

## Supporting information

### Synthesis and Optical Properties of Lead-Free Cesium Germanium

#### Halide Perovskite quantum rods

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This Supplementary Information file replaces that originally published on 21<sup>st</sup> May 2018, due to an error in the “Characterization and measurements” section. The first sentence has been changed from “The as-prepared samples were characterized by X-ray powder diffraction (XRD), and transmission electron microscopy (TEM)” to “The as-prepared samples were characterized by X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM)”. There was no XRD data reported, therefore the ESI has been updated to reflect this change.

#### Experimental section

##### Materials

Germanium (II) chloride ( $\text{GeCl}_2$ , 99.999%), Germanium (II) bromide ( $\text{GeBr}_2$ , 99.999%), Germanium (II) iodide ( $\text{GeI}_2$ , 99.999%), cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , reagent Plus, 99%). Octadecylamine (ODA, 97%), octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 90%), oleic acid (OA, 90%), diethylenetriamine (DIEN, 99%), trioctylphosphine oxide (TOPO, 99%) and the spiro-OMeTAD were purchased from Sigma-Aldrich. Absolute ethanol (Alfa Aesar, 99.8%), toluene (Sigma-Aldrich, 99.8%), and hydrochloric acid (Alfa Aesar, 36.5%). Titanium diisopropoxide bis (acetylacetonate) were purchased from Alfa Aesar.

### **Synthesis CsGeX<sub>3</sub> (X = Cl, Br, I) quantum rods by solvothermal route**

In a typical synthesis, 0.7 g of GeBr<sub>2</sub> (2.3 mmol) (or 0.45/0.86 g of GeCl<sub>2</sub>/GeI<sub>2</sub>, respectively), 60 mL of ODE, 6 mL of OA and 6 mL of OLAM were loaded in a 100 mL four-neck flask and dried under a vacuum for 1 h at 120 °C. Then, a mixture of 10 mL of ODE with 5 mL of previously synthesized Csoleate (2 g of Cs<sub>2</sub>CO<sub>3</sub> degassed in 60 mL of ODE and 5 mL of OA at 120 °C for 1 h), hydrochloric acid (1 mg), TOPO and DIEN were heated with stirring at 80 °C, while purging continuously with nitrogen for 1 h. The reagents were loaded into a 50 mL Teflon lined autoclave, which was then filled with anhydrous DIEN up to 80% of the total volume. The autoclave was sealed and was maintained at 180 °C for 6 h, and then quantum rods solution was quickly cooled down to room temperature with an ice bath (~-4°C), and the products were transferred to a glovebox. After this step, the solution was filtrated, washed by excess octane, hexane, and toluene by centrifugation, respectively. Finally, dried in a vacuum at 80 °C for 3 h and prepared products were redispersed in toluene for further use.

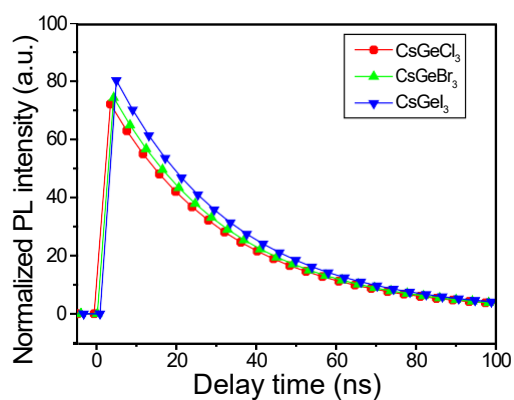
### **Fabrication of the lead-free all inorganic perovskite devices**

To fabricate the all-inorganic CsGeX<sub>3</sub> (X=Cl, Br and I) perovskite hybrid solar cell (Fluorine tin oxide (FTO) /TiO<sub>2</sub>/ CsGeX<sub>3</sub>/ HTM /Ag). FTO glass (15 Ω sq<sup>-1</sup>) was cleaned using a three step ultrasonic process of ethanol, distilled water and acetone for 10 min, respectively. After drying under a nitrogen stream, substrates were further cleaned by UV ozone for 6 min. Subsequently, TiO<sub>2</sub> precursor (titanium diisopropoxide bis(acetylacetonate) and TiO<sub>2</sub> porous) were then coated onto the FTO substrate by two consecutive spin coating steps, at 2000 rpm for 60 and 10 s, respectively. After each spin coating, the film was baked at 180 °C for 5 min under nitrogen. The obtained substrate was then sintered at 550 °C for 15 min in the N<sub>2</sub>-filled tube furnace. To avoid oxygen and moisture, the substrates were transferred into a nitrogen filled glove box. Sequentially, precursor solutions of CsGeI<sub>3</sub> perovskites (90mg/ml) in toluene were spin coated at 1000 rpm for 10s and 5000 rpm for 20s, then dried on hot-plate at 100 °C for 5 min. At 5000 rpm for 20 s, the wet spinning film was quenched by dropping 50 μl of anhydrous toluene. After spin coating, the film was annealed at 100 °C for 10 min. The spiro-OMeTAD hole transporting materials (HTM) solution (10 mg/ml) in toluene was

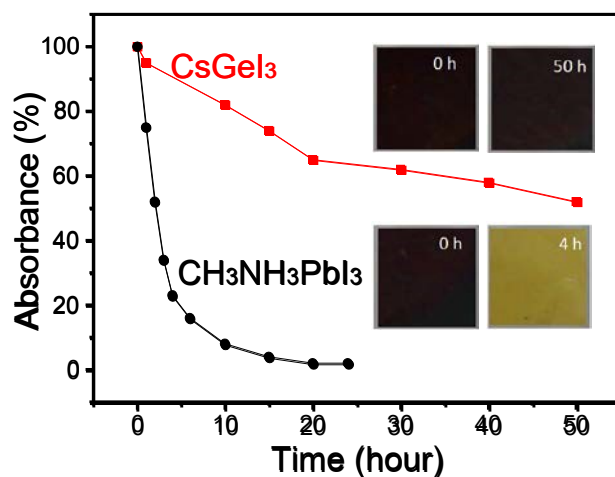
spin-coated at 2000 rpm for 30s on top of perovskite layer. Finally, silver electrodes were deposited under vacuum ( $< 10^{-6}$  Torr) on top of the HTM by thermal evaporation. The device area was fixed to  $0.16 \text{ cm}^2$ . All device fabrications were conducted below 50% of relative humidity.

### **Characterization and measurements**

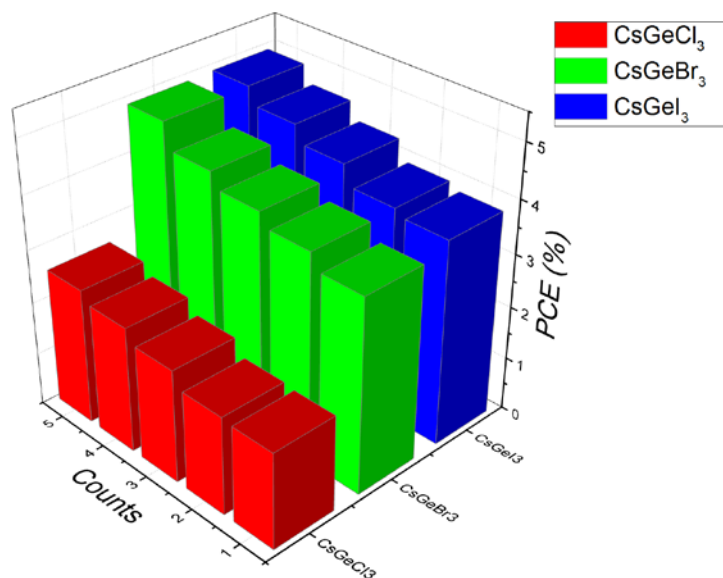
The as-prepared samples were characterized by X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). TEM characterization was conducted on a JEM-2000EX system using an acceleration voltage of 160 kV. The average rod diameter and the aspect ratio of the beads were calculated from the TEM images. PL was performed on PerkinElmer LS55 luminescence spectrometer made by PerkinElmer Company in United States, excited by a wavelength of 532 nm line of a pulse xenon lamp at room temperature. XPS measurements were carried out using PHI 5000 VersaProbe X-ray Photoelectron Spectroscopy (ULVAC-PHI, Inc., Japan). Current–voltage measurements were performed using a Keithley 2400 source meter. Solar cells were masked using a non-reflective metal aperture of  $1 \text{ cm}^2$  which defined the active area. The EQE spectra were measured by combining a monochromated 450 W xenon lamp (Oriel) with a sourcemeter (Keithley 2400) and calculated using a calibrated Si photodiode (OSI-Optoelectronics).



**Figure S1.** Time-dependent PL decays of various CsGeX<sub>3</sub> quantum rods prepared with different halide (CsGeCl<sub>3</sub>, CsGeBr<sub>3</sub>, and CsGeI<sub>3</sub>) in toluene, averaged across measurements from 5 samples.



**Figure S2.** Absorbance relative intensity at 660 nm as a function of time under same conditions. The temperature was 25 °C for all measurements; the light intensity was 1500 mW cm<sup>-2</sup>. (Red: CsGeI<sub>3</sub>, black: CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.)



**Figure S3.** Efficiency distribution of the optimized the lead-free perovskite quantum rods perovskite solar cells.

**Table S1.** Measured CsGeX<sub>3</sub> quantum rods Composition

	Precursor atomic ratio	Measured by EDS <sup>a</sup>	Measured by XPS <sup>b</sup>
Cs:Ge:Cl	1:0.96:2.82	1:0.87:2.73	1:0.82:2.74
Cs:Ge:Br	1:0.95:2.74	1:0.82:2.75	1:0.78:2.72
Cs:Ge:I	1:0.92:2.52	1:0.85:2.88	1:0.72:2.84

<sup>a</sup>EDS measurements have an error of ca.  $\pm 2$  atom %.

<sup>b</sup>XPS measurement have an error of  $\pm 0.2$  atom % for Cs,  $\pm 0.1$  atom % for Ge,  $\pm 0.5$  atom % for Cl, Br and I.

**Table S2.** Summarized photovoltaic parameters derived from current– voltage curves recorded within 24 h (after device fabrication) for the different perovskite devices with different halide ratio.

	atomic ratio	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
Cs:Ge:Cl	1:0.96:2.82	0.75	18.57	0.44	2.57
Cs:Ge:Br	1:0.95:2.74	0.49	19.49	0.52	4.92
Cs:Ge:I	1:0.92:2.52	0.52	18.78	0.51	4.94