ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Self-Healing Photochromic Elastomer Composites for Wearable UV-Sensors

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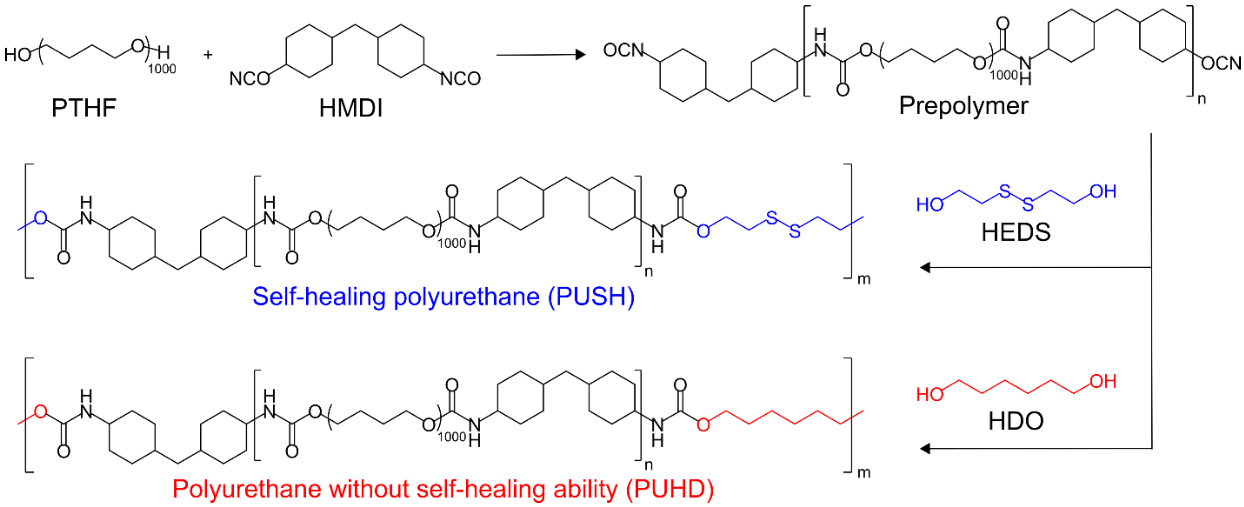

Figure S1. Synthetic routes for the preparation of self-healing polyurethane (PUSH) and polyurethane without self-healing ability (PUHD).

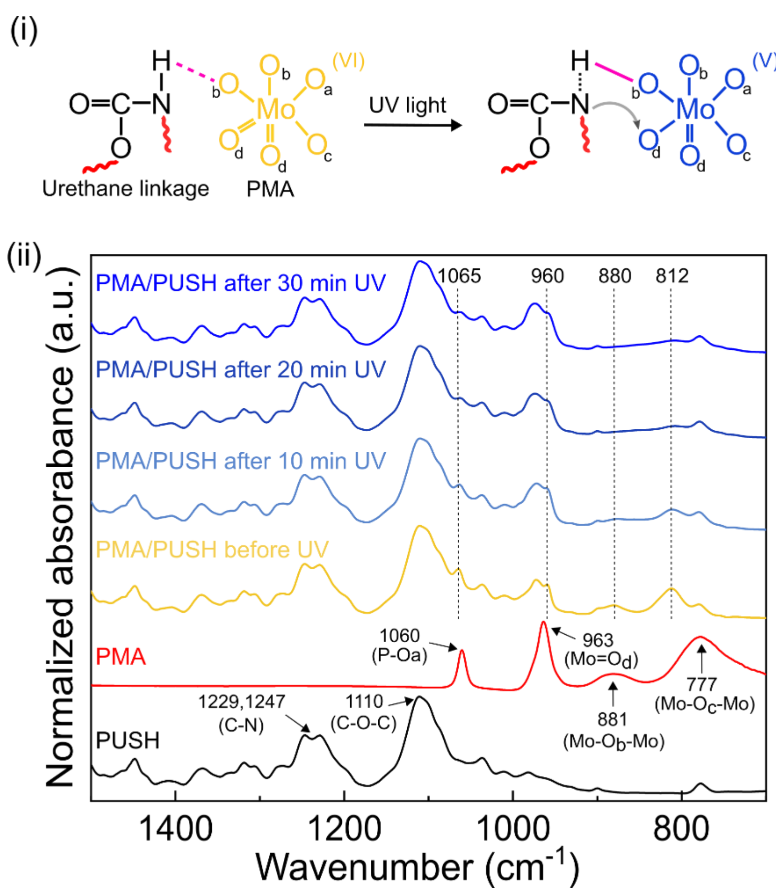

Figure S2. (i) A photochromic mechanism between phosphomolybdic acid hydrate (PMA) molecules and urethane linkages in a self-healing polymer network. (ii) FTIR spectra of PUSH polymer, PMA, and photoPUSH (5.7 wt% PMA) before and after being exposed to UVA light for 10–30 min.

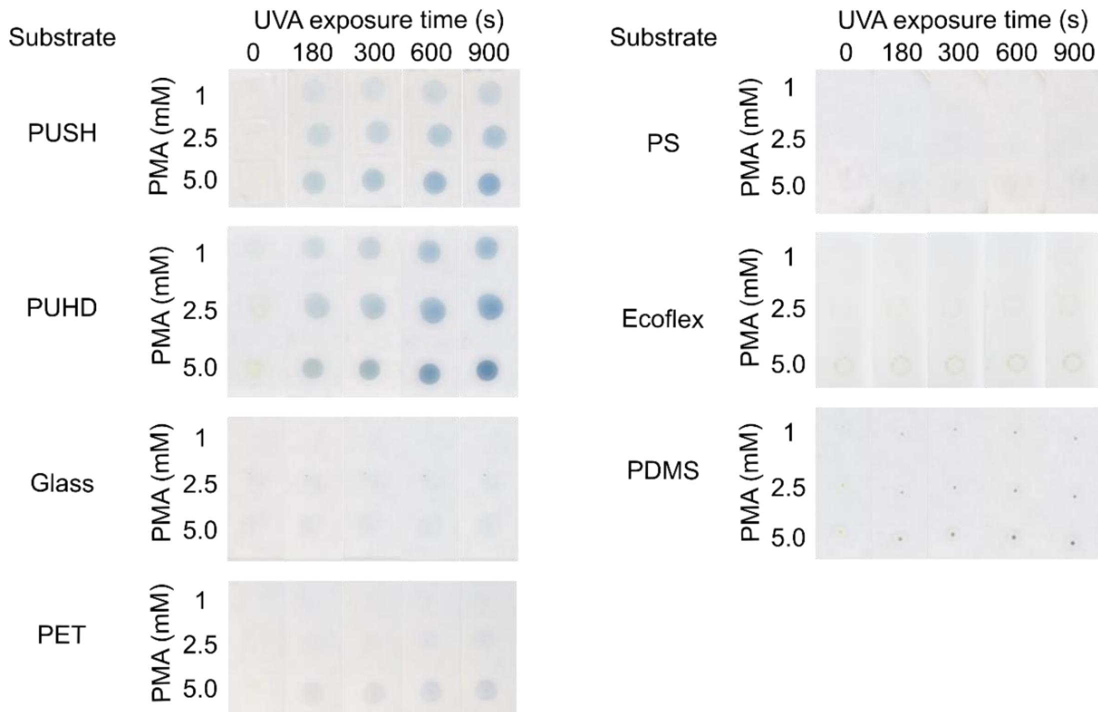

Figure S3. PMA deposited on different substrates, showing color change after exposure to UVA light at a wavelength of 368 nm with an increasing exposure time.

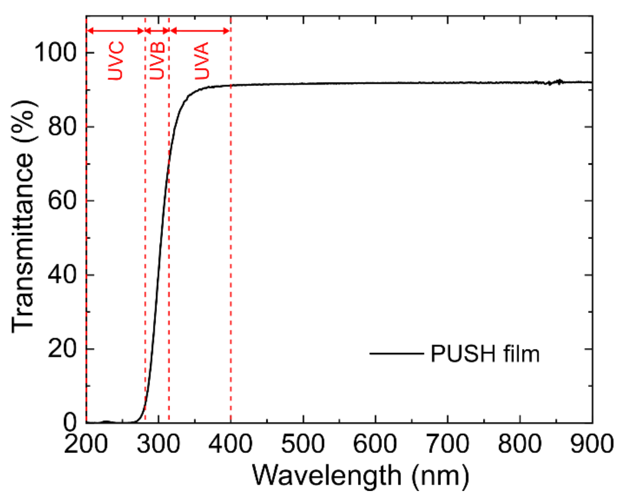

Figure S4. Ultraviolet–visible (UV–vis) light transmittance spectra of PUSH film (thickness = 0.09 mm).

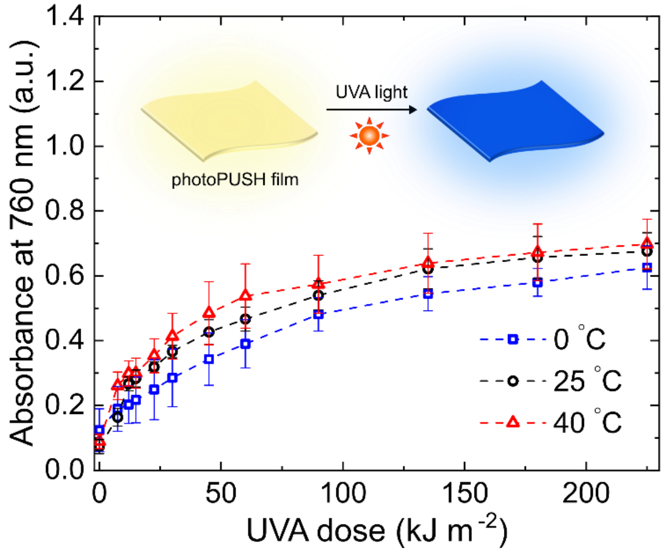

Figure S5. UV absorbance at a wavelength of 760 nm as a function of UVA light (λ_{max} = 365 nm) dose for photoPUSH films with 5.7 wt% PMA under different temperatures.

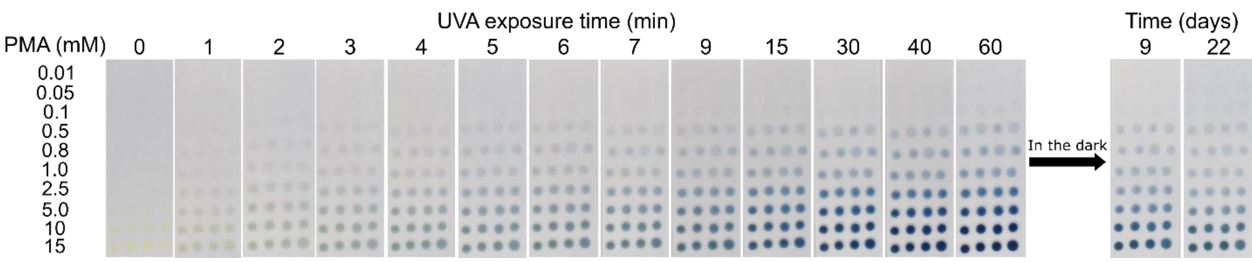

Figure S6. Photographs of a PUSH film with different amount of PMA after being irradiated under UVA and kept in the dark at 25 °C.

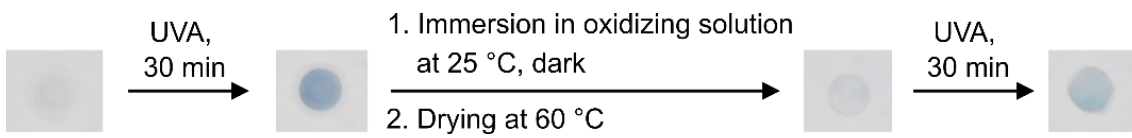

Figure S7. Photographs showing the reversible color transition of a photoPUSH composite with 11.4 wt% PMA upon oxidation with an aqueous solution of hydrogen peroxide.

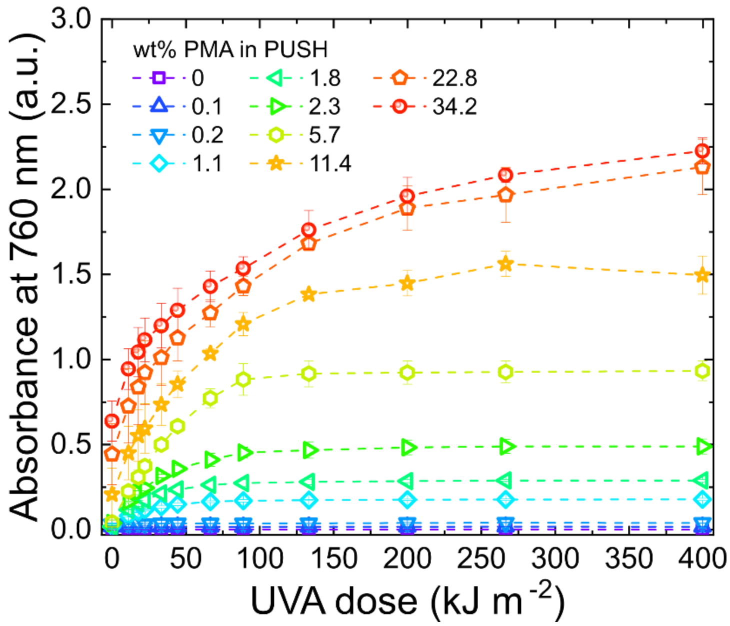

Figure S8. UV absorbance at a wavelength of 760 nm as a function of UVA light (λ_{max} = 368 nm) dose for photoPUSH films with different PMA amounts.

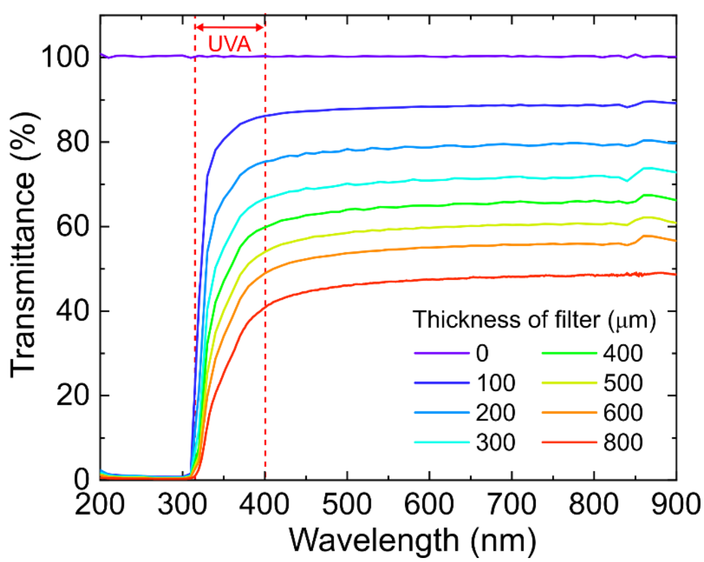

Figure S9. Melanin-mimic UV filters (polyethylene terephthalate (PET) thin films) with different thickness. The wavelength range for UVA, B, and C is marked with dash lines at 200–280 nm, 280–315 nm, and 315–400 nm, respectively.

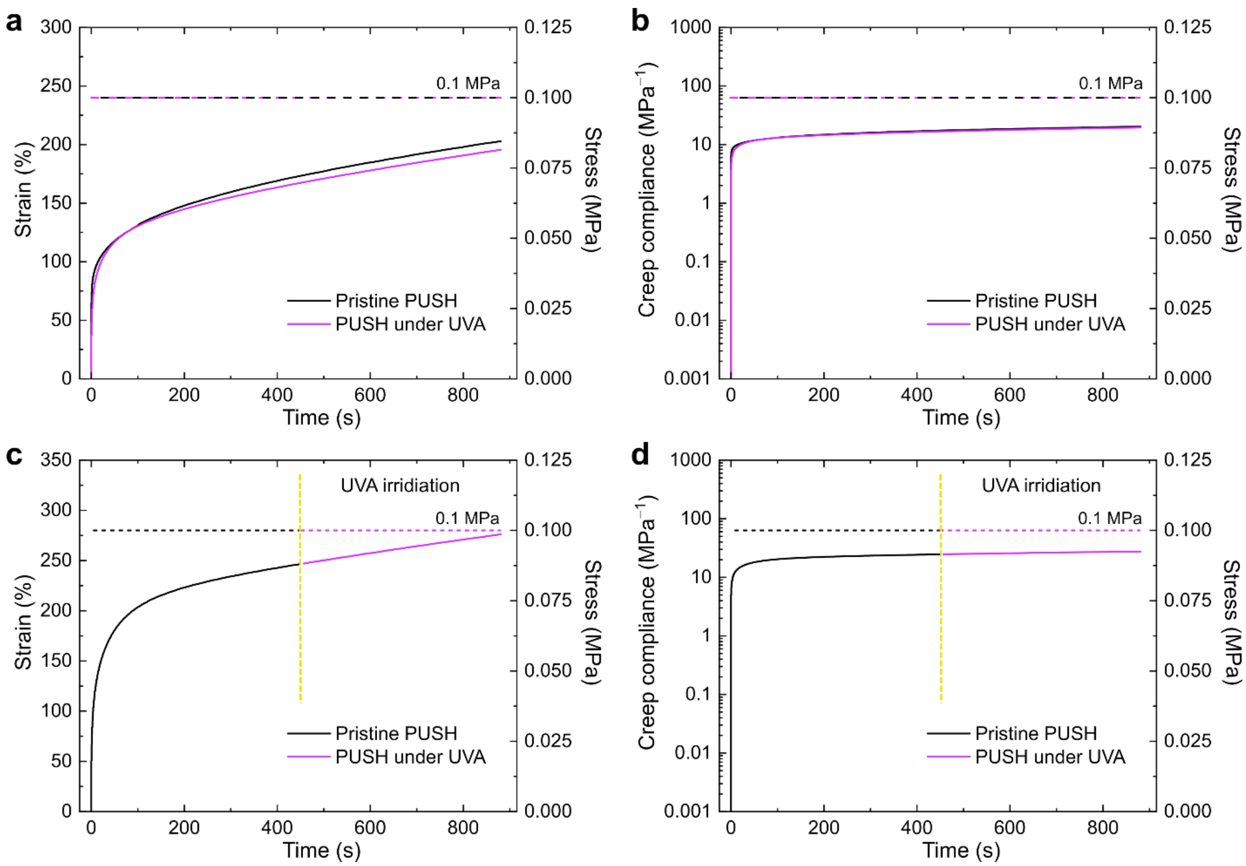

Figure S10. Comparison of shear strain (%) and creep compliance of (a,b) two different PUSH films and (c,d) a PUSH film under constant stress of 0.1 MPa with and without UV light exposure.

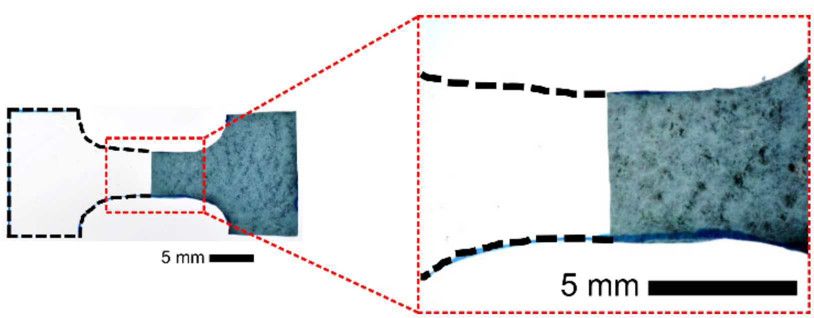

Figure S11. A photograph showing a healed dog-bone shaped sample between PUSH (transparent, in black dashed line region) and photoPUSH (blue). The magnified image on the right showed the healed position.

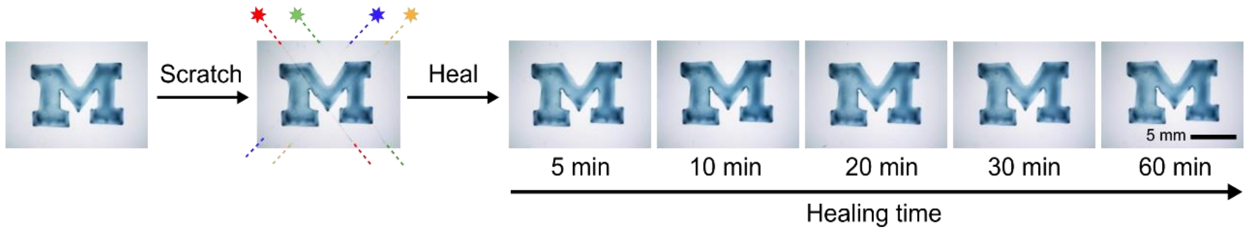

Figure S12. A "M"-shaped photoPUSH film was scratched and then healed at 70 °C for different healing times.

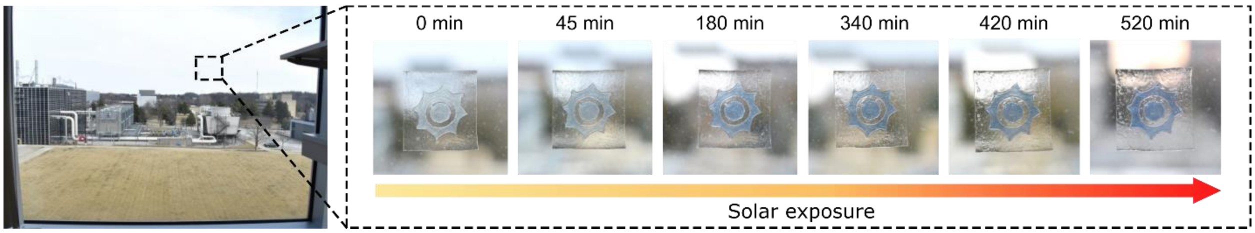

Figure S13. Photographs of a UV-sensor (photoPUSH composite on a PUSH sticker film) attached to a window for natural sunlight exposure monitoring.

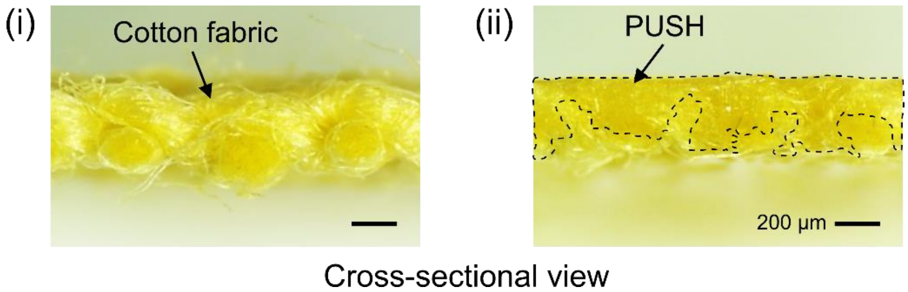

Figure S14. Optical images showing cross-sectional view of (i) original cotton textile and (ii) PUSH penetrating through the cotton textile.

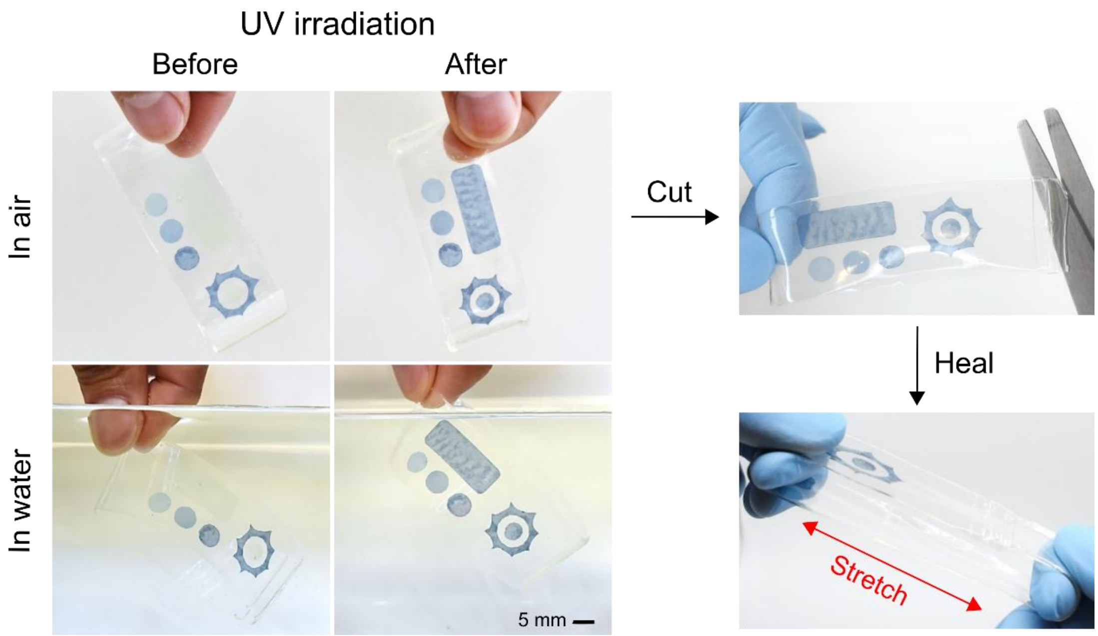

Figure S15. A UV detection wristband exhibits color change with UV light in air and in water. The wristband was cut and subsequently healed at 70 °C, recovering the mechanical and photochromic properties.

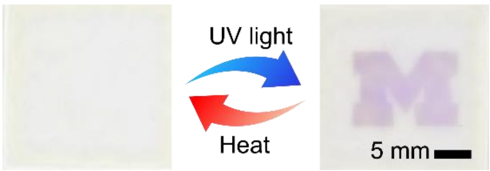

Figure S16. Reversible photochromism of a self-healing SP/PUSH composite film upon UVA light (λ_{max} = 365 nm) irradiation with a M-shaped photomask and heating at 60 °C.

Table S1. Benchmark of representative photoelectric wearable UV sensor technologies. Adapted from ref.[1]

Fabrication			Specificity		Selectivity	Sensitivity		Real-time monitoring		Practical applicability					Ref
Functional materials	**Substrates**	**Fabrication techniques**	**Visible blind**	**Detection wavelength**	**Spectral selectivity**	**Light intensity (mW cm^{-2})**	**MED range**	**Intensity**	**Cumulative dose**	**Reusability**	**Naked eye detection[a]**	**Custom for different skin types**	**Stretchability**	**Self-healing ability**	
ZnO/ Graphene	Cellulose paper	ZnO pencil writing	✓	365 nm	✗	0.5–3.9	✓	✓	✗	✓	✗	✗	✗	✗	[2]
Te/ZnO, Te/TiO_2	Paper	Brush writing	Partial	350 nm	✗	N/A	N/A	✓	✗	✓	✗	✗	✗	✗	[3]
ZnO	Paper	Screen printing	✗	254 nm	✗	3.8	✗	✓	✗	✓	✗	✗	✗	✗	[4]
ZnO	PI	Inkjet printing	✓	365 nm	✗	9.1×10^{-3}	✓	✓	✗	✓	✗	✗	N/A	✗	[5]
ZnO/rGO	mica	Laser Writing	N/A	365 nm	✗	0.66–20.03	✓	✓	✗	✓	✗	✗	N/A (bending)	✗	[6]
p-CuZnS/n-TiO_2	Ti wires	Chemical bath	✗	350 nm	✗	1.26	✓	✓	✗	✓	✗	✗	✗	✗	[7]
TiO_2/GO	Parylene-C	Spraying	Partial	270 nm	✗	0–2.5 × 10^{-2}	✓	✓	✗	✓	✗	✗	N/A (bending)	✗	[8]
TiO_2/GO	Gold-on-glass interdigitated electrodes	AC electrophoresis deposition	Partial	Solar simulator	✗	3.2	✓	✗	✓	N/A	✗	✗	✗	✗	[9]
PANI/TST/ PAG/CNTs	PI	Laser printing dip coating	✓	365 nm	✗	40	✓	✗	✓	✗	✗	✗	N/A (flexible)	✗	[10]
CNTs	Cellulose thread	Dip coating	✓	254, 365 nm	✓	2–4	✓	✓	✗	✓	✗	✗	N/A (flexible)	✗	[11]
CNTs	Glass, PI	Drop casting	N/A	254 nm	N/A	0.2–2	✗	✓	✗	✓	✗	✗	✗	✗	[12]
ZnO/SiO_2/ TiO_2	Glass	Direct deposition	✓	370 nm	✓	8.6×10^{-2}	✓	✓	✗	✓	✗	✗	✗	✗	[13]
Photodiode arrays	Copper, PI	N/A	N/A	365, 305 nm	✓	2.2, 0.16	✓	✓	✓	✓	✗	App-customi-zable	✗	✗	[14]
Black phosphorus	SiO2/Si, PEN,PI	N/A	✗	365, 208 nm	✓	2	✓	✓	✗	✓	✗	✗	✗	✗	[15]
PMA	Self-healing polyurethane	Solution blending/ casting, assemblability	N/A	UVA, B, C (368, 365, 306, and 265 nm)	✓	2–5.6	✓	✗	✓	✓	✓	✓	✓	✓	This work

a) The "naked eye detection" here refers to the state where the sensor response is detectable directly by the eye and thus offers the user the sensing results without external interfaces.

Table S2. Benchmark of representative photochromic wearable UV sensor technologies. Adapted from ref.[1]

Fabrication			Specificity		Selectivity	Sensitivity		Real-time monitoring		Practical applicability					Ref
Functional materials	**Substrates**	**Fabrication techniques**	**Visible blind**	**Detection wavelength**	**Spectral selectivity**	**Light intensity (mW cm^{-2})**	**MED range**	**Intensity**	**Cumulative dose**	**Reusability**	**Naked eye detection**	**Custom for different skin types**	**Stretchability**	**Self-healing ability**	
C1H/MG, DPIC/TB	PVB	Spin coating	✓	Solar simulator	✗	UVI 5	✓	✗	✓	✗	✓	✗	✗	✗	[16]
PDPPS-TF/CVL PDPPS-TF/CR	PDMS	Screen printing	✓	UVA, UVB	✓	UVA 1.8 UVB 0.17	✓	✓	✓	✗	✗	✓	✓	✗	[17]
TiO_2/brilliant blue FCF/PVP	Photo paper	Inkjet printing	✓	Solar simulator	✗	3.2	✓	✗	✓	✗	✓	✓	✗	✗	[18]
TiO_2/RBBR/ glycerol	hydroxyethyl cellulose	Spin coating	✓	368 nm	✗	1.5	✓	✗	✓	✗	✓	✗	N/A	✗	[19]
Prussian Blue/TiO_2	polyethylene terephthalate	Cyclic voltammetry	✓	365 nm	✗	0.2–10	N/A	✓	✗	✓	✓	✗	✗	✗	[20]
DTEC	LDPE	Solution casting	✗	Solar simulator	✓	100	✓	✗	✓	✗	✓	✗	✗	✗	[21]
PMA/LA	Filter paper	Pen writing	✓	UVA, B, C	✓	0.5	✓	✗	✓	✗	✓	✓	✗	✗	[22]
Hackmanite $(Na,M)_8Al_6Si_6O_{24}(Cl,S)_2$	N/A	N/A	✗	Solar simulator	✓	UVI 0–6	✓	✓	✓	✓	✗	✗	✗	✗	[23]
UV-bleachable dye/LED	PDMS	Spin casting	✓	Solar simulator	✗	4.2	✓	✗	✓	N/A	✗	✗	✓	✗	[24]
PMA-ONB	PEN	Drop casting	N/A	Solar simulator	✗	100	✓	✗	✓	✗	✓	✗	N/A (bending)	✗	[25]
PMA	Self-healing polyurethane	Solution blending/ casting, assemblability	N/A	UVA, B, C (368, 365, 306, and 265 nm)	✓	2-5.6	✓	✗	✓	✓	✓	✓	✓	✓	This work

Table S3. Benchmark of commercial wearable UV sensor technologies. Adapted from ref.[1]

Category	Product	Format	Battery-free/Self-powered	UVA/UVB differentiation	Cumulative dose	Activation-free	Sunscreen applicable	Custom for different skin types	Reusable[a]	Water-proof	Work on its own	Stretchability	Self-healing ability	Ref
Electronic	Microsoft Band	Wristband	✗	✗	✗	✗	✗	✗	✓	✗	✓	✗	✗	[26]
Electronic	My skin track UV	Clip	✓	✓	✓	✓	✗	✓	✓	✓	✗	✗	✗	[27, 28]
Electronic	Shade	Magnetic clip	✗	✓	✓	✓	✗	✓	✓	✓	✗	✗	✗	[29]
Electronic	Sunsprite	Clip	✓	✗	✓	✓	✗	✗	✓	✗	✓	✗	✗	[30]
Electronic	Qsun	Clip	✗	✓	✓	✓	✗	✓	✓	✗	✓	✗	✗	[31]
Electronic	Stella	Wristband	✗	N/A	✓	✓	✗	✓	✓	✓	✓	✗	✗	[32]
Electronic	Violet	Clip	✗	✓	✓	✓	✗	✓	✓	✓	✓	✗	✗	[33]
Electronic	Sunfriend	wristband	✗	✗	✓	✓	✗	✓	✓	✓	✓	✗	✗	[34]
Colorimetric/ Electronic	My UV patch	Sticker	✓	App-differentiable	✓	✓	✓	App-customi-zable	✗	✓	✗	✗	✗	[27, 35]
Colorimetric	Sundicator	Sticker/wrist band	✓	✗	✗	✗	✓	✗	✗	✓	✓	✗	✗	[36]
Colorimetric	Smartsun	Sticker/wrist band	✓	✗	✗	✓	✓	✗	✗	✓	✓	✗	✗	[37]
Colorimetric	SPOTMYUV	Sticker	✓	✗	✗	✗	✓	✗	✗	✓	✓	✗	✗	[38]
Colorimetric	Logicink	Sticker	✓	✗	✓	✓	✓	✗	✗	✓	✓	N/A	✗	[39]
Colorimetric	photoPUSH	patch/sticker /wristband	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	This work

a) Reusable is defined as the potential capability of the sensor to be reset and reused after the first day's usage, such that the previous exposure data does not affect the ongoing performance of the sensor.

Abbreviations

AC	Alternating current
C1H	Chloral hydrate
CNTs	Carbon nanotubes
CR	Congo red
CVL	Crystal violet lactone
DPIC	Diphenyliodonium chloride
DTEC	(2Z,6Z)-2,6-bis(2-(2,6-diphenyl-4H-thiopyran-4-ylidene)ethylidene) cyclohexanone
FCF	Brilliant blue FCF
GO	Graphene oxide
LA	Lactic acid
LDPE	Low-density polyethylene
LED	Light-emitting diode
MG	Malachite green
N/A	Not available
ONB	Ortho-nitrobenzyl
PAG	Photoacid generator
PANI	Polyaniline
PDMS	Polydimethylsiloxane
PDPPS-TF	4-phenoxyphenyl)diphenylsulfonium triflate
PEN	Poly(ethylene naphthalate)
PI	Polyimide
PMA	Phosphomolybdic acid
PVB	Poly(vinyl butyral)
PVP	Polyvinylpyrrolidone
RBBR	Remazol brilliant blue R
rGO	Reduced graphene oxide
SiO2	Silicon dioxide
TB	Thymol blue
Te	Tellurium
TiO2	Titanium dioxide
TST	Triphenylsulfonium triflate
ZnO	Zinc oxide

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