

Supplementary Information

Tailorable and Photochromic Multifunctional Methyl Viologen/Cellulose Nanocrystal (CNC) Films

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1. Materials and Methods

Aqueous suspensions of CNCs were purchased from CelluForce as the sodium-neutralized form (CNC-Na⁺, 6.1 wt%, pH = 6.5). Deuterated solvents D₂O were purchased from Cambridge Isotope Laboratories. All reagents and solvents were purchased from Sigma-Aldrich, Oakwood, and ASTAMAN, and were used without further purification unless otherwise mentioned. PVA (Mw = 2000 Da) and HPC (Mw = 80 kDa) were purchased from Sigma-Aldrich and used without further purification. Methyl viologen dichloride was synthesized following reported methodologies.¹ The NMR data (Fig. S2) matched with the reported data.¹ Deionized water was used throughout.

¹H NMR spectra were recorded on a Bruker AVIII HD 400 MHz spectrometer and a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to residual protonated solvent. EPR spectra were measured with a Bruker FLEXSYS E 500 EPR spectrometer operating at X-band. SEM micrographs were captured using a Zeiss XB350 Field Emission-SEM at 1 kV. Samples for SEM were sputter-coated with 3.19 nm Au using a Cressington sputter coater. The mechanical properties of the MV-polymer films were measured using a 5969 Series Universal Testing System (Instron) with a 2 kN loading cell under the testing rate of 10 mm/min. Thermogravimetric analysis (TGA) was performed on a Netzsch TG209 F1 Libra. Samples were heated at 10 °C in a nitrogen atmosphere. The elemental analysis of HPC was performed with a Thermo Flash 2000 Elemental Analyzer. Circular dichroism (CD) spectra were recorded on a Jasco J-815 CD spectrophotometer. UV-vis spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer using a solid sample holder. Infrared spectroscopy was performed on a PerkinElmer Frontier FT-IR spectrometer equipped with an attenuated total reflectance accessory. Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer. All photographs were taken with an iPhone XR. For UV irradiation, analytikjena UVM-28 EL series UV lamp (8 W) was used in a black box at a distance of 8.3 cm from the sample.

2. Preparation of MV-embedded films

PVA and HPC were prepared as 6.1 wt% aqueous solutions. The films were made by casting and mixing 1 mL 6.1 wt% polymer solution and a certain amount of 100 mM MV dichloride solution on a polystyrene dish (a regular hexagon with side length 13 mm). Films were air-dried at room temperature overnight. The thicknesses of MV-CNC films were measured with a micrometer and are listed in Table S1.

Table S1. Amount of MV used to prepare each MV-CNC film and corresponding film thickness.

	0.5 wt% MV-CNC film	1.1 wt% MV-CNC film	1.6 wt% MV-CNC film	3.0 wt% MV-CNC film	4.3 wt% MV-CNC film	6.4 wt% MV-CNC film
The volume of MV solution added (μL)	12.5	25	37.5	70	100	150
MV concentration in the mixed solution (mM)	1.25	2.5	3.75	7	10	15
MV wt% in the corresponding film	0.5	1.1	1.6	3.0	4.3	6.4
Film thickness (mm)	0.12	0.10	0.12	0.10	0.13	0.14

The morphology of CNCs was examined with a FEI Tecnai Spirit 120kV transmission electron microscope (TEM). The samples were sonicated for 10 minutes before 3 μL were deposited onto glow-discharged Formvar coated 200 mesh Copper TEM grids (Ted Pella). The solution was allowed to rest on the TEM grid for 3 minutes before wicking off the excess liquid with a wedge of filter paper. The grid with adsorbed samples was then negatively stained with 3 μL of 2% uranyl acetate for 1 minute before wicking off the excess stain. After fully drying, the samples were imaged using the TEM. All images of CNCs were obtained at 80 kV operating voltage. Analysis of the particle size using ImageJ and Origin (160 particles counted) showed that the size of CNCs is 217 ± 38 nm.

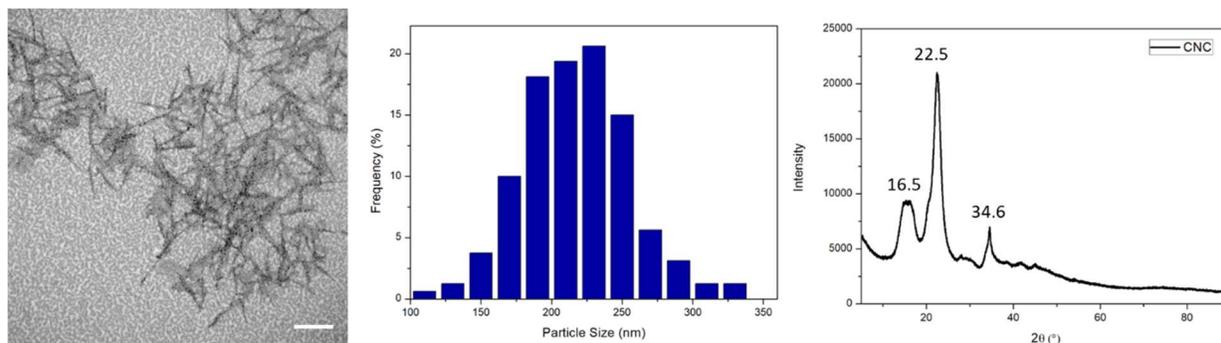


Fig. S1. TEM image (left), size distribution histogram (middle), and powder X-ray diffractogram (right) of CNCs used in our experiments. Scale bar = 200 nm.

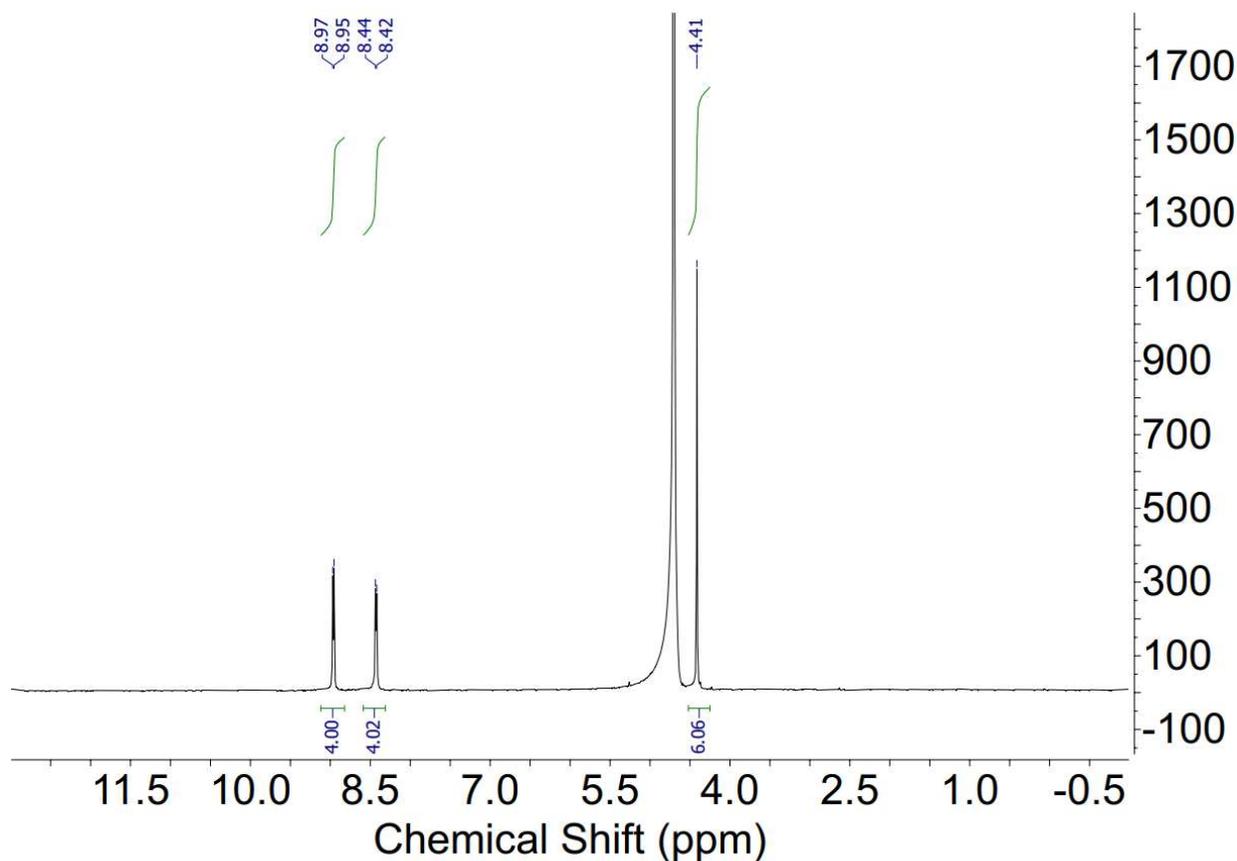


Fig. S2. ^1H NMR spectrum (400 MHz, D_2O , 25 $^\circ\text{C}$) of methyl viologen dichloride.

3. Estimation of the number of hydroxyl groups on PVA, HPC and CNCs

PVA:

In the previous study, the number of hydroxyl groups on PVA could be obtained by hydroxyl group titration with KOH, and the hydroxyl number determined was 1220.85 mg KOH/g sample, which is equal to 21.80 mmol/g sample.² Based on the chemical structure of PVA, the theoretical number of hydroxyl groups is calculated as 22.73 mmol/g. In this study, we estimated the number of hydroxyl groups on PVA as 22.73 mmol/g since it is close to the experimental value.

Chemical structure of PVA: $(\text{C}_2\text{H}_4\text{O})_n$, each unit has one hydroxyl group

$$\text{Number of hydroxyl groups} = 1 * \frac{1 \text{ g}}{44 \text{ g/mol}} = 22.73 \text{ mmol g}^{-1}$$

HPC:

We can estimate the number of hydroxyl groups on HPC from the chemical structure.

Chemical structure of HPC: $((\text{C}_6\text{H}_{10}\text{O}_5) \cdot x(\text{C}_3\text{H}_6\text{O}))_n$, each unit has three hydroxyl groups.

Based on the elemental analysis of HPC, %C = 53.25%, so x could be calculated as 2.79

$$\text{Number of hydroxyl groups} = 3 * \frac{1\text{g}}{324\text{ g/mol}} = 9.27\text{ mmol g}^{-1}$$

CNCs:

The number of moles of hydroxyl groups per gram on the surface of CNCs can be estimated using a reported method.³ Using the nanocrystal dimension of $217 \pm 38 \times 17 \pm 2$ nm in this paper, the number of hydroxyl groups on the surface of CNCs varies between 0.96 mmol g^{-1} (0.38 mmol g^{-1} primary) and 1.31 mmol g^{-1} (0.48 mmol g^{-1} primary) for this dataset.

4. Characterization of MV-embedded films

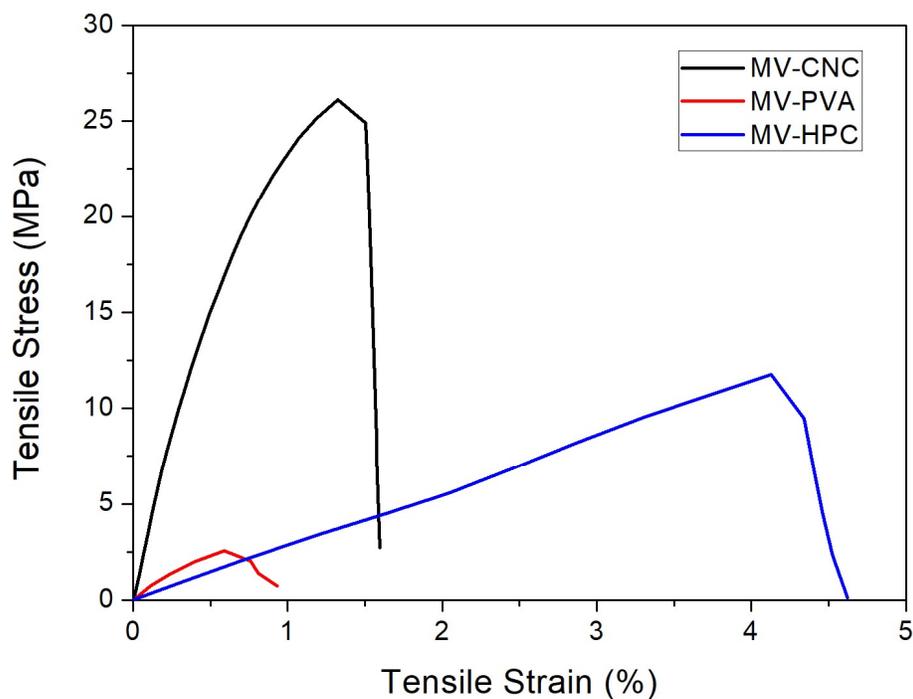


Fig. S3. Typical stress-strain curves of 3.0 wt% MV-CNC, MV-PVA and MV-HPC films.

Table S2. Maximum tensile stress, elongation at break and Young's modulus of 3.0 wt% MV-CNC, MV-PVA and MV-HPC films.

Film type	Maximum tensile stress (MPa)	Elongation at break (%)	Young's modulus (GPa)
MV-CNC	26.2	1.3	3.1
MV-PVA	2.6	0.6 </td <td>0.4</td>	0.4
MV-HPC	11.8	4.1	0.3

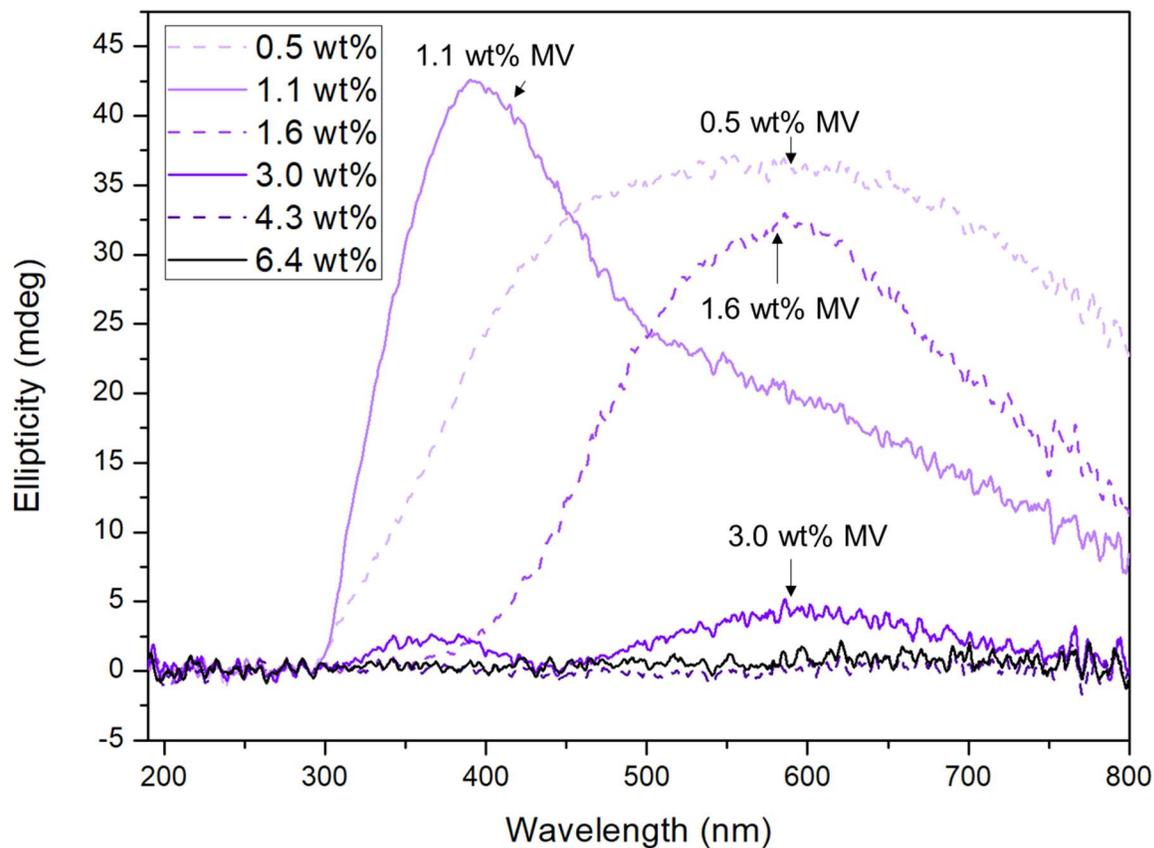


Fig. S4. CD spectrum of MV-CNC films with different wt% of MV.

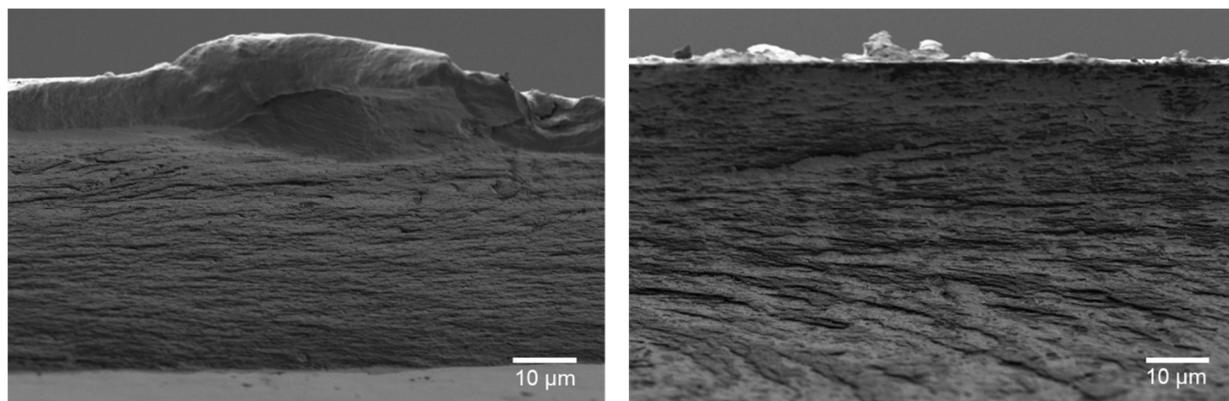


Fig. S5. SEM images of the cross section of 3.0 wt% MV-CNC film before (left) and after(right) UV irradiation.

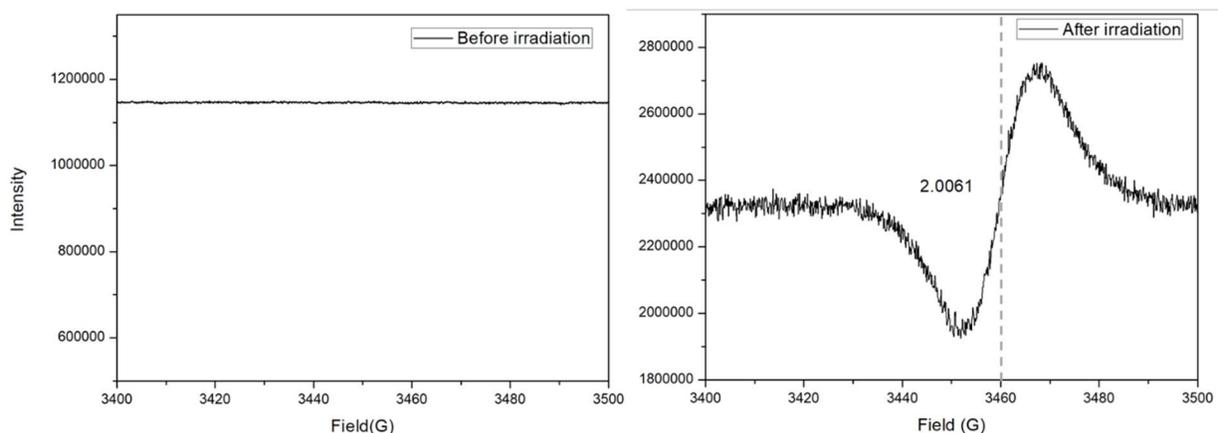


Fig. S6. EPR spectrum of 3.0 wt% MV-CNC film before (left) and after (right) UV irradiation. X-band frequency of EPR experiment is 9.714 GHz. Calculated g value at the magnetic field of 3459.6 G is 2.0061.

A MV-glucose NMR sample was prepared by dissolving UV-irradiated glucose (10 mg) containing 3.0 wt% of MV dichloride in DMSO- d_6 , under nitrogen and in a J. Young NMR tube. Once the blue solid was dissolved, the solution turned colorless, which means the radicals were quenched during dissolution and the solution contained just MV dications afterward, so we called this the initial state. The tube was then irradiated with UV light (302 nm) for 5 min, causing the solution to turn pale blue. After that, air was bubbled into the tube until the solution turned back to colorless. NMR spectra were recorded in each state. At the initial state, signals at 9.29, 8.75 and 4.43 ppm correspond to MV (Fig. S7). These signals disappeared once the solution was irradiated with UV light, meaning that MV ions transformed into radicals. Regeneration of MV resonances occurred after oxidation of MV radicals back to the dicationic form.

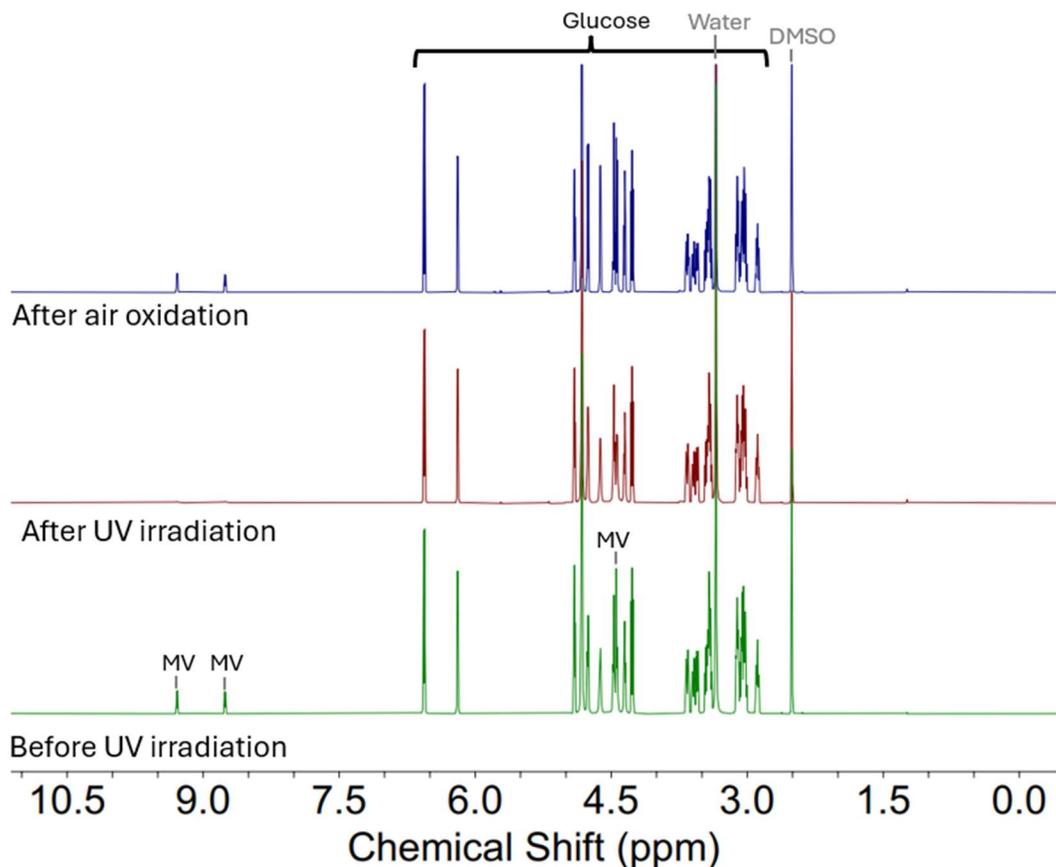


Fig. S7. ¹H NMR spectra (600 MHz, DMSO-*d*₆, 25 °C) of MV dichloride-glucose solution.

The FTIR spectra (Fig. S8) on the left shows that the major peaks of MV-CNC film with different MV loading have almost no differences between each other. The broad band at 3337 cm⁻¹ represented a stretching vibration for intermolecular O-H bonds. The sharp band at 2911 cm⁻¹ indicated the stretching vibration of C-H bonds. The C-O group stretching was observed at 1055 cm⁻¹. All these bands proved the presence of CNC substrate. Compared to CNC-Na⁺ film, 6.4 wt% MV-CNC film showed two unique peaks at 1508 and 1568 cm⁻¹, which correspond to the C=C bond stretching and C=N bond stretching in the pyridine ring, respectively.⁴ These two peaks demonstrated the appearance of MV in MV-CNC films.

The FTIR spectra on the right display almost no peak differences before and after UV irradiation, which might be because of the low concentration of formed radicals.

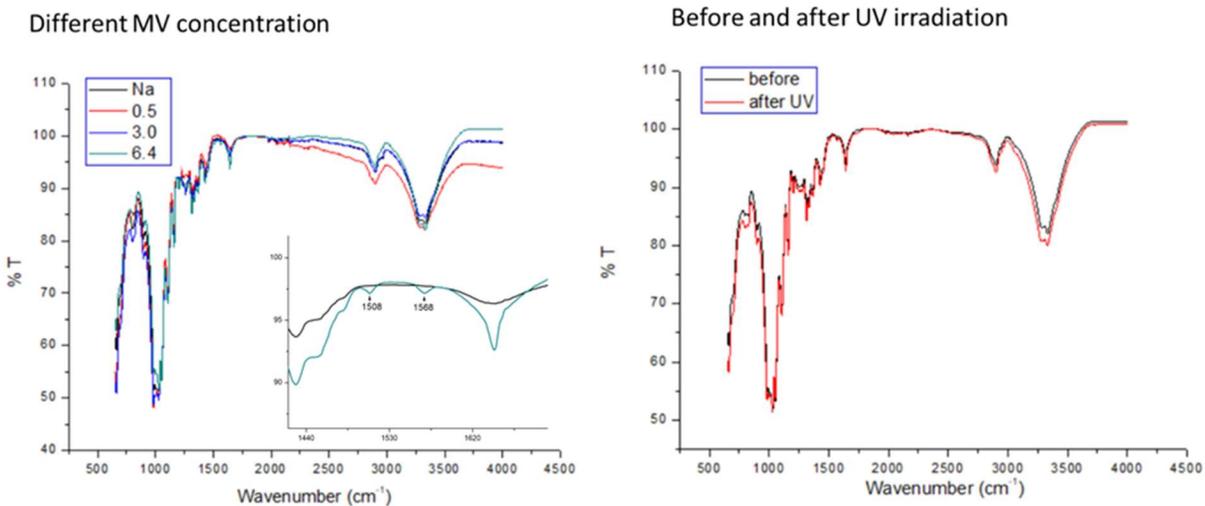


Fig. S8. FTIR spectra comparing MV-CNC films with different MV concentration(left) and MV-CNC films before and after UV irradiation (right). “Na” in the left legend means CNC-Na⁺ film without MV loading. The inset in the left figure shows an enlarged region comparing CNC-Na⁺ film with 6.4 wt% MV-CNC film.

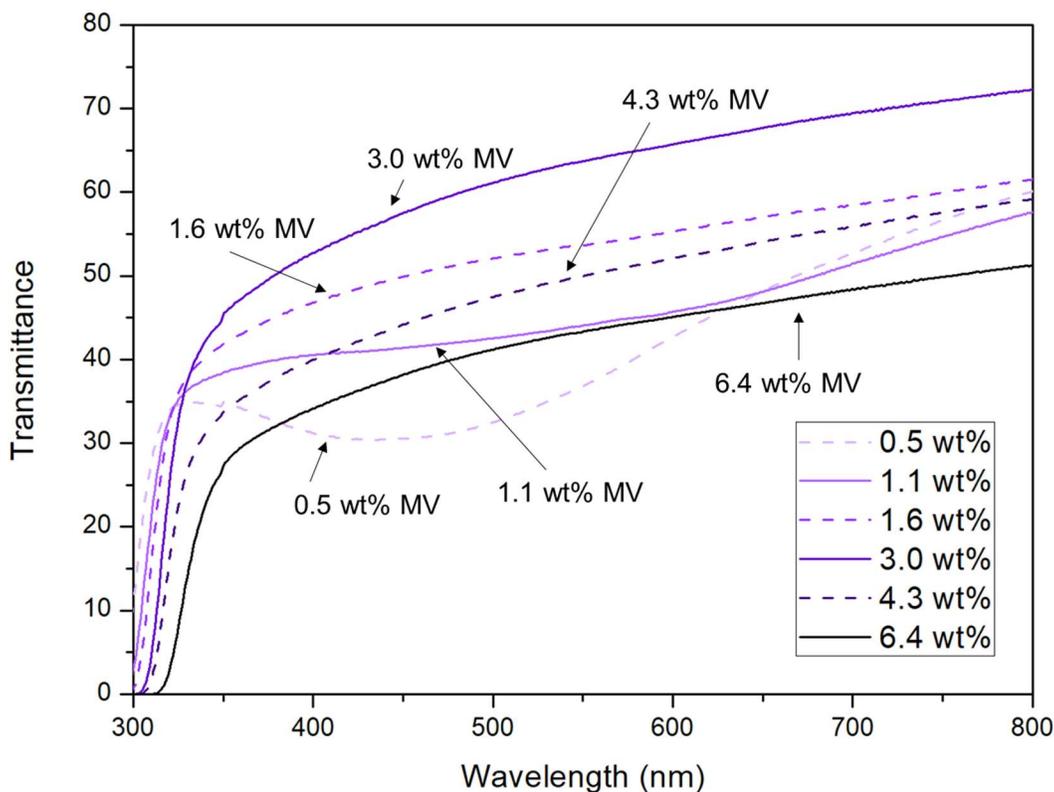


Fig. S9. Transmittance spectra of MV-CNC films with different wt% of MV.

MV-CNC films containing 3 wt% of the PF₆ viologen salt were made by mixing 1 mL of 6.1 wt% CNC suspension and 70 μL of a 100 mM MV dihexafluorophosphate solution prepared in acetonitrile. The sample was cast onto a polystyrene substrate (a regular hexagon with side length of 13 mm), and air dried at RT overnight. After 5 minutes of UV irradiation (302 nm), the colorless film turned pale blue (Fig. S10). The film changed back to colorless after two days.

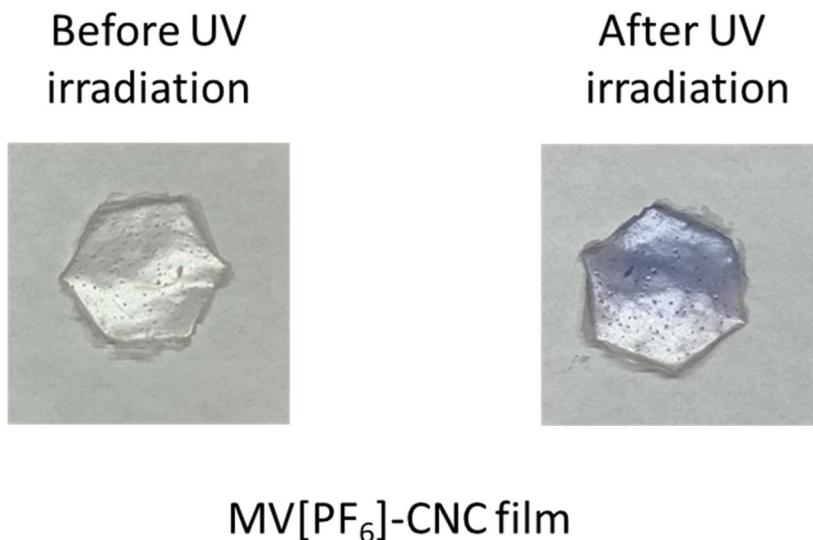


Fig. S10. Photographs of a 3.0 wt% MV-CNC film before and after UV irradiation. Sample prepared with hexafluorophosphate MV salt.

5. UV irradiation test on MV-embedded films

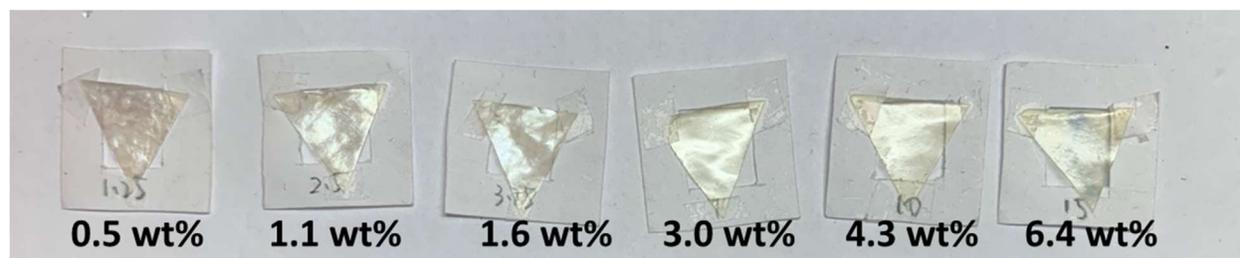


Fig. S11. Photograph of recovered MV-CNC films with different wt% of MV after 7 irradiation-oxidation cycles.

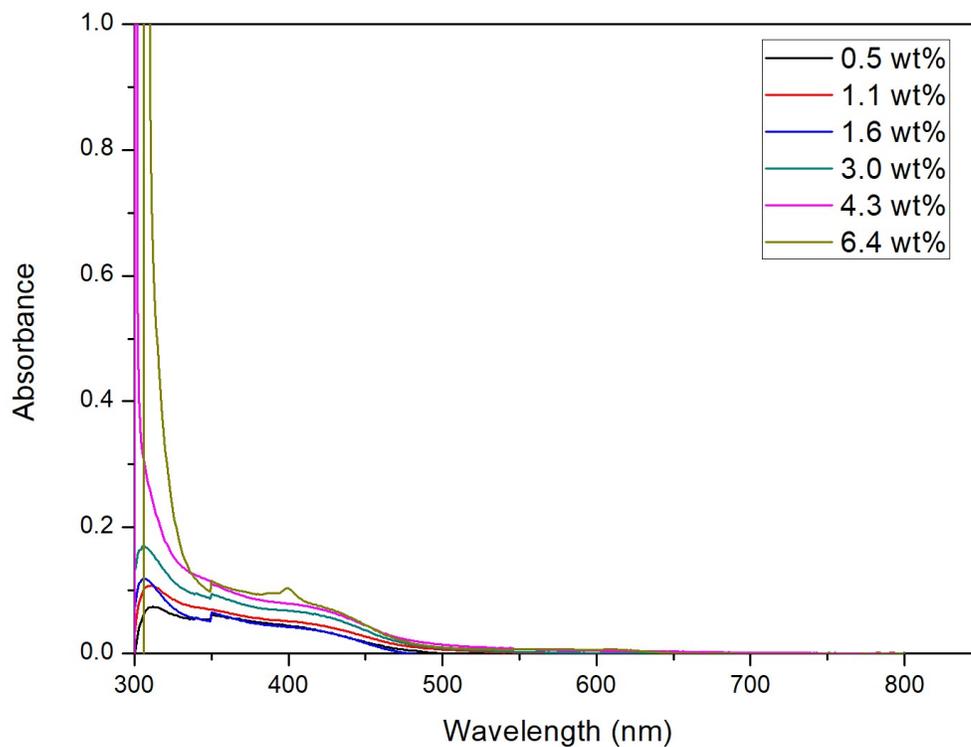


Fig. S12. UV-vis spectra of recovered MV-CNC films with different wt% of MV after 7 irradiation-oxidation cycles. Absorbances are recorded after oxidation step.

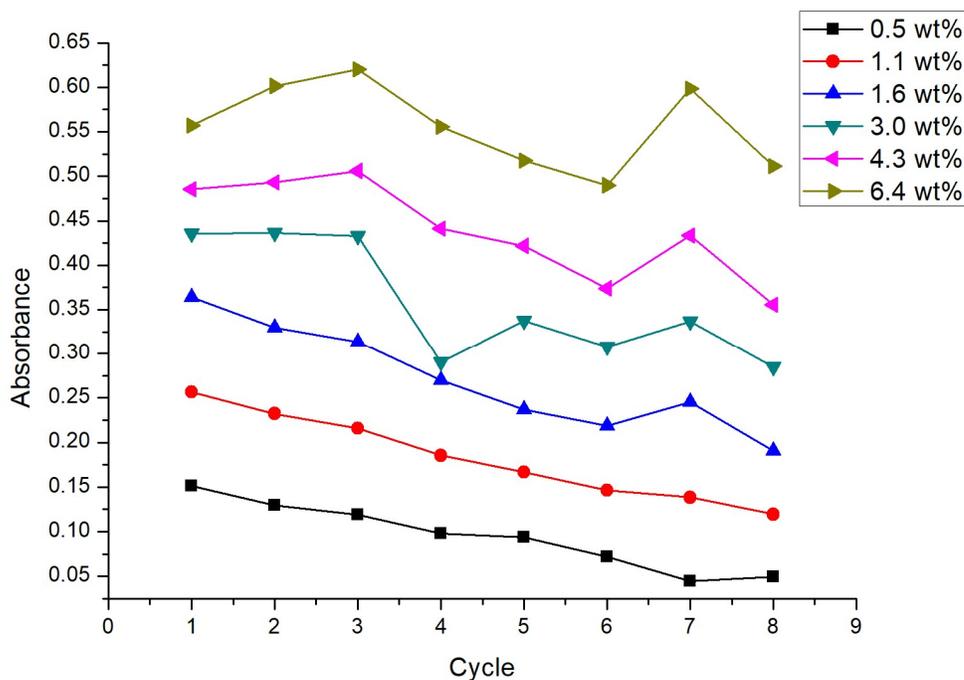


Fig. S13. Absorbance changes in irradiated MV-CNC films (from 0.5 wt% to 6.4 wt%) at 559 nm during 7 irradiation-oxidation cycles. Absorbances are recorded after each irradiation step.

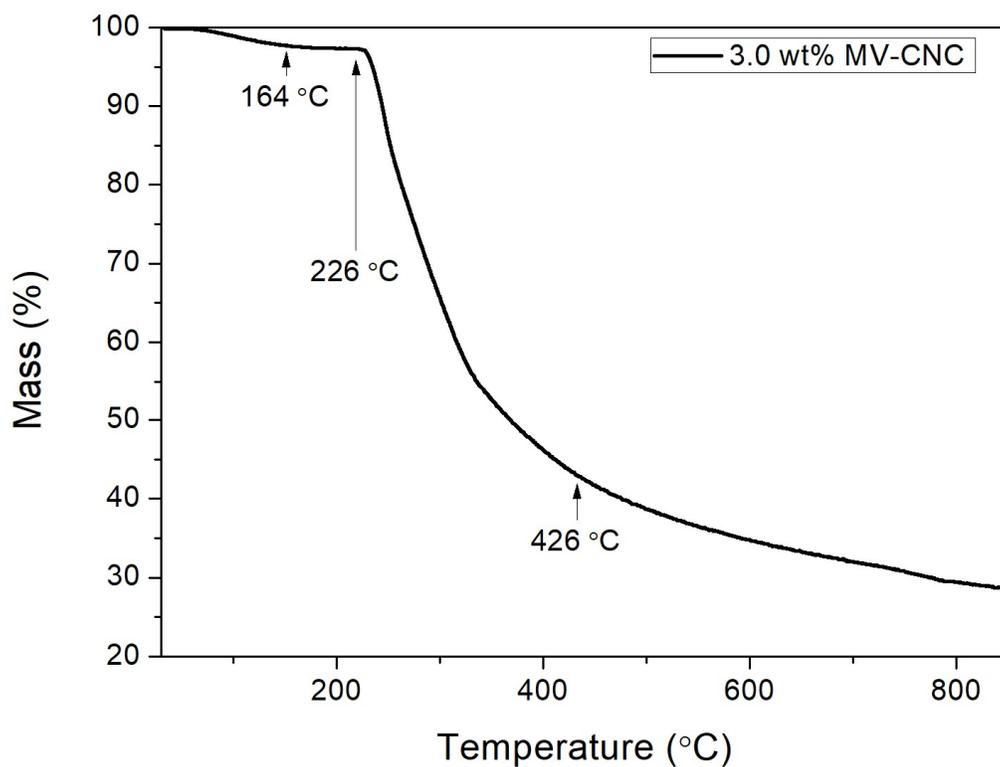


Fig. S14. TGA curve of 3.0 wt% MV-CNC film.

For environmental stability tests, 3.0 wt% MV-CNC films were sealed in vials overnight to reach equilibrium. After that, films were irradiated under UV light for 5 min and the irradiated films were characterized by UV-Vis spectroscopy. Fig. S15 shows the results. Conditions are listed as follows: Original = 20 °C, 30% RH, High T = 65 °C, 30% RH, Low T = -12 °C, 30% RH, High humidity = 20 °C, 75% RH.

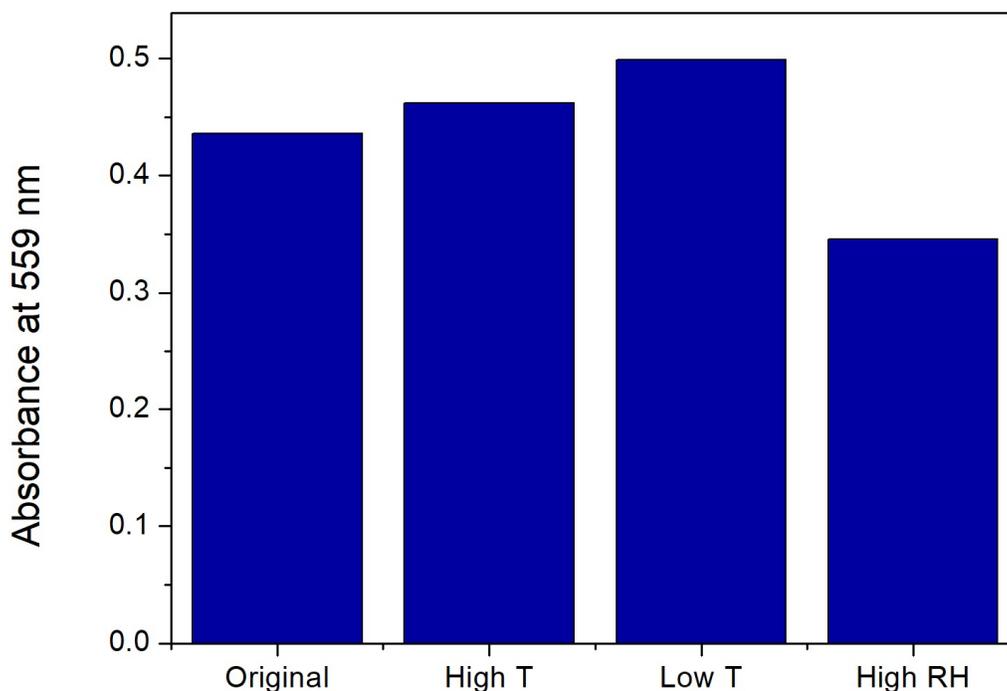


Fig. S15. Film absorbance at 559 nm under different environmental conditions.

6. Using MV-CNC film as UV index indicator

Table S3. 3.0 wt% MV-CNC film appearances under regular sun light with different UV index.

Sunshine duration (min)	20	20	20
UV index ⁵	1	3	6
MV-CNC film appearance			
Recommended actions ⁵	Safe. No protection needed.	Sun protection recommended.	Sun protection highly needed.

The colorimetry study was done by measuring the absorbance of 3.0 wt% MV-CNC film at 559 nm after irradiating for different lengths of time under UV lamp. A_{\max}^{559} represents the available maximum absorbance of irradiated film at 559 nm after 30 minutes irradiation, and A^{559} represents the absorbance of irradiated film at 559 nm after set irradiation time.

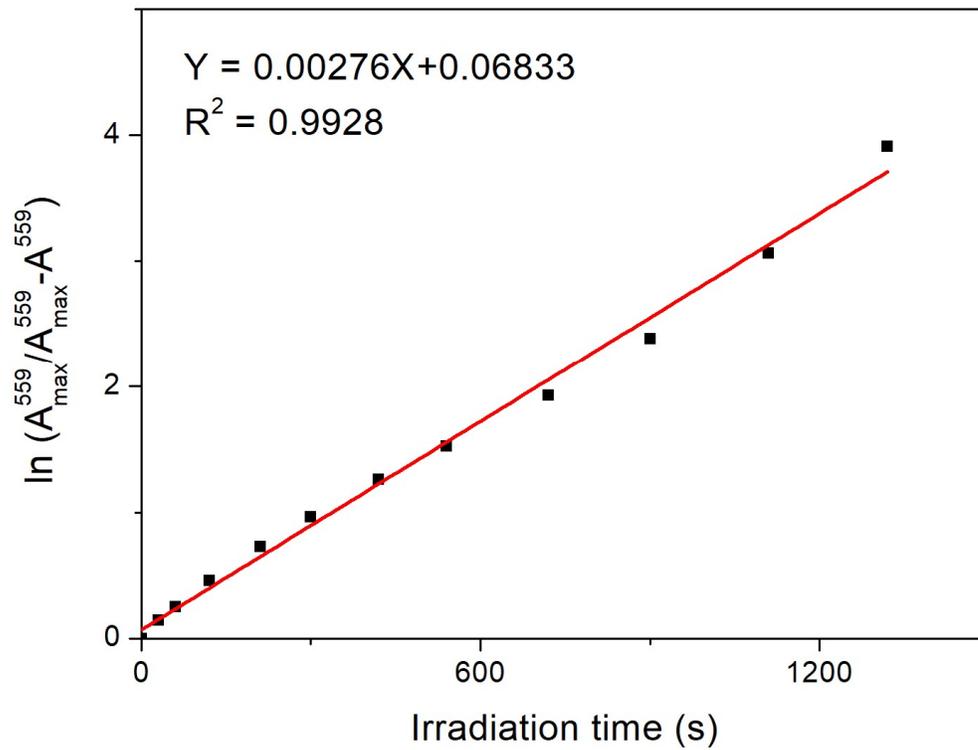


Fig. S16. Calibration curve between irradiation time and absorbance of the film at 559 nm.

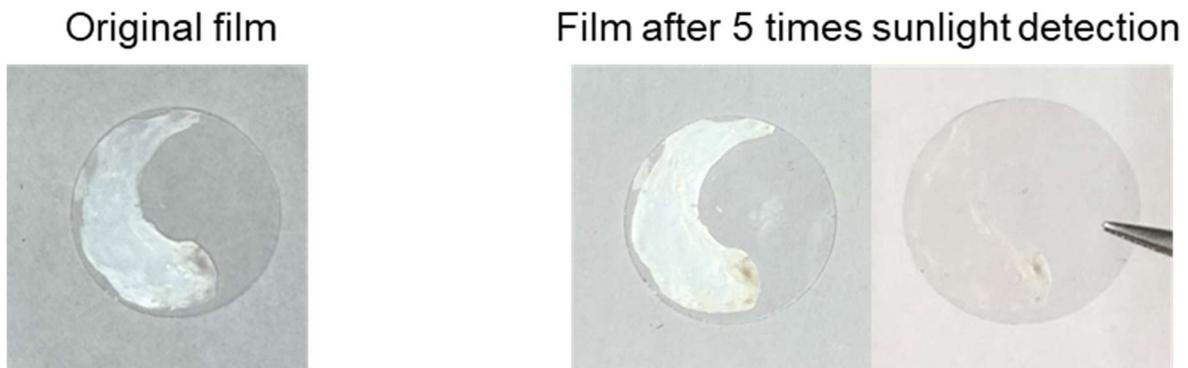


Fig.S17. Film appearance after 5 times sunlight detection.

References

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