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Lead Immobilization for Environmentally Sustainable Perovskite Solar Cells

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Preface

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

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

1. Introduction

Lead halide perovskites have attracted intense research attention since their first application as light harvesters in solid-state photovoltaics[1]. Certified record power conversion efficiencies (PCEs) of the state-of-the-art perovskite single junction and perovskite-Si tandem solar cells have reached 25.7% and 31.3%[2], respectively. Excellent operational stability over 9000 hours under international electrotechnical commission standards[3] and perovskite modules (64 cm^2) with efficiency above 20%[4] have been achieved. These achievements have enhanced the technology readiness of perovskite solar cells (PSCs) for commercialization.

However, the use of lead is a threat to the environment and human health due to its toxicity[5-8]. While lead occurs naturally in the Earth's crust, anthropogenic activity such as mining in the last few centuries and the use of lead in gasoline, paint, and electronics has increased the risk of exposure to humans and wildlife[9,10]. The use of lead has been systematically regulated with specific limitations designed for each application. This is mainly to minimize the risk of exposure to lead in each type of application, but also to consider the chemical form of the lead-containing compound in relation to bioavailability, which in turns influences both toxicity and bioaccumulation, *i.e.*, the compound's ability to enter living organisms[5,11,12]. The existing legislation around lead does not specifically mention perovskite-based electronics, and thus some urgent consideration is needed on the risk assessment of these materials to assist safe and responsible innovation with lead halide perovskites[5,6]. Recent efforts have strived to substitute the lead element by using divalent metals, such as tin[13-15], or combining monovalent and trivalent metals to construct double metal perovskites[16-18], but the performance of lead-free PSCs is significantly lower than their lead-based counterparts, indicating the essential role of lead in perovskites to realize high efficiency and long-term stability[19-22].

In this Perspective, we discuss the physico-chemical role of lead on optoelectronic properties of perovskite materials (**Box 1**)[23] and accompanying lead toxicity issues with relevant legislation[24,25]. The lead leaching and exposure pathways from PSCs during their lifespan will be discussed [25-29], at which point the end-of-life device can be possibly recycled for reuse by specialists with minimized exposure risk[30]. However, occasional lead leakage from operating devices is out-of-control and hence potentially more harmful. The resultant environmental impacts need to be quantified by considering the concentration and bioavailability of the exposed lead compounds[26,31-33]. We discuss here chemical approaches to fundamentally resolve the issue, categorized into 1) regulating solubility and diffusivity of lead ions in the device[34-51] and 2) chemical adsorption of the leaking lead ions via lead−adsorbing materials[52-57]. Beyond these approaches, we propose possible routes for fundamental mitigation of lead toxicity through chemical immobilization.

2. Lead in PSCs

2.1 Lead toxicity and relevant legislation

The toxicity of lead to humans became apparent in the mid-twentieth century[9], and the concerns of lead exposure to humans include the incidental ingestion of Pb from soil[10] or contaminated foods such as vegetables[58], although water is a main cause of oral exposure[59]. Pb is adsorbed via the small intestine into the blood and bioaccumulates in internal organs, including the liver, kidneys and the central nervous system. Pb is also deposited in the skeleton and can be remobilized during pregnancy, causing exposure to the foetus[60]. Public health concerns from chronic Pb exposure include neurotoxicity, impaired cognitive development and growth in children, effects on renal function, immunity, and the risk of cancer[61]. Clinical monitoring via measuring total Pb concentrations in blood or urine is possible[8,62]. However, the best way to protect the population is to prevent the exposure by setting limits on total Pb concentrations in soil, water, food, medicines and other consumer products.

The legislation with respect to human health includes some internationally agreed standards. For example, The World Health Organisation (WHO) recommends a limit on total Pb in drinking water of 10 µg L^{-1} [63]. In the USA, the ninety percentile for action on Pb concentrations in drinkable water is 15 µg L^{-1}, and has been continuously updated every 3-7 years with a desire for zero Pb in drinking water in the future[64]. With respect to protecting the agricultural food chain to humans, the upper limit of lead content in agricultural soil is set to 250 mg kg^{-1} in China[65]. The maximum tolerable lead content in canned beverages and foods is 150 and 250 mg kg^{-1}, respectively, set by the Food and Agriculture Organization (FAO) of the United Nations[66]. In the USA, the Centre for Disease Control (CDC) indicates a reference value for blood lead concentration of 3.5 µg dL^{-1} [67].There are also regulations for the disposal of solid wastes. For example, in the USA, the safe-to-use level of lead leakage (leaching from solid waste) is set to 5 µg L^{-1} [56]. There are also restrictions on the use of sludge containing metals, including Pb, in the EU[68]. EU legislation limits the content of lead in “homogenous materials” to 0.1% by weight. With that said, photovoltaic panels, “intended to be used in a system that is designed, assembled and installed by professionals for permanent use at a defined location”, are already exempt from this limitation[69]. However, this exemption does not apply to devices embedded in consumer electronics or portable systems — and so lead immobilization could represent a way toward compliance for consumer devices incorporating PSCs, but specific legislation regulating this issue will be needed in the future[70].

2.2 Environmental impacts of PSCs

2.2.1 Life cycle assessment of PSCs

Life cycle assessment has been employed to evaluate environmental impacts of PSCs by considering all stages of their life cycle from the extraction, purification and preparation of lead-related raw materials, to the manufacturing, installation and maintenance of PSCs and the handling of the products at the end of their lifespan[32,71,72]. An evaluation of PSC life cycle has concluded that PSC can be considered more sustainable than other technologies such as commercially available Si solar cells. Regarding the amount of lead used in a PSC, only an approximately 1 μm thick perovskite layer is used owing to their extremely high absorption coefficient, and lead concentrations are often very low in complete PSC devices (around 0.015 mg $L^{-1}dm^{3}$), which is similar to the amount of lead in solder conventionally used to assemble crystalline silicon solar panels. Around 17,000 metric tons of Pb is embodied in the production of the perovskite layer for a yearly 2400 GW electricity generation, representing only 1.1% of the 1.6 million metric tons of lead consumed in the U.S. domestic market each year[32]. We must also consider that in Europe already 56% of lead comes from secondary sources, that do not require mining and concentration of the material; these are the most energy-intensive processes of the production from primary sources, and so the use of secondary sources can reduce potential overall environmental impacts[73]. Despite these positive aspects, Pb leakage from PSCs still represents a major concern because, after installation, the panels will spend most of their lifetime subjected to uncontrolled atmospheric conditions, and possible damage to the panel will lead to dissolution and spreading of the lead due to rainwater[12,74].

2.2.2 Bioavailability of perovskites

Life cycle analysis and leaching studies might identify the potential exposure concentrations, but the effects on human health or the environment depend on how much of the total Pb is bioavailable to the organism, and also whether the bioavailable fraction presents a concern for toxicity. Even though potential lead leakage from PSCs might be relatively low, there is an ethical concern around lifetime exposure to trace amounts of Pb from the products because the internal organs will eventually accumulate sufficient Pb to cause adverse biological effects. However, the organ concentrations at the threshold of adverse effect are not well defined yet. Instead, epidemiology approaches are used to associate lifetime Pb exposure with specific diseases (*e.g.*, Parkinson's disease[75]), or to relate organ concentrations with specific effects (e.g., kidney Pb concentrations and renal function[76]). The toxic effect of lead halide perovskite is strongly dependent on the cellular properties and metabolic activity of cell types. For instance, human dopaminergic neuroblastoma cells and murine primary hippocampal neurons are very sensitive to the toxicity of $MAPbI_3$[77], while human lung epithelial cells are less sensitive[77,78]. In addition, lead toxicity is also related to the type of lead source, and the toxicity of different lead sources has been shown to follow the order of Pb^{2+} > perovskites > PbI_2 = PbO[79]. Moreover, the pH of the environment and the size of the perovskite nanoparticles also influences perovskite toxicity. Acidic conditions will accelerate the dissolution of Pb from the particles, and at low pH values the Pb is present as the bioavailable Pb^{2+} species, which readily binds to biological membranes. There may also be particle-size effects, and smaller perovskite nanoparticles with a high specific surface area are more toxic than larger ones[80,81].

The bioavailability of Pb in soils depends on Pb speciation in the water, the chemical composition of the soil (e.g., ionic strength, pH, natural organic matter) and the type of soil (clay soil, loamy soil, etc.). Inevitably, Pb uptake by plants and other soil organisms will be influenced by these factors and the source of the Pb. Perovskite has been shown to be more bioavailable, such that the lead uptake coefficient greatly increased in the order: native soil < PbI_2 < perovskites. The reason was attributed to organic cations from the perovskites, which can alter the pH values of the soil and impact the lead uptake ability of the plants[31]. Thus, for environmental or human health risk assessments, the form of the Pb, its chemical transformations, and the surrounding chemical matrix should be considered.

Lead weekly intake (LWI) by humans was taken as health-based guidelines for lead exposure, and the upper limit was set at 0.025 mg kg^{-1} body weight by the FAO of the United Nations[82]. By assuming that all the lead contained in a broken PSC panel would leak and reach the environment in a finite amount of time[83], the level of LWI under different percentage dispersion and environmental spreading scenarios is estimated. The scheme shown in **Fig.1** was calculated in order to estimate the possible level of LWI taking into account different possible scenarios. From it we can deduce a low fraction of the total lead needed for PSC reaching the food chain can represent a risk for humans, as in many scenarios the LWI would be higher than the levels estimated for the humans of 3000-5000 years ago and adult LWI limit withdrawn in 2010[84].

3 Lead immobilization in PSCs

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

3.1 Grain encapsulation

By wrapping the perovskite grains within hydrophobic organics (e.g., polystyrene[87,88]), water resistant oxides (e.g., TiO_2[89], SiO_2[44,45,90], Al_2O_3[91]) or insoluble lead salts (e.g., PbS[92], $PbSO_4$[46], $Pb(OH)_2$[47]), the pathways for water ingress and ions outflow can be effectively blocked. The utility of isolation strategy is dependent on the water permeability of the capping layers, which usually employ materials with strong hydrophobicity, high compactness and full coverage on perovskite grains. For instance, the condensation of small molecules along with perovskite crystallization[44,45] or depositing hydrophobic molecules[43] or functional salts (e.g., sulfonics[37,93], sulfates[46], sulfides[92,94,95]) atop the perovskite layer in post treatments enabled an in-situ encapsulation of grain boundaries and surface. Well grain-encapsulated lead-containing perovskites manifested robust water stability, which even demonstrated promising application as scintillators for in-vivo bio-imaging without significant cytotoxicity on target animals[90,96,97], indicating reduced bioavailability. In addition, inserting water resistant layers into the PSCs for inner[98-101] or external encapsulation[102-106] can also prevent water permeation, but these approaches are ineffective in case of device breakage. Even though some self-healing characteristics were endowed by mixing curable materials with the encapsulants[102], the protection effectiveness might be problematic because the curing process of the damaged encapsulants usually requires external stimulus (e.g., UV radiation, heating), which are not always available in emergency case.

3.2 Chemical complexation

To mitigate water contamination, the solubility of lead compounds from degraded perovskites needs to be decreased by forming low solubility products (K_{sp}) of lead-additive complexes via rational additive engineering. Typically, the additives should consist of both electron-donating Lewis base functional groups (e.g., carbonyl[34,36,37], thiol[107], sulfonic[53], sulfide[108], porphyrin ring[35], crown ethers[38]) coordinating with Lewis acidic Pb^{2+} ions via an acid/base interaction and hydrophobic backbone or side chains being endowed with water-repelling moieties (e.g., long alkyl chains, fluorine groups, carbon nanotubes[34]) allowing them to precipitate from water after complexation. Thus, the as-formed complexes become hydrophobic after the chelation of the functional groups with Pb^{2+}. For example, the addition of polyacrylic acid grafted carbon nanotubes (CNT-PAA) into the perovskite precursor can effectively suppress the lead leakage of the corresponding PSCs.[34] Briefly, the CNT-PAA exhibited a high Pb^{2+}-capturing capability due to the presence of large amount of carboxyl groups on the wall of CNTs. After the occupation of hydrophilic groups by Pb^{2+}, the self-aggregation of water insoluble CNTs allowed them to form precipitation in water. As a result, the leaked lead from the CNT-PAA doped device was well below the hazardous waste limit upon water immersion[34].

3.3 Structure integration

Water (moisture) induced perovskite decomposition usually initiates from water adsorption at the crystal surface, followed by deep penetration into the interior of the bulk and dramatically accelerated perovskite fragmentation and ions release[40]. Integration of perovskite structure within the device by improving binding strength of the constituent elements, intergrain connectivity and interfacial cohesion is able to increase energy barrier for water penetration, structural fragmentation and layer delamination, thus boosting the structural stability against water dissolution and lead leaking[49,109]. For instance, interfacial/intergrain bridge via strong coordination or dipole-dipole interaction can enhance the interconnectivity of the device, resulting in extremely stable perovskites in highly salty, acidic (pH=1) and basic (pH=13) aqueous conditions[110]. Sole enhancement of chemical interaction at perovskite top-surface has proven effective to resist crystal collapse and retard lead release[40], but it might be ineffective in case of device damage. Alternatively, the whole structure including the surface, bulk and interface of the perovskite layer needs to be integrated.

The integration of perovskite grains can be achieved by implementing polymerizable monomers into the perovskite layer to construct perovskite/polymer matrix.[41,42] For example, acrylamide monomers were employed as additives in the preparation of perovskite films[41], which were polymerized *in-situ* to form polyamides along with the perovskite transformation. The –C=O groups from the polyamides can interact with undercoordinated Pb^{2+} at grain boundaries and surface of the perovskite to form a robust chelation structure in the as-deposited thin films[41]. Also, the polyamides are prone to form hydrogels when exposed to water, which can further prevent the dissolution and diffusion of Pb^{2+} from the device into water[41]. Moreover, the agglomeration effect of the monomers during polymerization can induce compressive strain within the perovskite layer, which can increase the activation energy for ions migration[111] and barrier for water permeation[112], leading to improved crystal stability in high humidity conditions. Additionally, the infiltration of perovskite into rigid and mesoporous structure is also expected to prevent structural collapse.

3.4 Adsorption of leaked lead

In addition to *in-situ* immobilization, lead-adsorbing materials can be integrated into PSCs to capture leaking ions in case of device damage. Similarly, an effective lead-adsorbent should contain lead binding groups (e.g., phosphonates[54,113], thiols[107,114], sulfonates[56], tetraethylene glycol[115]) to form water insoluble lead products with extremely low K_{sp} values[116-119].

All functional layers located at interior or exterior of the devices *e.g.* charge transport layers (CTL)[107,113,115,120], electrodes[121] or encapsulants[54-56,114,122] may be considered as hosts for lead-adsorbents. Since the lead sequestration efficiency (SQE) is directly correlated with the density of adsorbing sites, the loaded materials should be abundant to ensure sufficient lead-adsorbing capacity. Thereby, the implementation of Pb adsorbents into interior layers of the device might be insufficient because of the limited scavenging capacity by layers. The conductivity of the electrode would decay if too much insulating materials were infiltrated[121]. Also, CTLs are at most a few hundred/ten nanometer thick which offer a low capacity to capture all Pb^{2+} contained in the perovskite film. Therefore, embedding lead-adsorbing materials into the exterior encapsulation is a better option, where the device performance is not restricted by the loading amount[56]. Given the random lead diffusion pathways, both front and back sides of the device can be simultaneously protected. A good example was given by Li *et al.* [54], where a highly transparent Pb-adsorbent was deposited on top of the front glass without filtering the incident light, and a blend of polymer encapsulants and Pb^{2+} binding materials was inserted between the back electrode and encapsulating cover. Owing to the remarkable lead-adsorbing capability on both sides, such chemical approaches can substantially reduce lead leakage by 96%[54]. Moreover, lead-adsorbing materials with different activity in various temperature and pH conditions should be combined. For instance, the employment of lead-adsorbents consisting of phosphonic and methylenephosphonic acid groups within one device can retain high *SQE* over a large temperature range due to the varied temperature dependent deprotonation effect[54].

As summarized in **Table 1**, the aforementioned four lead-immobilization strategies are systematically compared from the aspects of work mechanism, protection effectiveness and their influence on device performance. Notably, interior lead-immobilization strategies (i.e., isolation, complexation, integration) demonstrate high selectivity and fast responsibility because the Pb^{2+} ions are pre-protected before leakage, but relatively low SQEs (~60-80%). It is known that the lead-immobilizing capacity is correlated to the density of functional sites in the embedded additives, especially for the method of complexation. However, most of these additives are insulating and in some case light absorbing, which can undermine charge transport and photon harvesting, and the interaction between the additives and the Pb precursors can affect perovskite crystallization. Therefore, a trade-off between PCE and SQE might occur when the additive concentration exceeds the tolerance of perovskite materials[123]. Nevertheless, a rational dose of Pb-immobilizing additives in the perovskite layer can advantageously lead to PCE increase and lifetime increase (**Table 1**), which are defined by the PCE and lifetime ratio of best optimized device to pristine device, respectively. In addition, owing to the inert character of grain encapsulation and insolubility of the as-formed lead complexes, these approaches for grain isolation and chemical complexation would challenge the lead recycling process, which relies on the ease of extraction of the lead from the device. Also, the formation of homogenous capping layer at the perovskite grain boundaries might be problematic, especially in large scale manufacturing, because of the difficulties in controlling the layer thickness, restricting the upscaling of PSCs. In these aspects, the structure integration seems to be more promising, in which the lead-immobilizing capacity is related to the structural stability rather than the chelating sites of the additives, leading to relatively higher SQEs of ~80%.

In contrast, the implementation of lead-adsorbents at exterior of the device is more effective in the suppression of lead leakage with SQE approaching 100% because a large amount of materials can be loaded without influence on device performance. However, it still suffers from several drawbacks that may reduce their effectiveness. First, the lead-adsorbents are specifically designed to capture the Pb ions after their release from the perovskite lattice, and the sorption speed should be extremely fast otherwise the capturing efficiency might be limited if the water flux is fast or the Pb^{2+} concentration is high at the initial stage of device damage. Second, the variation of environmental pH and temperature, and the presence of other metal ions (e.g., Ca^{2+}, Mg^{2+}) within the water may defunctionalize the Pb-adsorbents. Third, the lead adsorbents, in addition to showing excellent Pb-adsorbing capacity, should also support scratching resistance, UV stability and high selectivity of lead ions.

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

4. Conclusions and Future Prospects

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

4.1 Toward lead immobilization in PSCs

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

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

Further investigation of the temporal dynamics of lead escape from PSCs and lead capturing from water at different environmental conditions (e.g., pH, temperature) can also provide guidelines for the optimization of lead-immobilization strategies toward practical application[124]. To guarantee sufficient lead-immobilizing capacity and resistance to re-dissolution, researchers should choose additives abundant anchoring sites, such as by grafting the lead-chelating functional groups on a backbone with high specific surface area (e.g., CNT[34], graphene[56], metal of framework[57]), and persistent binding energy with Pb^{2+} at a broad range of environmental conditions. Moreover, some environmentally friendly and degradable agents such as magnetic nanoparticles, chitosan composites, which exhibit promising activity to remove lead from wastewater in a wide range of pH and temperature[125-127], might be explored as lead-adsorbents in PSCs to improve their availability at various weather conditions without further pollution. Even though the bioavailability of immobilized lead is significantly reduced, these compounds might be re-dissolved and cause potential hazards during long-term exposure. In this respect, lessons from hydrogel of polyamides[41] or self-bundling of CNT[34] to precipitate the lead products from water, and integration of perovskite layer within the device to prevent its delamination and fragmentation in environmental water, are desirable.

4.2 Considering the full life cycle of PSCs

Lead leakage should be avoided when considering the full life cycle of PSCs. Starting with the preparation of lead halide perovskite films for PV applications, the overwhelming majority of researchers have adapted spin coating as their method of choice; this should be replaced by other solution processing methods such as slot die coating, screen printing or doctor blading, as these waste only a very small percentage of the perovskite precursors compared with spin-coating. Also, lead-immobilization strategies can be introduced into the precursor solutions to reduce the bioavailability of lead-containing waste. PSCs should be specifically optimized to prevent lead leakage according to their application. For example, flexible electronics are directly accessible to humans because of their potential applications in daily life, and the plastic substrates are prone to damage because they are sensitive to light, heat, scratching, and bending. Therefore, self-curing ability by mixing healable materials[102] and strain modulation to facilitate stress relaxation[128] should be endowed in flexible PSCs to improve their mechanical resistance.

Strategies should also be developed to dispose end-of-life perovskite devices. Ideally, all components of the multilayered PSCs should be recycled for reuse to save their energy-payback-time, especially the lead compounds because of their toxicity. Techniques of lead-recycling from PSCs were generally based on electrochemical deposition[129], selective solvent extraction[130-132], desorption from precipitated lead compounds[6,133], and so on[30,134]. Even though very high recycling yield can be achieved[6,129-133], these lead-recycling methods involve a large amount of organic solvents and complex energy-consuming processes, which increase the recycling cost and challenge their large-scale application. In addition, we should note that lead-immobilization with highly complexed Pb^{2+} would be a challenge for lead recycling, so the potential for lead-recycling should be considered as one of the criteria for the selection of lead-immobilization strategies.

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

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Author contributions

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. and M.G. contributed to the writing. N.G.P. edited the manuscript. All authors commented on the manuscript. H.Z., J-W.L., A.A. and N-G.P. contributed to the preparation of the figures.

Competing interests

The authors declare no competing interests.

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Figure legends

Fig. 1: Lead leakage pathways from PSCs and estimation of their potential environment impact. Schematic illustration of lead leakage pathways to the underground water during device fabrication and out-door operation, and estimation of their impact to the level of human lead weekly intake (LWI), which was calculated by considering the world population and total PSC leads required for electricity generation in 2050, compared with the adult LWI limit and human LWI 3000-5000 years ago.

Fig. 2: Lead immobilization methodologies in PSCs. Grain isolation with hydrophobic polymers, oxides or insoluble lead salts to block water ingress; Complexation of additive and lead compounds with low K_{sp} allowing to precipitate from environmental water; Structural integration with enhanced interconnectivity to prevent structure fragmentation and layer delamination; adsorption of lead ions using embedded lead-adsorbents at exterior of the device.

Fig. 3: Proposed lead leakage measurements and device structure for lead immobilization. **a**, schematic illustration of detection of leaking leads in case of water soaking of the perovskite layer and water dripping from the perovskite layer with precisely defined metrics, *e.g.* lead leakage ratio (LR), leaked lead concentration (c_{LL}) and lead sequestration efficiency (SQE), and the evaluation of potential impact of the leaked leads on the growth of plants and animals, and **b**, proposed device structure for Pb-immobilization including interior and exterior strategies.

Table 1: Quantitative analysis of lead-immobilization strategies

	Grain isolation	***Lead complexation***	***Structure integration***	***Chemical adsorption***
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 (*LR*), leaked lead concentration (c_{LL}) and *SQE*.	$LR = \frac{\text{leaked lead from perovskite}}{\text{lead contained in perovskite}} \times 100\%$ $c_{LL} = \frac{\text{leaked lead from perovskite}}{\text{volume of exposed water}}$ $SQE = \left(1 - \frac{\text{leaked Pb from immobilized perovskite}}{\text{leaked Pb from pristine perovskite}}\right) \times 100\%$

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

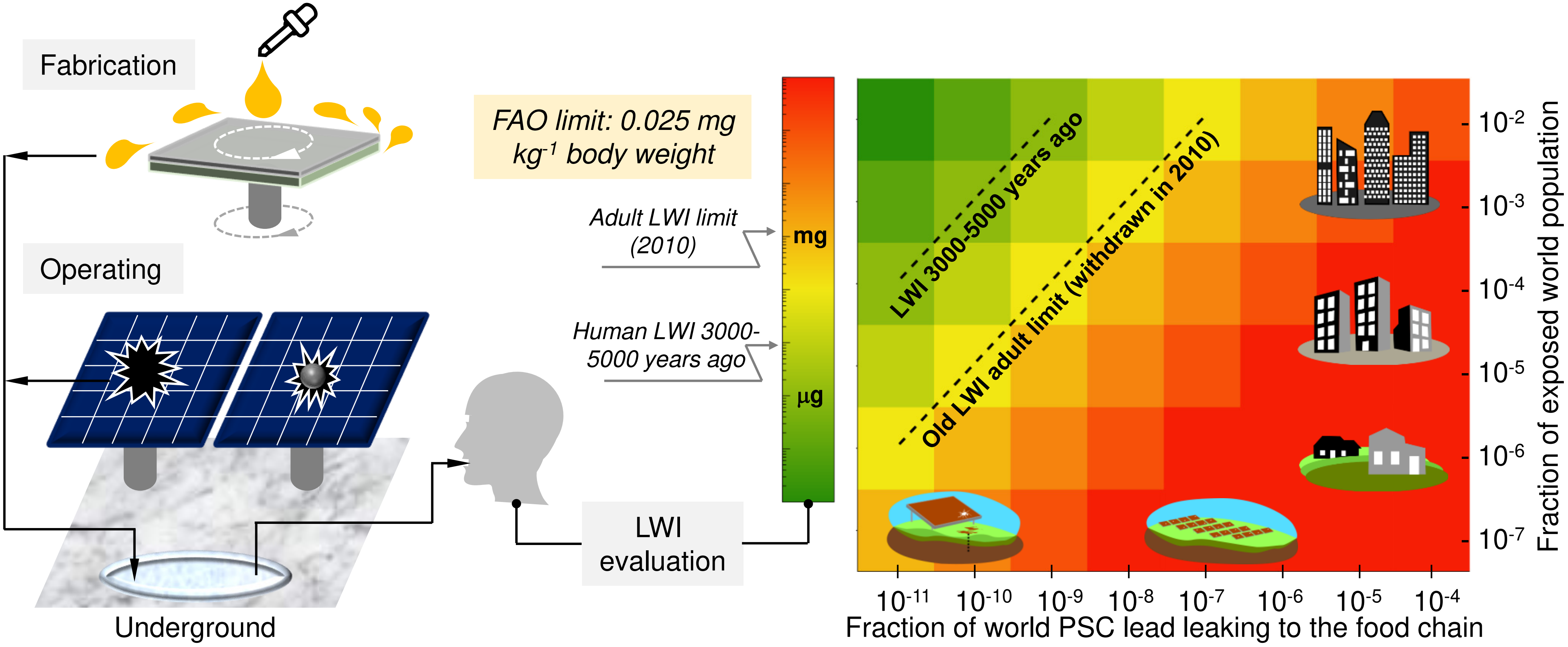
The prototypical ABX_3 metal halide perovskites consist of three-dimensional corner sharing BX_6^{4-} octahedra with A^+ cations occupying cubo-octahedral sites. The A is a monovalent organic or alkali metal cations (*e.g.*, MA^+, FA^+, or Cs^+), B is a divalent metal cation (*e.g.*, Pb^{2+} or Sn^{2+}),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

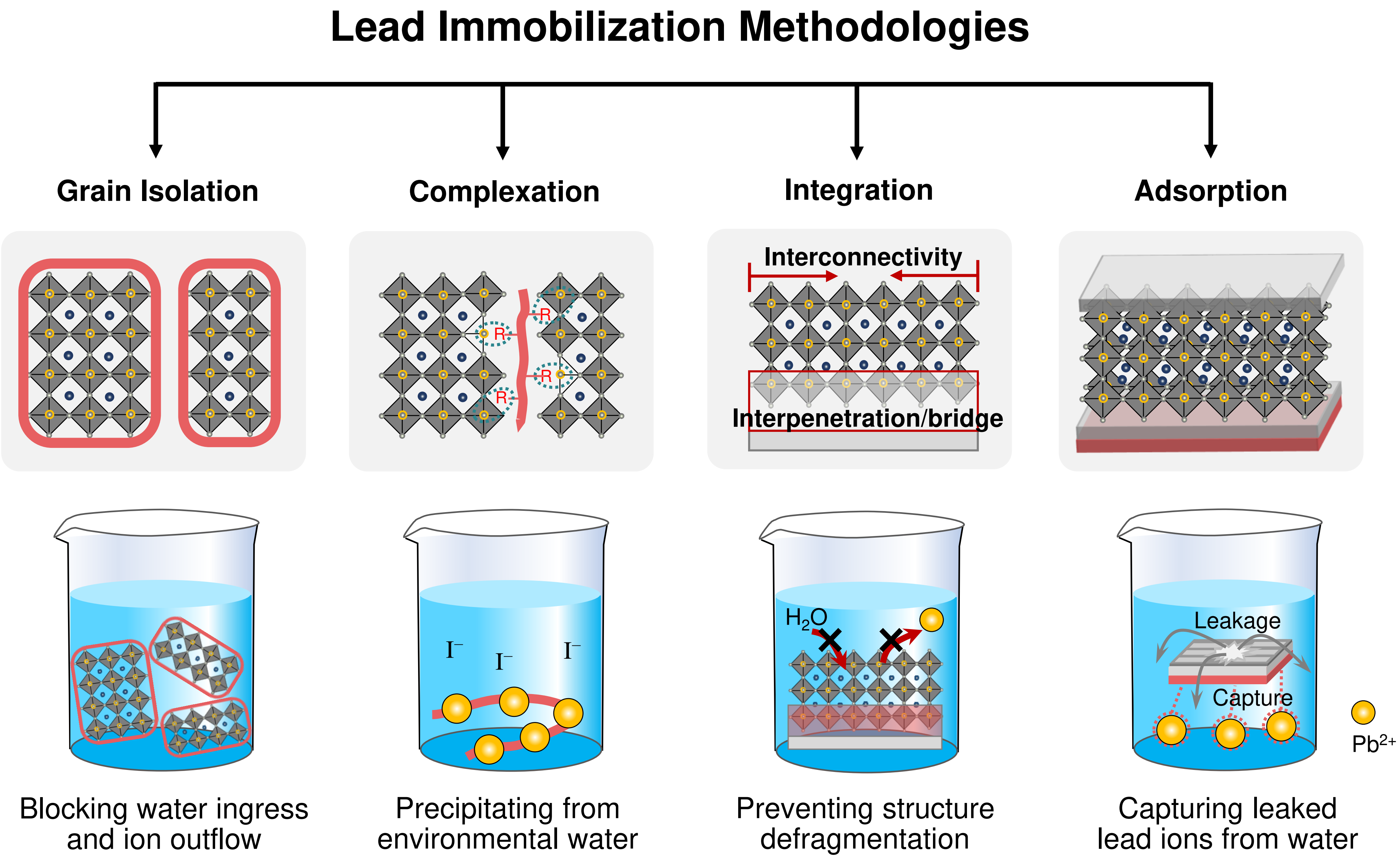
A fundamental question around the toxicity issue of the perovskite is if it is possible to realize the excellent optoelectronic properties of the perovskite without Pb. Although some progress has been made, the PCE and stability of the lead-free PSCs are still far lower than that of lead halide perovskite photovoltaics. In consideration of characteristic orbital mixing configuration contributing to excellent optoelectronic properties of the lead halide perovskites, there have been attempts to replace the Pb with other metals of similar orbital configurations. Owing to the identical valence shell electron configuration, the Group IV elements have been adopted. Among them, the most widely studied material is tin (Sn)-based perovskites[16]. The Sn^{2+} has similar ionic radius (118 pm) with Pb^{2+} (119 pm) alongside lone pair 5*s* and empty 5*p* orbitals whose effective nuclear charges (Z_{eff}) are 10.63 and 9.10, respectively[135,136]. However, the Sn^{2+} has tendency to be oxidized to Sn^{4+} (standard reduction potential, $E_0 = 0.15$ V for Sn^{2+}/Sn^{4+} versus $E_0 = 1.67$ for Pb^{2+}/Pb^{4+})[137], probably due to lack of lanthanide contraction resulting in relatively smaller Z_{eff} for 5*s* lone pair electrons than those for 6*s* ones in Pb^{2+} [14]. Consequently, unintended generation of Sn^{4+} in perovskite films results in high defect densities and thus poor optoelectronic properties[13]. Meanwhile, the acute toxicity of the SnI_2 was suggested to be rather higher than that of PbI_2[138]. Germanium (Ge) is another Group IV element with the identical valence electron configuration[139]. However, its smaller ionic radius (73 pm) and even higher tendency to be oxidized (E_0 = 0.0 V for Ge^{2+}/Ge^{4+}) cause poor optoelectronic properties and stability[140-142]. In effort to search for stable lead-free perovskites, other composition based on ns^2-containing Bi^{3+} and Sb^{3+} have been also explored. However, these compositions form lower dimensional crystal structures with relatively wider bandgaps and poor charge transporting capabilities[16-18]. Double perovskites consisting of Ag^+-Bi^{3+} or Ag^+-Sb^{3+} or other combinations of M^+ and M^{3+} ions form a structurally three dimensional corner sharing octahedra network, but their lower electronic dimensionality hampers efficient carrier transport[17]. Thus, at present, Pb is the most promising element with respect to optoelectronic properties, and thermodynamic and environmental stability of the perovskite crystals (**Table**).

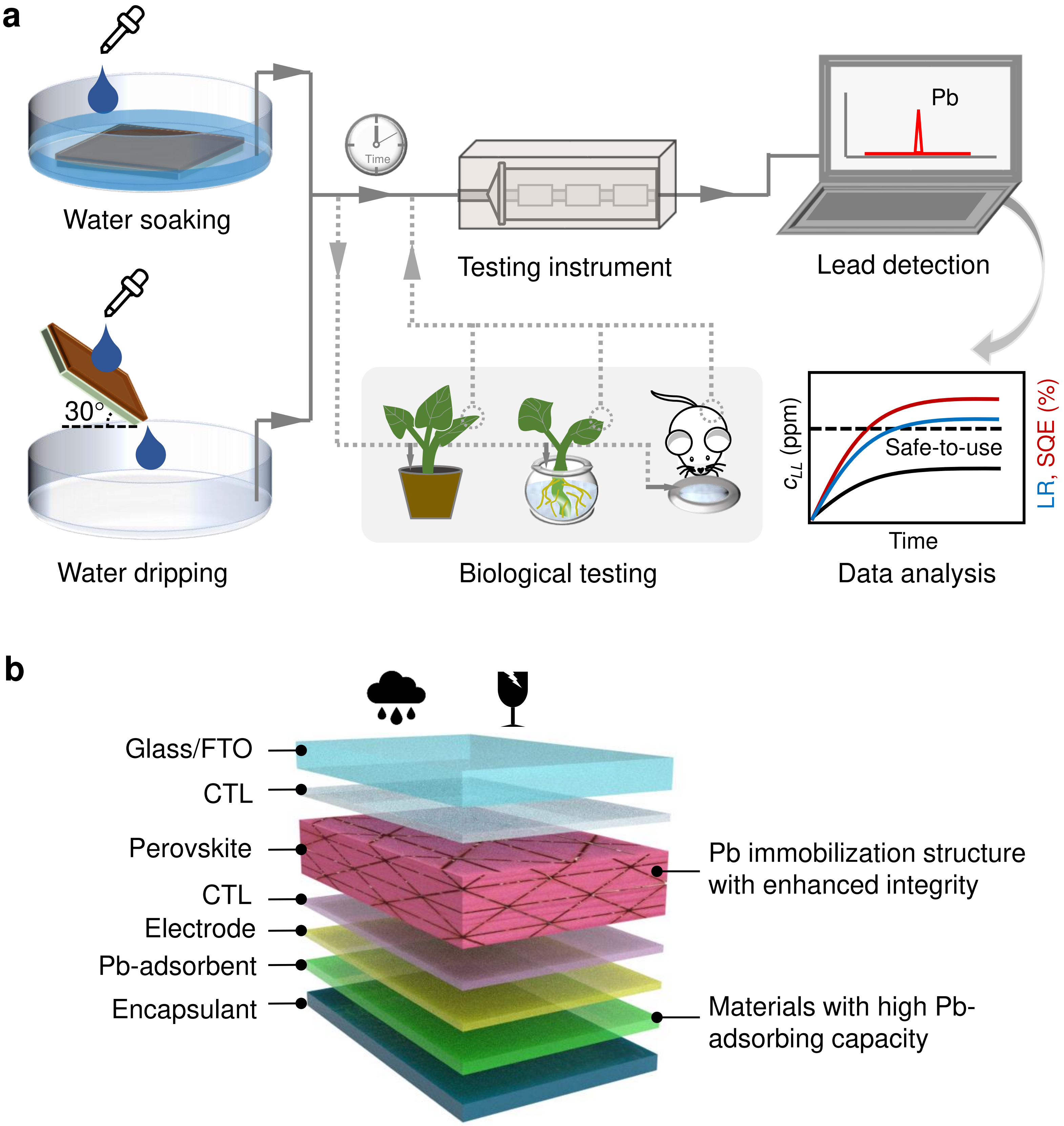
Table: Typical properties of lead and other alternative ions and halide perovskites (related) compounds containing those ions[15,17,18,137,139,142]

	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 (MX_6 connectivity)	O	O		X (1D)		X (electronically 0D)

O: achievable, X: unachievable


Fabrication
Operating
Underground
FAO limit: 0.025 mg kg^{-1} body weight
Adult LWI limit (2010)
Human LWI 3000-5000 years ago
mg
µg
LWI evaluation
LWI 3000-5000 years ago
Old LWI adult limit (withdrawn in 2010)
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
Fraction of exposed world population
10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4}
Fraction of world PSC lead leaking to the food chain


Lead Immobilization Methodologies
Grain Isolation
Complexation
Integration
Adsorption
R
R
R
R
Interconnectivity
Interpenetration/bridge
I⁻
I⁻
I⁻
H_2O
Leakage
Capture
Pb^{2+}
Blocking water ingress and ion outflow
Precipitating from environmental water
Preventing structure defragmentation
Capturing leaked lead ions from water


a
Water soaking
Water dripping
30°
Time
Testing instrument
Pb
Lead detection
Biological testing
c_{LL} (ppm)
LR, SQE (%)
Safe-to-use
Time
Data analysis
b
Glass/FTO
CTL
Perovskite
CTL
Electrode
Pb-adsorbent
Encapsulant
Pb immobilization structure with enhanced integrity
Materials with high Pb-adsorbing capacity