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1 **Lead Immobilization for Environmentally Sustainable**
2 **Perovskite Solar Cells**

3

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22 **Preface**

23 Lead halide perovskites are promising semiconducting materials for solar energy harvesting,
24 however, the presence of the heavy metal lead ions is problematic when considering potential
25 harmful leakage into the environment from broken cells, and also from a public acceptance
26 point of view. Moreover, strict legislation on lead usage around the world has driven innovation
27 in development of strategies in recycling end-of-life products via environmentally friendly and
28 cost-effective routes. Lead immobilization is a strategy to transform water-soluble lead ions
29 into insoluble, nonbioavailable and nontransportable forms over a large pH and temperature
30 range, and suppress lead leakage if the devices are damaged. An ideal methodology should
31 ensure sufficient lead chelating capability without significantly influencing the device
32 performance, production cost and recycling. Herein, we analyse chemical approaches to
33 immobilize Pb^{2+} from perovskite solar cells, such as grain isolation, lead complexation,
34 structure integration, and adsorption of leaked leads, based on their feasibility in suppressing
35 Pb leakages to a minimal level. We highlight the need for a standard lead leakage test and
36 related mathematical model to be established for reliable evaluation of the potential
37 environmental risk of perovskite optoelectronics.

38 **One sentence summary:** The presence of the heavy metal lead ions in perovskite solar
39 cells is problematic when considering potential harmful leakage into the environment from
40 broken cells, which should be rationally immobilized to eliminate their ecotoxicity to a safe-
41 to-use level prior putting them into the market.

42

43 **1. Introduction**

44 Lead halide perovskites have attracted intense research attention since their first application
45 as light harvesters in solid-state photovoltaics¹. Certified record power conversion efficiencies
46 (PCEs) of the state-of-the-art perovskite single junction and perovskite-Si tandem solar cells
47 have reached 25.7% and 31.3%², respectively. Excellent operational stability over 9000 hours
48 under international electrotechnical commission standards³ and perovskite modules (64 cm²)
49 with efficiency above 20%⁴ have been achieved. These achievements have enhanced the
50 technology readiness of perovskite solar cells (PSCs) for commercialization.

51 However, the use of lead is a threat to the environment and human health due to its toxicity⁵⁻
52 ⁸. While lead occurs naturally in the Earth's crust, anthropogenic activity such as mining in the
53 last few centuries and the use of lead in gasoline, paint, and electronics has increased the risk
54 of exposure to humans and wildlife^{9,10}. The use of lead has been systematically regulated with
55 specific limitations designed for each application. This is mainly to minimize the risk of
56 exposure to lead in each type of application, but also to consider the chemical form of the lead-
57 containing compound in relation to bioavailability, which in turns influences both toxicity and
58 bioaccumulation, *i.e.*, the compound's ability to enter living organisms^{5,11,12}. The existing
59 legislation around lead does not specifically mention perovskite-based electronics, and thus
60 some urgent consideration is needed on the risk assessment of these materials to assist safe and
61 responsible innovation with lead halide perovskites^{5,6}. Recent efforts have strived to substitute
62 the lead element by using divalent metals, such as tin¹³⁻¹⁵, or combining monovalent and
63 trivalent metals to construct double metal perovskites¹⁶⁻¹⁸, but the performance of lead-free
64 PSCs is significantly lower than their lead-based counterparts, indicating the essential role of

65 lead in perovskites to realize high efficiency and long-term stability¹⁹⁻²².

66 In this Perspective, we discuss the physico-chemical role of lead on optoelectronic properties
67 of perovskite materials (**Box 1**)²³ and accompanying lead toxicity issues with relevant
68 legislation^{24,25}. The lead leaching and exposure pathways from PSCs during their lifespan will
69 be discussed²⁵⁻²⁹, at which point the end-of-life device can be possibly recycled for reuse by
70 specialists with minimized exposure risk³⁰. However, occasional lead leakage from operating
71 devices is out-of-control and hence potentially more harmful. The resultant environmental
72 impacts need to be quantified by considering the concentration and bioavailability of the
73 exposed lead compounds^{26,31-33}. We discuss here chemical approaches to fundamentally resolve
74 the issue, categorized into 1) regulating solubility and diffusivity of lead ions in the device³⁴⁻⁵¹
75 and 2) chemical adsorption of the leaking lead ions via lead-adsorbing materials⁵²⁻⁵⁷. Beyond
76 these approaches, we propose possible routes for fundamental mitigation of lead toxicity
77 through chemical immobilization.

78

79 **2. Lead in PSCs**

80 **2.1 Lead toxicity and relevant legislation**

81 The toxicity of lead to humans became apparent in the mid-twentieth century⁹, and the
82 concerns of lead exposure to humans include the incidental ingestion of Pb from soil¹⁰ or
83 contaminated foods such as vegetables⁵⁸, although water is a main cause of oral exposure⁵⁹. Pb
84 is adsorbed via the small intestine into the blood and bioaccumulates in internal organs,
85 including the liver, kidneys and the central nervous system. Pb is also deposited in the skeleton
86 and can be remobilized during pregnancy, causing exposure to the foetus⁶⁰. Public health

87 concerns from chronic Pb exposure include neurotoxicity, impaired cognitive development and
88 growth in children, effects on renal function, immunity, and the risk of cancer⁶¹. Clinical
89 monitoring via measuring total Pb concentrations in blood or urine is possible^{8,62}. However,
90 the best way to protect the population is to prevent the exposure by setting limits on total Pb
91 concentrations in soil, water, food, medicines and other consumer products.

92 The legislation with respect to human health includes some internationally agreed standards.
93 For example, The World Health Organisation (WHO) recommends a limit on total Pb in
94 drinking water of $10 \mu\text{g L}^{-1}$ ⁶³. In the USA, the ninety percentile for action on Pb concentrations
95 in drinkable water is $15 \mu\text{g L}^{-1}$, and has been continuously updated every 3-7 years with a desire
96 for zero Pb in drinking water in the future⁶⁴. With respect to protecting the agricultural food
97 chain to humans, the upper limit of lead content in agricultural soil is set to 250 mg kg^{-1} in
98 China⁶⁵. The maximum tolerable lead content in canned beverages and foods is 150 and 250
99 mg kg^{-1} , respectively, set by the Food and Agriculture Organization (FAO) of the United
100 Nations⁶⁶. In the USA, the Centre for Disease Control (CDC) indicates a reference value for
101 blood lead concentration of $3.5 \mu\text{g dL}^{-1}$ ⁶⁷. There are also regulations for the disposal of solid
102 wastes. For example, in the USA, the safe-to-use level of lead leakage (leaching from solid
103 waste) is set to $5 \mu\text{g L}^{-1}$ ⁵⁶. There are also restrictions on the use of sludge containing metals,
104 including Pb, in the EU⁶⁸. EU legislation limits the content of lead in “homogenous materials”
105 to 0.1% by weight. With that said, photovoltaic panels, “intended to be used in a system that is
106 designed, assembled and installed by professionals for permanent use at a defined location”,
107 are already exempt from this limitation⁶⁹. However, this exemption does not apply to devices
108 embedded in consumer electronics or portable systems — and so lead immobilization could

109 represent a way toward compliance for consumer devices incorporating PSCs, but specific
110 legislation regulating this issue will be needed in the future⁷⁰.

111 **2.2 Environmental impacts of PSCs**

112 **2.2.1 Life cycle assessment of PSCs**

113 Life cycle assessment has been employed to evaluate environmental impacts of PSCs by
114 considering all stages of their life cycle from the extraction, purification and preparation of
115 lead-related raw materials, to the manufacturing, installation and maintenance of PSCs and the
116 handling of the products at the end of their lifespan^{32,71,72}. An evaluation of PSC life cycle has
117 concluded that PSC can be considered more sustainable than other technologies such as
118 commercially available Si solar cells. Regarding the amount of lead used in a PSC, only an
119 approximately 1 μm thick perovskite layer is used owing to their extremely high absorption
120 coefficient, and lead concentrations are often very low in complete PSC devices (around 0.015
121 $\text{mg L}^{-1}\text{dm}^3$), which is similar to the amount of lead in solder conventionally used to assemble
122 crystalline silicon solar panels. Around 17,000 metric tons of Pb is embodied in the production
123 of the perovskite layer for a yearly 2400 GW electricity generation, representing only 1.1% of
124 the 1.6 million metric tons of lead consumed in the U.S. domestic market each year³². We must
125 also consider that in Europe already 56% of lead comes from secondary sources, that do not
126 require mining and concentration of the material; these are the most energy-intensive processes
127 of the production from primary sources, and so the use of secondary sources can reduce
128 potential overall environmental impacts⁷³. Despite these positive aspects, Pb leakage from
129 PSCs still represents a major concern because, after installation, the panels will spend most of

130 their lifetime subjected to uncontrolled atmospheric conditions, and possible damage to the
131 panel will lead to dissolution and spreading of the lead due to rainwater^{12,74}.

132 **2.2.2 Bioavailability of perovskites**

133 Life cycle analysis and leaching studies might identify the potential exposure concentrations,
134 but the effects on human health or the environment depend on how much of the total Pb is
135 bioavailable to the organism, and also whether the bioavailable fraction presents a concern for
136 toxicity. Even though potential lead leakage from PSCs might be relatively low, there is an
137 ethical concern around lifetime exposure to trace amounts of Pb from the products because the
138 internal organs will eventually accumulate sufficient Pb to cause adverse biological effects.
139 However, the organ concentrations at the threshold of adverse effect are not well defined yet.
140 Instead, epidemiology approaches are used to associate lifetime Pb exposure with specific
141 diseases (e.g., Parkinson's disease⁷⁵), or to relate organ concentrations with specific effects
142 (e.g., kidney Pb concentrations and renal function⁷⁶). The toxic effect of lead halide perovskite
143 is strongly dependent on the cellular properties and metabolic activity of cell types. For instance,
144 human dopaminergic neuroblastoma cells and murine primary hippocampal neurons are very
145 sensitive to the toxicity of MAPbI₃⁷⁷, while human lung epithelial cells are less sensitive^{77,78}.
146 In addition, lead toxicity is also related to the type of lead source, and the toxicity of different
147 lead sources has been shown to follow the order of Pb²⁺ > perovskites > PbI₂ = PbO⁷⁹. Moreover,
148 the pH of the environment and the size of the perovskite nanoparticles also influences
149 perovskite toxicity. Acidic conditions will accelerate the dissolution of Pb from the particles,
150 and at low pH values the Pb is present as the bioavailable Pb²⁺ species, which readily binds to

151 biological membranes. There may also be particle-size effects, and smaller perovskite
152 nanoparticles with a high specific surface area are more toxic than larger ones^{80,81}.

153 The bioavailability of Pb in soils depends on Pb speciation in the water, the chemical
154 composition of the soil (e.g., ionic strength, pH, natural organic matter) and the type of soil
155 (clay soil, loamy soil, etc.). Inevitably, Pb uptake by plants and other soil organisms will be
156 influenced by these factors and the source of the Pb. Perovskite has been shown to be more
157 bioavailable, such that the lead uptake coefficient greatly increased in the order: native soil <
158 PbI₂ < perovskites. The reason was attributed to organic cations from the perovskites, which
159 can alter the pH values of the soil and impact the lead uptake ability of the plants³¹. Thus, for
160 environmental or human health risk assessments, the form of the Pb, its chemical
161 transformations, and the surrounding chemical matrix should be considered.

162 Lead weekly intake (LWI) by humans was taken as health-based guidelines for lead exposure,
163 and the upper limit was set at 0.025 mg kg⁻¹ body weight by the FAO of the United Nations⁸².
164 By assuming that all the lead contained in a broken PSC panel would leak and reach the
165 environment in a finite amount of time⁸³, the level of LWI under different percentage dispersion
166 and environmental spreading scenarios is estimated. The scheme shown in **Fig.1** was calculated
167 in order to estimate the possible level of LWI taking into account different possible scenarios.
168 From it we can deduce a low fraction of the total lead needed for PSC reaching the food chain
169 can represent a risk for humans, as in many scenarios the LWI would be higher than the levels
170 estimated for the humans of 3000-5000 years ago and adult LWI limit withdrawn in 2010⁸⁴.

171 **3 Lead immobilization in PSCs**

172 Owing to the soft and ionic character of perovskite, the first premise of lead leakage from
173 PSCs is ascribed to water induced decomposition of perovskite crystals into soluble lead
174 salts^{85,86}, which can outflow from the device and are then infiltrated into underground water or
175 soil along with rainwater, leading to damage to the ecosystem and human health. To prevent
176 such pollution, the pathways of water ingress and lead leakage need to be blocked via some
177 chemical lead-immobilizing approaches, which transform lead components into insoluble,
178 nontransportable or nonbioavailable forms as illustrated in **Fig.2**, so that the exposed lead from
179 PSCs is in a safe-to-use level.

180 **3.1 Grain encapsulation**

181 By wrapping the perovskite grains within hydrophobic organics (e.g., polystyrene^{87,88}),
182 water resistant oxides (e.g., TiO₂⁸⁹, SiO₂^{44,45,90}, Al₂O₃⁹¹) or insoluble lead salts (e.g., PbS⁹²,
183 PbSO₄⁴⁶, Pb(OH)₂⁴⁷), the pathways for water ingress and ions outflow can be effectively
184 blocked. The utility of isolation strategy is dependent on the water permeability of the capping
185 layers, which usually employ materials with strong hydrophobicity, high compactness and full
186 coverage on perovskite grains. For instance, the condensation of small molecules along with
187 perovskite crystallization^{44,45} or depositing hydrophobic molecules⁴³ or functional salts (e.g.,
188 sulfonics^{37,93}, sulfates⁴⁶, sulfides^{92,94,95}) atop the perovskite layer in post treatments enabled an
189 in-situ encapsulation of grain boundaries and surface. Well grain-encapsulated lead-containing
190 perovskites manifested robust water stability, which even demonstrated promising application
191 as scintillators for in-vivo bio-imaging without significant cytotoxicity on target animals^{90,96,97},

192 indicating reduced bioavailability. In addition, inserting water resistant layers into the PSCs for
193 inner⁹⁸⁻¹⁰¹ or external encapsulation¹⁰²⁻¹⁰⁶ can also prevent water permeation, but these
194 approaches are ineffective in case of device breakage. Even though some self-healing
195 characteristics were endowed by mixing curable materials with the encapsulants¹⁰², the
196 protection effectiveness might be problematic because the curing process of the damaged
197 encapsulants usually requires external stimulus (e.g., UV radiation, heating), which are not
198 always available in emergency case.

199 **3.2 Chemical complexation**

200 To mitigate water contamination, the solubility of lead compounds from degraded
201 perovskites needs to be decreased by forming low solubility products (K_{sp}) of lead-additive
202 complexes via rational additive engineering. Typically, the additives should consist of both
203 electron-donating Lewis base functional groups (e.g., carbonyl^{34,36,37}, thiol¹⁰⁷, sulfonic⁵³,
204 sulfide¹⁰⁸, porphyrin ring³⁵, crown ethers³⁸) coordinating with Lewis acidic Pb^{2+} ions via an
205 acid/base interaction and hydrophobic backbone or side chains being endowed with water-
206 repelling moieties (e.g., long alkyl chains, fluorine groups, carbon nanotubes³⁴) allowing them
207 to precipitate from water after complexation. Thus, the as-formed complexes become
208 hydrophobic after the chelation of the functional groups with Pb^{2+} . For example, the addition
209 of polyacrylic acid grafted carbon nanotubes (CNT-PAA) into the perovskite precursor can
210 effectively suppress the lead leakage of the corresponding PSCs.³⁴ Briefly, the CNT-PAA
211 exhibited a high Pb^{2+} -capturing capability due to the presence of large amount of carboxyl
212 groups on the wall of CNTs. After the occupation of hydrophilic groups by Pb^{2+} , the self-
213 aggregation of water insoluble CNTs allowed them to form precipitation in water. As a result,

214 the leaked lead from the CNT-PAA doped device was well below the hazardous waste limit
215 upon water immersion³⁴.

216 **3.3 Structure integration**

217 Water (moisture) induced perovskite decomposition usually initiates from water
218 adsorption at the crystal surface, followed by deep penetration into the interior of the bulk and
219 dramatically accelerated perovskite fragmentation and ions release⁴⁰. Integration of perovskite
220 structure within the device by improving binding strength of the constituent elements,
221 intergrain connectivity and interfacial cohesion is able to increase energy barrier for water
222 penetration, structural fragmentation and layer delamination, thus boosting the structural
223 stability against water dissolution and lead leaking^{49,109}. For instance, interfacial/intergrain
224 bridge via strong coordination or dipole-dipole interaction can enhance the interconnectivity
225 of the device, resulting in extremely stable perovskites in highly salty, acidic (pH=1) and basic
226 (pH=13) aqueous conditions¹¹⁰. Sole enhancement of chemical interaction at perovskite top-
227 surface has proven effective to resist crystal collapse and retard lead release⁴⁰, but it might be
228 ineffective in case of device damage. Alternatively, the whole structure including the surface,
229 bulk and interface of the perovskite layer needs to be integrated.

230 The integration of perovskite grains can be achieved by implementing polymerizable
231 monomers into the perovskite layer to construct perovskite/polymer matrix.^{41,42} For example,
232 acrylamide monomers were employed as additives in the preparation of perovskite films⁴¹,
233 which were polymerized *in-situ* to form polyamides along with the perovskite transformation.
234 The -C=O groups from the polyamides can interact with undercoordinated Pb^{2+} at grain
235 boundaries and surface of the perovskite to form a robust chelation structure in the as-deposited

236 thin films⁴¹. Also, the polyamides are prone to form hydrogels when exposed to water, which
237 can further prevent the dissolution and diffusion of Pb^{2+} from the device into water⁴¹. Moreover,
238 the agglomeration effect of the monomers during polymerization can induce compressive
239 strain within the perovskite layer, which can increase the activation energy for ions migration¹¹¹
240 and barrier for water permeation¹¹², leading to improved crystal stability in high humidity
241 conditions. Additionally, the infiltration of perovskite into rigid and mesoporous structure is
242 also expected to prevent structural collapse.

243 **3.4 Adsorption of leaked lead**

244 In addition to *in-situ* immobilization, lead-adsorbing materials can be integrated into PSCs
245 to capture leaking ions in case of device damage. Similarly, an effective lead-adsorbent should
246 contain lead binding groups (e.g., phosphonates^{54,113}, thiols^{107,114}, sulfonates⁵⁶, tetraethylene
247 glycol¹¹⁵) to form water insoluble lead products with extremely low K_{sp} values¹¹⁶⁻¹¹⁹.

248 All functional layers located at interior or exterior of the devices e.g. charge transport layers
249 (CTL)^{107,113,115,120}, electrodes¹²¹ or encapsulants^{54-56,114,122} may be considered as hosts for lead-
250 adsorbents. Since the lead sequestration efficiency (SQE) is directly correlated with the density
251 of adsorbing sites, the loaded materials should be abundant to ensure sufficient lead-adsorbing
252 capacity. Thereby, the implementation of Pb adsorbents into interior layers of the device might
253 be insufficient because of the limited scavenging capacity by layers. The conductivity of the
254 electrode would decay if too much insulating materials were infiltrated¹²¹. Also, CTLs are at
255 most a few hundred/ten nanometer thick which offer a low capacity to capture all Pb^{2+}
256 contained in the perovskite film. Therefore, embedding lead-adsorbing materials into the
257 exterior encapsulation is a better option, where the device performance is not restricted by the

258 loading amount⁵⁶. Given the random lead diffusion pathways, both front and back sides of the
259 device can be simultaneously protected. A good example was given by Li *et al.*⁵⁴, where a
260 highly transparent Pb-adsorbent was deposited on top of the front glass without filtering the
261 incident light, and a blend of polymer encapsulants and Pb²⁺ binding materials was inserted
262 between the back electrode and encapsulating cover. Owing to the remarkable lead-adsorbing
263 capability on both sides, such chemical approaches can substantially reduce lead leakage by
264 96%⁵⁴. Moreover, lead-adsorbing materials with different activity in various temperature and
265 pH conditions should be combined. For instance, the employment of lead-adsorbents consisting
266 of phosphonic and methylenephosphonic acid groups within one device can retain high *SQE*
267 over a large temperature range due to the varied temperature dependent deprotonation effect⁵⁴.

268

269 As summarized in **Table 1**, the aforementioned four lead-immobilization strategies are
270 systematically compared from the aspects of work mechanism, protection effectiveness and
271 their influence on device performance. Notably, interior lead-immobilization strategies (i.e.,
272 isolation, complexation, integration) demonstrate high selectivity and fast responsibility
273 because the Pb²⁺ ions are pre-protected before leakage, but relatively low *SQEs* (~60-80%). It
274 is known that the lead-immobilizing capacity is correlated to the density of functional sites in
275 the embedded additives, especially for the method of complexation. However, most of these
276 additives are insulating and in some case light absorbing, which can undermine charge transport
277 and photon harvesting, and the interaction between the additives and the Pb precursors can
278 affect perovskite crystallization. Therefore, a trade-off between PCE and *SQE* might occur
279 when the additive concentration exceeds the tolerance of perovskite materials¹²³. Nevertheless,

280 a rational dose of Pb-immobilizing additives in the perovskite layer can advantageously lead
281 to PCE increase and lifetime increase (**Table 1**), which are defined by the PCE and lifetime
282 ratio of best optimized device to pristine device, respectively. In addition, owing to the inert
283 character of grain encapsulation and insolubility of the as-formed lead complexes, these
284 approaches for grain isolation and chemical complexation would challenge the lead recycling
285 process, which relies on the ease of extraction of the lead from the device. Also, the formation
286 of homogenous capping layer at the perovskite grain boundaries might be problematic,
287 especially in large scale manufacturing, because of the difficulties in controlling the layer
288 thickness, restricting the upscaling of PSCs. In these aspects, the structure integration seems to
289 be more promising, in which the lead-immobilizing capacity is related to the structural stability
290 rather than the chelating sites of the additives, leading to relatively higher SQEs of ~80%.

291 In contrast, the implementation of lead-adsorbents at exterior of the device is more effective
292 in the suppression of lead leakage with SQE approaching 100% because a large amount of
293 materials can be loaded without influence on device performance. However, it still suffers from
294 several drawbacks that may reduce their effectiveness. First, the lead-adsorbents are
295 specifically designed to capture the Pb ions after their release from the perovskite lattice, and
296 the sorption speed should be extremely fast otherwise the capturing efficiency might be limited
297 if the water flux is fast or the Pb²⁺ concentration is high at the initial stage of device damage.
298 Second, the variation of environmental pH and temperature, and the presence of other metal
299 ions (e.g., Ca²⁺, Mg²⁺) within the water may defunctionalize the Pb-adsorbents. Third, the lead
300 adsorbents, in addition to showing excellent Pb-adsorbing capacity, should also support
301 scratching resistance, UV stability and high selectivity of lead ions.

302

303 Importantly, the lead leaking from PSCs and their adsorption is strongly dependent on the
304 testing conditions, such as temperature, pH values and volume of the exposed water, and how
305 the devices are broken. However, the reported SQE values in Table 2 were measured in
306 completely different conditions. In order to quantitatively evaluate the lead leakage from PSCs
307 and compare the utility of different lead-immobilization techniques from worldwide
308 laboratories, a standard lead leakage test supported by computational modeling needs to be
309 established. Also, some metrics e.g., total leaked lead concentration (C_{LL}), leakage ratio (LR),
310 SQE are recommended to be measured in a standard way, and two occasions (i.e., water soaking,
311 water dripping) of perovskite exposure in case of a harsh weather conditions (acidic and heavy
312 rain) are mimicked as listed in **Table 2** and illustrated in **Fig. 3a**. Moreover, the aged perovskite
313 films instead of completed devices, together with or without delaminated encapsulants, should
314 be used in the lead leakage measurement to simulate the case of full exposure of perovskite
315 layer to water. In addition, biological tests can also be performed to evaluate the influence of
316 the leaked leads on the growth of plants or animals.

317 **4. Conclusions and Future Prospects**

318 Research on lead based PSCs has advanced rapidly both on the efficiency and stability front.
319 It is time now to examine how to pursue the next phase of implementing this promising
320 technology on the large industrial scale with sustainability in mind, avoiding any possible
321 leakage of lead in the environment from the preparation of the precursors to the long-term
322 working-life of the solar panel. The question is: which options researchers should focus on to
323 fulfill the goal of developing a safe technology that does not harm the environment or human

324 health, and which practices need to be abandoned.

325 **4.1 Toward lead immobilization in PSCs**

326 As already surveyed in this Perspective, techniques for lead scavenging in PSCs range from
327 *in-situ* grain encapsulation, reducing lead solubility, strengthening internal connectivity and
328 capturing leaked lead. Considering the available means to avoid lead contamination and
329 situations that may lead to device damage, a future blueprint for lead-immobilization can be
330 outlined.

331 In order to improve SQE without sacrificing device performance, the optical constants (e.g.,
332 refractive index, absorption coefficients) and electrical properties (e.g., conductivity, energy
333 levels) of the additives used at interior of the PSCs for lead-immobilization need to be further
334 optimized to eliminate their influence on photocharge generation and extraction. Moreover, the
335 interaction between the additives and lead precursors should be tuned by adjusting the
336 coordination strength, additive concentration or processing methods to improve perovskite
337 crystallinity. Different lead-immobilizing approaches can be combined within one device. For
338 instance, combining interior strategies (*i.e.*, structural integration) to prevent the majority of
339 lead escape from the device, and chemical capturing of leaking lead with lead-adsorbents in
340 encapsulants, as illustrated in **Fig. 3b**.

341 Further investigation of the temporal dynamics of lead escape from PSCs and lead capturing
342 from water at different environmental conditions (e.g., pH, temperature) can also provide
343 guidelines for the optimization of lead-immobilization strategies toward practical
344 application¹²⁴. To guarantee sufficient lead-immobilizing capacity and resistance to re-
345 dissolution, researchers should choose additives abundant anchoring sites, such as by grafting

346 the lead-chelating functional groups on a backbone with high specific surface area (e.g., CNT³⁴,
347 graphene⁵⁶, metal of framework⁵⁷), and persistent binding energy with Pb²⁺ at a broad range of
348 environmental conditions. Moreover, some environmentally friendly and degradable agents
349 such as magnetic nanoparticles, chitosan composites, which exhibit promising activity to
350 remove lead from wastewater in a wide range of pH and temperature¹²⁵⁻¹²⁷, might be explored
351 as lead-adsorbents in PSCs to improve their availability at various weather conditions without
352 further pollution. Even though the bioavailability of immobilized lead is significantly reduced,
353 these compounds might be re-dissolved and cause potential hazards during long-term exposure.
354 In this respect, lessons from hydrogel of polyamides⁴¹ or self-bundling of CNT³⁴ to precipitate
355 the lead products from water, and integration of perovskite layer within the device to prevent
356 its delamination and fragmentation in environmental water, are desirable.

357

358 **4.2 Considering the full life cycle of PSCs**

359 Lead leakage should be avoided when considering the full life cycle of PSCs. Starting
360 with the preparation of lead halide perovskite films for PV applications, the overwhelming
361 majority of researchers have adapted spin coating as their method of choice; this should be
362 replaced by other solution processing methods such as slot die coating, screen printing or doctor
363 blading, as these waste only a very small percentage of the perovskite precursors compared
364 with spin-coating. Also, lead-immobilization strategies can be introduced into the precursor
365 solutions to reduce the bioavailability of lead-containing waste. PSCs should be specifically
366 optimized to prevent lead leakage according to their application. For example, flexible
367 electronics are directly accessible to humans because of their potential applications in daily life,

368 and the plastic substrates are prone to damage because they are sensitive to light, heat,
369 scratching, and bending. Therefore, self-curing ability by mixing healable materials¹⁰² and
370 strain modulation to facilitate stress relaxation¹²⁸ should be endowed in flexible PSCs to
371 improve their mechanical resistance.

372 Strategies should also be developed to dispose end-of-life perovskite devices. Ideally, all
373 components of the multilayered PSCs should be recycled for reuse to save their energy-
374 payback-time, especially the lead compounds because of their toxicity. Techniques of lead-
375 recycling from PSCs were generally based on electrochemical deposition¹²⁹, selective solvent
376 extraction¹³⁰⁻¹³², desorption from precipitated lead compounds^{6,133}, and so on^{30,134}. Even though
377 very high recycling yield can be achieved^{6,129-133}, these lead-recycling methods involve a large
378 amount of organic solvents and complex energy-consuming processes, which increase the
379 recycling cost and challenge their large-scale application. In addition, we should note that lead-
380 immobilization with highly complexed Pb^{2+} would be a challenge for lead recycling, so the
381 potential for lead-recycling should be considered as one of the criteria for the selection of lead-
382 immobilization strategies.

383 Finally, practical deployment of optoelectronic devices based on lead halide perovskites
384 should be accompanied with in-depth occupational and local population risk assessments, and
385 the prevention of lead leakage during their operation and at end-of-life is not only legally
386 required but also an ethical obligation. Specific legislation on lead usage can drive innovation
387 on the development of strategies in lead immobilization and device recycling. Meanwhile,
388 emergency remediation must be planned to mitigate unintentional air-borne emission of lead
389 soil pollution in case of fire accidents. Moreover, the PSCs should pass a standard test to

390 evaluate the potential risk of lead leakage prior putting them into the market.

391

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398

399 **Author contributions**

400 N-G.P. and H.Z. conceived the idea for the study. H.Z. wrote the first draft. J-W.L., R.H., A.A.
401 and M.G. contributed to the writing. N.G.P. edited the manuscript. All authors commented on
402 the manuscript. H.Z., J-W.L., A.A. and N-G.P. contributed to the preparation of the figures.

403

404 **Competing interests**

405 The authors declare no competing interests.

406

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826

827

Figure legends

828

829

830 **Fig. 1: Lead leakage pathways from PSCs and estimation of their potential environment**

831 **impact.** Schematic illustration of lead leakage pathways to the underground water during

832 device fabrication and out-door operation, and estimation of their impact to the level of human

833 lead weekly intake (LWI), which was calculated by considering the world population and total

834 PSC leads required for electricity generation in 2050, compared with the adult LWI limit and

835 human LWI 3000-5000 years ago.

836

837 **Fig. 2: Lead immobilization methodologies in PSCs.** Grain isolation with hydrophobic

838 polymers, oxides or insoluble lead salts to block water ingress; Complexation of additive and

839 lead compounds with low K_{sp} allowing to precipitate from environmental water; Structural

840 integration with enhanced interconnectivity to prevent structure fragmentation and layer

841 delamination; adsorption of lead ions using embedded lead-adsorbents at exterior of the device.

842

843 **Fig. 3: Proposed lead leakage measurements and device structure for lead immobilization.**

844 **a,** schematic illustration of detection of leaking leads in case of water soaking of the perovskite

845 layer and water dripping from the perovskite layer with precisely defined metrics, *e.g.* lead

846 leakage ratio (LR), leaked lead concentration (c_{LL}) and lead sequestration efficiency (SQE),

847 and the evaluation of potential impact of the leaked leads on the growth of plants and animals,

848 and **b,** proposed device structure for Pb-immobilization including interior and exterior

849 strategies.

Table 1: Quantitative analysis of lead-immobilization strategies

	<i>Grain isolation</i>	<i>Lead complexation</i>	<i>Structure integration</i>	<i>Chemical adsorption</i>
Mechanism	Prevent water contact with perovskite	Decrease solubility of degraded Pb compounds	Prevent perovskite defragmentation	Capture leaked Pb ²⁺ from water
Materials	Hydrophobic oxides, polymers or lead salts.	Additives with lead-chelating groups.	Porous scaffold, cross-linkable monomers, etc.	Lead adsorbents.
Location	grain boundaries and surface	Perovskite bulk	Bulk, surface and interface of perovskite	Exterior of the device
Lead adsorbing capacity	Limited due to its effect on charge transport	Limited due to its effect on perovskite crystallization	Independent on the loading amount	Relatively high
Lead selectivity	High (pre-isolated Pb ²⁺)	High (pre-complexed Pb ²⁺)	High (pre-integrated Pb ²⁺)	Can be disturbed by environmental factors
Responsivity	Before leakage	Before leakage	Before leakage	After leakage
Lead recycling	Challenging because of the isolated Pb	Challenging because of low solubility of Pb complex	negligible influence	No influence
SQE (full device)	83% ⁴³	58.3% ³⁵ , ~73% ³⁸ , 62.5% ³⁷ , 58.4% ³⁶ , 70% ³⁴	71.9% ⁴⁰ , 94% ⁴¹ , 82.9% ⁴²	98% ¹²¹
SQE (broken device)	-	-	-	>99.9% ^{53,55-57}
PCE increase	+8.5% ⁴³ , +10% ⁴⁴ , +3.3% ⁴⁵	+9.5% ³⁵ , +17% ³⁸ , +1.9% ³⁷ , +15% ³⁶ , +14% ³⁴	+10% ⁴¹ , +6.5% ⁴⁰ , +9.4% ⁴²	-1.1% ¹²¹ , +1.5% ⁵⁴ , +0.4% ⁵⁶ , +1.9% ⁵⁵
Lifetime increase	>100% ⁴³⁻⁴⁵	>100% ³⁴⁻³⁹	+67% ⁴¹ , +87.5% ⁴⁰ , >100% ⁴²	negligible influence 56,90
Scalability	-	17.36% (19.32 cm ²) ³⁷	15.7% (19.16 cm ²) ⁴¹ , 16.75% (24 cm ²) ⁴²	16.3% (60.8 cm ²) ⁵³ , 14.98% (25 cm ²) ⁵⁶ , 18.5% (31.5 cm ²) ⁵⁵

Table 2: Recommend testing conditions of lead leakage for PSCs

	Conditions	Specifications
Water	pH = 4.2; 0.1 ppm Ca ²⁺ ; dripping speed: 5 ml h ⁻¹ per cm ² device; soaking with 120 ml water per 1 cm ² device; room temperature or mediated temperature.	The pH values and competing Ca ²⁺ ions are used to mimic acidic rain. The water volume and flow rate is to simulate one day soaking and dripping under heavy rainfall (50 mm h ⁻¹).
Samples	Aged perovskite films.	To mimic the case of full exposure of perovskite layer to water.
Metrics	Lead leakage ratio (<i>LR</i>), leaked lead concentration (<i>c_{LL}</i>) and <i>SQE</i> .	$LR = \frac{\text{leaked lead from perovskite}}{\text{lead contained in perovskite}} \times 100\%$ $c_{LL} = \frac{\text{leaked lead from perovskite}}{\text{volume of exposed water}}$ $SQE = \left(1 - \frac{\text{leaked Pb from immobilized perovskite}}{\text{leaked Pb from pristine perovskite}}\right) \times 100\%$

855 **Box 1 | The physico-chemical roles of lead in perovskite devices**

856 The prototypical ABX_3 metal halide perovskites consist of three-dimensional corner sharing
857 BX_6^{4-} octahedra with A^+ cations occupying cubo-octahedral sites. The A is a monovalent
858 organic or alkali metal cations (*e.g.*, MA^+ , FA^+ , or Cs^+), B is a divalent metal cation (*e.g.*, Pb^{2+}
859 or Sn^{2+}), and X is a halide anion (*e.g.*, I, Br^- , or Cl^-). While any ions satisfying the geometrical
860 constraints can be considered to build perovskite structure, not all the compositions qualify for
861 the light absorber of high-performance photovoltaics.

862

863 A fundamental question around the toxicity issue of the perovskite is if it is possible to realize
864 the excellent optoelectronic properties of the perovskite without Pb. Although some progress
865 has been made, the PCE and stability of the lead-free PSCs are still far lower than that of lead
866 halide perovskite photovoltaics. In consideration of characteristic orbital mixing configuration
867 contributing to excellent optoelectronic properties of the lead halide perovskites, there have
868 been attempts to replace the Pb with other metals of similar orbital configurations. Owing to
869 the identical valence shell electron configuration, the Group IV elements have been adopted.
870 Among them, the most widely studied material is tin (Sn)-based perovskites¹⁶. The Sn^{2+} has
871 similar ionic radius (118 pm) with Pb^{2+} (119 pm) alongside lone pair 5s and empty 5p orbitals
872 whose effective nuclear charges (Z_{eff}) are 10.63 and 9.10, respectively^{135,136}. However, the Sn^{2+}
873 has tendency to be oxidized to Sn^{4+} (standard reduction potential, $E_0 = 0.15$ V for Sn^{2+}/Sn^{4+}
874 versus $E_0 = 1.67$ for Pb^{2+}/Pb^{4+})¹³⁷, probably due to lack of lanthanide contraction resulting in
875 relatively smaller Z_{eff} for 5s lone pair electrons than those for 6s ones in Pb^{2+} ¹⁴. Consequently,
876 unintended generation of Sn^{4+} in perovskite films results in high defect densities and thus poor

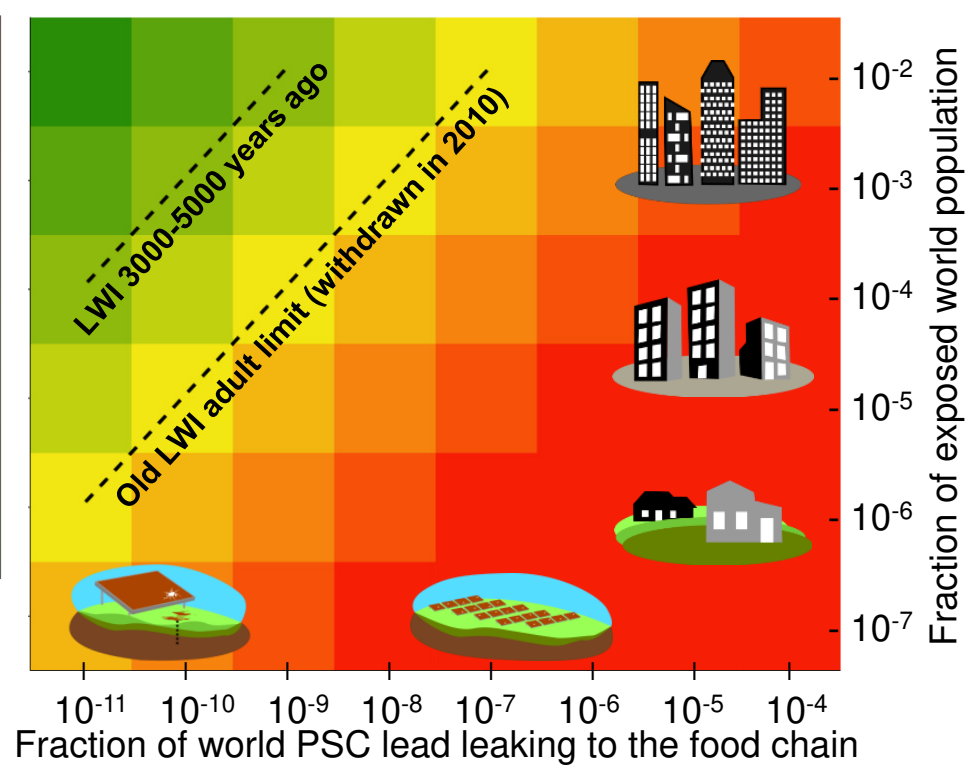
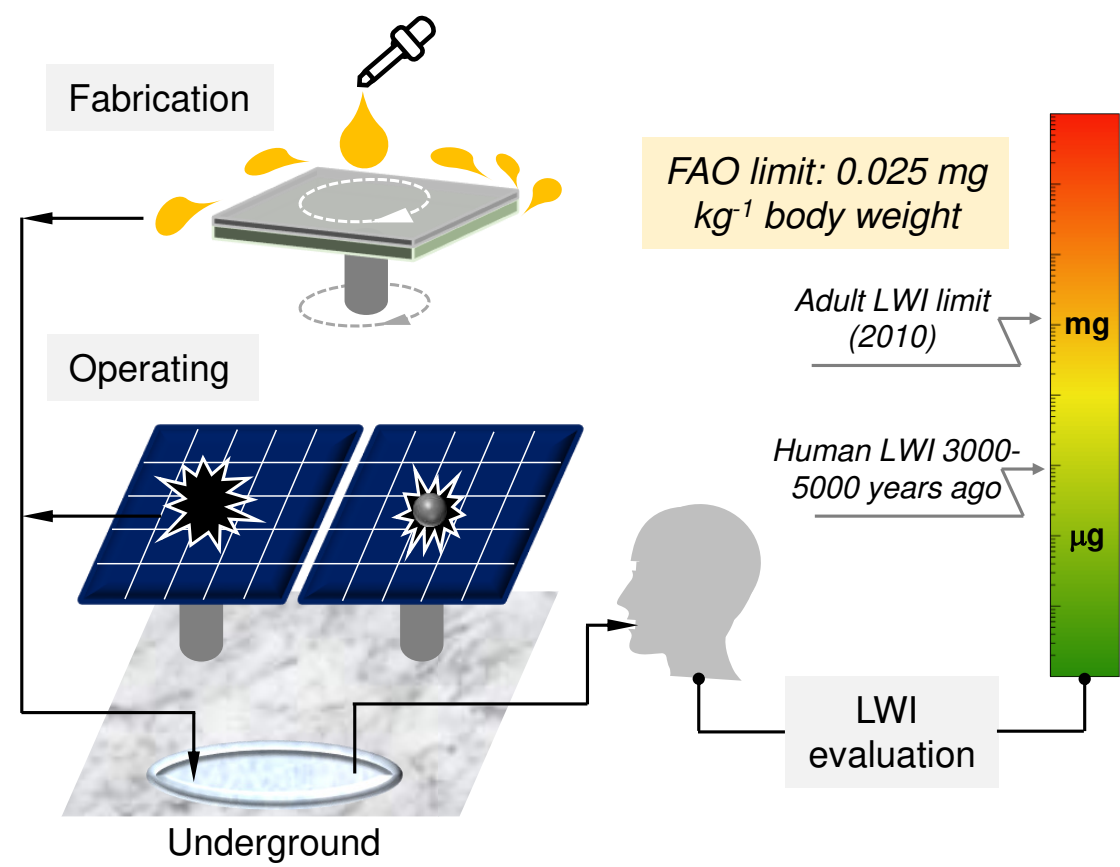
877 optoelectronic properties¹³. Meanwhile, the acute toxicity of the SnI₂ was suggested to be rather
 878 higher than that of PbI₂¹³⁸. Germanium (Ge) is another Group IV element with the identical
 879 valence electron configuration¹³⁹. However, its smaller ionic radius (73 pm) and even higher
 880 tendency to be oxidized ($E_0 = 0.0$ V for Ge²⁺/Ge⁴⁺) cause poor optoelectronic properties and
 881 stability¹⁴⁰⁻¹⁴². In effort to search for stable lead-free perovskites, other composition based on
 882 ns²-containing Bi³⁺ and Sb³⁺ have been also explored. However, these compositions form lower
 883 dimensional crystal structures with relatively wider bandgaps and poor charge transporting
 884 capabilities¹⁶⁻¹⁸. Double perovskites consisting of Ag⁺-Bi³⁺ or Ag⁺-Sb³⁺ or other combinations
 885 of M⁺ and M³⁺ ions form a structurally three dimensional corner sharing octahedra network,
 886 but their lower electronic dimensionality hampers efficient carrier transport¹⁷. Thus, at present,
 887 Pb is the most promising element with respect to optoelectronic properties, and thermodynamic
 888 and environmental stability of the perovskite crystals (**Table**).

889

890 **Table: Typical properties of lead and other alternative ions and halide perovskites (related)**
 891 **compounds containing those ions**^{15,17,18,137,139,142}

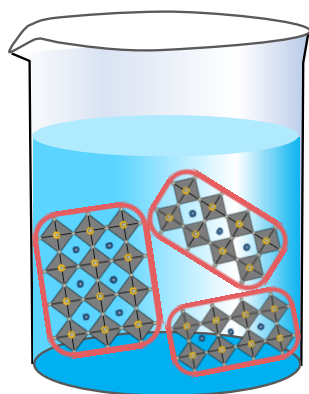
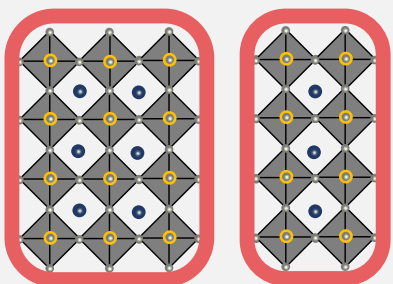
	Pb ²⁺	Sn ²⁺	Ge ²⁺	Bi ³⁺	Sb ³⁺	M ⁺ -M ³⁺
Effective ionic radius	119 pm	118 pm	73 pm	103 pm	76 pm	-
Oxidation state stability	O	X		O		O
3D Perovskite formability	O	O		X		O (double perovskite)
Defect-tolerant orbital configuration	O	O		O		O
Suitable bandgap	O (direct, ~1.5-3.0 eV)	O (direct, ~1.2-3.5 eV)		X (indirect, ~2.0-3.0 eV)		X (indirect, ~2.0-3.0 eV)
High isotropic carrier transport capabilities (MX₆ connectivity)	O	O		X (1D)		X (electronically 0D)

892 O: achievable, X: unachievable



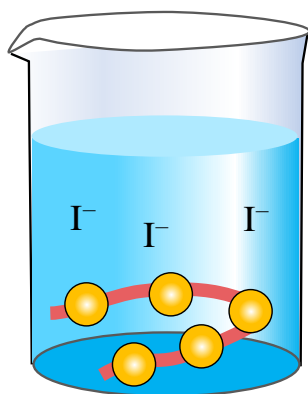
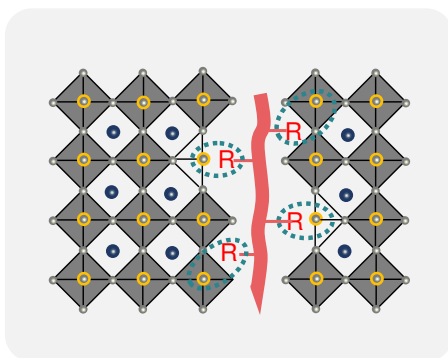
Lead Immobilization Methodologies

Grain Isolation



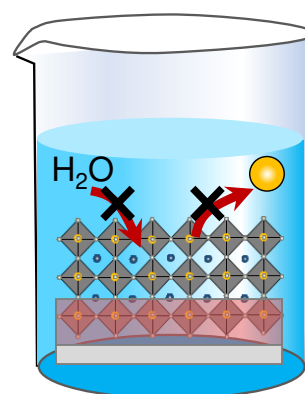
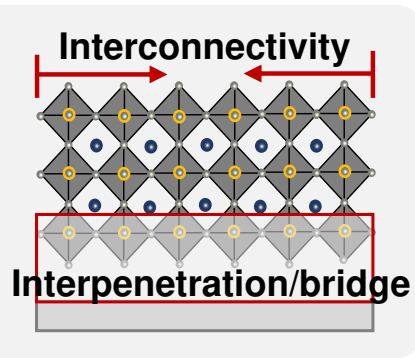
Blocking water ingress and ion outflow

Complexation



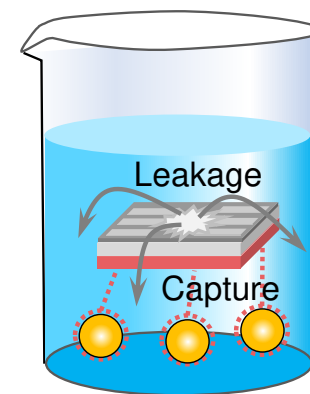
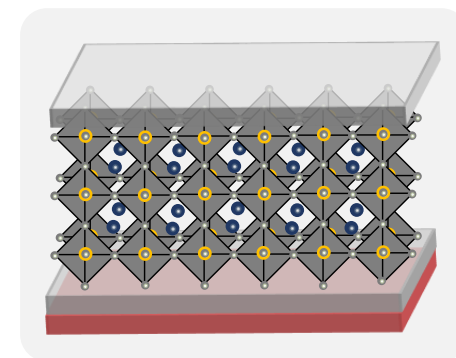
Precipitating from environmental water

Integration



Preventing structure defragmentation

Adsorption



Capturing leaked lead ions from water

