Supporting Information

Binary halides, ternary perovskite-like, and perovskite-derivative nanostructures: general hot injection synthesis, optical and photocatalytic properties

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Experimental section

Chemicals

All the chemicals were used as received. Potassium carbonate (K_2CO_3, 99.995%), Rubidium carbonate (Rb_2CO_3, 99.8%), Cesium Carbonate (Cs_2CO_3, 99.995%), Rubidium iodide (RbI,99.9%), Lead (II) chloride (PbCl2, 99.999%), Tin(II) chloride ($SnCl_2$, 99.99%), Tin (II) bromide ($SnBr_2$, 99.99%), Tin (II) iodide (SnI_2, 99.999%), Octadecene (ODE, 90% Aldrich), Oleic acid (OA, ≧99%), Oleylamine (OLA, 70%), Trioctylphosphine (TOP, 97%), N-Methyl-2-pyrrolidone (NMP, anhydrous 99.5%) were purchased from Aldrich.

Synthesis

(1) Halide nanoparticles

Preparation of alkali metal oleate solution:

Alkali metal (K, Rb, Cs) oleate solution were prepared. 0.1 mole K_2CO_3, Rb_2CO_3, Cs_2CO_3,RbI were loaded into 3-neck flask with 15 mL ODE or NMP (RbCl for NMP) and 1.2 mL OA, degassed under vacuum at 120 °C for 1h, the solution was then heated to 150-180 °C under Ar (KCl, KBr, RbBr, RbI at 180°C) until all the alkali metal precursors reacted with OA.

Synthesis of AX nanoparticles (A= K, Rb, Cs, X=Cl, Br, I):

5 mL ODE and 0.2 mole $PbCl_2$ or SnX_2 (X = Cl, Br, I) were loaded into 3-neck flask with 1-2.5 ml OLA or TOP (1 mL OLA for KCl, KBr, RbBr or RbI and 2 mL OLA for CsBr, CsI or RbCl , 2.5 mL TOP for CsCl) degassed under vacuum at 120 °C for 1 h, and then 2 mL OA

were injected and heated to 150-200 °C under Ar, the solution was kept at certain temperature for 1 h (CsBr, CsI or RbCl for 150 °C and KCl, KBr, RbBr or RbI for 180 °C, CsCl for 200 °C). After complete dissolved of the PbX_2 or SnX_2, 0.6 mL alkali metal oleate solution was then quickly injected and heat up to 180-240 °C (RbCl at 180 °C, CsBr at 200 °C, KCl, KBr, CsI, RbBr or RbI at 240 °C) for 30 min to 2 h under Ar (CsCl for 2 h).

(2) Perovskite-like nanoparticles

Preparation of alkali metal oleate solution:

Alkali metal (K, Rb) oleate solution was prepared. 0.1 mole Rb_2CO_3, K_2CO_3 were loaded into 3-neck flask with 15 mL ODE and 1.2 mL OA and degassed under vacuum at 120 °C for 1 h, the solution was then heated to 180 °C under Ar until all the alkali metal precursors reacted with OA.

Synthesis of APb_2Cl_5 nanoparticles (A = K, Rb):

5 mL ODE and 0.2 mole $PbCl_2$ were loaded into 3-neck flask with 1-2 mL OLA (1mL OLA for KPb_2Cl_5, 2 mL OLA for $RbPb_2Cl_5$) degassed under vacuum at 120 °C for 1 h, and 2 mL OA was injected. The temperature was then raised to 180 °C under Ar for 1 hr. After complete dissolved of the $PbCl_2$, 0.6 mL alkali metal oleate solution was then quickly injected and heat up to 220-240 °C ($RbPb_2Cl_5$ at 220 °C, KPb_2Cl_5 at 240 °C) for 30-40 min (KPb_2Cl_5 for 30 min, $RbPb_2Cl_5$ for 40 min).

(3) Perovskite derivative nanoparticles

Preparation of alkali metal oleate solution:

Alkali metal (Rb, Cs) oleate solution was prepared. 0.1 mole Rb_2CO_3, Cs_2CO_3 were loaded into 3-neck flask with 15 mL ODE and 1.2 mL OA and degassed under vacuum at 120 °C for 1 h, the solution was then heated to 150-180 °C (Cs_2CO_3 at 150 °C, Rb_2CO_3 at 180 °C) under Ar until all the alkali metal precursors reacted with OA.

Synthesis of A_2SnCl_6 nanoparticles (A = Rb, Cs):

5 mL ODE and 0.2 mole $SnCl_2$ were loaded into 3-neck flask with 1-2 mL OLA (1 mL OLA for Rb_2SnCl_6; 2 mL for Cs_2SnCl_6) degassed under vacuum at 120 °C for 1 h, and 2 mL OA was injected. The temperature was then raised to 180-200 °C (Rb_2SnCl_6 at 180 °C; Cs_2SnCl_6 at 200 °C) under Ar for 1 h. After complete dissolved of the $SnCl_2$, 0.6 mL alkali metal oleate solution was then quickly injected and heat up to 220-240 °C (Cs_2SnCl_6 at 200 °C, Rb_2SnCl_6 for 240 °C) for 30-40 min (Cs_2SnCl_6 for 30 min, Rb_2SnCl_6 for 40 min).

Photocatalytic testing

The photocatalytic activities of perovskite-likes and perovskite-derivatives nanoparticles were tested by degrading an organic dye, Rh6G in THF solution. In the photocatalytic experiments, 30 mg of as-synthesized nanomaterials was added to a beaker containing 100 mL of Rh6G THF solution with

concentration of 2 mg/L, and the solution was stirred in the dark for 1 h to reach adsorption–desorption equilibrium between the catalyst and Rh6G. The mixture was then irradiated using a 20 W 360 nm UVA lamp. The reaction mixture was irradiated for a certain period; about 3 mL of the suspension was taken out and immediately centrifuged for UV-Vis measurement.

Characterization and Measurement

The phase structure of the as-synthesized products were examined by X-ray diffraction (XRD, Rigaku Ultima IV X-ray diffractometer, Cu Kα λ = 1.54178 Å, 1°/min). The microstructure was observed using the field emission scanning electron microscope (SEM, Hitachi SU8010) and transmission electron microscope (TEM, JEOL JEM-ARM200FTH and Philips TECHAI20). UV-Vis spectra were obtained using Hitachi U-4100 UV-Vis spectrophotometer. Photoluminescence (PL) spectra were obtained using Horiba Scientific FluoroMax-4 spectrofluorometer. All optical measurements were obtained by nanomaterials dispersed in THF which were contained in quartz cuvette with 1 cm path length.

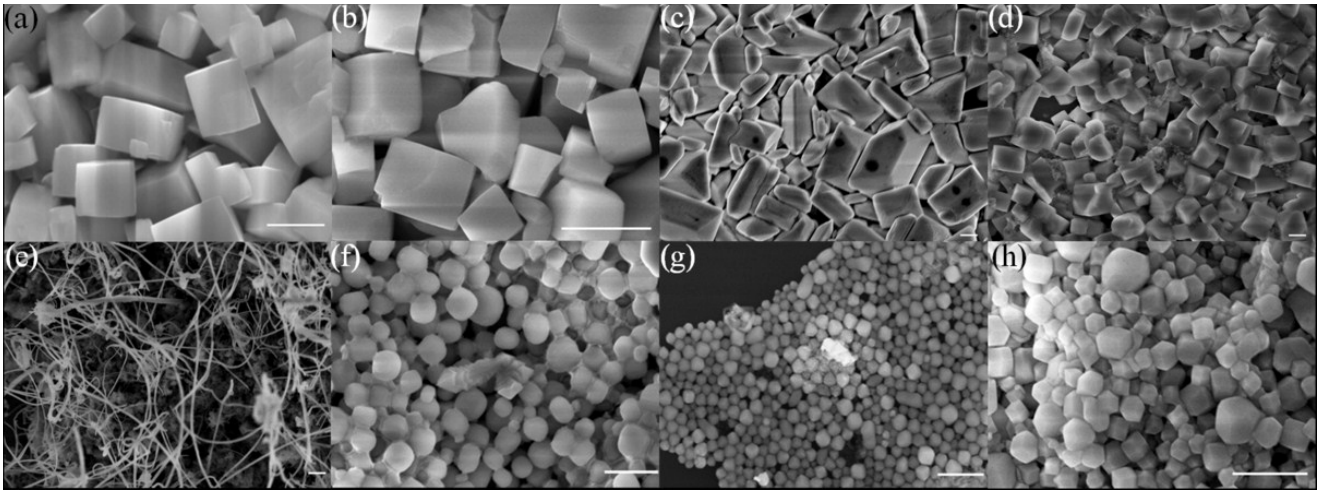

Fig S1: Representative low-resolution SEM image of as-grown halides, (a) KCl (b) KBr (c) RbCl (d) RbBr (e) RbI (f) CsCl (g) CsBr (h) CsI. Scale bar. 1 μm

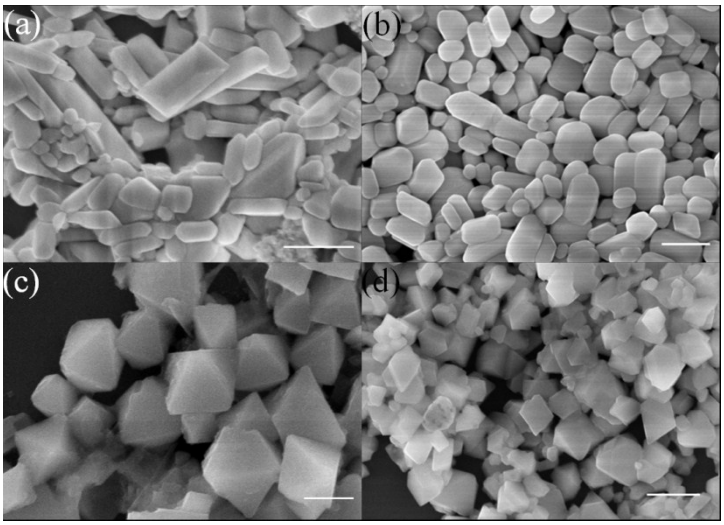

Fig S2: Representative low-resolution SEM image of as-grown perovskite-likes and perovskite-derivatives, (a) KPb_2Cl_5 (b) $RbPb_2Cl_5$ (c) Rb_2SnCl_6 (d) Cs_2SnCl_6.
Scale bar, 500 nm

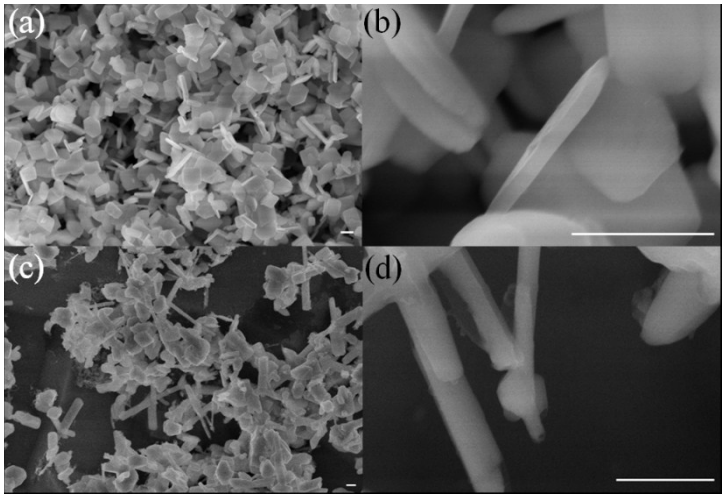

Fig S3: Representative SEM image of perovskite-derivatives Rb_2SnCl_6. (a), (b) plates; (c), (d) whiskers. Scale bar, 500 nm

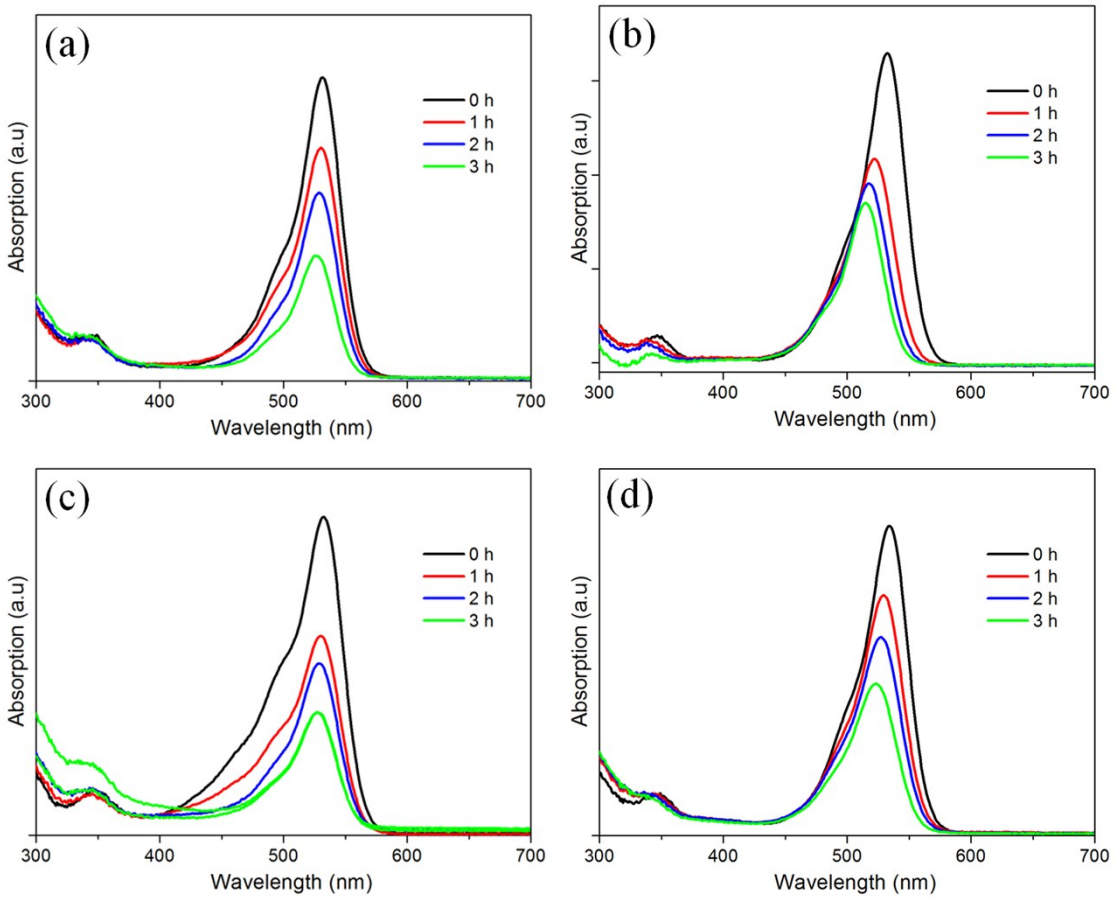

Fig S4 Time-dependent UV-vis spectra recorded during the photocatalytic degradation of Rhodamine 6G by using (a) KPb_2Cl_5, (b) Rb_2SnCl_6, (c) Rb_2PbCl_5, (d) Cs_2SnCl_6

Table S1: Synthetic conditions and results for various halides, perovskite-likes and perovskite derivatives

Compound	Precursor	ODE/NMP (mL)	OLA/TOP (mL)	Reaction Temperature (°C)	Reaction Time (min)	Morphology, size
KCl	K_2CO_3 $SnCl_2$	15 ml ODE	1 ml OLA	240	30	Cuboid, 300 nm-1 μm
KBr	K_2CO_3 $SnBr_2$	15 ml ODE	1 ml OLA	240	30	Cuboid, 300 nm-1 μm
RbCl	RbI $PbCl_2$	15 ml NMP	2 ml OLA	180	30	Cuboid or irregular shape, 500 nm-2μm
RbBr	Rb_2CO_3 $SnBr_2$	15 ml ODE	1 ml OLA	240	30	Cuboid, 500 nm-2μm
RbI	Rb_2CO_3 SnI_2	15 ml ODE	1 ml OLA	240	30	Wire-like, 30-50 nm in diameter
CsCl	Cs_2CO_3 $SnCl_2$	15 ml ODE	2.5 ml TOP	200	120	Sphere, 300-500 nm
CsBr	Cs_2CO_3 $SnBr_2$	15 ml ODE	2 ml OLA	200	30	Yarn ball, 100-300 nm
CsI	Cs_2CO_3 SnI_2	15 ml ODE	2 ml OLA	240	30	Cube, 100-300 nm
KPb_2Cl_5	K_2CO_3 $PbCl_2$	15 ml ODE	1 ml OLA	240	30	Short rod or cuboid, 200- 500 nm
$RbPb_2Cl_5$	Rb_2CO_3 $PbCl_2$	15 ml ODE	2 ml OLA	220	40	Short rod or cuboid, 200- 500 nm
Rb_2SnCl_6	Rb_2CO_3 $SnCl_2$	15 ml ODE	1 ml OLA	200	40	Octahedral 300- 500 nm
Cs_2SnCl_6	Cs_2CO_3 $SnCl_2$	15 ml ODE	2 ml OLA	200	30	Octahedral 300- 500 nm
Cs_2SnCl_6	Cs_2CO_3 $SnCl_2$	15 ml ODE	2 ml TOP	180	30	Plates 300- 500 nm
Cs_2SnCl_6	Cs_2CO_3 $SnCl_2$	15 ml ODE	2 ml TOP	200	30	Whiskers, 50-100 nm in diameter