Supporting Information for

Reversible Light-Mediated Compositional and Structural Transitions between $CsPbBr_3$ and $CsPb_2Br_5$ Nanosheets

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EXPERIMENTS SECTION

Chemicals. $PbBr_2$ (Aladdin, 99.9%, Shanghai, China), CsBr (Aladdin, 99.9%, Shanghai, China), polyvinylpyrrolidone (PVP, M_w=58000, Aladdin, Shanghai, China), dimethylformamide (DMF, 99.9%, Sinopharm Chemical Reagent Co., Ltd., China), dichloromethane (>99.5%, Sinopharm Chemical Reagent Co., Ltd., China), ethanol (>99.7%, Sinopharm Chemical Reagent Co., Ltd., China), and toluene (99.9%, Sinopharm Chemical Reagent Co., Ltd., China) were purchased and used without further purification.

Synthesis of $CsPbBr_3$@PVP nanoparticles. Solution A: $PbBr_2$ (0.08 mmol) and PVP (4.5 mmol) was dissolved in DMF (10 mL). Solution B: CsBr (0.08 mmol) was first dissolved in 100 μL H_2O, then mixed with 10 mL DMF. The solution A and solution B were mixed with 1:1 volume ratio to obtain the precursor solution. 0.2 mL precursor solution was added into 2 mL toluene and slowly become green turbid liquid.

Synthesis of $CsPbBr_3$@PVP nanosheets. Solution A: $PbBr_2$ (0.08 mmol) and PVP (4.5 mmol) was dissolved in DMF (10 mL). Solution B: CsBr (0.08 mmol) was first dissolved in 100 μL H_2O, then mixed with 10 mL DMF. The solution A and solution B were mixed with 1:1 volume ratio to obtain the precursor solution. 1 mL precursor solution was added into 10 mL dichloromethane and slowly become yellow colloidal solution. The as-prepared $CsPbBr_3$@PVP nanosheets can be easily precipitated by centrifugation at 7000 rpm, and transferred to ethanol for further phase transition studies.

Phase transition experiments. The as-prepared $CsPbBr_3$@PVP nanosheets was precipitated by centrifugation at 7000 rpm, and transferred to triple volume of ethanol. Then the solution was placed in a dark room at least 1 day to complete phase transition from orthorhombic $CPbBr_3$ to tetragonal $CsPb_2Br_5$. The tetragonal $CsPb_2Br_5$ was placed in photochemical reactions instrument, and the working current of the xenon lamp is 10 A. The incubation time was at least 30 min to complete phase transition from tetragonal $CsPb_2Br_5$ to orthorhombic $CPbBr_3$. The *in-situ* PL measurements to reveal the dynamic PL evolution were obtained with a Horiba PTI Quanta Master 400 steady-state fluorescence system (Japan) excited by 450 nm under ambient conditions. The XRD samples for reversible phase transition cycles were obtained by centrifugation at 7000 rpm, and the XRD measurement is *ex-situ*. The TEM samples for the transformed $CsPb_2Br_5$ nanosheets were obtained after 24 hours storage under light-off conditions, and the TEM samples for the transformed $CsPbBr_3$ nanosheets were obtained after 2 hours light-on conditions.

Characterization. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 electron microscope (USA) operating at 200 kV. X-ray powder diffraction (XRD) was measured with a Bruker AXS D8 X-ray diffractometer (USA) equipped with monochromated Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was performed using an achromatic Al Kα source (1486.6 eV) and a double pass cylindrical mirror analyzer (ULVACPHI 5000 VersaProbe) (Japan). Photo induced phase transition experiments were used a photochemical reactions instrument (CEL-LAB500, CEAULIGHT, China) combing with a xenon lamp. Ultraviolet and visible absorption (UV−Vis) spectra were recorded with a Shimadzu UV-3600 plus spectrophotometer under ambient conditions. The photoluminescence (PL) spectra of orthorhombic $CPbBr_3$ and tetragonal $CsPb_2Br_5$ and PL monitoring dynamic process of phase transition

excited by 450 nm were obtained with a Horiba PTI Quanta Master 400 steady-state fluorescence system (Japan) under ambient conditions. The lifetimes of PL were detected by Nikon Ni-U Micro-fluoresce Lifetime system (confotec MR200, SOL, Belarus) with a 375 nm picosecond lasers.

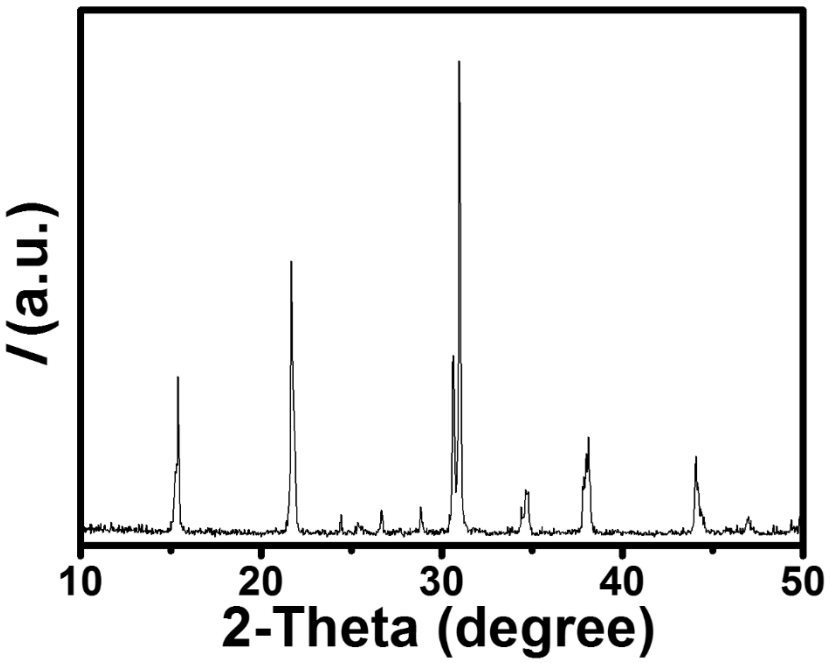

Figure S1. X-ray diffraction (XRD) patterns of as-prepared $CsPbBr_3$ nanosheets.

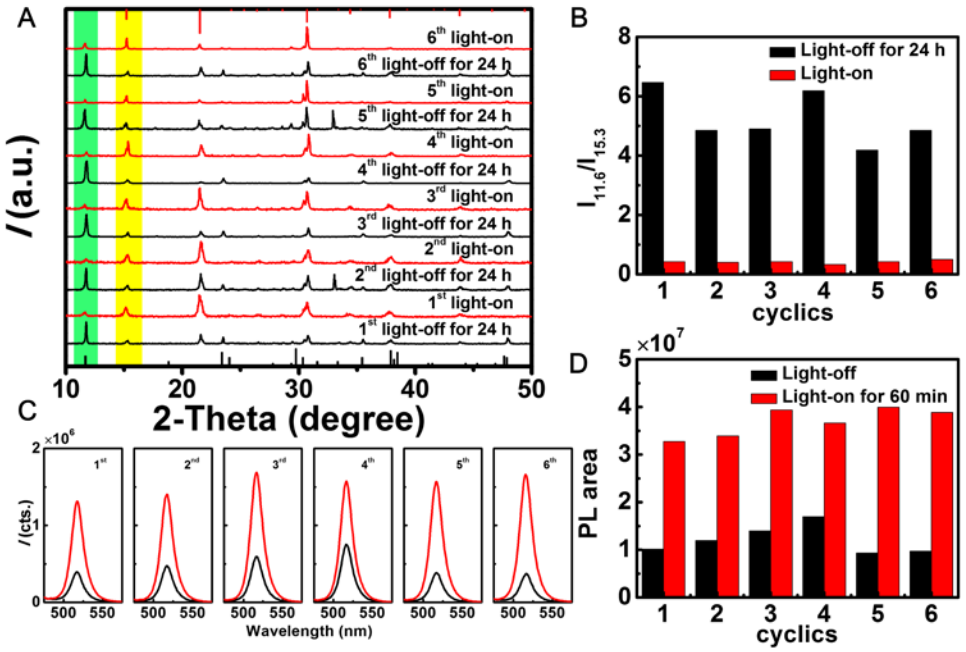

Figure S2. (A, B) XRD measurement to monitor six reversible phase transition cycles, and the corresponding tetragonal/orthorhombic ratio ($I_{11.6}/I_{15.3}$) to quantitatively demonstrate the phase transitions between light-on and after 24 h storage under light-off conditions. (C, D) PL measurement monitoring the phase transition cycles from tetragonal $CsPb_2Br_5$ to orthorhombic $CsPbBr_3$ in the case of the light-on illumination, and the corresponding peak areas of PL under light-off conditions and after 60 min continuous light-on illumination.

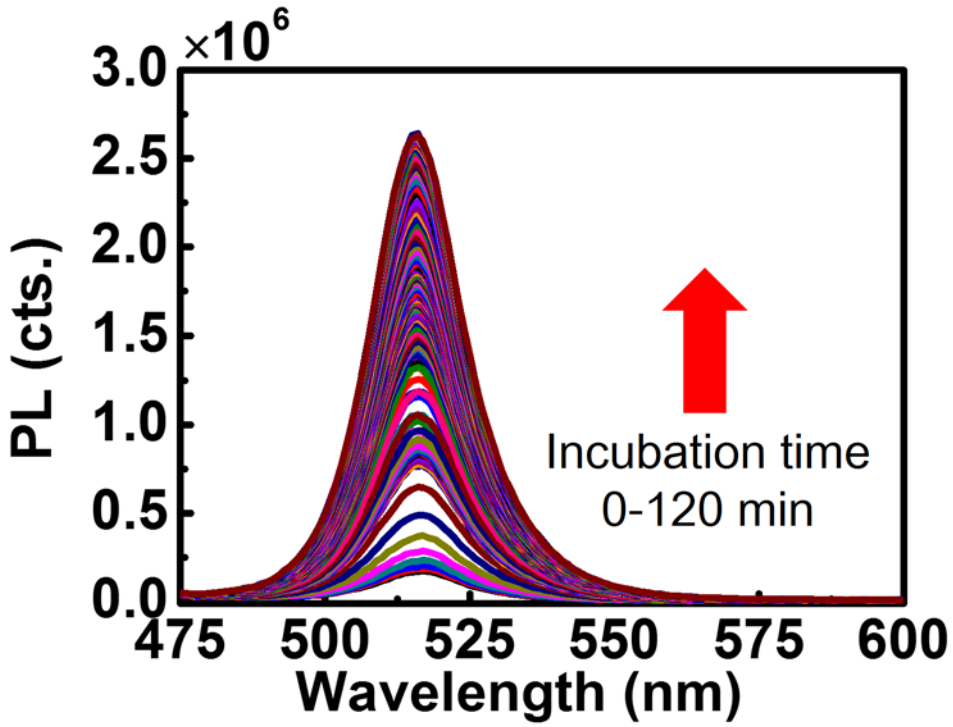

Figure S3. PL measurement monitoring the dynamic process of phase transition from tetragonal $CsPb_2Br_5$ to orthorhombic $CsPbBr_3$ in the case of the continuous illumination.

Table.S1 Fitting results of time-resolved PL decay curves.

	as-prepared $CsPbBr_3$	**transformed $CsPb_2Br_5$**	**transformed $CsPbBr_3$**
τ_1 (ns)	4.7 (70.0%)	23.5 (1.8%)	13.9 (44.6%)
τ_2 (ns)	17.9 (30.0%)	1.8 (86.9%)	4.7 (55.4%)
τ_3 (ns)	-	6.0 (11.3%)	-
A_1	2.29	0.05	0.22
A_2	0.26	27.83	0.82
A_3	-	1.08	-
τ_{ave} (ns)	8.7	2.7	6.8

Time-resolved PL decay curves were fitted by a triexponential (see eqs 1 and 2) function: $A(t) = A_0 + A_1\exp-(t-t_0)/\tau_1 + A_2\exp-(t-t_0)/\tau_2 + A_3\exp-(t-t_0)/\tau_3$ (eqs 1); The average lifetimes were calculated using $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$ (eqs 2).

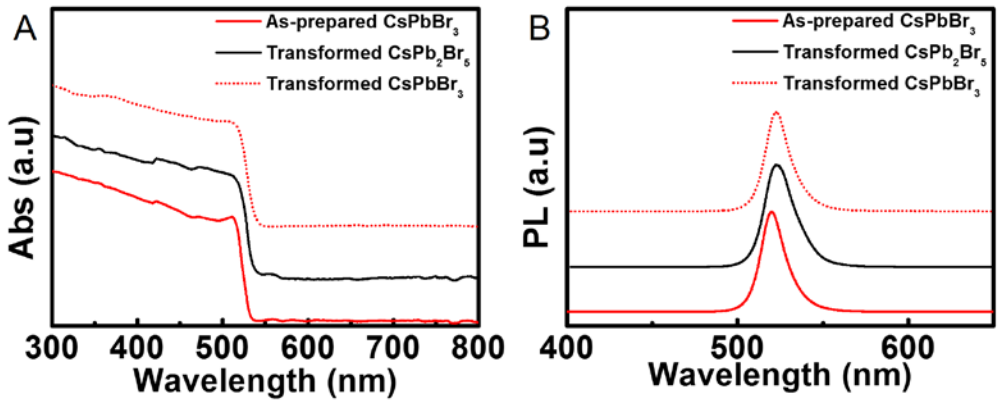

Figure S4. The solid state diffuse reflectance absorption (**A**) and PL emission (**B**) spectra of as-prepared $CsPbBr_3$ nanosheets, transformed $CsPb_2Br_5$ nanosheets, and transformed $CsPbBr_3$ nanosheets.