RESEARCH HIGHLIGHTS

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Failure pathways of perovskite solar cells in space

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High power-to-weight ratio, good radiation resistance, and low manufacturing cost enable perovskite solar cells (PSCs) to be possibly used in space[1]. Different from terrestrial applications, PSCs used in space will face cosmic radiation, e.g., electrons, protons, neutrons, gamma rays, X-rays, ultraviolet (UV) rays, etc. (Fig. 1(a)), harming their long-term operational stability. Electrons are the most common high-energy particles in space. A series of terrestrial experiments mimicking electrons in the space environment were carried out, showing that PSCs can be deteriorated upon exposure. Al-Jassim *et al.* elucidated two failure pathways for perovskite films under electron-beam (e-beam) exposure through cathodoluminescence (CL) signals variation, which are knock-on-induced defect formation and heat-induced phase transformation[2]. Gao *et al.* revealed the decomposition process of $MAPbI_3$ under e-beam exposure by in-situ TEM[3]. The structural change was initiated by the loss of I ions to form $MAPbI_{2.5}$, followed by the loss of MA ions to form $MA_yPbI_{2.5-z}$, and ended up with PbI_2 (Fig. 1(b)). Yan *et al.* observed severe short-circuit current density (J_{sc}) decrease after electron exposure, which was mainly attributed to the reduced substrate transmittance caused by glass "coloring" (Fig. 1(c))[4]. Similar phenomenon was also observed when soda-lime glass was irradiated by protons[5] and gamma rays[6], thus the irradiation tolerance of space-used substrate is demanded.

Compared with electrons, protons have a higher mass and may cause severe damage. So far, the influence of proton irradiation has been studied mostly on unencapsulated PSCs under low-energy proton irradiation (50 or 150 keV) and encapsulated PSCs under high-energy irradiation (20 and 68 MeV). Low-energy protons could induce more damage because most of them stop in the device interior, while high-energy protons pass through the device[5]. Nickel *et al.* studied the irradiation hardness of $MAPbI_3$ PSCs under 68 MeV proton irradiation with a total dose of 1.02×10^{13} p/cm^2. The device performance unexpectedly increased after irradiation, which was attributed to the reduced SRH recombination loss (Fig. 1(d))[7]. They speculated that the proton-doping-induced shallow energy-level defects compensated the impact of MA-escape-induced deep energy-level defects. In their subsequent study, they conducted proton irradiation test on $Cs_{0.05}MA_{0.17}FA_{0.83}Pb(I_{0.83}Br_{0.17})_3$ PSCs under the same condition. The photoluminescence (PL) decay curves indicated that the carrier lifetime was prolonged after 68 MeV proton irradiation. A kinetic model, in which the trap states induced by proton irradiation slowly release the trapped minority carriers, could perfectly fit the experimental results[8].

When cosmic rays (e.g. protons) passing through the atmosphere at low earth orbit (LEO) or spacecraft shielding, a certain amount of neutrons are created. Cacialli *et al.* reported that fast neutrons (energy $\geqslant$ 1 MeV) interact with perovskite, causing atomic displacement[9], which induces Frenkel defects. These defects acted as unintentional dopants, increasing open-circuit voltage (V_{oc}) and reducing leakage current. Noticeably, unlike light-induced degradation, fast neutron-induced degradation is permanent and irreversible.

Gamma rays, with energy from a few keV to ~8 MeV, have the strongest energy in the electromagnetic spectrum and the highest penetrating ability. Huang *et al.* used gamma rays of 0.42 rad/s to irradiate $Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}$ solar cells[6]. The power conversion efficiency (PCE) decreased to 85% of the initial value after first 2 h, declined slowly between 2–100 h, and kept stable between 100–1410 h. The initial PCE attenuation was attributed to ion displacement in the perovskite. Then, ions slowly returned to their original lattice positions, leading to the recovery of PCE. Yang *et al.* irradiated $FA_{0.945}MA_{0.025}Cs_{0.03}Pb(I_{0.975}Br_{0.025})_3$ PSCs at a higher intensity (50 rad/s) and observed the formation of δ-phase $FAPbI_3$[10]. Troshin *et al.* irradiated perovskite by using gamma rays of 4.2 rad/s with an accumulated dose up to 50 krad. PL spectra exhibited an increase in peak intensity and a red shift in peak position. They thought that gamma rays promote phase segregation *via* forming I-rich and Br-rich domains[11]. By excluding the influence of glass, they compared the stability of different perovskites upon gamma rays irradiation. $MAPbI_3$ presented the highest stability because of its unique self-healing nature (Fig. 2(a)). At the surface, $MAPbI_3$ can easily decompose into CH_3I, NH_3 and PbI_2. Under gamma rays irradiation, radicals of the volatile species will form and react to form MAI again, which will further react with PbI_2 to form $MAPbI_3$[12].

By using 1486 eV X-ray to radiate $MAPbI_3$, the perovskite surface was damaged, causing the formation of crystalline PbI_2 and the evaporation of NH_3I[13]. Cappel *et al.* indicated that different perovskites followed different decomposition modes under strong X-ray irradiation. For $CsPbBr_3$, X-rays caused the formation of metallic Pb, CsBr and Br_2, evidenced by a significant decrease in bromine content (Fig. 2(b)). For $Cs_{0.17}FA_{0.83}PbI_3$, X-rays caused the degradation of FA^+, yielding a Pb/I ratio of 1 : 2 but without the formation of metallic Pb[14].

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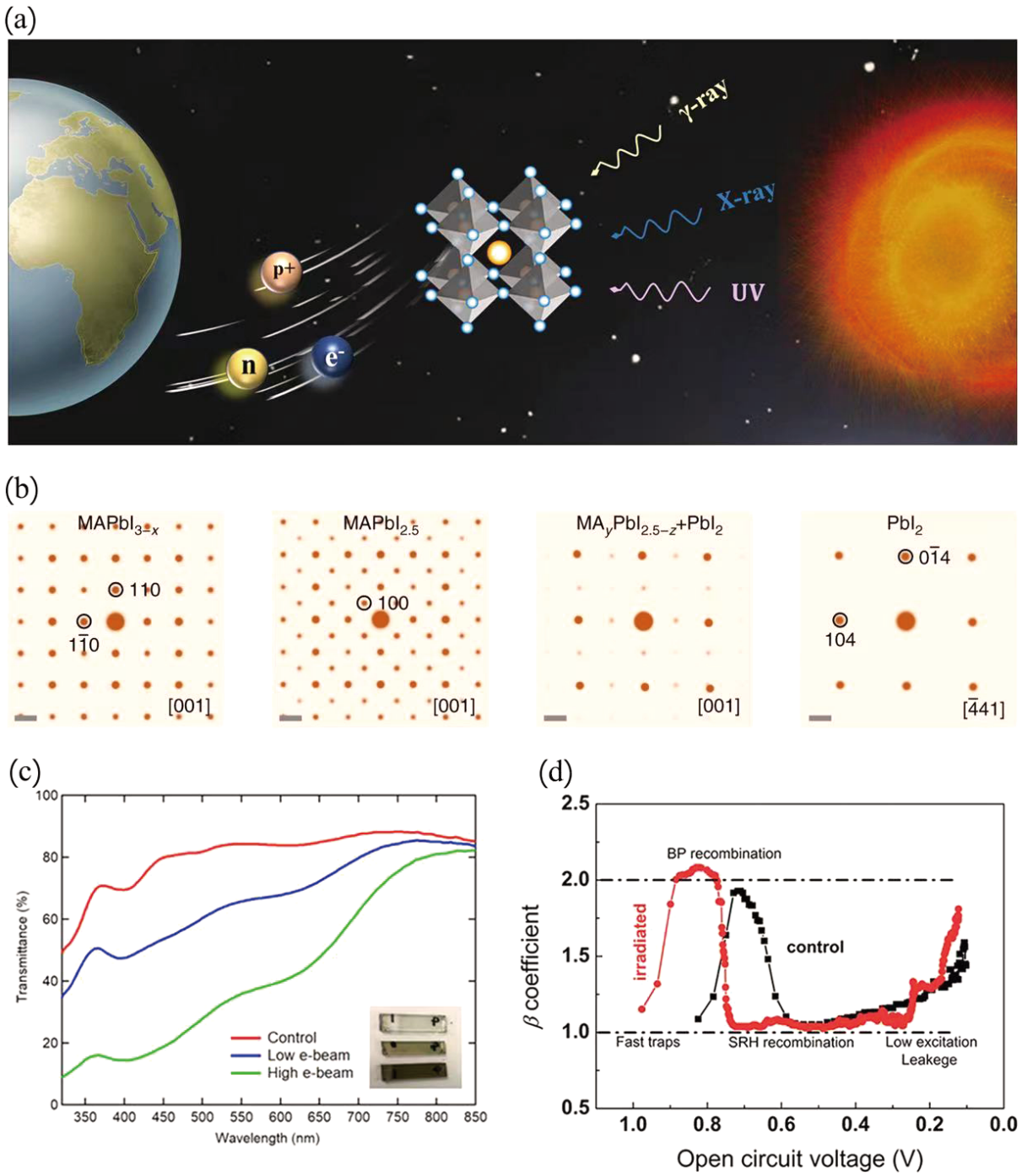

Fig. 1. (Color online) (a) Perovskite solar cells in space suffer various radiations. (b) Simulated electron diffraction patterns showing the structural evolution of $MAPbI_3$ under e-beam irradiation. Reproduced with permission[2], Copyright 2018, Springer Nature. (c) Transmittance spectra for glass substrates after e-beam irradiation. Reproduced with permission[3], Copyright 2020, American Chemical Society. (d) β coefficient *vs* V_{oc} curves. Reproduced with permission[7], Copyright 2017, Wiley.

In space, the solar spectrum becomes AM0, which comprises additional UV irradiation than AM1.5. Generally, water and oxygen could participate in the degradation of perovskites under UV light[15]. Recently, Li *et al.* indicated that the stability of PSCs with a TiO_2 layer was affected by UV light even in inert environment. The UV-induced degradation pathway is described in Fig. 2(c)[16]. Under UV light, Ti^{3+}-V_O (oxygen vacancy) reacts with the photogenerated holes and transforms to active Ti^{4+}-V_O trap states, leading to a loss of photocarriers. Ti^{4+}-V_O oxidizes I^- and produces I_3^-. I_3^- species further accelerate the decomposition of perovskite[17]. Al_2O_3, Zn_2SnO_4, $ZnTiO_3$ and NiO_x serving as photocatalysts may follow a similar degradation mechanism.

PSCs demonstrate superior stability than silicon solar cells under cosmic rays, but they are certainly not indestructible. Some degradation mechanisms are proposed and more are yet to be explored.

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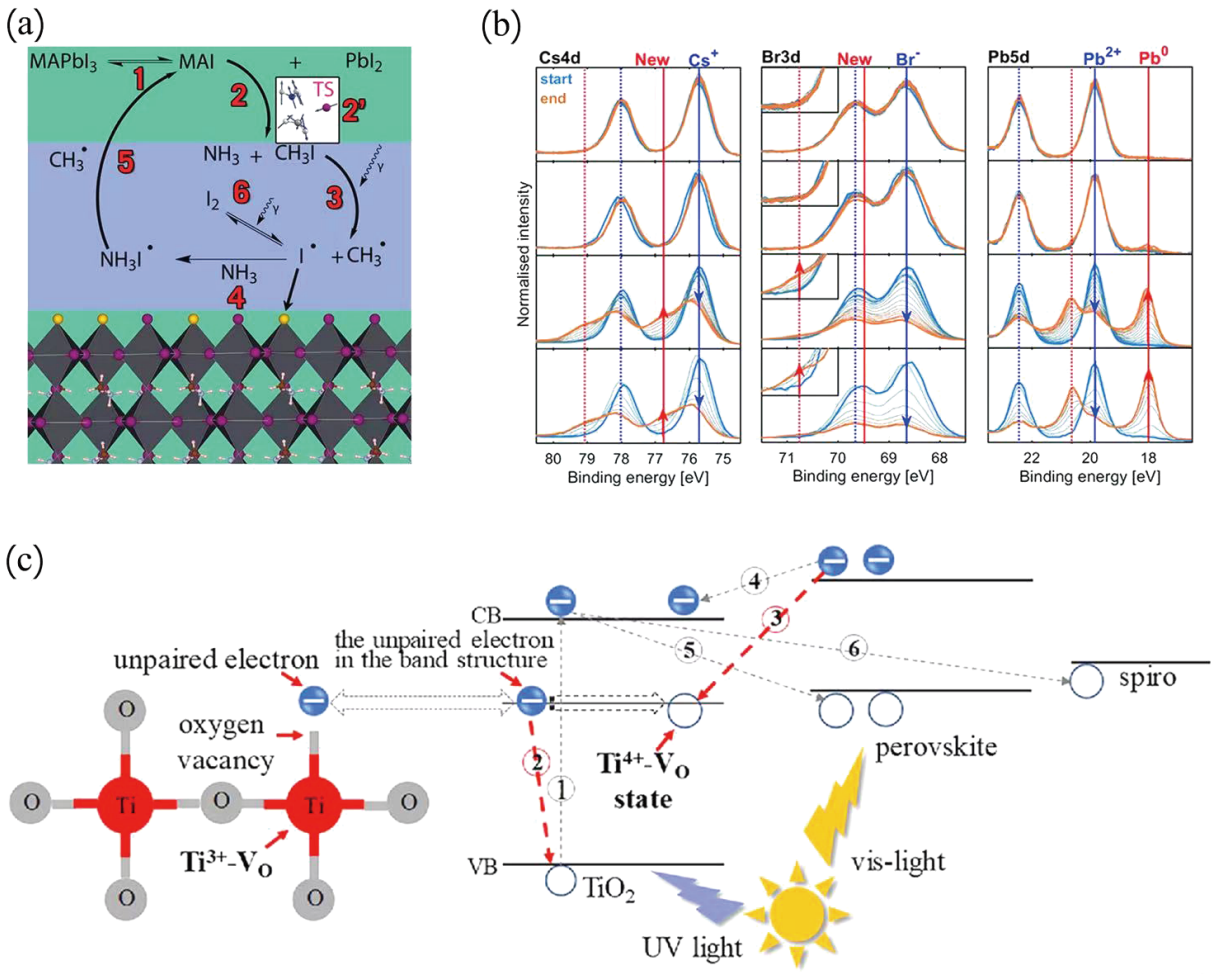

Fig. 2. (Color online) (a) Schematic for self-healing mechanism in $MAPbI_3$. Reproduced with permission[12], Copyright 2020, American Chemical Society. (b) Cs 4d, Br 3d, Pb 5d XPS spectra for $CsPbBr_3$. Reproduced with permission[14], Copyright 2021, Royal Society of Chemistry. (c) Schematic for UV-induced degradation of perovskite. Reproduced with permission[16], Copyright 2021, Royal Society of Chemistry.

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