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Electronic Supplementary Information

Perovskite chemical gardens: Highly fluorescent microtubes from self-assembly and ion exchange

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Description of experiments

We grew hundreds of $CaCO_3$ microtubes on a Nafion 117 membrane (FuelCellStore) that was placed between two scintillation vials held together by a 3D printed threaded connector. The bottom flask contained 1.0 M $CaCl_2$ (EMD Millipore) dissolved in 1% w/w agar gel (Sigma) while the upper one was filled with a 1.0 M Na_2CO_3 solution (VWR Chemicals). Precipitates developed only in the latter solution. We note that the distribution of sizes was heterogeneous, with most tubes having a characteristic length of 1 mm, and about 5-20 tubes per preparation being longer than 5 mm. After one week, the precipitates were collected in a Petri dish filled with water, washed several times, and then placed in water again for an additional 1 h to remove excess reactants. They were then transferred to a 10 mM lead acetate solution (Sigma-Aldrich) prepared with N_2 purged water and converted for 24 h to cerussite and hydrocerussite bearing-structures. $PbCO_3$ tubes were rinsed and dried at 22 ˚C under N_2 gas. The dried material was then exposed to 200 µL of a 100 mg/5 mL solution of $MAPbBr_3$ (98%, Aldrich) in isopropyl alcohol (Fisher Scientific). Upon drying, the tubes changed color from white to yellow/orange. The process was repeated three times.

Experiments focusing on long conversion times followed the same protocol described in the previous paragraph with the difference that the tubes were exposed to Pb^{2+} solution for as long as 35 days. To minimize reactant loss, the lead acetate solution was replaced after 6 h, 24 h, 48 h, and then every week. Samples were removed at specific time intervals and then mounted for SEM/EDS analyses. A few samples collected at day 35 were later converted to perovskite, initially under the same protocol described in the previous paragraphs, followed by full immersion in the MABr solution for 12 h, drying under ambient conditions, and rinsing with IPA to remove excess MABr.

Techniques

Photographs

Photographs of the tubes and the experimental setup were recorded using a Nikon D3300 camera (shutter speed of 1/10 s). For optical micrographs, the camera was connected to a LEICA DM-IRB inverted microscope. Fluorescence images utilized a hand-held UV light (shutter speed of 30 s).

SEM/EDS

Samples were mounted on carbon-tape covered aluminum stubs and sputtered with a 10 nm thick Iridium coating. Scanning electron micrographs were obtained with a FEI NOVA 400 instrument operating at 20 kV with a spotsize 3.0. EDS data were acquired using an Oxford 100 mm^2 UltimMax SDD EDS X-ray detector.

XRD

A Rigaku SmartLab instrument equipped with a copper rotating anode (Cu-Ka, λ = 0.154 nm, 40 kV, 44 mA) and D/teX Ultra detector was used in the powder X-ray diffraction analyses. The 2θ range was 10 to 80°

with a step size of 0.03° and speed of 5°/min. The XRD patterns are analyzed using a whole pattern profile fitting with Rietveld refinement.

Raman

Raman spectroscopy was carried out at an excitation wavelength of 633 nm using a Horiba JY LabRam HR evolution spectrometer. The laser beam was focused on the sample at 1 mW power through a 50x objective. The grating density was 600gr/mm. Spectra were averaged over three runs of 120 s each.

ICP/MS

Inductively coupled plasma mass spectrometry analyses were perfomed using a Thermo Scientific iCAP RQ ICP-MS with a detection limit of < 0.5 ppt, a mass stability of ≤ ± 0.025 u per day.

Photoluminescence

Laser-induced transient emission spectra and kinetics were studied using an Edinburgh Instruments LP980-KS Laser Flash Photolysis Spectrometer. The pump laser was a Nd:YAG laser (10 Hz repetition rate) operating at 355 nm (third harmonic) to pump an Optical Parametric Oscillator (OPO). The system was operated at 1 Hz. The probe was a 150 W pulsed Xenon arc lamp for kinetic and spectral measurements from multi-ns up to 300 µs. Powder samples placed in a NMR quartz tube were analyzed at λ_{exc} = 365 nm.

SI 3D structure

Object file of a threaded connector used to join scintillation vials. The design was created on Tinkercad and printed on an Ender-3 3D printer.

SI Movie 1

The movie shows vaterite tubes being exposed to Pb^{2+} solution for a total of 90 s.

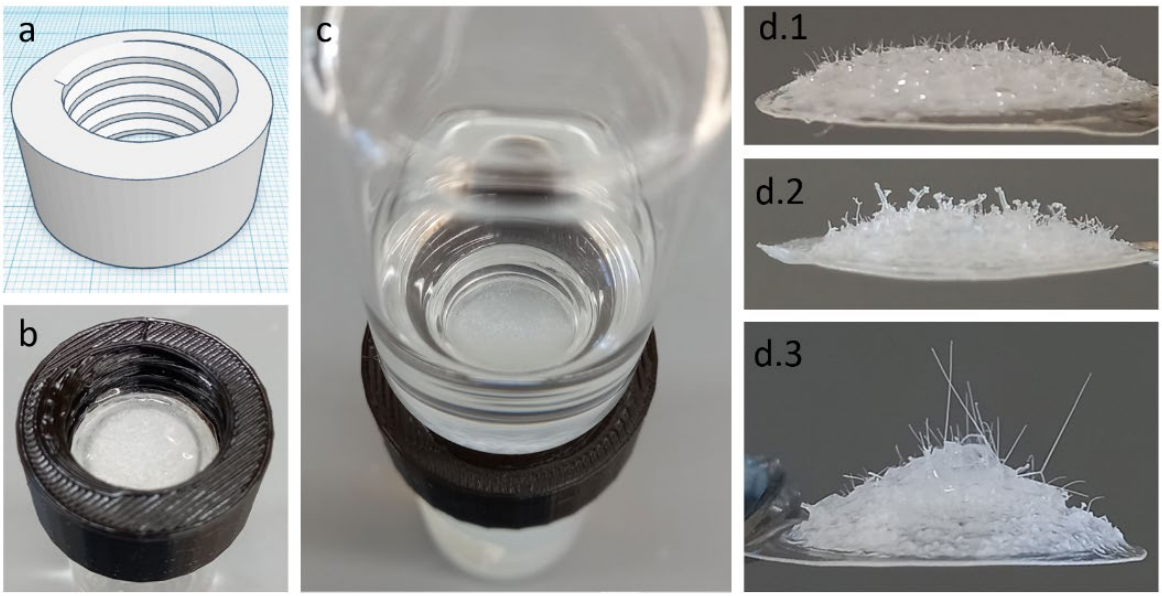

Fig. S1 Photographs of the experimental setup used to grow microtubes. (a) 3D model and (b) 3D-printed threaded connector used to join two scintillation vials together. Outer diameter: 3.2 cm. (c) Precipitate structures and tubes grown on a Nafion membrane placed between the vials. The microtubes are only seen on the Na_2CO_3 side. Pictures d.1-3 show membranes collected after 2, 4, and 7 days, respectively.

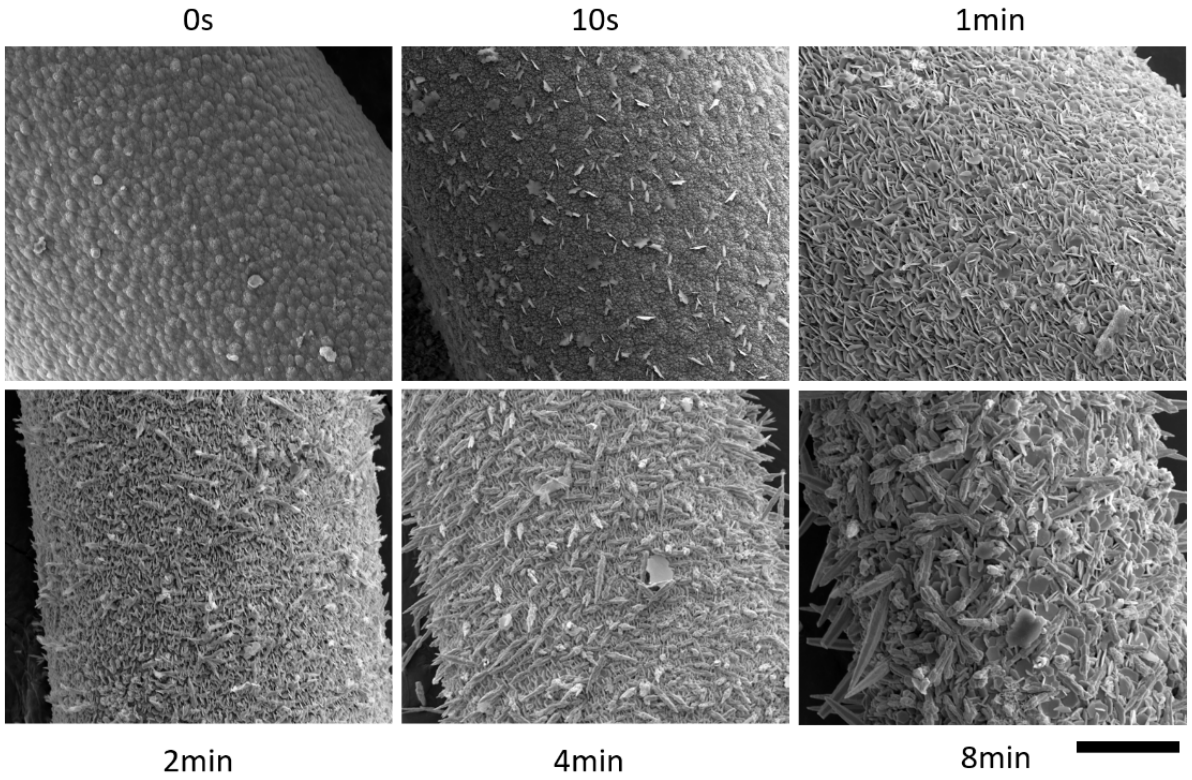

Fig. S2 SEM images of vaterite tubes exposed to 10 mM Pb^{2+} solution for increasing periods of time. Upon contact, the tubes become initially covered with hexagonal plates that are tentatively assigned to hydrocerussite. Over time, needle-like crystals start to grow and, eventually, cover the entire outer surface. They have a typical size of 20 µm but can reach 50 µm when the packing is not tight. XRD and Raman analyses indicate a cerussite composition. Scale bar: 50 µm. We note that the majority of tubes are covered with needle-like structures after 24 h. A small fraction remains covered with hexagonal plates only. These crystals are tightly packed and might exhibit long-range order.

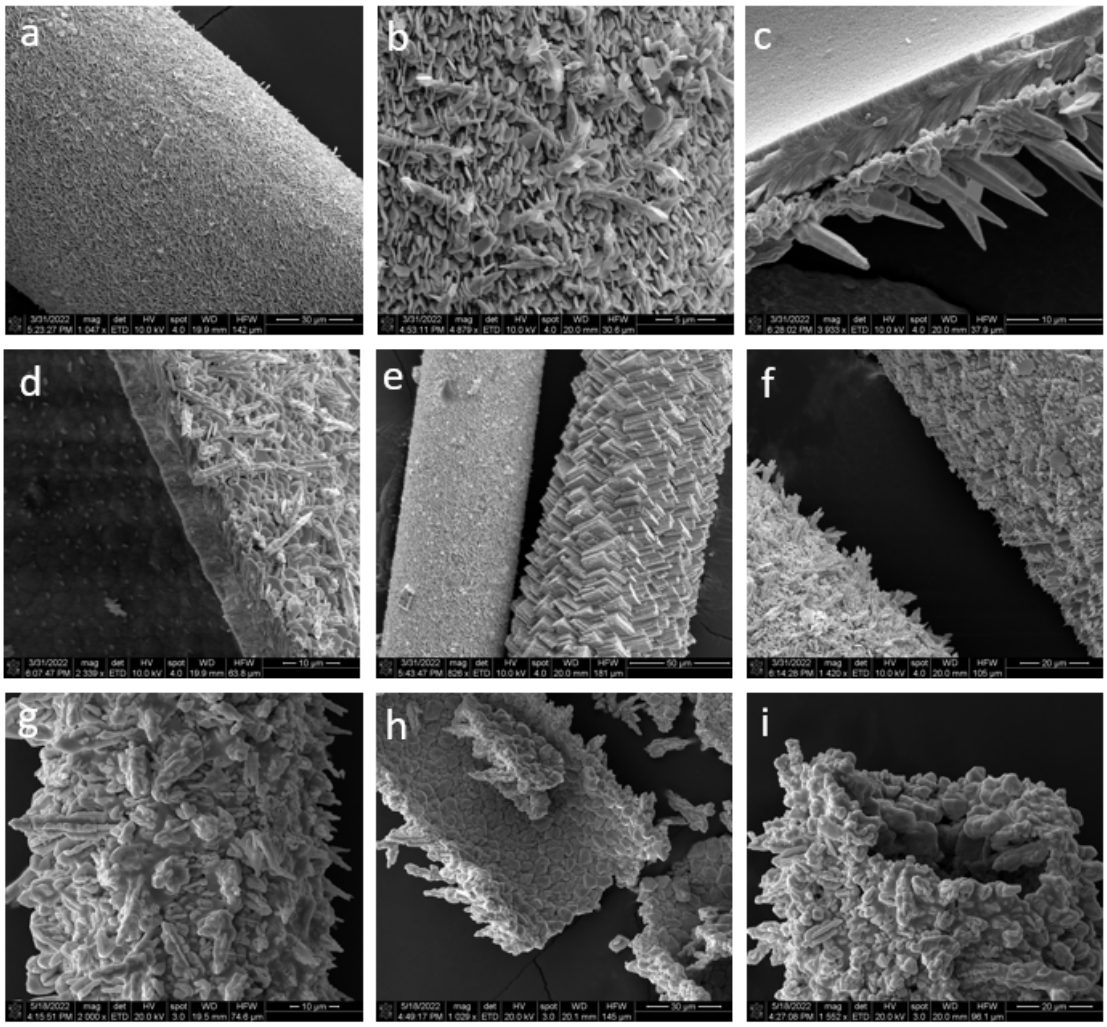

Fig. S3 SEM images of $PbCO_3$ and perovskite tubes. (a,b) Tube covered with hexagonal hydrocerussite platelets and early cerussite structures. (c,d) Cross-section images of tubes converted to cerussite. (e,f) Comparison between vaterite and calcite tubes exposed to Pb^{2+} solution for 24 h. (g-i) Surface and cross-section images of perovskite tubes. Scale bars are shown individually.

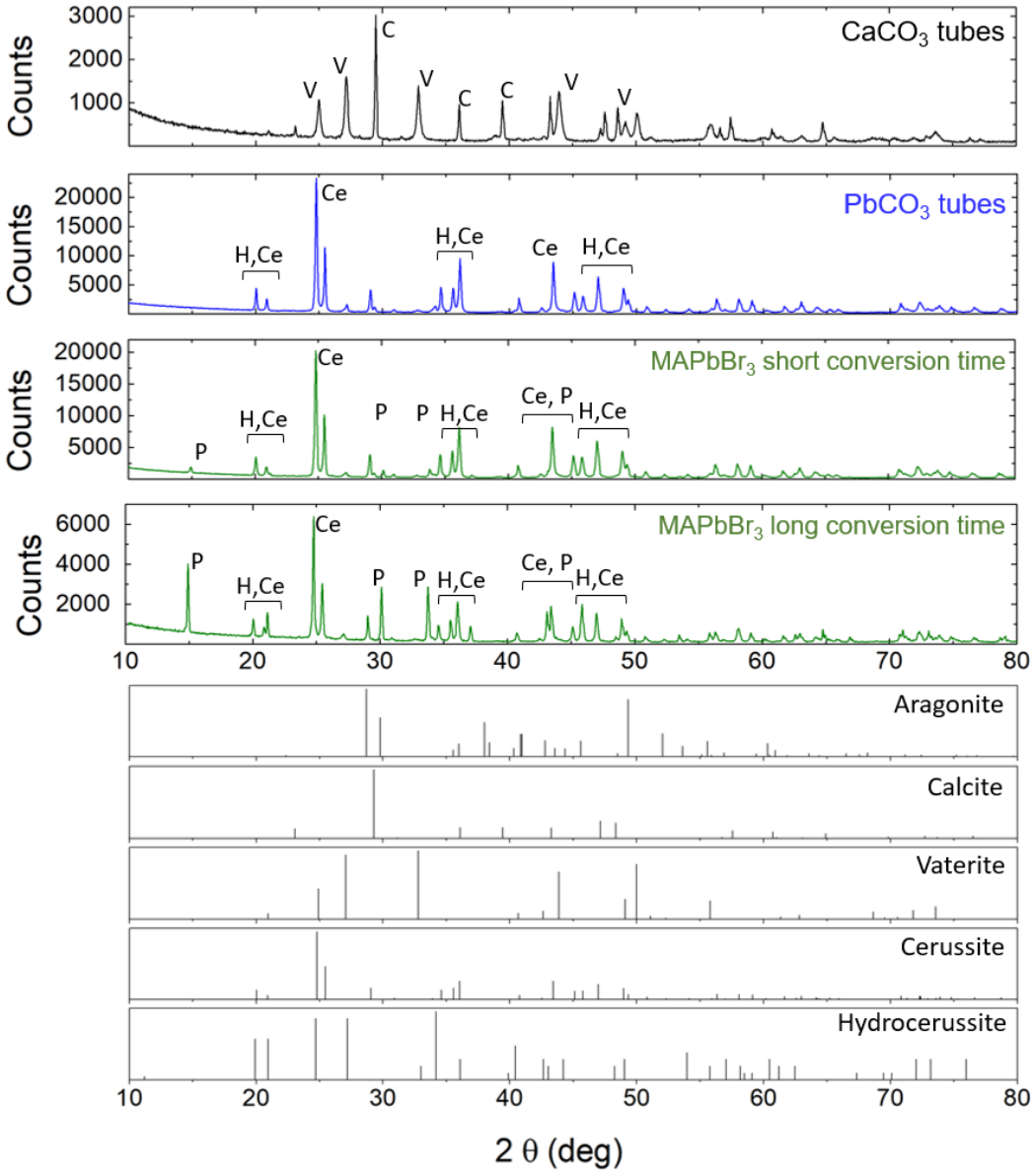

Fig. S4 XRD patterns obtained for powdered samples collected during different stages of the synthesis process. The outer surface of calcite and vaterite tubes is converted to cerussite and hydrocerussite structures. These are, in turn, converted to perovskite during the last stage. The panels at the bottom show typical diffraction patterns for well-known polymorphs of $CaCO_3$ and $PbCO_3$ (source: Cambridge Crystallographic Data Centre).

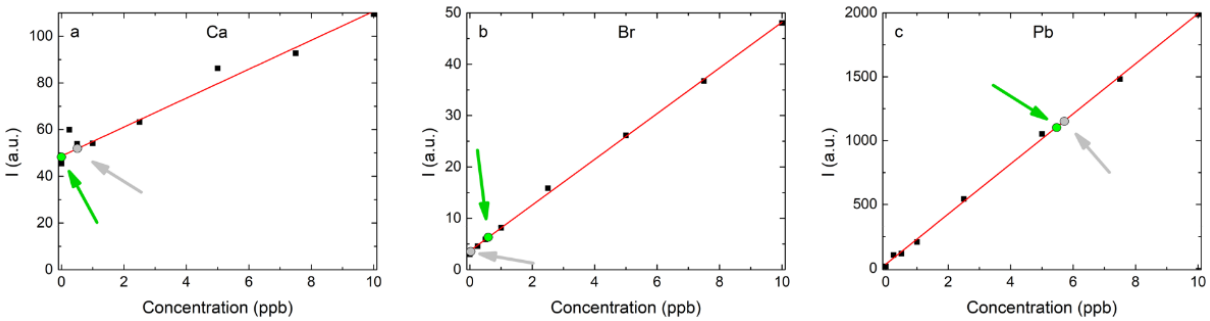

Fig. S5 ICP-MS signal intensities of Ca, Br, and Pb obtained for $PbCO_3$ tubes (gray arrow) and perovskite tubes (green arrow). The samples were digested in 2% (w/v) HNO_3.

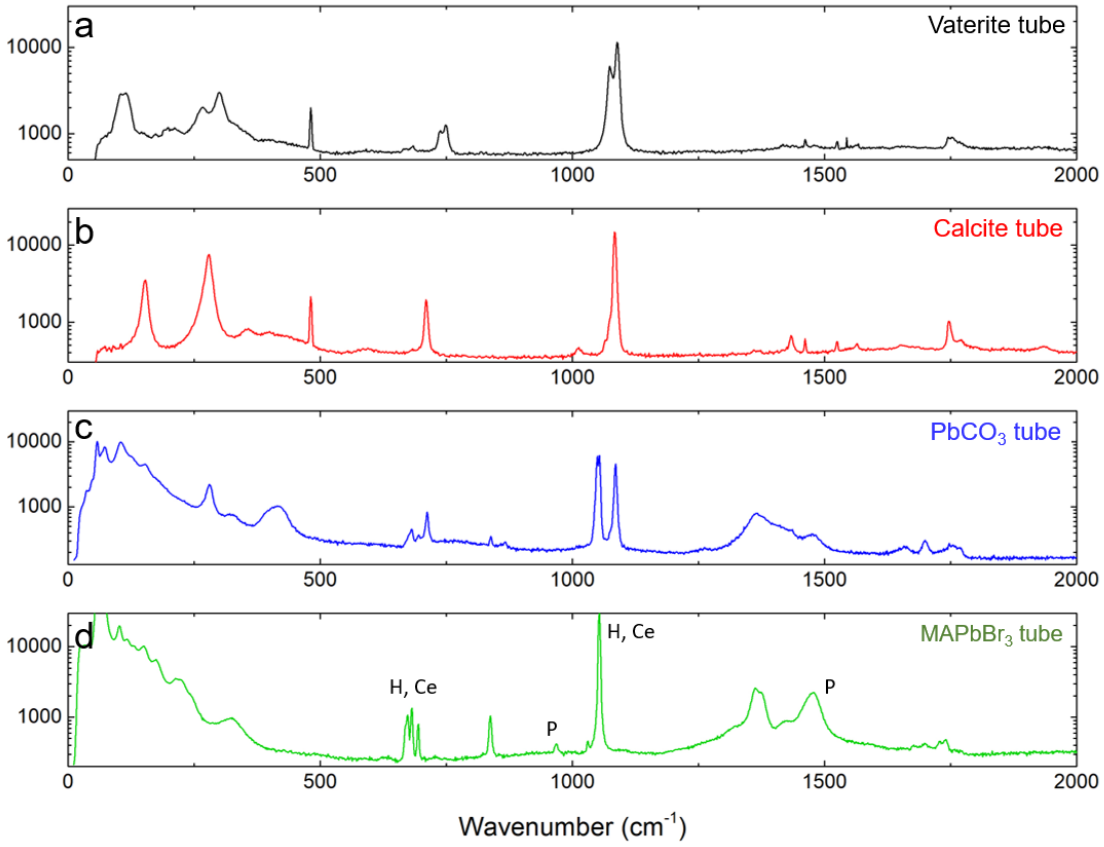

Fig. S6 Micro-Raman spectra obtained during different stages of the conversion process. Spectra collected on (a) vaterite and (b) calcite surfaces of unconverted $CaCO_3$ tubes. Spectra collected on (c) a cerussite crystal of a $PbCO_3$ tube and (d) a perovskite tube.

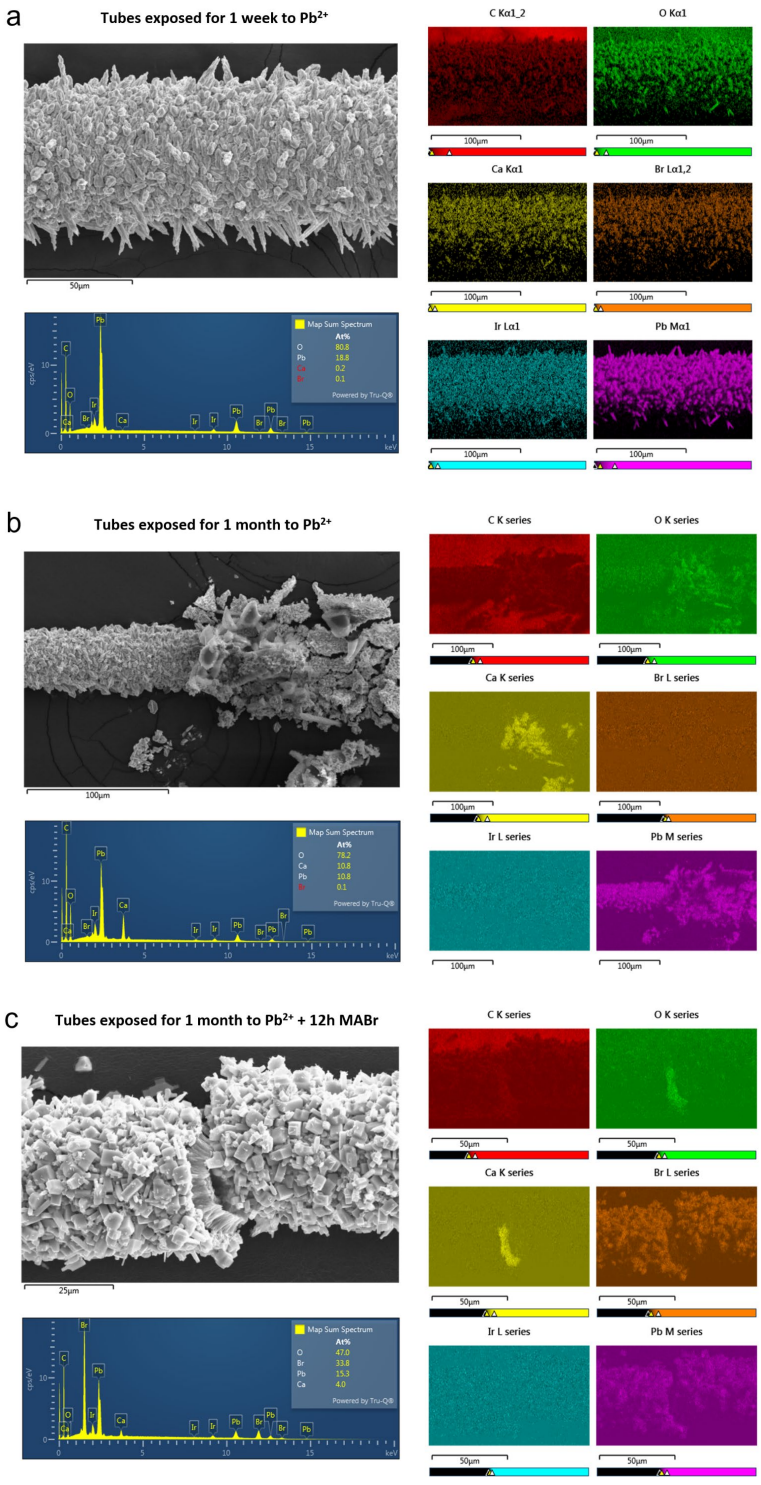

Fig. S7 SEM and EDS maps of samples exposed to Pb^{2+} and MABr for different periods of time. (a) A tube exposed to Pb^{2+} solution for one week reveals no trace of calcium on the outside surface; (b) a tube exposed to Pb^{2+} solution for one month (and subsequently crushed) has calcium in its interior; (c) a tube exposed to Pb^{2+} solution for one month and to MABr solution in IPA for 12 h (and subsequently crushed) also reveals calcium in its interior.

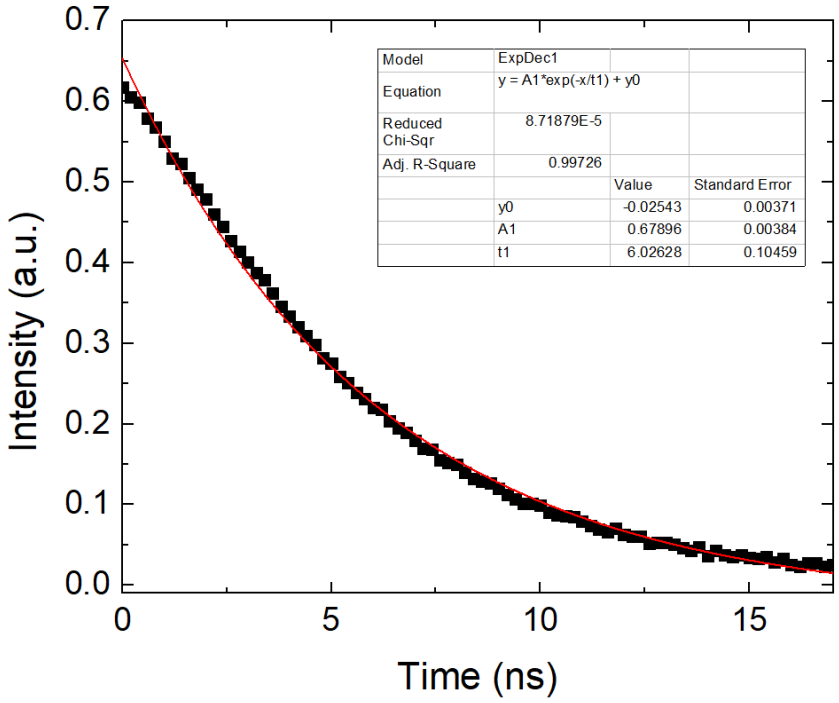

Fig. S8 Photoluminescence decay experiment with a single exponential curve fitted. The measurement was performed at λ_{exc} = 365 nm.

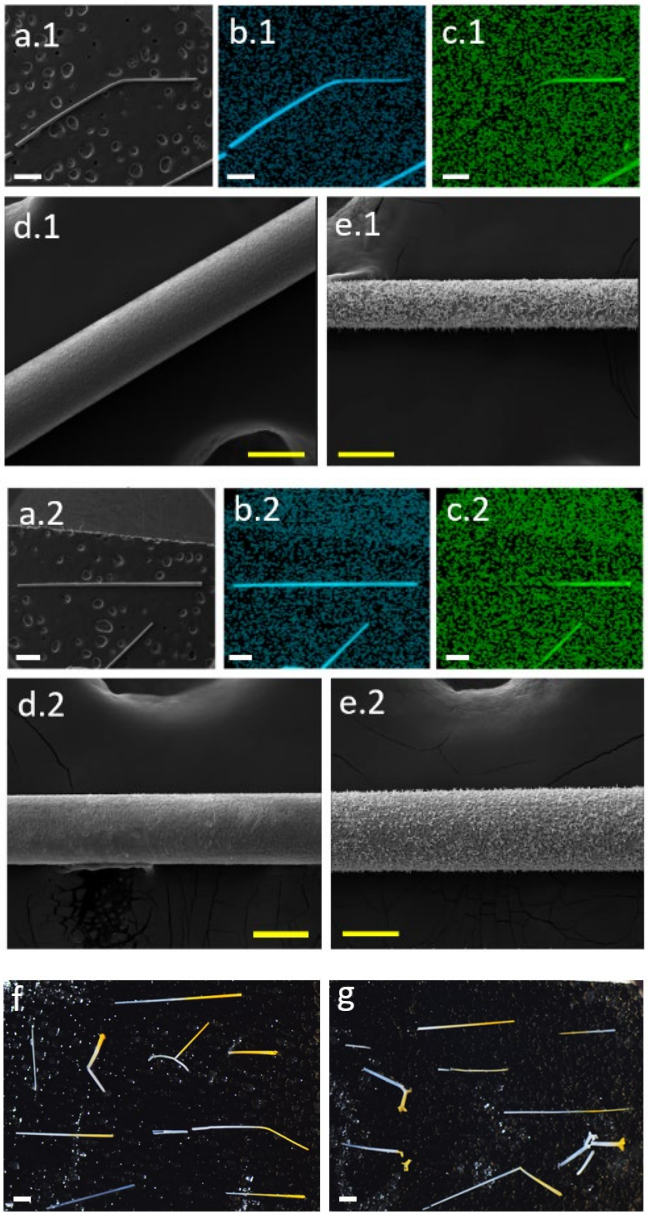

Fig. S9 Janus tubes prepared by partial immersion of vaterite tubes in Pb^{2+} solution for 1 min followed by immersion in MABr solution (three times for three seconds each). (a-c) SEM images and EDS maps of Ca and Pb, respectively. (d,e) Microstructure of the (d) unconverted and (e) perovskite-containing sides. (f,g) Examples of Janus tubes prepared. Scale bars: 500 µm (white), 50 µm (yellow).