Supporting Information:

Hydrothermal Synthesis of Organometal Halide Perovskites for Li-ion Batteries

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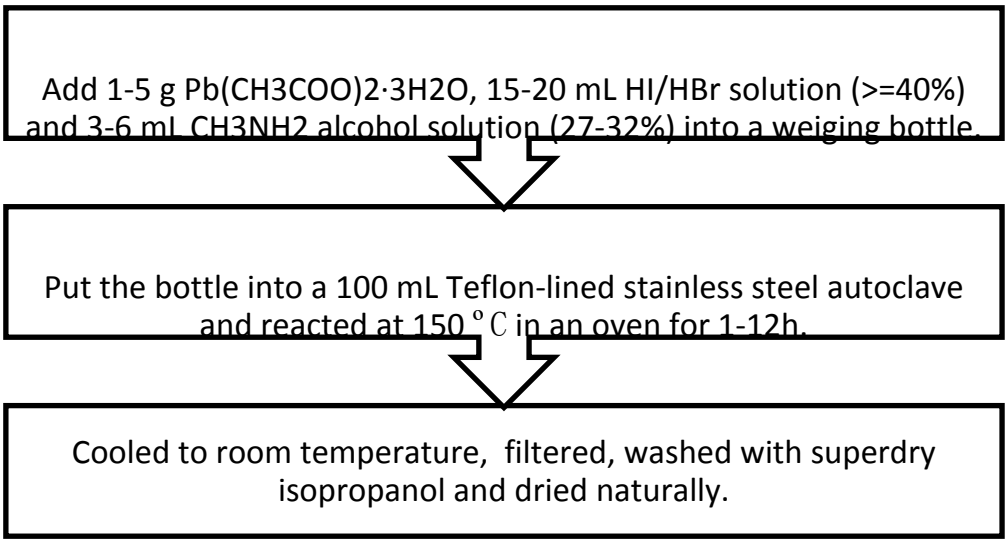
1. Synthesis of perovskite $CH_3NH_3PbX_3$(X=Br, I)

In a typical process, 1-5 g lead acetate ($Pb(CH_3COO)_2 \cdot 3H_2O$, $Pb(Ac)_2 \cdot 3H_2O$; Analytical Reagent, AR; Beijing Chemical Reagent Company) was added into a weighing bottle with the size of 30 × 70 mm. Then, 15-20 mL HI/HBr solution (HI, ≥ 45%; AR; Sinopharm Chemical Reagent Co., Ltd; HBr, ≥ 40%; AR; Sinopharm Chemical Reagent Co., Ltd) and 3-6 mL methylamine alcohol solution (CH_3NH_2, 27.0-32.0%; CP; Sinopharm Chemical Reagent Co., Ltd) were added into the bottle. After that, put the bottle into a 100 mL Teflon-lined stainless steel autoclave, and heated at 150 ℃ in an oven for 1-12 h. Finally it was taken out and cooled down to room temperature naturally. The obtained product was filtered, washed with superdry isopropanol (99.5%; J&K Scientific) and dried naturally.

To make the process clearer, the synthesis scheme for $CH_3NH_3PbX_3$ was described in Scheme S1.



Scheme S1. Synthesis process of the perovskite $CH_3NH_3PbX_3$.

2. Material Characterizations of the perovskite $CH_3NH_3PbX_3$

A Rigaku D/max-rA12kW X-ray diffraction system equipped with a Cu Kα X-ray tube operated at 40 kV and 100 mA using a step size of 0.02°at a scanning rate of 8 degree per min was used to characterize the crystal structure of the obtained powder. The EDX (Energy Dispersive X-Ray Spectroscopy) spectrum of the product was measured under a FEI Tecnai G2 T20 TEM (transmission electron microscopy) to analyze the composition. And a field-emission gun FEI Quanta 600F SEM (scanning electron microscopy) was used to characterize the morphology of the materials.

3. Electrochemical Characterization

Standard CR2032 coin cells were assembled in an argon-filled glove box with the moisture content less than 1 ppm to test the electrochemical performance of the as-synthesized product. The test electrodes were made of perovskite $CH_3NH_3PbBr_3$ (or $CH_3NH_3PbI_3$), conductive carbon black and PVDF binder in an 80:10:10 mass ratio, which were coated on circular copper-foil current collectors with the diameter of 12 mm. Lithium metal electrode with the diameter of 16 mm and the thickness of 0.6 mm was used as the counter electrode. Two electrodes were separated by a layer of 25 μm polymer membrane (Celgard®, average pore size: 43 nm) with 1 mol/L $LiPF_6$ solution in EC+EMC+DMC (ethylene carbonate+ ethylmethyl carbonate+ dimethyl carbonate, volume ratio=1:1:1) as the electrolyte.

A LAND BT2013A 8-channel automatic battery test system (Wuhan Lanbo Test Equipment Co., Ltd) was used to measure the charge-discharge capacity and cycle performance. Cyclic voltammetry was tested on a CHI660C electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd) at a sweep voltage range of 0.01-2.0 V with the rate of 1 mV/s.

Table S1. Refined XRD result of the synthesized perovskite $CH_3NH_3PbBr_3$ (a=5.9394 Å, space group=Pm-3m) and comparative results with standard perovskite material $CH_3NH_3PbBr_3$ (a=5.9334 Å, space group=Pm-3m, Ref. 12 in the text)[1].

hkl	d (Å)	Exp. d (Å)	2-theta (°)	Exp. 2-theta (°)	Ref. d (Å)	Ref. 2-theta (°)
100	5.9394	5.9686	14.903	14.83	5.939482	14.91526
110	4.1998	4.2308	21.137	20.98	4.19655	21.15379
111	-	-	-	-	3.42647	25.98318
200	2.9697	2.9829	30.067	29.93	2.96741	30.09099
210	2.6562	2.665	33.715	33.6	2.65413	33.74296
220	2.0999	2.1045	43.039	42.94	2.09828	43.07498
300	1.9798	1.9828	45.793	45.72	1.97827	45.83172
310	1.8782	1.8798	48.424	48.38	1.87676	48.46513
222	1.7146	1.7146	53.392	53.39	-	-

320	1.6473	1.6489	55.758	55.7	-	-
321	1.5874	1.5891	58.058	57.99	-	-
400	1.4849	1.4863	62.498	62.43	-	-
410	1.4405	1.4415	64.651	64.6	-	-
330	1.3999	1.3993	66.765	66.8	-	-
420	1.3281	1.3282	70.9	70.89	-	-
421	1.2961	1.2959	72.927	72.94	-	-
430	1.1879	1.1867	80.85	80.95	-	-
510	1.1648	1.1643	82.797	82.84	-	-
432	1.1029	1.1021	88.598	88.68	-	-

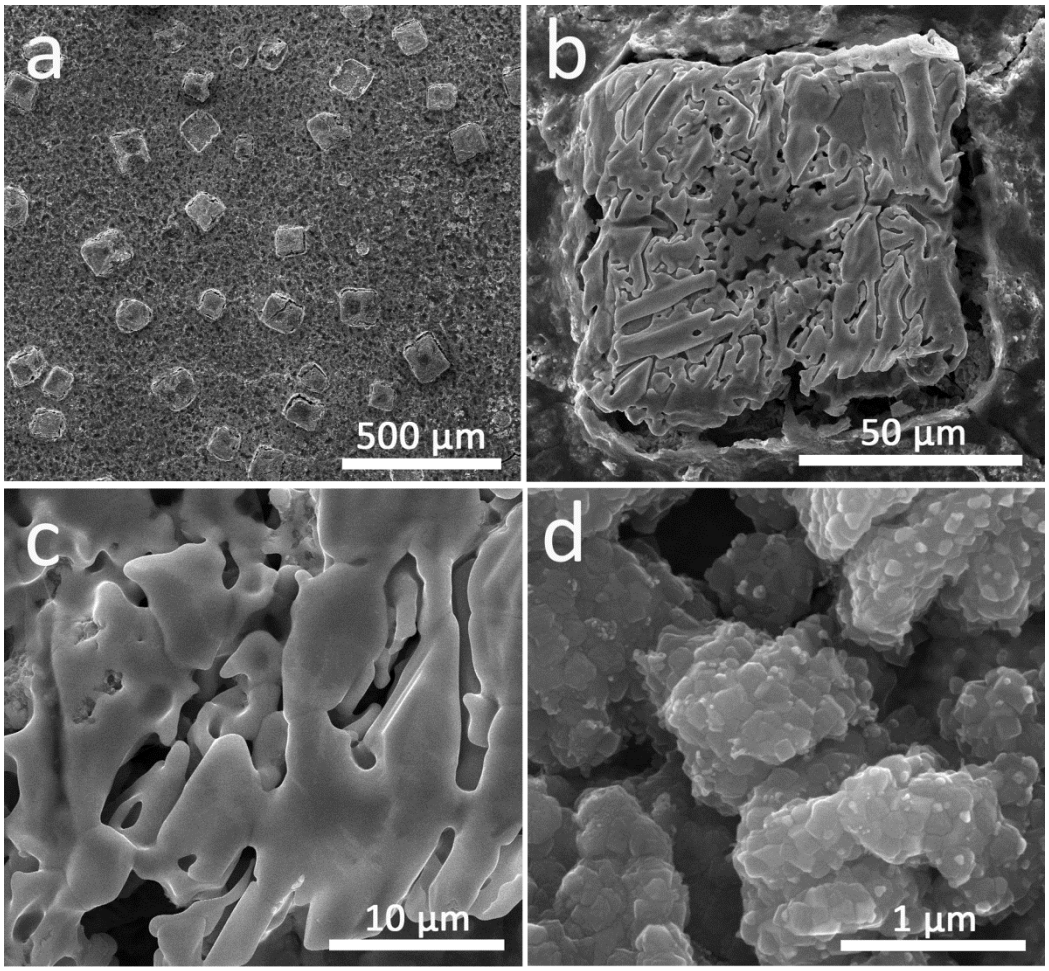


Fig. S1 SEM images of the as-prepared $CH_3NH_3PbBr_3$ test electrode with different magnifications (scale bar: 500 µm for a, 50 µm for b, 10 µm for c, 1 µm for d).

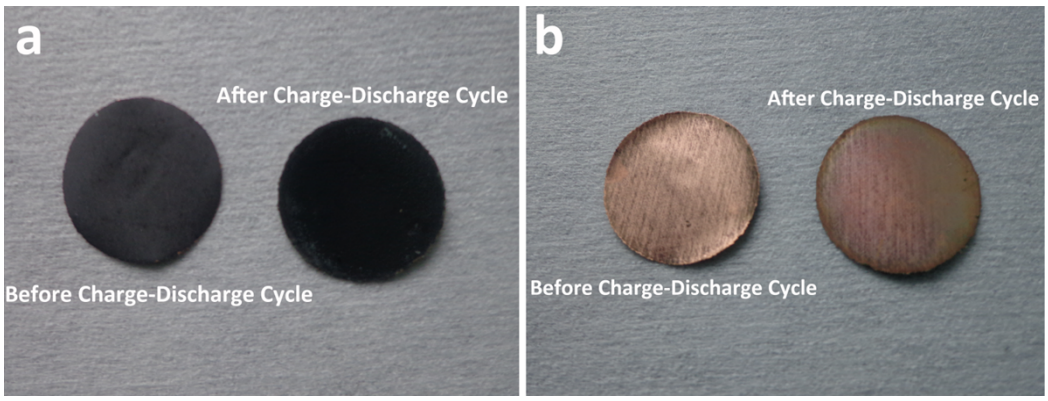


Fig. S2 Photographs of the test electrodes before and after charge-discharge cycles: (a) One side with active material $CH_3NH_3PbBr_3$. (b) The other side of the Cu foil with diameter of 14 mm.

REFERENCE

1. L. C. Schmidt, A. Pertegás, S. González-Carrero, O. Malinkiewicz, S. Agouram, G. Mínguez Espallargas, H. J. Bolink, R. E. Galian and J. Pérez-Prieto, *J. Am. Chem. Soc.*, 2014, **136**, 850-853.