

An Independent Post-Publication Bioindicator Study Supplementing the Environmental-Safety Discussion of Fiber-Based Perovskite Solar Cells

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Method Article

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Abstract

Fiber-based perovskite solar cells (fb-PSCs) offer a mechanically adaptable photovoltaic platform, but the possible release of lead (Pb) from damaged devices remains a concern for environmental deployment. In this independent post-publication study, we examine whether polyolefin elastomer (POE) encapsulation suppresses Pb transfer from Ti-fiber-based MAPbI₃ devices into a simplified soil-plant system. *Pogonatherum crinitum* served as the bioindicator, and flame atomic absorption spectroscopy (FAAS) was used to monitor the Pb signal in plant-derived extracts over 90 days. The encapsulated and unencapsulated devices were compared across three spatial configurations, including surface placement, burial and lateral separation from the plant. The encapsulated groups exhibited substantially lower Pb signals, with the reported signal after 90 days approximately one tenth of the unencapsulated control. We discuss the observed contrast in terms of the low-polarity POE backbone, unfavorable ionic partitioning, restricted diffusion, reduced water ingress and mechanically resilient coverage. The interpretation concerns Pb migration under the tested conditions and does not establish Pb speciation or a comprehensive ecotoxicological risk profile. Finally, we outline opportunities to improve the photovoltaic efficiency, bending durability and Pb containment of fb-PSCs through coordinated materials and interface engineering.

1. Introduction

Fiber-based perovskite solar cells (fb-PSCs) have attracted attention as lightweight, deformable and wearable photovoltaic devices [1, 2]. Compared with planar perovskite solar cells (PSCs), fb-PSCs can be woven, wrapped or integrated into curved surfaces. Consequently, they offer opportunities for self-powered wearable electronics and portable energy systems. However, the practical utility of fb-PSCs depends on more than the power conversion efficiency (PCE), the mechanical resilience and the storage durability. The environmental compatibility is equally important. A lead-containing perovskite (PVK) layer may release Pb-containing species when the device is damaged, degraded or exposed to moisture [3, 4]. Therefore, the encapsulation must be evaluated not only for device stability but also for its ability to limit Pb leakage [5–7].

In the published work on polymer-enhanced fb-PSCs, the primary emphasis was placed on the optimization of the electron transport layer (ETL), the PVK layer and the hole transport layer (HTL) [8]. The study also examined the anti-bending ability, optical response and durability under artificial perspiration [9, 10]. Polyolefin elastomer (POE) encapsulation was applied to improve the environmental robustness of the device [5, 8]. Nevertheless, the broader question of whether the encapsulation reduces Pb transfer into a soil-plant environment requires a separate experimental assessment. A plant-based bioindicator method provides a useful route for this purpose. *Pogonatherum crinitum* can absorb and accumulate heavy-metal species from its growth environment [11, 12]. The plant therefore provides a biologically relevant indicator of Pb migration from degraded or exposed PSC devices. Although the bioindicator test cannot replace a complete ecotoxicological assessment, it provides complementary evidence of the protective role of the encapsulation [3, 13].

This post-publication research note presents an independent bioindicator-based assessment of Pb leakage from POE-encapsulated fb-PSCs. The device architecture and photovoltaic background originate from the previously published fb-PSC study [8]. By contrast, the plant-growth experiment, Pb-extraction procedure, flame atomic absorption spectroscopy (FAAS) measurements, data analysis and interpretation form the independent research record presented here [14]. The objective is to strengthen the environmental-safety discussion of the original work. Accordingly, the present work compares the encapsulated and unencapsulated devices under different device-plant spatial configurations. It also examines the time-dependent Pb signal in the plant-derived extracts. The results assess whether the POE encapsulation suppresses Pb migration into the simplified soil-plant system. The conclusions are limited to the laboratory bioindicator evidence and do not constitute a full environmental risk assessment [13].

2. Experimental methods

2.1. Plant materials, soils and photovoltaic devices

Pogonatherum crinitum seedlings with similar initial size and visible health status were obtained from Beijing Florascape Co., Ltd., China. The seedlings served as the bioindicator plants in the independent post-publication Pb-leakage experiment. Sandy loam soil was purchased from Beijing Florascape Co., Ltd., China, and sieved through a 2.0 mm stainless-steel mesh before use. According to the supplier-provided batch information, the soil was dominated by sand and silt fractions, with a nominal pH range of 6.5–7.2 and an organic-matter content of approximately $15\text{--}30\text{ g}\cdot\text{kg}^{-1}$. The encapsulation layer was a commercial polyolefin elastomer (POE) photovoltaic film supplied by Hangzhou First Applied Material Co., Ltd., China. The film was based on Dow ENGAGE-grade polyolefin elastomer. The POE film had a nominal thickness of $100\text{--}150\text{ }\mu\text{m}$, a density of approximately $0.86\text{--}0.88\text{ g}\cdot\text{cm}^{-3}$, and a melt index of approximately $1.0\text{--}5.0\text{ g}\cdot 10\text{ min}^{-1}$ according to supplier specifications. The fiber-based MAPbI₃ perovskite solar-cell devices used in this bioindicator study were taken from the same device batch as the previously reported fb-PSC work. The devices contained Ti fiber substrates, compact SnO₂ electron-transport layers, MAPbI₃ perovskite absorbers, spiro-OMeTAD hole-transport layers and Au top electrodes. The soil-plant exposure experiment used only the completed devices, either with or without POE encapsulation. No additional perovskite precursor salts, charge-transport-layer precursors, dopants or coating solvents were used for new device fabrication in this independent bioindicator study.

2.2. Chemicals, standards and analytical solutions

Ultrapure H₂O with a resistivity of $18.2\text{ M}\Omega\cdot\text{cm}$ was used for the plant irrigation, sample rinsing, reagent dilution and blank preparation. The Hoagland nutrient solution was prepared from a commercial stock formulation purchased from Beijing Solarbio Science & Technology Co., Ltd., China. The stock was diluted with ultrapure H₂O before use. Hydrochloric acid (HCl, 36.0 wt%), nitric acid (HNO₃, 65.0 wt%), hydrofluoric acid (HF, 40.0 wt%) and perchloric acid (HClO₄, 70.0 wt%) were purchased from Shanghai

Aladdin Bio-Chem Technology Co., Ltd., China, and used for the digestion of the plant powder. Ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$, was dissolved in ultrapure H_2O to prepare a $20.0 \text{ mg}\cdot\text{mL}^{-1}$ matrix-modifier solution when required. Standard Pb in HNO_3 solution, TraceCERT grade, $1000 \text{ mg}\cdot\text{L}^{-1}$, was purchased from Merck and diluted with 1.0–2.0 vol% HNO_3 to prepare Pb calibration standards of 10.0, 20.0, 30.0, 40.0 and $50.0 \text{ }\mu\text{g}\cdot\text{L}^{-1}$. Ethanol and diethyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd., China, and used for the preparation of the operationally defined plant-derived extract. All diluted solutions were freshly prepared before measurement and stored in acid-washed polypropylene tubes.

2.3. Laboratory equipment and FAAS instrumentation

Polytetrafluoroethylene (PTFE) digestion crucibles with a nominal volume of 30–50 mL and matched PTFE mask caps were purchased from Nanjing Binzhenghong Instrument Co., Ltd., China. Polypropylene centrifuge tubes with capacities of 15 mL and 50 mL were purchased from Corning Inc. or Jiangsu Kangjian Medical Apparatus Co., Ltd., China. Agate mortars and pestles with an inner diameter of 80–100 mm were purchased from Shanghai Titan Scientific Co., Ltd., China. The Kimtech Science Kimwipes lint-free wipes were purchased from Kimberly-Clark Professional. They were used to remove residual surface water after the plants were rinsed. Stainless-steel scissors, tweezers and soil meshes were cleaned with dilute HNO_3 and rinsed with ultrapure H_2O before use. Plant samples were dried in a DHG-9070A electric thermostatic drying oven purchased from Shanghai Yiheng Scientific Instrument Co., Ltd., China. A TG-16 high-speed benchtop centrifuge purchased from Sichuan Shuke Instrument Co., Ltd., China, was used for extract clarification. The FAAS measurements were performed using a TAS-990 atomic absorption spectrometer purchased from Beijing Purkinje General Instrument Co., Ltd. (PERSEE, China). The instrument was equipped with a Pb hollow-cathode lamp, a deuterium background-correction system and an air-acetylene flame burner. Acetylene gas with a purity of 99.9% was supplied by Beijing Haikeyuanchang Practical Gas Co., Ltd., China, and compressed air was supplied by the instrument air-compressor system.

The FAAS experiment was conducted to determine the Pb concentration in the plant-derived extracts. The prepared sample solution was introduced into the flame for analysis. The analytical wavelength was 283.3 nm, the lamp current was 6.0 mA, and the monochromator bandwidth was 0.2 nm. The air-acetylene flame was operated with an acetylene flow rate of $1.0 \text{ L}\cdot\text{min}^{-1}$. The flame height was maintained at 15 mm throughout the measurements. The deuterium lamp provided the background correction.

3. Results and discussion

3.1. Experimental configurations and Pb accumulation

The Pb released from PSCs may adversely affect the surrounding environment [3, 13]. *Pogonatherum crinitum* has been investigated as a heavy-metal-accumulating bioindicator plant [11, 12]. As illustrated

in Fig. 1a, the root system can absorb Pb from the soil. The vascular tissues can subsequently transport a fraction of the absorbed Pb into the aboveground parts, providing a measurable indicator of environmental exposure [12]. Against this background, we examined how the encapsulation of the fiber-based PSCs affected the Pb signal accumulated in the plant tissues. The Pb concentration in the prepared plant-derived extract was determined by FAAS [14].

Fig. 1. (a): Illustration of Pb leakage process from PSC to *pogonatherum crinitum*. (b): Illustrations of Pb leakage experimental settings. (c)~(d): Effect of environment storage time on Pb element content in the plant-derived extract for Conditions #1~#3.

Bundles of 30 PSC devices were arranged in three spatial configurations [8]. The devices were placed on the soil surface beside the plant, near the base of the pot at a depth of 15 cm, or on the opposite side of the elongated container, 25 cm from the plant (Fig. 1b, Condition #1~#3). The inflorescence and leaf mixture were sampled every 5 days to prepare the plant-derived extract. The resulting extracts were analyzed by FAAS to determine the Pb content. The time-dependent Pb content was then compared between the encapsulated and unencapsulated E1/P1 devices (Figs. 1c~1d) [8]. In all three configurations, after 90 days of exposure, the reported Pb concentration for the encapsulated groups was approximately 0.5 mg/mL, or around 10% of the unencapsulated control [5, 15]. The marked difference indicates the protective effect of the POE encapsulation.

3.2. Bioindicator response and methodological limitations

Pogonatherum crinitum is suitable as a bioindicator of Pb leakage because of several complementary characteristics. These include Pb tolerance, rhizosphere activation, intracellular complexation, antioxidant buffering and transport to the shoots. The perennial grass has exhibited Pb tolerance and an appreciable Pb-enrichment capacity in greenhouse and field studies [11, 12]. After Pb enters the rhizosphere, it can alter the local enzyme activities and microbial communities. Changes in the activities of acid phosphatase and urease can affect Pb solubilization, complexation and availability at the root surface [11]. The rhizosphere bacteria can also exhibit upregulation of pathways involving ABC transporters, quinone reductase and ATP-binding proteins [11]. Such responses indicate that the rhizosphere microenvironment is sensitive to Pb stress. Within the plant tissues, Pb stress also modifies the antioxidant enzyme systems and organic-acid metabolism [12]. Organic acids can lower the activity of free Pb^{2+} through carboxylate coordination. They can also promote Pb immobilization in the cell walls, vacuoles or organic-acid complexes. Together, the protective responses can mitigate damage to the chlorophyll fluorescence, photosystem II and cell membranes [12]. Therefore, *Pogonatherum crinitum* is relatively sensitive to Pb leakage and can convert Pb signals from soil or local contamination sources into detectable Pb contents in plant tissues [3, 4]. The resulting bioindicator assay has three practical advantages: a straightforward experimental configuration, low cost and modest instrumentation requirements. It converts the question of “whether the device leaks Pb” into the question of “whether a bioavailable Pb signal is generated”, making it closer to an environmental exposure scenario than the

direct measurement of soaking solutions alone. Moreover, the plant response can integrate the cumulative effects of trace, long-term and low-flux leakage [3].

Nevertheless, the Pb uptake by *pogonatherum crinitum* depends strongly on the soil pH, organic matter, root development, microbial communities, irrigation conditions, Pb chemical speciation and inter-individual variability [13, 16]. The Pb signal measured by FAAS is defined by the selected extraction or digestion procedure. It cannot directly distinguish Pb^{2+} , PbI_2 , Pb-organic acid complexes or mineral-bound Pb [14, 17]. The signal therefore cannot, by itself, establish the ecological risk. Accordingly, *pogonatherum crinitum* is best treated as a laboratory bioindicator. The assay provides preliminary evidence that the POE encapsulation reduces the migration of bioavailable Pb, but it does not replace a complete ecotoxicological assessment [3, 4].

3.3. Physicochemical barriers to Pb migration in POE

The POE layer should not be regarded as absolutely impermeable to Pb. Instead, the encapsulation substantially retards Pb migration over the experimental timescale [5, 18]. This behavior can be understood through multiple energetic and kinetic barriers. Together, the barriers restrict the transfer of Pb from the perovskite layer through the surrounding soil and aqueous phases into the plant system [6, 7].

First, the Pb-blocking effect of POE originates primarily from the low-dielectric, low-coordination and low-free-volume transport environment formed by its nonpolar polyolefin backbone [5, 18]. Its molecular chains are mainly composed of saturated C-C and C-H σ bonds, with highly localized electron clouds. The frontier orbital levels of the polymer are energetically remote from the vacant Pb 6p states and the relevant states of the iodoplumbate complexes. Therefore, the interior of POE lacks active sites capable of effective orbital overlap, electron donor-acceptor interaction or Lewis acid-base coordination with Pb^{2+} . Unlike polar polymers containing carboxyl, hydroxyl, ether oxygen or amine groups, POE does not provide a continuous coordination-decoordination hopping network, nor does it form solvated microdomains capable of stabilizing Pb^{2+} [18, 19]. Furthermore, the relative dielectric constant of POE is generally only on the order of 2, which is far lower than that of aqueous phases and polar polymer phases. The entry of Pb^{2+} into POE therefore requires a transfer from a high-dielectric ionic environment into a low-dielectric hydrophobic phase. The transfer incurs the cost of hydration-shell stripping and an increase in electrostatic self-energy [16, 20]. It is also disfavored by the low interfacial partition coefficient. At the electronic-structure level, the σ -bonding states of POE lack delocalizable π electrons and lone-pair electrons, making it difficult to lower the energy of the migration transition state of Pb species. At the materials-transport level, the chain-entangled regions and the local crystalline domains of POE restrict the nanoscale free volume. Consequently, hydrated Pb^{2+} , PbI_3^- , PbI_4^{2-} or Pb-organic acid complexes have difficulty forming continuous diffusion pathways [21, 22]. Therefore, Pb species in POE lack both a thermodynamically stabilizing environment, and kinetically accessible migration channels, and their flux toward the external soil-water-plant system is weakened.

Second, when Pb^{2+} , PbI_3^- , PbI_4^{2-} and Pb-organic acid complexes enter POE from the perovskite degradation region, they encounter a pronounced energy barrier associated with solvation and the dielectric contrast between the phases. First, Pb^{2+} is strongly stabilized by hydration in the aqueous phase or in the wet degradation layer [13, 16]. The Pb-O coordination distance in the first hydration shell is on the Å scale. The hydration stabilization energy can reach the order of 10^3 kJ mol^{-1} . Therefore, Pb species must undergo hydration-shell stripping and reconstruction of the coordination environment before entering POE. The migrating species must then cross from the high-dielectric ionic phase into the low-dielectric polyolefin phase [20, 22]. The relative dielectric constant of water and wet ionic environments is generally on the order of several tens, whereas that of POE is only about 2. This sharp decrease in dielectric constant substantially increases the electrostatic self-energy of ions and generates Born-type desolvation penalties, image-charge repulsion and interfacial partition penalties. Furthermore, the σ -bond electrons in the POE backbone are highly localized. The polymer also lacks the lone-pair electrons and π -conjugated electron clouds that might stabilize an ionic migration state [18]. It is therefore difficult for POE to stabilize the Pb migration transition state through induced dipoles, orbital hybridization or inner-sphere coordination. In other words, Pb species in the POE phase simultaneously lack thermodynamic solvation gain and electronic-structure stabilization pathways. As a result, the low-polarity chain segments, the low ionic affinity and the restricted free volume jointly reduce the cross-interface partition coefficient and the effective diffusion coefficient, further suppressing the flux of Pb from the perovskite source term toward the external soil-water-plant system [7].

Third, the hydrophobic barrier effect of POE markedly reduces the chemical-potential gradient and permeation flux of water molecules into the perovskite degradation region [5, 21]. The POE consists of low-polarity polyolefin segments and has a low surface energy. Accordingly, its water contact angle generally falls within the hydrophobic range. Its equilibrium water uptake is far lower than that of oxygen- or nitrogen-containing polar polymers. Consequently, water molecules have difficulty forming a continuous hydrogen-bond network or penetrating hydrated nanochannels inside the POE [23, 24]. This process first suppresses the formation of hydrated intermediate phases in MAPbI_3 and weakens the solvated dissociation of MA^+ , I^- and PbI_2 . The conversion of PbI_2 into Pb^{2+} , Pb-I complexes or Pb-organic acid complexes is also constrained. The relevant reactions depend on an aqueous environment for ionic solvation, proton transfer and ligand exchange [25, 26]. Furthermore, from an electronic-structure perspective, the lone-pair electrons and high dipole moment of water molecules can stabilize the vacant 6p orbitals of Pb^{2+} and lower the local charge-separation energy after Pb-I bond cleavage. The interior of POE lacks this highly polarizable solvent field and therefore cannot effectively stabilize hydrated Pb transition states. From the perspective of diffusion kinetics, the reduction in the water flux also reduces the perovskite hydrolysis rate, the dissolved concentration of Pb species, the interfacial concentration gradient and the rhizosphere-available Pb activity [18]. As a result, Pb migration is not simply blocked at the downstream stage, but is continuously weakened from the initial steps of MAPbI_3 hydration, PbI_2 dissolution, Pb^{2+} solvation and plant-rhizosphere transport.

Fourth, the elastic chain segments of POE do not mean that high-flux ion channels exist inside the polymer. Instead, the crystalline lamellae, amorphous chain-entanglement regions and densely packed chain segments form a tortuous nanoscale diffusion network in the POE [5, 15]. Pb^{2+} , PbI_3^- , PbI_4^{2-} and Pb-organic acid complexes usually carry hydration shells in a humid environment, and their effective hydrodynamic radii are substantially larger than those of H_2O , O_2 or small organic molecules. Once the Pb species enter the POE, their transport is restricted by the pore size of the free volume, the segmental relaxation time and the interfacial partition coefficient. Furthermore, the nonpolar σ -bonded backbone of POE lacks polarizable coordination sites, and therefore cannot stabilize local charge rearrangement during Pb migration or lower the transition-state energy for ions crossing interchain voids [22, 27]. Thus, the Pb transport differs from simple diffusion driven by a concentration gradient. The effective migration is controlled by the activation barriers, pathway tortuosity and dynamic free volume. The ionic radius, solvation shell and complexation geometry amplify the steric-exclusion effects [18]. Accordingly, the effective diffusion coefficient may be several orders of magnitude below that of small water-vapor molecules. Ultimately, through semicrystalline blocking, chain-entanglement sieving, nanoscale free-volume compression and low-polarity interfacial repulsion, the POE encapsulation layer converts the migration pathway of Pb from the perovskite source term to the external environment into a low-flux, high-barrier and strongly hysteretic diffusion process [21].

Fifth, from an electronic-structure perspective, POE is a typical saturated polyolefin medium with a wide bandgap, low polarizability and low density of states. Its valence band is mainly composed of localized C-C and C-H σ -bonding orbitals, whereas its conduction band is dominated by high-energy σ^* antibonding orbitals, with a bandgap usually on the order of several eV [18]. Therefore, the POE provides virtually no continuous electronic states near the Fermi level for charge exchange. First, the vacant 6p orbitals of Pb^{2+} and the antibonding orbitals of Pb-I complexes are difficult to match energetically with the deep σ orbitals of POE. Second, POE lacks a π -conjugated backbone, lone-pair electron donors and highly polarizable heteroatoms [19, 23]. The orbital-overlap integral is therefore extremely small, and the charge-transfer matrix element is markedly suppressed. Furthermore, the migration of a Pb species may require local charge rearrangement and short-range electronic polarization to lower the activation barrier. The low dielectric response and low electronic polarizability of POE cannot provide this stabilization. As a result, Pb^{2+} , PbI_3^- , PbI_4^{2-} or Pb-organic acid complexes cannot establish continuous migration chains inside POE through redox coupling, Lewis acid-base coordination, inner-sphere complexation or electronically coupled assisted hopping [18]. Their transport is therefore dominated by unfavorable physical diffusion pathways. The large energy-level mismatch, weak orbital coupling, low polarization stabilization and absence of suitable electronic states impose additional restrictions. In other words, the suppression of Pb migration by POE arises not only from a geometric barrier, but also from its intrinsic insulating-barrier characteristics at the electronic-structure level: no available states to occupy, no orbitals to couple and no coordination sites to stabilize Pb species [7].

Sixth, the cross-phase migration of Pb^{2+} is also strongly limited by coordination-chemical selectivity. The Pb^{2+} ion has a relatively large ionic radius, high electronic polarizability and a pronounced soft Lewis-

acid character [20, 28]. It therefore favors chemical environments that provide strong coordination stabilization. Specifically, the I⁻, S sites, N sites, carboxylates, hydroxyl oxygen and inorganic oxygen defects can all stabilize the Pb center through lone-pair electron donation, inner-sphere coordination or hard-soft acid-base matching [6, 7]. The resulting Pb-I, Pb-S, Pb-N or Pb-O interactions can redistribute the local charge density and weaken the electrostatic penalty of the bare Pb²⁺ ions. They can also stabilize the asymmetric coordination environments associated with the 6s² lone pair. In contrast, POE contains only low-polarity C-C and C-H σ bonds. Its chain segments lack lone-pair electrons, π electrons, heteroatom coordination sites and dissociable functional groups, and thus exhibit extremely weak Lewis basicity and local dipole moments [22]. Therefore, after Pb species enter the POE phase, they cannot obtain effective coordination-field stabilization and can hardly form reversible adsorption-desorption sites. The transfer of Pb²⁺ from an I-, O-, N- or S-containing environment into the POE phase thus removes much of the initial coordination stabilization. This process is accompanied by a decrease in coordination number, loss of solvation free energy, interfacial partition penalty and local charge destabilization [18]. Therefore, Pb species have a higher chemical potential in POE and a markedly lower equilibrium partition coefficient. Ultimately, the POE acts neither as a favorable transport phase nor as an enrichment phase for Pb. Instead, it behaves more like a coordination-inert, low-polarity and low-affinity repulsive phase, thermodynamically suppressing the partitioning of Pb from the perovskite degradation region to the external environment.

Seventh, the POE encapsulation can reduce the generation of migratable Pb species at the source. The barrier limits the access of external oxygen, water and rhizospheric organic acids to the perovskite/metal-electrode interface [23, 24]. Under unencapsulated conditions, H₂O can induce MAPbI₃ lattice hydration, hydrogen-bond perturbation and MA⁺ destabilization. O₂ can participate in photoinduced superoxide-radical reactions. And, the acidic rhizospheric exudates can promote ligand exchange and complexation-driven dissolution of PbI₂. Together, the reactions can disrupt the Pb-I octahedral network. The degradation products may include PbI₂, Pb-O, Pb-OH, Pb-carboxylate and soluble Pb-organic acid complexes [22, 25]. By contrast, the low-polarity segments and the hydrophobic POE interface can reduce the permeability of O₂ and H₂O. The encapsulation also limits the contact of organic acids with the device edges, grain boundaries, pinholes and electrode defects. Furthermore, POE lacks a high-dielectric solvent field and proton-transfer network, and therefore cannot effectively stabilize the ionized transition state after Pb-I bond cleavage [5, 21]. As a result, the activation pathway for the conversion of MAPbI₃ from a solid-state lattice into soluble Pb species is elevated, while the interfacial reaction-rate constant and local Pb activity decrease simultaneously. Thus, the encapsulation does more than obstruct Pb after the migration begins. Rather, it reduces the strength of the Pb source term during the precursor reaction stages of hydration, oxidation, acid corrosion, complexation and dissolution, thereby markedly decreasing the Pb concentration available for subsequent diffusion and plant uptake [28].

Eighth, a continuous conformal POE coating alters the boundary conditions and the transport topology of Pb leakage from the fiber device. In unencapsulated devices, pinholes, microcracks, exposed grain-

boundary regions, Au-electrode edges and interlayer delamination zones can constitute high-flux percolation channels [5, 15]. The defect-rich regions have higher surface energies, stronger capillary uptake and shorter diffusion lengths. Consequently, water, O₂, organic acids and Pb species can migrate through the connected defect network. After POE coverage, the low-surface-energy polyolefin phase can fill or cover these high-energy defect sites and reduce the localized chemical-potential gradients at crack tips, grain-boundary steps and electrode edges [29, 30]. The adhesion between the POE and the outer device surface can also weaken capillary condensation, interfacial wetting and local electrolyte enrichment. The initially connected leakage network can therefore become divided into discrete and tortuous microdomains. At the electronic-structure level, POE lacks polar functional groups capable of stabilizing Pb²⁺ or Pb-I complexes [18]. Therefore, the blocked defect sites can hardly continue to act as coordination relay stations for Pb migration. As a result, the Pb transport shifts away from low-impedance defect diffusion and edge percolation. The remaining migration is constrained by the interfacial partitioning, bulk diffusion, segmental free volume and low-polarity repulsion [27]. Ultimately, through defect passivation, percolation-network disruption, reduced interfacial energy and extended diffusion pathways, the encapsulation layer suppresses the outward Pb leakage flux to a level that is difficult to accumulate significantly within the experimental time scale.

Ninth, even if trace Pb species enter the POE, their release on the outer side remains constrained by transient diffusion and the interfacial partition equilibrium [13, 16]. First, the effective diffusion of Pb²⁺, PbI₃⁻, PbI₄²⁻ or Pb-organic acid complexes in POE is not determined by a single concentration gradient, but is jointly controlled by the cross-interface partition coefficient, segmental free-volume distribution, diffusion-path tortuosity and local activation energy. The low-polarity environment of the POE also reduces the thermodynamic solubility of the Pb species in the encapsulation. Hence, a high internal source concentration does not necessarily produce a comparable concentration gradient at the outer surface. The encapsulation thickness, interfacial hysteresis and distribution of the nanoscale free volume further extend the characteristic diffusion time [18]. The Pb release may consequently be delayed. This process is no longer rapid ionic transport in an aqueous phase, but a low-flux mass-transport process limited by polymer-segment relaxation, transient void formation and interfacial redistribution. Meanwhile, plant rhizospheric uptake depends on soluble Pb activity, root-surface complexation, apoplastic transport and xylem loading [5, 21]. When the outward Pb flux is insufficient to establish a bioavailable rhizospheric concentration, the Pb signal accumulates only weakly in the plant tissues. Therefore, within the 90-day experimental time scale, POE can jointly reduce outer-side Pb release through a low partition coefficient, long diffusion pathway, low free-volume connectivity and strong temporal hysteresis, making it difficult for Pb to reach an effective concentration that can be stably absorbed by plant roots and transported to the shoots [28].

Tenth, the flexible encapsulation of POE can also suppress Pb exposure at the level of the mechanical source term. Under bending, friction with soil particles, wet-dry cycling and local compression, the fiber-based devices develop stress concentrations [15, 31]. The most vulnerable regions include the perovskite grain boundaries, interlayer interfaces, electrode edges and encapsulation defects. Without a

compliant encapsulation, the local tensile strain can be transferred directly to the brittle MAPbI₃ layer. This increases the stress intensity near crack tips and promotes grain debonding, interlayer delamination and perovskite pulverization [32, 33]. POE possesses a low elastic modulus, high elongation at break and pronounced viscoelastic energy-dissipation capability. Its elastic modulus is typically on the order of MPa to tens of MPa, far lower than those of inorganic perovskites and metal electrodes. Therefore, the POE can dissipate part of the mechanical loading through chain-segment relaxation, reversible conformational changes and interfacial shear [34]. Furthermore, the continuous coating of POE can reduce crack-tip opening displacement and weaken interfacial fatigue caused by wet-dry cycling. Its low-polarity σ -bonded backbone also reduces the adsorption capacity of water molecules and polar rhizospheric exudates at the interface, thereby alleviating water-induced plasticization, acid corrosion and interfacial embrittlement. As a result, the Pb source term in the device is less likely to be converted from an intact lattice or residual PbI₂ phase into detachable particles and soluble migratable species [5, 26]. Overall, the stress buffering and crack blunting reduce interfacial debonding, wet-dry fatigue and the formation of detached perovskite particles. These effects can change the Pb release from an abrupt damage-driven process to a slower process governed by the integrity of the encapsulation.

Taken together, the ten mechanisms describe a multiscale barrier rather than a simple physical cover [5, 18]. The proposed protection combines the low-polarity dielectric environment, limited water uptake, unfavorable ionic coordination, desolvation penalties and weak electronic coupling. The restricted free volume, tortuous diffusion paths, interfacial defect sealing and reduced generation of soluble Pb species provide additional contributions [7, 15].

3.4. Analytical limitations and future validation

The preceding analysis supports the use of FAAS as a practical and relatively inexpensive first assessment of Pb accumulation in the plant-derived extracts. Nevertheless, the resulting signal reflects the extractable or total Pb content only under the selected digestion and extraction protocol [14, 17]. It does not directly resolve Pb speciation, nanoscale distribution, root uptake pathways, or the dynamic release process from the encapsulated device. Future studies should therefore combine FAAS with more sensitive and spatially resolved techniques [13, 18]. Inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectroscopy (ICP-OES) could be used to quantify trace Pb with lower detection limits and broader elemental coverage. Graphite furnace atomic absorption spectroscopy (GFAAS) may further improve sensitivity for small-volume plant or soil extracts. X-ray fluorescence spectroscopy (XRF), micro-XRF and laser ablation ICP-MS (LA-ICP-MS) could map the Pb distribution in the roots, stems and leaves [16, 22]. The resulting maps would help distinguish Pb retained near the root surface from Pb transported into the shoots. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) would be particularly valuable for identifying Pb chemical states, coordination environments and possible Pb-O, Pb-S, Pb-I or Pb-organic ligand species [22, 28]. In addition, soil-pore-water analysis, sequential extraction, diffusion-gradient-in-thin-films methods, and isotope-labeling experiments could help distinguish soluble Pb, weakly adsorbed Pb, mineral-bound Pb and plant-bioavailable Pb. Therefore, the FAAS-based bioindicator experiment

provides initial laboratory evidence of reduced Pb migration with encapsulation. A full environmental-risk assessment would additionally require multi-technique quantification, chemical speciation, spatial imaging and longer-term soil-plant exposure tests [3, 13].

4. Prospects for further improvement of fiber-based perovskite solar cells

Beyond the environmental assessment, further advances in fb-PSCs require coordinated control of the photocarrier generation, interfacial recombination, cylindrical-film continuity, mechanical fatigue and Pb containment. In the previously published $\text{Ti/SnO}_2\text{:MAPbI}_3\text{/MAPbI}_3\text{:PJ71/spiro-OMeTAD/Au}$ architecture, the champion power conversion efficiency (PCE) reached 10.66%, with $J_{\text{sc}} = 14.38 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 1.038 \text{ V}$ and a fill factor (FF) of 71.43% [8]. The 25-device average PCE was $10.09 \pm 0.26\%$. After 500 bending cycles with a radius of 5.0 mm, the optimized device retained 84.3% of its initial PCE [8, 9]. For the 1.57 eV perovskite bandgap, the corresponding voltage deficit, $E_g/q - V_{\text{oc}}$, is approximately 0.532 V [35].

These figures identify three distinct priorities: increasing the absorption-limited current, reducing the nonradiative voltage loss and preserving electrically continuous pathways under repeated deformation. The 90-day plant-based Pb assay establishes a fourth consideration: the improved photovoltaic performance must be accompanied by effective containment of releasable Pb [5, 15].

4.1. Photovoltaic-layer chemistry and crystallization

At the photovoltaic-layer level, the first opportunity is to control the precursor coordination, nucleation kinetics and lattice microstrain on the curved Ti surface. The previously optimized PJ71 concentration of 100 ppm provides a reference for screening multifunctional conjugated polymers, including PJ71, P3HT, PTAA, PBDTTPD and thiophene-rich donor-acceptor copolymers [8, 36, 37]. The complementary polar additives include poly(vinylpyrrolidone), poly(ethylene oxide), poly(methyl methacrylate), thiourea, succinic acid, ammonium thiocyanate and ethylenediammonium diiodide [26, 38, 39]. The candidates could be investigated individually or as carefully controlled binary combinations [40]. S-, N- and O-donor groups can coordinate undercoordinated Pb^{2+} , while ammonium and halide species may regulate iodine vacancies, V_{I} , and local ionic redistribution [41–43]. A rational screening matrix could vary the additive concentration from 10 to 300 ppm and the layer thickness from 300 to 800 nm. The optimum should then be established experimentally, rather than inferred from planar devices. Mixed-A-site and mixed-halide formulations, including FAPbI_3 , CsPbI_3 and $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$, deserve comparison with MAPbI_3 for phase stability and bandgap control [36, 37]. The compositional screening should be accompanied by X-ray diffraction, grazing-incidence wide-angle X-ray scattering, spatially resolved photoluminescence and time-resolved photoluminescence [39, 44]. These measurements can distinguish genuine trap passivation from changes in the crystallization or optical absorption alone.

The second priority concerns the charge-selective contacts. The original $\text{SnO}_2\text{:MAPbI}_3$ electron-transport layer improved interfacial integrity, but residual hydroxyls, oxygen vacancies and poorly contacted

nanocrystals may still contribute to Fermi-level pinning and recombination [45, 46]. Ultrathin interlayers based on Al_2O_3 , MgF_2 , LiF , CsF , potassium salts or phosphonic-acid-functional molecules could be screened over nominal thicknesses of 0.5-3 nm [24, 46]. The electron tunneling pathway must remain sufficiently conductive [45]. Alternative electron-contact candidates include TiO_2 , Nb_2O_5 and appropriately modified ZnO , whose chemical compatibility with methylammonium perovskites must be tested [45]. At the upper junction, phenethylammonium iodide, fluorophenethylammonium iodides, butylammonium iodide and diammonium salts offer tunable surface dipoles and low-dimensional interfacial phases [24, 47]. The concentration, molecular orientation and phase thickness require careful control [40]. An excessively insulating two-dimensional layer can lower J_{sc} and FF even when V_{oc} increases [48, 49]. Spiro-OMeTAD could also be compared with PTAA, P3HT, NiO , CuSCN or CuI , with attention to work-function alignment, contact resistivity and bending-induced delamination [10, 50, 51]. As a quantitative benchmark, a tenfold increase in the calibrated external photoluminescence quantum yield would reduce the nonradiative voltage loss by approximately 59.5 mV at 300 K, provided that the generation rate and optical outcoupling remain comparable [35, 47].

The optical and electrical optimization should treat the fiber device as a cylindrical multilayer, rather than relying exclusively on a locally planar approximation. For a 250 μm -diameter Ti core, the circumferential incident angle and polarization vary continuously even under collimated illumination [1, 8]. Angle-resolved finite-difference time-domain calculations could incorporate the measured $n(\lambda)$ and $\kappa(\lambda)$ from spectroscopic ellipsometry [52, 53]. The resulting model could quantify the parasitic absorption in the Au contact, the redistribution of optical interference and the photogeneration profile over 300–900 nm. The reported 10 nm Au thickness is an appropriate starting point, although its continuity, optical transmission and resistance after bending must be measured jointly [8]. Hybrid transparent conductors that combine ultrathin Au with graphene, carbon nanotubes or Ag nanowire networks may improve the balance between the sheet resistance and the optical transparency [54, 55]. Such structures would require control of metal-ion diffusion and corrosion [56]. Outward-facing $\text{SiO}_2/\text{MgF}_2$ antireflection structures and optically textured POE could further improve angular light harvesting without exposing the perovskite to a reactive photocatalytic surface [57–59]. Importantly, the optical gain should be verified through an increase in the integrated J_{sc} , rather than inferred from the simulated absorptance alone [60, 61]. Earlier studies on crystalline and amorphous silicon nanostructures also provide transferable computational methods for broadband light management [62, 63]. However, their optical constants and charge-collection assumptions cannot be transferred directly to the fiber-based perovskite device [60, 61].

4.2. Mechanical fatigue and strain management

Mechanically, the Ti-core diameter sets an important first-order constraint. At a bending radius $R = 5.0$ mm, a 250 μm -diameter core experiences an approximate outer-surface geometric strain $\varepsilon_{\text{out}} \approx r/R = 2.5\%$, whereas a 100 μm core would approach 1.0% under the same idealized curvature [9, 32]. The estimates do not account for the redistribution of the strain among the perovskite, metal, polymer and encapsulation layers [9]. Nevertheless, they illustrate the potential benefits of a smaller substrate

diameter, higher interfacial fracture energy and displacement of the brittle layers toward the composite neutral axis [33, 64]. Elastomer-compatible materials, including thermoplastic polyurethane, styrene-ethylene-butylene-styrene, poly(vinylidene fluoride-co-hexafluoropropylene) and stretchable polyurethane acrylates, should be assessed as compliant interlayers rather than indiscriminately mixed into the photovoltaic phase [15, 31, 34]. The cross-sectional electron microscopy, nanoindentation, cyclic electrical mapping and cohesive-zone finite-element modeling could then connect the loss of layer conductance to the crack density, energy-release rate and interfacial adhesion [9, 56]. A prospective endurance benchmark is at least 90% PCE retention after 1000 cycles at $R = 5$ mm, followed by separate wet-dry and torsional fatigue tests [65, 66].

The final priority is to couple the efficiency improvements with quantitative Pb-containment engineering. The existing 100–150 μm POE encapsulation suppresses Pb transfer in the laboratory soil-plant configuration, but the polymer alone does not constitute an impermeable inorganic barrier [5, 8]. A multilayer encapsulation could combine the POE with conformal $\text{Al}_2\text{O}_3/\text{SiO}_2$ or $\text{Al}_2\text{O}_3/\text{HfO}_2$ nanolaminates [6, 27]. Mechanically segmented architectures may then help the inorganic barriers resist channel cracking. An independent, electronically insulated Pb-scavenging layer could contain thiol-functionalized mesoporous silica, phosphate-bearing particles, hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or immobilized chelating ligands [7, 20, 22]. Such a layer could intercept the Pb released after localized damage. Potential photochemical instability, ligand leaching and any adverse changes in moisture permeability must be excluded before deployment [19, 23]. The proposed screening targets include a water-vapor transmission rate no greater than $10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$ for the complete flexible barrier and stable maximum-power-point operation for 1000 h [65, 66]. The Pb release should also be reported in $\mu\text{g device}^{-1}$, as a fraction of the initial Pb inventory and per illuminated area [13]. These are proposed qualification targets, not measurements from the present study.

The combined opportunities can be illustrated using two numerical scenarios. If the contact, optical and microstructural improvements increased J_{sc} to 17.0 mA cm^{-2} , V_{oc} to 1.10 V and FF to 77%, the standard one-sun efficiency would reach 14.4% [8]. A more demanding combination of 20.0 mA cm^{-2} , 1.13 V and 80% would correspond to an efficiency of 18.1% [35, 49]. The higher value would require experimental verification of the spectral response, voltage losses and aperture-area normalization. Neither value is an achieved device result or a prediction that a single additive will deliver. The central research objective is therefore to co-optimize the defect thermodynamics, carrier-selective energetics, full-circumference light harvesting, strain-driven damage kinetics and Pb-release mass balance. A fiber photovoltaic platform that improves all five quantities simultaneously would offer a more meaningful advance than maximizing peak PCE without demonstrating mechanical and environmental durability [32, 65].

5. Conclusions

In conclusion, the laboratory bioindicator results indicate that the POE encapsulation substantially suppresses Pb migration from the fiber-based MAPbI_3 devices under the tested soil-water-plant

exposure conditions. The reduced Pb signal detected in *pogonatherum crinitum* is consistent with a multiscale physicochemical barrier, rather than a passive plastic cover. The encapsulation limits the migration of Pb species available to the plant. This effect arises from the intrinsically nonpolar polyolefin backbone, low dielectric constant, low water uptake, absence of coordination sites and restricted nanoscale free volume of POE. The features jointly impose desolvation penalties, interfacial partition barriers, weak electronic-state coupling and tortuous diffusion pathways for Pb^{2+} , iodoplumbate complexes and Pb-organic acid species. In addition, the hydrophobic conformal coating limits the ingress of H_2O , O_2 and rhizospheric organic acids. The barrier can consequently suppress MAPbI_3 hydration, PbI_2 dissolution, ligand exchange and the formation of soluble Pb species at the device interface. The viscoelastic POE also mitigates bending-induced cracking, wet-dry fatigue, interfacial delamination and perovskite pulverization. Consequently, the risk of mechanically triggered abrupt Pb release is reduced. Importantly, *pogonatherum crinitum* should be regarded as a laboratory bioindicator that reports bioavailable Pb migration rather than a complete ecotoxicological model. FAAS quantifies the total Pb signal under defined digestion conditions and cannot resolve Pb speciation or fully represent ecological risk. Nevertheless, the combined encapsulation and bioindicator strategy provides a practical approach for evaluating the Pb-retention performance of perovskite devices. The results demonstrated the POE as an effective, low-cost and mechanically compatible encapsulation layer for reducing Pb exposure risks in flexible perovskite technologies.

Declarations

Author's Note

This independent post-publication study provides a laboratory bioindicator assay to evaluate whether POE encapsulation can suppress the Pb leakage from fiber-based perovskite solar cells. The resulting evidence concerns the laboratory bioindicator response. It does not constitute a complete ecotoxicological risk assessment.

The purpose of the preprint is to provide readers with a fuller account of the environmental-safety rationale behind my fiber-based perovskite solar-cell study. The published journal article focused mainly on device optimization, mechanical durability, and photovoltaic performance. After its publication, I independently carried out additional experiments related to encapsulation, lead-leakage suppression, and environmental compatibility. Because the additional results cannot be incorporated retrospectively into the published article, they are reported here in an independent open research note.

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Figures

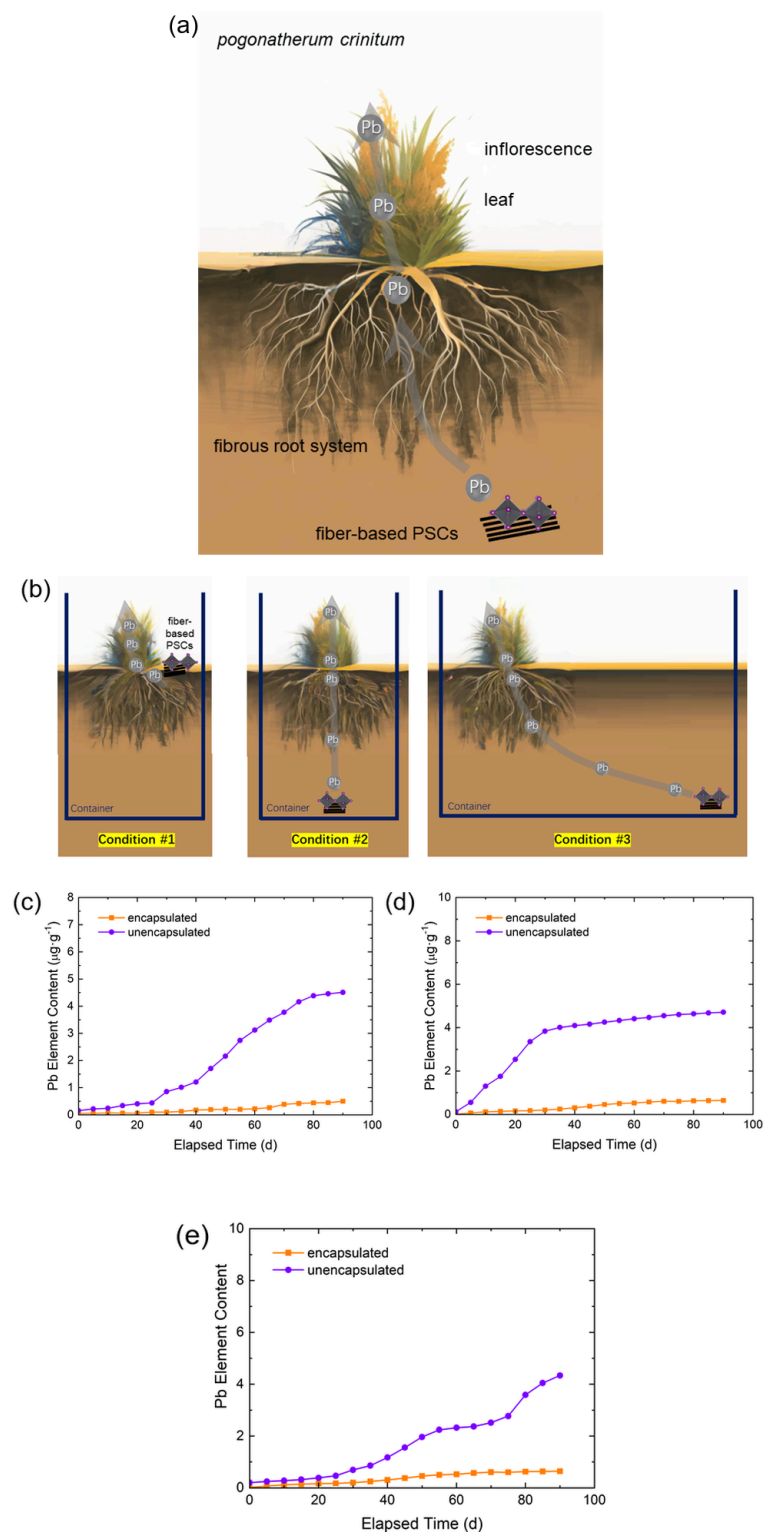


Figure 1

(a): Illustration of Pb leakage process from PSC to *pogonatherum crinitum*. (b): Illustrations of Pb leakage experimental settings. (c)~(d): Effect of environment storage time on Pb element content in the plant-derived extract for Conditions #1~#3.

Supplementary Files

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