**ABSTRACT:** Lead halide perovskites are seriously considered for next generation photovoltaic technology. They have a unique combination of easy synthesis, high efficiency, and cost-effective techniques. Still, the major concern is the toxicity of lead used in perovskite devices. The research community is still debating whether the amount of lead used in a solar cell really poses a danger or not. However, it is pretty clear that mitigating the lead leakage from the lead halide perovskite device is of utmost importance. In this review, we discuss new material chemistry approaches that can be applied to reduce the lead leakage/wastage from damaged lead halide perovskite solar cells. ECR (encapsulate, capture, and recycle) approaches have the potential to significantly reduce the environmental and health hazard risks of lead halide perovskite devices. Encapsulation by a self-healing material and rigid glass can help the perovskite survive the extreme conditions and avoid exposure of the perovskite layer to the external environment. Capturing of lead can also be done by an encapsulant layer that can very quickly and efficiently bind to lead, in the case that it leaks from the damaged perovskite device. Moreover, the recycling of damaged or decommissioned devices helps to avoid the lead wastage and contamination in the environment. Finally, we also discuss the potential of lead-free perovskite for optoelectronic applications.

**1. INTRODUCTION**

Demand for energy is increasing day by day. Fossil fuel alone would not fulfill all those needs. Furthermore, environmental sustainability is important. Harvesting solar energy has the potential to address these issues. The technology for harvesting solar energy is already there, such as with Si, CdTe, CIGS, and GaAs photovoltaic (PV) cells, with some pros and cons. The recent introduction of lead halide perovskites (LHPs) as the PV cell absorber provides us with an opportunity for solution-processed cost-effective solar cells with high power conversion efficiency (PCE). Hybrid LHP has seen a meteoric rise in the PV cell industry, achieving a PCE of 25.2% from just 3.8% within a few years of research. The meteoric rise in its efficiency is assigned to its exceptional optoelectronic properties such as long carrier diffusion length, long carrier lifetime, and defect tolerance. There are companies who have already started looking for commercialization of perovskite PV cells either as stand-alone PV technology or in tandem with silicon PV technology. However, the two major concerns of LHP are its instability and toxicity. For the instability problem, researchers have achieved significant success and have developed LHP PV cells with reasonable working stability. That is a good sign. Likewise, researchers are making significant progress to suppress issues related to lead toxicity, as well. Not only PVs, with the new proposed applications like light-emitting diodes (LEDs), photodetectors, and lasers, it is important to have a discussion on the environmental and health hazard that these LHP compounds pose.

While lead will always remain a toxic element, innovative chemistry approaches are coming up to suppress the chances of lead toxicity from LHP devices. The focus of this mini-review is to discuss the recent progress in this direction. In the beginning, we will discuss how the degradation of LHPs gives rise to concerns of lead toxicity and then compare the status with existing technologies like lead acid batteries and electronic solders with LHP PVs. Then, we will discuss new encapsulating materials, such as self-healing polymers, glass, and lead sequestration layers that suppress leakage of lead from LHP devices to the environment. Subsequently, recyclability issues of damaged or decommissioned devices and opportunities of lead-free perovskites will be discussed.

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2. LHP Degradation and Its Toxicity

LHPs are easily degraded by the action of heat and water/moisture. Figure 1a shows the heat-induced decomposition mechanisms of LHP by taking the example of widely studied CH₃NH₃PbI₃ or MAPbI₃. It can be seen that the exact product of the decomposition of MAPbI₃ varies depending on the temperature it encounters.

For a relatively lower temperature (<200 °C), MAPbI₃ degrades to volatile species HI, CH₃NH₂, and solid PbI₂. However, at a higher temperature (>200 °C), it degrades to thermodynamically more stable volatile species like NH₃, CH₃I, and solid PbI₂. Figure 1b shows the degradation of MAPbI₃ in the presence of water. The treatment of MAPbI₃ with water converts it to its monohydrate phase, that is, MAPbI₃·H₂O. The monohydrate phase consists of one-dimensional [PbI₃]⁻ double chains. Further hydration of this phase causes it to degrade into PbI₂ and aqueous MAI solution. It is clear that PbI₂ is the main lead-containing byproduct of LHP degradation.

Lead toxicity has a long history of affecting human health and the environment. Pb has been long used for making water pipes, pots, coins, and household paints, resulting in a serious health hazard. Toxicity of lead also stems from the fact that it can mimic other biological important ions such as Ca²⁺, Fe²⁺, and Zn²⁺. It is known to be carcinogenic. If ingested, lead gets accumulated in bones as lead phosphate and has a half-life of 40–50 years. Lead poisoning results in anemia, kidney damage, hypertension, and neurological disorder. Children and pregnant women are especially more vulnerable to it as it is known to cause severe intellectual retardation and behavioral problems. A concentration of lead >5 μg/dL in the blood is considered to be a case of lead poisoning. To treat the lead poisoning, chelation therapy is used. EDTA (ethylenediaminetetraacetate) and other chelating-agent-based drugs are used which bind to the lead and decrease its concentration in the body.

Given such toxicity of lead, Regulation of Hazardous Substances (RoHS) has restricted the amount of lead that can be used in electrical and electronic applications. A report by Dedecker et al. compiled the total amount of lead in different devices, wasted amount, lead concentration in soil, and the safe limit. Figure 1c shows the amount of lead required to manufacture and then the waste released from various lead-based applications. The amounts of lead required to generate electrical energy for the U.S. and the whole world (total energy generation in the year of 2011) based on LHP PV are 160 and 1000 t/year (t/year = tons/year), respectively. The calculation is carried out assuming the MAPbI₃-based PV device has an active layer thickness of 300 nm and an efficiency of 25%. Lead energy intensity, that is, the amounts of lead required to generate unit electricity for MAPbI₃, is 38 μg/kWh. So, multiplying this by the total energy requirement gives the required amount of lead needed for LHP PV devices, whereas the amounts of lead required for electric solder and lead acid batteries are 6200 and 1,000,000 t/year, respectively. Similarly, the waste generated by considering all LHP PV device dissolution would be only 1000 t/year, which would still be far less than the lead waste generated (around million t/year) by lead acid battery technology.

Figure 1d shows the lead concentration in the soil, which is contaminated by a LHP device. It also shows the average lead concentration in natural soil and the limit set by the U.S. Environmental Protection Agency (EPA) for the maximum allowed lead contamination in soil. Hailegnaw et al. did the calculation for determining the concentration of lead in soil by the degradation of the LHP PV cell, considering a 1 m² solar...
panel having a 300 nm thick MAPbI$_3$ layer. This layer contains 0.42 g of lead, which then if fully degraded would increase the concentration of lead in soil to 70 ppm (assuming soil density of 1.95 $\times$ 10$^3$ g/m$^3$) in the first centimeter of the soil below the LHP PV panel. With the effect of rain, this concentration would decrease because of the dispersion of lead in the further depth of the soil. The natural soil has lead concentration varying from 30 to 200 ppm depending on the geographical region and the industrial activities around it.\(^{14}\) The EPA has set the limit for the lead concentration in bare soil (play areas) as 400 ppm, whereas for urban soil, it is around 1200 ppm (nonplay areas).\(^{10}\) The study by Wixson et al.\(^{15}\) has proposed a limit of lead concentration of 300 ppm in the soil to prevent contamination due to LHP PV. However, the answer to the question of whether lead toxicity of LHPs remains an important concern for commercial application of these perovskite semiconductors is not an easy one to answer. There is simply a lack of enough studies looking at this matter. On one hand, the amount of lead contained in the LHP PV module is minute, and so the lead contamination due to LHP PV is very small compared to lead generated from coal power plants, lead acid batteries, and electronic solders. However, on the other hand, even the small amount of lead released is very harmful because of the increased bioavailability of its water-soluble salts. PbI$_2$ is commonly used as a precursor for the fabrication of LHP PV devices and is also regenerated when the perovskite degrades (see Figure 1a,b). PbI$_2$ has reasonable solubility in water and can enter the groundwater once the perovskite PV module breaks. \(^{14}\) Consequently, this form of lead is easily bioavailable to plants and other organisms and so can enter our food chain.

### 3. BIOAVAILABILITY OF LEAD LEAKED FROM PEROVSKITE PV MODULE

The number of experimental studies on health hazards caused by lead used in perovskite PV is limited. One such recent study by Li et al.\(^{16}\) has shown that the lead uptake by plants in LHP-contaminated soil is not linear with the lead concentration in the soil. To simulate the LHP contamination, they have added MAI + PbI$_2$. They have found that the lead from LHP contamination of the soil and water can enter the plant and subsequently in our food cycle more effectively than the other lead contaminants, such as electric solders or lead acid batteries. The increased bioavailability of lead from LHP is attributed to the presence of an organic cation in LHP, which helps with more uptake by plants. The LHP-like MAPbI$_3$ degrades to PbI$_2$, CH$_3$NH$_2$, and HI. HI decreases the soil pH and makes it more acidic. The solubility of lead salts is more in an acidic condition and thus increases their bioavailability to plants and animals.

Figure 2 shows the comparison of the concentration of lead in roots, stems, and leaves of mint plants grown in natural soil, with the mint plants grown in perovskite-contaminated soil after 20 days of the growth period. The natural soil (refers to the soil having lead contamination from other anthropological events such as mining, electronic waste, etc.) has a lead concentration of 36.3 mg kg$^{-1}$. The perovskite-contaminated soil has a lead concentration of 250 mg kg$^{-1}$. Although the perovskite-contaminated soil has only 7-fold higher lead content, the lead uptake in plant gets increased by 366 times. This excessive lead content in the studied mint plants showed blackening and rotting, indicating lead poisoning and then the death of the plants.

### 4. CHEMISTRY APPROACHES TO SUPPRESS LEAD TOXICITY

The amount of lead used in LHP PV devices is small, but preliminary studies suggest that the lead from LHP-contaminated soil and water probably has more propensity to become bioavailable. More research work is needed to better understand how lead from LHP enters the chain of plants, microorganism, and, finally, to our food chain. Nevertheless, lead toxicity of LHPs remains an important concern for commercial application of these perovskite semiconductors. Can developing new material chemistry provide potential solutions to this issue? We will discuss this question in this section. There are subsections discussing (i) developing novel encapsulation material for devices, (ii) recycling the decommissioned devices, and (iii) opportunity for lead-free perovskite semiconductors.

#### 4.1. Novel Encapsulation Material for PV Module

An enhanced strategy for encapsulation of PV cell can reduce the risk of lead leakage when the LHP PV cell is subjected to accidental or environmental damage. Two major natural ways by which a solar panel can be damaged are hail storm and fire. We will discuss both cases one after another.

##### 4.1.1. Hail Storm Safety by Self-Healing Polymer

PV cell module breakage by a natural agent such as a hail storm, which then combined with the action of rain or humidity, would result in LHP perovskite degradation to PbI$_2$. This sparingly soluble lead salt washes off with rainwater and goes into the soil and groundwater and thus contaminating them. One way to suppress such lead contamination is by encapsulating the module using self-healing material. Such encapsulation self-heals and thus avoids exposure of the perovskite layer to the environment. Jiang et al.\(^{17}\) recently showed such a possibility. They simulated a hail test on the LHP PV cell having different encapsulation materials by dropping a metallic ball and breaking the PV cell module. The different encapsulation methods for LHP PV tested in their study are shown in Figure 3a. Device in method A is not encapsulated, whereas in method B, the encapsulation is provided by a back glass cover and UV resin. In method C, the extra encapsulation (compared

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**Figure 2.** Concentration of lead in different parts of mint plants measured in leaves, stems, and roots after 20 days of growth in (a) control sample of soil having a lead concentration of 36.3 mg kg$^{-1}$ and (b) soil deliberately contaminated by LHP having a lead concentration of 250 mg kg$^{-1}$. Blackening of roots, stems, and leaves is observed, giving an indication of the lead toxicity in the plants. The soil sample used in the study is from Fujian Agriculture and Forestry University, China. Panels (a) and (b) are adapted with permission from ref 16. Copyright 2020 Springer Nature.
Figure 3. (a) Different encapsulation methods of the LHP PV device studied for hail storm safety test. The encapsulation method is categorized as method A (having no encapsulation), method B (encapsulation by bottom glass cover and UV resin), method C (extra protection by self-healing polymer, Surlyn), and method D (compared to method C, instead of Surlyn, tailor-made ER polymer is used for encapsulation). (b) Schematic showing the self-healing mechanism of ER polymer. First to simulate the damage to the LHP perovskite, the ER polymer has been cut by knife and then heated at 45 °C for 4 h, which is above its glass transition temperature (42 °C), to introduce the self-healing process where broken polymer chains cross-link with each other. (c) LHP PV cell module after broken by hammer ball is subjected to different weather conditions. Four weather conditions are shown here: rain for 4 h and then cloudy for 4−72 h (i and v); continuous rain for 72 h (ii and vi); rain for 4 h, sunlight for a total of 4 h, and then rain again for 24 h (iii and vii); sunlight for 4 h and then continuous rain for 200 h (iv). The black dashed line in iv, vi, and vii represents the maximum Pb that can leach out from the damaged LHP solar module. (d) Schematic of a fire safety test on Si/perovskite tandem PV cell where the PV cell module is placed in the hot zone of a tube furnace at 760 °C. Six substrates (placed vertically) are also kept downstream to capture the burnt species carried by air. (e) PV cell module after the degradation from fire. The red colored letters (a, c, d, f) on the module show where the lead is found, whereas green colored letters (b, e) show where no lead is found. Panels (a), (b), and (c) are adapted with permission from ref 17. Copyright 2019 Springer Nature. Panels (d) and (e) are adapted from ref 18. Copyright 2019 American Chemical Society.
to method B) is provided by having the self-healing polymer "Surlyn" (developed by DuPont having a glass transition temperature of 85°C) along with the top glass cover. In method D, tailor-made epoxy resin (ER) is used as self-healing polymer film that can self-repair when heated above its glass transition temperature of 42°C.

Figure 3b shows the mechanism of the self-healing property of ER. The tailor-made ER polymer encapsulant has a composition of diglycidyl ether of bisphenol A (DGEBA) epoxy resin, n-octylamine, and m-xylylenediamine (MXDA) in the ratio of 4:2:1, respectively. To simulate the damage to ER, it is cut by a knife. Cutting causes the polymer chain to break. After that, it is heated at 45°C for 4 h. The heating allows the ER to self-heal by cross-linking the polymers chains. The low glass transition temperature of the above tailor-made ER polymer makes it very much achievable in regular sunlight heating or during the normal operating temperature of the PV device.

In Figure 3c, the exposure of differently encapsulated PV devices after the hail storm condition and the corresponding lead leakage in water are shown. The weather conditions that are tested include the following: rain for the first 4 h and then cloudy until 72 h (i and v); continuous rain for 72 h (ii and vi); rain for the first 4 h, then sun for a total 4 h, and then rain again from 48 to 72 h (iii and vii); finally, sunny for the first 4 h and then rain for a total of 200 h (iv). The response time mentioned is the time after which the damaged LHP PV cell is found and repaired. Results suggest that the self-healing polymer significantly reduces the leakage of lead in rainwater. The lead leakage is reduced by a factor of 375 when using ER polymer as an encapsulant layer compared to method A, method B, and method C, subjected to weather condition iv. These results suggest that developing self-healing polymer encapsulation for LHP devices is an effective approach to suppress leakage of lead from damaged devices.

4.1.2. Fire Safety Test. Residential and commercial structures often encounter fire, and thus the rooftop PV cell module installed would be exposed to the flames. The typical temperature that reaches structural fire is around 700−900°C. Thus, if the LHP PV cell gets destroyed and the toxic lead releases into the environment in the form of toxic fumes and vapors, it would cause serious health concerns as well as an increase in the local concentration of lead in the environment over time. Thus, a study of fire safety of LHP PV cell module is required. Conings et al.18 have simulated the effect of structural fire on a Si/perovskite tandem PV module by placing it at a temperature of 760°C in the hot zone of a tube furnace, as shown in Figure 3d. The PV solar module used here consists of three LHP PV cells (1 in. × 1 in.) connected in series. The PV solar module is heated in the presence of a constant supply of fresh air and also six substrates are placed downstream to capture the burnt species coming out of the burnt PV solar module. Note that the architecture used for PV device encapsulation is glass/ethylene vinyl acetate (EVA)/PV/EVA/glass architecture. In Figure 3e, the damaged PV solar module after experiencing a fire-like heating condition is...
shown. The letters mentioned in red (a, c, d, and f) show the region where lead concentration is found, whereas the letters mentioned in green (b and e) show the representative area where lead concentration is not found. Treating the PV solar module to this fire-like temperature causes the glass cover to soften, and thus the individual PV cell moves away from their original position a little bit, leaving some areas uncovered by the glass cover. This is actually the region of the solar module, where some lead concentration is found, whereas the areas which are still covered by the glass do not show the presence of lead concentration. They have proposed that, in the exposed area of the module, the LHP perovskite is first degraded to PbI₂, which then evaporates and consequently oxidizes to PbO and PbO₂. A majority of these species go as fumes, and very little is stuck on the solar module. On analyzing the glass-encapsulated area, the lead concentration in the glass is nearly similar to the initial lead concentration in the perovskite film. This suggests that the degraded perovskite (in the form of an oxide counterpart, PbO/PbO₂) gets absorbed by the glass. Thus, the glass cover acts as a built-in tool for capturing oxidized lead species.

So, a robust device encapsulation of the solar panels is needed to stop the leaching of the lead in the environment. This calls for designing a new material for encapsulation. For example, additives can be added to the encapsulated glass to increase its melting temperature to minimize its damage in the event of a fire and so it can fully capture the Pb and its oxidized species. Combining the technology of both self-healing encapsulant and rigid glass encapsulant would enhance the mechanical as well as fire stability of the PV module.

4.1.3. Encapsulation by Lead Sequestration Layer. In the previous section, we discussed about what are the possible solutions that can stop leakage of lead from a damaged LHP PV cell to the environment. In the worst-case scenario, say the PV solar module breaks and the lead has started to leach out. Employing a “safe by design” approach, where a lead-absorbing material is used as an extra encapsulant layer that binds with the leaked lead from the damaged PV panel thus avoids lead contamination to the environment.

Li et al.19 reported such a design for a LHP PV cell having a coating of lead-absorbing material film on the front and back side of the PV device. The schematic of the device stack is shown in Figure 4a. On the front side (glass side), a film of transparent \(P,N^{′}-d(2-ethylhexyl)\text{methanediphosphonic acid (DMDP)}\) coated that has a property to absorb lead. The two phosphonic acid groups in the DMDP molecule strongly bind to the \(\text{Pb}^{2+}\) ion. These DMPD molecules are insoluble in water but have good permeability to water. So, the film allows water to sweep in and thus bind to any leaked \(\text{Pb}^{2+}\) in the rainwater wash off. On the back side (metal electrode side), an opaque polymer film (PEO = poly(ethylene oxide)) blended with a lead-chelating agent (EDTMP = \(N,N',N'',N'''-\text{ethylenediaminetetrais(methylene phosphonic acid)})\) is coated, which also has the lead-absorbing ability.

In Figure 4b, the efficiency of lead capturing by DMDP film is shown. The DMDP film is soaked in 50 mL of \(\text{PbI}_2\) aqueous solution. The initial concentration of lead was 4 ppm in the aqueous solution, which decreases down to 0.08 ppm (detection limit of the atomic absorption spectrometer applied) within 30 min of treatment with DMDP film. They have tested this strategy of lead capturing by having DMDP and EDTMP/PEO film on a \((\text{CsPbI}_3)_{0.05}(\text{FAPbI}_3)_{0.85}-(\text{MAPbBr}_3)_{0.15}\)-based LHP PV device. They have intentionally damaged the PV cell by shattering the front side with a hammer and scratching the backside with a blade. The damaged PV cell is then dipped in 40 mL of pure water to study the lead-capturing ability. Figure 4c compares the lead concentration with time in the water by dipping the damaged LHP PV device having a lead-capturing layer and one with the absence of a lead-capturing layer (pristine device). The experiment is conducted at room temperature and 50 °C. Higher temperature causes an increase in lead leakage. In the case when the lead-capturing layer encapsulation is present, the lead leakage is only about 0.2 ppm at both room temperature and 50 °C. In contrast, in the case of the pristine device, the lead leakage increases with time as well as temperature, reaching a lead concentration of 12 ppm for 50 °C and 9 ppm for room temperature conditions. This shows that the lead-sequestering films can effectively capture most of the leaked lead from the damaged LHP PV device. The amount of lead captured is calculated by the sequestration efficiency (SQE) defined as

\[
\text{SQE} (\%) = \left(1 - \frac{\text{Pb leakage with Pb absorbers}}{\text{Pb leakage without Pb absorbers}}\right) \times 100
\]

where "Pb leakage with Pb absorbers" is the Pb leakage from the device with Pb absorbers on both sides and "Pb leakage without Pb absorbers" is the Pb leakage from devices without any Pb absorbers. They have shown that, applying this approach, more than 98% of lead sequestered even when another interfering cation like Ca\(^{2+}\) is present. They have also verified that applying this lead-absorbing layer does not negatively impact the PCE of the PV cell.

Huckaba et al.20 have proposed a porous metal—organic framework (MOF) polymer composite known as FeBTC/PDA (FeBTC = iron(III) benzene tricarboxylic acid, PDA = poly(dopamine)) for the absorption of lead from the degraded PV cell devices. The PDA polymer resides in the cage of FeBTC MOF. Figure 4d shows the schematic of the absorption of the lead from the degraded LHP device in water by the FeBTC/PDA composite. First, the aqueous \(\text{PbI}_2\) solution is prepared. Second, the lead is absorbed from the solution by the FeBTC/PDA composite. The \(\text{PbI}_2\) solution is subjected to two successive treatments with 5 mg of FeBTC/PDA composite at 50 °C for 3 h, leading to lead removal of >97%. Figure 4e shows the mechanism of lead removal by the PDA polymer in the presence and in the absence of FeBTC MOF. In the presence of MOF, the amine-type and catechol-type functional groups act as a chelating agent for \(\text{Pb}^{2+}\). Whereas in the absence of MOF, the catechol-type functional group acts as a chelating agent for \(\text{Pb}^{2+}\). They have found that lead uptake by an amine functional group is greater than that with a catechol functional group. Thus, applying this MOF–polymer composite as the encapsulant layer in halide PV architecture can effectively sequester the Pb and thus can prevent leakage of Pb in the environment. A rough calculation of cost for using the FeBTC/PDA composite in the PV solar panel at a commercial scale gives an estimate of <30 USD/m². This indicates that the FeBTC/PDA can be incorporated in PV device installation at an industrial scale without causing any major financial burden on industry or the end consumer.

These results show that sequestration of lead from the PV device presents a novel way to stop the potential Pb leakage in the environment. Developing new lead-absorbing material which can be applied to PV devices and also cheaper is the new
direction of research for LHP PV technology to make it attractive and safe for commercial applications.

4.2. Recycling of PV Cell Panel. The other question is what happens after the LHP PV cell gets damaged and replaced or gets decommissioned after completing its lifetime. Does the lead gets wasted and released into the environment, or can it be salvaged? Recycling would not only solve the issue of dumping of toxic lead back to the environment in a landfill but also reduce the cost per watt of perovskite PV cell modules and reduce the energy payback time (time required for a PV cell module to produce an equivalent amount of energy as consumed during the production of the module itself). A calculation shows that the FTO glass constitutes around 58% of the cost, whereas the hole transport layer (HTL) and Au cost around 23% and 15% of the total cost of the LHP PV cell (excluding the cost of other encapsulating layers), respectively. Therefore, reusing these materials is also interesting from an economical point of view.

Kim et al. have carried out the selective dissolution of the LHP PV cell and reused the material for fabrication of a fresh PV cell. Polar protic solvent (ethanol, water) or polar aprotic solvent (N,N-dimethylformamide = DMF, dimethyl sulfoxide = DMSO) can be applied for selective dissolution of a perovskite layer, leaving the m-TiO$_2$ (mesoporous TiO$_2$)-coated fluorine-doped tin oxide (FTO) glass intact. To selectively dissolve the perovskite layer, they used DMF. The degradation of LHP in DMF is faster because of the easy bonding of PbI$_2$ with DMF via a Pb−O bond. To recycle the lead from the dissolved solvent, they used a two-step process where they carried out solvent extraction (from DMF to ether) and then carried out an ion exchange reaction with an efficiency of 99.99%. Hydroxyapatite (Ca$_{10}$(PO$_4$)$_3$(OH)$_2$) is used for an ion exchange reaction where Pb$^{2+}$ undergoes a cation exchange reaction with Ca$^{2+}$. Figure 5a shows the recycling strategy adopted by them for the LHP PV device. Starting from the pristine device, the gold metal electrodes are

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Figure 5. (a) Schematic of the process for the recycling of LHP PV cells via selective dissolution process. Step 1 involves the removal of Au electrode and the HTL (hole transport layer). Step 2 involves the dissolution of a perovskite layer in DMF and then the cleaning and drying of m-TiO$_2$/FTO substrate. Step 3 shows the fabrication of a new perovskite layer from recycled PbI$_2$. Finally, in step 4, the HTL and Ag electrode are deposited to complete the fabrication of a recycled LHP PV device. (b) Device performance of recycled devices corresponding to scheme a (normalized to the performance of the pristine device) shows that it remains similar in PCE, suggesting high reproducibility of this strategy. (c) In situ recycling of PbI$_2$, where the LHP is degraded by high temperature, and the remaining PbI$_2$ layer is converted to a MAPbI$_3$ layer using MAI solution. (d) Device performance of the recycled device shown in Figure c. Sample 1 is a pristine device; sample 2 is a recycled device made from a low concentration of MAI; sample 3 is a recycled device made from a high concentration of MAI, and sample 4 is a two times recycled PbI$_2$-based device. Panels (a) and (b) are adapted with permission from ref 22. Copyright 2016 Springer Nature. Panels (c) and (d) are adapted with permission from ref 25. Copyright 2017 John Wiley & Sons, Ltd.
peeled off, and then the LHP PV device is immersed in DMF solvent to dissolve HTL and LHP layer. Step 2 is then carried out where the substrate m-TiO2/FTO is rinsed and dried for reuse in a fresh device. Step 3 refers to the regeneration of the perovskite layer from the recycled PbI2 from the solvent. Finally, in step 4, the fresh LHP PV is fabricated by depositing HTL and Au electrode. Figure 5b shows the normalized PCE of the fresh device and the devices formed from the recycled PbI2 and m-TiO2/FTO substrate. They have shown that the recycling process of m-TiO2/FTO can be carried out up to 10 times without any significant decrease in PCE. Binek et al.23 have also adopted a similar approach for the recyclability of the LHP PV device. They have stripped the PV cell in layer-by-layer fashion until the m-TiO2 layer and then extracted the PbI2 and reused it for the fabrication of a new PV cell. However, they do have to use fresh m-TiO2 in each recycling process of the device, which would amount to some increase in cost as sintering of TiO2 requires significant energy input. Chhillar et al.24 have also shown that the recycled PbI2 from degraded LHP and the reformed perovskite film from it has equally good optoelectronic properties and is viable for the fabrication of fresh LHP PV devices.

Xu et al.25 have adopted a slightly different strategy for recycling of LHP PV cell. They have done in situ recycling of PbI2 (from thermally degraded MAPbI3 film) to form a fresh MAPbI3 perovskite film. Figure 5c shows the steps involved in the recycling process for the LHP PV device. First, the Ag electrodes are peeled off using adhesive tape followed by the removal of HTL by dissolving it in chlorobenzene. In step 3, the MAPbI3 perovskite is thermally degraded, leaving behind PbI2 layer. In step 4, the new MAPbI3 perovskite layer is formed by spin-coating a solution of MAI on PbI2 layer. Step 5 and step 6 involve the deposition of HTL and Ag electrode, respectively, to fabricate a fresh recycled PV device. Figure 5d shows the J−V (current density vs voltage) curve of a pristine device compared with the different recycled devices. Sample 1 is the pristine device; sample 2 is the first time recycled device formed from a low concentration of MAI; sample 3 is the first time recycled device formed from a high concentration of MAI, and sample 4 is the two times recycled device formed from a high concentration of MAI. It shows that the device
performance of sample 1 and sample 2 remains similar. However, a decrease in performance of sample 3 and sample 4 is observed probably because of the inability of PbI₂ to completely convert to MAPbI₃ at the perovskite/TiO₂ interface, which blocks the electron transportation.

A cost-effective and sustainable way to recycle the LHP is undoubtedly a way forward. A refurbished PV cell would reduce the strain on the demand of raw materials. Thus, recycling has the dual benefit of taking care of the environment as well as overall lowering the cost. A detailed calculation in terms of cost of installation, transportation, and recycling is required to have a better idea of the feasibility of the recycling process. Also, the recycling process of other encapsulant layers such as laminate polymer also needs to be considered.

4.3. Lead-Free Alternatives. It is always desirable to use environmentally benign material if efficiency is not too much compromised. Given the potential risk of release of lead, researchers have looked at lead-free perovskites. Figure 6a shows the PCE of the different lead-free system compared with the LHP. As can be seen, the efficiency of these devices still lags far behind that of LHP.²⁶ The closest competitor is Sn-based perovskite PV cells. However, the Sn-based perovskites are very unstable because of easy oxidation of Sn²⁺ to Sn⁴⁺. A quantum jump in research activity is required to stabilize Sn-based perovskite PV cells as well as achieving high PCE. However, this is not the only problem with Sn-based perovskite, and its toxicity effect is also debated in the literature.²⁷ Babayigit et al.²⁸ have carried out a comparison between the toxicity of PbI₂ and SnI₂ on zebrafish and have shown that LC₅₀ (lethal concentration for 50% of the population) is 0.09 and 0.83 × 10⁻³ M for SnI₂ and PbI₂ respectively. This increased toxicity of SnI₂ is due to increased acidification by the formation of HI. More detailed studies are required for assessing the environmental concern of Sn-based perovskites.

It is to be noted that the lead-free perovskites might find applications other than PV cells. Lead-free perovskites can be used for light-emitting diodes, sensors, and catalysis. Compounds like Cs₅AgInCl₆ can be obtained by replacing two Pb²⁺ in CsPbCl₂ (can be written as Cs₅Pb₂Cl₆) with one monovalent (M⁺ = Ag⁺) and one trivalent (M³⁺ = In³⁺) metal ion. Such CsₓM⁺M³⁺Cl₆ compounds are termed as double perovskites. These metal halide double perovskites are environmentally benign and more stable compared to LHP. However, these double perovskites typically have either a wider or an indirect band gap, reducing their potential for optoelectronic applications in the visible and near-infrared region. Introducing midgap states by lattice doping has been employed as a strategy to introduce optical functionality. Nandha et al.²⁹ have reported Mn²⁺-doped Cs₅AgInCl₆ achieving red-orange emission because of d–d transitions of Mn²⁺. Figure 6b shows the photoluminescence spectra of undoped and Mn²⁺-doped Cs₅AgInCl₆ microcrystals. The undoped sample does not have significant photoluminescence in the visible region, whereas the Mn²⁺-doped samples show the photoluminescence peak centered at 632 nm. Similarly, to achieve optical functionality in the near-infrared region, double perovskites are doped with lanthanide ions such as Er⁴⁺ and Yb⁵⁺.³⁰ Similarly, double perovskites can also be used for catalysis reactions. Zhou et al.³¹ have used Cs₂AgBiBr₆ for the photocatalytic reduction of CO₂ to CO and CH₄. CO₂ reduction to solar fuels is desirable because of both an environmental and an energy benefit. Figure 6c shows the energy alignment and mechanism of CO₂ reduction by Cs₂AgBiBr₆ nanocrystals.

Efficient blue LEDs are still a challenge. Leng et al.³² have shown that the compositions of MA₂Bi₂Br₈ nanocrystals passivated with the chloride (Cl⁻) exhibit intense blue photoluminescence. As they have varied and increased the Cl⁻ content, blue shift in photoluminescence has been observed. Figure 6d shows the digital photograph of the MA₂Bi₂(Cl,Br)₈ nanocrystals dispersion under UV light (325 nm) as Cl⁻ varies from 0, 33.3, 50, 66.7, and 100%. The text written in white shows the percentage of added Cl⁻ with respect to Br⁻, whereas the text in the red shows the photoluminescence quantum yield corresponding to that composition. The maximum value is observed for the Cl⁻ = 33.3% sample, reaching photoluminescence quantum efficiency of 54.1%. The reported value is one of the highest for lead-free nanocrystals emitting in the blue or deep blue region.

These examples discussed above show that while lead-free halide perovskites lag behind solar cell performance compared to LHPs, such lead-free perovskites can certainly be used for other applications including phosphor-converted LEDs, electroluminescent LEDs, and CO₂ reduction. The lead-free systems offer stability and nontoxicity, which makes them preferred for applications compared to LHPs.

5. CONCLUSIONS

To sum up, though LHP has created a new hope towards efficient and cheaper PV technology, still, the toxicity of lead remains a major issue which is yet to be resolved to make it safe for commercial applications. The actual environmental and health impacts of LHP PV are debated, but it is very desirable that, if possible, the alternative lead-free system should be used. However, the lead-free PV technology still lags behind lead-halide-based ones. Until some other technology catches up with the lead-halide-based ones in terms of efficiency, cost, and flexibility, we should focus our effort on making LHP devices safer for the environment and human health. Fortunately, some interesting approaches have been reported, which can address the toxicity issues of LHP PV devices to environment and health. In this context, encapsulation with a self-healing polymer or with a rigid glass has been shown to be effective against damage from hail storm or fire. For the worst-case scenario, if the lead leaches out when the PV device is damaged, another new chemical avenue of introducing a lead-absorbing layer with the LHP PV device itself is introduced. Another way is recycling the LHP PV device itself, once it is broken/damaged or its lifetime is over (decommissioned). The recycling strategy of lead in the form of PbI₂ and then fabricating a fresh LHP PV device with a similar PCE is also discussed. Such recycling not only reduces the lead wastage but also abates the demand for raw materials, thereby providing an overall decrease in cost and environmental impact of the LHP PV devices. The combination of these new material approaches should be implemented for LHP PV devices to make it environmentally safe. Therefore, a cheaper and efficient way of integrating these encapsulation methods and recycling strategies should be the focus of future research.

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