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Supporting Information

A Novel ZnO/Viologens Photochromic Composite Film with Rapid UV Response for Rewritable Paper, Solar UV Detection, Smart Windows and Anti-Counterfeiting

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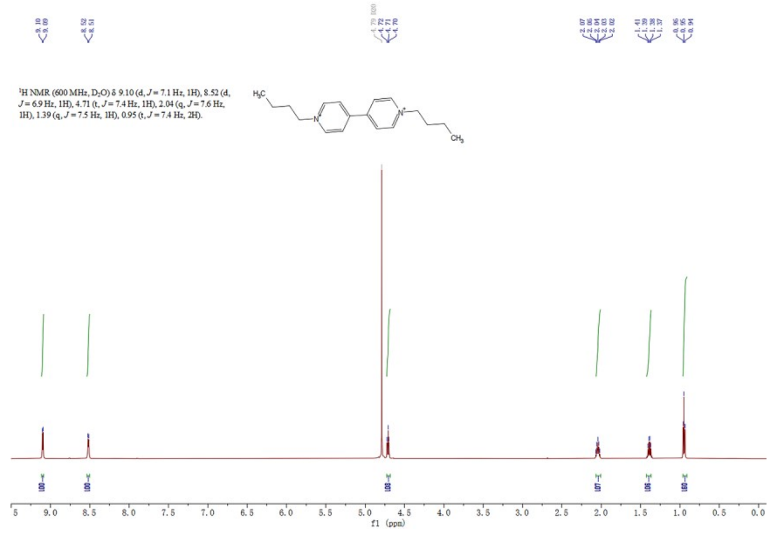

Fig. S1 V_1 NMR spectrum.

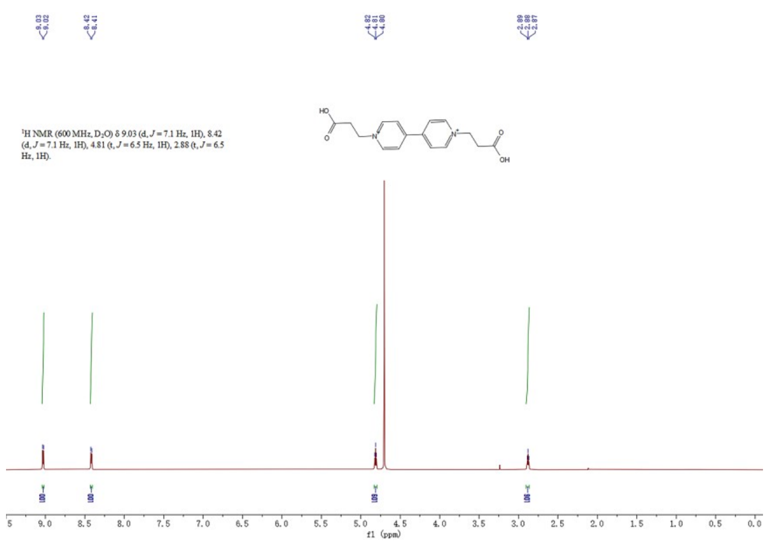

Fig. S2 V_2 NMR spectrum.

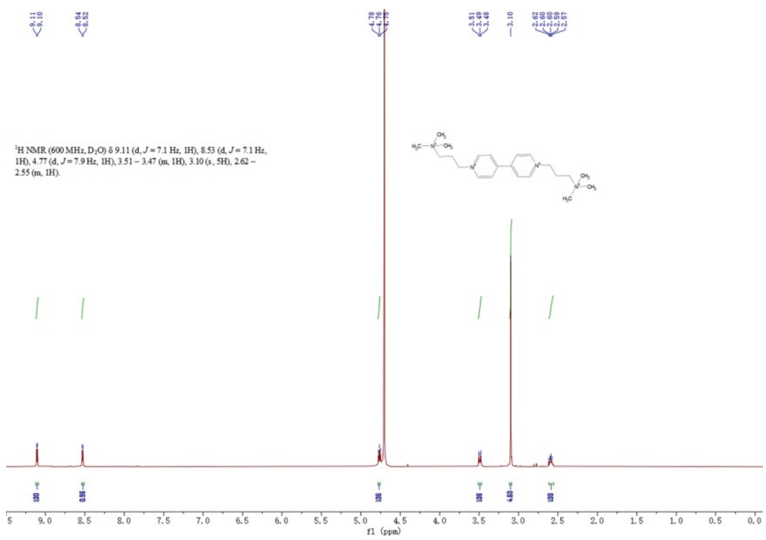

Fig. S3 V_3 NMR spectrum.

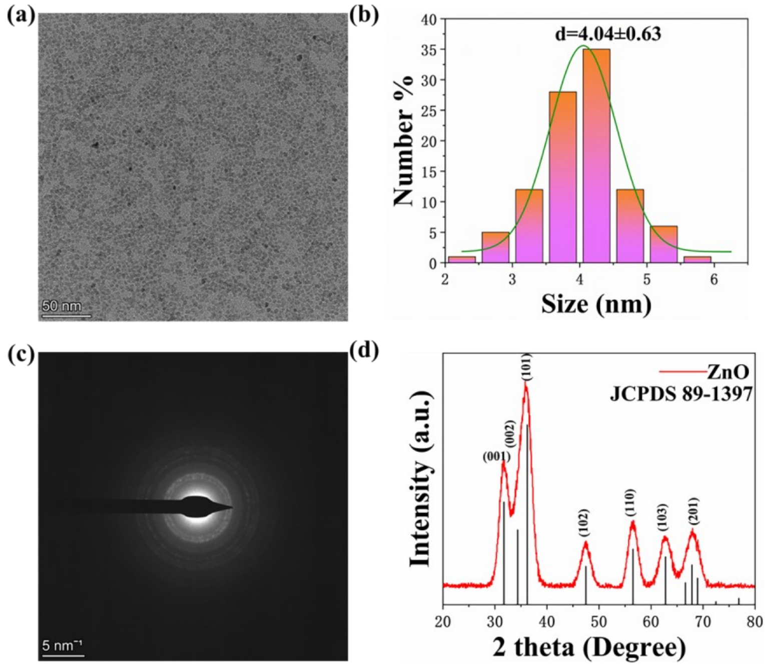

Fig. S4 Crystal structures of ZnO NPs (a) TEM images; (b) nanoparticle size distribution; (c) electron diffraction patterns; (d) XRD patterns.

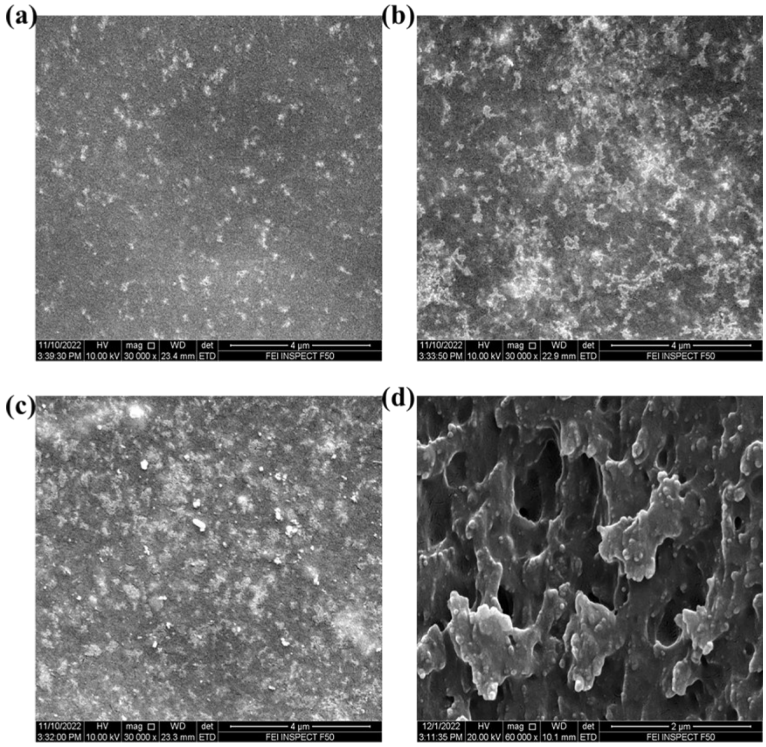

Fig. S5 SEM images of the surface of (a) HCP/V_2^{2+}/5.5 wt% ZnO, (b) HCP/V_2^{2+}/8.5 wt% ZnO and (c) HCP/V_2^{2+}/10 wt% ZnO films. (d) Cross-sectional SEM image of HCP/V_2^{2+}/5.5 wt% ZnO film.

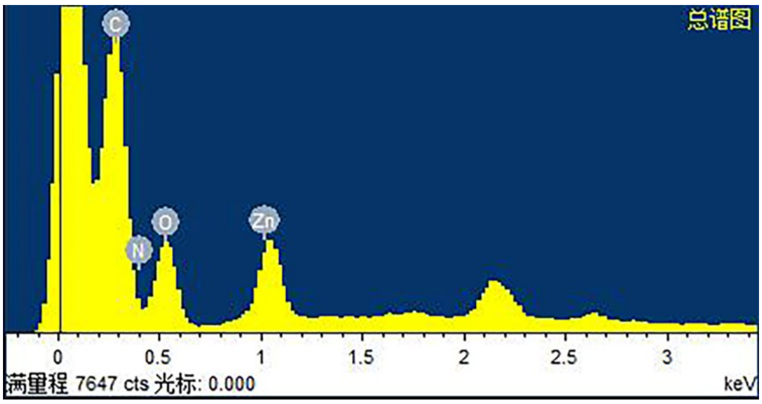

Fig. S6 The EDS spectrum of HCP/V_2^{2+}/5.5 wt% ZnO film.

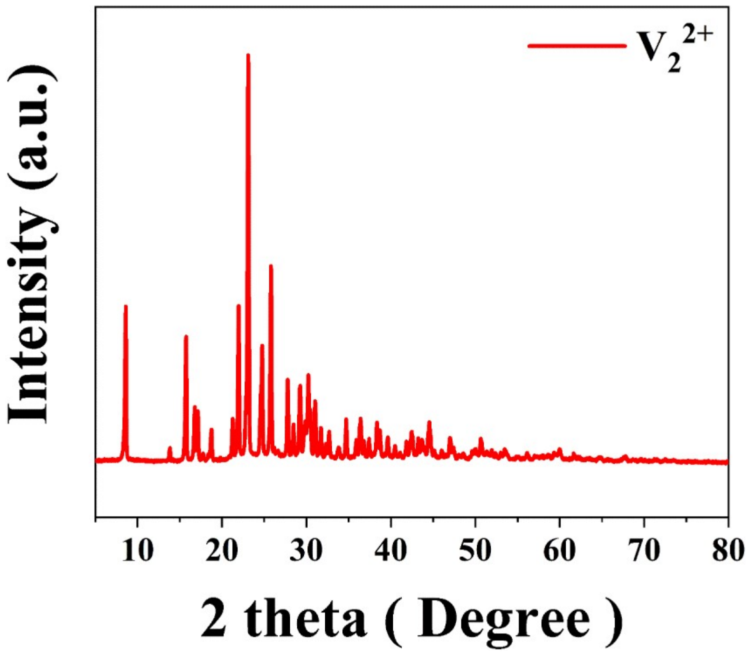

Fig. S7 V_2^{2+} XRD spectrum.

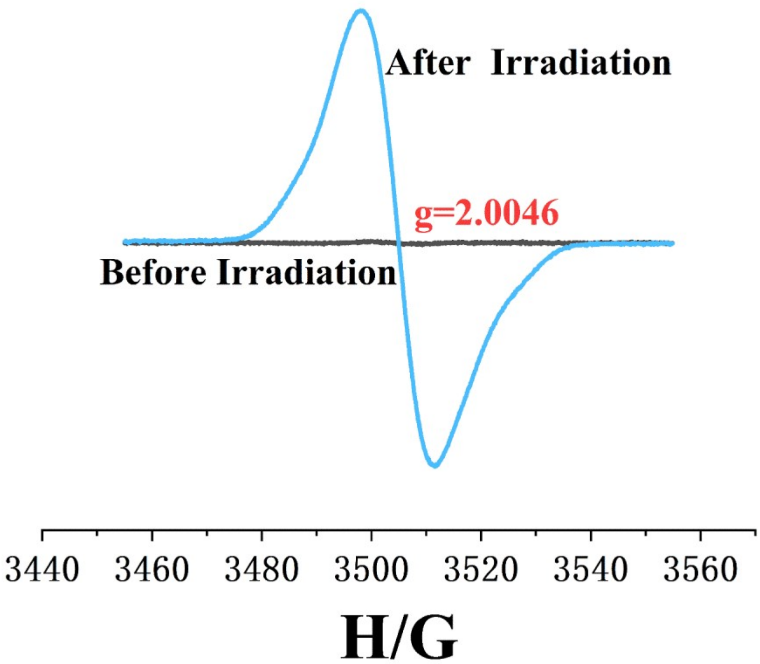

Fig. S8 The EPR spectra of the composite film before irradiation and after irradiation at room temperature.

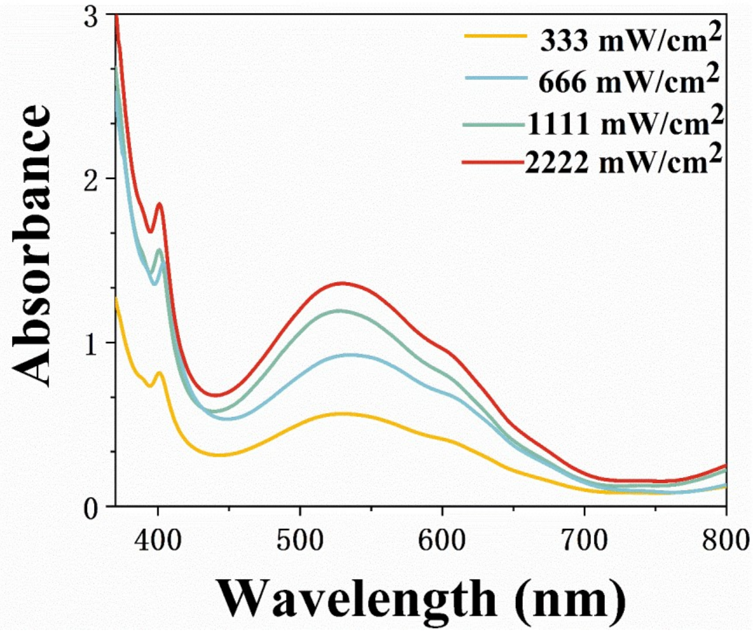

Fig. S9 The effects of different UV intensities on the photochromic performance of the HCP/V_2^{2+}/5.5 wt% ZnO film. (By placing the film at the same distance from the UV lamp (3 W, 6 W, 10 W, 20 W), the UV intensity can be determined using the formula: UV intensity (mW/cm^2) = Lamp output (mW) / (distance from lamp) ^{2}.

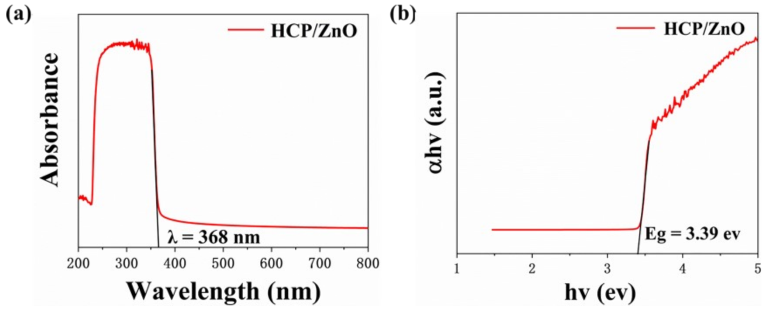

Fig. S10 Energy level evaluation of ZnO NPs.

The determination of the conduction band (CB) and valence band (VB) edge positions of zinc oxide (ZnO) depends on various factors, such as the bulk bandgap (Eg, bulk), size-dependent quantum confinement effect, and electron-hole pair Coulomb interaction. To estimate the position of the CB and VB, the following equations are used:[1, 2]

$$E_e = E_{CB} + \frac{m_h}{m_e + m_h}\left[E_{g,QD} - E_{g,bulk} + \frac{1.8e^2}{4\pi\varepsilon R}\right] \quad \text{Eq.S1(a)}$$

$$E_h = E_{VB} + \frac{m_e}{m_e + m_h}\left[E_{g,QD} - E_{g,bulk} + \frac{1.8e^2}{4\pi\varepsilon R}\right] \quad \text{Eq.S1(b)}$$

The CB and VB edge positions of bulk ZnO are -4.19 eV and -7.39 eV, respectively, while the effective masses of electrons and holes are 0.26 m_0 and 0.59 m_0, respectively. Here, m_0 represents the free electron mass[3]. The bandgap of a QD is 3.39 eV, as shown in Figure S10, while the bandgap of the bulk is 3.2 eV. The dielectric constant of bulk ZnO is $3.7\varepsilon_0$, where ε_0 is the dielectric constant of free space. As depicted in Fig. S4b, the QD radius (R) is 2 nm. E_e and E_h are calculated as -4.02 eV and -7.21 eV, respectively. For molecules, the reduction potentials are as follows: -0.590 V (vs. Ag/AgCl), -0.542 V, and -0.473 V for V_1^{2+}, V_2^{2+}, and V_3^{2+}, respectively. Then the reduction potentials with respect to VAC can be obtained as:

$$E_{VAC} = -4.5 - eE_{NHE} \quad \text{Eq.S2}$$

Therefore, the energy levels of the viologens (vs. VAC) are -4.10 eV, -4.16 eV, -4.23 eV for V_1^{2+}, V_2^{2+} and V_3^{2+} respectively. The driving force (CS) for electron transfer from ZnO to viologens is calculated by the energy difference between conduction band edge position and viologen reduction potentials.

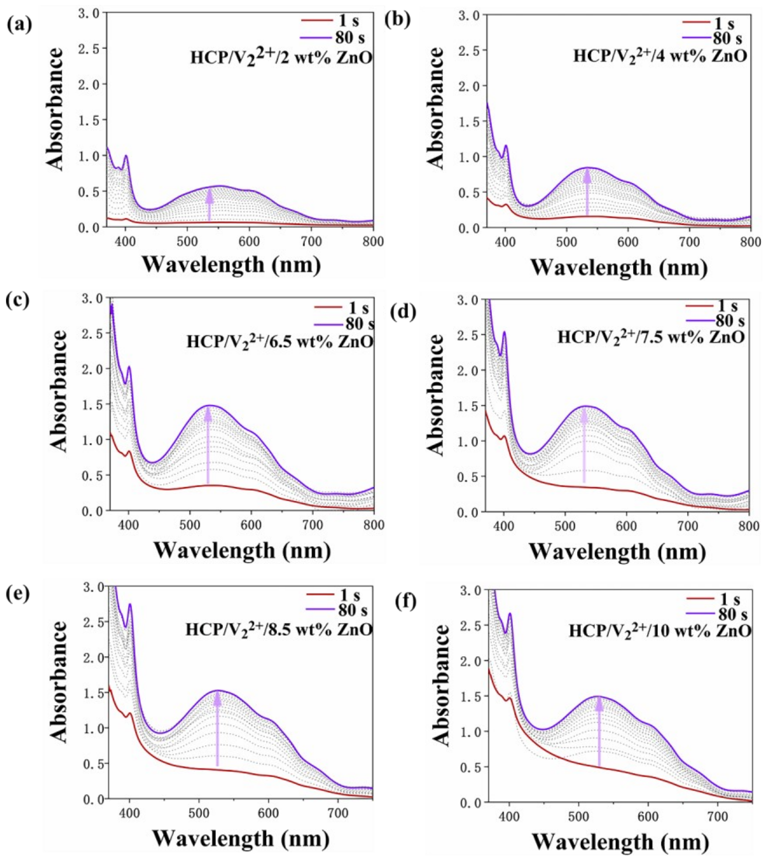

Fig. S11 UV-vis spectra of the films with different ZnO content.

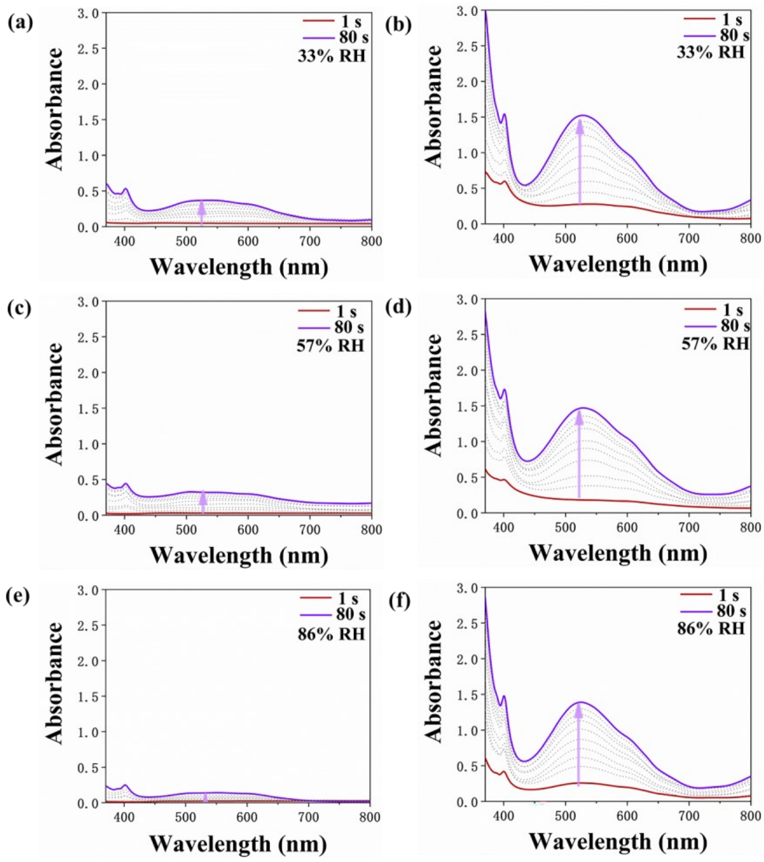

Fig. S12 (a), (b) and (c) are UV-vis spectra of HCP/V_2^{2+}/0 wt% ZnO at different RH environments. (d), (e) and (f) are UV-vis spectra of HCP / V_2^{2+} / 5.5 wt% ZnO at different RH environments.

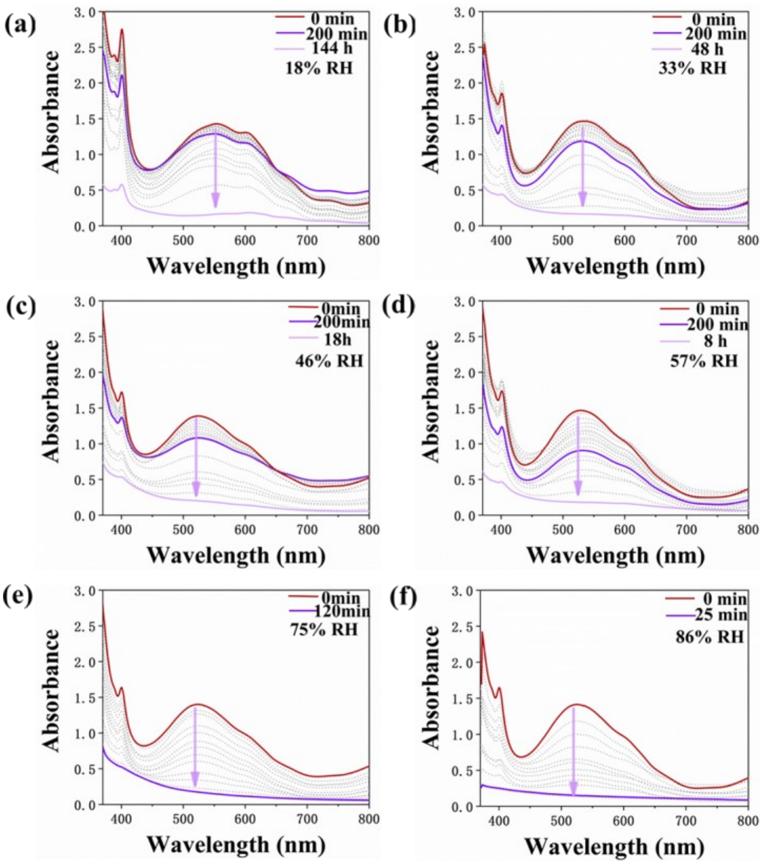

Fig. S13 UV-vis spectra of HCP/V_2^{2+}/5.5 wt% ZnO film in the decoloration state at different RH environments.

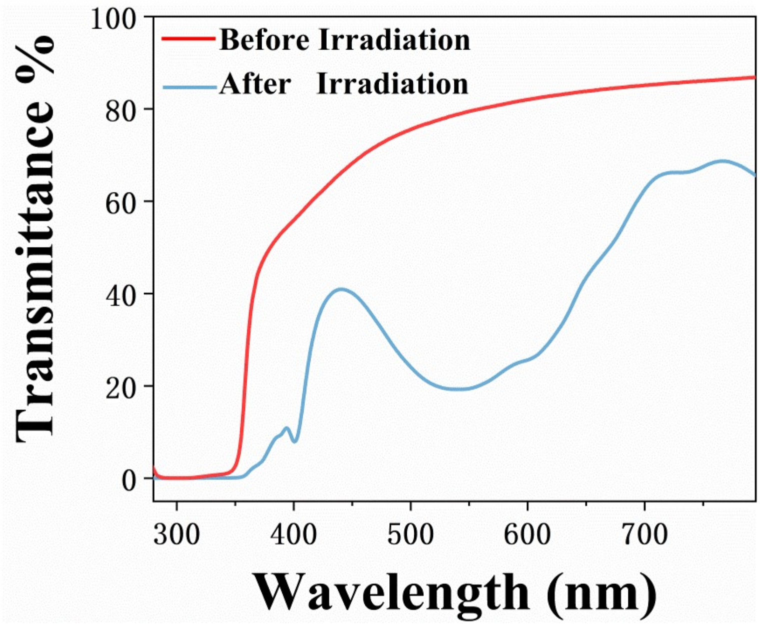

Fig. S14 The transmittance curves of the HCP/V_2^{2+}/5.5 wt% ZnO glass coating were recorded before and after exposure to outdoor environments with UV index of 9 for 20 seconds.

References

1. Q. Shao, H. Lin and M. Shao, *ACS Omega*, 2020, **5**, 10297-10300.
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