Ambient-Air-Stable Inorganic Cs_2SnI_6 Double Perovskite Thin Films via Aerosol-Assisted Chemical Vapour Deposition

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Electronic Supplementary Information†

Peeling and scratching tests for adhesion to the substrate.

In order to evaluate adherence between Cs_2SnI_6 film and ITO-glass substrate, we conducted sticking and scratching tests for films fabricated by AACVD and spin coating. The sticking test was carried out using adhesive tape of width of 1 cm. This was fastened to the films and then peeled off rapidly. For the scratching test, a needle was used to scratch the films by moderate force.

(A)

(B)

(C)

(D)

Figure S1 Photographs of Cs_2SnI_6 films fabricated *via* AACVD (A&B) and spin coating (C&D). A shows the as fabricated AACVD film and B following the peel and scratch tests. C and D are equivalent tests

for the spin-coated film. It is clear that the AACVD-grown film shows very little change following the scratch and peel tests. The tape remains clear of black powder and no line can be seen on the substrate following scratching. The spin coated film, on the other hand, shows significant removal by both the tape and scratching.

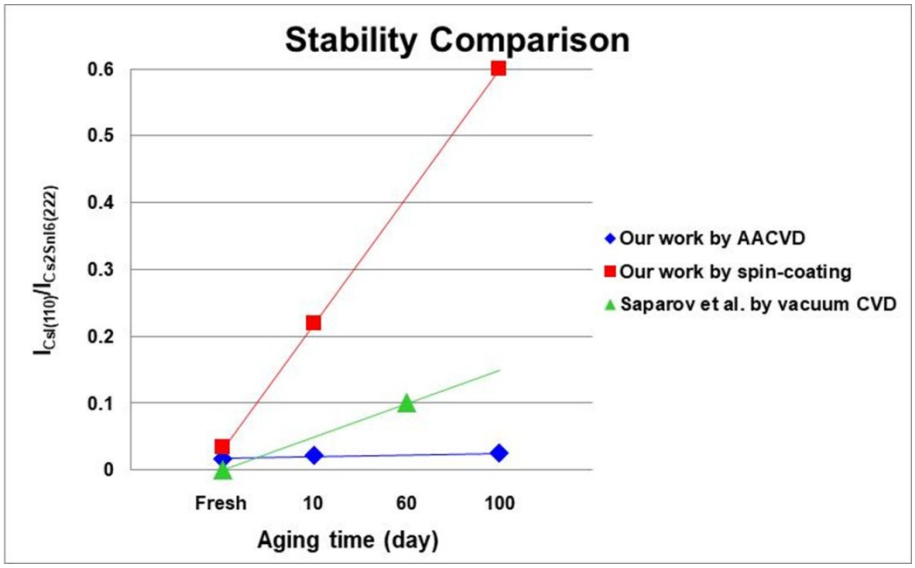


Figure S2 CsI-impurity-level comparison between the work reported by Saparov *et al.* through vacuum CVD and this work *via* AACVD and spin-coating showing the values of $I_{CsI(110)}/I_{Cs2SnI6(222)}$ determined from the XRD results as a function of aging up to around 100 days, as shown in Table 1. Note the data points obtained from the work of Saparov and the co-workers are estimated through measurement of the height of the corresponding reflections.

Table S1 Quantified atomic concentrations of various elements from the XPS spectra of Cs 3d (Figure 5), Sn $3p_{3/2}$ (Figure S3), and I 3d core levels. All elemental concentrations are normalised to [Cs] = 2.0 as in the ideal stoichiometry Cs_2SnI_6. Excess Sn (excess I) refers to the amount of Sn (I) that cannot be accounted for in the Cs_2SnI_6 (Cs_2SnI_6+CsI) phase(s).

Sample ID	**Total Cs**	**Cs in CsI**	**Cs in Cs_2SnI_6**	**Sn**	**I**	**Excess Sn**	**Excess I**
Ideal stoichiometry	**-**	**-**	**2.0**	**1.0**	**6.0**	**0.0**	**0.0**
AACVD (+HI) fresh	2.3 ± 0.2	0.3 ± 0.1	2.0 ± 0.2	4.1 ± 0.4	18.2 ± 1.8	3.1 ± 0.3	11.9 ± 1.2
AACVD (+HI) 100 days	2.4 ± 0.2	0.4 ± 0.1	2.0 ± 0.2	2.3 ± 0.2	6.8 ± 0.7	1.3 ± 0.1	0.4 ± 0.1
AACVD (-HI) fresh	2.7 ± 0.3	0.7 ± 0.1	2.0 ± 0.2	8.9 ± 0.9	9.2 ± 0.9	7.9 ± 0.8	2.5 ± 0.3
Spin-coated (+HI) fresh	2.4 ± 0.2	0.4 ± 0.1	2.0 ± 0.2	3.4 ± 0.3	7.2 ± 0.7	2.4 ± 0.2	0.8 ± 0.1
Spin-coated (+HI) 10 days	2.7 ± 0.3	0.7 ± 0.1	2.0 ± 0.2	2.8 ± 0.3	7.2 ± 0.7	1.8 ± 0.2	0.5 ± 0.1

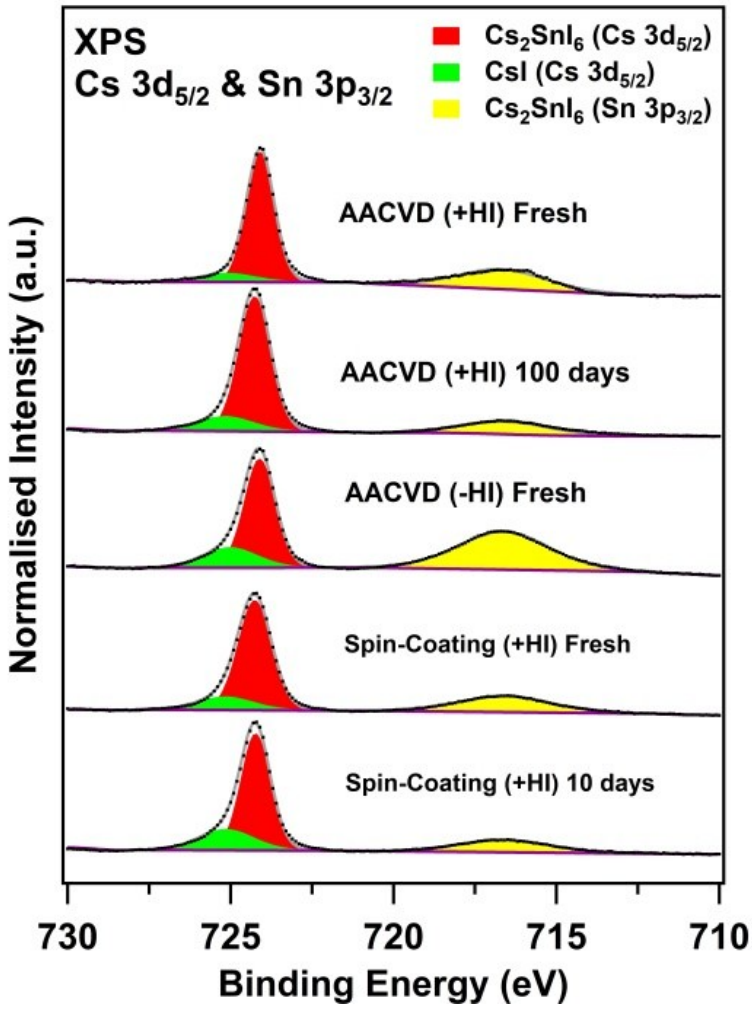
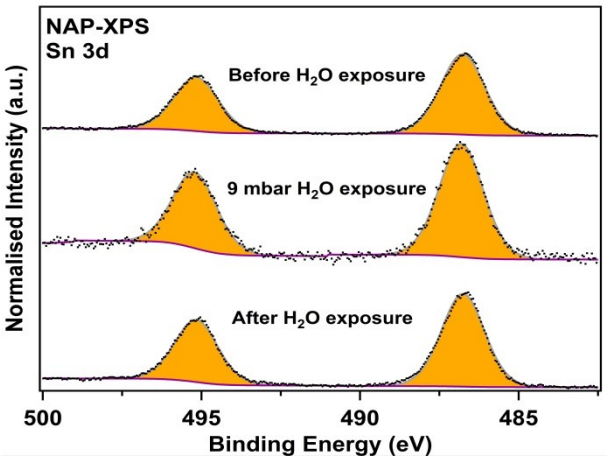
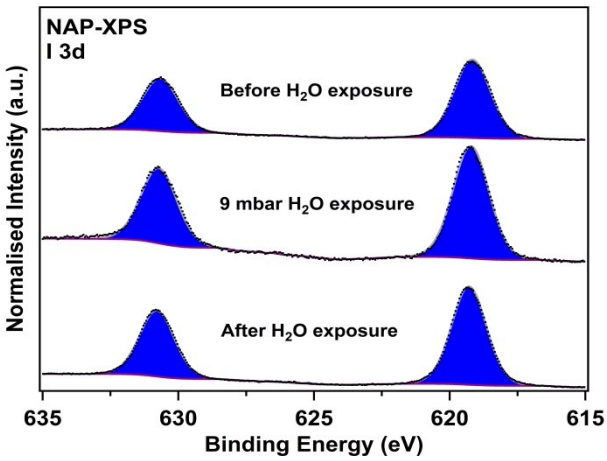


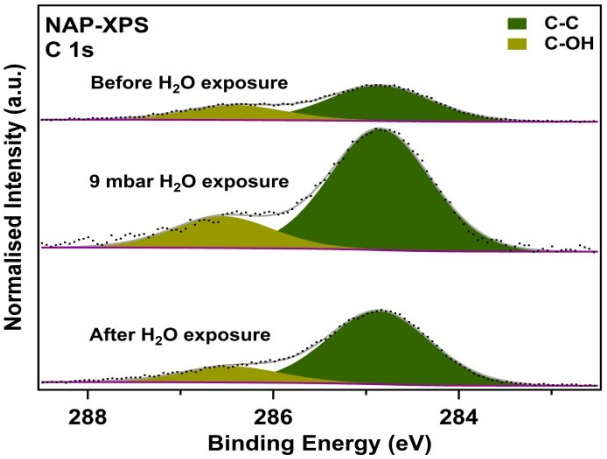
Figure S3 Sn $3p_{3/2}$ with Cs $3d_{5/2}$ core-level XPS spectra of various films prepared by AACVD or spin-coating. All spectra are normalised to the Cs $3d_{5/2}$ area for comparison of the relative concentrations of atomic Sn.


NAP-XPS
Sn 3d
Before H_2O exposure
9 mbar H_2O exposure
After H_2O exposure
Normalised Intensity (a.u.)
500
495
490
485
Binding Energy (eV)

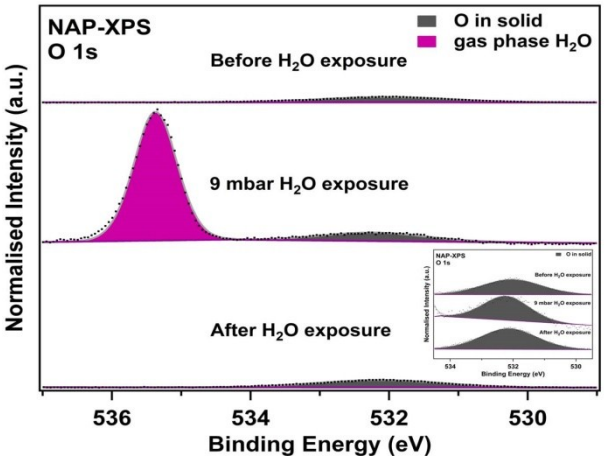
(A)


NAP-XPS
I 3d
Before H_2O exposure
9 mbar H_2O exposure
After H_2O exposure
Normalised Intensity (a.u.)
635
630
625
620
615
Binding Energy (eV)

(B)

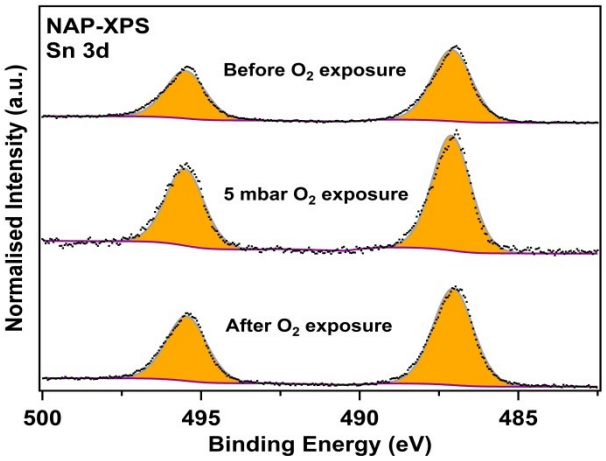

NAP-XPS
C 1s
C-C
C-OH
Before H_2O exposure
9 mbar H_2O exposure
After H_2O exposure
Normalised Intensity (a.u.)
288
286
284
Binding Energy (eV)

(C)

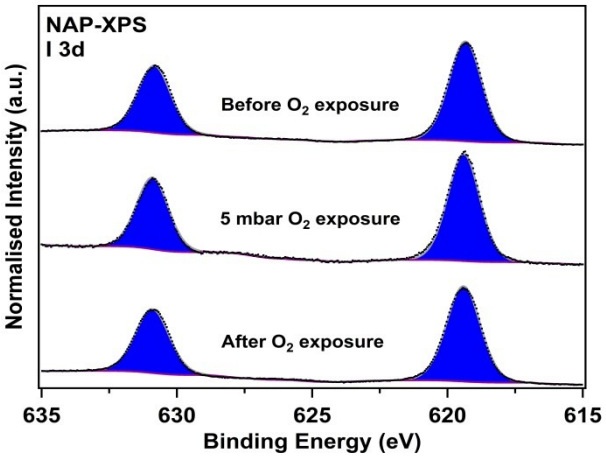


(D)

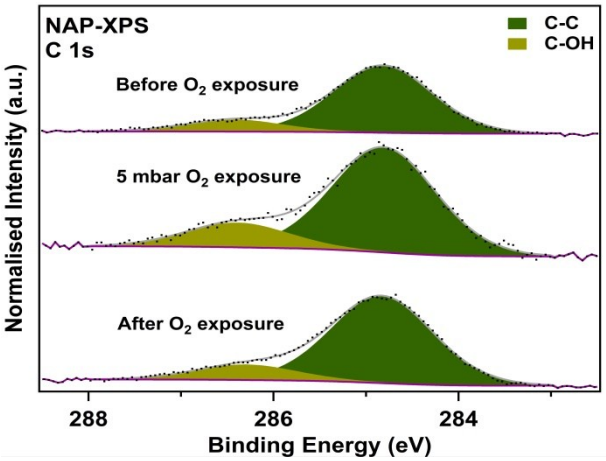
Figure S4(A) Sn 3d, (B) I 3d, (C) C 1s, and (D) O 1s core-level NAP-XPS spectra of AACVD (+HI)-grown film, recorded before, during, and after exposure to 9 mbar H_2O vapour. All spectra are normalised to the relevant Cs $3d_{5/2}$ area for comparison.


NAP-XPS
Sn 3d
Before O_2 exposure
5 mbar O_2 exposure
After O_2 exposure
Normalised Intensity (a.u.)
500
495
490
485
Binding Energy (eV)

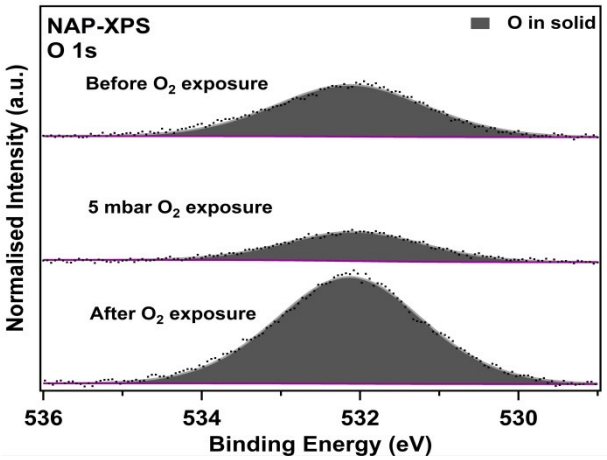
(A)


NAP-XPS
I 3d
Before O_2 exposure
5 mbar O_2 exposure
After O_2 exposure
Normalised Intensity (a.u.)
635
630
625
620
615
Binding Energy (eV)

(B)


NAP-XPS
C 1s
C-C
C-OH
Before O_2 exposure
5 mbar O_2 exposure
After O_2 exposure
Normalised Intensity (a.u.)
288
286
284
Binding Energy (eV)

(C)



(D)

Figure S5 (A) Sn 3d, (B) I 3d, (C) C 1s, and (D) O 1s core-level NAP-XPS spectra of AACVD (+HI)-grown film, recorded before, during, and after exposure to 5 mbar O_2. All spectra are normalised to the relevant Cs $3d_{5/2}$ area for comparison.

Table S2 Quantified atomic concentrations of C–O (BE: 286.3 ± 0.1 eV) from the C 1s NAP-XPS spectra and O–C (BE: 532.1 ± 0.1 eV) from the O 1s NAP-XPS spectra of AACVD (+HI)-grown films. All elements are normalised to Cs (using [Cs] = 2.0), consistent with Tables 1&2. Spectra were measured under UHV conditions before and after exposure to water or O_2.

Fresh AACVD (+HI)	C–O	O–C
UHV before H_2O exposure	15.8 ± 1.6	12.0 ± 1.2
UHV after H_2O exposure	26.5 ± 2.7	16.1 ± 1.6
UHV before O_2 exposure	5.4 ± 0.5	4.7 ± 0.5
UHV after O_2 exposure	9.2 ± 0.9	9.2 ± 0.9