Supporting Information

Interfacial Chemistry Triggers Ultrafast Radiative Recombination in Metal Halide Perovskites

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Experimental Procedures

Materials
Perovskite precursors (cesium halide and lead halide) and anhydrous solvents (dimethylsulfoxide and chlorobenzene) were purchased from Sigma-Aldrich and used without any further treatment. 4” Fused silica wafers (thickness = 500 μm) were purchased from Microchemicals.

Fabrication and modification of perovskite films
Perovskite precursor solutions were prepared by dissolving cesium halide and lead halide with a molar ratio of 1:1 in anhydrous dimethylsulfoxide. In a typical preparation, the cesium halide and lead halide were added in dimethylsulfoxide, stirred at 60 °C for 2 h, and filtered through a 0.2 μm polytetrafluoroethylene filter, yielding 0.25 M CsPbClBr2, 0.48 M CsPbBr3 and 1M CsPbBr1.5I1.5 perovskite precursor solutions. The perovskite films were obtained through spin-coating, during which ~100 μL anhydrous chlorobenzene was dropped onto the perovskite precursor layer, followed by annealing at 100 °C for 10 min. Aluminum oxide films were fabricated via plasma-enhance atomic layer deposition (PEALD, FlexAL, Oxford Instruments).

Structure characterizations
The morphology of as-prepared perovskite films was characterized by a profilometer (DektakXT, Bruker), a scanning electron microscope (SEM, Hitachi SU8010) and an atomic force microscope (AFM, Vecco Nanoscope IIIa, Bruker). The film components were measured through Energy-dispersive X-ray spectroscopy on the SEM and X-ray photoelectron spectrometer (XPS, ESCALab250Xi, Thermal Scientific). The perovskite crystal structures were examined by X-Ray diffraction (XRD, PANalytical Empyrean).

Optical measurements
The absorption spectra were recorded on a UV-Vis spectrophotometer (Hatachi UH4150). The fluorescence microscopy images were taken with a microscope (FluoView-500, Olympus). The optical measurements were carried out using a micro-photoluminescence system equipped with a mode-locked Ti:sapphire laser (400 nm, Spectra Physics), a microscope, a charge-coupled device camera, and a spectrophotometer (Princeton Instruments). The PL quantum yields were measured using an integrating sphere. The temperature dependent photoluminescence was measured in a helium flow cryostat system. The time-resolved photoluminescence was measured by a fluorescence lifetime imaging setup (PicoQuant). For reliable analyses and discussions, all PL measurements were carried out no less than three times on different positions of the individual perovskite films. We select and plot the PL spectra and decay profiles that can represent the average properties of the perovskite films. All PL derived data shown in the manuscript are averages of the ≥ 3 measurement results.

Theoretical calculations
The Density Functional Theory (DFT) calculations were performed with the Vienna Ab Initio Simulation Package (VASP) program. Electron exchange-correction energy was described by the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional. Electron-ion interactions were treated by the projector augmented-wave (PAW) method, van der Waals interactions were described by the Grimme DFT-D3 functional. A 3 × 3 × 1 gamma-centered Monkhorst-Pack k-point mesh was applied for geometry optimizations. The Kohn-Sham wave functions were expanded in plane waves up to 400 eV. The convergence criteria were set as 10⁻² eV in energy and 0.02 eV/Å in force. The effective masses of the electron and hole are calculated by fitting the conduction band minima and valence band maxima, respectively, with the following formula, $E(k)-E(0) = \frac{\hbar^2 k^2}{2m}$.
Results and Discussion

Table S1. Summary of representative works reporting the enhancement of intrinsic radiative recombination rates in metal halide perovskites.

| Perovskite               | Method                  | Increase in radiative recombination rate | Reference |
|--------------------------|-------------------------|------------------------------------------|-----------|
| FAPbBr₃ nanocrystal      | Quantum confinement      | 3.7                                      | [6]       |
| α-CsPbI₃ nanocrystal     | Quantum confinement      | 6.8                                      | [7]       |
| CsPbBr₃ nanocrystal      | Quantum confinement      | 10                                       | [8]       |
| (PEA)ₓ(MA)ₓ₋₁PbnIₙ₋₁ film | Quantum confinement      | 85                                       | [9]       |
| (PEA)ₓ(MA)ₓ₋₁PbnIₙ₋₁ film | Quantum confinement      | 93                                       | [10]      |
| CsPbBr₃ nanocrystal      | Ion doping               | 1.7                                      | [11]      |
| CsPbBr₃ nanocrystal      | Ion doping               | 3.5                                      | [12]      |
| CsPbBr₃ nanocrystal      | Ion doping               | 4.1                                      | [13]      |
| Cs₂(Ag₀.₆Na₀.₄)InCl₆ film| Ion doping               | 95                                       | [14]      |
| CsPbBr₃ film             | Interfacial modification | 5000                                     | this work |

Quantum confinement and ion doping are two typical strategies for enhancing the intrinsic radiative recombination of metal halide perovskites. However, these strategies suffer from limited increases (< 100 times) in the radiative recombination rate. In this work, we demonstrated an interfacial chemistry strategy of modifying metal halide perovskites to dramatically enhance their radiative recombination rate up to an unprecedented 5000 times.
The thicknesses of CsPbBr₃ perovskite films were measured with a profilometer (Figure S1a). Statistical analysis indicated a mean thickness of 124.9 ± 4.5 nm for the perovskite films (Figure S1b).
**Figure S2.** Atomic force microscopy images (AFM) of the CsPbBr\(_3\) perovskite films without and with the Al\(_2\)O\(_3\) coating.

The bare and Al\(_2\)O\(_3\)-coated CsPbBr\(_3\) films have very similar morphologies with the root mean square roughness of 27.4 and 26.4 nm, respectively.
Figure S3. X-ray photoelectron spectroscopy (XPS) spectra of Cs 3d and Br 3d of the CsPbBr$_3$ perovskite films without and with the Al$_2$O$_3$ coating.

The XPS spectra of Cs 3d and Br 3d of the CsPbBr$_3$ perovskite remain unchanged after Al$_2$O$_3$ coating, indicating that no new chemical bond forms with the surface Cs and Br elements.
A systematic study was carried out on the PL of the CsPbBr₃ films coated with Al₂O₃ of different ALD cycles. The PL intensity of the CsPbBr₃ film gradually increases with the ALD cycle up to 20 and levels off with further increase of the ALD cycle. When the ALD cycle is above 40, the PL enhancement exceeds 500 fold.
Figure S5. PL decay profiles of the CsPbBr$_3$ films coated by Al$_2$O$_3$ with different ALD cycles.

We systematically investigated the PL decay dynamics of the CsPbBr$_3$ films coated with Al$_2$O$_3$ of different ALD cycles. The PL lifetime of the CsPbBr$_3$ film gradually decreases with the ALD cycle up to 20 and levels off with further rise of the ALD cycle. When the ALD cycle is above 40, the PL lifetime reduction exceeds 10 fold. The decrease of the PL lifetime against the ALD cycle is in sync with the increase of the PL intensity, which indicates that the PL enhancement mainly originates from the acceleration of radiative recombination.
Figure S6. Absorption spectra of a CsPbBr$_3$ perovskite film before and after Al$_2$O$_3$ modification.

Because the chemical modification only occurs at the perovskite surface, the light absorption coefficient of the CsPbBr$_3$ perovskite film remains nearly unchanged after Al$_2$O$_3$ modification.
We fabricated the CsPbClBr$_2$ and CsPbBr$_{1.5}$I$_{1.5}$ perovskite films. After Al$_2$O$_3$ coating, the CsPbClBr$_2$ (CsPbBr$_{1.5}$I$_{1.5}$) film exhibits a ~200 (~310) fold enhanced PL intensity and a ~2.2 (~4.3) fold reduced PL lifetime, revealing a ~400 (~1300) fold increase in the radiative recombination rate. This indicates that the interfacial chemistry strategy of enhancing radiative recombination is universal for the perovskites with different halogen compositions.
Figure S8. PL spectra and decay profiles of the bare and Al₂O₃-modified CsPbBr₃ perovskite films measured from the substrate side under the same UV excitations.

We measured the PL characteristics of the bare and Al₂O₃-modified CsPbBr₃ perovskite films from the substrate side. After Al₂O₃ coating, the PL intensity increases ~480 times and the PL lifetime decreases ~10 times. Apparently, the ultrafast radiative recombination in the Al₂O₃-modified CsPbBr₃ film detected from the substrate side are almost same as those from the perovskite surface (Figure 2). This is attributed to the large carrier diffusion length (up to ~ 10 μm) of the CsPbBr₃ perovskite.[15] Because the carrier diffusion length is much larger than the film thickness of ~125 nm, almost all photogenerated carriers in the bulk phase, no matter from which side the sample is excited, can diffuse rapidly to the perovskite surface and are captured by the CsPbBr₃ surface states with a larger exciton binding energy. As a result, almost all radiative decay of the photogenerated carriers in the Al₂O₃-modified CsPbBr₃ perovskite films occur through the surface ultrafast recombination pathway.
SUPPORTING INFORMATION

Figure S9. Schematic diagram of a micro-photoluminescence measurement system.

Optically pumped amplified spontaneous emission (ASE) was measured on a far-field optical system equipped with a mode-locked Ti:sapphire laser, a microscope, a charge-coupled device camera, and a spectrophotometer. The 400 nm excitation pulses were generated by frequency doubling of the fundamental output from a regenerative amplifier (Spectra Physics, 800 nm, 100 fs, 1 kHz), which was in turn seeded by a mode-locked Ti:sapphire laser (Mai Tai, Spectra Physics, 800 nm, 100 fs, 80 MHz). The excitation laser was filtered using a 720-nm short-pass filter and then was focused down to a spot of ~100 μm in diameter through an objective (Nikon CFLU Plan, 20×, N.A = 0.8). The power at the input was altered by the neutral density filters. The emissions from the perovskite films were collected by the same objective with the back-scattering configuration, then imaged on the CCD camera and analyzed by the spectrometer after removing the excitation beam with a 420 nm long-pass filter.
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Author Contributions

H.D., L.M. and O.G.S. conceived the idea. H.D., C.Z., Y.S.Z., and L.M. designed the experiments. H.D., S.D., C.N.S., and M.Z. prepared the samples. H.D., C.Z. and M.T. performed the structure characterizations. H.D., C.Z. and W.N. performed the optical measurements. H.D. and C.Z. performed the numerical simulation. H.D., L.M., Y.S.Z. and O.G.S. wrote the paper. All authors participated in the data analyses and discussions.