

Electronic Supplementary Information

Enabling sunlight driven response of thermally induced shape memory polymers by rewritable $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite coating

Yang Yang,^[a] Fusheng Ma,^[b] Zhen Li,^[a] Juan Qiao^{*[b]}, Yen Wei^{*[a, b]} and Yan Ji^{*[a]}

1. Sample preparation

Materials

Triazobicyclodecene (TCI, 98%), adipic acid (TCI, > 99.0%) and diglycidyl ether of bisphenol A (Sigma-aldrich, D.E.R. 332) were used directly without further purification. Multiwalled carbon nanotubes (MWCNTs) were obtained from *Chengdu Organic Chemicals Co. Ltd.*, Chinese Academy of Sciences (CVD, purity 95+%, diameter < 8 nm, as-produced length 10-30 μm) with no functionalization. Aqueous solution of hydroiodic acid (57 wt.% in H_2O , Sigma-Aldrich), methylamine (in methanol, Sigma-Aldrich) and PbI_2 (99%, Sigma-Aldrich) were used directly without further purification. Carbon black was obtained from *Energy-Chemical Co. Ltd.* and used directly without further purification.

Synthesis of epoxy

The epoxy was prepared according to our previous work.¹ As shown in Fig. S1, stoichiometric amount of diglycidyl ether of bisphenol A (0.340 g, 1 mmol) and adipic acid (0.146 g, 1 mmol) were mixed and heated to 180°C. After the mixture was melted, triazobicyclodecene (10 mol% to the COOH) groups was introduced and stirred manually till homogeneous. As the mixture became very viscous, it was cooled to room temperature to obtain a solid product which was not completely crosslinked. Then the solid was sandwiched between two plates to be cured by a hot press for 4 h at 180°C. A spacer was placed between two plates to control the thickness of film. The applied pressure was 3 MPa. Fourier transform infrared spectroscopy (FTIR, *Perkin Elmer spectrum 100*) was used to monitor the reaction

progress. The epoxy peak at 912 cm^{-1} totally disappeared after curing for 4 h, indicating the complete reaction.

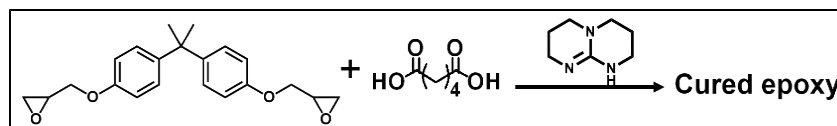


Fig. S1. Synthesis of epoxy.

Preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated epoxy

$\text{CH}_3\text{NH}_3\text{PbI}_3$ was prepared following the procedure described by Im *et. al.*² It was synthesized from $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 . Equimolar pre-synthesized $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in gamma-butyrolactone were stirred overnight at 60°C . After drop-casting the above solution onto glass substrates, heating to 100°C and annealing for 30 min, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ product was obtained. A $\text{CH}_3\text{NH}_3\text{PbI}_3$ DMF solution (0.02 g $\text{CH}_3\text{NH}_3\text{PbI}_3$ dissolved in 0.2 mL DMF) was used to prepare $\text{CH}_3\text{NH}_3\text{PbI}_3$ coating.

The coating process involves two stages. Firstly, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ DMF solution is coated onto the epoxy by spin-coating at a spin speed 3000 rpm for 20 s or drop-coating by a pipette. Secondly, the composite is annealed at 110°C to obtain a thin layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite (Fig. S2, sp1).

Preparation of carbon nanotube coated epoxy and gold nanoparticle coated epoxy

Carbon nanotubes (CNTs) coated epoxy is prepared by the same method which is used to prepare the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer. Firstly, 0.02 g CNT is suspended in 0.2 mL DMF and sonicated for 30 min. Secondly, the CNT-DMF solution is dropped on the surface of the epoxy and annealed at 110°C . The obtained carbon nanotube layer is inhomogeneous and aggregates can be easily observed by naked eyes (Fig. S2a, sp2).

Gold nanoparticle coated epoxy was prepared by spraying gold using the *ETD-2000* auto sputter coater (*Elaborate Technology Development Co. Ltd.*, China) with a current of 10 mA for 60 s (Fig. S2a, sp3).

Carbon black coated epoxy is prepared by the same method which is used to prepare the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer. Firstly, 0.02 g carbon black is suspended in 1 mL DMF and sonicated for 30 min. Secondly, the carbon black-DMF solution is dropped on the surface of the epoxy and

annealed at 110°C. The obtained carbon black layer is inhomogeneous and aggregates can be easily observed by naked eyes (Fig. S2b).

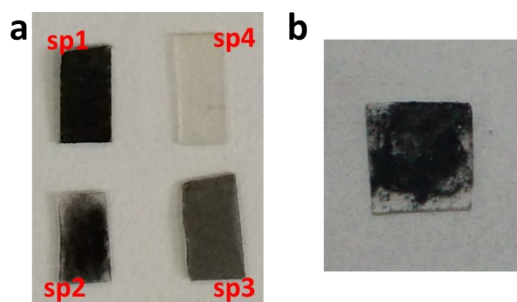


Fig. S2. (a) Photo of the four samples: $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated-epoxy (sp1), carbon nanotube coated epoxy (sp2), gold nanoparticle coated epoxy (sp3) and pure epoxy (sp4). (b) Photo of carbon black coated epoxy.

2. Characterizations of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer on epoxy

The microstructure of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was observed using scanning electron microscope (SEM) (*Hitachi SU8020*).

X-ray Diffraction (XRD) was performed on a *Bruker D8 ADVANCE* instrument. The result of $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated epoxy and pure epoxy are shown in Fig. S3b, which proves that a $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer exists on the surface of epoxy.

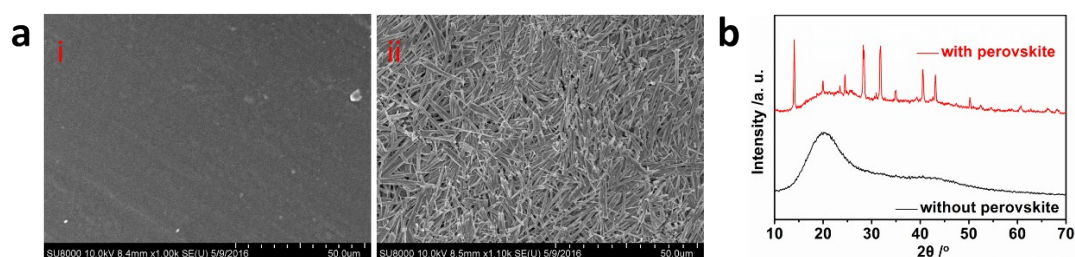


Fig. S3. (a) SEM graphs of surface topography of pure epoxy (i) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated epoxy (ii). (b) XRD graph of pure epoxy and $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated epoxy.

3. Thermal and mechanical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated epoxy

Differential scanning calorimetry (DSC) was performed using *TA instruments Q2000* operated at a scanning rate of 10 °C/min (Fig. S4a).

Stress-strain test was performed on a *TA instruments Q800* dynamic mechanical analyzer (DMA) apparatus in the tension film geometry under the controlled force mode, with a rectangular tension film dimension of 10.0 mm × 2.5 mm × 0.15 mm (Fig. S4b). The strain was measured while the sample was stretched at a ramp force of 0.5 N/min to 18.0 N.

The thermal stability was measured with a *TA instruments Q50* thermal gravity analysis (TGA) under air atmosphere at a ramp rate of 20 °C/min to 900°C. The decomposition temperatures of both CH₃NH₃PbI₃ coated epoxy and pure epoxy are about ~ 275°C (Fig. S4c).

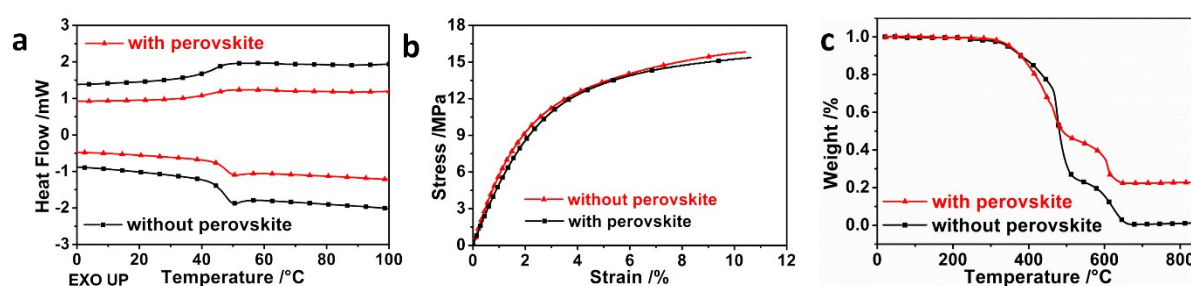


Fig. S4. (a) DSC traces of CH₃NH₃PbI₃ coated epoxy and pure epoxy (10 °C/min for both heating and cooling). The glass temperatures (T_g) are both about 45°C. (b) Stress-strain curves of CH₃NH₃PbI₃ coated epoxy and pure epoxy measured at 25°C. (c) TGA curves of CH₃NH₃PbI₃ coated epoxy and pure epoxy under air atmosphere (Heating rate: 20 °C/min).

4. Light responsive properties of CH₃NH₃PbI₃ coated epoxy

UV-vis absorption spectrum of the CH₃NH₃PbI₃ coated epoxy was performed by *Perkin Elmer Lambda 750* integrating sphere.

Two solar simulators were used in this paper. One was a solar simulator (CEL-S500/300, Aulight, Beijing, China) without filtering any specific wavelength. Unless special noted, we used this solar simulator for all the experiments. Another was a solar simulator (ABET Technologies, Sun 2000).

The original CH₃NH₃PbI₃ coated epoxy film and pure epoxy film used to lift heavy objects are shown in Fig. S5. Both samples were stretched by about 40% at 80°C before being irradiated.

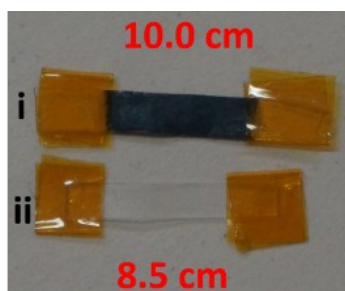


Fig. S5. Photograph of the original $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated epoxy film and pure epoxy film.

We investigated the correlation between the photo-thermal effect and thickness of the epoxy film, as well as the correlation between the photo-thermal effect and the thickness of the perovskite layer. As shown in Table S1a, when the thickness of the epoxy film increases, the responsive time for shape recovery increases. This is because the thermal conductivity of thick epoxy film is low, it needs more time to recover to its original shape. Here we used the solar simulator (ABET Technologies, Sun 2000) with a light intensity of 120 mW/cm^2 .

When the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer is very thin ($3 \mu\text{m}$), the responsive time is long. And when the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer is thicker ($9 \mu\text{m}$), it seems that the responsive time increases slightly. This might be because there is too much perovskite, which hinders the thermal transfer to epoxy. Here we used the solar simulator (ABET Technologies, Sun 2000) with a light intensity of 120 mW/cm^2 .

Without special specification, we used the epoxy thickness of 0.15 mm and $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer thickness of $6 \mu\text{m}$ in all the other experiments.

| (a) | Thickness of epoxy (mm) | Responsive time (s) | (b) | Thickness of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer | Responsive time (s) |
|-----|-------------------------|---------------------|-----|---|---------------------|
| | 0.05 | 8 | | 3 | 54 |
| | 0.10 | 17 | | 6 | 30 |
| | 0.15 | 30 | | 9 | 35 |
| | 0.20 | 39 | | | |
| | 0.25 | 50 | | | |
| | 0.30 | 64 | | | |

Table S1. (a) The correlation between the responsive time and the epoxy's thickness. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer's thicknesses of all these samples were $6 \mu\text{m}$. (b) The correlation between the responsive time and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thickness. The epoxy's thicknesses of all these samples were 0.15 mm .

We measured the temperatures at different simulated sunlight intensities. It can be seen from Fig. S6a, the temperature increases along with the sunlight intensities. And in the natural sunlight (intensity of 35.8 mW/cm²), the temperature induced by photo-thermal effect is almost stable at ~37°C (Fig. S6b), which is within the range of T_g .

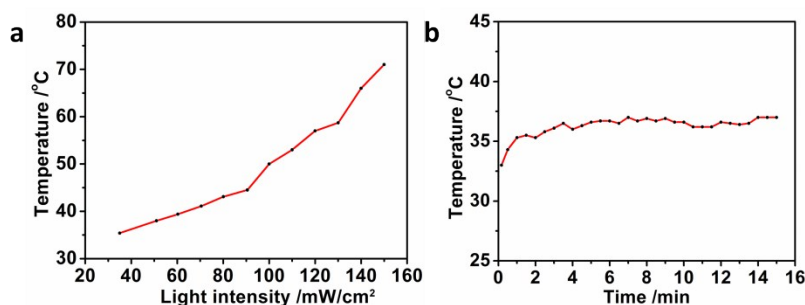


Fig. S6. (a) Temperature change with simulated sunlight intensity. (b) Temperature change with time at an intensity of 35.8 mW/cm².

5. Light responsive properties of another CH₃NH₃PbI₃ coated SMP

To show that this method can be generalized to other kind of SMPs, besides normal epoxy, here we also used a liquid crystalline SMP as a substrate, which was prepared as the reference 3. The glass transition temperature is about 50°C. After drop-coating a CH₃NH₃PbI₃ layer on the surface of liquid crystalline SMP and shaping it into a temporary shape, the temporary shape recovered to flat after being irradiated for 50 s under simulated sunlight (light intensity: 120 mW/cm²). Here we used the solar simulator (ABET Technologies, Sun 2000) with a light intensity of 120 mW/cm².



Fig. S7. Shape recovery of CH₃NH₃PbI₃ coated liquid crystalline SMP.

References

- 1 Y. Yang, Z. Pei, X. Zhang, L. Tao, Y. Wei, Y. Ji, *Chem. Sci.* **2014**, *5*, 3486.
- 2 J.H. Im, C.R. Lee, J.W. Lee, S.W. Park, N.G. Park, *Nanoscale* **2011**, *3*, 4088.
- 3 Z. Pei, Y. Yang, Q. Chen, E. M. Terentjev, Y. Wei, Y. Ji, *Nat. Mater.* **2014**, *13*, 36.