Green Revolution in Perovskite Solar Cells: Advancements in Lead-Free Perovskite Solar Cells and Eco-Friendly Fabrication Processes

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Abstract:

Perovskite solar cells (PSCs) have attracted considerable attention in the field of photovoltaics owing to their high power conversion efficiency (PCE), cost-effective production methods, and versatile applications. However, the widespread use of lead (Pb)-based materials in PSCs poses challenges related to their toxicity and environmental sustainability. This review explores recent advances in the development of Pb-free perovskite materials, such as tin (Sn)-based, germanium (Ge)-based, and other B(IV) and B(III) cation alternatives, while assessing their electronic properties, stability, and performance-enhancing strategies. Additionally, we discuss the use of green solvents and fabrication techniques to minimize their environmental impact. This review aims to guide future research toward safe, efficient, and environmentally sustainable PSC technologies, ensuring that the benefits of solar energy can be harnessed without compromising human health or the environment.

1. Introduction

Perovskite solar cells (PSCs) have emerged as a ground-breaking technology in the field of photovoltaics owing to their unique crystal structure and exceptional optoelectronic properties—including tunable direct bandgap, high absorption coefficient, long carrier lifetime, and extended diffusion length. Their versatility in material composition and fabrication methods enables the creation of flexible, lightweight, and semitransparent solar cells, potentially revolutionizing the solar energy market.

The perovskite structure is generally represented by the formula ABX3, where ‘A’ denotes a monovalent cation (such as methylammonium (MA), formamidinium (FA), or cesium (Cs)), ‘B’ denotes a divalent metal cation (usually lead (Pb)), and ‘X’ denotes a halide anion, as shown in Figure 1A. In the perovskite crystal structure, the central cation is octahedrally arranged with six anions. Figure 1B compares the electronic structures of two types of semiconductors—that is, typical III–V, II–VI, and group IV semiconductors (left) and lead halide perovskites (right). The left-hand side of the diagram shows semiconductors with “deep states,” defects within the bandgap that cause charge carrier recombination and reduce efficiency. By contrast, the lead halide perovskites shown on the right-hand side have “shallow states,” where defects are near the conduction or valence band edges, making them less likely to trap charges and less harmful to the carrier lifetime.1 Since methylammonium lead iodide (MAPbI3) PSCs were developed in 2009, PSCs have rapidly achieved power conversion efficiencies exceeding 26%, comparable to traditional silicon-based solar cells.2 However, the widespread use of Pb-based compounds in traditional PSCs has resulted in considerable toxicity and environmental challenges. Exposure to Pb can cause serious health problems, particularly neurological damage in children, and poses risks to multiple organs, even at low levels (Figure 1C). Additionally, Pb can leach into soil and water during the production, operation, and disposal of PSCs, leading to widespread contamination. The environmental impact of PSCs is exacerbated by their instability under moisture, heat, and ultraviolet (UV) light, which accelerate their degradation and increase the risk of Pb release. Moreover, conventional PSC fabrication processes rely heavily on toxic and volatile organic solvents—such as N, N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO)—which pose considerable environmental pollution and health risks (Figure 1D). Addressing these challenges is crucial for the sustainable development of PSC technology. To address these concerns, ongoing research has been focused on developing Pb-free perovskite materials and green solvent-based perovskites that can maintain or enhance the performance and stability of PSCs. This review examines recent advances in low-toxicity perovskite materials and environmentally friendly solvents, providing insights into the efficiency, stability, and future of eco-friendly PSCs.

2. Lead (Pb)-free Perovskite Materials

With growing concerns about the toxicity of Pb in PSCs, research has intensified to find suitable alternatives that maintain high efficiency while reducing environmental and health risks. This section explores the advancements in developing Pb-free perovskite materials, including the substitution of Pb with homovalent and heterovalent elements such as tin (Sn), germanium (Ge), and other B(IV) and B(III) cations. It also discusses the strategies employed to enhance the stability and performance of these Pb-free PSCs.

2.1 Homovalent-substituted lead (Pb)-free perovskites

In the quest to develop Pb-free PSCs, substituting Pb with homovalent elements like Sn and Ge has gained significant attention. These elements share similar electronic properties with Pb, making them promising candidates for maintaining the desirable optoelectronic characteristics of perovskite materials. However, replacing Pb introduces new challenges, such as increased material instability and the formation of defects, which need to be addressed to achieve commercially viable Pb-free PSCs.

2.1.1 Sn-based PSCs

Sn has emerged as a promising candidate to replace Pb in PSCs because of its similar electronic configuration and the presence of lone-pair orbitals in both elements, offering a potential solution to environmental and health concerns associated with Pb toxicity. Extensive research on Sn halide perovskites has shown that Sn halide perovskites possess favorable properties for photovoltaic applications—such as a high light absorption coefficient, small exciton binding energy, and high charge carrier mobility.3,4,5,6

Figure 2A illustrates the progress in the power conversion efficiency (PCE) of the Sn-based PSCs over time. From 2015 to 2024, there has been a notable increase in efficiency with different compositions, including MASnI3, FASnI3, and CsSnI3. In 2014, Kanazidis achieved a PCE of 5.73% for Sn-based Pb-free PSCs using methylammonium tin iodide (CH₃NH₃SnI₃) perovskite semiconductors.7 Figure 2B shows Sn-based perovskite materials—such as MASnI38, FASnI39, and CsSnI310—with bandgaps of 1.26 eV, 1.4 eV, and 1.3 eV, respectively. These three materials exhibit type-II band alignment, with a considerable conduction-band mismatch (exceeding 0.3 eV). This mismatch increases the recombination rate, resulting in a severe open-circuit voltage (VOC) loss. This effect is more pronounced in highly p-doped Sn-based perovskites, where the type-II band alignment further promotes carrier recombination, adversely affecting device performance. Figure 2C shows a schematic representation of the molecular orbital and band gap formation in the alloy MA(Pb1–xSnx)I3. Here, the valence-band maximum is composed primarily of antibonding states from the Sn s and I p orbitals, whereas the conduction-band minimum involves antibonding interactions between the Sn p and I p orbitals. Compared to lead halide perovskites—which feature “shallow states” near the band edges—Sn-based perovskites may exhibit “deep states” owing to defects, which lead to increased charge carrier recombination and reduced efficiency. This highlights the role of Sn and Pb in determining the electronic properties of alloys. Figures 2D and 2E show the Frost diagrams for Sn and Pb constructed by Saidaminov et al., revealing that the +2 oxidation state is thermodynamically favored for both Pb and Sn. Moreover, the more positive reduction potential of Pb⁴⁺ relative to Sn⁴⁺ indicates a greater thermodynamic driving force for the reduction of Pb⁴⁺. Consequently, Sn²⁺ exhibits a higher propensity for oxidation compared to Pb²⁺.11 The oxidation of Sn²⁺ is often considered a primary cause of the degradation of Sn-based perovskites, leading to device instability. Consequently, suppressing the oxidation of divalent Sn ions is crucial for improving the performance of Pb-free, Sn-based PSCs.

2.1.2 Strategies to mitigate oxidation in Sn-based PSCs

The realization of highly efficient Sn-based PSCs can be hindered by Sn²⁺-induced defects owing to low defect tolerance, leading to Sn vacancies and easy oxidation to Sn²⁺. To overcome these challenges, multiple methods—including additive strategies and surface passivation techniques—have been explored to prevent or reduce Sn2+ oxidation and improve the longevity and effectiveness of Sn-based PSCs.

One common method involves the incorporation of antioxidants—such as SnX₂ (X = F⁻, Cl) and their derivatives—which can act as Sn sources to suppress Sn oxidation and stabilize the perovskite phase. For example, Mathews et al. and Mhaisalkar et al.24 and Hatton et al.25 demonstrated that the addition of SnF₂ and SnCl₂ in CsSnI₃-based solar cells effectively suppressed Sn vacancies and pinholes during formation, leading to considerably enhanced device performance and high fill factors. Additionally, the addition of metallic Sn powder to the precursor solution26 and chlorine doping27 exhibited a substantial oxidation-inhibiting effect, suppressing the formation of detrimental Sn4+ defects and improving the overall device performance.

In addition to tin halides (SnX2) and their derivatives, hydrazine, and other organic additives have been introduced to suppress Sn oxidation. For example, hydrazine and its derivate hydrazine dihydrochloride28,29 have been incorporated in Sn-based PSCs to restrain the formation of Sn⁴⁺ impurities and passivate defect states and hysteresis, resulting in improved PCE. Moreover, guanidine thiocyanate (GASCN)30 has been reported to effectively passivate trap states and prevent Sn²⁺ oxidation, leading to improved charge carrier dynamics and device stability. Even with antioxidants introduced to prevent rapid oxidation, they often degrade into inactive byproducts after a single redox reaction. To address this problem, vanillin—a novel dual-stage antioxidant—has been proposed to enhance the stability and efficiency of Sn-based PSCs. Moreover, vanillin effectively suppresses Sn²⁺ oxidation, improves perovskite crystallization, and enhances light absorption, as shown in Figure 3A. The resulting devices exhibit high efficiencies and remarkable stability recovery upon microwave irradiation.31

Although antioxidative additives primarily address the issue of Sn²⁺ oxidation in Sn-based PSCs, surface passivation can be employed to mitigate the adverse effects of defects at grain boundaries and the perovskite/charge transport layer (CTL) interface. Yin and Zhang et al. demonstrated that thioamide-based surface passivation was effective for enhancing the optoelectronic properties of CsSnI perovskite thin films. As shown in Figure 3B, Sn²⁺-induced defects can be situated both at the surface and within the bulk of the perovskite crystal grains. The passivation strategy effectively reduces the defect density, leading to improved carrier dynamics and device performance. The resulting all-inorganic CsSnI₃ solar cells exhibit a PCE of 8.20% with remarkable stability.32 Hayase, Shen, and Chen also reported that the efficacy of trimethylsilyl-halide-based surface passivation in enhancing the performance and stability of Sn-based PSCs; the trimethylsilyl-halide-based surface passivation strategy effectively improved film quality, reduced defect density, and formed a hydrophobic protective layer. The resulting devices exhibited an improved PCE (from 10.05% to 12.22%) and considerably improved long-term stability.33

Beyond antioxidant additives and passivation strategies, in 2023 Hayase, Shen, and Zhang et al. reported a novel method to suppress Sn⁴⁺ formation and reduce trap densities by introducing a bi-interface optimization strategy involving the insertion of thin Sn metal layers at both perovskite interfaces. As shown in Figure 3C and Figure 3D, the experimental results reveal that Sn⁴⁺ ions predominantly accumulate on the surfaces of Sn-based perovskites; the optimization strategy involving thermal evaporation of Sn metal at the interfaces of the perovskite layer is shown in Figure 3D, where Sn metal is inserted into both interfaces, though its uneven distribution leaves the bottom Sn layer ineffective in altering the wettability of the perovskite precursor on the PEDOT surface. This method effectively suppresses Sn⁴⁺ formation and reduces trap densities, resulting in a high PCE of 14.31% and enhanced device stability.34

2.1.3 Ge-based PSCs

Germanium (Ge)—a group IVA element similar to Pb—is a promising environmentally friendly alternative for PSCs. Substituting Pb with Ge, combined with inorganic cations such as cesium (Cs) and rubidium (Rb), offers a pathway toward high-performance, stable devices coupled with the incorporation of inorganic cations, and presents a promising pathway toward high-performance and stable perovskite devices.

As shown in Figure 4A, Kanatzidis et al. synthesized Ge-based perovskites—such as CsGeI3, FAGeI3, and MAGeI3—featuring [GeI₃]⁻ building blocks arranged around A-cation spacers. These compounds exhibit three structural types, with CsGeI3, FAGeI3, and MAGeI3 forming 3D frameworks of corner-sharing [GeI₆]⁴⁻ octahedra, demonstrating different unit cell parameters based on cation size.35 Mathews and Asta et al. measured the valence and conduction-band energies of CsGeI3, MAGeI3, and FAGeI3. Valence band (VB) positions for CsGeI3, MAGeI3, and FAGeI3 perovskites were experimentally determined to be -5.10 eV, -5.2 eV, and -5.5 eV, respectively. Conduction band (CB) energies were calculated from optical bandgap values, resulting in -3.47 eV, -3.2 eV, and -3.15 eV, respectively. A systematic decrease in VB energy was observed upon replacing Cs with MA and FA cations, revealing trends consistent with those of other metal halides (Figure 4B). Tauc plot analysis showed bandgap values of 1.63, 2.0, and 2.35 eV for CsGeI₃, MAGeI₃, and FAGeI₃, respectively (Figure 4C). While all three compounds exhibit bandgaps exceeding the Shockley-Queisser limit, CsGeI₃, with a bandgap closely matching that of CH₃NH₃PbI₃, holds particular promise for single-junction solar cell applications. The wider bandgap perovskites are well-suited for tandem solar cell configurations to achieve high open-circuit voltages. 36

Mixed Sn–Ge perovskites have also emerged as potential Pb-free alternatives. Liu’s first-principles calculations (Figure 4D) demonstrated that while localized and deep within the bandgap at x = 0.25 and 0.75, the defect state which is occupied by a single electron becomes delocalized and shallow at x = 0.5. This behavior is attributed to variations in orbital hybridization strength between the defective Ge atom and its neighboring cations. Weaker hybridization at x = 0.5 results in a higher energy occ1 state. These findings highlight the influence of alloy composition on defect state characteristics within the CsGe₁₋ₓSnₓI₃ system. The CsGe₀.₅Sn₀.₅I₃ composition effectively mitigates the adverse effects of both SnI and GeI anti-site defects, highlighting the role of alloying in optimizing the material properties, offering new avenues for optimizing perovskite materials and device performance.37 Additionally, Rath et al. enhanced device performance by incorporating bromide ions into methylammonium germanium iodide perovskite, achieving a peak PCE of 0.57% for MAGeI₂.₇Br₀.₃-based solar cells (Figure 4E and Figure 4F).38 Although this represents considerable progress, improving device stability remains a critical area for future research.

2.2 Hetero and Other Alternatives to lead (Pb) in perovskite solar cells

Although Sn and Ge are the primary candidates for replacing Pb in PSCs, other alternatives including tetravalent B(IV) and trivalent B(III) cations also showed a potential to substitute Pb. Tetravalent B(IV)39 cations— such as Ti4+ or Zr4+—require the perovskite structure to transform from the ABX₃ to the A₂BX₆ stoichiometry40, leading to a vacancy-ordered double perovskite structure with B-site vacancies to compensate for the increased cationic charge. This transformation typically results in a rock salt arrangement owing to the considerable charge difference between the remaining B-site cations and vacancies. Trivalent B(III) cations41,42 (Bi³⁺ and Sb³⁺), owing to their lone-pair electron configurations, alter the structure A₃B₂X₉ stoichiometry, creating cation vacancies.43 These materials typically exhibit dimeric or layered structures, with the dimeric structure featuring isolated [B₂X₉] bioctahedra and the layered structure resembling a vacancy-ordered layered perovskite. For example, compounds such as Cs₃Bi₂I₉ adopt a 0D structure with isolated [Bi₂I₉]³⁻ anions, whereas Cs₃Sb₂I₉44, Rb₃Sb₂I₉45, and Rb₃Bi₂I₉ exhibit 2D layered structures with corner-sharing MI₆ octahedra.

These structural variations dramatically influence the physical and optoelectronic properties of the materials. Studies have shown that the bandgap of these materials increases systematically from Cs₃Sb₂I₉ to Cs₃Bi₂I₉ as the structure evolves from a 2D layer to a 0D molecular form, influencing their optical properties. Additionally, the broad photoluminescence (PL) emission bands evident in these materials suggest strong electron-phonon interactions, which affect charge carrier dynamics by creating polarons, similar to the behavior observed in other materials such as alkali halides, AgBr, and organic-inorganic halide perovskites. Although Sn and Ge remain the primary candidates to replace Pb, B(IV) and B(III) cations provide alternative pathways, each with unique structural and optoelectronic characteristics that affect the performance and stability of Pb-free PSCs.

2.3 Stability

Stability can be a major challenge in the development of Pb-free PSCs because of their chemical reactivity and susceptibility to environmental factors (such as moisture, oxygen, and light). For example, Sn-based PSCs often oxidize from Sn²⁺ to Sn⁴⁺, creating defect states that degrade device performance. The organic-inorganic hybrid structure can also contribute to instability under operational conditions.

To address these problems, various strategies have been explored. Yin and Zhang adopted a thioamide passivation strategy using thiosemicarbazide (TSC) to interact with charge defects, enhance the carrier lifetime, and reduce nonradiative recombination. TSC-treated CsSnI3 PSCs achieved a PCE of 8.20% and retained over 90% of their initial efficiency after 500 h of continuous illumination, compared to 71% for untreated cells (Figure 5A).

Kim and Kwak et al. demonstrated that incorporating formate ions into formamidinium tin triiodide perovskites effectively mitigated Sn oxidation and passivates defects, resulting in enhanced device stability and efficiency. Figure 5B and Figure 5C show that under ambient air and continuous illumination conditions, formate-treated devices exhibit superior long-term stability compared to pristine devices, retaining over 80% of their initial efficiency after 180 min and 400 h,46 respectively.

Rath et al. introduced bromide ions into the methylammonium germanium iodide perovskite, leading to a considerable improvement in the solar cell performance along with a slight enhancement in the stability of the germanium perovskite.38 Figure 5D shows that bromide-containing perovskites exhibit reduced degradation, confirming the stabilizing effect of bromide. Additionally, a bi-interface optimization strategy—which involves the insertion of a thin Sn metal layer at both perovskite interfaces—was found to suppress Sn4+ formation and reduce trap densities, resulting in excellent operational and long-term stability (Figure 5E). This strategy shows promise for the commercialization of stable Pb-free PSCs.34

3. Less Toxic Fabrication of Perovskite Solar Cells

Despite the rapid advances in vacuum deposition techniques for PSC fabrication, high-efficiency PSCs still rely predominantly on solution-processing methods that use organic solvents. These solvents often pose considerable environmental and health hazards because of their inherent toxicity, volatility, and flammability. This section reviews the progress in the development of solution-processing techniques for PSC fabrication using less toxic and environmentally friendly solvents. It also highlights the challenges that need to be overcome and discusses the sustainability of eco-friendly processes.

3.1 Green solvents to fabricate perovskite thin films

The fabrication of PSCs using solution-processing techniques involves a well-defined sequence of steps—that is: (1) precursor solution preparation, (2) coating or printing the precursor solution, (3) solvent removal, and (4) crystallization of the thin film. The initial step involves preparing a precursor solution by carefully selecting the solvents that play a pivotal role in dissolving the perovskite precursors, influencing the crystallization process, and ultimately determining the quality of the perovskite film.

Polar aprotic solvents with high dielectric constants are typically used to dissolve these salts effectively. Dipolar aprotic solvents such as DMF, DMSO, gamma-butyrolactone (GBL), 2-methoxyethanol (2ME), N-methyl-2-pyrrolidone (NMP), and dimethylacetamide (DMAc) facilitate the dissolution of perovskite precursors through Lewis acid-base interactions. They act as Lewis base donors and coordinate with Lewis acid halide salts. This interaction promotes the dissociation of the halide salts and their subsequent dissolution in the solvent.

The choice of solvent is not merely a matter of dissolving the precursors; it affects the perovskite crystallization process and the overall quality of the perovskite film. Solvents influence the kinetics of crystallization, morphology of perovskite grains, and optoelectronic properties of the resulting film. Consequently, careful selection of the solvent is crucial for achieving highly efficient and stable PSCs.

The combination of DMF as the primary solvent and DMSO as the co-solvent has emerged as the most widely employed and successful approach for preparing perovskite precursor solutions. However, its widespread use is hindered by the inherent toxicity of DMF. DMF is associated with a range of adverse health effects including liver damage, digestive disturbances, and potential reproductive toxicity. These concerns have led to a workplace exposure limit of 15 mg⋅m−3, restricting the scalability of DMF-based fabrication processes for large-scale production.

Although DMSO is considered less toxic than other commonly used solvents, its high boiling point (189 °C at standard atmospheric pressure) poses a major concern. This elevated boiling point makes it difficult to remove DMSO completely from the perovskite precursor solution during film formation. Residual DMSO—even in small amounts—can have detrimental consequences on the long-term stability of PSCs.

Consequently, researchers are continuously exploring new green solvents and solvent combinations to optimize the fabrication process and enhance the performance of PSCs. An ideal solvent should possess the following characteristics:

1. High precursor solubility;
2. Intermediate phase formation ability leading to a uniform morphology and high crystallinity of the perovskite film;
3. Controlled solvent evaporation and crystallization kinetics to provide a wide processing window during coating or printing processes; and
4. Process safety, low toxicity, and environmental friendliness.

Antisolvents are often employed after the deposition of the precursor solutions for the fabrication of PSCs via solution processing. Although their application to large-area module fabrication can be challenging, antisolvents are widely used in single-step spin-coating processes to fabricate high-efficiency small-area devices. By introducing an antisolvent before the complete drying of the spun precursor wet film, rapid solvent extraction occurs, quenching the film microstructure. Subsequent thermal annealing controls the nucleation-growth process, enabling the formation of compact and uniform perovskite thin films.

The selection of antisolvents is primarily guided by their polarities and boiling points. The polarity influences the ability to extract solvents from the precursor film and the solubility of solutes. Generally, antisolvents with polarity values between 2.0 and 4.5 are employed. Moreover, the boiling point is associated with the contact time between the antisolvent and perovskite film, which affects the morphology and surface morphology of the film. The commonly employed antisolvents used for fabricating high-quality perovskite layers include diethyl ether (DEE), chlorobenzene (CB), chloroform (CF), and toluene (Tol). However, these solvents pose fire hazards and can be detrimental to human health.

Owing to the larger volume of antisolvent used compared to the precursor solution, the identification and application of green antisolvents with high safety and low toxicity are particularly crucial. Moreover, antisolvent-free fabrication methods are suitable for large-area scalable processes. In this review, we focus on the combined use of green solvents as precursor solutions and green antisolvents as well as the exploration of green solvents without antisolvents in the fabrication of PSCs.

Table 1 summarizes the key parameters and outcomes of the reviewed studies, including the main and cosolvents in the precursor solution, type of antisolvent employed, safety and toxicity considerations, fabrication process and structure of the PSCs, and efficiency and long-term stability of the resulting devices.

Here, we describe the environmental, health, and safety implications of these solvents according to a globally harmonized system (GHS). Hazard statements within the GHS are codified with an “H” followed by three digits. These codes are categorized by hazard type—that is, physical hazards (H200 series), health hazards (H300 series), and environmental hazards (H400 series). Table 1presents only the codes associated with “danger” hazard statements.

Among the solvents used for perovskite precursor solutions, water is the most readily available, safe, and least toxic. However, lead iodide (PbI2)—a commonly used Pb compound—has low solubility in water. Lead nitrate (Pb(NO3)2) has been used as the precursor and water as the solvent. Hsieh *et al.*62 and Feng *et al.*63 developed two-step processes to form MAPbI3 layers, as shown in Figure 6A and Figure 6B. In this method, a Pb(NO3)2 aqueous solution is spin coated onto a TiO2 electron transport layer (ETL) and then placed in contact with an MAI solution in isopropanol (IPA). Because of the high surface tension of aqueous solutions, wetting problems can arise, necessitating surface treatment with UV-ozone or surfactants. The reaction between Pb(NO3)2 and MAI to form MAPbI3 is considerably slower than that between PbI2 and MAI, resulting in prolonged processing times, poor perovskite film morphology, and incomplete transformation. Zahi *et al.*47 overcame these limitations by fabricating a halide-free aqueous nanofluid based on a Pb(NO3)2 solution and spin-coating it. The nanofluid acted as a nucleation seed, improving the kinetics of perovskite film formation. The effectiveness was maximized when using a PbCO3-based nanofluid, leading to a PCE of up to 23.95% for MAPbI3-xClx perovskite films combined with a mesoporous TiO2 ETL and spiro-OMeTAD hole transport layer (HTL). Moreover, the fabricated PSCs exhibited long-term stability, maintaining 95.2% and 93.1% of their initial efficiency after 800 h under maximum power point tracking (MPPT) conditions and 85 °C shelf testing, respectively.

Alcohols—such as ethanol and IPA—are among the most commonly used organic solvents and are representative green solvents. However, the perovskite precursors do not dissolve in ethanol, necessitating the use of additional additives. Yun *et al.*48 developed ethanol-based perovskite precursor solutions by incorporating DMAc or DMSO—which act as Lewis bases—with alkylammonium chloride (RNH3Cl). These ethanol-based FAPbI3 precursor solutions enabled the fabrication of highly dense and uniform crystalline α-FAPbI3 films without antisolvent treatment or high-temperature annealing. Despite its reproductive toxicity, DMAc—when used in conjunction with ethanol—yielded a remarkable PCE of 28.08%, whereas the use of the green solvent DMSO as a co-solvent resulted in a PCE of 21.3%. The fabricated devices exhibited long-term stability, maintaining over 90% of their initial efficiency after 700 h under MPPT conditions.

Although ethanol and IPA are green solvents, their high vapor pressures and low boiling points necessitate precautions against fire and solvent evaporation-induced concentration changes during large-scale scalable processes. γ-Valerolactone (GVL)—a green solvent with a high boiling point (208 °C) and low vapor pressure (0.3 mm Hg at room temperature)—offers a promising alternative. Their biodegradability and low toxicity further enhance their environmental value. Miao *et al.*49 demonstrated the effectiveness of GVL in a single-step spin-coating method using n-butyl acetate as an antisolvent. This approach yielded an impressive PCE of 25.09% for a 0.085 cm2 cell and 20.23% for a 12.25 cm2 mini-module. Notably, GVL-based precursor solutions enabled the direct formation of α-FAPbI3 without an intermediate δ-phase, resulting in high-quality perovskite films. The fabricated PSCs exhibited remarkable stability, retaining 89% and 95% of their initial efficiencies after 2160 h of storage under ambient conditions (ISOS-D1) and 1000 h under MPPT conditions, respectively.

Owing to its low volatility, minimal toxicity, and lack of carcinogenic or mutagenic properties, triethyl phosphate (TEP) has emerged as a promising green solvent for PSC fabrication. Cao *et al.*51,52 demonstrated the effectiveness of TEP by fabricating a (FAPbI3)0.95(MAPbBr3)0.05 perovskite film using TEP as the solvent and DEE as the antisolvent. The resulting PSC achieved a PCE of 19.0% and exhibited remarkable stability, retaining 90% of its initial efficiency after 450 h of storage under dark nitrogen conditions. This study also highlights the potential of a fabrication process with fully green solvents by employing water and anisole as solvents for the ETL and HTL, respectively. However, the use of DEE as an antisolvent poses a potential safety hazard because of its high volatility and flammability, which limits its suitability for large-scale module production. To address this concern, Sajid *et al.*50 developed a 2-step solvent-free process using TEP as the sole solvent for both PbI2 and MAI/FAI precursor solutions. The fabricated PSC exhibited an impressive PCE of 20.98% and demonstrated exceptional stability, retaining 98.3% of its initial efficiency after 720 h of storage under 25 °C temperature and 65% relative humidity (RH) conditions.

DMSO is a common co-solvent with considerable promise in sustainable precursor formulations. However, its high boiling point, low vapor pressure, and strong binding to PbI2 make its removal challenging, particularly for large-scale processes. To address these limitations, researchers have investigated the use of more volatile noncoordinating solvents as cosolvents. Acetonitrile (ACN), dimethylpropyleneurea (DMPU), 2-methyltetrahydrofuran (2-MeTHF), and ethanol have been used as cosolvents. Doolin *et al.*55 developed a DMSO-based solvent system guided by Hansen solubility metrics, donicity, and environmental, health, and safety (EHS) considerations. A mixture of 40% DMSO, 30% DMPU, 20% 2-MeTHF, and 10% ethanol (vol%) was used to prepare the perovskite precursor solutions. The solution was spin coated and treated with the green antisolvent ethyl acetate (EA) to form the MAPbI3 film. In combination with the SnO2 ETL and spiro-OMeTAD HTL, a PCE of 16.05% was achieved.

Abate *et al.*53 developed a technique for coating large-area CsPbI2.77Br0.23 films using slot-die coating by preparing a solution of ACN and DMSO. The high volatility of ACN provided a high nucleation rate during the drying process, enabling the formation of black-phase perovskite films without separate heat treatment. In combination with the TiO2 ETL and Spiro-OMeTAD HTL, a PCE of 19.05% was achieved in small-area single-unit devices and 16.03% in 2.5 × 2.0 cm2 mini-modules. The devices exhibited long-term stability, maintaining over 90% of their initial PCE after a month of storage in air at a RH below 20% and 90% of their initial efficiency after 200 h under MPPT conditions.

Kim *et al.* 54 developed a novel process that employed IPA to effectively eliminate DMSO after forming a PbI2-DMSO film to address the persistent problem of DMSO removal. This method not only eliminated DMSO but also created a mesoporous morphology through DMSO extraction. This unique morphology enhanced the reaction rate with MAI in the IPA solution, enabling high-speed large-area coating. The fabricated PSCs—comprising a MAPbI3 film prepared by slot-die coating, SnO2 ETL, and Spiro-OMeTAD HTL—exhibited a remarkable PCE of 18.3%.

ACN is a green solvent used for perovskite precursor solutions. However, its limited ability to dissolve the perovskite precursors necessitates the addition of methylamine, typically in the form of an ACN/MA solution, as shown in Figure 6C and Figure 6D. This combination has been primarily employed for MAPbI3 film formation. Two methods for incorporating methylamine into ACN have been reported—that is, bubbling methylamine gas into ACN and mixing a solution of ACN and methylamine in ethanol. Ramadan *et al.*58 and Noel *et al.*59 achieved PCEs of approximately 19% by spin coating MAPbI3 films from ACN/MA precursor solutions and post-treating with IPA containing MACl. The rapid evaporation rate and low toxicity of ACN solutions make them suitable for large-area scalable coating processes. Belay Adugna *et al.*56 and Rezaee *et al.*57 successfully demonstrated scalable coating processes using n-i-p and p-i-n structures, achieving efficiencies of 20.3% and 19.5%, respectively.

1,3-dimethyl-2-imidazolidinone (DMI) is generally regarded as a less toxic solvent, although it is sometimes classified as toxic according to GHS Hazard statements. Chang *et al.*60 developed a precursor solution by dissolving Pb(Ac)2 and MAI in DMI. Figure 6E shows a scalable fabrication process for PSCs using only green solvents. The process involves the sequential blade coating of water-dispersed SnO2—a DMI precursor solution—and spiro-OMeTAD dissolved in EA. The fabricated PSCs exhibit a remarkable maximum efficiency of 18.26%.

Ionic liquids—which are molten salts based on MA at room temperature—offer an alternative approach to perovskite film fabrication without organic solvents. Methylammonium acetate (MAAc) molten salt—characterized by its high viscosity, negligible vapor pressure, and non-hazardous nature—is well suited for scalable fabrication processes under ambient air conditions without major humidity concerns. Chao *et al.*61 demonstrated the formation of MAPbI3 films from an MAAc solution containing PbI2 and MACl, as shown in Figure 6F and Figure 6G, achieving a PCE of 20.05%. The hydrogen bonding interactions between the MAAc molecules, PbI2, and MACl enhance the colloidal concentration of the precursor solution, leading to the formation of dense, pinhole-free, and high-quality perovskite films. The higher stability of MAPbI3 films formed using MAAc is evident in the performance of unencapsulated devices; after 1000 h of storage in ambient air, they retained 93% of their initial efficiency, and after 700 h of operation under light stress in a glovebox, they maintained over 80% of their original PCE.

**3.2 Green solvents for charge transport layers**

The discussion on the use of green solvents in solution-processed CTL formation has primarily focused on the solvents used to form the HTL in n-i-p structures, as summarized in Table 2. In p-i-n structures, NiOx and self-assembled monolayers are commonly used as HTLs, and polar solvents (such as alcohols) are typically employed to form the HTL. The ETL is formed primarily by the deposition of C60 in p-i-n structured devices. Titanium oxide or tin oxide are commonly used as the ETLs in n-i-p structures, and solvents such as water or alcohols are employed. Spiro-OMeTAD has been the most efficient HTL material for PSCs since its early stages of development. It is typically dissolved in nonpolar solvents, with CB being the most widely used solvent. However, owing to the toxicity of halogenated organic solvents, there is a need for green solvents to replace CB for commercialization.

Figure 7A (left) highlights alternative solvents to CB for dissolving Spiro-OMeTAD—including anisole, EA, p-xylene, and tetrahydrofuran (THF). Anisole and EA are the most commonly used solvents to replace CB for Spiro-OMeTAD coating. As previously discussed, Cao *et al.* demonstrated the feasibility of fabricating all layers (ETL/perovskite/HTL) using green solvent-based coating by employing anisole as the Spiro-OMeTAD solvent. Anisole exhibits low toxicity with a median lethal dose (LD50) of 3700 mg⋅kg-1 (rat, oral).64 Yavari *et al.*65 further demonstrated the comparable performance of anisole to CB by fabricating devices with a PCE of 20.2% using anisole as both the solvent and antisolvent.

EA, which has been previously employed as a green antisolvent for perovskite solar cell fabrication, can also be used as a solvent for spiro-OMeTAD. Guo *et al.*66 demonstrated the potential of EA by fabricating PSCs with a remarkable PCE of 23.3%. EA facilitates faster oxidation of spiro-OMeTAD compared to CB, eliminating the need for post-oxidation or additional oxidation agents. Additionally, a high efficiency could be achieved using a thinner spiro-OMeTAD layer, which reduced the amount of hole transport material required, favoring mass production.

Siegrist *et al.*68 employed *p*-xylene as a green solvent for spiro-OMeTAD. Although *p*-xylene carries the H304 danger code in the GHS hazard statement, it is considered a relatively safe non-halogenated organic solvent with an LD50 of 3700 mg⋅kg-1(rat, oral). A less toxic process was used for the fabrication of the perovskite layer, involving the thermal evaporation of PbI2 and CsI, followed by blade coating with a solution containing FAI, MABr, and MACl in IPA. The device achieved a PCE of 18.7% with the SnO2 ETL formed by the blade coating of an aqueous colloidal solution, and the Spiro-OMeTAD HTL formed by the blade coating of the Spiro-OMeTAD solution.

THF has also been proposed as a potential replacement for CB. Jiang *et al.*69 demonstrated that Spiro-OMeTAD films prepared from THF via dynamic spin coating exhibited enhanced crystallinity and higher hole mobility, enabling the efficient operation of PSCs without the need for additional dopants. The device employed a thinner Spiro-OMeTAD layer formed using a smaller amount of material than CB-based devices. An MoO3 buffer layer was deposited to enhance the HTL formation, and SnO2 was used as the ETL. The fabricated PSC achieved a PCE of 16.9% and retained 70% of its initial efficiency after 200 h of storage under ambient conditions (25–30% RH), demonstrating higher stability compared to CB- and dopant-based devices.

Spiro-OMeTAD requires dopants—such as Li-TFSI or tBP—for efficient charge transport. However, these dopants diminish the thermal and moisture stability of Spiro-OMeTAD. Consequently, novel materials have been developed to achieve high efficiency without dopants and can be formed using green solvents instead of CB. These new HTL materials typically possess large π-conjugated frameworks, facilitating hole transport. However, this can also hinder solubility, making solution-processed film formation a challenge. To address this problem, researchers have introduced materials by appending polar functional side chains to the conjugated main chain or to asymmetric structures, as shown in Figure 7 (right). Lee *et al.*71 synthesized a novel donor–acceptor (D–A) type polymer—that is, alkoxy-PTEG—composed of benzo[1,2-b:4,5:b′]dithiophene and tetraethylene glycol (TEG)-substituted 2,1,3-benzothiadiazole. The polymer achieved PCEs of 19.9% and 21.2% when using 3-methylcyclohexanon (3-MC) and 2-methylanisole (2-MA) solvents, respectively. Additionally, the PSC exhibited 88% stability after 30 d under ambient conditions (40–50% RH and room temperature).

In 2017, Lee *et al.* further designed an asymmetric D–A polymer (asy-PBTBDT) and fabricated PSC devices with a maximum PCE of 20.0% using 2-MA solvent.72 The device demonstrated remarkable long-term stability, retaining 91% of its initial efficiency after 30 d without encapsulation under 50–75% RH conditions. Cheng *et al.* combined these two strategies by introducing asymmetric polar oligo(ethylene glycol) side chains into the design of BDT-C8-3O. Fabricated PSC devices with BDT-C8-3O as the HTL, formed using 3-MC solvent and SnO2 as the ETL, achieved a PCE of 23.53%. The devices exhibited impressive operational and high-temperature stability, retaining over 84% and 79.5% of their initial efficiencies for 2000 h, respectively.

Moreover, p-i-n-structured PSCs have been fabricated using HTLs derived from D-A type small molecules and green solvents. Yu *et al.*75 designed a star-shaped donor-acceptor-donor (D-A-D) molecule—namely, BTP-1—which incorporated a 3,5-dicarbonitrile pyridine core. Employing 2-MA as a green solvent, the BTP-1-based HTL achieved an impressive efficiency of 24.34% in inverted perovskite solar cells with a C60 ETL. This represents the highest efficiency among PSCs using green solvents and small D–A-type HTLs. The device also exhibited remarkable long-term stability, retaining 98% of its initial efficiency after 1000 h of illumination under 1 sun intensity in a N2 atmosphere.

Researchers have combined backbone flexibility with rigid conjugate engineering modulation to overcome the tradeoff between solubility and hole mobility. Zhao *et al.*73 synthesized A-EDOT by incorporating flexible amide chains, polar-solubilizing ethylenedioxythiophene (EDOT) units, and conjugated binaphthalene groups. The polymer was dissolved in 2-MA to form the HTL. The fabricated p-i-n PSC with PCBM as the ETL achieved an efficiency of 20.23%. A strategy in which the conjugated unit was assembled by the rigid binaphthylamine core and the amide bond constituting the flexible backbone was also employed.74 Polar-solubilizing units ethylenedioxythiophene and thiophene were used as bridges to construct two kinds of polymers—namely, EDOT-SMe and T-SMe, respectively. Using 2-MA solvent to form the HTL and PCBM as the ETL, a maximum PCE of 20.25% was achieved.

4. Strategies for mitigating the leakage of lead (Pb)

As Pb-based encapsulated devices are poised for commercialization, effective module encapsulation has emerged as a means of mitigating potential Pb leakage from future devices. The encapsulation of PSCs protects the device from external degradation factors, such as moisture and oxygen, while preventing the leakage of internal materials, including Pb. However, physical encapsulation carries the risk of Pb leakage and environmental contamination if the device is damaged by external forces or if the encapsulation seal is compromised by degradation. To minimize this risk, material technologies have been developed to chemically capture Pb from perovskite materials, PSCs, and encapsulants between the device and cover glass.

Table 3 summarizes the strategies used to prevent Pb leakage from Pb-based PSC devices. Typically, materials containing functional groups—such as phosphate, carbonyl, carboxyl, sulfonate, and thiol groups—which can chemically bind Pb2+ ions, are widely used. To increase the number of absorption sites, mesoporous structures, metal-organic frameworks, and polymers have been introduced.

4.1 Lead (Pb) sequestration in perovskite films

One approach to prevent Pb leakage from PSCs involves introducing additives into the perovskite light-absorbing layer, which can form strong chemical bonds with Pb2+ ions. Horváth *et al.*80 added (NH4)2HPO4 to perovskite to form a water-insoluble lead phosphate to suppress Pb leakage. Yang *et al.*81 added 2-hydroxypropyl-β-cyclodextrin (HPβCD) and 1,2,3,4-butane tetracarboxylic acid (BTCA) to capture Pb2+ ions within the HPβCD cavities and/or the interconnected network of the additives, minimizing Pb leakage.

Additives introduced into perovskite materials simultaneously passivate defect sites (such as uncoordinated Pb), thereby considerably improving the performance of PSCs. Xu *et al.*76 added a polymer rich in hydrogen bonds and carbonyl groups, as shown in Figure 8A, achieving a maximum PCE of 23.1% through defect passivation and immobilization Pb2+ ions within the perovskite. Zhang *et al.*82 added an organic small molecule (octafluoro-1,6-hexanedioliacrylate) to perovskite, undergoing *in-situ* thermal crosslinking to form a polymer, passivating Pb- and I-related defects, and achieving a high efficiency of up to 24.76%. The devices exhibited high long-term stability, retaining 86% of their initial efficiency after 2000 h under conditions of RH = 80 ±5% and T = 25 °C, 90% after 1000 h at 85 °C in a nitrogen-filled glovebox, and 90% when tracking the maximum power point (MPP) under a nitrogen atmosphere. This study demonstrated that the carbonyl group of the additive bound to Pb2+ ions, suppressing Pb leakage.

4.2 Passivation layer on perovskite films

Perovskite film surfaces contain numerous defect sites, necessitating surface passivation strategies to fabricate highly efficient and stable solar cells. When a passivation material possesses abundant functional groups capable of binding Pb2+ ions, it can effectively suppress the diffusion and leakage of Pb from the perovskite film. Hu *et al.*85 introduced water-insoluble sunscreen benzimidazole sulfonic acid (PBSA) onto a perovskite surface. The device achieved PCEs of 24.14% (0.09 cm²) and 17.36% (19.32 cm²), respectively, while effectively suppressing Pb leakage. Moreover, under continuous 1-sun illumination in a nitrogen atmosphere, the device exhibited long-term stability with a T90 of 1130 h and a T80 of 2000 h. Meng *et al.*77 introduced diphosphatidyl-glycerol (Di-g) as a self-shielding interface in the perovskite layer. Figure 8B shows its amphipathic nature. Di-g can simultaneously bind tightly to the divalent Pb ions and provide interfacial water resistance, suppressing Pb leakage by 96%.

4.3 Lead (Pb) leakage suppression with charge transport layer

ETLs and HTLs are formed in contact with the upper and lower layers of the perovskite light-absorbing layer, respectively, for the purpose of electron and hole transport. Consequently, incorporating materials capable of chemically absorbing Pb into charge transport materials or introducing functional groups into charge transport materials that can capture Pb can reduce Pb leakage from PSCs.

Wu *et al.* employed a Zr(IV)-based thiol-functionalized 2D conjugated metal-organic framework blended with bis-C60 as the ETL in a p-i-n PSC, as shown in Figure 8C. This approach not only ensures efficient electron transport but also enables the capture of most Pb2+ ions leaked from the degraded perovskite solar cell by forming water-insoluble solids. The resulting device exhibited a PCE of 22.02% and demonstrated long-term stability, retaining 90% of its initial efficiency after 1100 h under ambient conditions with 75% RH and 92% after 1000 h of MPPT at 85 °C in a nitrogen-filled glovebox. Mokhtar *et al.* and Zhang *et al.* introduced hydroxyapatite and a mixture of amino trimethylene phosphonic acid (ATMP) and KOH into conventional TiO2 and SnO2 nanoparticle layers, respectively, which are commonly used as ETLs in n-i-p structures, thereby endowing them with the ability to chemisorb Pb2+ ions.

Organic charge transport layers can be designed to incorporate functional groups capable of binding Pb, thereby inhibiting Pb leakage. Xu *et al.*88 designed an *in-situ* co-polymerized interfacial layer (Spiro-NPU) based on Spiro-OH and 1,5-naphthalene diisocyanate (NDI) monomers, which enhanced moisture resistance and Pb blocking owing to the spiro block and NCO and carbonyl groups. The incorporation of Spiro-NPU improved the photovoltaic performance considerably, achieving peak PCEs of 23.26%. For long-term stability, no PCE decay was evident after 3000 h of aging in air at 60% RH. Over 90% of the initial efficiency was maintained after 500 h of aging at 85% RH and 25 °C (or at 55% RH and 85 °C), and 97% was retained after 200 h of MPPT under 1-sun illumination (AM1.5G) in a nitrogen atmosphere without external encapsulation. Additionally, an alkoxy-PTEG HTL—previously introduced as a material that can be formed using green solvents—can chelate Pb ions via its TEG groups.89

4.4 Preventing lead (Pb) leakage through external capping of PSCs

Ethylene vinyl acetate (EVA) and polyolefin elastomer (POE)—which are widely used as encapsulation materials for solar cells—provide physical cushioning between the solar module and cover glass but lack the ability to adsorb Pb. Encapsulant materials for PSCs require transparency, low-temperature processability, and the ability to adsorb Pb. To prevent Pb leakage, various encapsulation strategies have been proposed, including:

1. Coating the PSC surface with molecules, polymers, or resins that possess functional groups capable of adsorbing Pb,
2. Replacing conventional encapsulant materials with materials that can adsorb Pb, and
3. Incorporating Pb-adsorbing materials into conventional encapsulation materials.

Chen *et al.*91 introduced low-cost and chemically robust cation-exchange resins (CERs) into PSCs. These CERs effectively capture Pb2+ ions through their sulfonate groups. By integrating CERs with carbon electrodes and layering them on the glass surface of modules, Pb leakage was reduced to 14.3 parts per billion, well below drinking water safety standards. Moreover, Chen *et al.*92 developed a novel device structure by incorporating a cation-exchange resin comprising a cross-linked styrene-divinylbenzene copolymer with sulfonic acid groups in the perovskite layer, forming a mesoscopic scaffold on top of the HTL. This structure immobilizes Pb within the perovskite layer, effectively suppressing Pb leakage while maintaining device efficiency.

Valastro *et al.*93 prevented Pb leakage by depositing a transparent TiO₂ sponge structure with columnar mesopores onto the PSCs, cover glass, and polymeric foils using sputtering, as an alternative to organic materials. This TiO₂ sponge structure—with its large surface area—captured Pb through chemical interactions between Pb and O, and could sequester Pb at concentrations ranging from 24 to 63 g⋅cm⁻², equivalent to the amount of Pb contained in the perovskite layers with thicknesses from 200 to 500 nm.

Several studies have demonstrated the effectiveness of replacing conventional encapsulation materials with novel materials to mitigate Pb leakage. Jiang *et al.*95 employed epoxy resin (ER)-based polymers with a glass transition temperature (*Tg*) of approximately 42 °C as an encapsulation material for PSCs. The ER endowed the device with self-healing properties, allowing it to effectively protect the device from Pb leakage, even after encapsulation damage. Luo *et al.*97 designed bioinspired cage traps (BCTs)—eco-friendly and low-cost structures—by implanting a functional Pb-capturing molecular structure (CONH-R-NH₂) based on ethylenediamine (EDA) into mesoporous matrices. The BCTs effectively suppressed Pb leakage through capillary adsorption facilitated by the mesoporous structure and the chemical absorption by the -CONH-NH₂ and -CONH-R-NH₂ anchoring sites. PSCs encapsulated with BCTs exhibited 8.4% of the Pb leakage compared to unencapsulated PSCs, while maintaining a PCE of 22.20%.

Numerous studies have demonstrated the effectiveness of combining conventional encapsulants—such as EVA, POE, and polydimethylsiloxane (PDMS), with additional materials to prevent Pb leakage while maintaining compatibility with the PSCs, as shown in Figure 8D. Zhang *et al.*94 coated polyvinyl alcohol modified with sulfosuccinic acid (SMP) onto PDMS as a Pb absorbent. The sulfonic acid groups in SMP chemically absorbed Pb, reducing leakage by over 99%. Li *et al.*99 introduced an encapsulation strategy for PSCs involving the coating of P,P′-di(2-ethylhexyl)methanediphosphonic acid (DMDP) on the glass side of the front transparent conducting electrode and a mixture of N,N,N,’ N′-ethylenediaminetetrakis(methylenephosphonic acid) (EDTMOP) and a POE on the back metal electrode side, followed by an EVA encapsulation layer. This approach enabled on-device sequestration of over 96% of Pb leakage caused by severe device damage. Li *et al.*96 adapted a standard encapsulation process used in silicon-based solar cells by applying an encapsulant composed of a standard solar EVA film and a pre-laminated DMDP layer on both sides of the PSC. This encapsulation method, enabled by the chemisorption of phosphonic groups, captured over 99.9% of Pb leakage from severely damaged PSCs.

Li *et al.*98 introduced a composite encapsulant comprising CER and UV resin for application to the metal side of devices to mitigate Pb leakage. The sulfonic acid groups within the CER attracted Pb²⁺ ions in aqueous solution, forming a precipitate. This approach reduced the Pb leakage to less than 5 ppm in both rigid and flexible PSCs. Subsequently, the same research group spin-coated sulfonated graphene aerogels mixed with PDMS on both sides of flexible devices to function as Pb-absorbing encapsulants.79 These encapsulants captured over 99% of Pb²⁺ ions with chemical absorption by sulfonate groups from degraded devices under simulated conditions.

Xiao *et al.*100 synthesized an ionogel encapsulant for PSCs using acrylic acid (AA) as the Pb-binding monomer, methylene-bis-acrylamide (MBAA) as the covalent cross-linker, azobisisobutyronitrile (AIBN) as the thermal initiator, and tributyl(methyl)phosphonium dimethyl phosphate (TPDP) as the ionic liquid. The phosphonium ionic liquid not only stabilized the gel by preventing solvent evaporation but also increased the number of Pb-binding sites through phosphate anions. Carboxyl groups in the AA further captured Pb²⁺ ions. When this ionogel was combined with the conventional POE encapsulant, undetectable levels of Pb (< 1 ppb) escaped from the damaged perovskite module after a simulated hail test, followed by 24 h of water immersion.

5. Conclusions

The development of Pb-based PSCs is a crucial step toward sustainable and environmentally friendly photovoltaic technologies. This review highlights promising alternatives to Pb-based PSCs, focusing on Sn- and Ge-based perovskites, as well as other cation substitutions, such as B(IV) and B(III). Although Sn-based perovskites show potential owing to their electronic similarity to Pb, they are challenged by oxidation and defect formation, necessitating innovative strategies—such as antioxidative additives, surface passivation, and bi-interface optimization—to enhance stability and performance. Ge-based perovskites are another viable alternative, with their favorable bandgap tunability and environmental benefits, although their stability requires further improvement. Moreover, the development of green fabrication processes—including the use of less toxic solvents—has shown promise for reducing the environmental footprint of PSCs. Innovations in precursor solution preparation, solvent selection, and process optimization have contributed to improvements in the performance and stability of PSC devices. Green solvent processing is expected to play a crucial role in the commercial viability of PSCs. However, future studies should focus on identifying and optimizing nontoxic, eco-friendly solvents that can produce high-quality perovskite films with minimal environmental impact. Additionally, scaling up these green processing techniques from the laboratory to industrial scale will be a critical step toward the widespread adoption of Pb-free PSCs. The inherent instability of Pb-free perovskites—particularly under environmental stress—remains a critical area for future research. By integrating advanced materials, device engineering, and eco-friendly fabrication methods, this field could advance toward the commercialization of sustainable high-performance PSCs.

AUTHOR CONTRIBUTIONS

Shanshan Gao and Jeong-Ju Bae wrote the original draft. Da Seul Lee contributed to the review and editing. Tae-Youl Yang and Seong Sik Shin supervised.

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**CONFLICT OF INTEREST**

The authors declare no competing interests.

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**도표, 텍스트, 종이접기, 디자인이(가) 표시된 사진

자동 생성된 설명Figure 1.** (A) Perovskite structure. (B) Electronic structure of typical III–V, II–VI, or group IV semiconductors (left) compared to the lead halide perovskite crystal structure (right). (C) Systems affected by lead toxicity. (D) Human health toxicity of solvents expressed in the disability-adjusted life years (DALYs) per kg of substance emitted to urban air.

텍스트, 도표, 스크린샷, 라인이(가) 표시된 사진

자동 생성된 설명**Figure 2.** (A) Efficiency development of Sn-based perovskite solar cells.12–23 (B) Schematic energy level diagram of MASnI3, FASnI3, and CsSnI3. (C) Schematic summarizing the origin of the band gap bowing in MA(Pb1–xSnx)I3. Shaded regions represent the valence and conduction bands with thick lines showing the molecular orbital picture of the formation of electronic bands in the alloy. (D–E) Frost diagrams for Pb and Sn under standard conditions.

텍스트, 스크린샷, 도표이(가) 표시된 사진

자동 생성된 설명**Figure 3.** (A) Schematic illustration of the 2-staged redox reaction between vanillin and Sn-based perovskite: i) Oxidation of Sn-based perovskite in absence of vanillin. ii) Reduction of Sn4+ back to Sn2+ and oxidation of vanillin to vanillic acid. iii) Reduction of Sn4+ back to Sn2+ and oxidation of vanillic acid. (B) Schematic illustrating defects formed at the surface and in interior of a CsSnI3 perovskite and its corresponding passivation strategy, including i) surface and interior Sn vacancy, ii) undercoordinated Sn ions, iii) proposed reaction pathway of superoxide production under photoexcitation, iv,v) Lewis acid-base interaction between TSC and CsSnI3, and the resistance of oxidation. (C) XPS depth profiling investigation for Sn4+ distribution in perovskite film. (D) Preparation process of Sn-based PSCs and designed device structure.

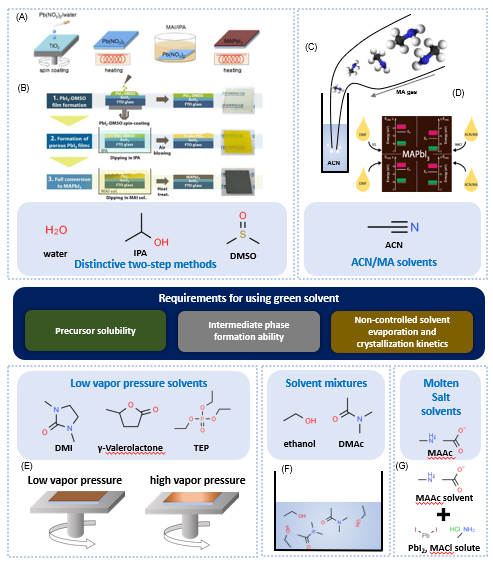
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**Figure 4.** Crystal structures of (A) CsGeI3, FAGeI3, and MAGeI3. (B) Schematic energy level diagram of CsGeI3, MAGeI3, and FAGeI3. (C) Optical absorption spectrum of CsGeI3, MAGeI3, and FAGeI3. (D) Schematic diagram depicting the influence of orbital hybridization strength on the energy of the hybrid orbitals. (E) JV curves measured in the dark and under 100 mW/cm2 illumination with and without 2.9 × 2.9 mm2 shadow mask, and (F) EQE spectrum and of an optimized MAGeI2.7Br0.3-based solar cell.

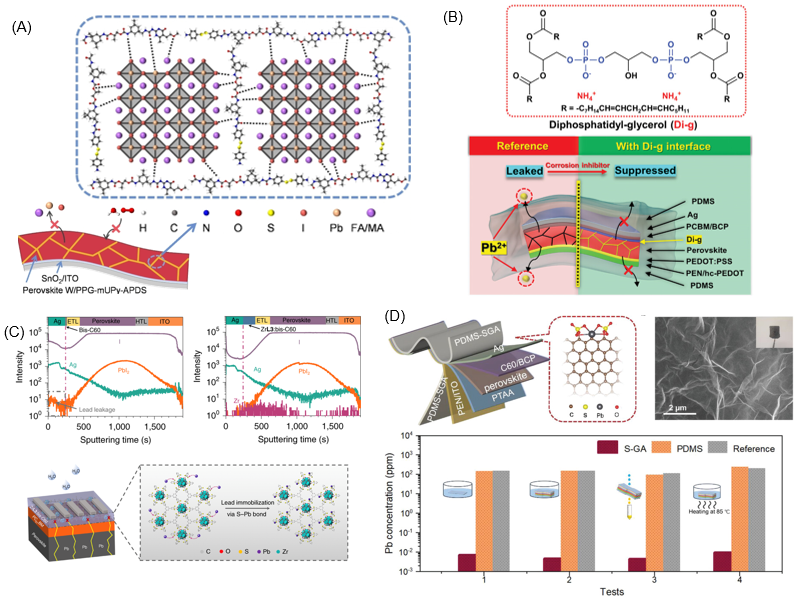
텍스트, 도표, 라인, 스크린샷이(가) 표시된 사진

자동 생성된 설명Figure **5.** (A) Stability measurements of pristine and TSC-passivated CsSnI3 perovskite solar cells with encapsulation. (B–C) Comparison of the unencapsulated device stability of FASnI3 and Fo–FASnI3 PSCs under ambient air conditions (approximately 30% humidity and 25 °C) and C) white LED illumination (100 Mw⋅cm−2). (D) Absorption intensity at 510 nm plotted versus time curve of the MAGeI3 and MAGeI2.7Br0.3 perovskite samples. (E) Maximum power point tracking test for the Sn-PVK-SnOX device during 1 sun illumination in 300 s with perovskite Cs0.02(FA0.9DEA0.1)0.98)0.98EDA0.01I3.

Figure **6.** Lesstoxic solvents to fabricate perovskite thin films. Procedure for the novel two-step method with (A) Pb(NO3)2/water62 and (B) PbI2-DMSO system,54 (C) schematic of infusing MA into the ACN solvent, (D) comparison of band diagrams between perovskite films produced with conventional solvent and ACN/MA system,58 (E) schematic of uniformity as function of solvent vapor pressure in thin films produced by spin coating, (F) schematic of homogeneous solvent mixture, and (G) molecular structures of ionic liquid and perovskite precursor.

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자동 생성된 설명**Figure 7.** Green solvents to dissolve Spiro-OMeTAD (left, green) and organic alternatives charge transport materials to replace Spiro-OMeTAD for using green solvents (right, blue)



**Figure 8.** Various strategies to mitigate lead leakage. (A) Schematic of the interaction of PPG-mUPy-APDS with a perovskite film.76 (B) Molecular structure of the Di-g (upper) and schematic of the Di-g film that suppresses Pb2+ ions leaking from perovskite at the interface (lower).77 (C) ToF-SIMS depth profiles of perovskite solar cell with the immobilization effect of ZrL3 on leaked Pb2+ ions.78 (D) Schematic of perovskite solar module encapsulated with mixture of S-GA/PDMS and SEM image of S-GA/PDMS (upper). Comparison of the amount of lead leakage according to encapsulation methods under various test conditions (lower).79

Tables and Captions

**Table 1.** Less toxic solvents to fabricate the perovskite films.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Ref | Main solvent | GHS Hazard code | Co-solvent | | GHS Hazard code | Antisolvent | GHS Hazard code | Cell structure | Method | PCE (%) | Stability |
| 47 | Water | - | Isopropanol | | H225 | - | - | FTO/c-TiO2/mp-TiO2/MAPbI3-xClx//Spiro-OMeTAD/Au | Pb(NO3)2 spin coating + MAI:MACl immersion | 23.95 | MPP 800 h: ~95.2% 85 °C dark 800 h: ~93.1% |
| 48 | Ethanol | H225 | Dimethylacetamide | | H360 |  | H225 | FTO/SnO2/FAPbI3/Spiro-OMeTAD/Au | Single-step spin coating + antisolvent quenching | 25.08 | MPP 700 h: ~90% |
| 49 | γ-valerolactone | - | - | | - | N-butyl acetate | - | FTO/c-TiO2/SnO2/FAPbI3/Spiro-OMeTAD/Ag | Single-step spin coating + antisolvent quenching | 25.09 | MPP 1000 h: ~95% 85 °C dark 240 h: ~68% ISOS-D1: 90% (2160 h) |
| 50 | Triethyl phosphate | - | - | | - | - | - | FTO/SnO2/MAFAPbI3/Spiro-OMeTAD/Au | PbI2 spin coating + FAI:MAI spin coating | 20.98 | 25 °C -65% RH dark 720 h: 98.3% |
| 51 | Triethyl phosphate | - | - | | - | Dibutyl ether | H225 | FTO/SnO2/(FAPbI3)0.95(MAPbBr3)0.05/Spiro-OMeTAD/Au | Single-step spin coating + antisolvent quenching | 20.13 | N2 dark 450 h: 86.4% |
| 52 | Triethyl phosphate | - | - | | - | Diethyl ether | H225 | FTO/SnO2/ (FAPbI3)0.95(MAPbBr3)0.05/Spiro-OMeTAD/Au | Single-step spin coating + antisolvent quenching | 19.0 | -  N2 dark 480 h: 91.6% |
| 53 | Dimethyl sulfoxide | - | Acetonitrile | | H225 | - | - | FTO/c-TiO2/CsPbI2.77Br0.23/Spiro-OMeTAD/Au | Slot-die coating | 19.05 | Air (< 20% RH) dark: 90% 85 °C dark 60 h: ~80% MPP 200 h: 90% |
| 54 | Dimethyl sulfoxide | - | Isopropanol | | H225 | - | - | FTO/SnO2/MAPbI3/Spiro-OMeTAD/Au | Slot-die coating + MAI:MACl immersion | 18.5 | - |
| 55 | Dimethyl sulfoxide | - | Dimethylpropyleneurea | H318 | | Ethyl acetate | H225 | FTO/SnO2/MAPbI3/Spiro-OMeTAD/Au | Single-step spin coating + antisolvent quenching | 16.05 | - |
| 2-methyltetrahydrofuran | H225  H318 | |
| Ethanol | H225 | |
| 56 | Acetonitrile | H225 |  | | H225 | - | - | FTO/c-TiO2/mp-TiO2/MAPbI3/Spiro-OMeTAD/Ag | Blade coating | 20.3 | - |
| 57 | Acetonitrile | H225 | Ethanol | | H225 | - | - | ITO/Cu:NiOx/MAPbI3/PC60BM/BCP/Ag | Bar coating with gas quenching | 19.5 | - |
| 58 | Acetonitrile | H225 | Isopropanol | | H225 | - | - | FTO/SnO2/MAPbI3/Spiro-OMeTAD/Ag | Single-step spin coating | 18.7 | - |
| 59 | Acetonitrile | H225 | Isopropanol | | H225 | - | - | FTO/TiO2/C60/MAPbI3/Spiro-OMeTAD/Au | Single-step spin coating | 19.0 | - |
| 60 | 1,3-dimethyl-2-imidazolidinone | H311 H318 | - | | - | - | - | FTO/SnO2/MAPbI3/Spiro-OMeTAD/Au | Blade coating | 18.26 | Air (40–50% RH) Dark 1680 h : 86.5% |
| 61 | Methylammonium acetate | - | - | | - | - | - | ITO/CPTA/BACl/MAPbI3-xClx/Spiro-OMeTAD/MoO3/Au | Single-step spin coating | 20.05 | AM 1.5G illumination 700 h: 80% |
| H225: Highly flammable liquid and vapor [Danger flammable liquids], H311: Toxic in contact with skin [Danger acute toxicity, dermal], H318: Causes serious eye damage [Danger serious eye damage/eye irritation], H360: May damage fertility or the unborn child [Danger reproductive toxicity] | | | | | | | | | | | |

**Table 2.** Less toxic solvents to fabricate charge transport layers.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Ref | Solvents for CTLs | GHS Hazard code | Target materials | | Solvents for perovskite/antisolvent | Cell structure | Method | PCE | Stability |
| 67 | Anisole | - | Spiro-OMeTAD | | Triethyl phosphate / Diethyl Ether | FTO/SnO2/ (FAPbI3)0.95(MAPbBr3)0.05/Spiro-OMeTAD/Au | Spin coating | 19.0 | N2 dark 480 h: 91.6% |
| 65 | Anisole | - | Spiro-OMeTAD | | DMF:DMSO / Anisole | FTO/c-TiO2/mp-TiO2/Cs0.05(MA0.17FA0.83)0.95Pb(I0.83Br0.17)3/Spiro-OMeTAD | Spin coating | 20.2 | - |
| 68 | P-xylene | H304 | | Spiro-OMeTAD | IPA (Thermal evaporation of inorganic iodide) | IOH/SnO2/(Cs,FA,MA)Pb(I,Br)3/Spiro-OMeTAD/Au | Blade coating | 18.7 | - |
| 66 | Ethyl acetate | H225 | Spiro-OMeTAD | | DMF:DMSO:IPA | ITO/SnO2/FAMAPbI3/Spiro-OMeTAD/MoO3/Ag | Spin coating | 23.3 | - |
| 69 | Tetrahydrofuran | H225 | Spiro-OMeTAD | | DMF:DMSO / Chlorobenzene | ITO/C60/MAPbI3-xClx/Spiro-OMeTAD/MoO3/Ag | Spin coating | 16.94 | Ambient condition (25–30% RH) 200 h: 70% |
| 70 | 3-methylcyclohexanon | - | BDT-C8-3O | | DMF:DMSO:IPA | ITO/SnO2/perovskite/BDT-C8-3O/Au | Spin coating | 23.53 | MPP 2000 h: 84% 85 °C N2 2000 h: 79.5% |
| 71 | 2-Methylanisole (3-methylcyclohexanon) | - | Alkoxy-PTEG | | DMF:DMSO / Chlorobenzene | FTO/SnO2/Cs0.06FA0.78MA0.16Pb0.94I2.4Br0.48/HTL/Au | Spin coating | 21.2 (19.9) | Air (40–50% RH), Dark 30 d (~720 h): 88% (unencap), 100% (encap 100 °C 4 d (~100 h): 94% (encap) |
| 72 | 2-methylanisole | - | Asy-PBTBDT | | DMF:DMSO / Chlorobenzene | FTO/SnO2/Cs0.06FA0.78MA0.16Pb0.94I2.4Br0.48/HTL/Au | Spin coating | 20.0 | - |
| 73 | 2-Methylanisole | - | A-EDOT | | DMF:DMSO / Chlorobenzene | ITO/A-EDOT/MAPbI3/PCBM/BCP/Ag | Spin coating | 20.23 | 85 °C N2 255 h: 62% |
| 74 | 2-Methylanisole | - | T-Sme | | DMF:DMSO / Chlorobenzene | ITO/T-SMe/MAPbI3/PCBM/BCP/Ag | Spin coating | 20.05 | - |
|  | EDOT-Sme | | ITO/EDOT-SMe/MAPbI3/PCBM/BCP/Ag | 20.25 | - |
| 75 | 2-methylanisole | - | BTP | | DMF:DMSO / Chlorobenzene | ITO/BTP1-2/Cs0.05(FA0.98MA0.02)0.95Pb(I0.98Br0.02)3/C60/BCP/Ag |  | 24.34 | N2 1 sun illumination 1000 h: ~100% 85 °C N2 528 h: 85% |
| H304: May be fatal if swallowed and enters airways [Danger aspiration hazard] | | | | | | | | | |

**Table 3.** Strategies to prevent lead (Pb) leakage from Pb-based PSC devices.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Ref | Type | Materials | Mechanism | Leakage test | PCE | Stability |
| 80 | Additive in perovskite | Na2HPO4, KH2PO4, (NH4)2HPO4 in MAPbI3 | Formation of water-insoluble lead phosphates | Soaking mixed powder into water | - | - |
| 81 | Additive in perovskite | 2-hydroxypropyl-β-cyclodextrin (HPβCD) and 1,2,3,4-butane tetracarboxylic acid (BTCA) | Chemical adsorption and physical blocking effect to capture the Pb ions inside the cavities of HPβCD and/or nano-/meso-pores of the interconnected network | Water-scouring test | 22.14% | In ambient air with ~30 ±10% RH: 96% after ~4000 h  At 85 °C in a N2-filled glovebox : 80% after 300 h |
| 76 | Additive in perovskite | polymer with poly(propylene glycol) (PPG), mUPy motifs and aromatic disulfides (APDS) with chain extender isophorone diisocyanate (IPDI)\ | Chemical adsorption of Pb2+with the carbonyl functional groups | Soaking PSCs into water | 23.10% | In ambient air (23 ±2 °C and 30 ±10% RH: 89% after 2000 h |
| 82 | Additive in perovskite | OF-HDDA polymer (POF-HDDA) | Defect passivation by carbonyl groups (C=O) and -CF2- units | Soaking perovskite films into water | 24.76% (0.09 cm2) 20.66% (14 cm2) | Storage in the air: 100% after 1050 h, 90% after 4300 h  RH = 80 ±5%, T = 25 °C; 86% after 2000 h  85 °C in a N2-filled glove box : 90% after 1000 h  MPPT in a N2 environment: 90% after 1000 h |
| 83 | Additive in perovskite | Fullerene-porphyrin dyad | Chemical reaction with porphyrin ring with dissociative lead ions and formation of a stable and water-insoluble fullerene-based metalloporphyrin (FPD-Pb) complex | Soaking perovskite films into water | 23.00% | MPPT of unencapsulated devices: > 83% after 1500 h |
| 84 | Additive in perovskite | (Poly)acrylamide | Chemical interaction between C=O of amide group and Pb2+ | Soaking unencapsulated PSC modules into water | 22.1% 15.7% (19.16 cm2) | Continuous one-sun equivalent illumination in ambient air: T80 > 1000 h |
| 85 | Perovskite surface passivation | Benzimidazole sulfonic acid | Chemical absorption by the interaction between Pb2+ and sulfonic group | Soaking unencapsulated PSC modules into water | 24.14% (0.09 cm2)  17.36% (19.32 cm2) | Under continuous 1 sun illumination in N2 atmosphere: 1130 h (T90) and 2000 h (T80) |
| 77 | Perovskite surface passivation | Diphosphatidyl-glycerol (Di-g) | Chemical adsorption of Pb2+ with two hydrophilic phosphonic acid groups in each Di-g molecule | Soaking unencapsulated PSCs into water | 20.29% (1.01 cm2) 15.01% (21.82 cm2) | Light-dark cycles (in air, the humidity is 45%) for 2.25 h respectively: ~100% after 20 cycles |
| 78 | ETL | 2-D conjugated MOF | Chemical absorption by the interaction between Pb2+ and thiol group | Soaking unencapsulated PSCs into water | 22.02% | In ambient environment (with a RH of 75%): 90% after 1100 h  MPPT at 85  °C in a N2-filled glovebox: 92% after 1000 h |
| 86 | ETL | TiO2-hydroxyapatite (Ca10(PO4)6(OH)2) composite | Bonding formation between Pb2+ and phosphate (PO43-) | Soaking damaged PSCs into water | 20.98% | Aging of non-encapsulated cells stored under ambient conditions: > 85% after 38 d |
| 87 | ETL | Amino trimethylene phosphonic acid (ATMP) | Chemical absorption by phosphonic acid groups | Soaking ETL films in Pb-containing water | 23.52% | Aging at room temperature in a N2 atmosphere, dark: 93% after 1000 h  Unencapsulated PSCs stored in an ambient environment with 30–50% RH: 90% after 1200 h |
| 88 | HTL | Spiro-NPU | Chemical interaction between acylamino groups and Pb2+ | Soaking unencapsulated PSCs into water | 23.26% | Aging in air at 60% RH: 100% after 3000 h  Aging at 85% RH and 25 °C: > 90% after 500 h  MPPT at 50 °C in N2 : 97% after 200 h |
| 89 | HTL | alkoxy-PTEG, composed of benzo[1,2-b:4,5:b′]dithiophene and tetraethylene glycol (TEG)-substituted 2,1,3-benzothiadiazole | Chemical interaction between alkoxy-PTEG and Pb2+ | 1H NMR and UV-Vis spectroscopy in the solution of the mixed monomer of alkoxy-PTEG and lead iodide in dimethylformamide | 21.20% | Aging in dark with RH of 40%–50% at RT: 88% after 30 d at 100 °C: 94% after 4 d |
| 90 | Capping layer on perovskite films and  electrodes | 1H,1H,2H,2H-perfluorodecanethiol (PFDT) | Chemical interaction between thiol groups and Pb2+ | Soaking perovskite films and PSC devices into water | 21.79% | MPPT of unencapsulated PSCs in a N2-filled box on a heating plate at 85 °C: 90.1% after 500 h  Aging in humid air (85 ±10% RH): > 90% after 500 h |
| 91 | Capping layer / Additive in electrodes | cation-exchange resins | Chemical absorption by the interaction between Pb2+ and sulfonate group | Soaking damaged modules into water | 18.00% | Thermal cycling from −40 to 85 °C (IEC 61215), ~75% after 50 cycles |
| 92 | Capping layer / scaffold in perovskites | cation-exchange resins, cross-linked styrene-divinyl benzene copolymer with the sulfonic acid groups | Chemical absorption by the interaction between Pb2+ and sulfonate group in mesoporous structure | Soaking damaged modules into water | 20.1% (6.08 mm2) 16.3% (60.8 cm2) | MPPT at 45 °C in ambient conditions: ~85% after 500 h |
| 93 | Capping layer on devices | TiO2 sponges | Chemisorption by Pb-O bonds | Soaking PSCs into water | 11.70% | Aging at ~55% RH and 24 °C: 17% after 60 d |
| 94 | Encapsulant | Modifying polyvinyl alcohol with sulfosuccinic acid (SMP) + PDMS | Chemisorption with sulfonic acid groups and ester groups | Soaking damaged PSCs into water | 21.20% | MPPT in N2 at 50 ±5 °C: 86% after 270 h |
| 95 | Encapsulant | Epoxy resin-based polymers | Self-healing characteristics | Water dripping on damaged modules | 14.3%  (mini-module) | - |
| 96 | Encapsulant | Ethylene vinyl acetate (EVA) film and a pre-laminated P,P′-di(2-ethylhexyl)methanediphosphonic acid (DMDP) layer | Chemical absorption by the encapsulant | Soaking unencapsulated PSCs into water | 21.22% | Under dark at 55 °C in ambient condition (20–35% RH) : ~ 90% after 800 h |
| 97 | Encapsulant | Bioinspired cage traps: mesoporous amino-grafted-carbon net | Capillary adsorption in mesoporous matrices & chemical chelation between the -CONH and Pb2+ | Soaking damaged PSCs into water | 22.20% | Continuous light at AM1.5 G, 100 mW/cm2 with 60 ±5 °C: 81% after 360 h  25 °C and 50% RH: 92% after 1000 h  25 °C and 85% RH: 98% after 600 h |
| 79 | Encapsulant | Sulfonated graphene aerogels mixed with polydimethylsiloxane | Chemical absorption by the interaction between Pb2+ and sulfonate groups | Soaking module into water | 22.7% (2.25 cm2) | In ambient air (40–50% RH, 25 °C): ~ 90% after 500 h  In ambient air (40–50% RH, 25 ℃) and under 30 W LED illumination: ~100% after 7 d |
| 98 | Encapsulant | Purolite C100 (in a Na+ form) in ultraviolet-cured resin (UVR-C) | Chemical absorption by bountiful sulfonic acid groups | Soaking PSCs into water/water dripping | ~21% | In ambient air: ~100% for > 500 h |
| 99 | Encapsulant | P,P′-di(2-ethylhexyl)methanediphosphonic acid (DMDP) film | Chemical absorption by two phosphonic acid groups | Soaking PSCs into water/water dripping | 20.27% | Continuous operation at 1 sun simulated illumination intensity in the air at approximately 50 ℃: 80% after 500 h |
| 100 | Encapsulant | Poly-AA (PAA) ionogel with acrylic acid (AA), methylene-bis-acrylamide (MBAA), azobisisobutyronitrile (AIBN), and tributyl(methyl)phosphonium dimethylphosphate (TPDP) | Chemical absorption by phosphate groups of TPDP and carboxyl groups of PAA | Soaking damaged mini-modules into water | 22.9% 18.5% (31.5 cm2) | Damp heat test at 85% RH and 85 °C environment: 95.2% after >1000 h  Thermal cycling test (IEC 61215): 96.1% after 210 cycles |
| 67 | Post-lead sequestration | Metal–organic framework (MOF) polymer composite, FeBTC/PDA (FeBTC = Iron (III) benzene tricarboxylic acid, PDA = poly(dopamine) | Chemisorption by catechol and amine functional groups | Soaking unencapsulated PSCs into water | - | - |