Supplementary Information for

Solid-solid Chemical Bonding Featuring Targeted Defect

Passivation for Efficient Perovskite Photovoltaic

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* Corresponding author E-mail address: zhaoqing@pku.edu.cn **Note S1.** Comparison of solution and solid phase processing for surface defect passivation.

Surface defect passivation is crucial for the preparation of high-efficiency PSCs, since the defects of perovskite films are mainly distributed on the film surface.¹ Solution-processed surface defect passivation is usually performed at high spin-coating speeds, which limits the compatibility of this method to surface passivation of large-area perovskite films for industrial production. However, in solid-phase passivation, passivator films with any desired size can be prepared in advance by various methods, which gives solid-phase passivation the opportunity for size compatibility, especially for future commercial development. Therefore, it possesses great potential to transfer the successful experience of fabricating high-efficiency small-area devices to large-area devices.

In solution processing, the passivator should be generally soluble in isopropyl alcohol (IPA) or chlorobenzene (CB), which inevitably limits the selection range of passivator. In solid-phase passivation, theoretically, passivator films can be prepared by various methods because it is pre-prepared on an independent substrate, including solution processing (spin coating, blade coating, spray coating) and solution-free processing (vapor deposition, magnetron sputtering, etc.). Therefore, this feature may greatly broaden the selection range of passivator and provide the possibility for more exploration regarding passivation materials and mechanism.

In solution processing, the passivator is usually dissolved in IPA or CB, these solvents may slightly dissolve the organic salts (such as FAI, MAI) on the surface of the underlying perovskite film,² thus disturbing the perovskite surface stoichiometric ratio, which may create new defects. While, this can be completely avoided in solvent-free solid-phase surface passivation.

In solution-processed surface defect passivation, the passivators spread indiscriminately on the underlying perovskite film. Although passivators are beneficial for surface defect sites, for defect-free regions, this may lead to passivator residues, and these residual low-conductivity passivators may hinder carrier extraction. In solidphase passivation, only those passivators that chemically interact with the defect sites remained on the surface of perovskite films (Fig. S1). For defect-free regions, passivator molecules will be removed when detaching the passivator film substrate. Therefore, this unique targeted defect passivation may avoid the undesired surface residue of low-conductivity passivators.

	Solution process	Solid-solid process
State of passivator	Liquid	Solid
Depth of processing	Certain depth of surface	Only the surface
	(IPA or CB will penetrate	
	downward)	
	<u>;;</u>	•
Size compatibility	(High-speed spin coating	(Pre-prepared passivator
	limits large-scale	film makes it size
	applications)	compatible)
	~	•
Passivator selection	(Only passivators that can be	(Pre-prepared passivator
	dissolved in IPA, CB, etc.)	film makes the selection
		of passivator wider)
Surface composition damage	~	•
	(Surface organic salts will be	(No solvent dissolves the
	dissolved by the solvent)	surface components)
	~	<u>.</u>
Passivator residue	(Indiscriminate coverage of	(Only the defect sites can
	passivator)	bond with the passivator)



Fig. S1 Comparison between solution spin coating and solid phase method.



Fig. S2 TOF-SIMS result of untreated perovskite film.



Fig. S3 XPS results of control, SPP-10 and SPP-20. (a) XPS full spectra. (b) XPS spectra of I 3d.



Fig. S4 Raman mapping image of SPP-20 sample at 205 cm⁻¹ (characteristic signal of Pb-S),³ scale bar is 20 μ m.



Fig. S5 Calculated binding energies for three coordination bonds based on density functional theory (DFT). The calculation of van der Waals force is rather challenging, but it is a weak force with a value of about 0.4-4 KJ/mol.⁴⁻⁶



Fig. S6 Obtaining defect-rich perovskite films. (a) The picture of aged PSC under MPP tracking for 800 h. (b) The Au electrode of the aged PSC was stripped off by adhesive

tape. (c) The Spiro-OMeTAD of the aged PSC was washed off by chlorobenzene, and the perovskite film with more defects than the fresh control film was obtained.



Fig. S7 XPS mapping characterization. (a) Before SPP, the I mapping of defect-rich film aged by MPP tracking. (b) Before SPP, the I mapping of fresh perovskite film. (c) After SPP, the S mapping of defect-rich perovskite film aged by MPP tracking. (d) After SPP, the S mapping of fresh perovskite film.



Fig. S8 TRPL result of defect-rich perovskite film aged by MPP tracking and fresh control perovskite film before and after SPP.

Note S2. Further confirmation of targeted passivation.

Targeted passivation means that the passivator molecules will not be anchored on defect-free region. Although we cannot directly observe targeted passivation from a microscopic perspective, we can confirm this from a more macroscopic perspective (Fig. S9). Ideally, if we can obtain defect-rich perovskite film (region A) and completely defect-free perovskite films (region B), after solid phase passivation, if the passivator molecules are only distributed in region A and no passivator molecules are detected in region B, such passivation behavior can be firmly confirmed as targeted passivation---the passivator molecules will not remain at the defect-free region. Given that it is impossible to obtain absolutely defect-free perovskite films. Therefore, it can be reasonably concluded that the more defects, the more anchored passivator molecules, the fewer defects and the fewer anchored passivator molecules.

We prepared defect-less perovskite region by only passivating half of the one perovskite film to eliminate the effect of batch variation on the experimental results. We first covered half of the perovskite film with adhesive tape (Fig. S10a, b), then passivated the surface defects of the other half of the perovskite film by spinning coating octylammonium iodide (Fig. S10c),7 so as to obtain the passivated halfperovskite film (Fig. S10d). The passivated half perovskite film exhibits significantly longer carrier lifetime (Fig. S10e) and stronger PL intensity (Fig. S10f), indicating significantly lower defect density. Therefore, we obtained defect-less and defect-rich half-perovskite film in one sample (Fig. S10g). We then removed the adhesive tape and treated this sample by solid phase passivation. After solid phase passivation (Fig. S10h), we separately dissolved the exactly equal amounts of powder of passivated halfperovskite and unpassivated half-perovskite into DMF (Fig. S10i) for elemental quantification by inductively coupled plasma optical emission spectrometer (ICP-OES). We found that both the passivated and unpassivated half-perovskite films have similar Pb concentrations after solid phase passivation (Fig. S10j). However, passivated half-perovskite film (defect-less) contain significantly lower S content (8.04 mg/L) than that of unpassivated half-perovskite film (defect-rich) (9.54 mg/L), confirming the key feature of targeted passivation: The fewer defects, the fewer anchored passivator molecules.



Fig. S9 Schematic illustration of designing experiments to confirm targeted passivation.



Fig. S10 Confirmation of targeted passivation. (a) Photo of adhesive tape and original perovskite film. (b) Covering half of the perovskite film. (c) Passivating half of the perovskite film. (d) Obtaining the passivated and unpassivated half-perovskite film. (e, f) TRPL and PL characterizations of the passivated and unpassivated half-perovskite film. (g) Obtaining the defect-less (passivated) and defect-rich (unpassivated) half-perovskite film in one sample. (h) The photo of the perovskite sample after solid phase passivation. (i) After solid phase passivation, the passivated and unpassivated half-

perovskite film was separately dissolved into DMF. (j) Elemental characterization results of Pb and S by ICP-OES.



Fig. S11 GIWAXS characterization of control perovskite film with different X-ray incident angles.



Fig. S12 GIWAXS characterization of SPP-10 perovskite film with different X-ray incident angles.



Fig. S13 GIWAXS characterization of SPP-20 perovskite film with different X-ray incident angles.



Fig. S14 Top-view scanning electron microscopy (SEM) images of control, SPP-10 and SPP-20 films, the scale bars are 1 μ m.



Fig. S15 SEM image of perovskite films treated by blank substrate without passivator. **a**, SEM image of perovskite film treated by blank substrate at 70°C for 20 min without additional pressure. **b**, SEM image of perovskite film treated by blank substrate under 0.3 MPa for 20 min without additional heating. **c**, SEM image of perovskite film treated by blank substrate under the same conditions as SPP, the scale bars are 1 μ m. The blank substrate without passivator to treat the perovskite film under the same conditions as SPP but without additional pressure (0 MPa, 70 °C, 20 min) or without heating (0.3 MPa, 25 °C, 20 min) will not lead to morphology change of perovskite films. Even we simultaneously applied the same temperature and pressure to the blank substrate to perform the same process as SPP, there is no any change in the surface morphology of the perovskite film, firmly confirming that only heat or press will not lead to morphology change of perovskite films in Fig a-d. Only hot pressing without passivator will not affect the photovoltaic performance of PSCs.

Note S3 The formation mechanism of PbI₂-complex.

We designed an experiment to treat pure PbI₂ film by same SPP process to study the formation of the found PbI₂-complex, and evident PbI₂-complex peak appeared in XRD characterization result (Fig. S16), indicating a strong coordination anchoring ability between the passivator and Pb²⁺. Raman scattering was measured in order to gain more information on the formation of PbI₂-complex by artificially synthesizing it (See the experiment section). The characteristic peaks of PbI₂ disappear completely in PbI₂-complex (Fig. S17a, b).⁸ In addition, the stretching vibrations of C-N (1261 cm⁻¹)⁹. ¹⁰ are shifted towards lower wave numbers (Fig. S17c and d). The ¹H liquid nuclear magnetic resonance of passivator and PbI₂-complex showed obvious shift, probably due to the formed N-H...I hydrogen bond between the passivator and I⁻ (Fig. S17e). The N-H vibration in FTIR spectra of PbI₂-complex shifted toward lower wavenumber, which supports the formation of hydrogen bonds in PbI₂-complex (Fig. S17f). These findings suggest that the selected passivator has strong interaction with Pb²⁺.³



Fig. S16 The XRD result of pure PbI₂ and PbI₂ treated by the same SPP-20 process.



Fig. S17 The Raman spectroscopy characterization of passivator and PbI_2 -complex. (a) The Raman spectroscopy characterization of passivator and PbI_2 -complex. (b) A

magnified view of the Raman spectrum of PbI₂-complex in Fig. S17a, the typical Raman bands of PbI₂ (75, 96, 112, 164 cm⁻¹) was completed vanished in PbI₂-complex. (c) The stretching vibrations of C-N in passivator shifted towards lower wavenumber after forming complex with PbI₂ due to the bidentate coordination effect. (d) The laser confocal Raman spectroscopy mapping of passivator and PbI₂-complex performed at 1258 cm⁻¹, which can be assigned to C-N bond. (e) ¹H liquid nuclear magnetic resonance of passivator and PbI₂-complex. (f) The FTIR spectra of passivator and PbI₂-complex.



Fig. S18 Investigation on energy band structure of PbI_2 -complex. (a) The UV absorption spectroscopy of PbI_2 -complex. (b) band gap of test of PbI_2 -complex. (c) UPS characterization of PbI_2 -complex. (d) Schematic diagram of I-type band alignment between perovskite grains and PbI_2 -complex at GB.



Fig. S19 Solid phase passivation for the perovskite films without PbI_2 . (a) SEM of perovskite film without PbI_2 . (b) XRD results before and after SPP treatment of perovskite films without excessive PbI_2 . (c) *J-V* curves of control (without PbI_2) perovskite solar cell and after SPP treated perovskite solar cell. (d) Statistical distribution of V_{OC} of control and SPP-treated perovskite solar cells without PbI_2 .



Fig. S20 Optical Characterization. (a) Photoluminescence spectrum of control, SPP-10 and SPP-20 perovskite films. (b) UV absorption spectrum of SPP-10 and SPP-20 perovskite films. (c) Band gap calculation. (d-f) The confocal laser scanning microscope (CLSM) images of control, SPP-10 and SPP-20 perovskite films, scale bars are 2 μ m.



Fig. S21 The UPS spectrum of control and SPP-20 perovskite films.



Fig. S22 ps-TA characterization. (a) Schematic diagram of optical path. (b, c) TA twodimensional mapping of control and SPP-20 samples. (d, e) TA spectrum of control and SPP-20 samples at different time delays. (f) Normalized kinetic traces of control and SPP-20 samples for photobleaching probed at 760 nm.



Fig. S23 The dark current density-voltage (J-V) characterization.



Fig. S24 Defect characterization based on device. (a) The electrochemical impedance spectroscopy of control and SPP-20 PSCs. (b) The TPV measurement result of control and SPP-20 PSCs. The lifetime of TPV measurement is longer than that of TRPL measurement because the TPV characterization is based on the complete device containing electrodes, and the voltage decay includes the influence of electrode capacitance, so the measured lifetime is significantly extended. ^{11, 12} The device configuration and thickness of each layer are the same for control and SPP samples, so the contribution of electrode capacitance is the same. The only difference between control and SPP devices is whether the perovskite films were optimized, so the final difference in TPV result should be due to the difference in the perovskite film itself.



Fig. S25 External quantum efficiency (EQE) spectra of control and SPP-20 PSCs, their integrated J_{SC} are 24.82 and 24.85 mA/cm², respectively.



Fig. S26 SPP-20 PSC with $V_{\rm OC}$ of 1.20 V.



Fig. S27 Certificated PV performance from an accredited photovoltaic certification institution (Photovoltaic and Wind Power Systems Quality Test Center, IEE, Chinese Academy of Sciences), the certificated efficiency is 24.65%.



Fig. S28 The second certificated PV performance from an accredited photovoltaic certification institution (National PV Industry Measurement and Testing Center, Fu Jian Metrology Institute) after two months of storage, the certificated efficiency is 24.29%.



Fig. S29 The statistical distributions of V_{OC} , J_{SC} and FF of control and SPP PSCs. Significant defect passivation contributed to significantly increased V_{OC} , more effective suppression of non-radiative recombination, more uniform surface potential distribution, and suppressed surface leakage current resulted in the slight increase in FF.



Fig. S30 Preparation of passivator film by drop coating. (a) Schematic diagram of passivator film prepared by drop-casting. (b) Schematic diagram of the obtained passivator film. (c) Photo of passivator film obtained by drop casting. (d) J-V curve of perovskite solar cells treated by passivator film prepared by drop casting.



Fig. S31 Photovoltaic parameters of 1 cm^2 devices. (a) The *J-V* curves of SPP-20 PSC under forward scan. (b) SPO of SPP-20 device at MPP. (c-f), The statistical distributions of photovoltaic parameters of control and SPP-20 PSCs.

Fig. S32 The effect of temperature on SPP. (a) The XRD of perovskite films treated by SPP with different temperatures. 50 °C can't initiate SPP, so the sample treated at 50 ° C remained in its original state (excessive PbI₂). However, when the temperature rises, we could find that the diffraction peak intensity of PbI₂ gradually decreases, accompanied by the increase of the diffraction peak intensity of $(2-MP)_x$ -PbI₂. This is because the SPP process gradually transforms PbI₂ at the grain boundary into $(2-MP)_x$ -PbI₂ with better light stability. (b, c) Photoluminescence spectrum and TRPL of perovskite films treated by SPP with different temperature. (d-g) *J-V* curves of PSCs treated by SPP with different temperature. (h-k) Statistical distributions of photovoltaic parameters of the devices obtained at 70 °C and 80 °C.

Fig. S33. Photovoltaic parameter statistics for the relationship between pressure in SPP and PCE of obtained PSCs.

Fig. S34 Solid phase passivation based on 2-TM. (a) Molecular structure of 2-TM. (b) *J-V* curves of control and 2-TM solid phase passivated perovskite solar cells.

Fig. S35 Comparison of solution method and SPP. (a, b) PL and TRPL results of perovskite films treated by solution and solid phase methods.

Fig. S36 Comparison of solution method and SPP. **a**, SEM image of perovskite film treated by conventional solvent method, the scale bar is 1 μ m. **b**, *J-V* curves of champion PSCs treated by solution method and SPP based on the same passivator (2-MP). The champion efficiency of solution treated perovskite solar cells is 23.33%, while the efficiency can be further improved to 24.89% by solid phase defect passivation. **c-f**, Statistical distribution of photovoltaic performance of PSCs treated by solution method and SPP based on the same passivator (2-MP).

Fig. S37 The water contact angle of control, SPP-10 and SPP-20 perovskite films.

Fig. S38 Moisture stability test. (a) Schematic diagram of the humidity stability test, the perovskite films and a glass of water are simultaneously covered by a petri dish to create a high humidity environment. (b) Pictures of control and SPP-20 perovskite films over time under high humidity.

Fig. S39 XRD results of PbI₂ and PbI₂-complex after different illumination time.

Fig. S40 UV absorption spectra of toluene solution after soaking control and SPP-20 perovskite films for 48 hours under light.

Fig. S41 Time-dependent photoluminescence intensity of control and SPP-20 perovskite films under heating at 85 °C.

Sample	Number	PLQY (%)	Ave (%)	
Control	1	0.66		
	2	0.97		
	3	0.76	0.77	
	4	0.72		
	5	0.74		
SPP-10	1	2.25		
	2	2.24		
	3	1.77	2.03	
	4	1.68		
	5	2.25		
SPP-20	1	2.28		
	2	2.78		
	3	2.44	2.67	
	4	3.12		
	5	2.77		

Table S1 The PLQY of control and SPP samples.

Table S2 Photovoltaics parameters of SPP-20 PSCs treated by the reusable passivator film.

Times	$V_{ m oc}\left({ m V} ight)$	$J_{\rm sc}~({ m mA~cm^{-2}})$	FF	PCE (%)
1	1.19	25.21	0.813	24.4
2	1.17	25.22	0.830	24.5
3	1.19	25.18	0.811	24.3
4	1.18	25.17	0.815	24.2
5	1.19	25.18	0.818	24.5

Table S3 Statistical distribution of photovoltaic performance of PSCs treated by solution method and SPP based on the same passivator (2-MP).

		Max	Min	Ave
$V_{\rm OC}$ (V)	Spin coating	1.16	1.12	1.142
	SPP-20	1.20	1.16	1.182
$J_{\rm SC}~({ m mA/cm^2})$	Spin coating	25.26	25.08	25.148
	SPP-20	25.26	25.08	25.155
FF	Spin coating	0.808	0.772	0.794
	SPP-20	0.839	0.804	0.819
PCE (%)	Spin coating	23.33	21.69	22.80
	SPP-20	24.89	23.66	24.38

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