Long-term stability in γ -CsPbI₃ perovskite via an ultraviolet-curable polymer network

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Black-colored (α , γ -phase) CsPbI₃ perovskites have a small bandgap and excellent absorption properties in the visible light regime, making them attractive for solar cells. However, their long-term stability in ambient conditions is limited. Here, we demonstrate a strategy to improve structural and electrical long-term stability in γ -CsPbI₃ by the use of an ultraviolet-curable polyethylene glycol dimethacrylate (PEGDMA) polymer network. Oxygen lone pair electrons from the PEGDMA are found to capture Cs⁺ and Pb²⁺ cations, improving crystal growth of γ -CsPbI₃ around PEGDMA. In addition, the PEGDMA polymer network strongly contributes to maintaining the black phase of γ -CsPbI₃ for more than 35 days in air, and an optimized perovskite film retained ~90% of its initial electrical properties under red, green, and blue light irradiation.

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Halide perovskites are considered as the next-generation optoelectronic materials because of their excellent optoelectronic properties owing to inherent direct band gaps, high absorption coefficients, long exciton diffusion lengths, and low-cost solution process availabilities^{1–3}. Among them, organic–inorganic hybrid perovskites in which organic cations such as methylammonium^{4,5} or formamidinium^{6,7} are applied to the position A of ABX₃ structure have been preferentially studied for realizing a cubic structure by satisfying the Goldschmidt tolerance factor ($0.81 < t < 1.1$, $t = (r_A + r_X)/\sqrt{2}(r_B + r_X)$, where r_A , r_B , and r_X are the ionic sizes of A, B, and X, respectively)^{8,9}. However, due to the inherent volatility problems of the organic cations^{10,11}, all-inorganic perovskite (CsPbX₃, X = I, Br, Cl) which replaced the organic cation with cesium is drawing attention recently^{12–17}. Particularly, in the case of CsPbI₃ in which the iodine is in the X position, it is intensively studied as a visible light detection material because it can effectively absorb the entire visible light^{18–20}.

In general, cubic α -CsPbI₃ (black phase) has a suitable low bandgap (~ 1.70 eV) that can effectively absorb the visible region. Unfortunately, α -CsPbI₃ is unstable below 330 °C and undergoes rapid phase transition to undesirable large bandgap (~ 2.80 eV) orthorhombic δ -CsPbI₃ (yellow phase) at the room temperature²¹. Recently, adding hydroiodic acid (HI) enables lower formation energy of perovskite that is to realize relatively stable orthorhombic γ -CsPbI₃ (~ 1.69 eV, black phase) in a low-temperature process at about 100 °C^{22–24}. However, there is still a challenge of phase transition occurrence to δ -CsPbI₃ upon prolonged exposure of γ -CsPbI₃ to ambient conditions.

To secure the long-term stability of the black phase CsPbI₃ under ambient conditions, two approaches have been developed: partial substitution of anion or cation^{25–28}, and surface passivation using organic additives^{29–32}. One of the partial substitution methods, CsPbI_{*n*}Br_{3–*n*} implemented by partially replacing bromide at the iodide position possesses a wider bandgap than α and γ -CsPbI₃, thereby it is a compromise way which is difficult to effectively absorb visible light²⁵. The surface passivation method using organic additives, another approach to achieving improved stability, deteriorates the electrical properties of perovskite due to excess additives (10–70 wt%)²⁹ for realizing long-term stable black phase CsPbI₃. The above methods obviously provide a roadmap for CsPbI₃ to stabilize the black phase in the long-term, but still contain the issues of bandgap widening and electrical properties deterioration.

Herein, we propose a robust strategy by employing infinitesimal (≤ 3 wt%) ultraviolet (UV)-curable polyethylene glycol dimethacrylate (PEGDMA) to ensure the structural and electrical long-term stability of the γ -CsPbI₃ under ambient conditions. Oxygen lone-pair electrons of the PEGDMA capture Cs⁺ and Pb²⁺ cations and considerably improve the crystal growth of γ -CsPbI₃ around PEGDMA. In addition, polymer network of PEGDMA processed by UV exposure strongly contributes to maintaining the γ -CsPbI₃ structure tight for more than 35 days in ambient conditions. To evaluate the photo-electronic properties, two-terminal photoresistors were fabricated and evaluated, the optimized UV-cured γ -CsPbI₃ (3 wt% PEGDMA) film showed that $\sim 90\%$ of the initial electrical values responding to red, green, and blue lights, were stably maintained even after 35 days in the ambient conditions.

Results and discussion

Feasibility of long-term stable perovskite CsPbI₃ by UV-curable polymer network. Figure 1 shows the feasibility of long-term stabilized black phase CsPbI₃ under ambient conditions when UV is irradiated to thin film prepared by the spin coating method with CsPbI₃ precursor solution containing a small amount of PEGDMA with photo-initiator (2-hydroxy-2-

methylpropiophenone; HMPP). The reference CsPbI₃, and the CsPbI₃ with or without UV-curing after the addition of PEGDMA showed absorbance peaks from ~ 730 nm in the fresh state (Fig. 1a). As a result of recalculating the UV-vis spectroscopy analysis data and deriving the Tauc's plot, the optical bandgap of reference CsPbI₃ is 1.72 eV, and the CsPbI₃ with or without UV-curing after the addition of PEGDMA are 1.69 eV, all samples exhibit black color to the naked eye (Fig. 1c). After the above three CsPbI₃ samples were left in the air for 5 days, CsPbI₃ with or without UV-curing after adding PEGDMA maintained an optical bandgap of 1.69 eV. However, in the case of the reference CsPbI₃ without PEGDMA, an undesirable phase transition (yellow colored) occurred, which means that the optical bandgap derived to 2.82 eV. Even adding PEGDMA, the CsPbI₃ that did not undergo UV irradiation maintained a bandgap of 1.69 eV, but the phase transition is progressing slowly, and it shows slightly brown to the naked eye after 5 days (Fig. 1b, d). However, the CsPbI₃ with UV-curing after the addition of PEGDMA stably maintained a bandgap of 1.69 eV and the color of black even after 5 days. These results indicate that the UV-cured PEGDMA network is a direct clue to keeping the perovskite's lattice structure firmly under atmospheric conditions. Using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, we measured the IR absorbance of PEGDMA containing photo-initiator before and after UV irradiation to perform a qualitative investigation for the conversion of C=C double bonds in the methacrylate group of PEGDMA (Fig. 1e). Each PEGDMA has two methacrylate end groups, which, when exposed with UV, react with four other methacrylate groups through radical polymerization by HMPP to make a covalent bond, and the PEGDMA forms a cross-linked network (Supplementary Fig. 1)³³. When no UV irradiation was applied after HMPP was added to PEGDMA, the inherent C=C double bond peak of PEGDMA was clearly maintained and even matched exactly with all the intrinsic peaks of PEGDMA. This means that HMPP does not have any influence on the PEGDMA molecular structure when UV is not irradiated. However, when UV lights were irradiated after HMPP was added to PEGDMA, the C=C peak of the methacrylate group of PEGDMA disappeared. In addition, as the C=C peak at 1637 cm^{−1} disappeared, the C=O peak was blue-shifted from 1716 to 1722 cm^{−1} due to the C=C double bond being converted to a C–C single bond, so that is clear evidence the PEGDMA with HMPP was fully UV-cured³⁴. Through the XRD analysis, with the fresh state, the reference CsPbI₃, the CsPbI₃ with or without UV-curing after the addition of PEGDMA showed Bragg peaks at 14.16°, 14.33°, 28.54°, and 28.89°, which corresponded to the (200), (100), (400), and (220) planes of the orthorhombic γ -CsPbI₃ (*Pbnm* space group) crystallites, respectively^{20,23}. However, after exposure to ambient conditions for 7 days, the only CsPbI₃ with UV-cured PEGDMA network maintained stably the black γ -CsPbI₃ phase (Fig. 1g).

A conceivable mechanism for the introduction of the PEGDMA UV-curing strategy to improve the long-term stability of CsPbI₃ is proposed in Fig. 2. In a previous study, Li et al.³⁰ reported that the electronegative acylamino group of the poly-vinylpyrrolidone (PVP) molecule attracts the cation of the CsPbI₃ precursor to help the CsPbI₃ nucleus formation and growth from the vicinity of the PVP molecule. Similarly, the acrylate group of PEGDMA also exhibits electronegative properties. The rich oxygen lone pair electrons of the acrylate group effectively attract Cs⁺ and Pb²⁺ cations in the precursor solution to induce CsPbI₃ nuclei formation and crystal growth from the PEGDMA molecular backbone chain. The PEGDMA molecules prevent the aggregation of perovskite crystals grown in the precursor solution due to the intermolecular rejection effect^{30,32} of each other and help to form a stable colloid (Fig. 2a). After the spin-coating process, the CsPbI₃

Fig. 1 Feasibility of long-term stable perovskite by UV-curable polymer network. **a, b** The UV-vis spectrum of the reference CsPbI₃, and CsPbI₃ with or without UV-curing after the addition of PEGDMA, at the fresh state (**a**), and after 5 days left in the ambient conditions (**b**). **c, d** Tauc's plot derived from the UV-vis spectroscopy analysis data of the fresh state (**c**), and after 5 days left in the ambient conditions (**d**). Inset: photographic images of the reference CsPbI₃, and CsPbI₃ with or without UV-curing after the addition of PEGDMA. **e** ATR-FTIR spectroscopy analysis to investigate qualitatively for the conversion of C=C double bonds in the methacrylate group of PEGDMA whether UV irradiation. **f, g** XRD patterns of the reference CsPbI₃, and CsPbI₃ with or without UV-curing after the addition of PEGDMA, at the fresh state (**f**), and after 7 days left in the ambient conditions (**g**). Asterisk (*): HPB_{13+x}²⁰.

Fig. 2 A conceivable mechanism for the introduction of the PEGDMA UV-curing strategy to improve the long-term stability of CsPbI₃. **a** Step 1: Induced CsPbI₃ nuclei formation and crystal growth from the PEGDMA molecular backbone chain by the PEGDMA's oxygen lone pair electrons in the precursor solution. **b** Step 2: UV-curing process immediately before cooling, on the spin-coated and annealed CsPbI₃ after the addition of PEGDMA. UV irradiation: 365 nm, 400 mW cm⁻² for 5 s. **c** Step 3: Establishment of the robust γ -CsPbI₃ with the UV-cured PEGDMA polymer network.

with PEGDMA annealed at 90 °C for 5 min and exposed UV for 5 s immediately before cooling, which induces to photopolymerization between PEGDMAs, thus CsPbI₃ crystals in the thin film were fixed more compactly without any extra byproducts (Fig. 2b). Therefore, the PEGDMA induces CsPbI₃ nuclei formation and crystal growth from the PEGDMA molecular backbone chain, the γ -CsPbI₃ structure, which is tightly fixed by the UV-cured PEGDMA polymer network, can maintain the robust γ -phase under ambient conditions (Fig. 2c).

The correlation between PEGDMA content and black γ -CsPbI₃ optical long-term stability. We investigated in-depth the effect of the content of UV-cured PEGDMA polymer network inside CsPbI₃

thin film on the atmospheric stability of γ -CsPbI₃. Figure 3 shows the effect on the optical long-term stability of γ -CsPbI₃ by splitting the PEGDMA content added to the CsPbI₃ precursor solution into 0, 0.5, 1, 3, and 5 wt%, respectively. For convenience, the group of γ -CsPbI₃ thin-film samples with adding different wt% of PEGDMA cured by UV after spin coating are briefly referred to as γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA), respectively. Figure 3a–e is the result of accumulating UV-vis absorbance spectra while exposing γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) to the ambient conditions for 35 days. The variation of an optical property of γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) for 35 days were measured at ambient conditions with 20.50 ± 1.10 °C for temperature and $26.81 \pm 2.56\%$ for relative humidity, respectively (Supplementary

Fig. 3 The effect on the optical long-term stability of γ -CsPbI₃ by splitting the PEGDMA content added to the CsPbI₃ precursor solution. **a–e** Accumulated UV–vis absorbance spectra while exposing γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) to the ambient conditions for 35 days. **f** FE-SEM top view images of γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA). Scale bar: 2 μ m. **g** Time-dependent photographic results obtained by observing the optical color change of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) thin films during 35 days in ambient conditions. The red square box represents the limitation of γ -phase stability that begins to transition from the γ -phase to the δ -phase. **h–k** XPS analysis on the fresh γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) at full range (**h**), Pb 4f (**i**), I 3d (**j**), and Cs 3d (**k**).

Fig. 2 and Supplementary Tables 1 and 2). The achromatic lines (black and gray) indicate the date of which the perovskite represents a stable black phase, and the chromatic lines (from red to yellow) indicate the date at which the perovskite can no longer maintain the black phase. The γ -CsPbI₃ (0 wt% PEGDMA) was rapidly changed to δ -CsPbI₃ as the phase transition began 3 days after exposure to the ambient conditions, but γ -CsPbI₃ (0.5, 1, 3, and 5 wt% PEGDMA) were kept stable black phase in the long term as the PEGDMA content increased. Especially, both γ -CsPbI₃ (3 wt% PEGDMA) and γ -CsPbI₃ (5 wt% PEGDMA), even after 35 days after exposure to the ambient conditions, the absorbance peak was stably observed at $\sim$ 730 nm, and the spectrum change was almost negligible. Interestingly, as the PEGDMA content increased, the absorbance peak intensity at the 720 nm position of all fresh γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) follows a linear relationship with the PEGDMA content (Supplementary Fig. 3). This means that PEGDMA directly affects the growth of perovskite grain, and this tendency is clearly confirmed through the field emission scanning electron microscopy (FE-SEM) images in Fig. 3f.

Figure 3g shows the time-dependent photographic results obtained by observing the optical color change of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) thin films, which were continuously exposed to the ambient conditions. The red square box represents the limitation of γ -phase stability that begins to transition from the γ -phase to the δ -phase, which perfectly matches the UV–vis spectral trend of Fig. 3a–e. The XPS analysis was performed on the fresh γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) to confirm the CsPbI₃ lattice binding energy varying

with PEGDMA content (Fig. 3h–k). In the case of pure γ -CsPbI₃ (0 wt% PEGDMA), the Cs 3d spectra show two peaks at 723.5 and 737.2 eV corresponding to the binding energies of Cs 3d_{5/2} and Cs 3d_{3/2}, respectively. The Pb 4f spectra show two peaks at 137.6 and 142.5 eV corresponding to the binding energies of Pb 4f_{7/2} and Pb 4f_{5/2}, and the spectra of I 3d also exhibit two peaks at 618 and 629.3 eV corresponding to I 3d_{5/2} and I 3d_{3/2}, respectively. However, in cases of γ -CsPbI₃ (0.5, 1, 3, and 5 wt% PEGDMA), as the PEGDMA content increases, Cs 3d and Pb 4f binding energy were significantly lowered by 0.7 eV, and I 3d was also slightly shifted to the low binding energy. This tendency indicates that the PEGDMA content increases, the oxygen lone pair sites also increase linearly, so the binding energy of Cs 3d and Pb 4f peaks are lowered by causing a stronger interaction between the cations of the γ -CsPbI₃ and oxygen lone pairs of PEGDMA. Since the binding energy of Cs⁺ and Pb²⁺ ions forming the γ -CsPbI₃ lattice was lowered, the anion I 3d peaks was also shifted slightly to the lower binding energy as a side effect. As a result of XPS analysis, it was confirmed that effective Coulombic interactions exist between the oxygen lone pairs and the Cs⁺, Pb²⁺ cations inside the CsPbI₃ thin film. We performed dynamic light scattering (DLS) analysis to determine whether these Coulombic interactions originated from the PEGDMA added CsPbI₃ precursor solution (Supplementary Fig. 4).

Through the DLS analysis, the colloid size of the CsPbI₃ (0 wt% PEGDMA) precursor solution was confirmed that the solution contained the monodispersed CsPbI₃ colloids which have a diameter of 1.32 nm. However, as the content of PEGDMA

Fig. 4 The electrical properties of Au/ γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA)/Au photoresistors under irradiation of various LED light sources. **a–e** Photoresponse I - V characteristics of photoresistors including fresh γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA), under irradiation of 0.4 mW cm⁻² of red (635 nm), green (532 nm), and blue (450 nm) LED light sources. **f, g** The comparison of additional optical response parameters between as-prepared and after 35 days of Au/ γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA)/Au photoresistors. Unit of the parameters: EQE(%), $J_{\text{photo}}/J_{\text{dark}}$, R (A W⁻¹), D^* (Jones).

increases from 0.5 to 5 wt%, an additional satellite peak was observed, unlike the CsPbI₃ (0 wt% PEGDMA) solution. As the content of PEGDMA increases, the intensity of the reference CsPbI₃ colloid peak gradually decreased; on the contrary, the intensity of the satellite peak increased with the corresponding colloid size also increased to 173.09, 428.47, 614.62, and 1319.97 nm, respectively. The fact that the observed colloid size is clearly distinguished as the amount of added PEGDMA increases does mean that PEGDMA induces CsPbI₃ nucleation and directly affects crystal growth. Obviously, DLS analysis only provided information on the colloid size distribution trend in the liquid phase, therefore, another method for analyzing the grain size of perovskite thin film (solid phase) has been considered. We counted the perovskite grain size distribution in the solid phase using the Image J program based on the FE-SEM image (Supplementary Fig. 5 and Supplementary Table 3). Each γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) FE-SEM image was used to measure the areas of grains within the same area (610,000 nm²) and counted by 800 nm² size section. The average grain size of γ -CsPbI₃ (0 wt% PEGDMA) was 2131.95 $\pm$ 989.17 nm², and as the PEGDMA content increased, the γ -CsPbI₃ grain size tended to increase. This trend was effective until γ -CsPbI₃ (5 wt% PEGDMA), which grain size measured 7824.19 $\pm$ 4255.89 nm². This result indicates that the colloid size distribution result through DLS analysis of perovskite precursor solution (liquid phase) is directly related to the grain size inside the fabricated thin film (solid phase). Therefore, XPS, DLS, and Image J analysis results provide strong evidence supporting the mechanism of Fig. 2, as it can be seen that oxygen lone pairs of PEGDMA induce CsPbI₃ nucleation and crystal growth in the PEGDMA molecular backbone chain from the precursor solution state.

Photo-electrical properties and phase stabilities according to variation of the PEGDMA polymer network content in γ -CsPbI₃. To confirm the applicability of γ -CsPbI₃ with PEGDMA polymer network as a light detecting material, 2-terminal lateral photoresistors with channel length and width of 120, 1000 μ m,

respectively, were fabricated in Au/ γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA)/Au structure. Figure 4 shows the electrical properties of photoresistors under irradiation of 0.4 mW cm⁻² of red (635 nm), green (532 nm), and blue (450 nm) LED light sources. Figure 4a–e represents the photoresponse I - V characteristics of photoresistors including γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA). As the PEGDMA content increased, the dark current of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) device decreased. The dark current of the γ -CsPbI₃ (0 wt% PEGDMA) device showed a relatively large value of 8.0×10^{-10} A, while the γ -CsPbI₃ (5 wt% PEGDMA) device slightly decreased by 6.47×10^{-11} A. Since PEGDMA exhibits electrical insulating properties, the dark current tends to decrease as the amount of added PEGDMA increases. On the other hand, when red, green, and blue light was irradiated, the photocurrent of photoresistors including the γ -CsPbI₃ (0, 0.5, 1, and 3 wt% PEGDMA) tended to increase as the increment of PEGDMA content from 0 to 3 wt%. As mentioned in Fig. 3f and Supplementary Fig. 4, the increment of PEGDMA content attributes to the large growth of perovskite grains and within such large grains, photo-generated charge carriers generally exhibit a longer mean free-path which would yield a higher photocurrent. However, the photocurrent of γ -CsPbI₃ (5 wt% PEGDMA) did not follow the above trend. Since the γ -CsPbI₃ grains, irregularly overgrown when 5 wt% PEGDMA was added, the film shows poor roughness which hinders the charge carrier transport from the CsPbI₃ to the electrodes. In addition, the 5 wt% PEGDMA-added film suppresses the generation of effective photocurrent because it contains a large number of pin-holes that cause scattering of photogenerated charge carriers (Fig. 3f). As a result of measuring the I - V curve after continuously exposing these devices to the ambient conditions for 35 days, γ -CsPbI₃ (3 wt% PEGDMA) device showed ~90% of the photo-electrical performance compared to the initial state (Supplementary Fig. 6 and Supplementary Table 4). Figure 4f, g shows the comparison of additional optical response parameters between as-prepared and after 35 days of Au/ γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA)/Au photoresistors. To determine whether CsPbI₃ with

Table 1 Comparison of additional optical response parameters between fresh and after 35 days of Au/ γ -CsPbI₃ (0, and 3 wt% PEGDMA)/Au photoresistors at 40 V.

(At 635 nm)	Fresh				After 35 days			
PEGDMA contents (wt%)	$J_{\text{photo}}/J_{\text{dark}}$	R (A W ⁻¹)	EQE (%)	D^* (Jones)	$J_{\text{photo}}/J_{\text{dark}}$	R (A W ⁻¹)	EQE (%)	D^* (Jones)
0%	9.05×10^0	1.50×10^{-2}	2.61×10^0	3.26×10^{10}	1.92×10^0	2.83×10^{-4}	2.64×10^{-2}	2.06×10^9
	$\pm 1.63 \times 10^0$	$\pm 2.55 \times 10^{-3}$	$\pm 4.67 \times 10^{-1}$	$\pm 5.59 \times 10^9$	$\pm 9.78 \times 10^{-2}$	$\pm 2.65 \times 10^{-5}$	$\pm 3.33 \times 10^{-3}$	$\pm 1.28 \times 10^8$
3%	9.07×10^2	1.22×10^{-1}	2.38×10^1	9.30×10^{11}	7.55×10^2	9.74×10^{-2}	1.90×10^1	7.56×10^{11}
	$\pm 3.92 \times 10^1$	$\pm 4.05 \times 10^{-3}$	$\pm 7.88 \times 10^{-1}$	$\pm 1.21 \times 10^{10}$	$\pm 1.14 \times 10^2$	$\pm 2.09 \times 10^{-3}$	$\pm 4.10 \times 10^{-1}$	$\pm 5.94 \times 10^{10}$

Fig. 5 Time-resolved photoresponse and transient response time of the optimized γ -CsPbI₃ (3 wt% PEGDMA) photoresistor. a, b Photocurrent-time responses of the reference γ -CsPbI₃ photoresistor at fresh state (a) and after 35 days (b) at 40 V applied bias. **c, f** The transient response time of the γ -CsPbI₃ (3 wt% PEGDMA) photoresistor at fresh state (c) and after 35 days (f). **d, e** Photocurrent-time responses of the γ -CsPbI₃ (3 wt% PEGDMA) photoresistor at fresh state (d) and after 35 days (e). Photocurrent-time response was measured at 40 V applied bias in the dark and under illumination using the LEDs at 635, 532, 450 nm with fixed light intensity ($P_{\text{in}} = 0.4 \text{ mW cm}^{-2}$) and frequency (1 Hz). The transient response time was measured at the 10th period during the 2 Hz, 50% duty cycle with fixed light intensity ($P_{\text{in}} = 0.4 \text{ mW cm}^{-2}$).

UV-cured PEGDMA network continuously maintains the black phase and the photoelectric properties, we tested the response of the photoresistor on red-colored (635 nm) light in cases of fresh and after 35 days, respectively (Table 1). The γ -CsPbI₃ (3 wt% PEGDMA) device showed stable photoresponse characteristics in light of 635 nm as well as 450 and 532 nm even after exposure to ambient conditions for 35 days. The initial $J_{\text{photo}}/J_{\text{dark}}$ of the γ -CsPbI₃ (3 wt% PEGDMA) device for 635 nm light is 9.07×10^2 , and the $J_{\text{photo}}/J_{\text{dark}}$ after 35 days is 7.55×10^2 . Initial responsivity (R) is 0.122 A W^{-1} , and the responsivity after 35 days is 0.0974 A W^{-1} . In addition, normalized detectivity (D^*) showed a value of 7.56×10^{11} Jones after 35 days from the initial value of 9.30×10^{11} Jones. The initial value of the external quantum efficiency (EQE) is 23.8%, and the EQE after 35 days still retains 19%, which shows excellent electrical long-term stability.

Furthermore, to evaluate the repetitive driving stability of the optimized γ -CsPbI₃ (3 wt% PEGDMA) photoresistor, we measured the time-resolved photoresponse and transient response time (Fig. 5). Photocurrent-time response was measured at 40 V applied bias in the dark and under illumination using the LEDs at 635, 532, 450 nm with fixed light intensity ($P_{\text{in}} = 0.4 \text{ mW cm}^{-2}$) and frequency (1 Hz) (Fig. 5a, b, d, e). Unlike the reference γ -CsPbI₃ (Fig. 5a, b), the γ -CsPbI₃ (3 wt% PEGDMA)

photoresistor showed stable and consistent repetitive driving characteristics not only the fresh state but also after 35 days, and the photocurrent values were also matched with Fig. 4d and Supplementary Fig. 6d. In addition, rise times in response to red, green, and blue light of fresh γ -CsPbI₃ (3 wt% PEGDMA) were 65.1, 66.0, and 66.4 ms, and fall times were 66.8, 66.8, and 66.7 ms, respectively. Even after 35 days exposed in the ambient conditions, it shows an excellent fast response time that did not change much from the rise and fall time values of the initial device (Fig. 5c, f).

Conclusion

In summary, we suggest a robust strategy to ensure the structural, electrical long-term stability of γ -CsPbI₃ under ambient conditions by employing the infinitesimal amount ($\leq 3 \text{ wt\%}$) of UV-curable PEGDMA. The electronegative oxygen lone pairs of the PEGDMA attract Cs⁺ and Pb²⁺ cations from the CsPbI₃ precursor solution, which induce effective CsPbI₃ nucleation and growth from the PEGDMA backbone chain. In addition, the PEGDMA ($M_n \approx 330$) has short chain lengths with four repeating units, resulting in a dense network by the UV-curing, which acts to hold CsPbI₃ tightly, thus it is possible to suppress the additional distortion of the

γ -CsPbI₃ lattice. The PEGDMA polymer network formed by UV irradiation inside the γ -CsPbI₃ thin-film clearly contributed to maintaining a considerably stable black phase even when exposed to ambient conditions for 35 days. To evaluate the electrical long-term stability of the γ -CsPbI₃ thin-film employing with the PEGDMA polymer network, 2-terminal lateral photoresistors of Au/ γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA)/Au structure were fabricated, and the photoresistor including optimized UV-cured γ -CsPbI₃ (3 wt% PEGDMA) showed that ~90% of the initial electrical values were retained responding to red, green, and blue light even after 35 days in the ambient conditions. Consequently, despite the addition of a small amount of UV-cured PEGDMA network into the γ -CsPbI₃, the γ -CsPbI₃'s photoelectric parameters and light response speed remain robust even after prolonged exposure to ambient conditions. Therefore, applying an infinitesimal UV-curable polymer network with electronegative lone pair electrons to perovskite is an innovative strategy that can contribute effectively to long-term optical and electrical stability. It also indicates that this strategy can be applied not only to γ -CsPbI₃ but also to various halide perovskite materials.

Methods

Preparation of CsPbI₃ precursor solution containing a small amount of PEGDMA. The CsPbI₃ precursor solution was prepared by dissolving 0.48 M of cesium iodide (CsI, 99.999%, Sigma Aldrich) and lead iodide (PbI₂, 99%, Sigma Aldrich) in the mixed solvent of 2 mL of anhydrous N, N-dimethylformamide (DMF, 99.8%) and 72 μ L of HI (57 wt% in H₂O, Sigma Aldrich) and stirred vigorously at 700 rpm over 12 h²⁴. PEGDMA:HMPP mixture with 1 wt% of 2-hydroxy-2-methylpropiophenone (HMPP, 97%, Sigma Aldrich) added to poly(ethylene glycol) dimethacrylate (PEGDMA, $M_n \approx 330$, Sigma Aldrich) as a photoinitiator was added to the prepared CsPbI₃ precursor solution as 0, 0.5, 1, 3, 5 wt% of the total amount of CsI and PbI₂. Then stirred vigorously at 700 rpm over 6 h.

Fabrication process of Au/ γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA)/Au photoresistors. The prepared CsPbI₃ precursor solution containing a small amount of PEGDMA was spin-coated on a bare glass substrate in two steps. First, the spin-coating was performed at 2000 rpm for 25 s, and then spin-coating was immediately performed at 5000 rpm for 35 s. After 5 s of reaching 5000 rpm, the chlorobenzene was directly dropped onto the substrate to quickly remove the DMF solvent³⁵. After the spin-coating process, the CsPbI₃ with PEGDMA annealed at 90 °C for 5 min and exposed UV for 5 s immediately before cooling, which induces to photopolymerization between PEGDMAs. LED UV lamp (365 nm, Liim tech) was used as an ultraviolet light source. In this study, all UV-curing processes were performed at 400 mW cm⁻² for 5 s and the distance between the light source and substrate was fixed at 15 mm. Finally, 100 nm gold (Au) electrodes were deposited by the thermal evaporator, with a shadow mask with channel length and width of 120, 1000 μ m, respectively.

Characterizations of optical and photoelectrical properties. The current-voltage characteristics for all devices were measured in the voltage range -40 to 40 V at room temperature in a dark using the 4155B (Keysight) semiconductor parameter analyzer with the visible light irradiation using LED light sources (STF0A36C, SSC). The optical transmittance and absorbance of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) films are measured using a UV-Vis spectrometer (PerkinElmer Lambda 35). UV-cured PEGDMA structures are confirmed with ATR-FTIR (BRUKER, Alpha) at 4000–600 cm⁻¹ ranges. The crystallinity and morphology of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) films were obtained using FE-SEM (S-4800, Hitachi) and X-ray diffraction (XRD, D8 Advance, Bruker Co.) executed with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 150 mA (6 kW) with a grazing-incidence mode. X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Kratos) was used to analyze the chemical properties of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) films. Time-resolved photoreponse and transient response time were measured by B2902A (Keysight) two-channel source meter.

Data availability

The datasets that support all the findings of this study are available from the corresponding author (Y.S. Kim) upon reasonable request.

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Author contributions

N.-K.C. and H.-J.N. performed the fabrication of the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) films and photoresistors, and the γ -CsPbI₃ (0, 0.5, 1, 3, and 5 wt% PEGDMA) film's optical characteristics were carried out by N.-K.C., H.-J.N., and J.Y. The paper was written through contributions of all authors. The project was planned, directed and supervised by Y.S.K. All authors have given approval to the final version of the paper.

Competing interests

The authors declare no competing interests.

Additional information

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