Supporting Information

All-inorganic lead halide perovskite nanohexagons for high performance air stable Lithium Batteries

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Material synthesis and fabrication of the anode

Materials. All reagents were of relatively high-purity. The $PbBr_2$ (trace metals basis, 99.999 %), CsBr (anhydrous, 99.999 %), oleic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, technical grade, 90 %) and toluene (anhydrous, 99.8%) were purchased from Aldrich. The N,N-Dimethylformamide (DMF, anhydrous, 99.8 %) was purchased from Alfa-Aesar and the oleylamine ($CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2$, approximate C18-content 80-90 %) from ACROS Organics. The oleic acid has been degassed for 1 hour under vacuum at 120 °C and stored in the GloveBox. All the reagents were stored and handled under Ar atmosphere in a glove box (MBRAUN, UNILab).

Synthesis of all-inorganic perovskite nanocrystals. In a typical synthesis, a stock solution of $PbBr_2$ (0.4 mmoles) and CsBr (0.4 mmoles) in 10 ml of anhydrous DMF was prepared in a sealed vial closed under Ar in protective atmosphere of a GloveBox. The solution was maintained under stirring until the complete dissolution of the precursors. Then, 1 ml oleic acid (OA) and 0.5 ml oleylamine (OLAm) were added in the above solution. Afterwards, 0.9 ml of this solution was added rapidly in 10 ml of anhydrous toluene (10 ml) in a sealed vial under vigorous stirring (1000 RPM). This vial was placed in ice before the addition of the stock solution and sustained under stirring for 30 minutes. Subsequently, it was retained on the bench for a week under ambient conditions. Then, the perovskite nanocrystals were separated upon centrifugation at 1000 RPM for 5 min and finally re-dispersed in toluene.

Fabrication of assembly's structures. A small amount of 30 μl of the toluene perovskite nanohexagon solution has been dropped on a piece of ITO (1×0.5 mm) precoated glass to spread all over the substrate and dry for a few minutes. Then, repeated annealing cycles were carried out at 220 °C for 3 min for the perovskite nanocrystals depositions.

Pulsed laser deposition (PLD) of TiO_x coatings. The TiO_2 targets used in PLD were prepared by pressing (room temperature, 4 metric tons for 2 min) 1 gr of 99 % pure TiO_2 powder (Sigma Aldrich). Pulsed laser ablation of the solid targets and subsequent film deposition were performed into a high vacuum ($3x10^{-6}$ mbar) chamber using a KrF excimer laser (248 nm, 20 ns, pulse repetition rate 10 Hz) emitting an energy density (fluence) of 2 J/cm^2. The laser spot size was adjusted by a movable focusing lens, while the laser fluence was tuned by an optical attenuator. The target-to-substrate distance and number of the laser pulses used were 5 cm and 1000 respectively.

Characterization

a) SEM (JEOL 7000), equipped with an EDS (INCA PentaFET-x3), was used for the analysis of the samples. These experiments were performed on the perovskite hexagons before and after the electrochemical scans. For the size distribution diagrams, 150 individual nanohexagons were counted up.

b) XRD studies were performed on a Rigaku D/MAX-2000H rotating anode diffractometer with Cu Kα radiation, equipped with a secondary graphite monochromator. The XRD data were collected at room temperature over a 2θ scattering range of low angle, with a step of 0.02 ° and a counting time of 20 s per step. The perovskite hexagons have been measured before and after the electrochemical scans.

c) Low magnification and HRTEM images were recorded on a LaB6 JEOL 2100 transmission electron microscope operating at an accelerating voltage of 200 kV. All the images were recorded by the GatanORIUS TM SC 1000 CCD camera. For the purposes of the TEM analysis, a drop of the as-prepared toluene-based solution was deposited onto a carbon-coated copper TEM grid, which was eventually evaporated. The structural features of the nanohexagons were studied through FFT patterns obtained from the HRTEM images.

d) Electrochemical measurements: A standard three-electrode electrochemical cell[1-3] was utilized as reported previously using 0.05 M, LiCl aqueous solution, scan rate of 10 mV s^{-1} at potential ranging from -1.0 V to +0.5 V vs. Ag/AgCl reference electrode.[4, 5] The counter electrode was Pt and the working electrode was the all-inorganic lead halide perovskite nanohexagons grown on ITO precoated glass substrates. Cyclic voltammograms were also carried out at scan rates of 10, 25, 50, 75, 100 and 200 mV s^{-1} for the diffusion coefficient estimation. Galvanostatic measurements were obtained at specific current of 45, 90 and 200 mA g^{-1} and potential ranging -1 V to +0.1 V for a number of scans up to 100. Finally, electrochemical impedance spectroscopy (EIS) was performed for alternating current (AC) amplitude 5.0 mV and set potential -0.2 V over the frequency range 10 mHz - 100 kHz.

e) Crystal structures Visualization: The crystal structure in the Figure S6 is visualised using the Diamond 3.0 software.[6]

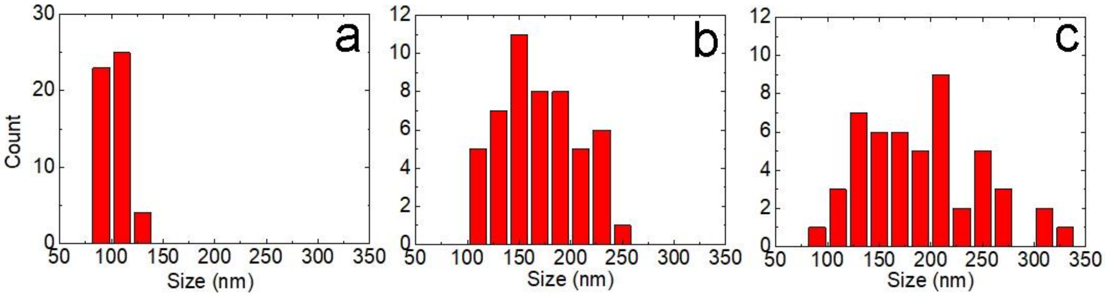
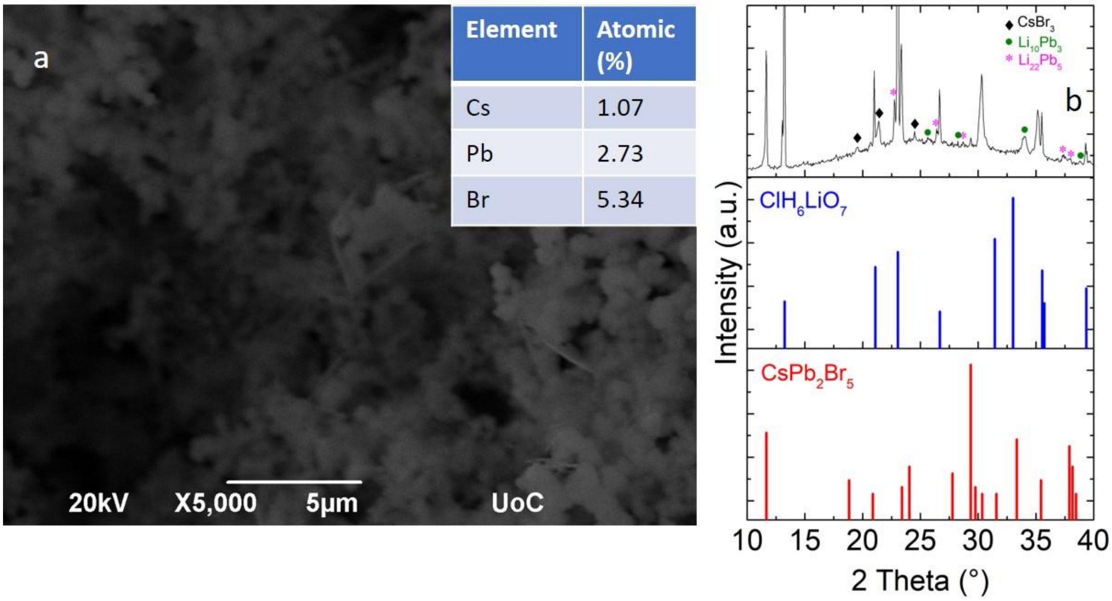


Figure S1. Size distribution diagrams of the non-annealed (a), 3-annealed (b) and 5-annealed (c) samples.



Element	Atomic (%)
Cs	1.07
Pb	2.73
Br	5.34

Figure S2. SEM image (a), EDS analysis (a-inset) and XRD pattern (b) of the 5-annealed sample after 100 scans.

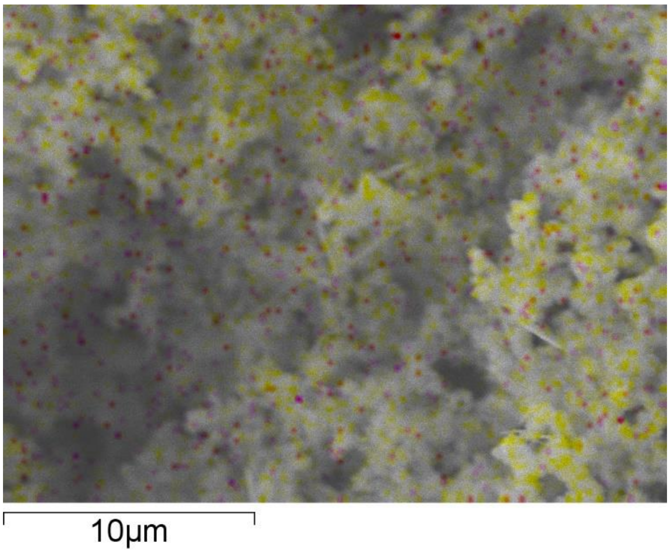
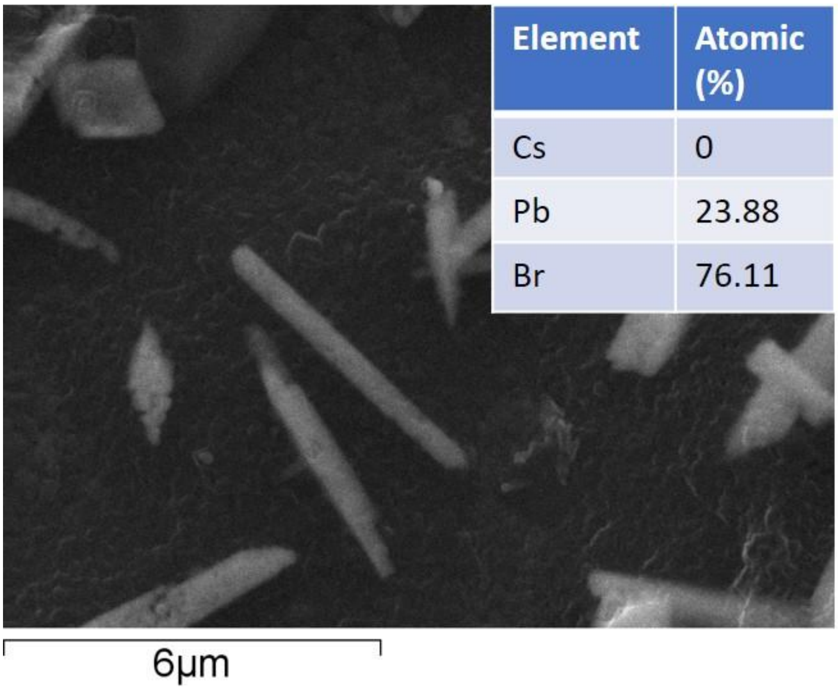


Figure S3. Energy Dispersive Spectroscopy (EDS) mapping for the titanium (yellow) and oxygen (magenta) elements of the same area of the Figure S1.



Element	Atomic (%)
Cs	0
Pb	23.88
Br	76.11

Figure S4. SEM image and EDS analysis of the 5-annealed sample after 40 scans. The rods are $PbBr_x$.

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6. *Diamond - Crystal and Molecular Structure Visualization*

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http://www.crystalimpact.com/diamond.