Cellulose Material with Humidity Color Responsiveness

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Abstract. In nature, there are a large number of structural color applications. To bio-bionic nature's structural color and response to environmental stimuli color changes, jute is prepared by acid hydrolysis into cellulose nanocrystals, and then by simply introducing small molecules as plasticizers and moisture absorbers to prepare a highly flexible, controlled rainbow colors and multi-stimulating cellulose nanocrystals (CNC). The presence of the additive polyglycol (PEG) doesn't prevent the self-assembly of CNC in the aqueous solution, but will result in increased mechanical toughness, which makes it possible to obtain a structurally adjustable independent Rainbow CNC color. The surface charge density of CNC is an important factor in controlling the spacing dimension of the chiral nematic structure of the dry solid CNC film, which can smoothly change the color of the structure by adjusting the chiral nematic structure. It is worth noting that the change is reversible, with alternating relative humidity between 40% and 100%, a discoloration material that makes biofilms widely used in color-coded sensors, anti-fouling techniques and decorative coatings.

1. Introduction

Compared to pigments or dyes, structural colors are generated by the interaction of light with nanoscale periodic structures, resulting in strong reflections within a clearly defined wavelength range [1-2]. Beautiful colors such as home flies [3] and green beetles[4] come from an array of ordered dots and fine lines that adjust their rainbow colors for camouflage and communication or as a warning to enemies. Inspired by nature, structural colors have been widely explored as optical materials [5]. Such as photonic paper [6], tunable bandgap films [7] and color-variable coatings. [8] More recently, the structural color of multi-layer coatings has become increasingly interesting to researchers, who are working to select suitable nanoparticles with regular form and good stability as alternative photon arrays. Inorganic nanoparticles, [9] silica opines [10] and ZnO nanorods [11] of gold nanocrystals are commonly used to make photonic crystal coatings or films. In addition, polystyrene microspheres and polyphenols with a regular diameter of 580 nm [12] also exhibit the best photonic bandgap. Located in a visible or near-infrared area. However, due to irregular dimensional and structural defects, 1D photonic crystals of nanorods often have a large percentage of air space and disappearing photon band gaps, and are not suitable for photon applications. [13]

Cellulose nanocrystal (CNC) nanorods have many unique properties, such as surface area, low thermal expansion coefficient, and optical liquid crystal, which have attracted great interest and application in recent years. Cellulose nanocrystals (CNC), usually prepared by acid catalyzing a large
amount of cellulose, can be well dispersed in water because of the introduction of sulfate groups and the resulting electrostatic rejection on their surfaces, which makes it possible to form a hand-to-column liquid crystal. Even after the evaporation of water to produce a solid film, if its spiral spacing is located in the visible wavelength area, CNC can maintain the liquid crystal structure and present the iridescent color,[14] and due to the adjustable spacing to control its rainbow color, different methods have been widely reported, including ultrasonic treatment, desulfurization, and the introduction of salt or water-soluble polymers.[15-16] However, the mechanism sensing environmental changes in chroma in the resulting CNC material is rarely described. Zhang et al.[16] prepared a thick CNC film in a petri dish using traditional solution casting methods, which showed the color of the humidity response. Liu and his colleagues used a layer-by-layer approach to develop a rainbow optical numerically controlled coating on a silicon wafer that could sense different vapors. However, it should be noted that due to the high vulnerability of CNC, these membranes are not independent. To overcome this deficiency, MacLachlan's group introduced pyridine and amino formaldehyde resin was injected into the CNC matrix and a medium-porous photonic CNC membrane sensitive to humidity and pressure was constructed. The presence of these thermoset resins does not interfere with the self-assembly of CNC, but it is difficult to avoid the volume shrinkage of this thermoset material or, worse, the apparent wrinkles in the CNC membrane.

2. Experimental section
Materials. Jute is provided by Jiangsu Wujiang Jinjiang Bridge Lu Cotton Textile Co., Ltd., sulfuric acid (H2SO4, 99.9%), acetic acid (HAc, 99.5%), ammonia solution (NH3·H2O, 25-28%) and hydrochloric acid (HCl, 36-38%), purity is pure analysis, purchased in Jiangsu Strong Functional Chemistry Co.Ltd., without further purification direct use, poly(ethylene glycol) (PEG) provided by Jiangsu Strong Functional Chemistry Co., Ltd.

2.1. Preparation of colloidal dispersion of CNC
As reported in our previous work[13], CNC was prepared by hydrolysis of jute in sulfuric acid solution (64%) at 50 °C for 2 h under continuous agitation, and the resultant slurry was diluted 5-fold with deionized water to quench the hydrolysis reaction. Subsequently, the resultant suspension was placed into regenerated cellulose dialysis tubing (MWCO = 8000–14,000) against recycled deionized water to remove acid residues and byproducts until the pH of dialysate finally reached around 5.5. The dialysate was then centrifuged at 12,000 rpm for 5 min to remove any impurities and coarse particles using high-speed centrifuge (HC-2061, Soochow University, China). Immediately after centrifugation, the diluted CNC dispersion was concentrated into colloidal suspension with a concentration of 1.5wt%. A mild mechanical sonication was performed for 30 min to obtain a homogenized colloidal dispersion of CNC in an ice bath sonicator. The attainable yield of CNCs was around 0.8 wt%.

2.2. Preparation of structural color CNC
A flexible and responsive chiral nematic solid CNC film was produced in a green and cost-effective two-step process, showing the uniform structural color in response to relative humidity by the addition of PEG. PEG (one of the most effective depleted polymer reagents in water) is assembled with the CNC in an aqueous suspension, followed by slow drying to form an iridescent solid film with a chiral nematic structure, which can be adjusted by changing the composition of the CNC and PEG. The pitch size of the meso-neutral nematic structure results in a composite film having a tunable photonic bandgap. The composite film response was gradually increased and the color change of RH between 40% and 100% were investigated.

3. Results and discussion
Here, the CNC was prepared by the previously reported method of acid hydrolysis.[12] By the TEM test, the prepared CNC had a rod-like morphology with an average length of 300 nm and an average diameter of 8 nm (Fig. 1a). Due to the presence of a negatively charged sulfate surface group, the CNC
can be uniformly dispersed in water without precipitation. The zeta potential and sulfur content of the CNC prepared in this work were -15.9 mV (Fig. 1b) and 0.0126 mol/g. According to previous reports, colloidal particles are prone to flocculation at a zeta potential below 25 mV. However, for CNC, once the zeta potential becomes below 15 mV, its reunion begins. As a result, the water-based CNC dispersions prepared in this paper are stable.

Figure 1. (a) TEM image of the as-prepared CNC; (b) zeta potential of CNC suspension.

Figure 2. (a) Reversible structural color change of the CNC-PEG (30%) film under different RH; (b) UV–vis extinction spectra of neat CNC and CNC-PEG films; (c) Reversible conversion of the stopband position of the CNC-PEG (20%) film by exposing alternately between RH 30% and 100% for ten cycles.

To prepare a rainbow CNC film, water is evaporated by conventional solution casting methods. A photograph of this CNC-PEG (30%) film taken in the vertical direction is shown in Figure 2a, where different rainbow colors can be seen, i.e., RH increases between 50% and 100% as the ambient humidity increases. And lower, and show structural color changes in the visible spectrum. At RH of 30% and 50%, the sample showed a similar green color. The different "coloring" in the film is due to the fact that
light of a certain wavelength is extinct as it passes through the film. Further quantitative analysis by UV-vis extinction spectroscopy indicated that with the incorporation of PEG, the gradual redshift of the maximum extinction wavelength occurred between 347 and 610 nm (Fig. 2b). Usually, rainbow colors are considered to be the result of Bragg reflections. The color change of the structure to red under high humidity is the expansion of the multilayer structure due to water permeation. Subsequently, as the RH decreases, the periodic multilayer structure changes are reversed. When RH is gradually reduced from 100% to 50% according to the increasing step, the transparent film returns to deep red, orange, brown, light blue, green, and the reflected color is completely reversible. The reversible conversion of the stopband position of the film is shown in Figure 2c when alternately exposed to 40% RH and 100% RH for 10 cycles.

It is well known that mechanical properties are very important for practical applications. However, for a neat CNC film, it is impossible to perform a tensile test due to high inherent brittleness. In contrast, the addition of PEG causes a significant increase in the tensile toughness of the CNC film. In particular, CNC-P (40%) has an elongation at break of more than 2% (Fig. 3a), which is larger than many previous reports. The detailed relationship between elongation at break and PEG is provided in Figure 3b.

![Figure 3.](image)

Figure 3. (a) Tensile property of neat CNC-PEG films; (b) elongation at break of CNC films.

In this regard, a simple application has been made in the anti-counterfeiting work of the RMB. Prepare a CNC-PEG (30%) film on the surface of the RMB, and then keep the RMB at an ambient humidity of 50%, 75%, 85%, and 90% for one hour, then take out and observe the color change. Figure 4 shows. It shows better difference under different environmental humidity conditions and can objectively reflect the change of color, so it will have potential immeasurable value in the anti-counterfeiting work of banknotes.

![Figure 4.](image)

Figure 4. Reversible structural color change of the CNC-PEG (30%) film under different RH in RMB.
4. Conclusion
Flexible and responsive chiral nematic CNC-PEG composite membranes with uniform and adjustable structural colors were successfully prepared by controlling the composition of the CNC and PEG or by varying the external relative humidity. The sulfur content of the CNC, that is, the surface charge density, is a very important factor in controlling the pitch of the chiral nematic structure of the dry solid CNC film. Careful selection of the starting materials and hydrolysis conditions produces a solid CNC film having a reflective color that covers the entire visible spectrum. The presence of PEG imparts high flexibility to the CNC film, can be bent and stretched, and has an elongation at break of more than 2%. A large, flat photonic composite film having a uniform bright structural color from blue to red was prepared. Due to the reversible expansion and dehydration of the chiral nematic structure, the CNC-PEG (30%) composite film also exhibits a reversible and smooth structural color change from green to transparent in response to an increase and decrease in RH between 40% and 100%. Composites also offer outstanding mechanical and thermal properties that complement versatility.

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