

Spherical hydroxyapatite nanoparticle scaffolds for reduced lead release from damaged perovskite solar cells

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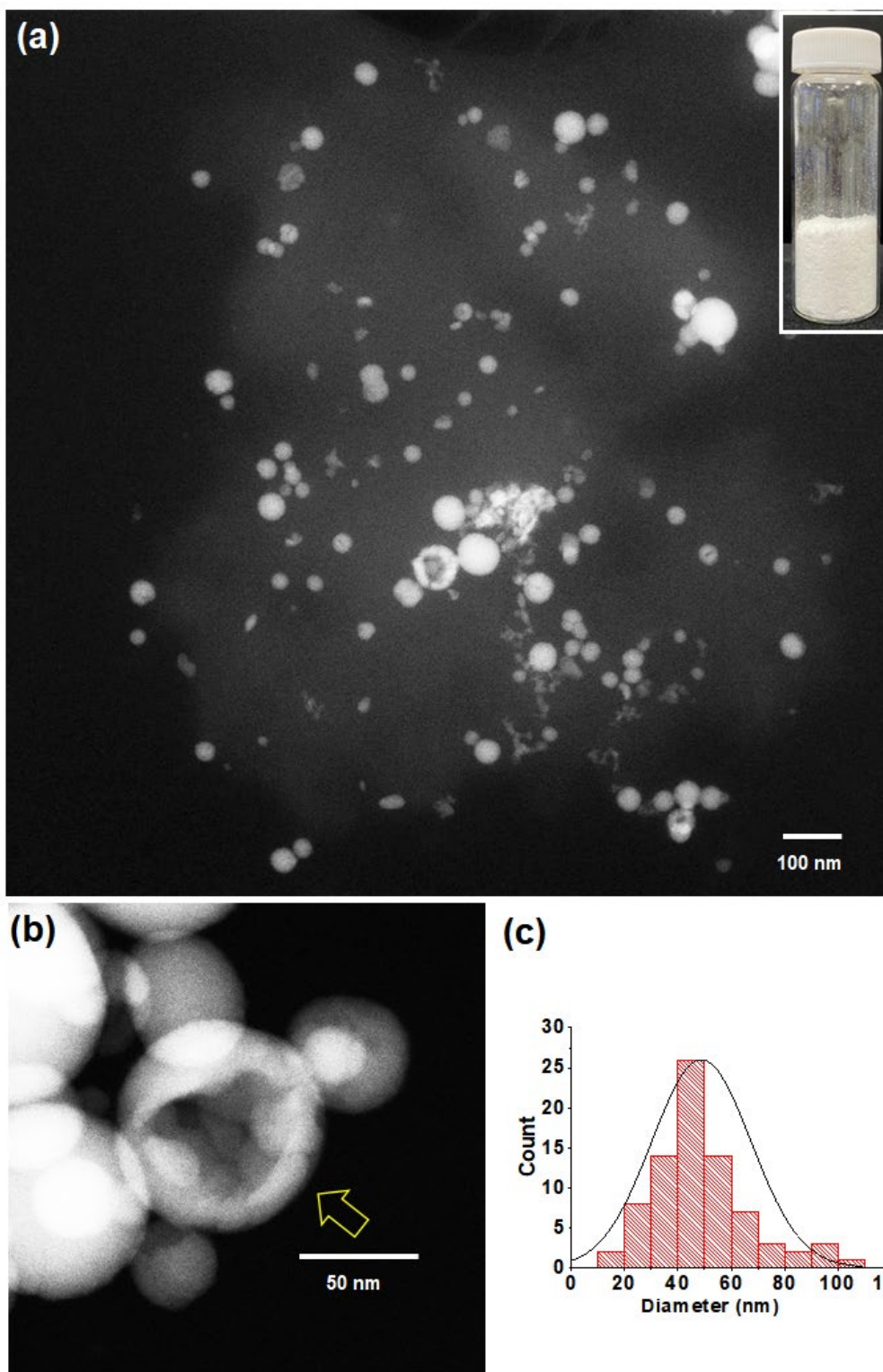
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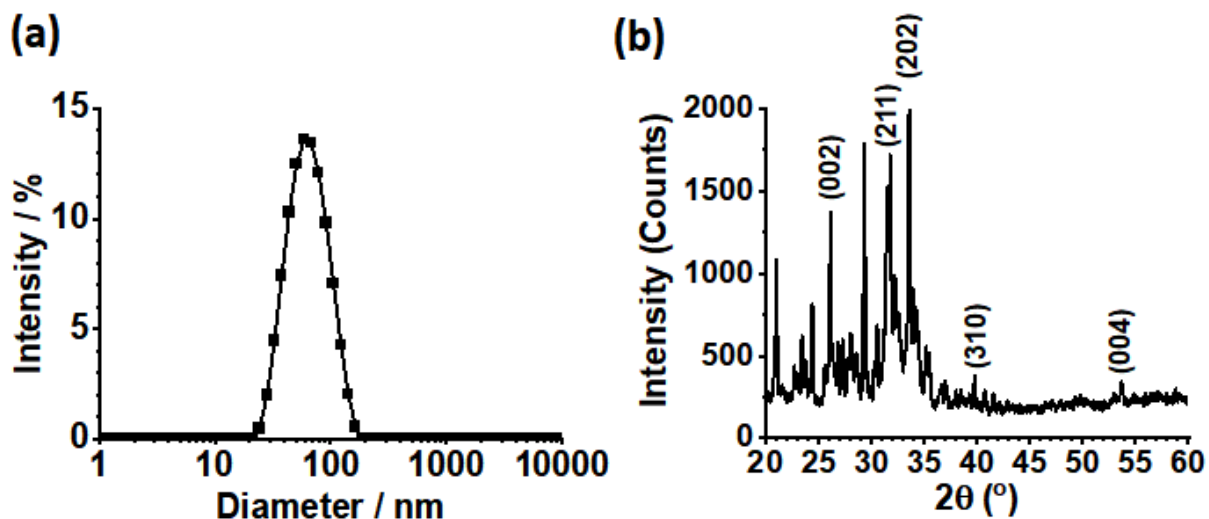
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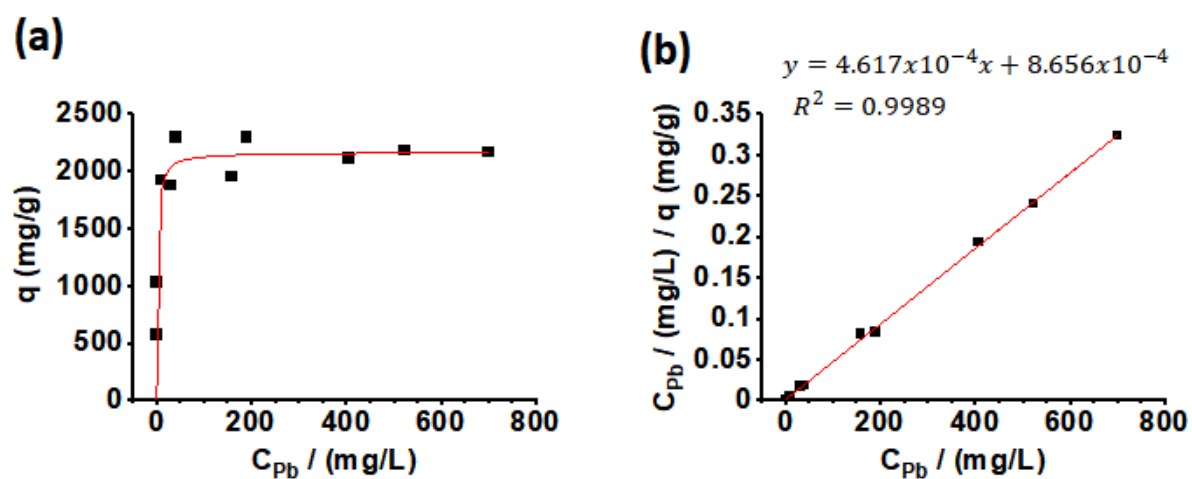
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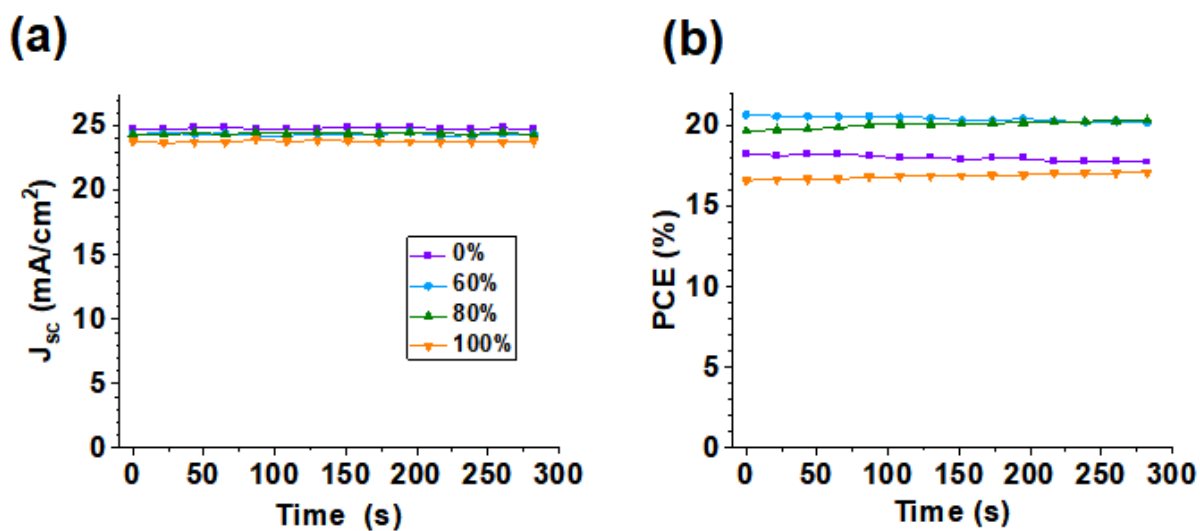
Supplementary Figure 1. s-HAP investigation using HAADF STEM. (a) Lower and (b) higher magnification TEM images for the s-HAP nanoparticles which were easily synthesized in multi-gram quantities (inset of A). (c) Distribution of s-HAP diameters obtained from the TEM images.



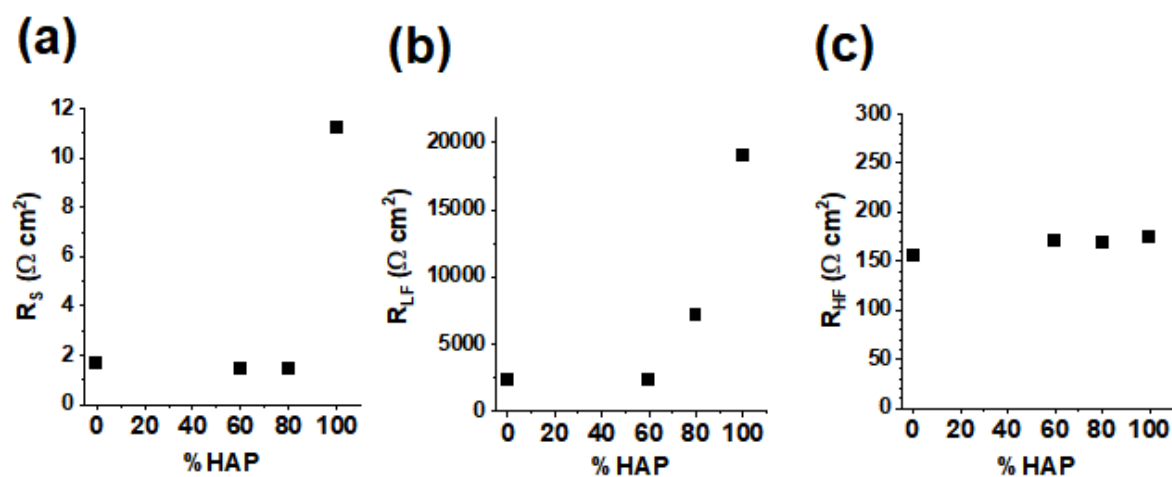
Supplementary Figure 2. s-HAP size and structure characterization. (a) Dynamic light scattering diameter distribution for s-HAP nanoparticles dispersed in isopropanol (IPA). (b) X-ray scattering profile for s-HAP.



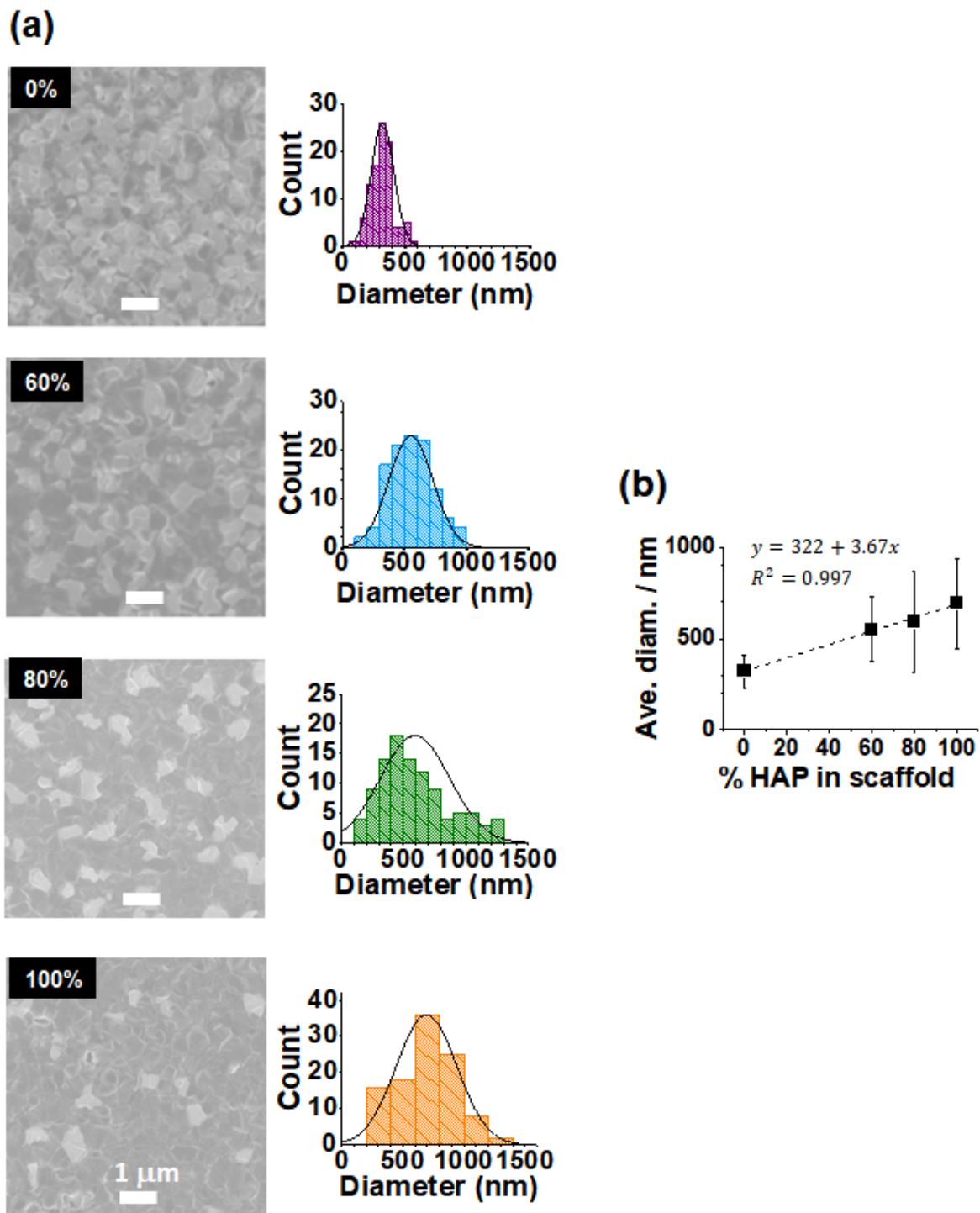
Supplementary Figure 3. Absorption of Pb by s-HAP. (a) Absorption isotherm data and **(b)** Data from (a) replotted to obtain the absorption capacity.



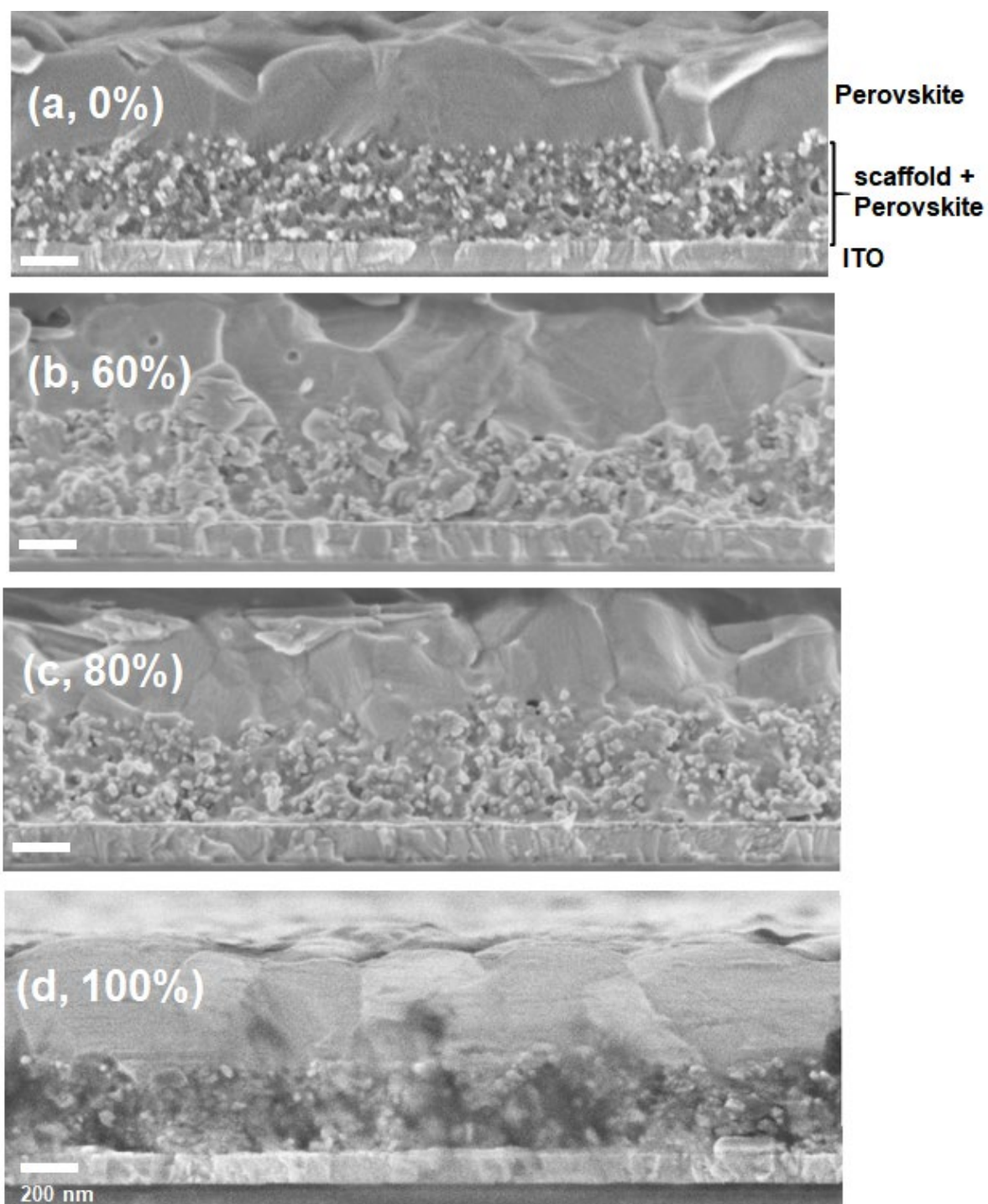
Supplementary Figure 4. Stabilized power output measurements. Variation of (a) short-circuit current densities and (b) power conversion efficiencies for the devices under illumination. The legend shown in (a) also applies to (b).



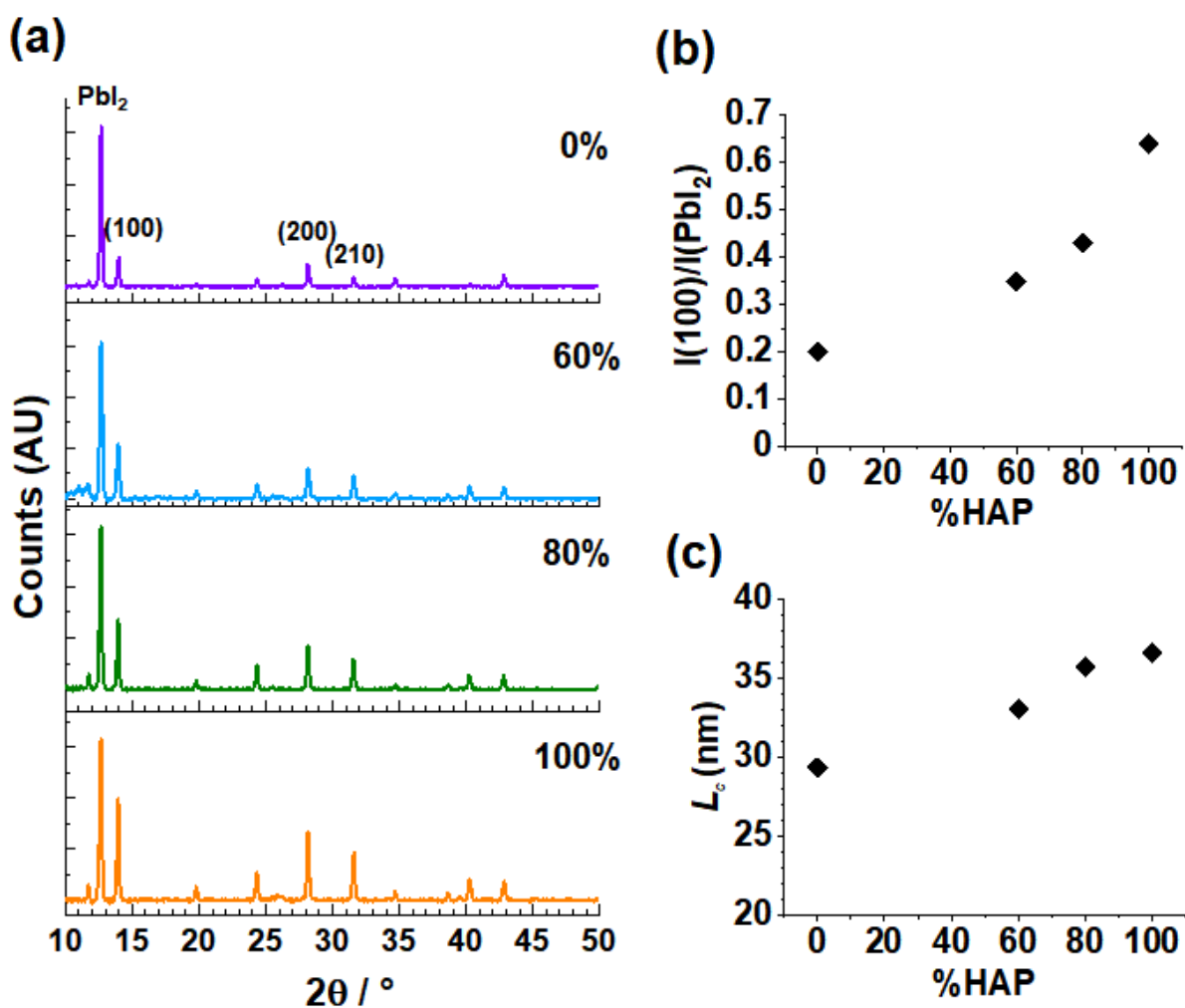
Supplementary Figure 5. Electrochemical impedance data analysis. Resistance parameters ((a) – (c)) obtained from fitting the model shown above Fig. 2e to the EIS data shown in that figure.



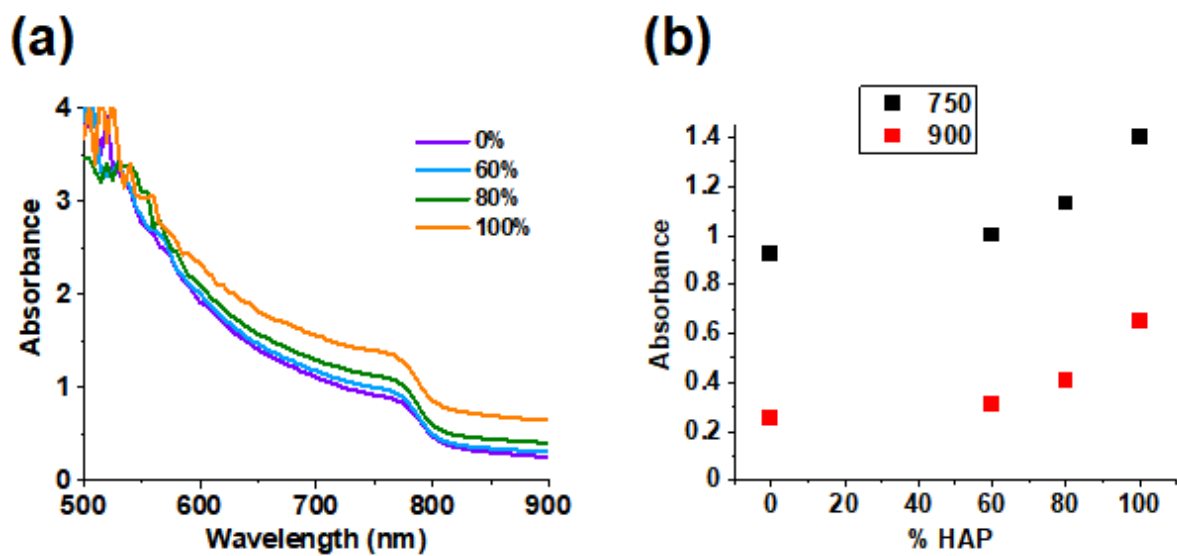
Supplementary Figure 6. Grain size analysis of perovskite films. (a) Lower magnification SEM images and grain size distributions for the various films. **(b)** Variation of average perovskite grain diameter with s-HAP content in the scaffolds. The error bars in (b) are the standard deviation.



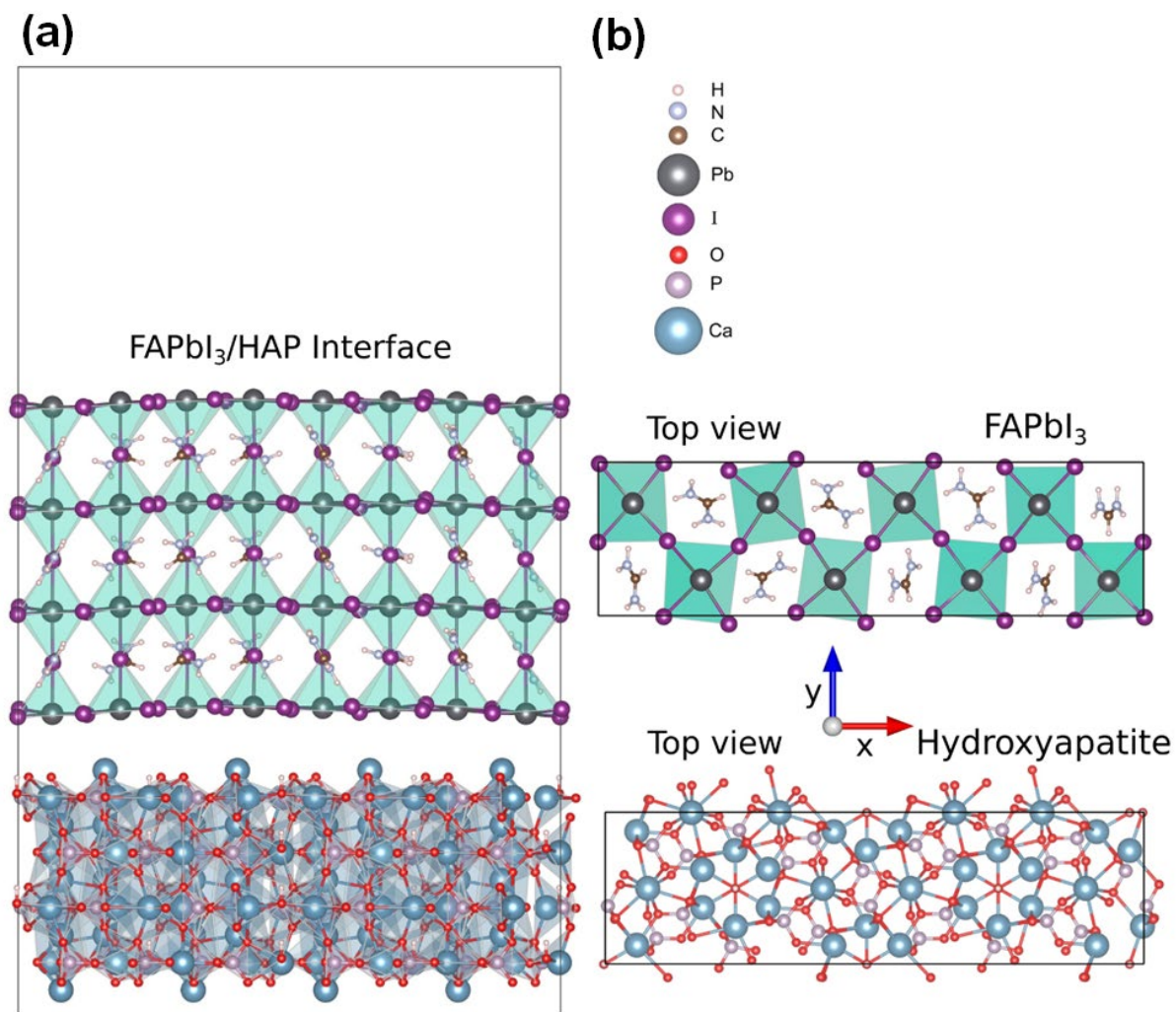
Supplementary Figure 7. SEM cross-sectional images for the films.



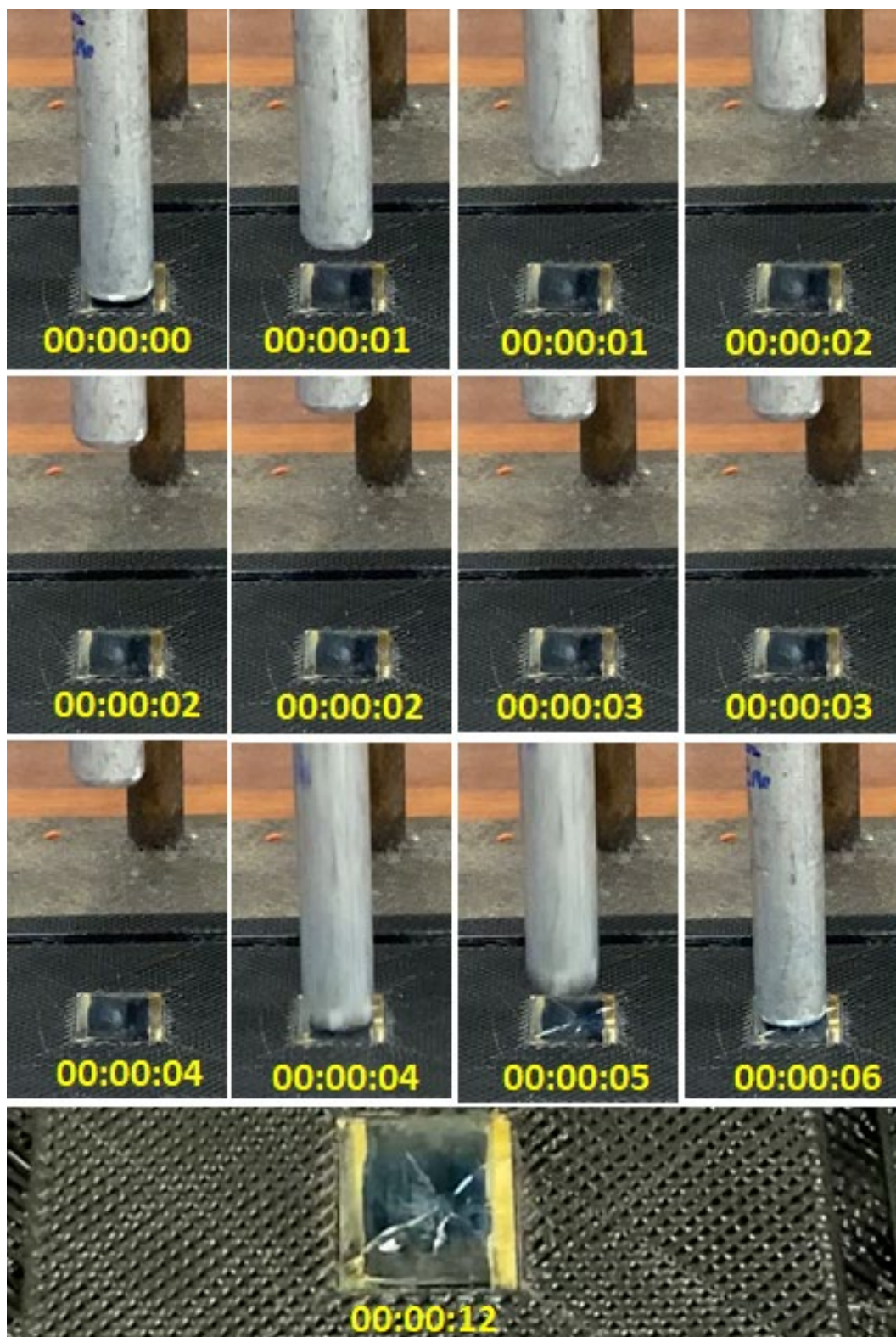
Supplementary Figure 8. Investigating perovskite structure. (a) 1D GIXRD profiles of the perovskite films grown on blended s-HAP/TiO₂ scaffolds. (b) Variation of the intensity ratio for the (100) perovskite peak to the PbI₂ peak with %HAP. (c) Variation of the coherence length calculated from the Scherrer equation with %HAP.



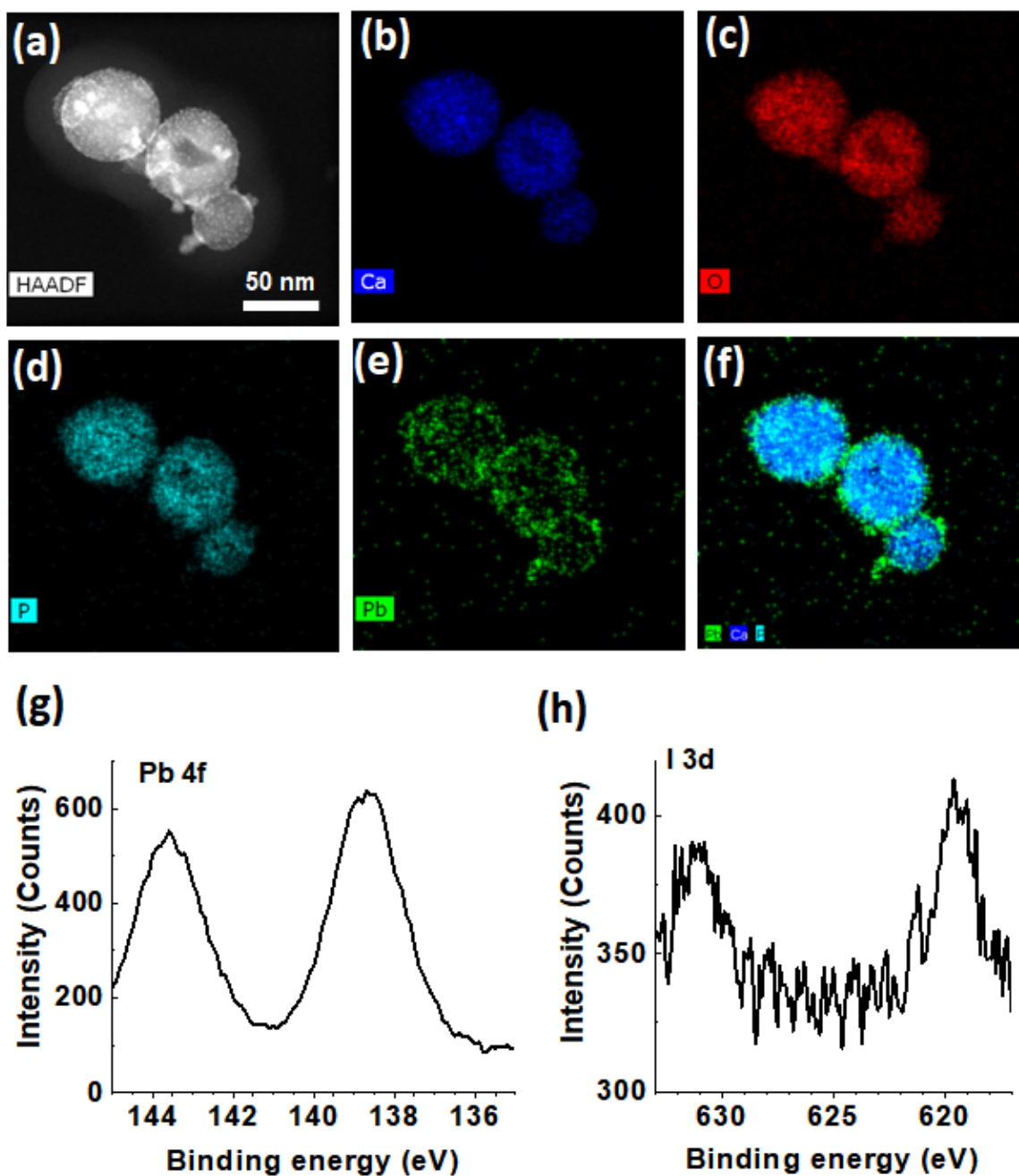
Supplementary Figure 9. (a) UV-visible spectra and (b) absorbance measured at 750 and 900 nm vs. s-HAP content in the scaffold from the data shown in (a).



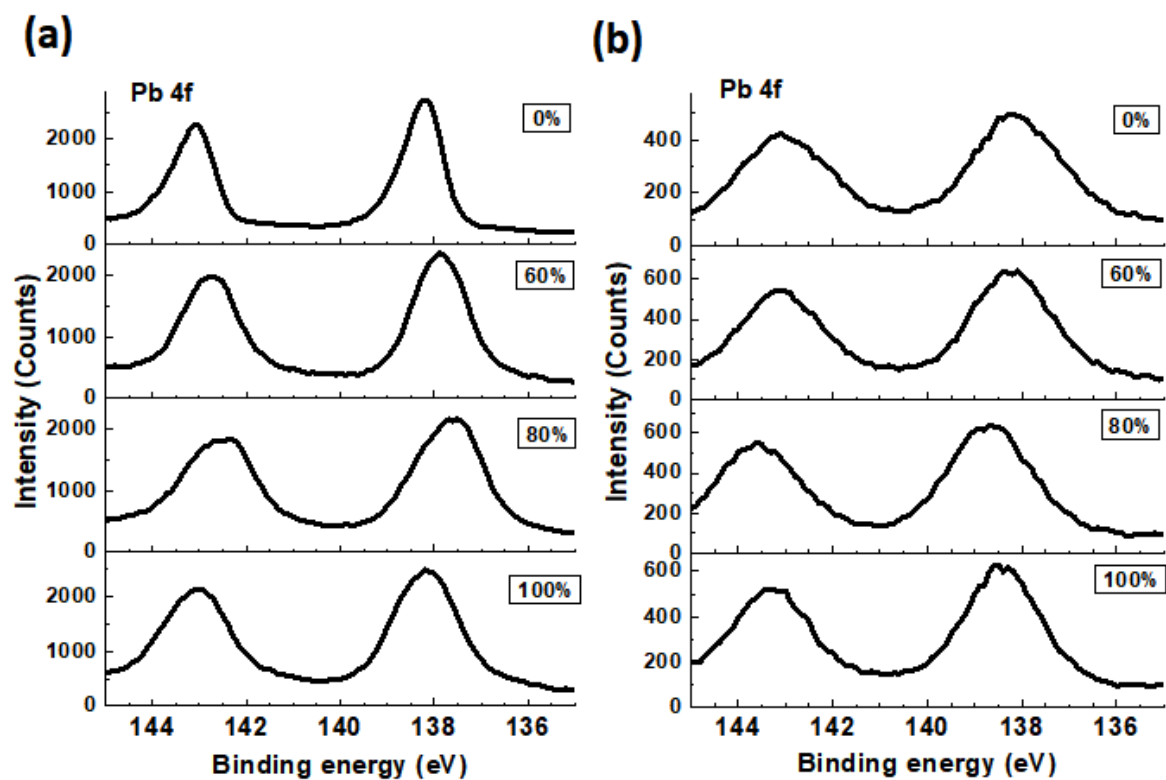
Supplementary Figure 10. Modelling HAP-perovskite interface. **(a)** Investigating energies of inequivalent configurations of O-H in HAP. **(b)** Top views of the simulated interface slabs of FAPbI₃ and HAP structures. The lattice mismatch along the *x*-axis is 4.8%. The perovskite was compressed by 2.4% and the HAP was elongated by 2.4%.



Supplementary Figure 11. Cell breaking procedure. Time lapse photos (sec) of breaking procedure for the PSCs. A rod (mass of 300 g) was used, and the height was 5.0 cm above the cell when it was released.



Supplementary Figure 12. Investigating the s-HAP encapsulation layer after the water-soaking experiments. HAADF STEM and STEM-EDS analysis ((a) – (f)) of a sample of the s-HAP encapsulation layer from the device containing an 80% HAP scaffold after absorption of Pb for 24 h. (f) is a composite colour image showing overlay of Pb, Ca and P elemental signals. XPS core level spectra of the encapsulation layer s-HAP after the water soaking experiment are shown for the (g) Pb 4f and (h) I 3d signals.



Supplementary Figure 13. Studying the Pb contents after water-soaking. XPS spectra for the (a) scaffold and (b) s-HAP encapsulation layers after the 24 h impact/soaking experiments.

Supplementary Discussion

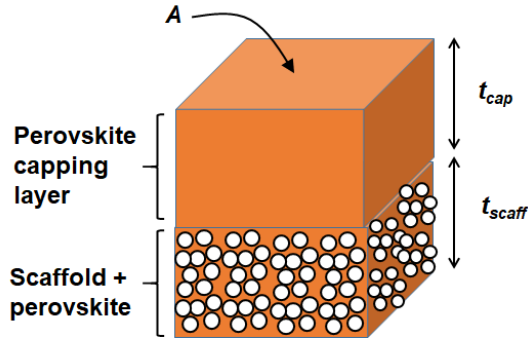
In the following we address two questions. The first question concerns the relative Pb content in the water phase and the 0% scaffold (100% meso-TiO₂ scaffold) after 24 h of water soaking. The second question (B) concerns the potential for the 100% s-HAP scaffold to absorb all of the Pb initially present in the device after water soaking.

The relative Pb content in the water phase and the TiO₂ scaffold can be estimated using the following approach. The mass of perovskite in the capping layer and scaffold using the cross-sectional thickness values is calculated. Then, the mass of Pb in solution after 24 h of release from the water soaking data is calculated. Comparison of the Pb masses from the latter and that initially in the film is then conducted to give the relative Pb content in water and remaining in the scaffold. The details of these calculations follow for the 0% (100% meso-TiO₂) system.

The idealized geometry for the film before fracture and water soaking is depicted in Supplementary Figure S14. The initial mass of perovskite in the film is given by:

$$m_{Perov} = \rho_{Perov} A (P t_{scaff} + t_{cap}) \quad (S1)$$

where ρ_{Perov} , A and P are the perovskite density, area of the film and porosity of the scaffold layer, respectively. The parameters t_{scaff} and t_{cap} are the thicknesses of the scaffold and capping layers, respectively. The values for the latter were 326 and 338 nm, respectively, based on the SEM in Fig. S7. We use a P value of 0.6 for the meso-TiO₂ layer[1]. The value of A was 3.0 cm². Using a perovskite density[2] of 4.1 g/cm³, equation S1 yields $m_{Perov} = 0.66$ mg. The Pb content of FAPI is 33 wt.%. Hence, the initial Pb content in the film is estimated as 0.22 mg. The error is estimated as ± 0.05 mg.



Supplementary Figure 14. Idealized geometry of the initial perovskite film.

The mass of Pb released into water over a period of 24 h is calculated as 0.29 ± 0.03 mg from the water soaking experiment (see Fig. 6d). Comparing this value to the Pb content initially estimated as being present (above) shows that the ranges for these values overlap. We conclude that the majority of the Pb initially present in the 0% device resides in the water phase after 24 h of soaking. The XPS data shown in Fig. 7i do indicate Pb was still present in that scaffold after 24 h. We attribute this to a minor proportion of PbI_2 that resided on the scaffold surface.

We next consider the question of whether there was sufficient absorption capacity within the 100% S-HAP scaffold to absorb all of the initial Pb present in the device. To arrive at this answer the mass of s-HAP in the scaffold must be calculated and the absorption capacity of s-HAP used to calculate the maximum possible Pb that could be absorbed by that scaffold.

The mass of the s-HAP scaffold is given by the following equation.

$$m_{\text{HAP}} = \rho_{\text{HAP}} A (1 - P) t_{\text{scaff}} \quad (\text{S2})$$

where ρ_{HAP} is the s-HAP density. We use the density of HAP (3.2 g/cm^3) for this calculation[3]. The value of P for the HAP scaffold is not known. For the purposes of this calculation we assume that P is the same as that used above for TiO_2 , i.e., 0.6. Furthermore, the 100% s-HAP scaffold thickness was 292 nm from Fig. S7d. Using $A = 3.0 \text{ cm}^2$, we

estimate a value for m_{HAP} of 0.11 mg. From the absorption capacity of 2165 mg g⁻¹ measured for s-HAP in this study, the maximum Pb²⁺ that can be absorbed by the 100% s-HAP scaffold is estimated as 0.24 mg. We caution that the latter should be considered as a nominal value. Nevertheless, it does appear as though there was, in principle, sufficient absorption capacity for the 100% s-HAP scaffold to absorb all of the Pb initially present.

Supplementary Table 1. Measured PSC performance data

HAP%^a	Scan direction	V_{oc} (volts)	J_{sc} (mA.cm⁻²)	FF (%)	PCE (%)
0	Fwd	1.03 ± 0.01	24.36 ± 0.61	69.72 ± 1.36	17.44 ± 0.29
	Rev	1.04 ± 0.01	24.32 ± 0.63	72.41 ± 1.24	18.25 ± 0.28
	Best	1.03	24.78	72.91	18.61
60%	Fwd	1.06 ± 0.01	24.24 ± 0.19	73.45 ± 1.35	18.80 ± 0.23
	Rev	1.07 ± 0.01	24.18 ± 0.33	76.28 ± 1.27	19.64 ± 0.28
	Best	1.06	24.35	78.03 ±	20.17
80%	Fwd	1.06 ± 0.01	24.44 ± 0.21	71.72 ± 2.05	18.60 ± 0.45
	Rev	1.07 ± 0.01	24.46 ± 0.19	75.32 ± 1.76	19.73 ± 0.39
	Best	1.08	24.34	77.60	20.32
100%	Fwd	1.01 ± 0.02	24.15 ± 0.55	64.41 ± 2.62	15.72 ± 0.44
	Rev	1.02 ± 0.02	24.28 ± 0.61	67.52 ± 2.63	16.72 ± 0.45
	Best	1.04	23.72	70.35	17.38

^a s-HAP concentration used to prepare the scaffold.

Supplementary References

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3. Larranaga, M. D.; Lewis, R. J.; Lewis, R. A., *Hawley's Condensed Chemical Dictionary*, 16th Ed. John Wiley and Sons 2016.