Supporting Information

Charge Transfer Boosting Moisture Resistance of Seminude Perovskite Nanocrystals via Hierarchical Alumina Modulation

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Experimental and Computational Methods

Synthesis of $h$-$Al_2O_3$: Alumina nanoflowers were synthesized by the hydrothermal method. Typically, $0.875 \text{ mmol } Al_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O}$ (99%), $0.345 \text{ mmol } \text{CTAB}$ (99%), and $5.245 \text{ mmol } \text{urea}$ (99%) were mixed into $35 \text{ ml}$ of distilled water at room temperature. After stirring for 30 min and undergoing ultrasonic processing for 10 min, the resulting solution was transferred to a $50 \text{ ml}$ teflon-lined stainless-steel autoclave sealing at $120^\circ\text{C}$ for 2 h and then heated at $180^\circ\text{C}$ for another 3 h. The precipitation was collected through centrifugation and dryness and then calcined at $700^\circ\text{C}$ for 3 h in air to get hierarchical $Al_2O_3$. Similarly, spherical $Al_2O_3$ was formed at $120^\circ\text{C}$ for 2 h. Lamellar $Al_2O_3$ was synthesized using $\text{AlCl}_3$ (99%) as the aluminum source.

Synthesis of $\text{CsPbX}_3@h$-$Al_2O_3$ composites: $\text{CsPbX}_3$ NCs were prepared according to the reference. For the in-situ synthesis of $\text{CsPbX}_3@h$-$Al_2O_3$ composites, in brief, $10 \text{ ml } \text{ODE}$ (90%), $0.376 \text{ mmol } \text{PbX}_2$ (99.999%), and $0.12 \text{ g } h$-$Al_2O_3$ were mixed in a 50 mL three-necked flask, degassed for 10 min, and then dried at $120^\circ\text{C}$ for 1 h in vacuum. Under $\text{N}_2$ protection, $1 \text{ ml } \text{OA}$ (90%) and $1 \text{ ml } \text{OLA}$ (80–90%) were injected into the flask at 20 $^\circ\text{C}$. The temperature was elevated to 170 $^\circ\text{C}$ until the solution became clear, and then 1 ml $\text{Cs-oleate}$ was quickly injected. Five seconds later, the solution was immediately cooled in an ice-water bath. Then, the cooled solution was stirred for 6 hours so that the NCs could fully anchor on the surface of the $h$-$Al_2O_3$. Finally, the $\text{CsPbX}_3@h$-$Al_2O_3$ composites were centrifuged and washed once by methyl acetate (99%), and then the precipitate was dried under vacuum at room temperature.

Equipment: Powder X-ray diffraction patterns of the samples were measured by using an Empyrean diffractometer equipped with monochromatic Cu Kα radiation ($\lambda = 1.54056$ Å). The morphologies of the samples were analyzed using MIRA3 TESCAN field-emission scanning
electron microscopy. Transmission electron microscopy images were collected using a 200 kV FEI TECNAI G2 F20 microscope. The photoluminescence spectra were recorded using F4500 spectrometry. The PL decay curves were collected on an FLS 980 spectrometer, and PLQY was measured in an integrating sphere using 365 nm as the excitation wavelength.

*Computational details:* To reveal the charge transfer between the perovskite NCs and the alumina surface, density functional theory (DFT) calculations with the GGA/PBE functional and the double zeta plus polarization orbitals basis set were carried out using the SIESTA code. Other detailed computational parameters were a $k$-point sampling of $1\times1\times1$, an energy cutoff of 300 Ry, a projected atomic orbital energy shift of 10 meV, a maximal force threshold of 0.02 eV/Å, and a density matrix tolerance of $1.0\times10^{-4}$. The (100) surface of Al$_2$O$_3$ was modeled with a $2\times2$ supercell to form the interface with CsPbBr$_3$. CsPbBr$_3$ have the perovskite structure, namely, Pb forms octahedral coordination bonds with six Br, and Cs is located in the cavity of octahedrons. Two possible contacts between CsPbBr$_3$ and the alumina surface were considered through the interactions of Pb, Br or Cs, Br atoms with O, and Al atoms. On the basis of the first-principles DFT calculation results, Bader code was used for the charge analysis.
Figure S1. Fluorescence photos of pure perovskite NCs and composites stored in water, (a) CsPbCl$_{1.5}$Br$_{1.5}$, (b) CsPbCl$_{1.5}$Br$_{1.5}$@h-Al$_2$O$_3$, (c) CsPbBr$_{1.2}$I$_{1.8}$ and (d) CsPbBr$_{1.2}$I$_{1.8}$@h-Al$_2$O$_3$.

Figure S2. Photographs of (a, b) pure perovskite NCs in hexane and (c, d) dried CsPbX$_3$@h-Al$_2$O$_3$ composite powders for well exhibiting perovskite body-color in sunlight and good photoluminescence under 365 nm light radiation. Blue: CsPbCl$_{1.5}$Br$_{1.5}$, green: CsPbBr$_3$, red: CsPbBr$_{1.2}$I$_{1.8}$.
Figure S3. SEM image of $h$-Al$_2$O$_3$ microspheres (looking like nanoflowers) with hollow structures.

Figure S4. Contact angles of (a) $c$-SiO$_2$, (b) CsPbBr$_3@c$-SiO$_2$, (c) $c$-TiO$_2$, (d) CsPbBr$_3@c$-TiO$_2$, (e) $c$-ZnO, (f) CsPbBr$_3@c$-ZnO, (g) $c$-Al$_2$O$_3$ and (h) CsPbBr$_3@c$-Al$_2$O$_3$ powders.

Figure S5. SEM images of (a) commercial ($c$-), (b) spherical ($s$-), and (c) lamellar ($l$-) Al$_2$O$_3$. 
Figure S6. Fabrication of dendritic SiO$_2$ ($d$-SiO$_2$) and CsPbBr$_3$@$d$-SiO$_2$ composite. $d$-SiO$_2$: (a) SEM, (b) and (c) TEM images. CsPbBr$_3$@$d$-SiO$_2$ composite: (d) SEM, (e) and (f) TEM images. (g) Element mappings of composite particles. (h) XRD patterns of the powders. Luminescent photos of CsPbBr$_3$@$d$-SiO$_2$ composites in water for (i) 0 day and (j) 2 days under the sunshine (left) and 365 nm irradiation (right).
Figure S7. PL spectrum comparison of CsPbBr$_3@$l-Al$_2$O$_3$ composite before washing and after washing 8 times using $n$-hexane. The inset shows that the upper hexane solution became clear and colorless.

Figure S8. (a) TEM image of the CsPbX$_3@$l-Al$_2$O$_3$ composite, (b–f) element mappings of the composite, (b) Al, (c) O, (d) Cs, (e) Pb and (f) Br. The green dotted lines draw the area of alumina.
Figure S9. The optimized geometries of perovskite CsPbBr$_3$ (a) and complex Al$_2$O$_3$/CsPbBr$_3$ (b) by first-principles DFT calculations (GGA/PBE). The interface Pb and Br atoms, the inside Pb-Br bonding layer, and the water-interacting Br layer are respectively framed by red, green, and blue dashed-lines. The DFT-optimized geometries of water attachment on perovskite CsPbBr$_3$-H$_2$O (c) and complex Al$_2$O$_3$/CsPbBr$_3$-H$_2$O (d) via a Br…H-O-H weak bond and Cs-O bond. The binding energies and atomic distances for water attachment on them are labeled besides. The lattice constants in all cases are $a = 16.83\ \text{Å}$, $b = 16.14\ \text{Å}$, $c = 50\ \text{Å}$, and $\alpha = \beta = \gamma = 90^\circ$. 
Figure S10. The Al-Br interatomic distances within 3 Å and electron populations on these Al-Br chemical bonds in the complex of Al₂O₃/CsPbBr₃ as shown in Figure S9 (b).

ps: Fewer Pb-O bonds shorter than 3 Å are also found at the interface of the complex.

Figure S11. TiO₂ rutile (110), ZnO (10-10), and SiO₂ (100) surfaces by first-principles DFT optimizations (GGA/PBE). The atomic charges are average values by Bader charge analysis and collected from the unsaturated atoms on surfaces.
**Table S1.** photoluminescence quantum yield (PLQY) and average lifetime of blue, green, red perovskite NCs and their composites.

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<th>Materials</th>
<th>PLQY (%)</th>
<th>Lifetime (ns)</th>
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<td>CsPbCl$<em>{1.5}$Br$</em>{1.5}$</td>
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<td>CsPbBr$<em>{1.2}$I$</em>{1.8}$@h-Al$_2$O$_3$</td>
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<td>106.2</td>
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**Figure S12.** (a) XPS spectra of CsPbBr$_3$, h-Al$_2$O$_3$ and CsPbBr$_3$@h-Al$_2$O$_3$. (b) XPS of Br 3d core levels for CsPbBr$_3$@h-Al$_2$O$_3$ and CsPbBr$_3$. 
Figure S13. Time-resolved decays curves of perovskite NCs and their composites, (a) blue-emitting materials, (b) red-emitting materials.

Figure S14. Thermal cycling stabilities. (a) CsPbBr$_3$@d-SiO$_2$ composites, (b) CsPbBr$_3$ NCs and CsPbBr$_3$@Al$_2$O$_3$ composites with different morphology of alumina, (c) blue CsPbCl$_{1.5}$Br$_{1.5}$ NCs and CsPbCl$_{1.5}$Br$_{1.5}$@h-Al$_2$O$_3$ composites, and (d) red CsPbBr$_{1.2}$I$_{1.8}$ NCs and CsPbBr$_{1.2}$I$_{1.8}$@h-Al$_2$O$_3$ composites.
REFERENCES

