Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

Solution Synthesis and Phase Control of Inorganic Perovskites for High-performance Optoelectronic Devices

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Methods

Synthesis of inorganic perovskite cesium lead halides ($CsPbX_3$, X = Br or I)

Inorganic perovskite $CsPbX_3$ were fabricated by a facile and low-cost solution-phase approach. Typically, 0.01 mol lead acetate ($Pb(Ac)_2$) and 0.01 mol cesium acetate ($Cs(Ac)_2$) were added into 25 mL haloid acid (HBr or HI, 47 wt.%) aqueous solution and stirred for 30 min. The mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and placed into an oven, and then heated at 150 °C for 2 h. After the reaction, the autoclave was token out from the oven and rapidly cooled to room-temperature by water flushing. The as-obtained product was washed with anhydrous isopropanol for several times and dried in a vacuum oven at 60 °C. For each batch of synthesis, the yields are around 7.0 g (~97%) for $CsPbI_3$ and 5.7 g (~98%) for $CsPbBr_3$, respectively.

Fabrication of y-$CsPbI_3$ and b--$CsPbI_3$ based photodetectors

Firstly, FTO glass substrate (with the FTO thickness of ~1 μm and the size of 2 × 2 cm) was etched by 2.0 M HCl and Zn powder to fabricate two separated FTO electrodes with a spacing of 3 mm. Subsequently, the FTO substrate was cleaned with acetone, ethanol, and deionized water, and then dried in air. Typically, 360 mg of y-$CsPbI_3$ product was put in an Ar-filled glovebox, dissolved into 1.0 mL dimethylformamide (DMF), and then spin-coated on the patterned FTO substrate to prepare y-$CsPbI_3$ film. To convert the orthorhombic phase y-$CsPbI_3$ to the cubic perovskite phase b-$CsPbI_3$, an additional step was carried out by heating the y-$CsPbI_3$ film to 335 °C for more than 1 min. To prevent the influence of ambient environment, the as-fabricated two-terminal photoreactor was encapsulated by a piece of cover glass using a hot-melt spacer (Surlyn 1702, 30 μm thick, Solaronix), as shown in the insets of Figure 3a,b.

Fabrication of b-$CsPbI_3$/carbon based all-inorganic perovskite solar cells

The FTO substrate were patterned and cleaned with the same method mentioned above. The c-TiO_2 layer was deposited on the FTO substrate by spin-coating a mixed ethanol solution of 0.5 M titanium isopropoxide and 0.5 M diethanol amine at 7000 rpm for 30 s, and the annealing in air at 500 °C for 2 h. The m-TiO_2 layer was deposited by spin-coating a mixture of TiO_2 paste (with average particle size of 20 nm) and ethanol with a weight ratio of 1:8 at 5000 rpm for 30 s and sintering at 500 °C for 30 min; subsequently, the FTO substrate was immersed into a 0.04 M $TiCl_4$ aqueous solution at 70 °C for 30 min, cleaned with water and ethanol, and then annealed at 450 °C for another 30 min. The b-$CsPbI_3$ film was coated on the FTO/c-TiO_2/m-TiO_2 or FTO/c-TiO_2 substrate with the same method for the fabrication of photoreactors as mentioned above. Finally, the carbon counter electrode was deposited by doctor-blade coating a layer of conductive carbon ink on the surface of b-$CsPbI_3$ film and then heated at 70 °C for 60 min.

Characterizations and measurements

The morphological features of the samples were examined by scanning electron microscopy (SEM, HITACH S-4800). X-ray photoelectron spectroscopy (XPS) was performed on a PHI-5000 VersaProbe X-ray photoelectron spectrometer with an Al Kα X-ray radiation. XRD spectra were collected with a Bruker D-8 Advance diffractometer using Cu *Kα* X-ray radiation. Optical absorbance spectra were collected with a UV-vis-NIR spectrophotometer (Shimadzu, UV-3600) in a wavelength range of 200-800 nm. The optoelectronic properties of $CsPbI_3$ based photodetectors were measured by an electrochemical workstation (CHI-760). The simulated solar AM 1.5G illumination was provided by a solar simulator (Oriel Solar Simulator, Model 91160). The monochromatic lights were obtained by applying optical filters with corresponding wavelengths. The J-V characteristics were recorded by a Keithley 2400 source meter.

Table S1. XPS binding energies and atomic ratios of Cs, Pb and I elements measured from the inorganic perovskite $CsPbI_3$ film.

	Cs $3d_{5/2}$	**Cs $3d_{3/2}$**	**$Pb4f_{7/2}$**	**$Pb4f_{5/2}$**	**I $3d_{5/2}$**	**I $3d_{3/2}$**
Binding Energy (eV)	723.6	737.6	137.4	142.3	618.3	629.9

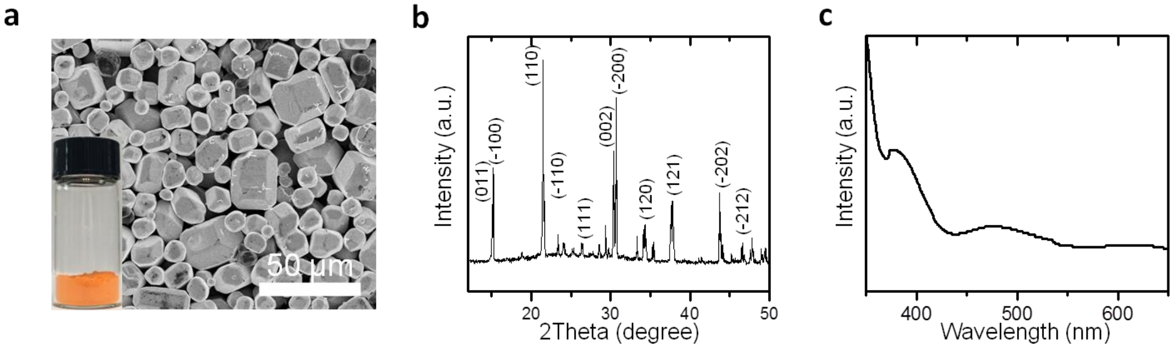

Figure S1. (a) SEM image, (b) XRD pattern and (c) UV-vis spectrum of as-prepared $CsPbBr_3$ microcrystals. The $CsPbBr_3$ is in the monoclinic phase (JCPDS card No. 18-0364)

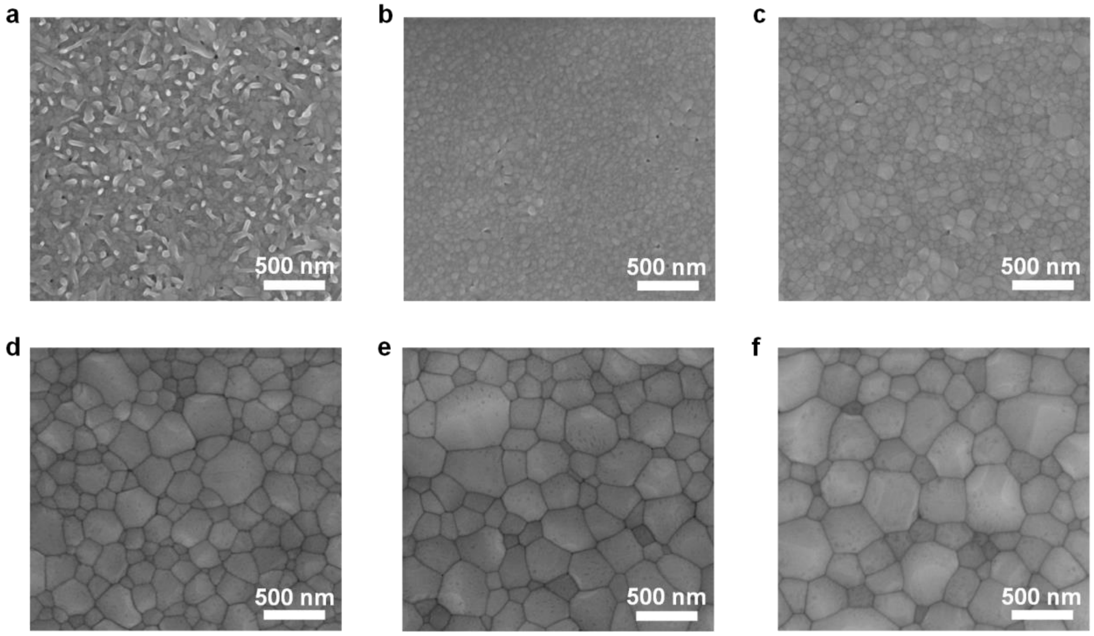

Figure S2. SEM images of (a) as-prepared y-$CsPbI_3$ film and annealed y-$CsPbI_3$ films after treating at (b) 100 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C and (f) 325 °C, respectively.

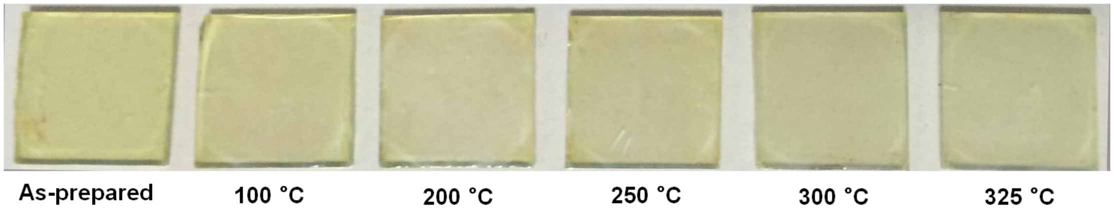

Figure S3. Optical images of as-prepared y-$CsPbI_3$ film and annealed y-$CsPbI_3$ films treated at 100 °C, 200 °C, 250 °C, 300 °C and 325 °C, respectively.

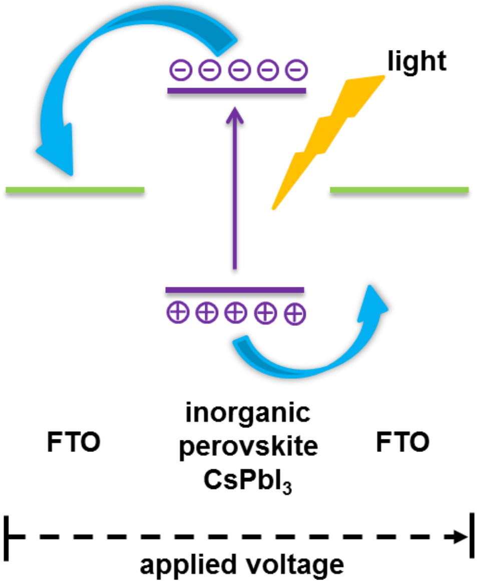

Figure S4. Working mechanism of the $CsPbI_3$-based two-terminal photodetectors.

Table S2. Photovoltaic parameters of IPSC-1 and IPSC-2, respectively.

Devices	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)
AIPSC-1	13.74	0.58	0.44	3.48
AIPSC-2	14.31	0.67	0.48	4.65