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$_2$CO$_3$, 99.995%), Rubidium carbonate (Rb$_2$CO$_3$, 99.8%), Cesium Carbonate (Cs$_2$CO$_3$, 99.995%), Rubidium iodide (RbI, 99.9%), Lead (II) chloride (PbCl$_2$, 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%), Trioctyolphosphine (TOP, 97%), N-Methyl-2-pyrroolidone (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$_2$CO$_3$, Rb$_2$CO$_3$, Cs$_2$CO$_3$, 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 1 h, 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

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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 PbX₂ or SnX₂, 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 Rb₂CO₃, K₂CO₃ 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 APb₂Cl₅ nanoparticles (A = K, Rb):
5 mL ODE and 0.2 mole PbCl₂ were loaded into 3-neck flask with 1-2 mL OLA (1mL OLA for KPb₂Cl₅, 2 mL OLA for RbPb₂Cl₅) 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 PbCl₂, 0.6 mL alkali metal oleate solution was then quickly injected and heat up to 220-240 °C (RbPb₂Cl₅ at 220 °C, KPb₂Cl₅ at 240 °C) for 30-40 min (KPb₂Cl₅ for 30 min, RbPb₂Cl₅ for 40 min).

(3) Perovskite derivative nanoparticles
Preparation of alkali metal oleate solution:
Alkali metal (Rb, Cs) oleate solution was prepared. 0.1 mole Rb₂CO₃, Cs₂CO₃ 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 (Cs₂CO₃ at 150 °C, Rb₂CO₃ at 180 °C) under Ar until all the alkali metal precursors reacted with OA.

Synthesis of A₂SnCl₆ nanoparticles (A = Rb, Cs):
5 mL ODE and 0.2 mole SnCl₂ were loaded into 3-neck flask with 1-2 mL OLA (1 mL OLA for Rb₂SnCl₆; 2 mL for Cs₂SnCl₆) degassed under vacuum at 120 °C for 1 h, and 2 mL OA was injected. The temperature was then raised to 180-200 °C (Rb₂SnCl₆ at 180 °C; Cs₂SnCl₆ at 200 °C) under Ar for 1 h. After complete dissolved of the SnCl₂, 0.6 mL alkali metal oleate solution was then quickly injected and heat up to 220-240 °C (Cs₂SnCl₆ at 200 °C, Rb₂SnCl₆ for 240 °C) for 30-40 min (Cs₂SnCl₆ for 30 min, Rb₂SnCl₆ 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$_2$Cl$_5$ (b) RbPb$_2$Cl$_5$ (c) Rb$_2$SnCl$_6$ (d) Cs$_2$SnCl$_6$. Scale bar, 500 nm

Fig S3: Representative SEM image of perovskite-derivatives Rb$_2$SnCl$_6$. (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) K\textsubscript{Pb}\textsubscript{2}Cl\textsubscript{5}, (b) Rb\textsubscript{2}SnCl\textsubscript{6}, (c) Rb\textsubscript{2}PbCl\textsubscript{5}, (d) Cs\textsubscript{2}SnCl\textsubscript{6}
Table S1: Synthetic conditions and results for various halides, perovskite-likes and perovskite derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Precursor</th>
<th>ODE/NMP (mL)</th>
<th>OLA/TOP (mL)</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (min)</th>
<th>Morphology, size</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>K₂CO₃ SnCl₂</td>
<td>15 ml ODE</td>
<td>1 ml OLA</td>
<td>240</td>
<td>30</td>
<td>Cuboid, 300 nm-1 µm</td>
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<tr>
<td>KBr</td>
<td>K₂CO₃ SnBr₂</td>
<td>15 ml ODE</td>
<td>1 ml OLA</td>
<td>240</td>
<td>30</td>
<td>Cuboid, 300 nm-1 µm</td>
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<tr>
<td>RbCl</td>
<td>RbI PbCl₂</td>
<td>15 ml NMP</td>
<td>2 ml OLA</td>
<td>180</td>
<td>30</td>
<td>Cuboid or irregular shape, 500 nm-2µm</td>
</tr>
<tr>
<td>RbBr</td>
<td>Rb₂CO₃ SnBr₂</td>
<td>15 ml ODE</td>
<td>1 ml OLA</td>
<td>240</td>
<td>30</td>
<td>Cuboid, 500 nm-2µm</td>
</tr>
<tr>
<td>Rbl</td>
<td>Rb₂CO₃ SnI₂</td>
<td>15 ml ODE</td>
<td>1 ml OLA</td>
<td>240</td>
<td>30</td>
<td>Wire-like, 30-50 nm in diameter</td>
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<tr>
<td>CsCl</td>
<td>Cs₂CO₃ SnCl₂</td>
<td>15 ml ODE</td>
<td>2.5 ml TOP</td>
<td>200</td>
<td>120</td>
<td>Sphere, 300-500 nm</td>
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<tr>
<td>CsBr</td>
<td>Cs₂CO₃ SnBr₂</td>
<td>15 ml ODE</td>
<td>2 ml OLA</td>
<td>200</td>
<td>30</td>
<td>Yarn ball, 100-300 nm</td>
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<tr>
<td>CsI</td>
<td>Cs₂CO₃ SnI₂</td>
<td>15 ml ODE</td>
<td>2 ml OLA</td>
<td>240</td>
<td>30</td>
<td>Cube, 100-300 nm</td>
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<tr>
<td>KPb₂Cl₅</td>
<td>K₂CO₃ PbCl₂</td>
<td>15 ml ODE</td>
<td>1 ml OLA</td>
<td>240</td>
<td>30</td>
<td>Short rod or cuboid, 200- 500 nm</td>
</tr>
<tr>
<td>RbPb₂Cl₅</td>
<td>Rb₂CO₃ PbCl₂</td>
<td>15 ml ODE</td>
<td>2 ml OLA</td>
<td>220</td>
<td>40</td>
<td>Short rod or cuboid, 200- 500 nm</td>
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<tr>
<td>Rb₂SnCl₆</td>
<td>Rb₂CO₃ SnCl₂</td>
<td>15 ml ODE</td>
<td>1 ml OLA</td>
<td>200</td>
<td>40</td>
<td>Octahedral 300- 500 nm</td>
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<tr>
<td>Cs₂SnCl₆</td>
<td>Cs₂CO₃ SnCl₂</td>
<td>15 ml ODE</td>
<td>2 ml OLA</td>
<td>200</td>
<td>30</td>
<td>Octahedral 300- 500 nm</td>
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<tr>
<td>Cs₂SnCl₆</td>
<td>Cs₂CO₃ SnCl₂</td>
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<td>30</td>
<td>Plates 300- 500 nm</td>
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<tr>
<td>Cs₂SnCl₆</td>
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<td>30</td>
<td>Whiskers, 50-100 nm in diameter</td>
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