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Preview

Radiation-tolerant organic solar cells for spacecraft

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Solar cells are often the preferred choice of power for space applications. However, the rapidly expanding near-Earth space activity demands spacecraft powered by photovoltaic materials that are of lower cost and radiation tolerant. While achieving radiation tolerance in mechanically soft matter appears counterintuitive, a recent paper from *Joule* demonstrates that organic semiconductors could offer a promising path forward to space power.

With the proliferation of the near-Earth space, the need to develop materials with electronic and optoelectronic properties suitable for extreme environments is increasingly critical. Solar wind traveling from the Sun toward Earth consists of energetic protons and electrons, which get trapped in Earth's magnetic field upon impact. These result in space radiation usually encountered by spacecraft. Additionally, for the orbits closer to Earth, this radiation strips off atmospheric oxygen, leading to atomic oxygen formation. In these high-radiation environments, such as the low earth orbit (LEO), which is a key deployment zone for satellite constellations, space assets encounter proton fluences ranging from 10^7 to 10^{14} cm^{-2} MeV^{-1}, potentially accumulating fluences exceeding 10^{12} cm^{-2} in a year.[1] While radiation is a key stressor, thermal cycling, atomic oxygen, and vacuum also pose challenges. The lack of gravity at high altitudes results in atmospheric pressures as low as 10^{-11} Torr, while temperature cycling in the range of $-50^{\circ}C$ to $+80^{\circ}C$ is usually expected every 90 min in LEO. Traditional semiconductor devices currently powering the near-Earth space, based on Si and III-Vs, are costly and employ thick encapsulation for radiation hardening. Materials with lower cost, lighter weight, and higher specific powers can aid the development of soft and printable semiconductors that can withstand the extreme environment.

Organic semiconductors, including polymers and small molecules, and organic-inorganic hybrid semiconductors, such as metal-halide perovskites, offer advantages in this perspective. Devices made from perovskites have demonstrated specific powers reaching 40 W/g, far exceeding those of silicon (1 W/g) and GaAs (3 W/g). However, the integration of organic semiconductors in space electronics has been considered implausible due to their vulnerability to space radiation, atomic oxygen, thermal cycling, and vacuum. High-energy radiation can break chemical bonds and create defects in organic semiconductor materials, leading to the degradation of their electronic properties.[2]

In a recent paper from *Joule*, Li and co-workers challenge this view and demonstrate unexpected radiation tolerance and self-healing in organic photovoltaics (OPVs).[3] The authors reveal insights into the radiation resistance of organic semiconductors, contrasting two separate classes—small molecules and polymers—when used as the photoactive layer in solar cells.[3] Their investigation of low-energy proton irradiation, a critical energy range particularly relevant for emerging photovoltaics in LEO conditions,[1] shows that vacuum-deposited small-molecule OPVs maintain their performance under proton radiation fluences up to 10^{12} cm^{-2}, challenging the popular perception about radiation sensitivity of organic materials. Using Monte Carlo simulations, 30 keV protons are shown to fully penetrate the entire active layer, resulting in atomic displacements. As expected, these protons are found to generate more vacancies than energies >100 keV, underlining the importance of using low-energy protons for maximizing radiation interaction with ultrathin device stacks and accurately testing these architectures.[1,4]

As protons travel through these organic solar cell device stacks, they lose energy via elastic non-ionizing energy loss (NIEL) and inelastic ionizing energy loss (IEL), as illustrated in Figure 1A for the case of halide perovskite crystal structures (ABX3).[5–7] NIEL is responsible for displacing atoms from their original positions, a phenomenon that is known to cause radiation damage in conventional Si and III-V semiconductors.[8] Hydrogen (H) atoms, which constitute the polymer side chains, are particularly easy to displace given their small mass. Via IEL, protons interact with electrons in the system, leading to ionization. While a deeper understanding of radiation effects in the materials reported by the authors is needed, it is likely that both NIEL and IEL effects are responsible for the changes observed.

Solar cell device architecture used for the proton irradiation experiments by Li and co-workers is illustrated in Figure 1B. The organic semiconductor active layer, made from either small molecules or polymers, was sandwiched between charge transport layers and electrodes for collecting photogenerated charges. While thermally evaporated small-molecule OPVs maintained their power conversion efficiencies (PCEs)

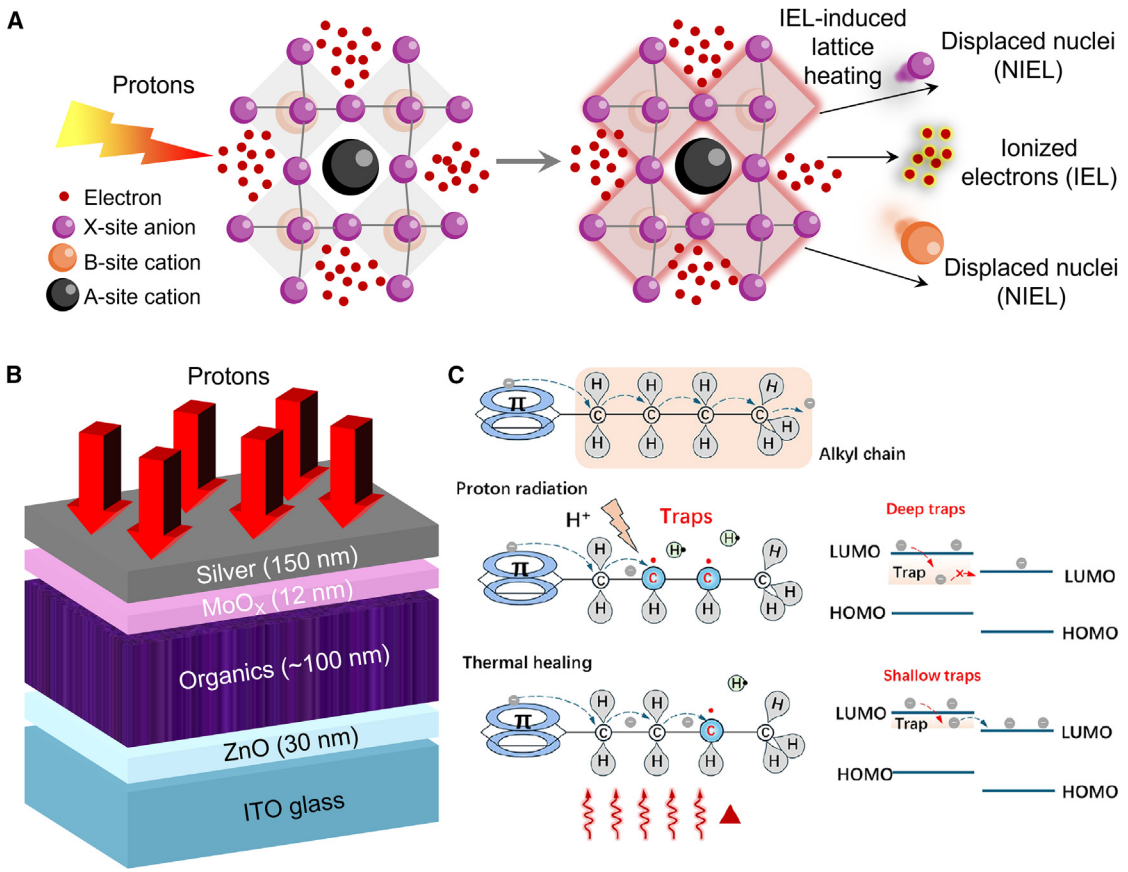

Figure 1. Radiation effects in emerging photovoltaic semiconductors and devices
(A) Radiation-matter interactions in soft lattice semiconductors (adapted from Kum et al.[4]).
(B) OPV device architecture used for proton irradiation.
(C) Proposed mechanism for radiation-induced degradation of the polymer absorber layer used in the OPV.

under 30 keV protons, the solution-processed polymer OPVs degraded to about 50% of their initial values. Experimental insights from nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) point toward dissociation of C–H bonds via H atom displacement and the subsequent cross-linking of polymeric chains. The cross-linked chains are responsible for the formation of deep traps, causing non-radiative recombination and subsequent device performance loss in the polymer-based OPVs (Figure 1C). In contrast, the observed radiation tolerance of the small molecules is ascribed to a lack of extended alkyl chains. These findings directly link the role of the molecular structure in organic semiconductors to radiation tolerance of the device and can lead to design principles for radiation-tolerant organic electronics and optoelectronics.

Particularly remarkable is the self-healing behavior observed by Li and coworkers in polymer-based devices. Thermal annealing of these irradiated devices between 65°C and 85°C renders the defects inactive, restoring up to 90% of their initial PCE. This result implies that defects created in these systems by the low-energy protons are thermally activated. Annealing at relatively modest temperatures (<100°C) substantially restored device performance, suggesting that the soft nature of these materials, often considered a disadvantage under extreme conditions, might contribute to their radiation tolerance through self-repair mechanisms.

This recovery behavior is similar to the radiation tolerance observed in metal halide perovskites (MHPs), where soft lattices, electron-phonon coupling, and low thermal conductivities combinedly contribute to radiation tolerance.[9] Due to this serendipitous combination, radiation-induced displacement defects in MHP semiconductors can be reversed via lattice heating caused by IEL from the incident protons.[5] This local heating of the perovskite lattice has the potential to rearrange NIEL-displaced atoms, partially restoring the lattice and its optoelectronic properties. Comparable behaviors in OPVs and PSCs suggest that materials with certain degrees of structural flexibility might possess atomistic mechanisms for mitigating radiation damage.

The role of polaronic effects, well documented in organic semiconductors, could be crucial in this context. The ability of these materials to accommodate structural deformations through polaronic effects might provide a mechanism for tolerating radiation damage without permanent degradation of electronic

properties. While these results are promising, further investigation is needed to clearly unravel radiation effects in such materials and the atomistic mechanisms involved. While the demonstrated tolerance is impressive, harsher orbit environments such as the upper LEO and medium earth orbit (MEO) present even more extreme radiation conditions. In addition, while the flexibility of organic semiconductors appears to activate radiation tolerance, this might make them vulnerable to high temperatures and thermal cycling.[9] The combined effects of radiation and thermal cycling for mission-specific orbits should be investigated.

Soft materials are generally characterized by lattice dynamics. Upon irradiation, these dynamics are expected to be exacerbated due to the NIEL and IEL effects. This can result in uncontrolled damage, leading to volatilization of the material. To circumvent this, ultralight conformal barrier layers might serve as a useful component in the OPV device stacks under irradiation. This strategy has recently been demonstrated for PSCs, where it was shown that despite incident protons fully penetrating the barrier and the device stack, the devices retained their performance.[10] Thus, while conventional barriers suppress moisture and oxygen ingress, conformal barriers might be necessary to inhibit egress, which is a likely outcome and failure mode of soft materials under stress.

Overall, these findings suggest that mechanical softness enhances extreme resilience and align with similarly counterintuitive observations in recent years for metal-halide perovskites. While major challenges related to thermal cycling stability, tolerance to ultraviolet radiation and atomic oxygen, and operation under vacuum remain, the results by Li and coworkers pave an exciting path forward in exploring organic semiconductors for space applications.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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