Bacterial cellulose wave plates for polarization-encryption applications

Experimental section

Materials

Disodium hydrogen phosphate (Analytical Reagent), sodium hydroxide (Analytical Reagent), ethanol anhydrous (Analytical Reagent), acetic acid (Analytical Reagent, 98%), and yeast extract were purchased from Beijing Chemical Reagent Company. D-Glucose anhydrous (AMRESCO, U.S.A.), peptone (Analytical Reagent, Beijing Aoboxing Biotechnology), and epoxy resin (Osborne Co., Ltd) were also used. Acetobacter xylinum HN001 was provided by Tianjin University, China. NOA-65 UV curing adhesive was purchased from Norland Product. All chemicals were used as received.

Preparation of BC pellicles

A fluid culture medium for xylinum was prepared by dissolving 25 g of D-glucose anhydrous, 10 g of peptone, 7.5 g of yeast extract, and 10 g of dipotassium hydrogen phosphate in 1 L of deionized water. The culture medium was then adjusted to pH = 5.0 by acetic acid and sterilized at 121 °C for 20 min. The acetobacter xylinum HN001 was inoculated into the sterilized culture medium and cultured under a static condition at 30 °C for 4-7 days. Thus-prepared BC pellicles were treated successively using 1 wt.% NaOH solution at 80 °C for 1 h and washed with amounts of deionized water until the pH ~7 to remove dead cells and residue chemicals.

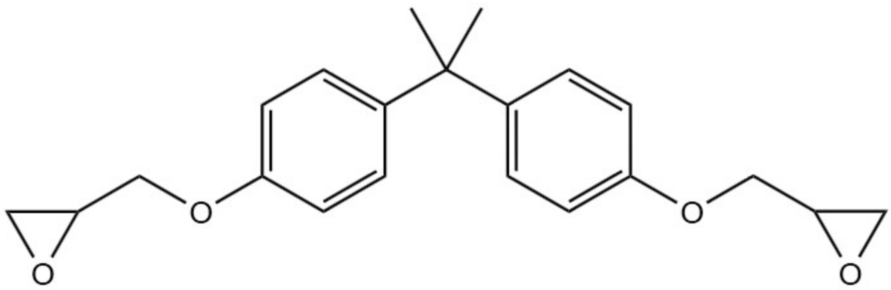
Preparation of transparent and birefringent OBC nanocomposite films

(1) Wet stretching

BC pellicles were cut into 10 mm*20 mm pieces and stretched using a universal material testing machine (SANS, CMT6203). The sample was first subjected to the 20% pre-stretching with a stretching speed of 2 mm/min. Subsequently, relax the pre-stretching BC pellicle by shaking it repeatedly and then stretch it further to the required stretching ratio.

(2) Air displacement with epoxy resin-filling

The oriented BC pellicles were dried at room temperature to obtain the OBC paper. The epoxy resin was prepared by mixing components A (2, 2'-[(1-methylenylethyl) bis (4, 1-phenylene formaldehyde)] diethylene oxide) and B (O, O'-bis(2-aminopropyl) polypropylene glycol) with a mass ratio of 3:1, then fully stirred and placed in a vacuum-drying oven for 30 minutes to remove bubbles. The chemical structure of epoxy resin is shown below. The OBC paper was first soaked in ethanol for 30 minutes to make it permeable, and then in epoxy resin with a weight ratio of 5.5 for another 30 minutes to fully fill the interstitial cavities inside the OBC film. Finally, the epoxy resin-OBC nanocomposite film was cured in the oven at 60℃ for 2 hours.



Preparation of the pixelated optical pattern

First, a transparent acrylic substrate was etched using 10.6 μm laser (CO_2-50 laser, 350W) to form 2 mm× 2 mm grids. Next, 2 mm×2 mm slices were cut from the center of OBC-9-40, OBC-19-40 and OBC-28-40, and used as the 1/4, 1/2 and 3/4 waveplates, respectively. Then according to the designed optical pattern, the pixelated OBC waveplates were glued to the corresponding position on the gridded acrylic plate using NOA 65 UV curing adhesive. Note that all the pixelated OBC waveplates have the same stretching direction along the y-axis in Figure 4d.

Characterization

Scanning electron microscopy (SEM) was performed using a JEOL-7800F field emission scanning electron microscopy at an accelerating voltage of 3.0 kV. Polarized optical microscopy (POM) images of OBC paper were acquired on a BA310Pol microscopy, and the stretching direction was at an angle of 45 degrees with the crossed linear polarizers. Two-dimensional X-ray diffraction (2D-XRD) images were recorded with a Xenocs Xeuss 2.0 equipped with a Pilatus 300K 2D detector (pixel size=172 μm) using a Cu Kα X-ray beam with a wavelength (λ) of 0.154 nm. Transmission spectra and polarized transmission spectra of OBC nanocomposite films were recorded on a SHIMADZU UV-1800 spectrophotometer with the preset wavelengths of visible region (400-700 nm) and near-infrared region (700-1100 nm). The polarizers with operating wavelengths of 400-700 nm (LPNIRE100-A) and 700-1100 nm (LPNIRE100-B) were purchased from Thorlabs.

Estimation of orientational birefringence in OBC nanocomposite films

According to Equations 1 and 2, R was calculated by the least square fitting method, and the accuracy of its value was determined by comparing it with the birefringent color of the Michel-Levy chart. In the case that the sample thickness was measured by the screw micrometer, Δn was calculated by Equation 5. Note this method does not apply to measure the wavelength-dependent birefringence.

Calculation of Hermans order parameter S

By analyzing 2D-XRD data with Fit2D, the diffraction intensity function $I(\varphi)$ of 2θ=22.9° (2θ presents the diffraction angle) was obtained, which corresponds to the (200) diffraction of cellulose Iβ of BC nanofibres. Herein, φ represents the directional angle of the (200) reflection in OBC relative to the stretching direction. Hermans order parameter S was calculated by integrating with Equations 3 and 4.

Calculation of Stokes vector and Drawing of the Poincare sphere

Using left/right-handed circularly polarized light as the incident light, the polarizer was, in turn, changed into a 0° linear polarizer, 45° linear polarizer, 90° linear polarizer and right-handed circular polarizer, and the intensities of the transmitting beam were recorded as I_0 , I_{45} , I_{90} , I_r respectively. Total light intensity $I = I_0 + I_{90}$. The Stokes vector was calculated by

$$M = 2I_0 - I\ ,\ C = 2I_{45} - I\ ,\ S = 2I_r - I\ ; \qquad \text{Stokes vector} = I\,(1\ ,\ M/I\ ,\ C/I\ ,\ S/I)^{\mathrm{T}} \qquad (6)$$

According to the Stokes vector, the coordinates of the points on the Poincare sphere were plotted by MATLAB.

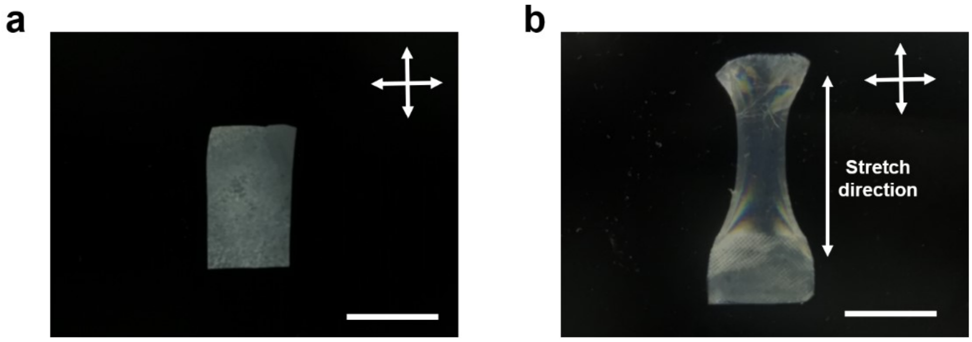


Figure S1. Photographs under crossed polarizers of the dried BC pellicle (**a**) and the OBC paper (**b**). The stretching direction is at a 0/90° angle to the direction of the polarizers. Scale bars: 1 cm.

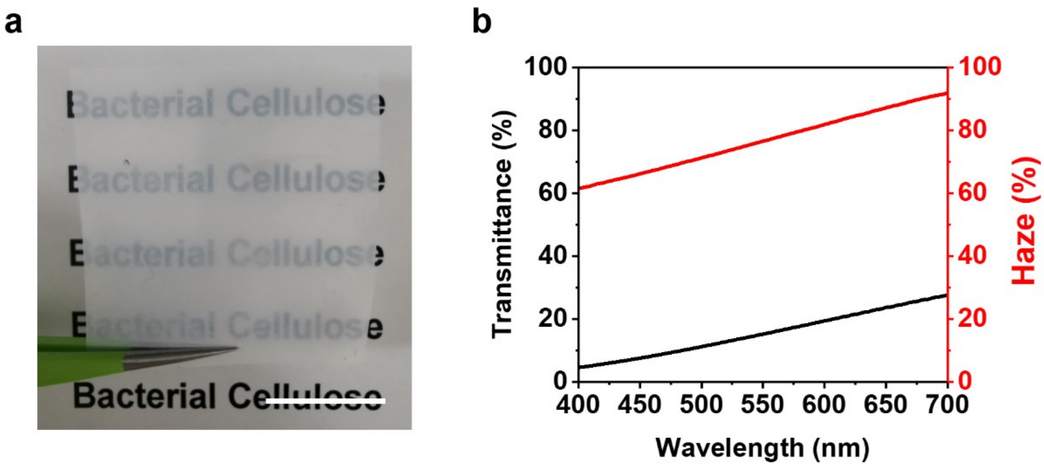


Figure S2. (**a**) Physical display of the dried BC pellicle before filling with epoxy resin. (**b**) Transmission and haze spectra confirm that the dried BC pellicle has low transparency and high haze. Scale bar: 1 cm.

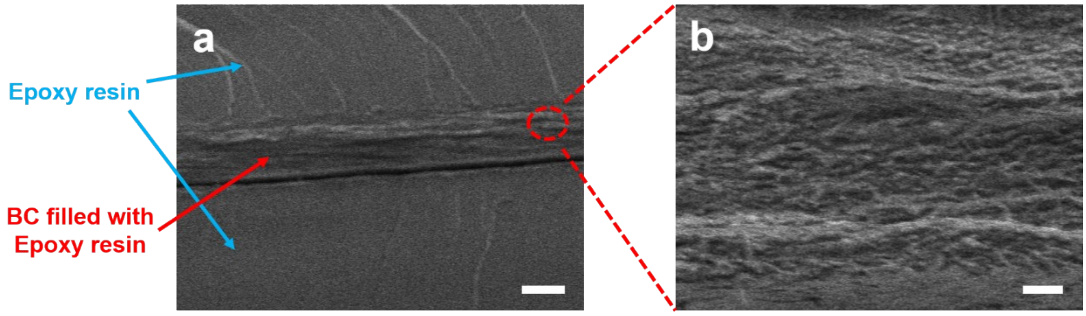


Figure S3. The cross-section SEM image of the dried BC pellicle after filling with epoxy resin (**a**) and the high-magnification SEM image circled by the red dotted line (**b**) show that the interstitial gaps between BC nanofibrils are filled with epoxy resin. Scale bars: 10 µm (**a**), 1 µm (**b**).

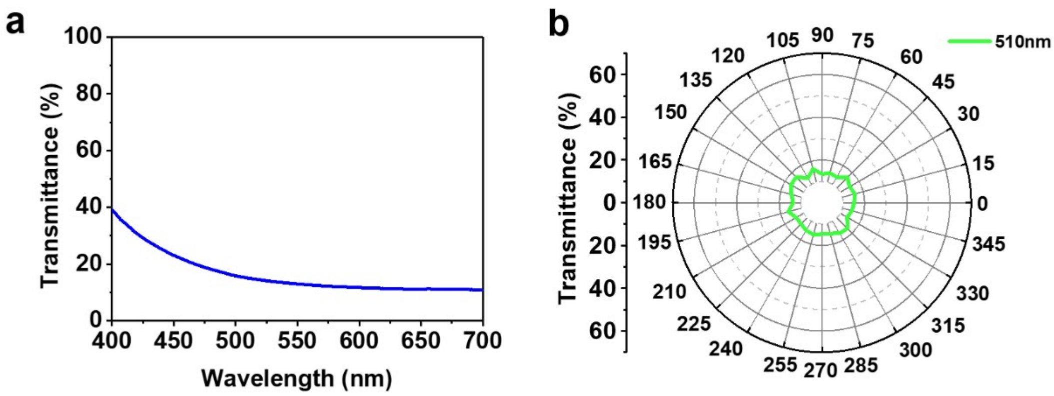


Figure S4. (**a**) Polarized transmission UV-vis spectrum of transparent unstretched BC nanocomposite film between crossed linear polarizers. (**b**) Polar plots of polarized light intensities of transparent unstretched BC nanocomposite film at 510 nm.

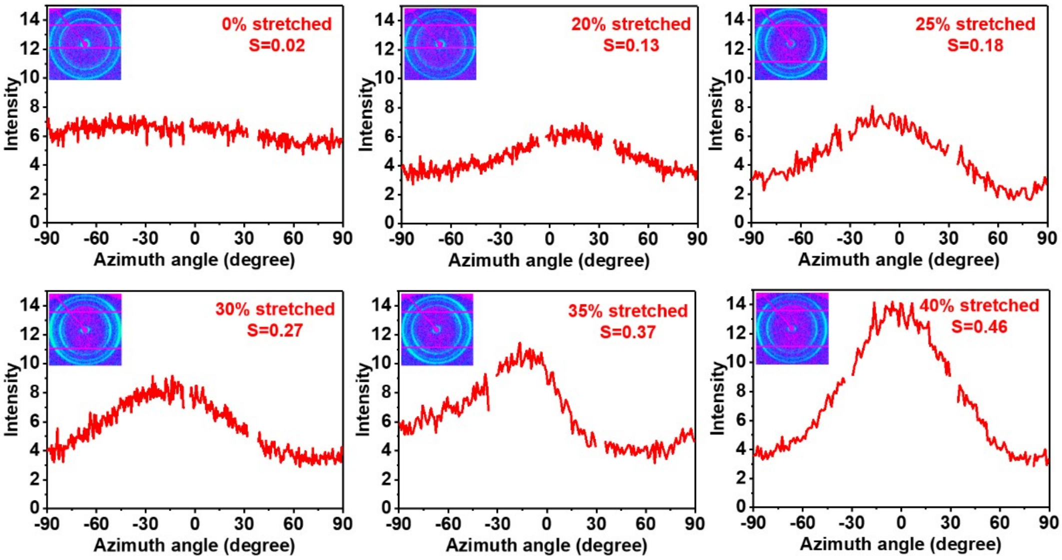


Figure S5. X-ray diffraction intensity of the (200) plane of dried BC pellicle before and after 20%-40% stretched with a diffraction angle 2θ of 22.9° (Hermans order parameter, *S* and 2D-XRD pattern inset).

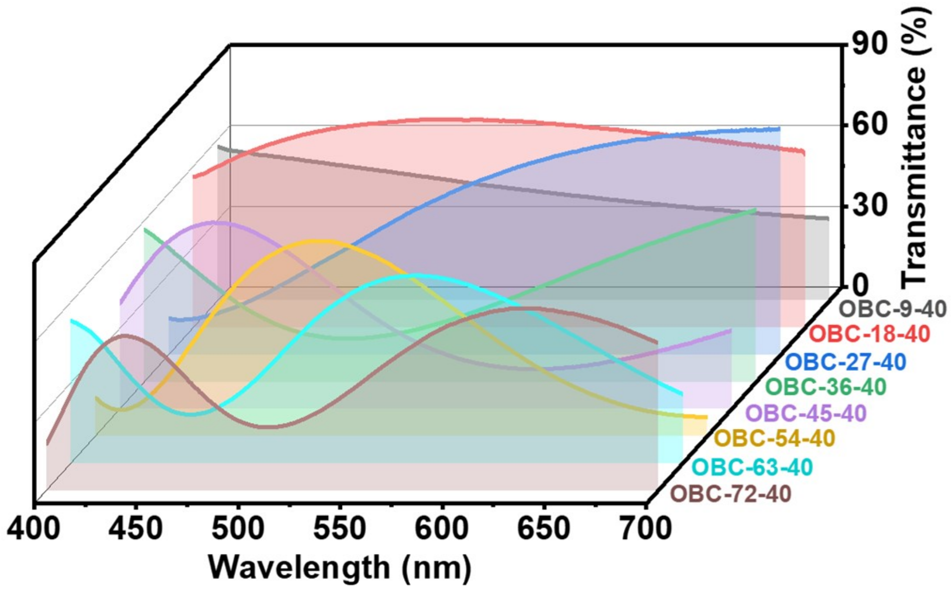


Figure S6. Polarized transmission UV-vis spectra of OBC-T-40 between crossed linear polarizers. T= 9, 18, 27, 36, 45, 54, 63, 72.

	LCP input	OBC-9-40	OBC-19-40	OBC-28-40
1	1	1	1	1
M/I	-0.239	-0.935	0.002	0.826
C/I	0.115	0.030	0.076	0.449
S/I	-0.944	0.075	0.956	0.159

	RCP input	OBC-9-40	OBC-19-40	OBC-28-40
1	1	1	1	1
M/I	-0.072	0.881	0.172	-0.916
C/I	0.154	0.294	-0.034	-0.208
S/I	0.935	-0.242	-0.951	0.071

Figure S7. Stokes vectors of OBC-T-SR when LCPL (**a**) or RCPL (**b**) as the input.

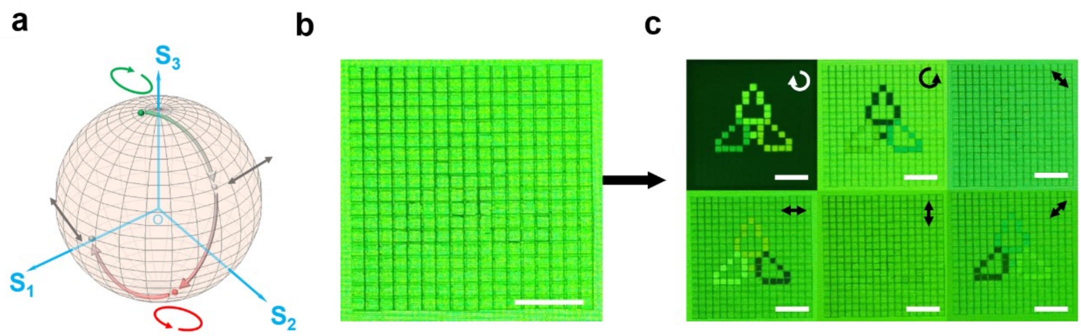


Figure S8. (**a**) Trajectories of the polarization change of the RCPL input at 532 nm passing through the OBC-based 1/4, 1/2 and 3/4 wave plates were represented on the Poincare sphere. (**b**) Photograph of OBC-based optical pattern under a 532 nm RCPL input. (**c**) Different optical patterns were observed by LCP, RCP, and LP as analyzers. (LCP/RCP refers to left/right-handed circular polarizer and LP refers to linear polarizer.) Scale bars: 1 cm.