Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Mechanochemical Syntheses of All-Inorganic Iodide Perovskites from Layered Cesium Titanate and Bismuth (and Antimony) Iodide

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Experimental section

Chemical and Reagents: Anatase (99.8%, Aldrich), Cs_2CO_3 (99%, Alfa Aesar), CsI (>99%, TCI), BiI_3 (Anhydrous, TCI), and SbI_3 (ultra-dry, 99.999% (metal basis), Alfa Aesar) were used without further purification.

Preparation of layered cesium titanate ($Cs_2Ti_5O_{11}$):

$Cs_2Ti_5O_{11}$ were prepared by solid-state reactions according to previously reported methods.[1] $Cs_2Ti_5O_{11}$ was synthesized by the heating of a mixture of Cs_2CO_3 and anatase at the molar ratio of 1:5 at 1000°C for 20 h.

Synthesis of $Cs_3Bi_2I_9$/Titanate (CBI/T) by mechanochemical reactions.

(i) By one-time addition: BiI_3 (173 mg) was added into $Cs_2Ti_5O_{11}$ (100 mg) in the solid-state. Then, A stoichiometric mixture was manually ground with an agate mortar and a pestle under ambient atmosphere for 30 min. The product was denoted as i1.

(ii) By portion-wise addition: A portion of BiI_3 (one-fourth of 173 mg, *ca.* 43 mg) was mixed with $Cs_2Ti_5O_{11}$ (100 mg) in an agate mortar and a pestle for 7 min (or until the orange solid was seen). Then, the subsequent addition of BiI_3 (*ca.* 43 mg) into the mixture was done and the operation was repeated for 4 times in total to reach a stoichiometric ratio of 1:2 for $Cs_2Ti_5O_{11}$ and BiI_3. (the amounts are given in the supporting information Table S1.)

Synthesis of $Cs_3B_2I_9$ (CBI) by mechanochemical reactions:

A mixture of CsI (76.3 mg) and BiI_3 (115.4 mg) was manually ground using an agate mortar and a pestle for 30 min (or until obtaining homogeneous orange powder).

Table S1. Weight of the starting materials employed.

Cs precursor	BiI_3				Sample's abbreviation
100 mg ($Cs_2Ti_5O_{11}$)	173 mg				i1
100 mg ($Cs_2Ti_5O_{11}$)	*ca.* 43 mg	*ca.* 43 mg	*ca.* 43 mg	*ca.* 43 mg	CBI/T
76.3 mg (CsI)	115.4 mg				CBI

*The weight loss of all the experiments based on the starting materials was ≤ 5%, which occurred during the collection of the products after the reaction.

Synthesis of $Cs_3Sb_2I_9$/Titanate (CSI/T) by mechanochemical reactions.

A mixture of SbI_3 (162.4 mg) and $Cs_2Ti_5O_{11}$ (100 mg) was manually ground with an agate mortar and a pestle under ambient atmosphere for 15 min.

Characterization

Powder X-ray diffraction patterns (XRD) of the products were recorded using Bruker New D8 Advance instrument equipped with Ni filter (Cu Kα radiation). The XRD patterns were recorded immediately after the grinding at the scan speed of 5.67°/min. Scanning electron micrographs and elemental mapping images were obtained on an Oxford energy dispersive X-ray fluorescence spectrometer (X-Max 150 mm^2) equipped with SEM (JEOL, JSM7610F) instrument without coating. UV-Vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda 1050 (PerkinElmer, U.S.A.) using integrated sphere and polytetrafluoroethylene as the reference. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-ARM200F high-resolution transmission electron microscopy. Elemental mapping was derived by an energy dispersive X-ray (EDS) analyses using EX-230BU EDS detector equipped with the JEOL JEM-ARM200F transmission electron microscope. Sample specimen was prepared by dispersing the sample in a hexane using ultrasonic homogenizer for a few minutes.

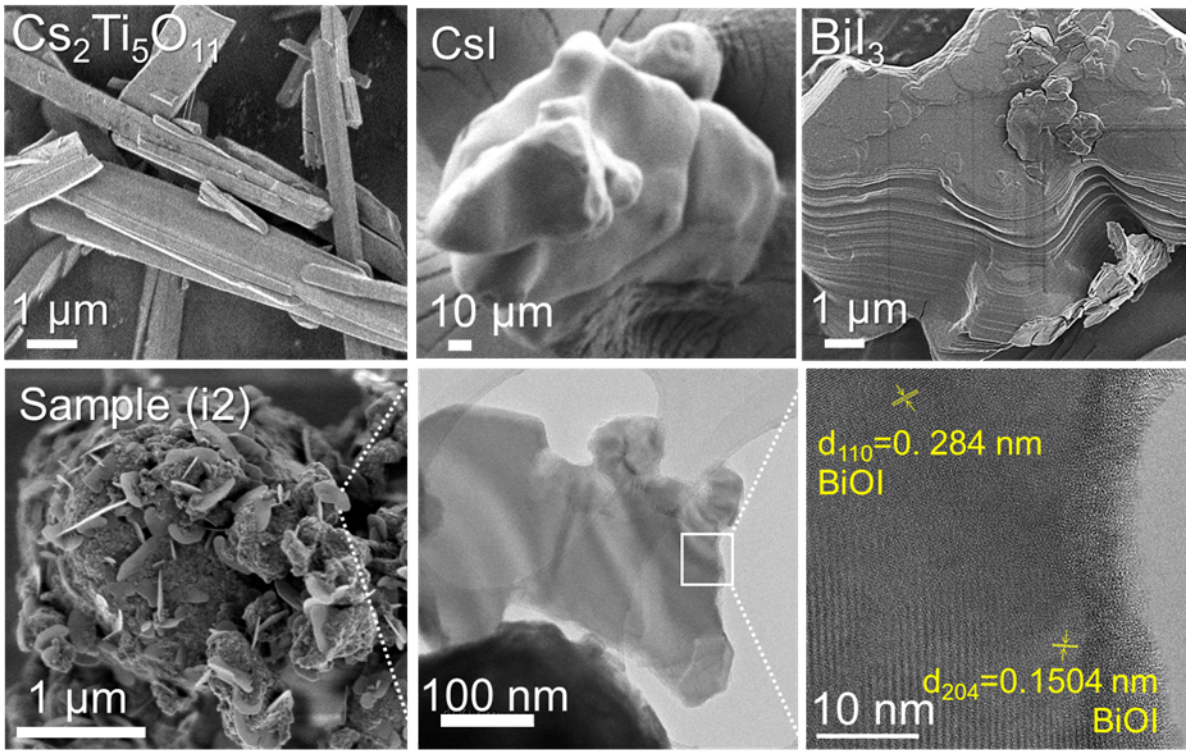

Fig. S1. SEM images of $Cs_2Ti_5O_{11}$, BiI_3, and CsI (top), and SEM, TEM, and HRTEM images of the sample (i2), which were obtained by one-time addition of BiI_3 to $Cs_2Ti_5O_{11}$ and subsequent grinding for an hour (bottom).

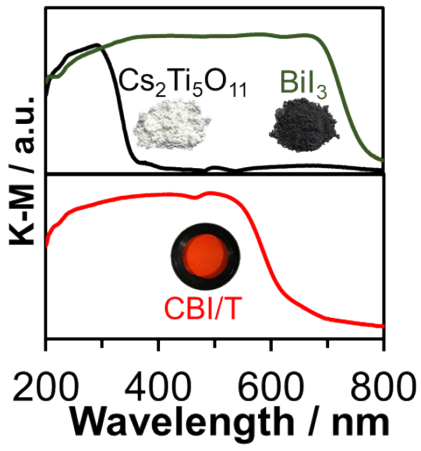

Fig. S2. UV-DRS spectra and the appearance of the starting materials ($Cs_2Ti_5O_{11}$ and BiI_3) and the CBI/T.

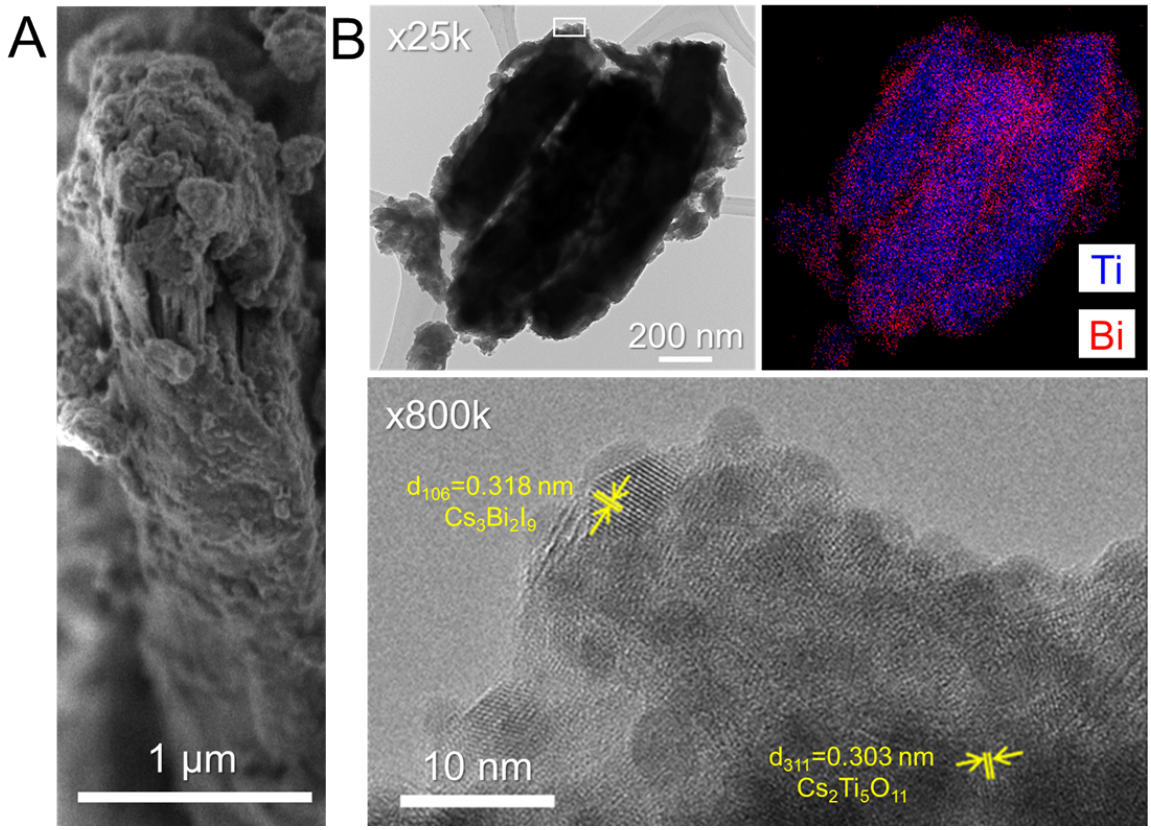

Fig. S3. (A) SEM, (B) TEM/EDX and HRTEM images (at the selected area) of CBI/T. The elements were presented by Ti (blue) and Bi (red).

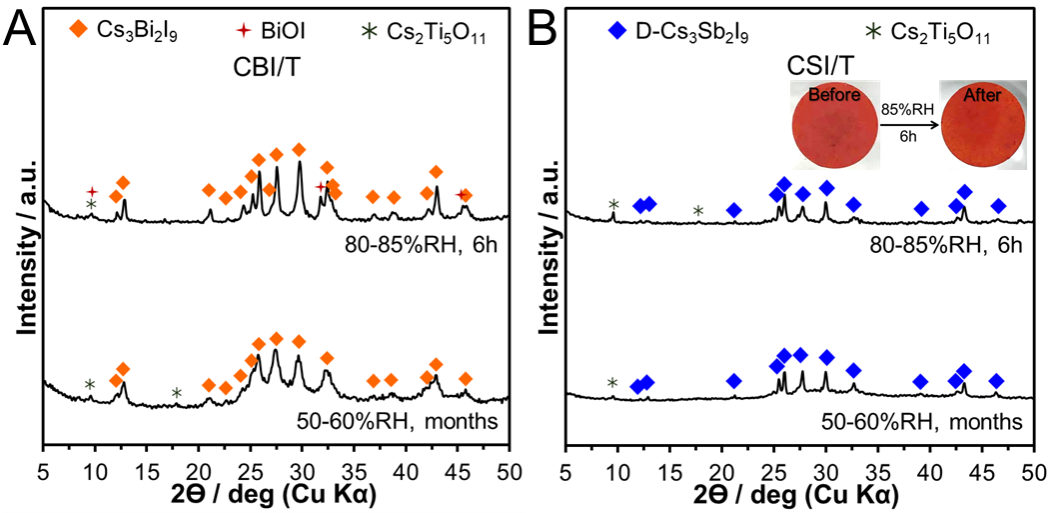

Fig. S4. XRD patterns of (A) CBI/T and (B) CSI/T stored under the relative humidity of 50-60% and 80-85%.

Reference

[1] I. E. Grey, I. C. Madsen, J. A. Watts, L. A. Bursill, J. Kwiatkowska. *J. Solid State Chem*. **1985**, *58*, 350-356.