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Reduction of lead leakage from damaged lead halide perovskite solar modules using self-healing polymer-based encapsulation

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Nowadays the major factors determining commercialization of lead halide perovskite photovoltaic technology are shifting from solar cell performance to stability, reproducibility, up-scaling, and in particular the concern of Pb leakage during solar cell operation. Here we simulate a realistic scenario that the perovskite solar modules with different encapsulation methods are damaged to a typical extent by mechanical impact (according to the modified FM 44787 standard) and quantitatively measure the lead leakage rates from the damaged modules. We demonstrate that an epoxy resin (ER) based encapsulation method reduces the Pb leakage rate by a factor of 375 compared to the encapsulation method using a glass cover with the UV-resin cured at the module edges. The excellent Pb leakage prevention characteristics is due to the self-healing property of ER and increased mechanical strength. These findings strongly suggest lead halide perovskite photovoltaic products can be used with minimal Pb leakage if appropriate encapsulation is employed.

1 Lead halide perovskites have garnered considerable attention as efficient light absorbers. Solar cell power
2 conversion efficiency (PCE) has reached 23.7% for single junction perovskite¹ and 28.0% for perovskite
3 silicon tandem structure (two-terminal)¹ on a laboratory scale, already surpassing the other well-
4 established commercial photovoltaic technologies, e.g., multi-crystalline silicon (22.3%) and thin film
5 copper indium gallium selenide (CIGS) (22.9%)², suggesting that PCE is no longer a major limiting factor
6 towards commercialization of this novel photovoltaic technology. Lifetime of a perovskite solar cell under
7 operation and the existence of toxic Pb in the perovskite absorber become significant concerns regarding
8 whether and how this technology should be developed.³⁻¹⁵ Encapsulation is a necessary and widely
9 employed approach to significantly increase the solar cell operational stability by preventing
10 environmental related degradation and enhancing the mechanical strength against external impact. A
11 variety of customized encapsulation methods have been developed for different types of solar cells. For
12 example, a stacked 5-layered structure of glass/ethylene vinyl acetate (EVA)/photovoltaic
13 module/EVA/backsheet is used to encapsulate Si solar panels;¹⁶ a stacked layer of glass/EVA or poly-vinyl
14 butyral (PVB)/photovoltaic module/transparent conductive electrode (TCO) is used to encapsulate CIGS
15 solar panels;¹⁷ a structure of TCO/photoanode/electrolyte/photocathode/TCO is encapsulated by surlyn
16 polymer in dye-sensitized solar cells.¹⁸ Encapsulation methods have been also developed aiming at
17 improving operational stability and reducing the environmental related degradation of perovskite solar
18 cells (PSCs) and modules. Benefiting from decreasing the oxygen and moisture diffusion in the lead halide
19 perovskite absorbers, the T_{80} lifetime of PSCs in ambient condition was improved from 656 h to over 3423
20 h after encapsulation.¹⁹ Using an EVA encapsulant, PSCs withstood temperature cycling and retained over
21 90% of their initial performance after 200 temperature cycles.²⁰ On the other hand, effectiveness of these
22 encapsulation methods against Pb leakage, which is equally important, has not been studied. Similar to Si
23 solar modules, perovskite solar modules for outdoor applications can get damaged or even broken due to
24 natural causes e.g., hailstones, snow and wind loading, fires during usage. The toxic Pb can penetrate

1 through the damaged region with rain water and contaminate the local environment (Supplementary Fig.
2 1). Therefore, it is imperative to study the effect of encapsulation on the Pb leakage from damaged
3 perovskite solar modules and to develop an encapsulation method that can effectively minimize the Pb
4 leakage.

5 In this work, we develop three encapsulation methods for perovskite solar modules, simulate a
6 realistic scenario in which the encapsulated perovskite solar modules are damaged by mechanical impact
7 such as hail impact, and quantitatively measure the Pb leakage rate from the damaged perovskite solar
8 modules, which to our best knowledge is the first attempt in the field. In addition, we use the semi-
9 empirical approximation based on the Noyes-Whitney equation to study the key parameter that
10 determines the lead leakage rate from damaged perovskite solar modules. Furthermore, we characterize
11 the self-healing property of the encapsulation polymer, i.e., epoxy resin (ER), which is used with a multi-
12 stack structure of glass/ER/perovskite solar module/UV-resin/glass to understand how the self-healing
13 property of ER influences the key factor in terms of reducing the Pb leakage rate.

14 **Experimental procedures to assess the Pb leakage**

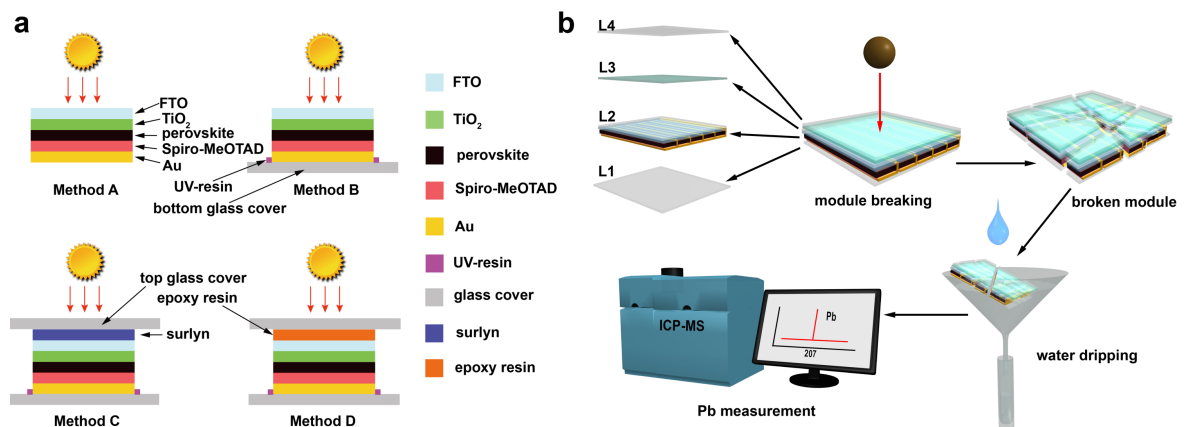
15 The $\text{Cs}_{0.07}\text{FA}_{0.93}\text{PbI}_3$ perovskite solar modules were prepared according to our reported method
16 (geometry of the perovskite solar module is shown in Supplementary Fig. 2).²¹ To ensure the relevance of
17 this study to the real solar cell applications, the perovskite solar modules used here are all working solar
18 modules with reasonable performance. Details of the transmittance and reflectance of the encapsulants
19 and the solar module performance are discussed in the Supplementary Information and shown in
20 Supplementary Fig. 3 and Supplementary Table 1. Four types of configurations, designated as Method A,
21 B, C and D, were studied. In Method A, perovskite solar modules with a structure of FTO/c-
22 $\text{TiO}_2/\text{Cs}_{0.07}\text{FA}_{0.93}\text{PbI}_3/\text{spiro-MeOTAD}/\text{Au}$ from top to bottom were used without further encapsulation (Fig.
23 1a). In Method B, perovskite solar modules were encapsulated by 1 mm thick glass substrates using a UV-
24 resin (XNR5570, NAGASE) at the bottom sides. The UV-resin was coated at the edges of the modules, and

1 cured under a 400 W UV lamp for 5 min. No encapsulation was performed at the top sides (Fig. 1a). In
2 Method C, perovskite solar modules were first encapsulated at the bottom sides similar to Method B, and
3 then encapsulated by 1 mm thick glass substrates using thermo-compressed surlyn adhesive resin films
4 (DuPont) at the top sides by annealing at 140 °C for 10 s (Fig. 1a). The surlyn films show the self-healing
5 property when the heating temperature approaches its melting temperature (T_m), e.g., 85 – 90 °C.²² This
6 encapsulation method has been commonly applied for organic photovoltaics and dye-sensitized solar
7 cells.^{18,23} In Method D, perovskite solar modules were first encapsulated at the bottom sides similar to
8 Method B, and then encapsulated by 1 mm thick glass substrates at the top sides using thermo-
9 crosslinking ER films. The ER films also show the self-healing property, i.e., they return from a deformed
10 state (temporary shape) to their original (permanent) shape induced by heating up at temperature higher
11 than the glass transition temperature, T_g .^{24,25} As a consequence, the ER films have shown promising
12 applications in manufacturing sensing devices or actuators for medical industries, because of the unique
13 self-healing and easy-processing properties.^{26,27} The ER films are formed by mixing diglycidyl ether of
14 bisphenol A type epoxy resin (DGEBA), *n*-octylamine (OA), and *m*-xylylenediamine (MXDA). The reaction
15 between DGEBA and OA forms linear polymers (Supplementary Fig. 4), which show strong physical
16 crosslinks by tail-to-tail associations among alkyl chains exhibiting the behavior of a physical network.^{28,29}
17 By substituting OA with MXDA while maintaining the overall stoichiometric ratio between epoxy and
18 amine, chemical crosslinks are also formed.³¹ These chemical crosslinks help improve the mechanical
19 properties of ER, which is evidenced by the increased T_g and T_m .^{28, 30} ER has the tendency to self-heal
20 when heated up at temperatures higher than its T_g (i.e., self-healing), but loses its physical strength when
21 heated up at temperatures higher than its T_m . We determined T_g and T_m of the ER films with three
22 different compositions using differential scanning calorimetry (DSC). Based on these results, we selected
23 the particular ER (DGEBA: OA: MXDA = 4: 2: 1) with a T_g of 42 °C and T_m of 88 °C as the encapsulant in
24 encapsulation Method D for our Pb leakage study, because such an ER film shows the self-healing property

1 and maintains its physical strength at the temperature most relevant to solar cell operation
2 (Supplementary Fig. 5a-d, Video S1-2). However, we claim that the local overheating (known as the hot-
3 spot heating) may occur on the current-limiting cell in a string, causing partial failure of the encapsulation.
4 Therefore re-adjustment of the polymer composition (OA to MXDA ratio) will be needed to increase the
5 T_m , especially at the hot regions. The ER film possesses excellent thermal stability with a thermal
6 degradation temperature of 246.1 °C determined by thermogravimetric analysis (TGA), which is
7 significantly higher than the typical solar cell operating temperature (Supplementary Fig. 6). Activation
8 energy (E_a) corresponding to thermal decomposition of the ER film is 72.6 kJ/mol (Supplementary Fig. 6).
9 To demonstrate the feasibility of this encapsulation method, we also evaluated the cost of the ER layer.
10 The price of the 800- μm -thick ER layer is \$12.3/ m^2 , which amounts to 4.4% of the total cost of the
11 encapsulated perovskite solar modules³¹⁻³⁴, suggesting that it is a very promising encapsulant from the
12 cost point of view. More detailed information for the cost evaluation can be found in the Supplementary
13 Fig. 7, Supplementary Table 2. The FTO side of the perovskite solar module is designated as the top side
14 allowing light to pass through, and the Au electrode side of the perovskite solar module is designated as
15 the bottom side (Fig. 1a).

16 To simulate the hail impact, we mechanically broke the encapsulated perovskite solar modules by
17 dropping a metal ball on top of them, similar to the Approval Standard for Rigid Photovoltaic Modules
18 (FM 44787)³⁵, a standard hail impact test for Si solar panels. We optimized the impact condition using FTO
19 substrates with the similar encapsulation methods to achieve a certain typical damage pattern, i.e., star-
20 shaped microcracks,³⁶ on damaged encapsulated modules, which can appear in typical-sized PV modules
21 under the standardized test conditions (Supplementary Figs 8 and 9a-h). We assume that the impact
22 intensity is 1 impact per 25 cm^2 , which represents an extreme case scenario. Subsequently each damaged
23 perovskite solar module was put in a funnel with a tilt angle of approximately 30° with respect to the
24 horizontal direction (Fig. 1b), which is the optimized tilt angle for countries/regions at 35° latitude

1 considering achieving the maximum energy throughout the year.³⁷ Water was dripped on the damaged
 2 region of the perovskite solar modules. Solubility of Pb^{2+} in the rain water strongly depends on the pH
 3 value of rain. To simulate the worst scenario, where perovskite solar modules experience a heavy acid
 4 rain after being damaged, acid water with a pH value of 4.2 determined by a pH meter was continuously
 5 dripped on the damaged part of the module for 1.5 h (Supplementary Fig. 10).³⁸ Note that the water
 6 dripping conditions used in this study are designed with the hope to simulate the actual conditions, but
 7 may not be exactly the same as the actual conditions (see details of water dripping tests on damaged
 8 perovskite solar modules in the Methods). All the leaked Pb species were collected in the water, which
 9 was detected using an inductively coupled plasma mass spectroscopy setup (ICP-MS) to determine the Pb
 10 concentration (Fig. 1b).



11
 12 **Fig. 1 | Assessment of Pb leakage from damaged perovskite solar modules.** (a) Schematic drawing
 13 showing the encapsulation methods A, B, C and D. (b) Schematic drawing showing the experimental
 14 procedure to assess the quantity of the toxic Pb leaked from a perovskite solar module that is damaged
 15 due to external impact (e.g., hail). Encapsulated perovskite solar modules are mechanically damaged by a
 16 metal ball mimicking a standard hail impact test (FM 44787) to achieve a certain typical damage pattern,
 17 i.e., star-shaped microcracks,³⁵ for encapsulated modules. The damaged module is placed in a funnel for
 18 water dripping testing to simulate a damaged module under rain. The water is collected and injected into
 19 the ICP-MS to measure the Pb concentration. Layer L1 is the bottom encapsulation glass. Layer L2 is the
 20 perovskite solar module with the structure of FTO/c- TiO_2 / $\text{Cs}_{0.07}\text{FA}_{0.93}\text{PbI}_3$ / Spiro-MeOTAD/ Au (from top to
 21 bottom). Layer L3 is the adhesive resin. Layer L4 is the top glass cover.

22 **The Pb leakage rate from damaged perovskite solar modules**

1 We prepared the first batch of 12 perovskite solar modules (3 perovskite solar modules in each
2 encapsulation method) for the Pb leakage tests (Figs 2a, 2e, 2i for Method A, Figs 2b, 2f, 2j for Method B,
3 Figs 2c, 2g, 2k for Method C and Figs 2d, 2h, 2l for Method D). Under the same impact energy, perovskite
4 solar modules with different encapsulation methods show dramatically different mechanical strength.
5 Perovskite solar modules without encapsulation (Method A) were broken into many pieces
6 (approximately 10 pieces) (Fig. 2m). Perovskite solar modules encapsulated with the Method B were
7 broken into 2-3 large pieces with star-shaped microcracks formed at the hitting position (Fig. 2n).
8 Perovskite solar modules encapsulated with the Methods C and D held in one piece with star-shaped
9 cracks at the hitting position (Figs 2o,p). Hail-typical damages on commercialized solar modules are star-
10 shaped microcracks, suggesting the impact performed on the perovskite solar modules is similar to the
11 real case.³⁶ We then performed the water dripping tests on the damaged perovskite solar modules. In the
12 real case there could be a period of time, defined as the response time, when the damaged perovskite
13 solar modules are found and replaced / repaired. The damaged perovskite solar modules can experience
14 different weathers, e.g., rainy or sunny during this period of time. We did three experiments to simulate
15 different weather conditions.

16 In the first experiment, we immediately dripped the acid water (pH = 4.2) on the 4 damaged perovskite
17 solar modules, an undamaged perovskite solar module encapsulated by Method D (designated as Control
18 E) and an FTO substrate (designated as Control F) for 1.5 h with a speed of 5 mL/h to mimic a heavy acid
19 rain right after the hail impact. For the perovskite solar modules after impact, color of some portions of
20 the perovskite solar modules changed from black to yellow after first several minutes of water dripping,
21 demonstrating that perovskite is decomposed to PbI_2 .³⁸ After 1.5 h water dripping, the yellow color is
22 extended to most of the regions for the perovskite solar modules encapsulated by Methods A and B (Figs
23 2q,r), but only limited to local regions around the star-shaped microcracks for the modules encapsulated
24 by the Methods C and D (Figs 2s,t). The observation demonstrates that the Pb leakage is via the micro-

1 cracks formed on the damaged FTO substrates for Sample C and D. Variation of the color changing rate
2 for the perovskite solar modules with different encapsulation methods suggests the different
3 decomposition rate of the perovskite films in the perovskite solar modules. The contaminated water that
4 dripped through perovskite solar modules and two control samples was collected to detect the Pb
5 concentration by ICP-MS. Pb concentration in Control F is 0.05 mg/L, which is the background Pb
6 concentration in the water that passes through the system. Sample Control E shows the same Pb
7 concentration as Control F and no color change, revealing that the encapsulation Method D works well.
8 Therefore the Pb leakage in Method C and D is not caused by encapsulation delamination at the module
9 edges. Pb concentrations in the contaminated water are similar for the encapsulation Methods A and B,
10 suggesting that the bottom encapsulation has a negligible effect on Pb diffusion rate under a normal hail
11 impact (Fig. 3a and Table 1). On the other hand, the Pb concentration is drastically decreased to ~14% for
12 the Method C and to ~6% for the Method D compared to the Method A (Fig. 3a and Table 1). This result
13 suggests that a thin adhesive resin film and a top glass cover can substantially enhance the mechanical
14 strength of the perovskite solar modules, result in substantially reduced Pb leakage.

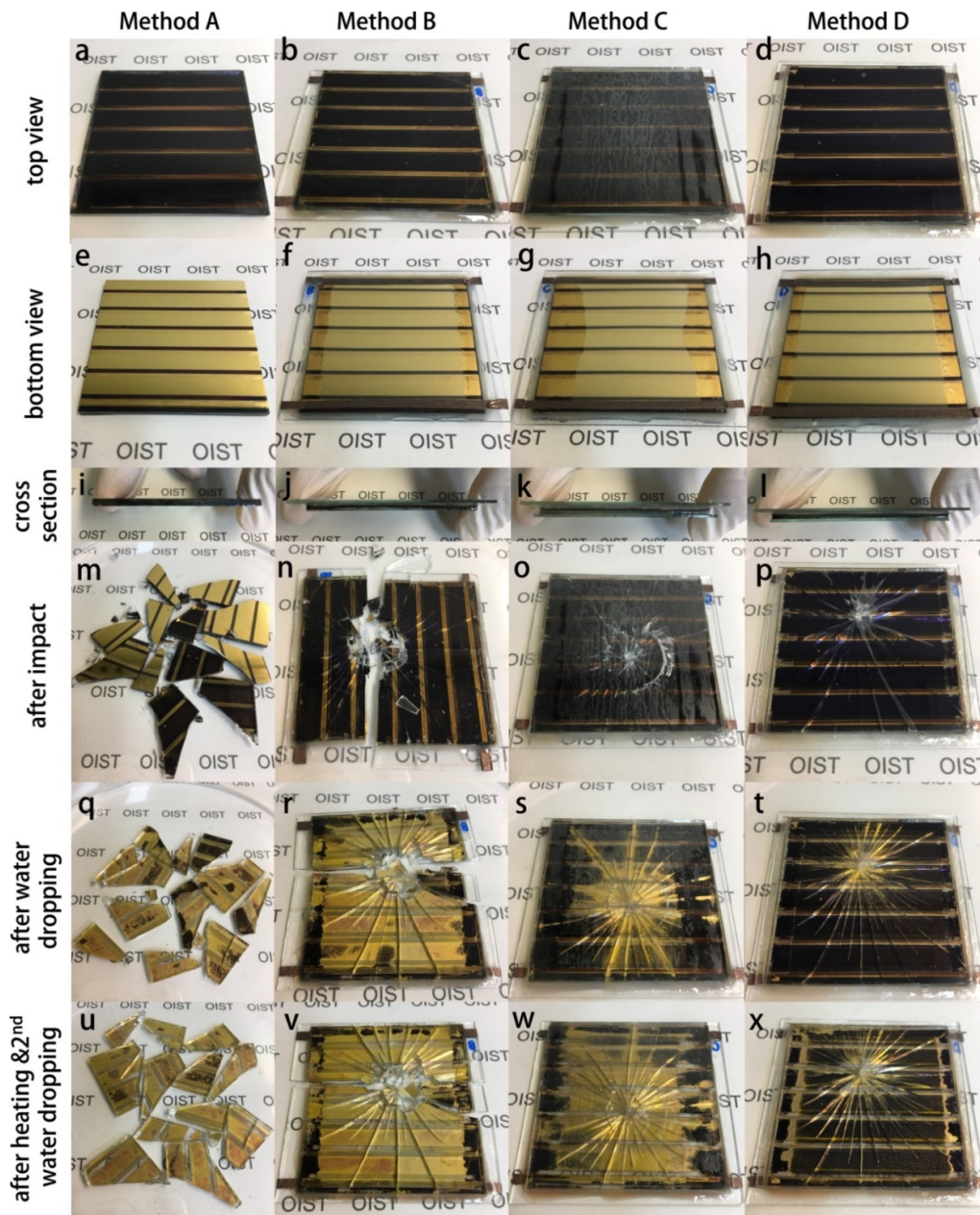
15 In the second experiment, we heated these decomposed perovskite solar modules at 45 °C for 4 h to
16 mimic a reasonable temperature and time range on a sunny day,^{39,40} then dripped the acid water again
17 on the damaged modules with a speed of 5 mL/h for 1.5 h to mimic another rain and measured the Pb
18 concentration in the contaminated water. Yellow color extended to almost all the area for perovskite solar
19 modules encapsulated by the Methods A and B (Fig. 2u,v), suggesting that the perovskite decomposed
20 more completely. Size of the yellow color regions is substantially increased for perovskite solar modules
21 encapsulated by the Method C (Fig. 2w) but only slightly increased for the Method D (Fig. 2x). When the
22 comparison is made between the first and second measurements, we found dramatic differences for
23 perovskite solar modules encapsulated by Method D compared to the others. Specifically, Pb
24 concentration ratios before and after annealing are all close to 1 for Sample A, B and C. However, the ratio

1 substantially decreased to 0.04 for Sample D (Figs 3a, 3b and Table 1). In the case of the Method D, the
2 average Pb concentration on the three samples is as low as 0.03 mg/L (with the background Pb
3 concentration in the water subtracted). The results reveal that our newly developed method (Method D)
4 reduces the Pb leakage significantly better than the incomplete encapsulation methods (Method A and
5 Method B) and the encapsulation method using the surlyn film (Method C), nicely making use of the
6 heating by the sunshine.

7 On the other hand, Pb concentration in the second dripping test could also be influenced by the first
8 water dripping test due to differences of the Pb residual amount. To study the effect of the Pb residual
9 amount on the Pb leakage, we conducted the third Pb leakage test. A second batch of 12 perovskite solar
10 modules (3 perovskite solar modules in each encapsulation method) were damaged at the same impact
11 condition, heated at 45 °C for 4 h and water dripped for 1.5 h. The Pb concentration in the contaminated
12 water for each condition is similar to that in the second experiment for all the 4 samples (Fig. 3c, Table 1),
13 revealing that the Pb leakage rates are similar if the Pb residual amount is still sufficient (There is still a lot
14 of yellowish colored PbI_2 as shown in Figs 2u-x).

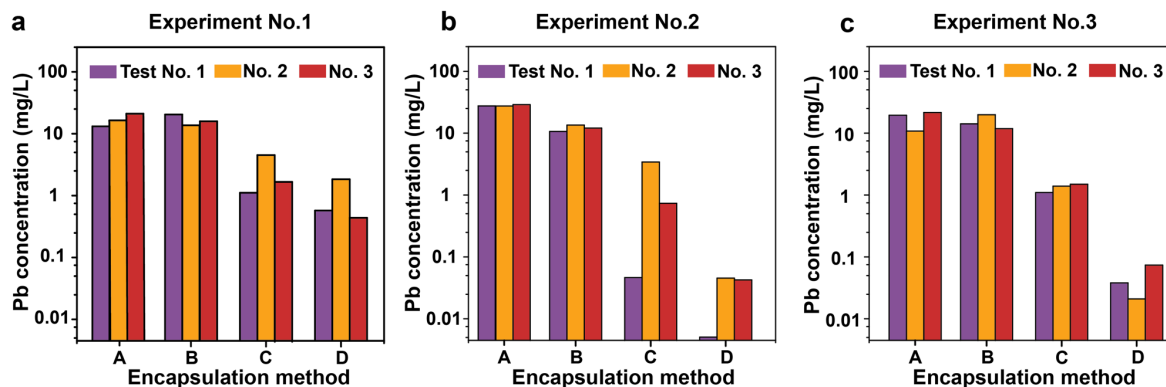
15 We calculated the Pb leakage rate according to the Pb concentration in the contaminated solution,
16 and the results are summarized in Table 2. The background Pb concentration obtained for the control
17 Sample E was subtracted for the calculation (see Supplementary Information for the calculation details).
18 The Pb leakage rate without sample heating was extracted from Experiment #1 and with sample heating
19 was extracted from Experiment #3, respectively. The Pb leakage rate is assumed to be approximately
20 constant under each condition. This assumption agrees well with another study of Ag and Zn leakage from
21 organic photovoltaic modules.⁴¹ The encapsulation Method D using a multi-stack structure of glass/
22 ER/perovskite solar module/UV-resin/glass shows much better performance against Pb leakage than
23 other encapsulation methods. For example, using Method D, the Pb leakage rate is reduced by a factor of

1 18 without heating by sunshine and by a factor of 375 with heating by sunshine, respectively, compared
2 to the perovskite solar module encapsulated using a glass sheet with UV-resin cured at the module edges
3 (Method B). Although there are different opinions in the literature regarding the environmental impact of
4 Pb contamination caused by perovskite solar modules^{38,42-48}, it is generally believed that rigorous
5 measures should be taken to prevent Pb from polluting environment. Because of the excellent
6 performance against Pb leakage, our newly developed encapsulation method D is expected to help
7 achieve this goal.



1

2 **Fig. 2 | Photographs of perovskite solar modules.** (a-l) Perovskite solar modules before being intact. (m-
 3 p) Perovskite solar modules after impact. (q-t) perovskite solar modules after first water dripping test. (u-
 4 x) perovskite solar modules after first water dripping test, heating at 45 °C for 4h and second water
 5 dripping test. (a,e,i,m,q,u) the perovskite solar module without encapsulation (Method A), encapsulated
 6 with (b,f,j,n,r,v) Method B; (c,g,k,o,s,w) Method C and (d,h,l,p,t,x) Method D. Different perovskite solar
 7 module encapsulation methods lead to different degrees of perovskite decomposition under the same
 8 impact and water dripping conditions.



1

2 **Fig. 3 | Pb leakage concentration in the contaminated water. (a)**, experiment No. 1. Water dripping tests
 3 are conducted on the perovskite solar modules. Pb concentration in the contaminated water was detected
 4 by ICP-MS. **(b)**, experiment No. 2. The perovskite solar modules were water dripped, heated at 45 °C for
 5 4h to simulate the sunny weather, and water dripped for the second time. Pb concentration in the second
 6 dripping water was tested. **(c)**, experiment No. 3. The perovskite solar modules were heated at 45 °C for
 7 4h and water dripped. The Pb concentration was tested. Three samples, named as Test No.1, No.2 and
 8 No.3 were tested at each condition. The Pb leakage concentration is substantially influenced by the
 9 encapsulation methods.

10 **Table 1 | Pb concentration in dripping water passing through damaged perovskite modules**

Experiment No.	Test condition	Pb concentration in the last dripping water (mg/L or ppm)					
		Method A	Method B	Method C	Method D	Control E	Control F
1	Water dripped	17±3	16±3	<2	<0.9	5 × 10 ⁻²	5 × 10 ⁻²
2	Water dripped, heated and water dripped again	27.5±0.6	12±1	<1	<8 × 10 ⁻²	-	-
3	Heated and water dripped	17±4	15±3	<1.3	<9 × 10 ⁻²	-	-

11 Water dripping test is conducted on (Control E) an undamaged perovskite solar module encapsulated by Method D and (Control F) an FTO
 12 substrate. No metal ball impact is performed for Samples control E and Control F. For methods A, B, C and D, three samples are tested at each
 13 condition. Data shown here are the average values. The error bars represent the standard deviations calculated based on the measurement
 14 results collected from 3 different samples.

15 **Table 2 | Pb leakage rate without and with the heating treatment**

	Method A	Method B	Method C	Method D
Pb leakage rate without heating (mg/(h × m ²))	34±6	32±6	<4	<1.8
Pb leakage rate with heating (mg/(h × m ²))	34±8	30±6	<2.6	<8 × 10 ⁻²

16 Pb leakage rate calculation: Pb ions are assumed to leak at a constant rate under each condition (i.e., using different encapsulation method and
 17 heating condition) when the Pb residual amount was sufficient to maintain the Cs at constant value (A_e, D, d and C_b values do not change with

1 time). The error bars represent the standard deviations calculated based on the measurement results collected from 3 different samples. See
2 Supplemental Information for the calculation details.

3 **Simulated assessment of the Pb leakage from damaged perovskite solar modules**

4 To understand how the encapsulation methods influence the Pb leakage rate, here we use the semi-
5 empirical approximation based on the Noyes-Whitney equation, which has been used by Celik et al. to
6 study the metal leakage from damaged perovskite solar cells.⁴⁵

$$7 \quad \frac{d_m}{dt} = A_e \left(\frac{D}{d} \right) (C_s - C_b) \quad (1)$$

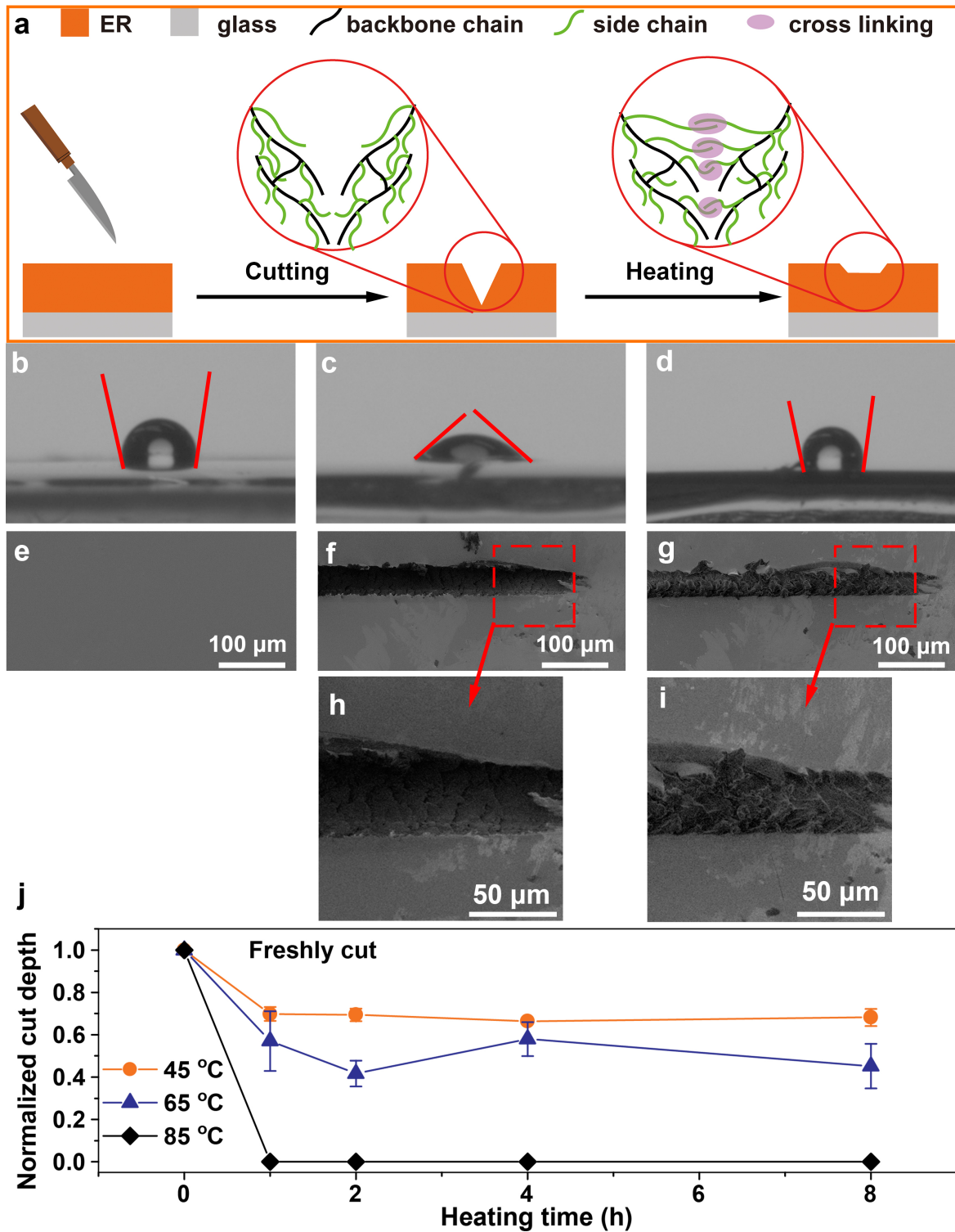
8 where m is the mass of the dissolved Pb, t is the diffusion time, A_e is the effective exposure area that Pb
9 exposed to the solvent, D is the diffusion coefficient of Pb^{2+} ion, d is the thickness of the encapsulation
10 boundary layer (polymer and the top glass cover), C_s is the saturated mass concentration at the surface of
11 the solution and C_b is mass concentration in the bulk solution. Because values of the parameters are
12 known either from literature (D , C_s and C_b),⁴⁵ or from our experimental results (d and dm/dt), we are able
13 to calculate the value of A_e , which is a key factor influencing the Pb leakage rate. Details of calculation are
14 shown in Supplementary Table 3. For the samples without heating treatment (experiment No. 1), A_e is
15 similar for Sample A (3.7 cm^2) and Sample B (3.4 cm^2), and substantially decreased for Sample C (0.49 cm^2)
16 and Sample D (0.33 cm^2). The reduction of A_e for Sample C and D comparing to Sample A and B is because
17 of the improved mechanical strength by putting the encapsulation polymer and the top glass cover on the
18 perovskite solar module. For the samples with heating treatment, A_e of Samples A, B and C do not change
19 after the heating treatment (Supplementary Table 3). On the other hand, A_e of Sample D after heating
20 treatment is dramatically reduced ($1.3 \times 10^{-2} \text{ cm}^2$) comparing with the same sample without heating (0.33
21 cm^2). We think the substantially reduced A_e for Sample D after heating is due to addition of the ER layer
22 between FTO and top glass cover. The ER film is known to possess the self-healing property in crushed
23 microstructure and damaged surface after heating, and therefore can prevent water from penetration
24 into the damaged perovskite solar modules.²⁵ In sharp contrast, the A_e for Sample C does not reduce after

1 heating because the heating temperature is too low to activate the self-healing property of the surlyn
2 film.²²

3 **Self-healing properties of the epoxy resin encapsulant**

4 To reveal the self-healing phenomenon of Method D during solar cell operation, we then focus on
5 characterization of the chemical and physical property of the ER film under the heating treatment that
6 can be caused by sunshine. We drop cast the ER films (DGEBA: OA: MXDA = 4: 2: 1) on glass slides and let
7 them cure at 70 °C for 10 min. The films were cut with a knife to achieve mechanical damages with a width
8 of approximately 40 μm and then heated at 45 °C for 4 h (Fig. 4a). We studied the effect of heating on the
9 surface hydrophobicity property of ER by conducting water contact angle (CA) measurements on the ER
10 film before cutting, after cutting but before heating, and after cutting and after heating. Water CA is
11 106.6±0.6° for the pristine ER film and 24.6±0.4° for the film with microcrack at the cutting region (Figs
12 4b,c). After heating, hydrophobicity at the cutting region is almost completely recovered showing a CA of
13 104±2° (Fig. 4d). The results reveal that the recovery of the surface hydrophobicity after heating leads to
14 reduction of A_e . Furthermore, we studied the morphology of the pristine ER films (3 samples) without
15 cutting, after cutting but before heating, and the ER films after cutting and 4 h heating by scanning
16 electron microscopy (SEM). The Surlyn films (3 samples) used as control samples were melt on the glass
17 slides at 120 °C for 2 min, which formed solid films after they cooled down to room temperature. The ER
18 films are relatively flat before cutting (Fig. 4e), while deep valleys are clearly visible on both the ER films
19 and the Surlyn films after cutting (Figs. 4f,h, Supplementary Fig. S11). After the heating treatment, the
20 valley on the ER films are re-filled by forming micro-structured ER (Figs. 4g,i). On the other hand, the valley
21 on the Surlyn film remains almost unchanged (Supplementary Fig. S11). These results suggest that only
22 the ER film shows the self-healing property under such a heating condition. To quantitatively study the
23 self-healing property at 45 °C, the cut depth, defined as the height difference between the baseline and
24 the bottom of the valley at the cutting region, was measured by a profilometer at different heating times

1 (the raw data can be found in Supplementary Figs 12-14, and Supplementary Table 4). We plotted a figure
2 showing the normalized cut depth, i.e., the cut depth value after a certain time of heating normalized with
3 respect to the initial cut depth value upon fresh cutting, as the function of the heating time. We observe
4 a clear reduction of the normalized cut depth after 1 h, which further decreases slightly after heating for
5 4 h (Fig. 4j). This is another piece of evidence confirming that the ER films heal after heating at 45 °C. Note
6 that although the heating temperature of 45 °C is selected in this study which represents a conservative
7 case, solar cells or modules can get even hotter during normal operation. Therefore, 85 °C is selected for
8 damp heat test and thermal cycle test in the IEC 61215 standard.⁴⁹ It is necessary to study the self-healing
9 property and stability of the ER film at higher temperatures to evaluate the durability of such an
10 encapsulant. We deposited 6 ER films on glass slides, cut and heated them at 65 °C and 85 °C, respectively
11 (3 samples for each heating condition). The cutting region heals much faster than the sample heated at
12 45 °C (Figs 4j, see the details in Supplementary Figs 12-14 and Supplementary Table 4). Especially for the
13 sample heated at 85 °C, almost no cutting trace is observed after 1 h (Fig. 4j). These results suggest that
14 the self-healing characteristics are more pronounced at elevated temperatures. On the basis of these
15 results, we can safely conclude that both the damaged hydrophobicity and crushed microstructure formed
16 on the ER film during the hail impact recover after heating, resulting in substantially reduced A_e . As a
17 consequence, the ER film can effectively prevent water from penetration into the perovskite solar
18 modules via star-shaped microcrack region leading to substantially reduced Pb leakage.



1

2 **Fig. 4 | Self-healing property of the epoxy resin encapsulant.** (a) Schematic drawing showing the self-healing process of the epoxy resin. The side-view photos showing the water contact angle on (b) the

3

1 pristine ER film, (c) the film after cutting, and (d) the film after cutting and heating at 45 °C for 4 h. The
2 top-view SEM images showing (e) the pristine ER film before cutting, (f) the film after cutting but before
3 heating, and (g) the film after cutting and heating at 45 °C for 4 h. (h) The SEM image showing the enlarged
4 region marked in (f). (i) The SEM image showing the enlarged region marked in (g). (j) The normalized cut
5 depth as a function of heating time under 3 different heating temperatures (45 °C, 65 °C, and 85 °C). The
6 cut depth is defined as the height difference between the baseline and the bottom of the valley at the
7 cutting region (the raw data can be found in Supplementary Figs 12-14, and Supplementary Table 4). The
8 normalized cut depth (i.e., the y axis value of Figure 4j) is the cut depth value after a certain time of heating
9 normalized with respect to the initial cut depth value upon fresh cutting. For example, for any heating
10 temperature, the normalized cut depth equals to 1 at the heating time of 0 h (i.e., in the state of being
11 freshly cut and without any heating). The error bars represent the standard deviations calculated based
12 on the measurement results collected from 3 different samples.

13 **Effect of the weather condition on the Pb leakage with different encapsulation**

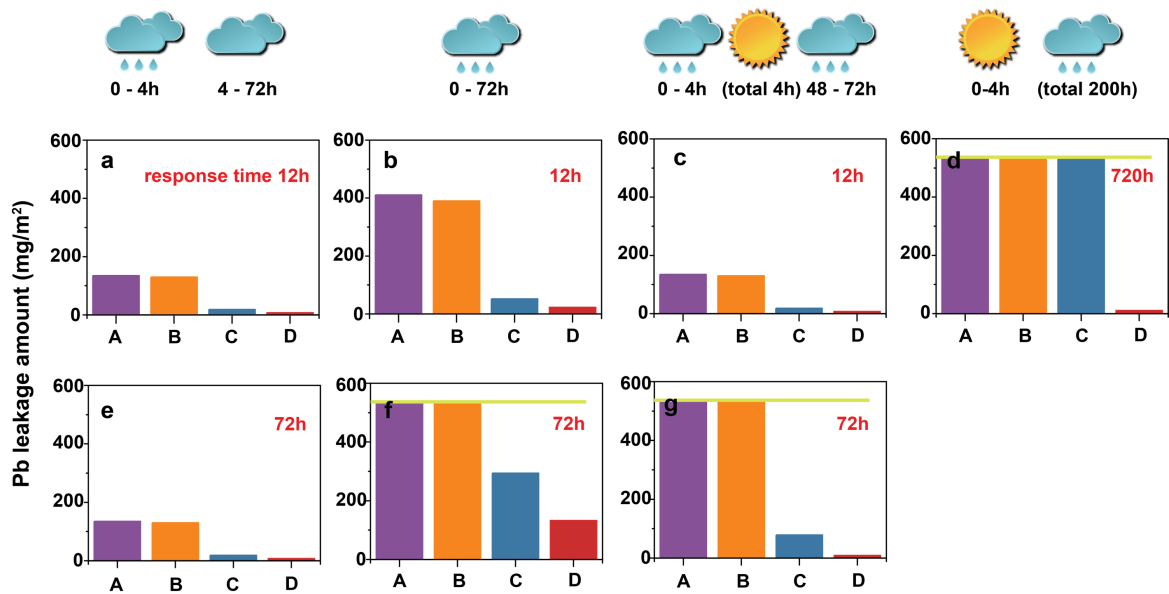
14 The damaged perovskite solar modules can experience different weather conditions within the response
15 time, which can affect the lead leakage amount. To comprehensively assess the Pb leakage amount for
16 different encapsulation methods, 4 possible weather conditions and 3 response times, namely 12 h (fast),
17 72 h (medium) and 720 h (slow), are simulated, amounting to a total number of 56 conditions. We
18 calculate the Pb leakage amount based on the leakage rate (Supplementary Table 5). Under a normal
19 weather condition when a short rain lasts for 4 h, the Pb leakage amount is similar for encapsulation
20 Methods A (140 mg/m²) and B (130 mg/m²) and decreased to C (16 mg/m²) and D (7 mg/m²) at both 12
21 and 72 h response time (Figs 5a, 5e). Comparing with the work by Hailegnaw et al., i.e., when ~70% of Pb
22 mass loss is observed after 1 h dripping test³⁸, the Pb leakage rate is much slower even for Sample A (~26%
23 Pb mass loss in 4 h). The different Pb leakage rates are due to different sample structures (a complete
24 device with the structure of FTO/TiO₂/perovskite/Spiro-MeOTAD/Au vs. a bare perovskite film) and
25 different water dripping directions (the FTO side versus the perovskite side). In a serious condition when
26 a heavy rain lasts for 72 h, the Pb leakage amount is increased for all the encapsulation methods. For
27 example, The Pb leakage amount reaches the maximum value (540 mg/m²) for Methods A and B at 72 h,
28 increases from 48 mg/m² at 12 h to 290 mg/m² at 72 h for Method C and increases from 22 mg/m² at 12
29 h to 130 mg/m² at 72 h for Method D (Figs 5b, 5f). Heating from the sunshine makes drastically different

1 Pb leakage amounts between perovskite solar modules encapsulated employing an ER layer (Method D)
2 and the other methods. If it rains for the first 4 h, with sun rises for 4 h in total and rains again starting at
3 48 h for 24 h, a huge Pb leakage amount variation is shown comparing to a fast and a medium response
4 time for encapsulation Method A (140 mg/m² at 12 h and 540 mg/m² at 72 h), B (130 mg/m² at 12 h and
5 540 mg/m² at 72 h) and C (16 mg/m² at 12 h and 78 mg/m² at 72 h), but show very little effect for
6 encapsulation Method D (7 mg/m² at 12 h and 9 mg/m² at 72 h) (Figs 5c, 5g). Under an extreme whether
7 condition when the damaged perovskite solar modules experience a sunny weather for 4 h and multiple
8 rains for 200 h and a slow response time of 720 h, the Pb leakage amount reaches the maximum value
9 (540 mg/m² at 720 h) for encapsulation Methods A, B and C (Fig. 5d). On the other hand, encapsulation
10 Method D shows an extremely small quantity of Pb (16 mg/m² at 720 h), suggesting the outstanding
11 protection of Method D in preventing the Pb from leakage. We interpret the data as follows.

12 (I) Encapsulation methods can dramatically influence the Pb leakage amount from a damaged perovskite
13 solar module. A complete encapsulation Method D using a multi-stack structure of glass/ER/perovskite
14 solar module/UV-resin/glass reduces the Pb leakage amount significantly better than other encapsulation
15 methods (Figs 5a-g).

16 (II) Weather condition is another factor influencing the Pb leakage amount. Shorter time of rainfall results
17 in a lower Pb leakage amount; Sunny weather right after the module being damaged shows very little
18 beneficial effect for Methods A, B, C, but drastically reduce the Pb leakage amount in the case of Method
19 D (Figs 5c, 5d, 5g).

20 (III) Response time also influences the Pb leakage amount. A longer response time results in a larger Pb
21 leakage amount.



1

2 **Fig. 5 | Effect of weather condition on Pb leakage with different encapsulation methods.** (a,e), it rains
 3 for the first 4 h and cloudy until 72 h. (b,f), it rains constantly for 72 h. (c,g), it rains for the first 4 h,
 4 with sun rises for 4 h in total and rains again starting at 48 h for 24 h. (d), it is sunny for the first 4 h and start
 5 for multiple rains for 200 h in total in 720 h. Yellow lines in (d,f,g) represent the maximum Pb amount that
 6 can leak from a damaged perovskite solar module. 4 different weather conditions are shown at the top of
 7 figure and 3 different response times (12 h, 72 h and 720 h) are labeled in red color in each figure.

8 **Conclusions and outlook**

9 In summary, we quantitatively measured the lead leakage from the damaged perovskite solar modules
 10 without encapsulation and as well as with 3 different encapsulation methods. The Pb leakage amount is
 11 strongly dependent on the encapsulation methods, weather condition and response time. With carefully
 12 designed experiments to simulate realistic conditions, we demonstrate that our customized encapsulation
 13 method with a multi-stack structure of glass/ER/perovskite solar module/UV-resin/glass which shows
 14 excellent performance against Pb leakage from the damaged perovskite solar modules. The results shed
 15 light on effective methods to solve the potential toxicity concern of Pb-based metal halide perovskite
 16 photovoltaic technology. Further works that can help further resolve this issue include establishment of
 17 perovskite photovoltaic industry standard, optimization of the perovskite solar cell encapsulation

1 methods, development of the rigorous maintenance, emergency processing and recycling programs to
2 meet the safety requirement of this technology.

3 **Methods**

4 **Perovskite solar module fabrication.** Perovskite solar modules, each containing 6 sub-cells connected in series with
5 a total active area of 12.0 cm², were fabricated according to our reported methods.²¹ The active area of the
6 perovskite solar modules is determined by the overlap regions of FTO and Au electrode (Supplementary Fig. 1).
7 Patterned FTO glasses (7-8 Ω/□, Opvtech.) were cleaned by sequentially sonicating in deionized water, ethanol and
8 acetone as substrates. UV-Ozone treatment was performed on the substrates just before use. A 40 nm c-TiO₂ layer
9 was deposited via magnetron sputtering at 180 W with a mask. A 550 nm Cs_{0.07}FA_{0.93}PbI₃ perovskite layer was
10 deposited on the TiO₂ layer via a three-step process. First, a PbI₂·DMSO film was spin-coated using 1:1 molar ratio of
11 lead iodide (TCl, 99.99%) and DMSO (99.9%, Sigma-Aldrich) in DMF (99.8%, Sigma-Aldrich) (1.3 M) and annealed at
12 100 °C for 5 min; Second, the PbI₂·DMSO film is converted to FAPbI₃ via CVD deposition of FAI (Dyesol) under a low
13 vacuum (1 Torr) for 2.5 h with the source and substrate zone temperature of 190 °C and 155 °C, respectively. Third,
14 the as prepared FAPbI₃ film is immersed in the cesium acetate (99.9%, Sigma-Aldrich) in IPA (98%, Sigma-Aldrich)
15 solution (2mg/mL) for 3 s at room temperature in a N₂ filled glovebox, followed by annealing at 150 °C for 20 min in
16 air. A 200 nm spiro-MeOTAD layer was spin-coated on the Cs_{0.07}FA_{0.93}PbI₃ perovskite layer with a solution containing
17 72.3 mg spiro-MeOTAD (Merck), 28.8 μL of 4-*tert*-butylpyridine (98%, Sigma-Aldrich) and 17.5 μL of lithium bis(trifl
18 uoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 mL acetonitrile (Sigma-Aldrich, 99.8 %)) in 1mL of
19 chlorobenzene. The perovskite and spiro-MeOTAD layers are partially removed by mechanical scratch using a second
20 mask. A 120 nm gold electrode was deposited via thermal evaporation (0.01-0.08 nm/s) on the spiro-MeOTAD layer
21 using a third mask.

22 **Characterization.** Transmittance and reflectance of the substrates with different top encapsulation methods was
23 characterized by UV/Vis spectrometer (JASCO Inc., V-670). Surface roughness measurements on the surlyn and ER
24 films were conducted using a profilometer (Dektak XT, Bruker). Morphology of the cutting region of surlyn and ER
25 films was measured by field emission scanning electron microscopy (Helios NanoLab G3 UC, FEI). The water contact
26 angle was obtained by a drop shape analyzer (krüss GmbH). Tg and Tm of the ER films with different compositions
27 were measured using a DSC (DSC 8500, Perkin Elmer) with a scan rate of 20 °C/min from -10 to 100 °C. An Indium
28 reference sample was measured for calibration. Thermal stability of the films was determined by TG measurements
29 using a Netzsch TG-DTA2000SE thermal analyzer. Measurements were performed in aluminum crucibles under a
30 stationary ambient air atmosphere with a scan rate of 15, 20 and 25 K/min from room temperature to 600 °C. Solar
31 cell performance was measured under AM 1.5 G one-sun illumination (100 mW/cm²) using a solar simulator
32 (Newport Oriel Sol A) and Keithley 2420 source meters. Intensities of the solar simulators were calibrated with a
33 calibrated silicon detector (Oriel Instruments Model 91150V). All the J-V characteristics were carried out in ambient
34 (RH ~ 60%) at room temperature. Scan rates were 0.2 V/s in the forward to backward direction. 10 s pre-illumination
35 and no pre-bias were applied for the measurement. Pb concentration in the dripping water was detected using an
36 inductively coupled plasma mass spectroscopy (Thermal Scientific, element 2).

37 **Perovskite solar module encapsulation.** Perovskite solar modules were encapsulated in Method A, B, C and D (Fig.
38 2a). In Method A, perovskite solar modules with a structure of FTO/c-TiO₂/ Cs_{0.07}FA_{0.93}PbI₃/spiro-MeOTAD/Au from
39 top to bottom were used without further encapsulation. In Method B, perovskite solar modules were encapsulated
40 by 1 mm thick glass substrates using a UV-resin (XNR5570, NAGASE) at the bottom sides. The UV-resin was coated
41 at the edges of the modules, and cured under a 400 W UV lamp for 5 min. No encapsulation was performed at the
42 top sides. In Method C, perovskite solar modules were first encapsulated at the bottom sides similar to Method B,

1 and then encapsulated by 1 mm thick glass substrates using thermos-compressed surlyn adhesive resin films (DuPont)
2 at the top sides by annealing at 140 °C for 10 s. In Method D, perovskite solar modules were first encapsulated at
3 the bottom sides similar to Method B, and then encapsulated by 1 mm thick glass substrates at the top sides using
4 thermo-crosslinking SHP films by mixing diglycidyl ether of bisphenol A type epoxy resin (Sigma-Aldrich), *n*-
5 octylamine (Sigma-Aldrich), and *m*-xylylenediamine (Sigma-Aldrich) with a molar ratio of 4:2:1 and annealing at 70
6 °C for 10 min. Thickness of the surlyn adhesive resin film is 80 μm. We optimized thickness of the SHP film to be
7 approximately 80 μm by performing a proper pressure during the annealing process for comparison.

8 **Impact tests of perovskite solar modules.** Perovskite solar modules were damaged mechanically similar to the
9 Approval Standard for Rigid Photovoltaic Modules (FM 44787)³⁵, where a metal ball (45 mm in diameter, 358 g) was
10 dropped from a certain height onto the perovskite solar modules. Because the size of our perovskite solar module
11 (25 cm²) was much smaller than the commercial Si solar panel which is used for standard hail impact test, e.g., FM
12 44787, we optimized the impact condition using FTO substrates with the similar encapsulation methods to achieve
13 a certain typical damage pattern, i.e., star-shaped microcracks,³⁶ on damaged encapsulated modules. Such damage
14 patterns can appear in typical-sized PV modules in the standardized test conditions (Supplementary Figs 8 and 9).
15 The breaking tests were performed on FTO substrates with the 4 types of encapsulation methods including FTO
16 substrates without encapsulation (designated as A); FTO substrates encapsulated with a 1 mm thick glass using a
17 UV-resin on the one side and a SHP film on the other side (designated as B); FTO substrates encapsulated with a 1
18 mm-thick glass on one side, a 80 μm-thick surlyn film and 1 mm-thick glass on the other side (designated as C); FTO
19 substrates encapsulated with a 1 mm-thick glass on one side, a 80 μm-thick SHP film and 1 mm-thick glass on the
20 other side (designated as D). When the distance was 10 cm, FTO substrates without encapsulation or top cover
21 (Method A) broke into many pieces (Supplementary Fig. 9e). FTO substrates encapsulated with Method B broke into
22 2-3 main pieces with star-shaped microcracks formed at the hitting position (Supplementary Fig. 9f). FTO substrates
23 encapsulated with Methods C and D remained in one piece and showed star-shaped microcracks at the hitting
24 position (Supplementary Figs 9g,h). We fixed the height to be 10 cm for hitting the perovskite solar modules. We
25 assume that the impact density is 1 impact per 5 cm × 5 cm, which represents an extreme case scenario. Based on
26 this assumption, the averaged distance between the two adjacent impacts is close (5 cm). Therefore, after the
27 formation of the first crack, an even higher impact for the adjacent second crack may be required to achieve a similar
28 crack pattern of the first crack because the broken module may yield better strength to the second impact stresses.
29 The actual situation could be that the Pb leakage rate per area is not as high as the results we have obtained.

30 **Water dripping tests on damaged perovskite solar modules.** Each of the damaged perovskite solar modules
31 (encapsulated by A, B, C, D) was placed in the in a funnel with ~30° relative to ground for the water dripping tests
32 (Supplementary Fig. 10). Glass slides were used to hold the broken pieces of the perovskite solar modules
33 encapsulated by Method A and B at the same angle for the test. Deionized water with pH of 4.2 determined by a pH
34 meter was continuously dripped on a bare FTO glass substrate for detection of the Pb background and the damaged
35 part of the perovskite solar modules using a syringe pump at 5 mL/h for 1.5 h. The rain contact area, defined as the
36 area that a water drop actually spread on the damaged glass cover, is around 1 cm² according to statistical results
37 of 50 water drops on a glass cover. (Supplementary Fig. 10) Therefore the rain intensity is 50 mm/h, which is in the
38 typical heavy rain range.^{38, 50} The Pb contaminated water was collected by centrifuge tubes. This method considers
39 the rain intensity and the drop size and assumes that the rainfall is uniformly distributed in the investigated region.
40 It does not consider the impact energy of the rain drops, therefore may not be exactly the same as the actual
41 condition. We are aiming at studying the worst scenario of Pb leakage from damaged perovskite solar modules.
42 However, the actual Pb leakage rates are expected to change dependent on the module size, hail size, impact density,
43 rainfall rate, etc.

44

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48

49 Author contributions

1 Y. B. Q. conceived the idea, initiated and supervised the work. Y. J. and L. Q. designed the experiment,
2 prepared the modules, tested the module breaking conditions and measured the Pb leakage amount. Y.
3 J. performed the J-V measurements and water contact angle measurements. L. Q. carried out the DSC
4 measurement. E. J. J. P. did the TG measurement. All authors contributed to writing the paper.

5 **Data availability**

6 The data that support the plots within this paper and other findings of this study are available from the
7 corresponding author on reasonable request.

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13 **Competing interests**

14 The authors declare no competing financial interests.