

Organohalide Lead Perovskites: More Stable than Glass under Gamma-Ray Radiation

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Organohalide metal perovskites have emerged as promising semiconductor materials for use as space solar cells and radiation detectors. However, there is a lack of study of their stability under operational conditions. Here a stability study of perovskite solar cells under gamma-rays and visible light simultaneously is reported. The perovskite active layers are shown to retain 96.8% of their initial power conversion efficiency under continuous irradiation of gamma-rays and light for 1535 h, where gamma-rays have an accumulated dose of 2.3 Mrad. In striking contrast, a glass substrate shows obvious loss of transmittance under the same irradiation conditions.

The excellent stability of the perovskite solar cells benefits from the self-healing behavior to recover its efficiency loss from the early degradation induced by gamma-ray irradiation. Defect density characterization reveals that gamma-ray irradiation does not induce electronic trap states. These observations demonstrate the prospects of perovskite materials in applications of radiation detectors and space solar cells.

Organohalide lead perovskites are suitable for optoelectronic devices that convert photons into electricity, given their intriguing optoelectronic properties of strong light absorption and large mobility-lifetime product, in addition to other advantages such as low material cost and simple fabrication process.^[1–6] Within a short period of research, the power conversion efficiency (PCE) of perovskite solar cells quickly increased, from 3.8% in 2009 to 23.3% in 2018, which already rivals other thin film solar cell technologies.^[7] Fast,

high-throughput fabrication of perovskite modules has also been demonstrated with simple processes such as blade coating with module efficiency close to 15%.^[8] It remains unclear as to whether the perovskite solar cells can operate over 25 years in a real-world environment that is filled with oxygen and moisture, which are their two major stressors. Enhanced encapsulation has clearly shown to elongate the operational lifetime of perovskite solar cells to a much longer duration, indicating that the intrinsic stability of perovskite solar cells may be much longer than expected.^[9–11] Nevertheless, perovskite solar cells may find their niche applications in space where oxygen or moisture does not exist. For space applications, there are new stressors such as radiation that may impose new threats to the stability of perovskite solar cells, while stability of solar cells under radiation has been rarely studied. The increasing interest in perovskite-based X-ray and gamma-ray detectors warrants an imperative study of the stability of perovskite materials and devices under ionizing radiation.^[12,13]


Less than a handful of studies have been performed to reveal the effects of proton, electron, and X-ray irradiation on perovskite so far.^[14–17] Miyazawa et al. irradiated perovskite solar cells with 1 MeV electrons and found that the devices retained 93% of their peak performance after irradiation with a fluence of $1 \times 10^{16} \text{ cm}^{-2}$.^[15] Experiments conducted by Lang et al.^[14] indicated a decrease in short-circuit current density (J_{sc}) by 20% for perovskite solar cells exposed to a proton dose of $1 \times 10^{13} \text{ p cm}^{-2}$. The perovskite self-healed with recovery on fill factor (FF) and open-circuit voltage (V_{oc}) after the proton irradiation terminated.^[16] The effects of soft X-ray exposure on uncovered perovskites were investigated by Motoki et al. who reported that soft X-ray irradiation resulted in the evaporation of perovskite surface with residual elements in the form of crystalline PbI_2 . Apart from above stability studies with different radiation sources, the stability of perovskite device under gamma-ray radiation is also important but remained virtually unexplored.^[18] Large amounts of gamma-rays are inevitably produced when the galactic cosmic rays, comprising mainly protons and alpha particles, undergo nuclear interactions with the constituent nuclei of the spacecraft, which poses a challenge to the perovskite materials for their long-term application in space. Moreover, organohalide perovskites also showed great

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promise in ionizing radiation (X-ray and gamma-ray) detection by direction conversion of radiation into current or voltage signal.^[19] Therefore, it is valuable to examine the stability of perovskite devices under high-dose gamma-ray irradiation. The stability study should be conducted under radiation and light simultaneously, because a large density of charges generated by visible light may induce physical changes in perovskite materials, such as light accelerated ion migration.^[20] However, it has not been taken into consideration in previous studies.

In this work, we perform a comprehensive study on the stability of the perovskite solar cells under gamma-rays and visible light simultaneously. Hybrid perovskites are found to be very stable after exposure to continuous light and gamma-ray irradiation for 1535 h with an accumulated gamma-ray radiation dose of 2.3 Mrad. The experimental results herein imply the superior stability of perovskites to gamma-ray radiation, compared with glass or crystalline silicon, and possible mechanism are discussed.

Figure 1a shows the structure of perovskite solar cells fabricated which has a p-i-n planar heterojunction configuration of glass/indium tin oxide (ITO)/poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA)/perovskite/fullerene (C₆₀)/bathocuproine (BCP)/copper (Cu). The devices with this structure have been shown to be hysteresis-free with average PCEs of $\approx 19\%$ (Figure S1 and Table S1, Supporting Information).^[21] Devices were encapsulated using epoxy resin with a cover glass before stability tests, which do not affect the performance of the devices (Figure S2, Supporting Information). Details about

the device fabrication and encapsulation can be found in the Experimental Section.

We conducted in situ efficiency measurements of perovskite solar cells under irradiation of both gamma-rays and light illumination, and the schematic diagram of the stability test system is shown in Figure 1b. The perovskite solar cells were placed inside a ¹³⁷Cs benchtop irradiator, which provided continuous gamma-ray irradiation. Visible light generated by a tungsten halogen lamp was also coupled into the solar cells by an optical fiber, and the light intensity was 4.98 mW cm^{-2} , calibrated by a silicon diode. To accurately estimate the dose at the location of our perovskite solar cells, a dosimeter was placed close to the perovskite solar cells during the in situ measurement. The dose rate of the devices was measured to be 1.5 krad h^{-1} . During the stability test, *J-V* curves of the device were monitored in situ by a Keithley 2612A. The photocurrents of the devices did not show obvious change under gamma-ray irradiation compared to that in the absence of gamma-rays, suggesting such dose rate of gamma-ray radiation was still too low to generate considerable current, despite that this dose rate is already high compared to what exists in space (Figure S3, Supporting Information).

The device for the test had an initial J_{SC} of 21.98 mA cm^{-2} , a V_{OC} of 1.06 V and an FF of 80.5% , and a PCE of 18.8% tested under AM 1.5G simulated light source with a reverse scan rate of 0.1 V s^{-1} (Figure 1c). At the beginning of the in situ stability test, the J_{SC} , V_{OC} , FF, and PCE of the device were measured to be 1.10 mA cm^{-2} , 0.907 V , 0.789 , and 16.0% , respectively, by

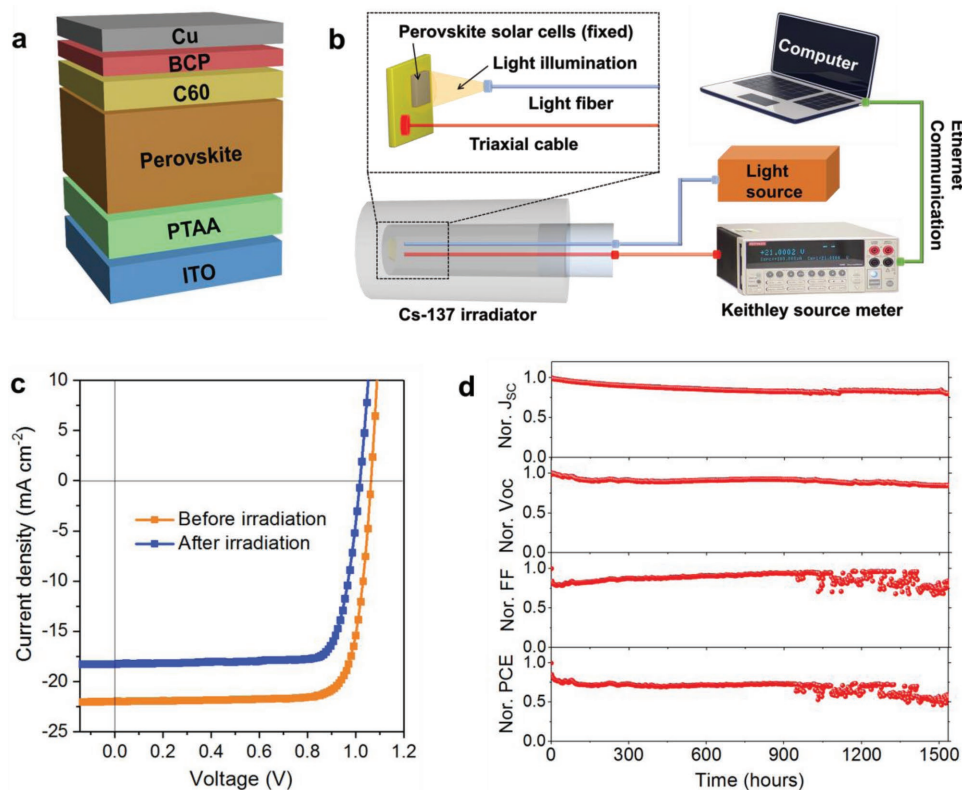


Figure 1. a) Illustration of the device structure of the p-i-n perovskite solar cells. b) Schematic of the stability test system. c) *J-V* curves of the perovskite device before and after irradiation test. d) Radiation stability of an encapsulated perovskite device.

the in situ stability test system, owing to the lower intensity of incident visible light from the optical fiber. Upon the irradiation of light and gamma-rays, the PCE of the solar cell initially reduced to 82% of the original value during the first 5 h, and then remained stable up to about 1000 h as depicted in Figure 1d and Figure S4 in the Supporting Information. The initial loss in performance is mainly caused by the reduction of FF to 82% of the initial value in the first 5 h. However, the FF recovered to 97% with continued radiation test after 1410 h. Similar phenomenon was also observed in three other devices, indicating that the self-recovery of the device performance is general (Figure S5, Supporting Information). Both the J_{SC} and V_{OC} gradually reduced to about 83% and 86% of the original value at 1410 h. Some noise in the FF and PCE was observed after testing for 960 h and the stability test was ended at 1535 h. It was later found that the noise was caused by the damage of the copper electrode by radiation, causing a crack in the electrode (Figure S6, Supporting Information).

After the long efficiency measurement, we took the device out of the testing system to examine the $J-V$ curve of this device again under simulated AM 1.5G illumination. The V_{OC} and J_{SC} of the irradiated device decreased to 1.02 V and 18.26 mA cm⁻², respectively, while the FF remained to be 80.2% (Figure 1c). The PCE of the device is thus 14.95% under simulated 1 sun illumination, in consistent with the in situ tracking measurement. Previous study reported that the degradation of perovskite devices can be partially reverted after aging in dark for about 12 h.^[22,23] Thus, the photovoltaic parameters were checked again by aging the device under 1 sun illumination for 2 h. No obvious recovery of PCE was observed after soaking in light as shown in Figure S7 in the Supporting Information.

As the stability tests were conducted under visible light and gamma-rays simultaneously, one needs to figure out whether the observed efficiency change, especially the fast initial burn-in occurred during the first 5 h, is caused by light or gamma-ray. Light-induced burn-in has been frequently observed in previous studies, which may be caused by light enhanced ion migration or generation of trap states.^[22,23] We therefore placed a perovskite solar cell under continuous light without gamma-rays, and then turned on the gamma-rays to find out the reason for the initial burn-in phenomenon. As shown in Figure 2, the photovoltaic parameters were stable during the first 8 h testing with only light illumination. However, when gamma-rays were turned on, obvious performance degradation shows up immediately. After gamma-ray irradiation for 2 h, the FF and PCE reduced to about 84% and 85% of their initial values, respectively. This experiment confirms that the initial burn-in should be caused by the ionization and displacement damage of gamma-rays. Figure 2 also shows that the device performance quickly stabilized under gamma-rays, indicating that the materials quickly adjust themselves which slow down the degradation. When the device is irradiated by only gamma-rays, the dark current gradually increased during 8 h (Figure S8, Supporting Information), which indicates that gamma-rays would impose a negative effect on perovskite and triggers the initial burn in solar cells.

It is noted that the color of glass substrates changed to dark brown after gamma-ray irradiation for 1535 h, as shown by the

photos in Figure 3a. It is not surprising that the color of the devices and the ITO substrates changed after receiving an accumulative dose of 2.3 Mrad, because of the generation of color centers due to displacement of ions by high-energy gamma-ray photons.^[24] However, the color change of glass prevents certain light from being incident on the perovskite material and thus, the efficiency of the device was underestimated. We measured the transmittance spectra of the ITO substrate before and after irradiation with the same gamma-ray dose to quantify the light loss, and the results are shown in Figure 3b. The transmittance of ITO glass reduced from about 90% over the entire visible light range to about 50–75% after irradiation. The difference of absorption spectra shown in Figure 3b reveals some features of the defects generated in glass by the gamma-rays. Intriguingly, there are two absorption bands centered at 625 and 430 nm of the darkened glass, which correspond to the absorption of defect sites of nonbridging oxygen hole centers (NBOHC:≡Si–O•) in soda-lime silicate glass, agreeing with previous radiation studies of glass.^[24] We thus calculated the maximum possible J_{SC} out of the device with colored ITO glass. The maximum possible external quantum efficiency (EQE) of the device after the stability test is calculated by the multiplication of internal quantum efficiency of the device before radiation with the transmittance of the glass after radiation, and the results are shown in Figure 3c. Before irradiation, the calculated J_{SC} by integrating EQE and sun spectrum is 21.4 mA cm⁻², in agreement with the $J-V$ measurement results shown in Figure 1c. If there is no degradation from the perovskite layer, the maximum J_{SC} of the device with colored glass

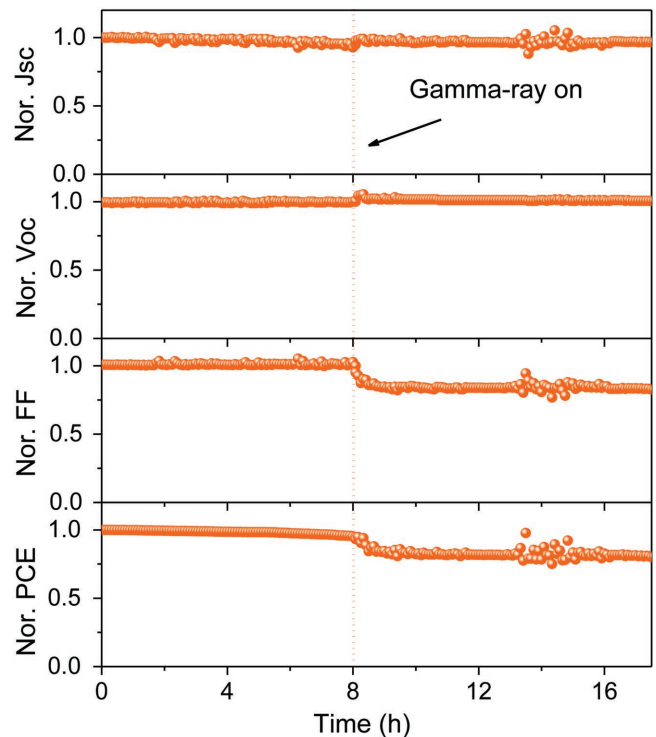


Figure 2. Influence of gamma-ray irradiation on the $J-V$ parameters of a typical perovskite solar cell. Gamma-rays were turned on at 8 h. The device was irradiated by simulated solar light of 49.8 W m⁻² during the entire test.

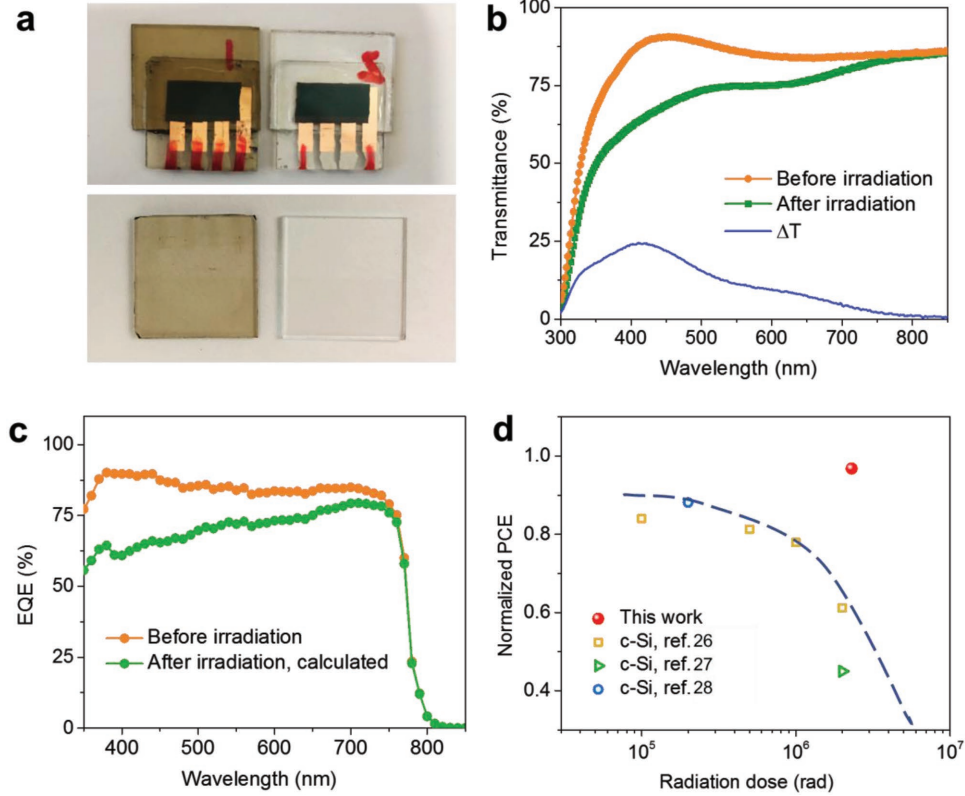


Figure 3. a) Pictures of devices (top) and ITO substrates (bottom) before (right) and after (left) gamma-ray irradiation. The radiation dose was 2.3 Mrad with duration time of 1535 h. b) Transmittance spectra of ITO glass before and after irradiation. ΔT is the loss in transmittance stemmed from irradiation. c) EQE spectra of the device before and after irradiation. The one after irradiation is calculated by transmittance results. d) Comparison of normalized PCE as a function of gamma-ray radiation dose of perovskite with crystalline silicon solar cells.

would be 18.4 mA cm^{-2} . The measured J_{SC} of 18.26 mA cm^{-2} shown in Figure 1c is actually very close to theoretically maximum value, indicating negligible J_{SC} loss after the stability test under gamma-rays and light irradiation. In fact, the slight reduction of V_{OC} of the irradiated device shown in Figure 1d should be partially caused by the reduced light intensity.^[25] To correct the light intensity in the J - V testing for the irradiated device, we calculated the irradiance received by the perovskite active layer between 350 and 800 nm, in which region contributes to the photovoltaic response. The received power incident visible light by the active layer are 46.7 and 38.4 mW cm^{-2} for the device before and after gamma-ray irradiation under 1 sun illumination. Therefore, the real test condition of the irradiated device is equivalent to ≈ 0.82 sun. The PCE of this device after irradiation is thus corrected to be 18.2% under 1 sun illumination. It is comparable to the initial PCE, indicating barely any degradation of perovskite solar cells under gamma-ray irradiation for 1535 h. The device performances before and after gamma-ray irradiation are summarized in Table 1. In Figure 3d, we compare the stability of our perovskite devices with previous reports of crystalline silicon solar cells. Clearly, the radiation hardness of perovskite-based device would be much better than silicon cells which retain only 61.2% of the initial PCE after irradiation by gamma-rays with an accumulated dose of ≈ 2 Mrad.^[26–28]

The primary effect of high-energy radiation, such as photons, on photovoltaics are both ionization and displacement

damage where atoms in the semiconductor lattice are knocked out from their equilibrium position to form point defects like vacancies, interstitials or defect complex, such as vacancy impurity clusters.^[24] In comparison, gamma-rays may cause displacement of atom if the recoil nucleus after photoelectric effect have acquired enough energy to break the bond.^[29] As the damage of perovskites usually accompanied with morphological variations, we first examined the perovskite layers after irradiation by scanning electron microscopy (SEM). The irradiated device was disassembled by exfoliating the Cu electrode using Scotch tapes. As shown in Figure 4a,b, there was no pin-hole or obvious change of perovskite film morphology after irradiation. It should be noted that there are residues of PCBM and C60 on the irradiated perovskite film, which makes the surface blurred. The cross-sectional SEM images of the devices further

Table 1. Photovoltaic parameters of a perovskite device before and after gamma-ray irradiation. J - V curves before and after irradiation were recorded under AM 1.5G simulated irradiation with a reverse scan rate of 0.1 V s^{-1} . Photovoltaic parameters after irradiation are corrected by adjusting the received light intensity of active layer to be ≈ 0.82 sun.

	$J_{SC} [\text{mA cm}^{-2}]$	$V_{OC} [\text{V}]$	FF	PCE [%]
Before irradiation	21.98	1.06	80.5%	18.8
After irradiation	18.18	1.02	80.2%	15.0
After glass transparency correction	18.18	1.02	80.2%	18.2

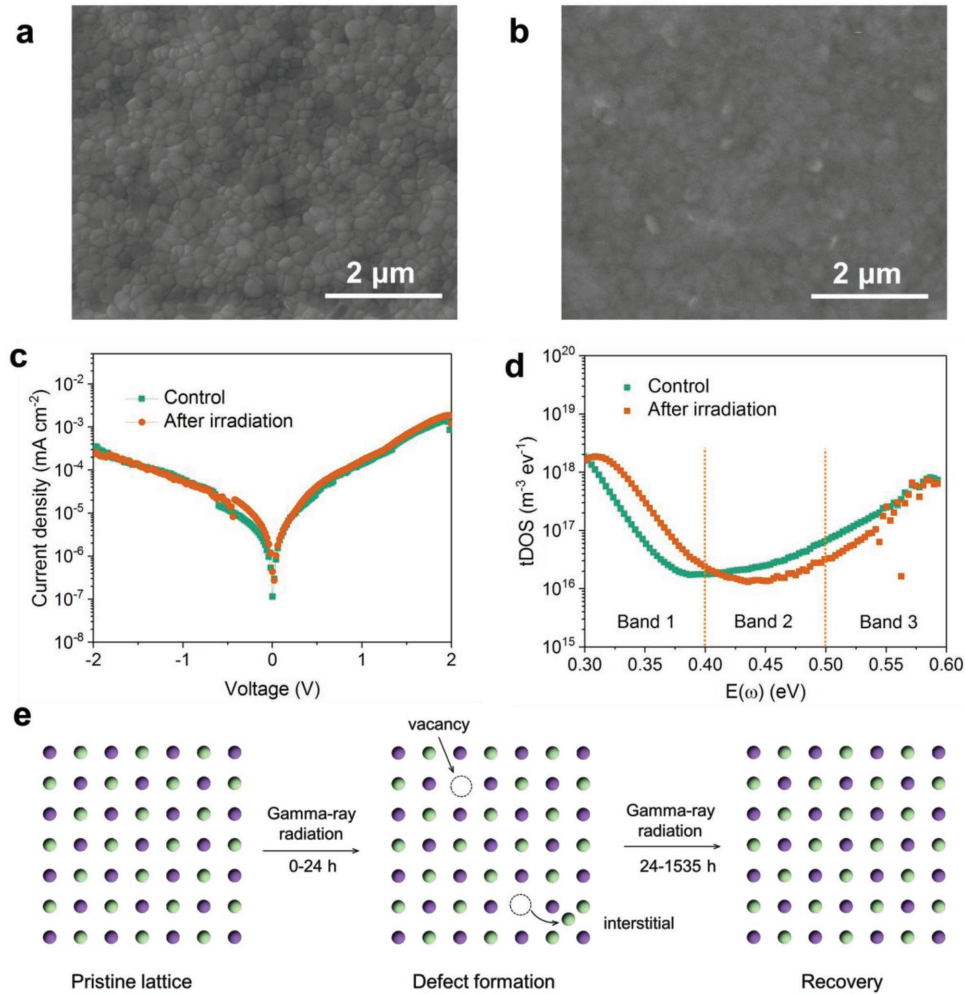


Figure 4. a,b) Top-view SEM images of a standard perovskite film and perovskite film after radiation test for 1535 h. c) Dark current characteristics and d) trap density of states obtained by TAS of the device before and after radiation tests for 1535 h. e) Self-healing mechanism of perovskites under gamma-ray radiation.

reveal the similar surface characteristics of the device without and with irradiation (Figure S9, Supporting Information).

Our previous results have identified that perovskites are highly ionic materials with ease of ion migration, whose morphological may be changed under irradiation.^[30] Figure 4c shows the dark current curves of a standard device (control) and the one after irradiation of 1535 h. Both devices exhibit small leakage current density lower than 10 mA cm⁻² even under a large reverse bias of 2 V, implying that gamma-ray irradiation has not caused leakage current by forming shunt pathways. To evaluate whether gamma-rays generate electronic defects in the perovskite film, we further conducted thermal admittance spectroscopy (TAS) to quantitatively characterize the charge trapping density in the devices.^[31] Figure 4d shows that the irradiated device has a slightly changed density of trap states (tDOS), while the variation is still within one order of magnitude which in many cases can be caused by device variation.

Gamma-rays should displace the ions in perovskite crystals from their initial location to form defects which is illustrated in Figure 4e. The occurrence of crystal defects are usually responsible for the reduction of photovoltaic parameters via

Shockley–Read–Hall process.^[32,33] We have also shown that initial degradation is caused by gamma-ray irradiation. After that, the maximum power output remained almost unchanged during the test between 100 and 1410 h (Figure 1c), despite the light intensity kept reducing during the measurement due to transparency loss from the ITO substrate. Thus, we can reasonably conclude that the real PCE should have increased and partially recovered during testing between 100 and 1410 h. The self-healing behavior of perovskites can be explained by ease of ion migration so that the displaced ions can move back to their lattice positions which are still thermodynamically lower energy sites.^[34,35] The light illumination also accelerated this recovery process, because of the light enhanced ion-migration behavior, which has been observed previously.^[20,36]

In summary, we have demonstrated excellent gamma-ray radiation hardness of hybrid perovskite layers under continuous light and gamma-ray irradiation with an accumulated gamma-ray dose of 2.3 Mrad, surpassing that of crystalline silicon solar cells. We have found that the PCE loss is mainly caused by the coloring of glass substrate under gamma-ray radiation, indicating that perovskites are even more stable than glass. After

the light intensity correction, we found that 96.8% of original PCE of the perovskite solar cell device retained after the long-term radiation stability test. It is noted that light loss can be alleviated by using different types of glass, for example, the cerium doped glass,^[37] which can avoid the formation of color centers under radiation in space. Self-healing behavior of the perovskite device was observed upon irradiation. The results presented here indicate that organohalide perovskites are radiation hard with great promise for radiation detection and space solar cells.

Experimental Section

Device Fabrication: Patterned ITO substrates were cleaned by ultrasonication with soap, acetone, and isopropanol. The hole transport layer PTAA with a concentration of 2 mg mL⁻¹ dissolved in toluene was spin-coated at a speed of 4000 RPM for 35 s and then annealed at 100 °C for 10 min. Before depositing perovskite films, the PTAA film was pretreated by spinning 80 μL dimethyl formamide (DMF) at 4000 RPM for 15 s to improve the wetting property of the perovskite precursor solution. The perovskite precursor solution composed of mixed cations (lead (Pb), cesium(Cs), formamidinium (FA), and methylammonium (MA)) and halides (I, Br) was dissolved in mixed solvent (DMF/DMSO = 4:1) with a chemical formula of Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}. Then 80 μL precursor solution was spun at 2000 RPM for 2 s and 4000 RPM for 25 s, and the film was quickly washed with 130 μL toluene at 20 s during spin-coating. The sample was annealed at 65 and 100 °C each, for 10 min. The devices were finished by thermally evaporating C60 (30 nm), BCP (8 nm), and copper (140 nm) in sequential order. A thin layer of CYTOP was first coated onto the back surface of device by blade coating, followed by annealing at 75 °C for 45 min on a hot plate. Then, a cover glass was attached onto the back surface for further protection by using epoxy resin.

Radiation Stability In Situ Measurement: The in situ experiment was conducted utilizing the ¹³⁷Cs benchtop irradiator at The Ohio State University Nuclear Reactor Lab. The devices were positioned securely at the center of the irradiator. The dose rate and accumulative dose received by perovskite devices were calibrated by a dosimeter (LANDAUER nanoDot®), which was placed close to the perovskite solar cells. The amounts of dose in two experiments were 347.74 and 801.48 cGy with irradiation time of 15.0 and 31.0 min, respectively. The gamma-ray dose rate provided by the irradiator was estimated to be ≈1.5 krad h⁻¹. A tungsten halogen lamp produced simulated sunlight illumination on the devices with constant density of 49.8 W m⁻² via light fiber (Light Source: Ocean Optics HL-2000-HP, Fiber: Ocean Optics QR600-7-UV-125F, Lens: Ocean Optics 74-UV). All devices were measured by a Keithley 2612A source-meter with scan rate of 0.017 V s⁻¹. The cells were connected to the source-meter close to the benchtop with a triaxial cable. The Keithley source-meter was controlled by a PC equipped with LabVIEW software and an in-house built LabVIEW program that performed I–V characterization at specific time intervals and saved the measurement data to a local disk. All experiments were performed at room temperature (23 ± 2 °C). Using this setup, the perovskite solar cell devices were characterized in situ while being subjected to the simulated sunlight illumination and gamma-ray irradiation. Figure 1c shows schematic of the in situ experimental setup.

Post-Irradiation Characterization: The morphology and structure of the samples were characterized by Quanta 200 FEG environmental SEM. The J–V analysis of solar cells was performed using a solar light simulator (Oriel 67 005, 150 W Solar Simulator) and the power of the simulated light was calibrated to 100 mW cm⁻² by a silicon (Si) diode (Hamamatsu S1133) equipped with a Schott visible-color glass filter (KG5 color-filter). All cells were measured using a Keithley 2400 source-meter with a scan rate of 0.1 V s⁻¹. EQE spectra were measured with a Newport QE measurement kit by focusing a monochromatic beam

of light onto the devices. The tDOS of solar cells were derived from the frequency-dependent capacitance (C–f) and voltage dependent capacitance (C–V), which were obtained from the TAS measurement performed by an inductance (L), capacitance (C), and resistance (R) LCR Meter (Agilent E4980A).

Correction of Light Intensity: To correct the light intensity of J–V testing for the irradiated device, the irradiance received by the perovskite active layer was calculated according to the following equation:

$$I = \int_{\lambda_1}^{\lambda_2} T \times SI \, d\lambda$$

where λ is wavelength, T is transmittance of ITO substrate, SI is spectral irradiance, and I is irradiance received by the active layer between λ_1 and λ_2 . The spectral irradiance data were referred to the standard tables for reference solar spectral irradiances: direct normal and hemispherical on 37° tilted surface (ASTM G173-03). As the visible light contributed mainly to the photovoltaic response, wavelength between 350 and 800 nm was selected. The received power of incident visible light by the active layer were estimated to be 46.7 and 38.4 mW cm⁻² for the device before and after gamma-ray irradiation under standard 1 sun illumination. Thus, the light intensity of the irradiated device was equivalent to be ≈0.82 sun after the light loss was deducted.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

gamma-ray radiation, organohalide perovskites, outer space, self-healing, solar cells, stability

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