or multi-domain texture when cast from solution in the absence of a coercive field. In this paper we show that a reversible shift in the iridescence of NCC films (dry state blue ↔ humid state red) occurs on cycling between dry and moist states. We propose that this color change is caused mainly by a humidity-induced variation of the pitch of the inherent reflection grating of the film.

2. Experiments

2.1. Synthesis, characterization and nanocrystalline cellulose (NCC) film formation

Sheets of softwood spruce fiber (Temalfa93, Tembec Inc., Temiscamingue, QC) were cut into 3 cm × 0.5 cm pieces and ground in a Willy mill, then passed through a 20-mesh screen. The NCC suspension was produced by hydrolysis of with sulfuric acid (Fisher) in a procedure adapted from Roman et al. [14]. A sulfuric acid to pulp ratio of 17.5 ml/g was used to prepare the NCC. Accordingly, pulverized pulp was added to 64% diluted acid and the mixture was maintained at 45 °C with constant stirring. The reaction was terminated by adding a ten-fold excess of de-ionized water (18 MΩ resistivity). The NCC suspension was isolated by centrifugation in repeated wash cycles to remove the excess acid. The pellets were re-suspended in water and dialyzed (spectro/Por membrane, molecular weight cutoff of 12000–14000). Dialysis continued for three days until the dialysis water was pH neutral. The resulting NCC particles were then dispersed by sonication (Vibracell Sonics & Materials Inc., Danbury, CT) for about 5 min. The colloidal dispersion was finally combined with a mixed bed ion exchange resin (Sigma–Aldrich) and stored for 3 days in the dark at room temperature. The final NCC suspension was concentrated to 4% by evaporation. 3 ml of this NCC suspension was filled into a 5 cm diameter Petri dish and allowed to evaporate over a 48 h period at ambient temperature to yield an iridescent NCC film.

2.2. Microscopy

The thickness of the film in its dry and wet state was measured via polarized optical microscopy (POM), and carried out with a Nikon Optiphot microscope connected to a SonyXCD-X710CR CCD camera equipped with IIDC (Instrumentation & Industrial Digital Camera) image capture software. The microscope was equipped with a 530 nm wave plate to enhance image edge contrast for film thickness measurement. A Hitachi 4700-S field emission gun scanning electron microscope (FEGSEM) was used to analyze the cross-sectional structure of the film. Films were sectioned perpendicular or fractured oblique to the film surface.

2.3. Spectral monitoring under controlled humidity

Color changes in NCC films were captured by digital camera. An Ocean Optics-2000 fiber spectrometer was used to monitor the spectrum of white light reflected from the NCC film. Reflection peaks from sample films were collected via optical fiber positioned at the center of the reflection color peak position with a light incident angle of 25° from normal. In this work, RH was measured at 20 °C. Humidity effects on the color spectrum of the NCC film were detected by observing changes in spectral reflectivity for RH

Download English Version:

<https://daneshyari.com/en/article/7149313>

Download Persian Version:

<https://daneshyari.com/article/7149313>

[Daneshyari.com](https://daneshyari.com)