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REVIEW

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Cite this: *Mater. Chem. Front.*, 2022, **6**, 2779

Challenges of lead leakage in perovskite solar cells

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Received 30th June 2022,
Accepted 20th July 2022

DOI: 10.1039/d2qm00632d

rsc.li/frontiers-materials

Solar energy is a promising energy source to resolve the expanded energy demand for global development. In recent years, perovskite solar cells (PSCs) have shown dramatic improvements, from device efficiency to operation lifetime. Their low-cost and simple preparation process, tunable bandgap, and customizable applications give them promise for commercialization. Among the perovskite materials for photovoltaic application, the lead-halide perovskites have achieved the highest efficiency of 25.7%, which is much better than that of Sn-based (13.4%) and Ge-based (7.11%) PSCs, and at the same time, the best stability. However, the toxicity risk of the Pb element makes people question its commercial application. Pb-polluted soil could affect the growth of plants, and the contaminated water environment influences the health of fish and other aquatic animals. Pb will eventually accumulate in human body through the food chain, damaging the central nervous system and causing cardiovascular diseases. Laws and regulations for heavy metals are well established, and only if the Pb leakage risk can be controlled within a certain range can the commercial application of PSCs be considered safe and reliable. This review summarizes the pathway for Pb leakage and its impact on health and the environment. Especially, strategies for preventing Pb from leaking are discussed. Finally, we propose strategies for PSCs to achieve a good balance between high efficiency, long-term stability, and environmental protection.

1. Toxicity of PSCs

Perovskite materials have achieved great developments in recent years,[1–5] however, it still suffer from stability issues, including ion migration, phase transition, phase segregation, and component volatilization, leading to material and device degradation, especially when working under high humidity, high temperature, and ultraviolet irradiation. Upon degradation of the material and device, the device performance decays dramatically, and at the same time, the components, which include the organic cation, halide anion, and highly toxic Pb(ɪɪ), also pose the risk of leaking into the environment, resulting in soil and water contamination.

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1.1 Pb Leakage of PSCs

Perovskites easily decompose when exposed to water. A typical $MAPbI_3$ perovskite, upon mixing with water, would experience a spontaneous and irreversible dissolution process.[6] Under the reaction between water molecules and Pb sites, the perovskite surface first undergoes a rapid dissolution, exposing I and forming stronger Pb–I bonds on the surface. However, the Pb–I bond will hydrate and form a hydrated phase, resulting in faster dissolution of the perovskite, which eventually decomposes completely.[7] In addition, humidity could also lead to structural collapse. Under high humidity, perovskite degrades through different mesophases and finally decomposes into toxic PbI_2.[8–10] Mixed-cation perovskites have demonstrated improved stability. However, under moisture and light, the mixed phases (*e.g.*, $FA_{0.85}Cs_{0.15}PbI_3$) gradually separate and degrade within 30 hours. In the first stage, the FAI evaporates and forms PbI_2 pits, and the $FACsPbI_3$ phase separates into needle-like δ_o–$CsPbI_3$ and large δ-$FAPbI_3$ particles, which gradually shrink and decompose to PbI_2 (Fig. 1c and d),[11] which dominates the Pb leakage kinetics. Besides water and oxygen, the photovoltaic performance of perovskite solar cells is also significantly reduced under UV irradiation due to the fragile resistance of perovskite to high-energy radiation,[12–14] which may also lead to structural collapse.

Under the synergistic influence of external stimuli, the perovskites eventually degrade into lead iodide or elemental lead. If water participates in this process, the degradation is further accelerated. After degradation, Pb exists in the form of Pb^{2+} and Pb^0, which have been proven harmful to the environment and human health. In the current research, the degradation of perovskite after long-term operation is unavoidable, so it is crucial to estimate the Pb leakage risk and avoid further contamination.

1.2 Toxicity of Pb after degradation

Upon material degradation and damage to the device, the Pb in perovskite may decompose into elemental lead and lead ions, then leak into the environment through the soil and water. In view of the importance of soil and water to the ecosystem, toxic Pb could have a serious impact on organisms. A series of studies have shown that the central nervous system[15] and cardiovascular system[16] of humans and other creatures can be greatly affected under Pb poisoning.[17]

An and coworkers characterized the teratogenic effects on Japanese medaka larvae at 16 dpf (days post fertilization) in water containing different concentrations of lead iodide. Fig. 2a shows that as the concentration of PbI_2 increased, different effects of teratogenicity appeared, including growth reduction, tail malformation, spine deformity, hemostasis, and edema deformation in organs, with a dramatically increased risk.[18] The impact of organic cations has also been raised; some studies demonstrated that the presence of organic cations promotes the absorption of Pb by organisms, and their bioavailability is ten times higher than the single PbI_2. As a result, the Pb^{2+} content in mint leaves planted in perovskite-contaminated soil was 50 times higher than that of leaves planted in natural soil (Fig. 2b).[19]

To sum up, Pb presents a high risk of leaking from degraded perovskite devices and modules, and its toxicity greatly impacts creatures and the environment. To avoid the potential damage, strategies for preventing Pb leakage have been developed, from microscopic material design to macroscopic device encapsulation.

2. Strategies for Pb leakage control

Laws and regulations have already been promulgated to restrict Pb pollution. Based on the EU Restriction of Hazardous Substances (RoHS) Directive and the US Resource Conservation and Recovery Act (RCRA) Pb regulations, Moody *et al.* evaluated the pollution risk of perovskite and found that the Pb leakage in perovskite devices exceeded current standards, and thus the Pb leakage problem could not be ignored.[20] To date, several strategies have been developed to minimize the leakage of Pb.

2.1 Encapsulation and barrier layers

Encapsulation is the most commonly used strategy to achieve long-term stability under the working conditions by preventing the invasion of moisture and oxygen. Generally, organic macromolecules and glass cover plates are used in encapsulation for physical protection, and at the same time, they also prevent Pb leakage. However, under extreme weather conditions, such as severe temperature changes and hail, the simple encapsulations are not intensively reliable; they may become cracked and destroyed, leaving the perovskite layer directly exposed to the environment.

Self-healing polymers have been proposed to enhance the robustness of encapsulation. Inspired by the self-healing feature of epoxy resin (ER)-based polymer at high temperature, Qi *et al.* suggested an encapsulation method using a combined ER and glass cover bonded with ultraviolet resin (Fig. 3a and b). The glass transition temperature (T_g) of the self-healing polymer material is about 42 °C, which is approximately equal to

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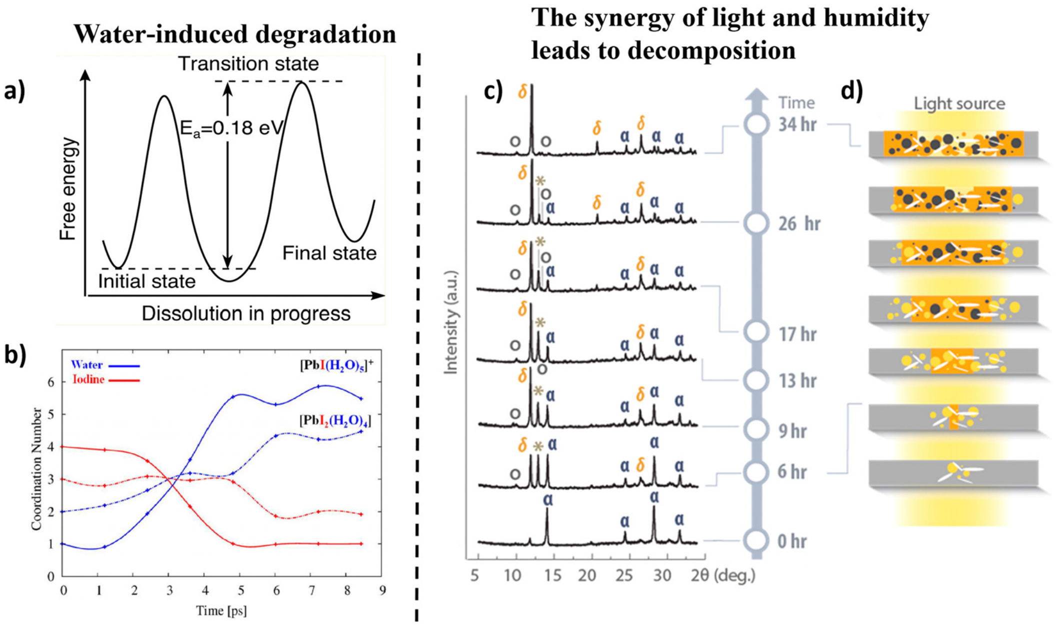

Fig. 1 (a) Low-energy barrier is formed during perovskite dissolution.[6] (b) The hydrated phase of lead iodide and water.[7] Reproduced from ref. 7 with permission from American Chemical Society, copyright 2015. (c) XRD at different degradation times under light and humidity. (d) Schematic representation of the degradation process.[11] Reproduced from ref. 11 with permission from American Chemical Society, copyright 2021.

the surface temperature of the module when directly exposed to sunlight (45 °C). The contact angle test verified that the ER could be re-crosslinked under direct sunlight illumination. To simulate hail damage conditions, the device was hit by a metal ball dropped from a fixed height. Compared with traditional encapsulation methods, the ER encapsulation reduced the Pb leakage rates of damaged devices from 30 to 0.08 mg h^{-1} m^{-2}. This result illustrated that ER encapsulation restored the protection of perovskite photovoltaic devices after the damage.[21] Furthermore, Wan *et al.* developed a "sandwich" encapsulant approach by combining two kinds of encapsulants, polyolefin (PO) and polyisobutene (PIB), as shown in Fig. 3c. The devices were damaged under the same conditions in Qi's work, and then immersed in solutions with different pH values (to simulate conditions of seawater, lake water, and rain) to evaluate the Pb leakage. The "sandwich" encapsulant alleviated the damage of hail and acid rain on the device to a certain extent. Under the protection of the "sandwich" package, Pb leakage into the soil dropped to 3.4 ppm,[22] which is much lower than the value of 70 ppm predicted by Hailegnaw in 2016.[23]

In addition to the traditional external encapsulation by polymer and glass cover, the Pb leakage can also be minimized by introducing internal encapsulations. Huang *et al.* converted the lead in perovskite to lead sulfate by an *in situ* reaction with octylamine sulfate, and a dense lead sulfate shelled structure was formed on the surface of perovskite films (Fig. 4b). With a low solubility product constant of about 10^{-18}, lead sulfate could be considered insoluble in water, which then acts as a barrier, preventing the invasion of water. Benefiting from the protection of this dense shell, the perovskite single crystal showed significantly enhanced stability without phase change and decomposition after being placed in water for over 60 s (Fig. 4c), resulting in reduced Pb leakage risk.[24] Jen *et al.* developed superhydrophobic self-assembled monolayers (SAMs) on top of silver electrodes by evaporating 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT), whose sulfhydryl group bonds to silver during evaporation and forms a superhydrophobic structure. It also bonded with Pb and passivated the defects, thus minimizing the Pb leakage to 2.05 ppm.[25]

Waterproof encapsulants could prevent Pb leakage; however, as a physical barrier, Pb leakage still cannot be avoided if the encapsulation becomes invalid under serious physical damage. Moreover, the encapsulants degrade under the stimulation of light and heat,[26] which could cause the generation of cracks and material deformation. Thus, simple encapsulation may be not enough to provide full protection for Pb leakage control.

2.2 Chemisorption layer

Besides the construction of a physical barrier, chemically absorbing the free-state Pb is also crucial for leakage control. The internal absorption layer can be set as the "frontline" for Pb leakage prevention. Although external encapsulation can block water and oxygen invasion, the perovskite could still degrade under continuous illumination and/or vacuum,[11] thus generating free-state Pb. The design principle of the internal chemisorption layer is that it can absorb Pb and/or form chelates to avoid Pb leakage. Sulfur-containing groups have been selected to pin the Pb without damaging the structure of the perovskite.

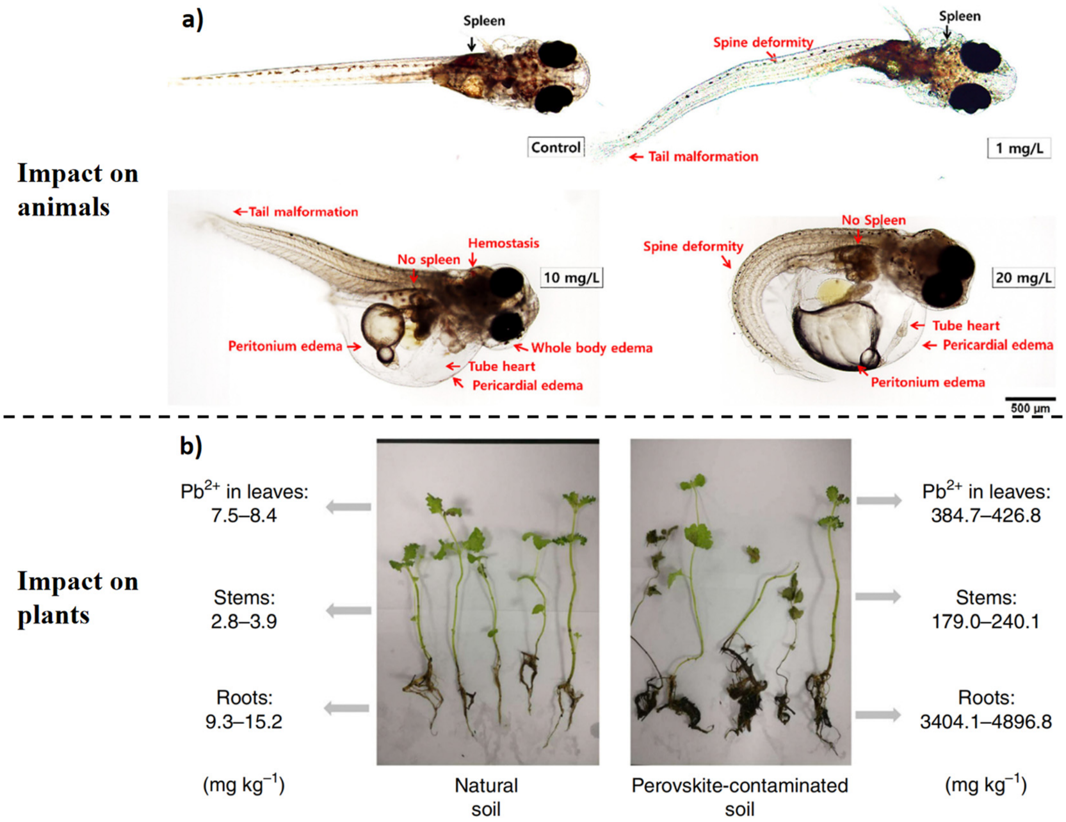

Fig. 2 (a) Appearance of surviving Japanese medaka larvae after exposure to 16 dpf of PbI_2. With increasing concentrations of PbI_2 exposure, PbI_2-treated Japanese medaka fry exhibited various adverse effects, as shown in the figure.[18] Reproduced from ref. 18 with permission from Elsevier B.V., copyright 2021. (b) The picture of mint plants grown on control soil (left) and 250 mg kg^{-1} Pb^{2+} perovskite–contaminated soil (right). The Pb concentration in mint leaves, stems, and roots grown in polluted soil is about 50 times, 70 times, and 350 times higher than that in natural soil.[19] Reproduced from ref. 19 with permission from Springer Nature, copyright 2020.

Lead is the only element in the IV_A group that can form a stable thiolate, which has been applied to the design of adsorbent molecules. The reaction of thiol (R-SH) and lead(II) salt can produce yellow lead thiolate precipitate. In clinical treatment, mercaptans are used as detoxification therapeutics for heavy metal elements such as lead, mercury, cadmium, *etc.*[27] Sulfur-containing groups such as sulfhydryl and sulfonate are also commonly used functional groups for Pb coordination.[28]

Cation exchange resin (CER) has been applied for Pb adsorption due to its high adsorption capacity. Huang *et al.* introduced a CER that contains sulfonate groups (structure shown in Fig. 5a) to decorate the metal electrodes, which effectively minimized the Pb leakage. Mixing the CER with carbon electrode resulted in a unique mesoporous structure with high binding energy towards Pb, leading to a stronger ability to inhibit Pb leakage with the higher adsorption efficiency. This strategy reduced the Pb leakage of carbon-based devices to the ppb level, at 14.3 ppb (1.43×10^{-2} ppm), a safe value for the environment.[29] This sulfonate resin was also used as a scaffold that grew directly on polytriarylamine (PTAA) and acted as the bottom substrate for perovskite growth. The application of this sandwiched Pb-absorbing resin further reduced the Pb leakage to 1.5×10^{-3} ppm, almost reaching the detection limit of ICP instruments. Moreover, this structure contributed to PCE improvement, from 19.4% to 20.4%.[30] Huang *et al.* also applied PAA (polyacrylic acid) ion gels for Pb adsorption. Compared with CER, this ion gel had better elasticity and healing properties after damage, which also prevented Pb leakage from the battery module even after extreme damage (such as car rolling).[31] Zhu *et al.* mixed the CER with UV resin to encapsulate the metal side of rigid and flexible devices. This CER (C100), containing sulfonic acid groups, not only was used as an encapsulant adhesive for mechanical enhancement but also absorbed the leached Pb. It can be seen from Fig. 5d that whether it is a device or a thin film, rigid or flexible substrate, the leakage of perovskite Pb after C100 encapsulation is greatly reduced to less than 5 ppm.[32]

Besides CER, metal porphyrins with thiols were also used to enhance the water resistance of perovskites. As shown in Fig. 6, porphyrin molecules have multiple reactive sites, like cobwebs in nature. Thiols pinned the Pb in the lattice by forming Pb–S bonds, and at the same time, the central Cu^{2+} ion and/or other metals in porphyrin copper could modulate the distribution of electrons in the porphyrin ring through π–I interactions, and

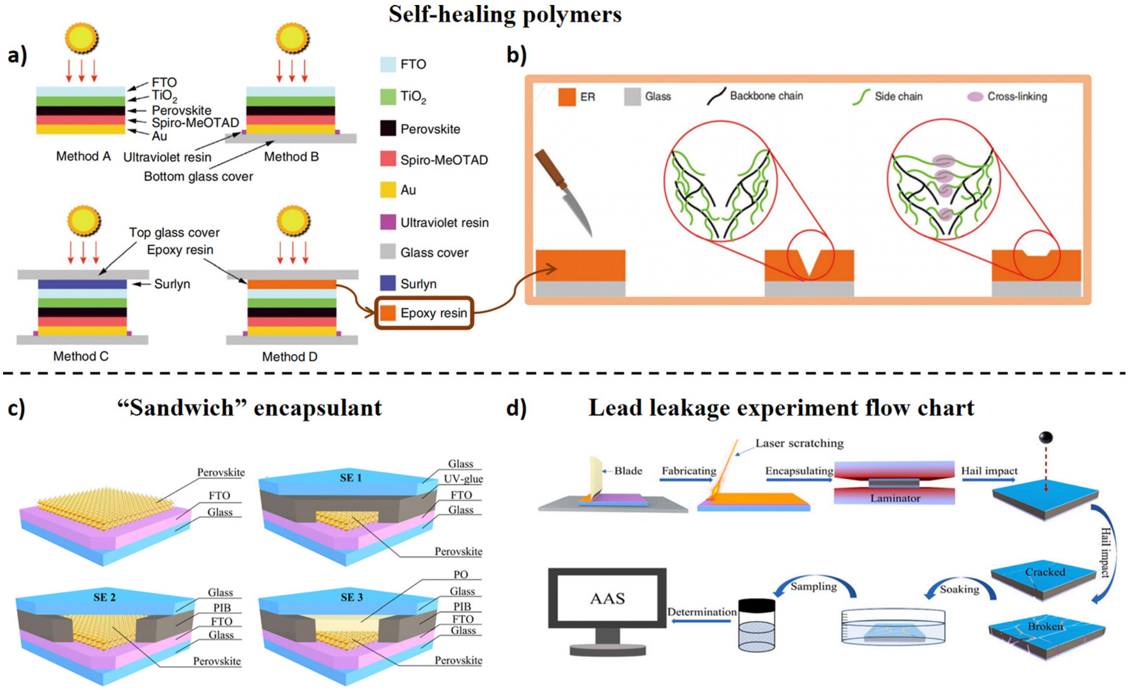

Fig. 3 Schematic showing the (a) encapsulation methods A, B, C, and D and (b) the self-healing process of the ER encapsulant.[21] Reproduced from ref. 21 with permission from Springer Nature, copyright 2019. (c) Unencapsulated perovskite devices and devices with different "sandwich" encapsulation methods. (d) The Pb leakage test process mainly includes device fabrication, packaging, simulated-hail metal ball impact test, dripping water or soaking, sampling, and lead ion concentration determination.[22] Reproduced from ref. 22 with permission from Elsevier B.V., copyright 2021.

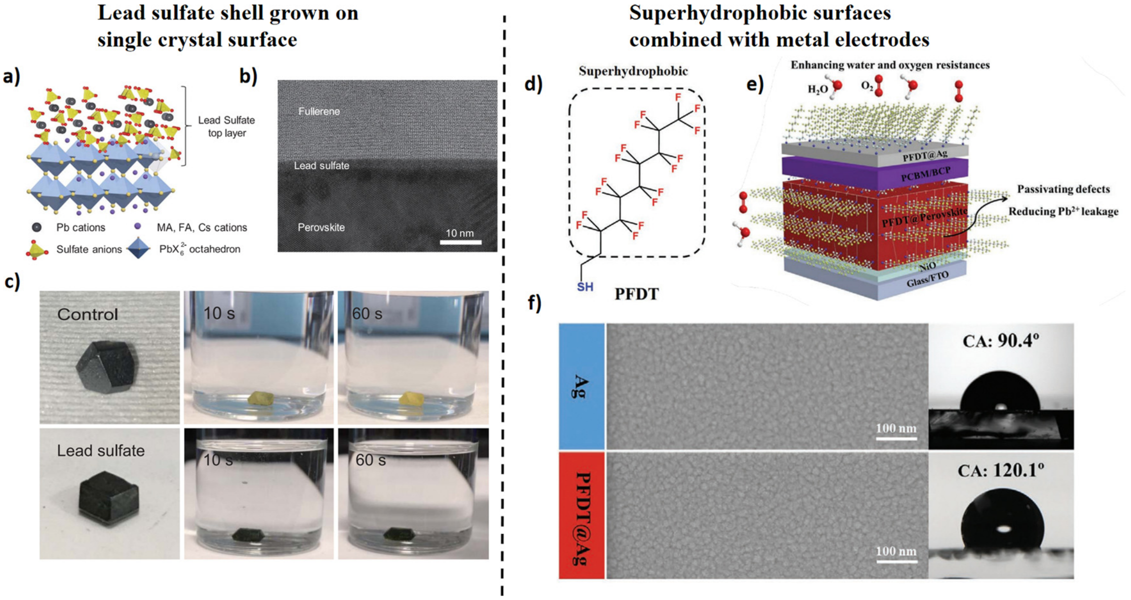

Fig. 4 (a) Schematic illustration of the *in situ* formation of lead sulfate dense layers on perovskite surfaces. (b) Cross-sectional HR-TEM image of the perovskite/lead sulfate/C60 interface. (c) Comparison of immersion effects on $MAPbI_3$ single crystal with and without lead sulfate shell in water.[24] Reproduced from ref. 24 with permission from American Association for the Advancement of Science, copyright 2019. (d) Schematic diagram of the structure of PFDT and (e) the function of blocking water and oxygen on the inverted device to prevent Pb leakage. (f) The water contact angle of the modified silver electrode surface increased from 90° to 120°, and the hydrophobicity was greatly improved.[25] Reproduced from ref. 25 with permission from Wiley-VCH GmbH, copyright 2021.

the hydrogen bond formed with side chains effectively combine the I^- and I_2 on the perovskite surface. The porphyrin molecule acts as a hydrophobic layer on the perovskite film, thus suppressing water invasion, and is strongly bonded to the

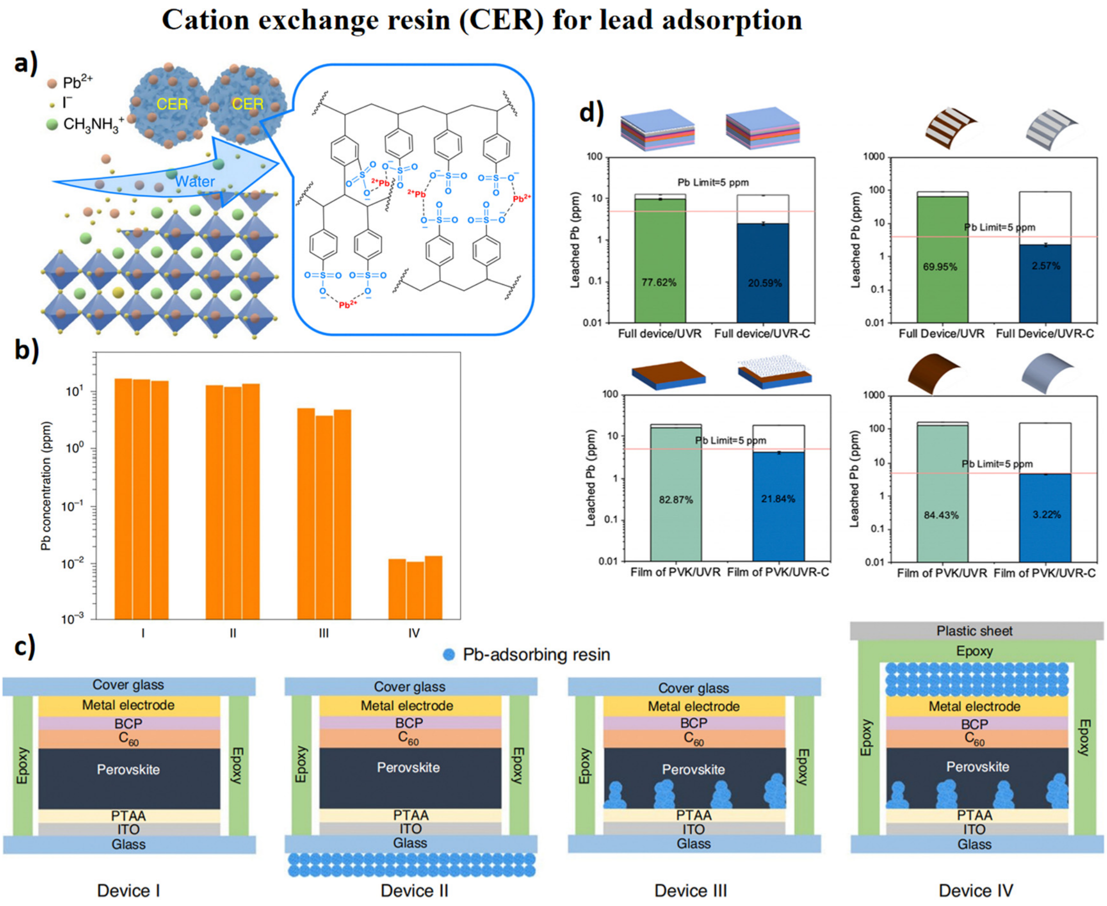

Fig. 5 (a) Schematic diagram of the cation exchange resin with sulfonic acid groups.[29] Reproduced from ref. 29 with permission from Springer Nature, copyright 2020. (b) Pb leakage detection in four types of encapsulation structures and (c) schematic diagrams of four encapsulation methods with CER in the lower interface bracket and the upper interface.[30] Reproduced from ref. 30 with permission from Springer Nature, copyright 2021. (d) Comparison of lead leaching from devices and films on glass and flexible substrates using UVR and UVR-C as encapsulant.[32] Reproduced from ref. 32 with permission from Elsevier Ltd, copyright 2022.

perovskite surface through chemical bonds. This molecule stabilized the perovskite in water for five minutes without decomposing and dissolved in the form of perovskite instead of decomposing into lead iodide, thus minimizing Pb leakage.[33,34] Studies have shown that Pb leakage of the perovskite film encapsulated by porphyrin molecules was effectively reduced to 1.5 ppm after being immersed in water for 10 minutes, which was half that of the unencapsulated device.[35]

In addition to introducing separated adsorption or barrier layers, Pb adsorption can also be realized by material functionalization. Jen *et al.* developed the electron extraction layer (EEL) into a two-dimensional metal–organic framework (MOF) with heavy metal absorption ability (shown in Fig. 7a). The organic framework of Zr-based MOF contained sulfhydryl groups to trap the leaked Pb^{2+} in perovskites by forming water-insoluble species, with a reduced Pb leakage of 7.6 ppm (38.4 ppm for reference). Furthermore, the Zr-based MOF-modified bis-C_{60} EEL enhanced the PCE and stability of perovskite devices.[36] Macromolecules that could form a chelate with Pb were also employed to prevent Pb leakage. Park *et al.* demonstrated a novel donor–acceptor-type polymer hole transport layer (HTL), alkoxy-PTEG (composed of benzo[1,2-*b*:4,5:b′]dithiophene and tetraethylene glycol (TEG)-substituted 2,1,3-benzothiadiazole). The alkoxy-PTEG showed a better blocking effect for Pb compared with the spiro-OMeTAD (Fig. 7b); however, the capture ability for Pb of this thin layer is weaker than the sulfhydryl-based encapsulant method.[37]

Aside from the capture ability of the functional group, the absorption efficiency also depends on the contact area between the absorber layer and the perovskite. Chen *et al.* implanted an *in situ* polymerized three-dimensional network between the perovskite grains (as shown in Fig. 8a and b), which increased the contact area between the Pb absorber layer and the perovskite, effectively minimizing the Pb leakage. They used dormant acrylamide (AAm) to react with Pb with a ratio of 1:1 to form a polyamide (i-PAM@PbI_2) network chelated with Pb at the crystal grains. By soaking the unencapsulated devices in water, they found that the i-PAM@PbI_2 device showed good water stability compared with the reference device. Further increasing the amount of AAm added to 20 mg mL^{-1}, the Pb leakage of the device was reduced by half, and for the highest

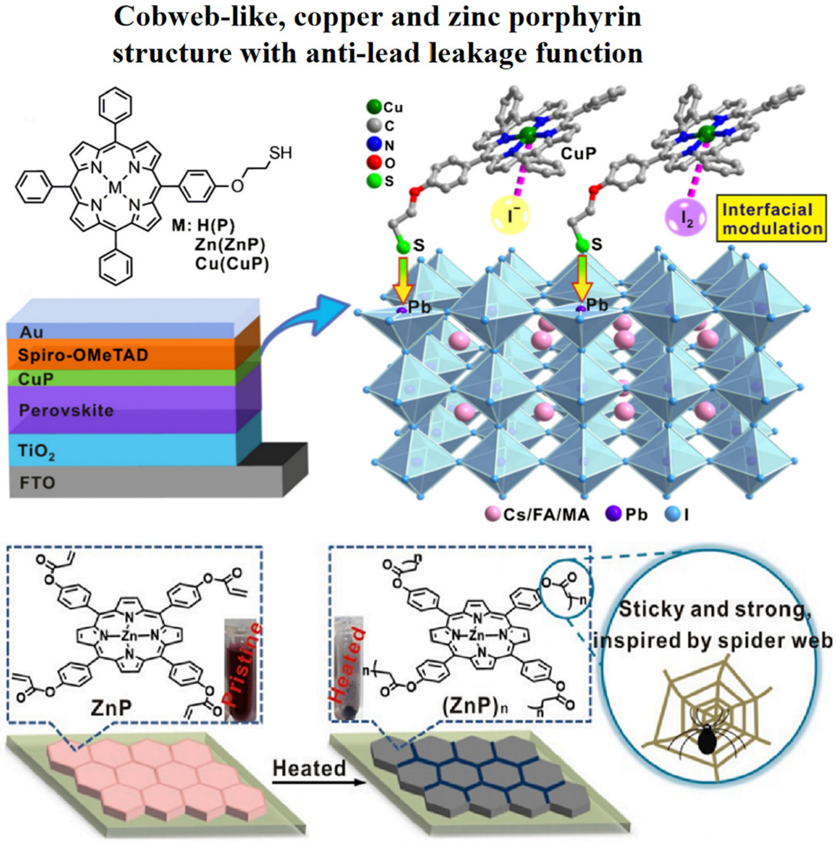

Fig. 6 Schematic diagram of the structure of metalloporphyrin, with multiple reactive sites that can coordinate with perovskite, and has the function of preventing lead leakage.[33,34] Reproduced from ref. 33 with permission from Elsevier B.V., copyright 2021. Reproduced from ref. 34 with permission from Chinese Chemical Society, copyright 2021.

concentration of AAm of 80 mg mL^{-1}, the Pb leakage was further decreased to only 0.79 ppm (Fig. 8c).[38]

It needs to be noted that the functionalized charge transport layer can only resist Pb leakage for a very short time, around 5–10 minutes, which provides a limited response time for replacing the damaged device, and a high risk of Pb leakage remains. Its primary function is to develop the device performance by acting as charge transport layer, passivation layer, and/or barrier layer. When the chemisorption layer adsorbs lead or forms chelates, it may lose its essential function, and the perovskite lattice collapses due to the reduction of lead. To our knowledge, no research has demonstrated a material that can temporarily store Pb and allow it to return to the crystal lattice under certain conditions, like a buffer layer. The design of this kind of material may resolve the Pb leakage problem and improve the stability of perovskites at the same time.

2.3 Recycling and reuse of Pb

According to previous discussions, the building of a physical barrier and/or chemical adsorption can be applied to minimize Pb leakage risk. However, the development of appropriate recycling methods still plays a more crucial role in the production lifetime for waste and pollution control.

2.3.1 Device reuse and Pb extraction. The cost of perovskite solar cells was estimated to be about 16 USD m^{-2} (Fig. 9a),[39] of which the glass substrates account for 50–70%.[40] When devices are discarded directly, they not only pollute the environment but also bring material waste. From the perspective of cost saving and environmental protection, the recycling of perovskite solar cells is necessary. Among the source materials of perovskite PV devices, the inorganic components such as glass substrates, electrode materials, and lead iodide are all recyclable.

The general idea of recycling is to layer the encapsulated perovskite solar modules and extract PbI_2 by solution method. Huang *et al.* dissolved the perovskite with *N*,*N*-dimethylformamide (DMF) and used carboxylic acid cation exchange resin to remove the lead ions in DMF. The lead ions adsorbed on the resin were further released into the aqueous solution through the regeneration process of nitric acid, and lead iodide was precipitated by adding sodium iodide. In this method, the lead recovery rate reached 99.9%.[41]

Pathak's team introduced another approach to recycling the lead iodide, in which the Pb source is not extracted separately, but directly reused in the form of PbI_2 film, and in which the degraded perovskite film is treated with acetic acid *via* a single-step method to remove the organic cations. It was found that the photoelectric performance of the perovskite devices fabricated from the reused PbI_2 film showed no obvious decrease, and it was even better than that from fresh PbI_2 films.[42]

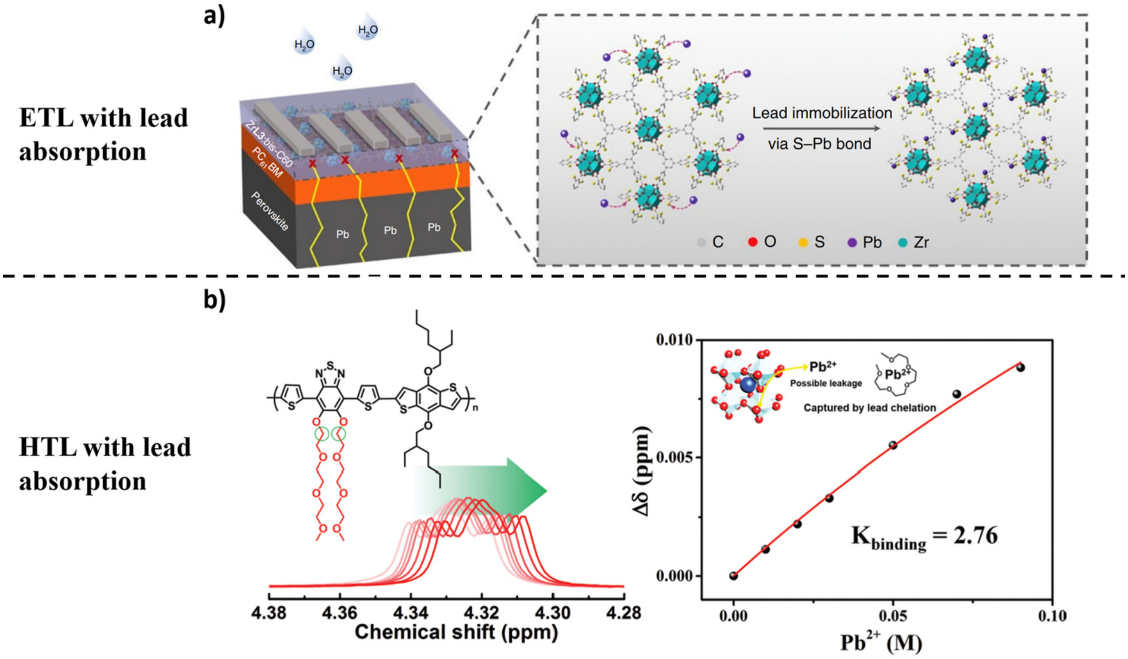

Fig. 7 (a) Schematic diagram of ZrL3 : bisC60 electron transport layer reducing Pb leakage.[36] Reproduced from ref. 36 with permission from Springer Nature, copyright 2020. (b) 1*H* NMR spectra and linear correlation plots of chemical shifts of alkoxy-PTEG monomer with increasing Pb^{2+} concentration.[37] Reproduced from ref. 37 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2020.

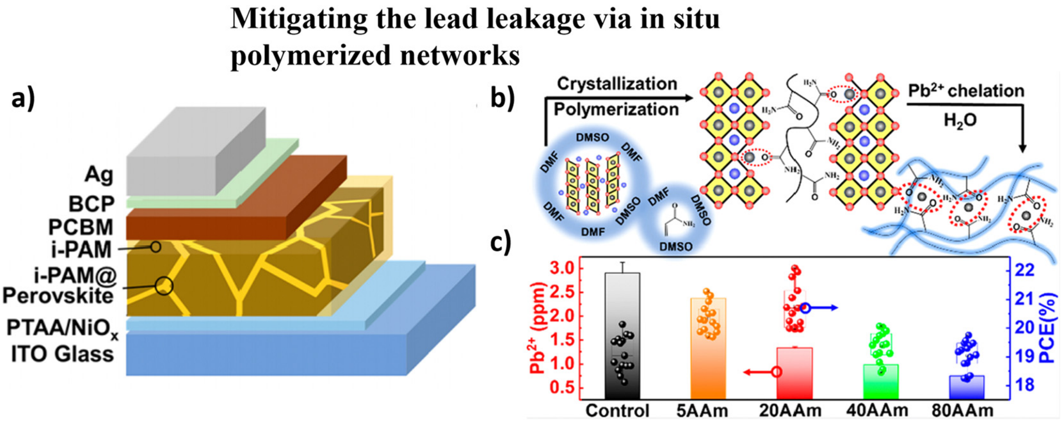

Fig. 8 (a) Device structure of PSC and schematic diagram of the i-PAM@PbI_2 organic network. (b) Formation process of i-PAM@PbI_2 *via in situ* polymerization. (c) Effects of different concentrations (mg mL^{-1}) of i-PAM@PbI_2 on device efficiency and Pb leakage inhibition.[38] Reproduced from ref. 38 with permission from American Chemical Society, copyright 2021.

2.3.2 Post-treatment of Pb leakage.

In case of Pb leakage after the device is damaged, the post-treatment methods for purifying the polluted water and soil are equally important. Current conventional methods for removing heavy metals from aqueous solutions and soil include chemical precipitation, electrochemical recovery, ion-exchange membranes/ion-chelating agents, solvent extraction/liquid membrane separation, and size exclusion.[43] However, these methods involve not only complicated pretreatment but also high cost. Compared with the above-mentioned industrial methods, Pb can be absorbed by using materials or organisms in nature. Some plants can absorb the heavy-metal elements for growth,[44,45] and the natural folds and porous structures can also absorb heavy-metal ions in water and soil.[46,47] The potential application of this kind of material can contribute to the repair of the environment after Pb contamination.

As a commonly used heavy-metal-chelating antidote, EDTA (ethylenediaminetetraacetic acid) has been applied in the post-treatment of Pb pollution. After continuous leaching of soil samples with EDTA solution, the Pb leaching rate can reach 80%.[48] EDTA can also be used to treat plants that adsorb Pb. When these treated plants are planted in the soil, their ability

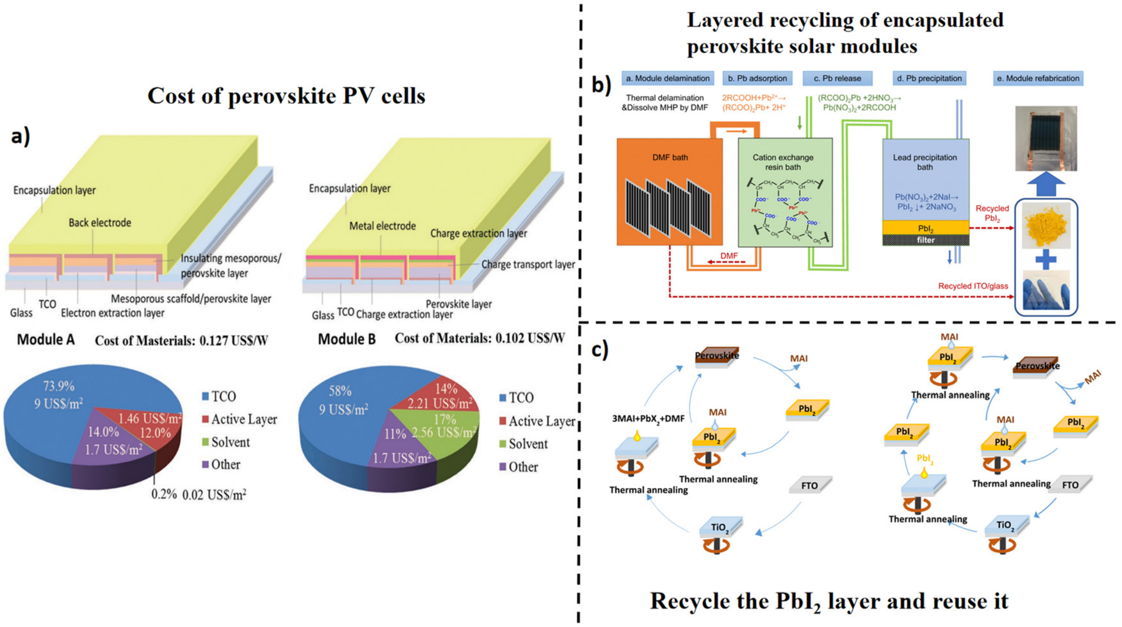

Fig. 9 (a) Schematic diagram of the perovskite photovoltaic device with mesoporous structure (module A) and planar inverted structure (module B) and their material allocation costs. Material costs are calculated based on the wholesale price and content of materials in a structure that takes into account 80% usage.[39] Reproduced from ref. 39 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2016. (b) Schematic diagram of the process of layered recovery of perovskite with different recycled materials.[41] Reproduced from ref. 41 with permission from Springer Nature, copyright 2021. (c) Removal of cations using chloride or acetate to recover and recycle PbI_2 to prepare new perovskite layers.[42] Reproduced from ref. 42 with permission from American Chemical Society, copyright 2019.

to adsorb Pb increased by up to 53 times.[49] Hussein *et al.* utilized an agricultural waste palm oil kernel shell (PKS) and found that under the condition of pH > 4, the adsorption capacity of PKS for Pb^{2+} can reach 90%. As an adsorbent, this PKS did not require any pretreatment and could easily achieve excellent adsorption effects as a filter, which reused the agricultural waste and reduced environmental pollution.[50] Algurb *et al.* also discovered a biosorbent that can be used for Pb adsorption. A pure natural Pb adsorbent was obtained by grinding the cone biomass of *Pinus sylvestris* and sieving, which was then used to filter the Pb in polluted water.[51]

2.4 Lead-free PSCs

As long as Pb is present in the crystal lattice, the risk of Pb leakage exists, so lead-free perovskites have also been widely investigated. According to the electronic structure, the IV_A and V_A elements close to Pb on the Periodic Table can be used to construct the perovskite structure of ABX_3 (X = tin, germanium,

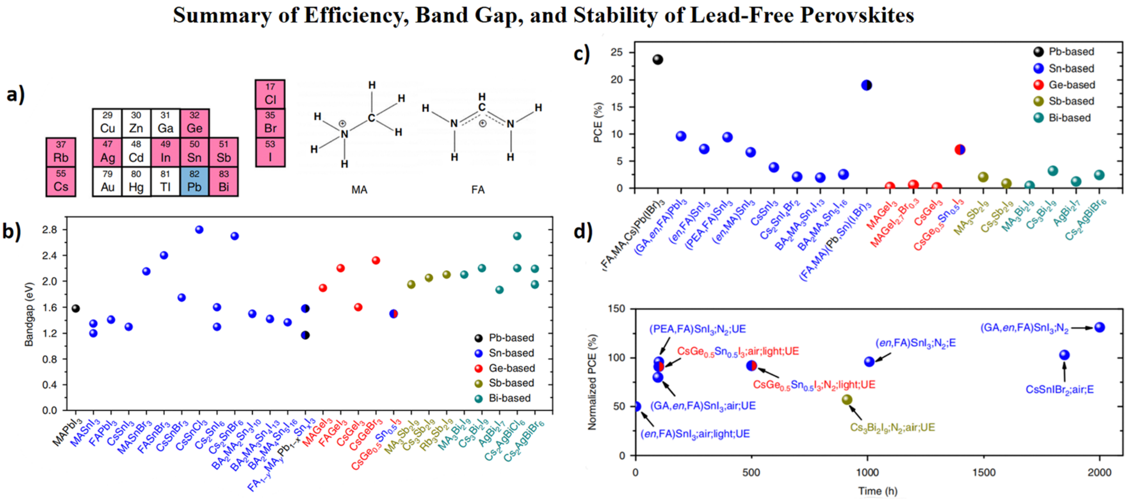

Fig. 10 (a) Potential cations, metals, and halogen atoms capable of forming perovskite structures; (b) the band gaps; (c) highest reported efficiencies; and (d) stability of the perovskites they form.[52] Reproduced from ref. 52 with permission from Springer Nature, copyright 2019.

antimony, and bismuth). For the selection of the substitute materials, the primary condition is low toxicity. Secondly, other factors, such as narrower bandgap, higher absorption coefficient, high mobility, long carrier lifetime, and good stability should be considered.

As shown by the statistical results in Fig. 10, among these materials, Sn-based materials are most likely to replace Pb due to their similar structure and bandgap. Comparing with Pb-based perovskites, the bandgap of Sn-based perovskites is more appropriate for high-efficiency photovoltaic design according to the Shockley–Queisser limit,[52] as the band gaps of $MASnI_3$, $FASnI_3$ and $CsSnI_3$ are 1.20 eV, 1.41 eV and 1.30 eV, respectively.[53] However, the oxidization of tin-based perovskite needs to be avoided to stabilize the three-dimensional structure. Its current maximum efficiency is only 12.4%,[54] which has been greatly developed but is still far from the Pb-based perovskites. Meanwhile, Boyen and Conings' work demonstrated that Sn exhibits faster and more lethal effects on organisms than Pb in terms of teratogenicity and lethality.[55] Germanium-based perovskites also attract great interest. Compared to Sn-based and Pb-based perovskites, the Ge-based perovskites exhibit wider band gaps except for $CsGeI_3$, which is 1.6 eV; the band gaps of other components are about 2 eV.[56] In addition, the efficiency of pure-phase germanium-based perovskite is not high enough. The current highest germanium-based efficiency reported is only 7.11% in a Sn–Ge binary $CsSn_{0.5}Ge_{0.5}I_3$ device.[57] Except for the IV_A elements, Bi-based, Sb-based, and In-based perovskites were also developed. However, their efficiency and stability are far from satisfactory, and most of them formed a low-dimensional structure from 0D to 2D, showing large binding energy and poor crystallinity, which were not appropriate for photovoltaic applications.[58]

In short, a tremendous improvement, especially in efficiency and stability, is expected for the Pb-free perovskites, and the benefits of utilizing PSCs with an eco-friendly feature would be appreciated.

3. Summary and outlook

In summary, as the essential component for PSCs, Pb has been proven to be a hazardous element to the environment and human health, and this is one of the major problems hindering the commercialization of PSCs. Several strategies, such as encapsulation, introducing chemisorption layers, establishing ion migration barriers, and constructing waterproof structures have been developed and show great effects on Pb leakage reduction. In addition, Pb-free PSC devices have also been proposed to resolve the Pb issue entirely; however, their lower efficiency and poor stability remain a problem. The PSC recycling procedures and environmental post-treatment methods are crucial for minimizing the influence after Pb leakage.

However, for commercialization, there are several issues to be aware of. Firstly, recent studies focus on the adsorption of leaked Pb, at the same time, retarding Pb dissolution from the kinetics view is also important. Understanding the dissolution route of PSCs will greatly benefit the selection of material for leakage control and the perovskite composition design. Secondly, the forms in which Pb exists, such as cluster, ion, solid *etc.*, need to be considered when verifying its concentration in the contaminated environment, to prevent the underestimation of undetectable species (limited by the instrument). Thirdly, suitable encapsulant materials which are not only compatible with perovskite but also with other functional layers need to be found. Last but not the least, one major advantage of PSCs is their low power generation cost (or production cost), and avoiding the rapid increase of manufacturing cost is crucial for the development and commercialization of this technology.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge funding support from the National Natural Science Foundation of China (52172182, 21975028, 22011540377, 22005035 and U21A20172) and the Beijing Municipal Natural Science Foundation (JQ19008).

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