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Shape Memory Cellulose-based Photonic Reflectors

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Supporting Information – PDF

The supporting video can be found here:

https://www.dropbox.com/s/t69wsja4ja6l0rn/00003s2.mpeg?dl=0

https://www.dropbox.com/s/08xzdo80z7twguo/00004s3.mpeg?dl=0

1) Experimental Section

Chemicals: Citric acid and 1,12-dodecanediol were purchased from Sigma-Aldrich and ethanol 99.5% from Panreac. All chemicals were used as received.

Fabrication of cellulose nanocrystals films: The cellulose nanocrystal suspension was provided by CelluForce. Films of cellulose nanocrystals were fabricated by EISA by pouring 2 mL of 1 wt% CNC suspension, at pH 5.5 into polystyrene Petri dishes of 3.6 cm diameter and allowed to dry at ambient conditions. To obtain respectively red, green and blue films the ionic strength of the initial suspension was adjusted by subjecting it to heat treatment in a water bath at 60 °C for 12 h, 21 h and 30 h respectively. The dry films were then detached from the substrates and cut into individual flakes of similar shape, avoiding the edge region affected by a coffee-ring strain.[1]

Prepolymer synthesis: A prepolymer composed of citric acid and 1,12-dodecanediol (mol ratio of hydroxyl to carboxyl groups 4:3) was prepared following a previously reported protocol**Error! Bookmark not defined.** and diluted in ethanol, at a concentration of 0.5 g.mL^{-1}, with the help of mild heating and sonication.

Preparation of SMP composites: Free-standing CNC flakes were immersed in the diluted prepolymer overnight, drained to remove the excess of prepolymer and finally left drying for ethanol evaporation. For further curing of the samples, they were held by three contact points, to prevent adhesion to a substrate, and thermally annealed at 80 ºC, in an oven for periods from 16 h to 20 h.

Optical characterization: Optical characterization was performed in reflection mode on a customized Zeiss Axio microscope using a halogen lamp (Zeiss HAL100) as a light source with Koehler illumination. The light reflected off the sample passes through a quarter wave plate and a polarizing filter, specifically oriented to select either left-circularly-polarized or right-circularly-polarized light before being split between a CCD camera (UI-3580LE-C-HQ, IDS) and an optical fiber mounted in confocal configuration and connected to a spectrometer (AvaSpec-HS2048, Avantes). This setup allowed for the spectra acquisition from specific areas in the sample; all the spectra were normalized to the reflection of a silver mirror.

Scanning Electron Microscopy: SEM images were acquired using a Leo Gemini 1530VP system, Zeiss, working in cross section at an angle of 90° with respect to the electron beam. The samples were placed on aluminum stubs using conductive carbon tape and sputter-coated with a few nanometer thick layer to Au/Pd (Emitech K550) to minimize the charging effect. The acceleration voltage used was 4 kV and the working distance was 3- 4 mm.

2) Supplementary Figures

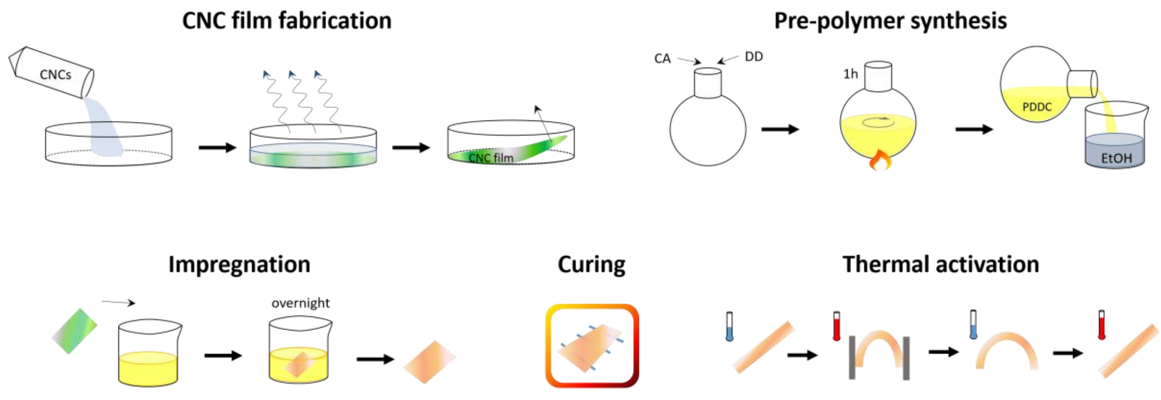

Figure S1. Fabrication procedure for the CNC/PDDC-HD hybrid structure and thermal activation steps.

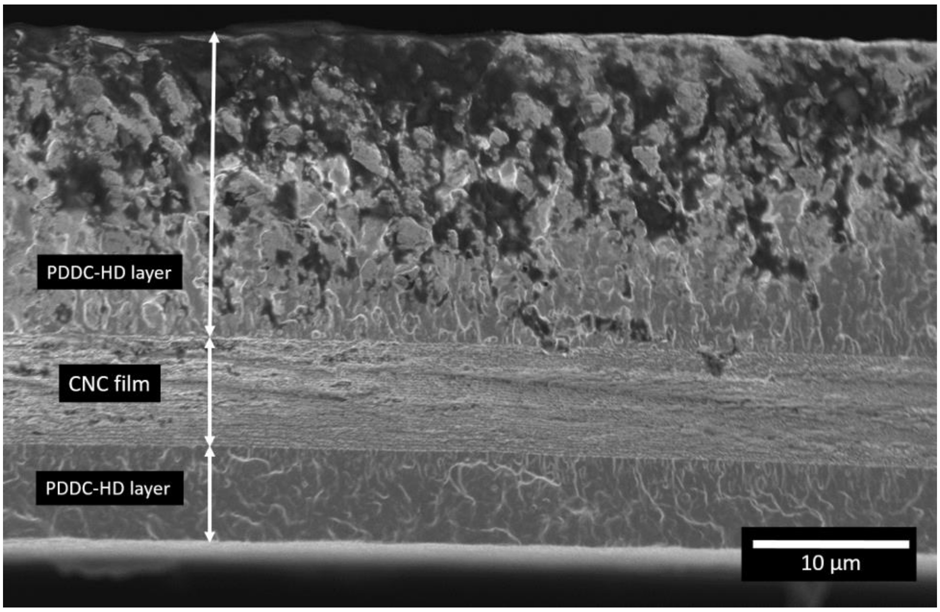

Figure S2. SEM image showing the layered structure of the CNC/PDDC-HD hybrid material. The CNC thin film is sandwiched between two layers of PDDC-HD as a result of the impregnation process.

3) Estimation of the Young modulus of a simplified hybrid CNC/PDDC-HD layered material

The Young modulus of pure CNC films, noted E_{cell}, has been evaluated in the literature as being in the range of few GPa (1.5 GPa,[2] 5.8 GPa[3]).

The Young modulus of pure PDDC-HD bulk polymer has been estimated to 13.7 MPa at room temperature and decreasing to a plateau of 2 MPa above T_{trans} = 30 °C.[4]

From the cross-section profile of the film displayed in Figure S2 and assuming that the Young modulus of the edge and the middle layers are given by the pure PDDC-HD and pure CNC ones, one can estimate an effective Young modulus of the overall material corresponding to the bending stress applied in a cantilever geometry using the following formula:[5]

$$A_1 = t_1 ; \quad A_2 = t_2 * E_{CNC}/E_{PDDC}; \quad A_3 = t_3; \quad A_T = A_1 + A_2 + A_3;$$

$$y_1 = t_1/2 ; \quad y_2 = t_1 + t_2/2; \quad y_3 = t_1 + t_2 + t_3/2; \; y_T = (y_1A_1 + y_2A_2 + y_3A_3)/A_T$$

$$I_i = A_i[(y_i - y_T)^2 + t_i^2/12] ; \quad I_T = \sum_{i=1}^{3} I_i; \; I_{PDDC} = (t_1 + t_2 + t_3)^3/12;$$

$$E_{hybrid} = E_{PDDC} * \frac{I_T}{I_{PDDC}}$$

From this simplified modeling, the effective Young modulus E_{hybrid} of the overall film is expected to increase by a factor ~2.7 as compared to pure PDDC-HD.

4) References

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(4) Espinha, A.; Serrano, M.; Blanco, A.; López, C. Thermoresponsive Shape-Memory Photonic Nanostructures. *Adv. Opt. Mater*. 2014, 2, 516-521.

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