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Electronic Supporting Information

Gelatin/PVA composited photochromic film for light printing with fast rewritability and long-term storage ability

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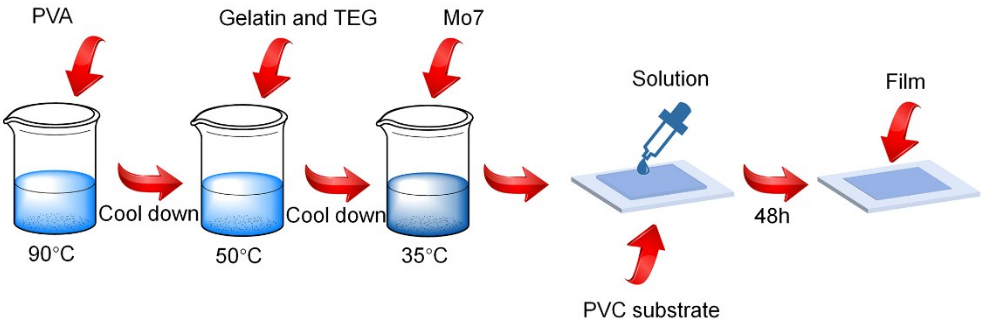
Experimental Section

Materials: Gelatin (gel strength ~250 g bloom), PVA (type 1788), TEG (98%) and Mo7 [$(NH_4)_6Mo_7O_{24}\cdot4H_2O$, 99%] were obtained from Shanghai Aladdin Reagent Co. Ltd.

Preparation of films: PVA25 and PVA50 were obtained as follows: gelatin and TEG were firstly dissolved in fresh PVA aqueous at 50°C. Then Mo7 was dissolved after the solution was cooled to 35°C. The solution was spread and dried on polyvinyl chloride (PVC) film substrates for 48 h in an indoor environment (20°C, 30% relative humidity (RH)) to obtain films. PVA0 was obtained as similar method but PVA aqueous was replaced with water. The preparation process was shown in **Scheme S1** and the recipes were shown in **Table S1**. In this experiment, the thickness of the film were approximately 150 μm.



Scheme S1. Preparation process of the films.

Table S1. Recipes of the films.

	Gelatin (g)	PVA (g)	TEG (g)	Mo7 (g)	H_2O (mL)
PVA0	2.0	0	2.0	0.9	30
PVA25	2.0	0.5	2.0	0.9	30
PVA50	2.0	1.0	2.0	0.9	30

Mechanical measurement: Mechanical measurement was performed on the equipment (SHIMADZU, model AGS-X, 100 N, Japan) at indoor environment. The samples were cut into 30*5 mm ribbons and the thickness was measured. The stretching rate was 2 mm min^{-1}.

Absorbance measurement: The UV-Vis spectra and transmission measurements were measured by equipment (Cary 5000, Agilent). The scanning range was 200-800 nm and the scanning rate was 1800 nm·min^{-1}.

Photochromic experiment: The samples were treated by a UV light source (Intelli-ray 600 Uvitron International). The distance between the sample and the light source was 20 cm.

Fourier transform infrared (FT-IR) test: The FT-IR spectra were measured using an FT-IR spectrometer (Nicolet iS 50) with a test range of 4000-400 cm^{-1} and scan for 32 times.

X-ray diffraction (XRD) analysis: The XRD test of the films were characterized using an X-ray diffractometer (Rikagu, Smartlab) with Cu Kα radiation at a scan speed of 5° min^{-1}.

Thermal gravimetric analysis (TGA): TGA (Q500, TA) was used to assess the thermal stabilities of the films under a nitrogen atmosphere. The temperature range was 50-600 °C.

Differential scanning calorimetry (DSC) analysis: DSC was performed on a METTLER TOLEDO from 25 to 100 °C, with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. To erase previous thermal history left from film preparation, The sample was scanned for three times and the third scan data was used.

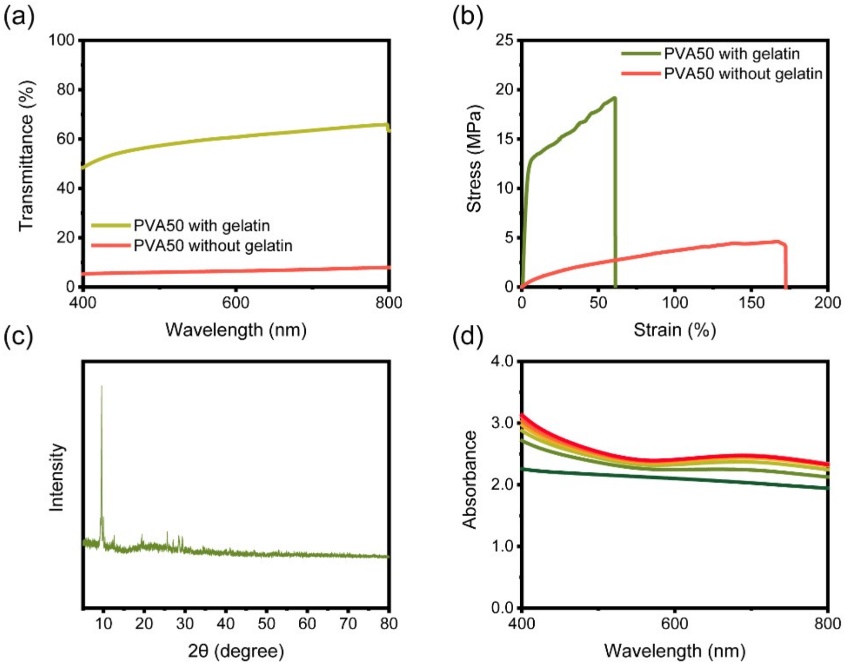


Figure S1. (a) Transmittance curves, (b) stress-strain tests curves of PVA50 films with and without gelatin, respectively. (c) XRD pattern of PVA50 film without gelatin and (d) UV-vis spectra of the film after different UV irradiation times (0-30s, interval was 5s).

The results showed that the transparency of PVA50 film without gelatin dropped significantly to less than 10%. At the same time, the mechanical properties changed significantly, the fracture stress decreased and the elongation at break increased. XRD pattern showed a series of sharp peaks, indicating that Mo7 precipitated as crystals in the PVA50 film without gelatin, which was the main cause of the decrease in transparency. Gelatin could form electrostatic interactions with Mo7, which allowed Mo7 to be uniformly dispersed in the film without precipitation. In addition, the rigid molecular chain of gelatin was also the key to achieve high mechanical properties of the film. Due to the optical opacity of PVA50 film without gelatin, only the surface Mo7 was involved in the photochromic process, which made the absorption spectra of PVA50 film without gelatin no longer changed significantly after 15 s of UV light irradiation and led to the decline of photochromic properties.

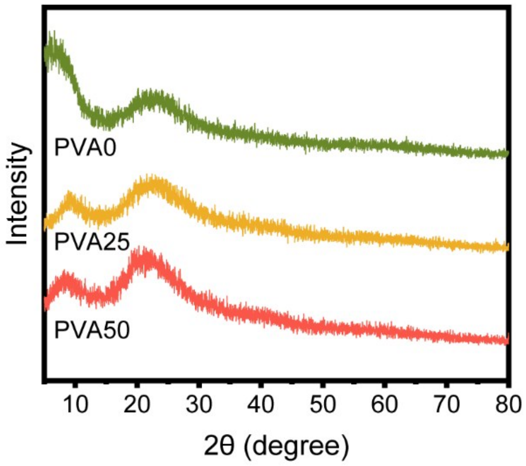


Figure S2. XRD pattern of all films

PVA tends to form crystalline regions, and the crystalline regions can cause the transparency decrease of materials. Thus, the transparency of PVA25 had declined and PVA50 was further reduced.

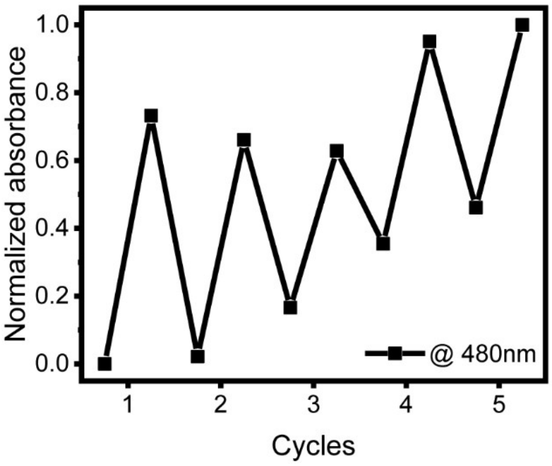


Figure S3. Normalized absorbance of PVA50 film with color-fading cycles.

The results showed that the film demonstrated good stability in the first two cycles, and the absorbance of the film gradually increased thereafter. It could be suspected that the decrease in cycle stability may be due to structural defects in the film after bleaching. Despite this, the photochromic properties of the film did not fail and still exhibit significant cycling capacity after five cycles.

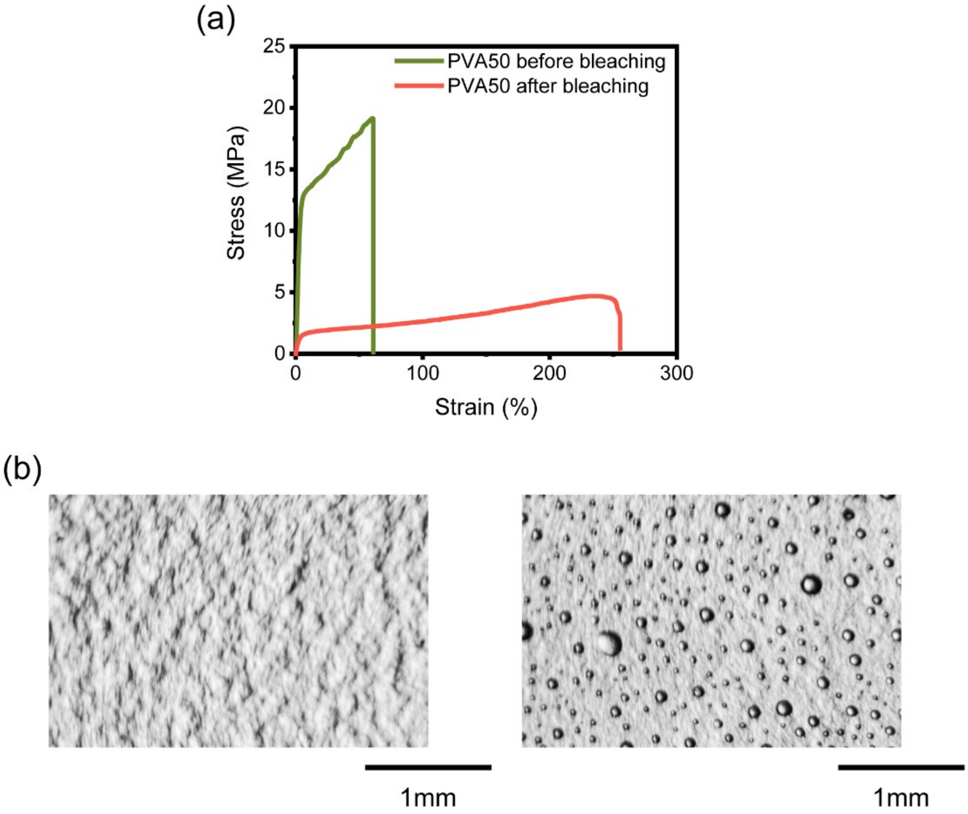


Figure S4. (a) Stress-strain tests curves of PVA50 films before and after bleaching at 90% at 70°C and (b) corresponding optical microscope images.

The mechanical properties of PVA50 film showed significant changes after bleaching: the fracture stress decreased significantly and the elongation at break increased significantly. In order to investigate the cause of this phenomenon, the optical microstructure of the film before and after bleaching was observed. The results showed that a large number of micron-sized bubbles were formed in the film after bleaching, leading to the decrease of the mechanical properties.

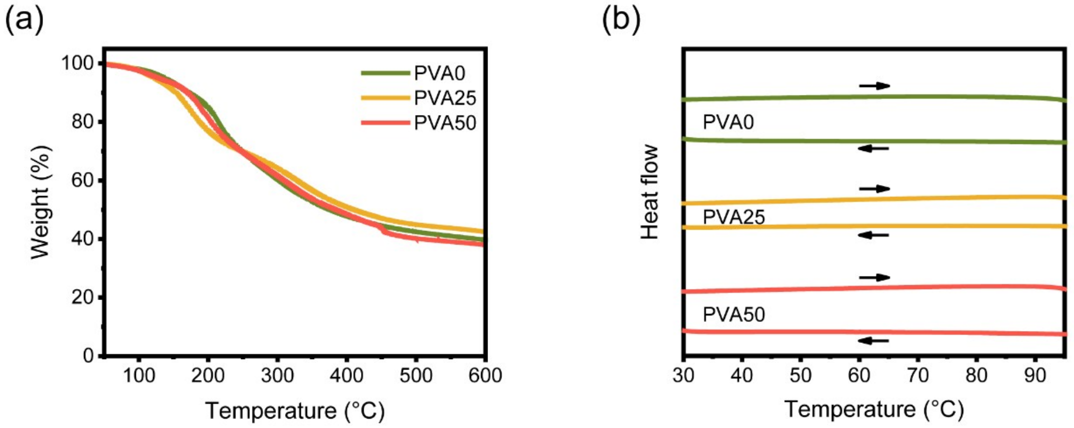


Figure S5. (a) TG and (b) DSC curves of the films.

These films showed multiple peaks in the TG curves. The most significant difference was the decomposition of PVA at 450°C. The intensity of this peak increased as the PVA content increased in the sample. The peak at around 120°C was derived from the release of water vapor. The temperature was slightly higher than the boiling point of water was due to hydrogen bonding between water and polymer chains in the films. The peaks at about 200°C corresponded to the decomposition of Mo7, and the peaks at about 325°C corresponded to the release of TEG. Despite this, it was clear that these films were stable over their operating temperature range (from 20°C to 70°C). DSC testing showed no significant endothermic/exothermic peaks of these films, indicating that the molecular structure within the film did not change significantly over the operating temperature range.