

## Electronic Supplementary Information

### In-situ Synthesis of High-Efficiency CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub>

#### Composite Nanocrystals in Aqueous Solution by Microemulsion

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## **Experimental Section**

### **Chemicals.**

PbBr<sub>2</sub> (Aladdin, 99.9 %, Shanghai, China), CsBr (Aladdin, 99.9 %, Shanghai, China), Cs<sub>2</sub>CO<sub>3</sub> (Aladdin, 99.9 %, Shanghai, China), 1-Octadecene (ODE, Sigma-Aldrich, 90%, America), Oleic acid (OA, Sigma-Aldrich, 90%, America), Oleylamine (OAm, Acros Organics, 80-90%, America), Sodium dodecylbenzenesulfonate (SDBS, Aladdin, 95.0%, Shanghai, China), HF (Aladdin, 40% in H<sub>2</sub>O, Shanghai, China), NaOH (Aladdin, 98.0%, Shanghai, China), HNO<sub>3</sub> (Aladdin, 65.0%, Shanghai, China), Li Bai cleaner essence (Guangzhou Liby Enterprise Group Co., Ltd., China), Chao Neng cleaner essence (Nice Group Co., Ltd., China), Diao Pai cleaner essence (Nice Group Co., Ltd., China), Frosch cleaner essence (Werner & Mertz Gruppe, Germany), toluene (99.9%, Sinopharm Chemical Reagent Co., Ltd., China), and commercial K<sub>2</sub>SiF<sub>6</sub>:Mn<sup>4+</sup> (Yantai Shield Advanced Materials Co., Ltd.) were purchased and used without further purification. The cleaner essence was rich in sodium dodecylbenzenesulfonate, sodium fatty alcohol ether sulfate, foaming agent, and solubilizer.

### **Preparation of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs by cleaner essence and the treatment with HF.**

Typically, PbBr<sub>2</sub> (0.1 g), CsBr (0.1 g), Li Bai cleaner essence (0.3 g) and deionized water (5.0 mL) were added into in a 40 mL centrifuge tube with vigorous stirring under the ambient conditions (the humidity was 45 ~ 65% and the temperature was 15~35 °C). After 10.0 min, 50 uL HF was added in 5 mL supernatant for 10.0 min. Then the produce was centrifuged at 5000 rpm for 3.0 min to remove the large particles and remaining impurities and keep the supernatant. Then the supernatant was recentrifuged at 12500 rpm for 5 min. The supernatant was discarded, and the precipitate was washed by toluene three times to obtain more purified perovskites solutions (Three times of washing would strip the surfactant and sodium dodecylbenzene-sulfonate from NCs and made the NCs can uniformly disperse in toluene). Finally, the precipitate was dispersed in 5.0 mL toluene for further test and use.

The Li Bai cleaner essence can be replaced by the Chao Neng cleaner essence, Diao Pai cleaner essence, Frosch cleaner essence to synthesize CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs.

The total volume of solution was enlarged by 20 times for the large-scale synthesis of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs.

#### **Preparation of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs without the treatment of HF.**

Typically, PbBr<sub>2</sub> (0.1 g), CsBr (0.1 g), Li Bai cleaner essence (0.3 g) and deionized water (5.0 mL) were added into in a 40 mL centrifuge tube with vigorous stirring under the ambient conditions (the humidity was 45 ~ 65% and the temperature was 15~35 °C). After 20.0 min, the produce was centrifuged at 5000 rpm for 3.0 min to remove the large particles and remaining impurities and keep the supernatant. Then it was recentrifuged at 12500 rpm for 5 min. The supernatant was discarded, and the precipitate was washed by toluene three times to obtain more purified perovskites solutions (Three times of washing would strip the surfactant and sodium dodecylbenzene-sulfonate from NCs and made the NCs can uniformly disperse in toluene). Finally, the precipitate was dispersed in 5.0 mL toluene for further test and use.

#### **Preparation of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs by SDDBS.**

Similar to the preparation of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs without the treatment of HF, the cleaner essence was replaced by 0.015 g SDDBS.

#### **Preparation of Cs-oleate precursor.**

Cs<sub>2</sub>CO<sub>3</sub>(0.407 g), OA (2.5 mL) and of ODE (17.5 mL) were mixed in a 50 mL 3-neck flask. This mixture was heated to 120 °C and degassed and dried in vacuum at 120 °C for 1 h. After degassing, the temperature was subsequently raised to 150 °C under N<sub>2</sub> until all Cs<sub>2</sub>CO<sub>3</sub> reacted with OA. The Cs-oleate precursor solution was stored in a three-neck flask under N<sub>2</sub> for the synthesis of perovskite NCs.

### **Preparation of CsPbBr<sub>3</sub> NCs.**

PbBr<sub>2</sub> (0.1468 g), ODE (10 mL), OA (1.0 mL), and OAm (1.0 mL) were mixed in a 50 mL three-neck bottle. Water and oxygen were removed under vacuum for 1 hour at 120 °C. Before raising the temperature to 180 °C, the solution was kept under N<sub>2</sub> environment. After maintaining the temperature at 180 °C for 10 min, the 0.8 mL Cs-oleate precursor, pre-heated at 110 °C, was injected into the solution. After 10 s, the three-neck flask was placed in an ice bath and cooled to room temperature. Finally, the crude solution was centrifuged at 10000 rpm. The precipitate was washed with toluene two times and dispersed in 5.0 ml toluene for further test and use.

### **Fabrication of the light-emitting diodes.**

White light-emitting diodes (WLED) were fabricated by combining blue-chip (457 nm, Shenzhen VANQ Technology Co. Ltd), different volumes of the as-prepared CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs or CsPbBr<sub>3</sub> NCs solution, and commercial red phosphor K<sub>2</sub>SiF<sub>6</sub>:Mn<sup>4+</sup>. In a typical process, a total of 2.0 mL of a toluene solution of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs or CsPbBr<sub>3</sub> NCs solution was added to the mixture of silicone resin (YD65-5A) and anhydride curing agent (YD65-5B) with vigorous stirring. And the weight of YD65-5A and YD65-5B were kept as 0.15 g and 0.15 g. After the mixture was heated to 40 °C for 30 min under vacuum to evaporate toluene, x g of K<sub>2</sub>SiF<sub>6</sub>:Mn<sup>4+</sup> (x=0, 0.01, 0.02, 0.03, 0.04, 0.05) were added with vigorous stirring. The obtained mixture slurry was directly coated onto blue chips by dipping and thermally cured in a vacuum oven at 50 °C for 3 h to obtain white LEDs. The white LEDs were operated at 3.5 V and a drive current 50 mA. The optical properties of white LEDs were measured by a light metrology system with an integrating sphere (Labsphere) and a spectrograph (CDS-600, Labsphere).

## **Characterization.**

**The powder X-ray diffraction (XRD)** was performed on a D-MAX 2200 VPC in the range of  $10^\circ < 2\theta < 60^\circ$  at a scanning rate of  $8^\circ/\text{min}$  with CuK $\alpha$ 1 radiation ( $\lambda = 1.5405 \text{ \AA}$ ) on a silicon wafer. **Transmission electron microscope (TEM)** images were acquired on an FEI Tecnai G2 Spirit instrument with an accelerating voltage of 120 kV. High-resolution TEM images, **High-Resolution TEM** have acquired on a JEOL-JEM 2100F transmission electron microscope an accelerating voltage of 200 kV and an energy dispersive detector. **The inductively coupled plasma mass spectrometer (ICP-MS)** was measured using the iCAP Qc and the solvent is 5 % HNO $_3$ . **Fourier transformation infrared (FTIR) spectra** were taken by using a Fourier transformation infra-red spectrometer (Bruker, EQUINOX 55). **The photoluminescence (PL) spectra** within the PL lifetime decay curves were measured using an Edinburgh Instruments FSP1000 Time-Resolved and Steady-State Fluorescence Spectrometers. **The absolute photoluminescence quantum yield (PL QY)** of the sample was performed at an excitation wavelength of 365 nm on the Hamamatsu instruments C9920. **The pH** of the sample was measured using EZDO® W6267 Waterproof Pen Type pH Meter. The pH of the HF solution was used **pH test paper**.

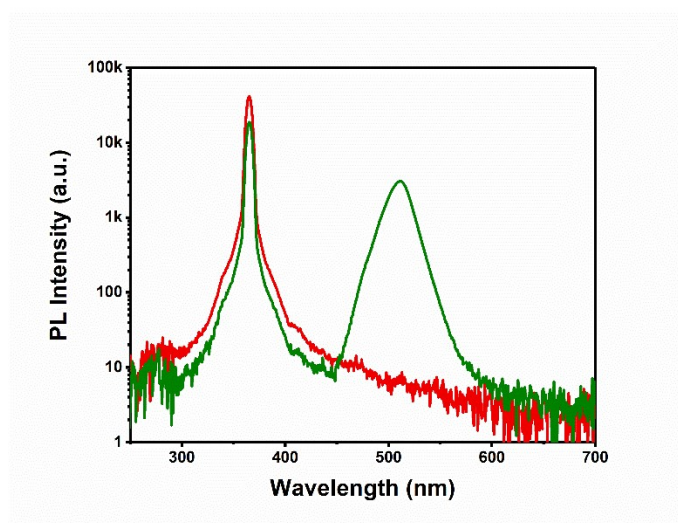


Figure S1. The PL QY spectra of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs.

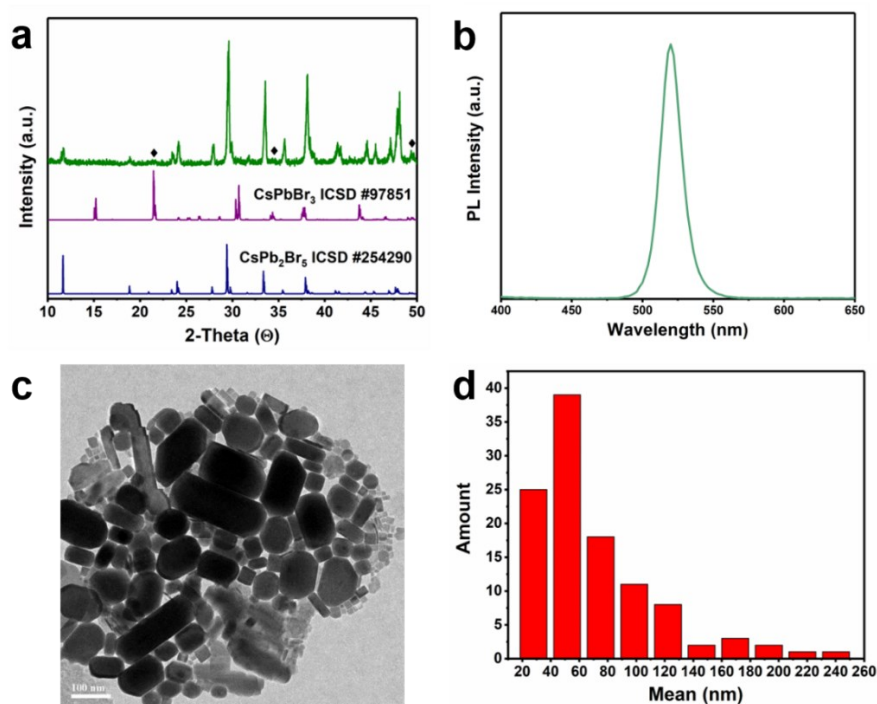


Figure S2. (a) XRD patterns of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. (b) The PL emission spectrum of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. (c) TEM image of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. (d) The size distribution of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. The CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs were prepared only using pure SDBS.

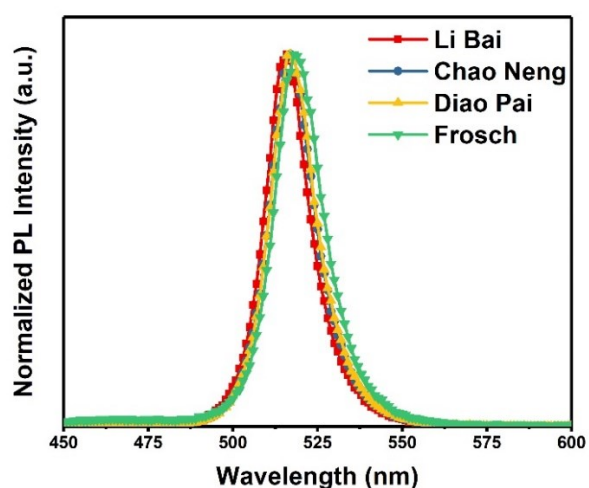


Figure S3. PL emission spectra of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs which were synthesized by different brands cleaner essences.

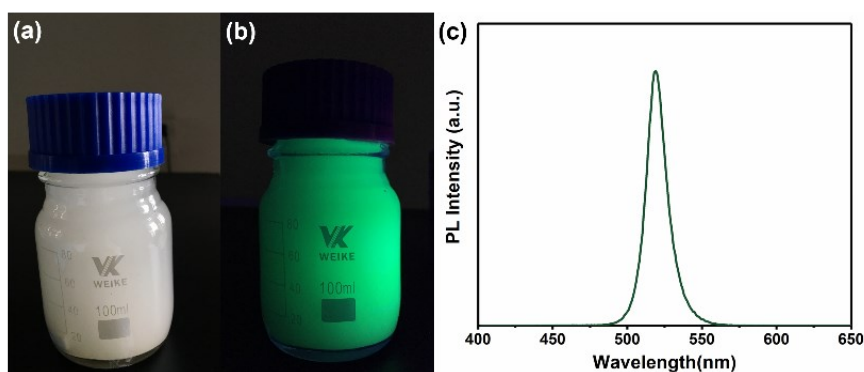


Figure S4. The pictures of the large-scale synthesized products under the natural light (a) and UV light (365 nm) (b) where the total volume of solution for a typical synthesis process was enlarged by 20 times. (c) The PL emission spectrum of the large-scale synthesized CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs.

Originally, a total volume of 5 ml solution was used to synthesize the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. We had tried to synthesize the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs in a large-scale. The total volume of the solution was enlarged by 20 times. Figure S4 shows the pictures of the large-scale synthesized products under the natural light and UV light (365 nm) as well as its PL emission spectrum. As shown in Figure S4(c), the large-scale synthesized CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs give a green emission at 519.0 nm with a full width at half maximum of 16.0 nm, which is consistent with the composite NCs synthesized in small scale. These results suggest that the method shows consistency.

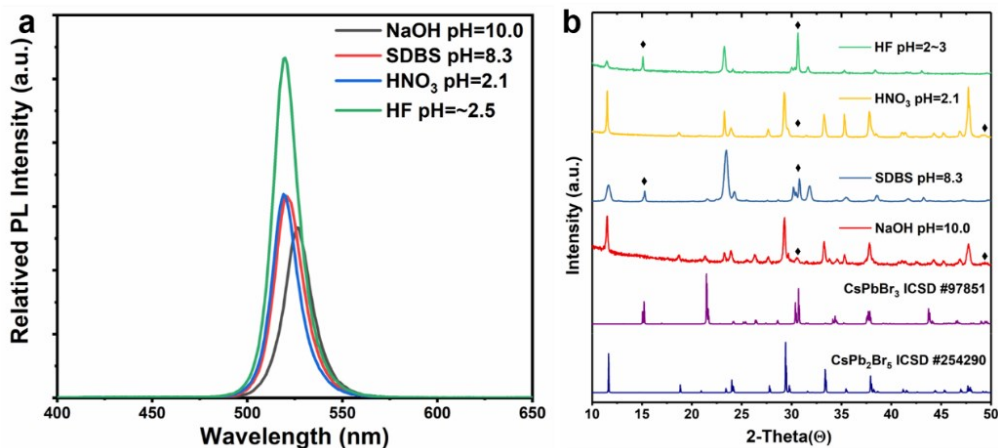


Figure S5. (a) The PL emission spectra and (b) XRD patterns of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs which were synthesized in different pH cleaner essence aqueous solution. The pH was adjusted by adding NaOH, HNO<sub>3</sub>, and HF in the SDBS solution.

The pH of the HF cleaner essence aqueous solution was tested by the pH test strips. For the sample of the NaOH, there was a little by-product of Pb<sub>2</sub>OBr<sub>2</sub>•H<sub>2</sub>O (JCPDs no. 06-0177).



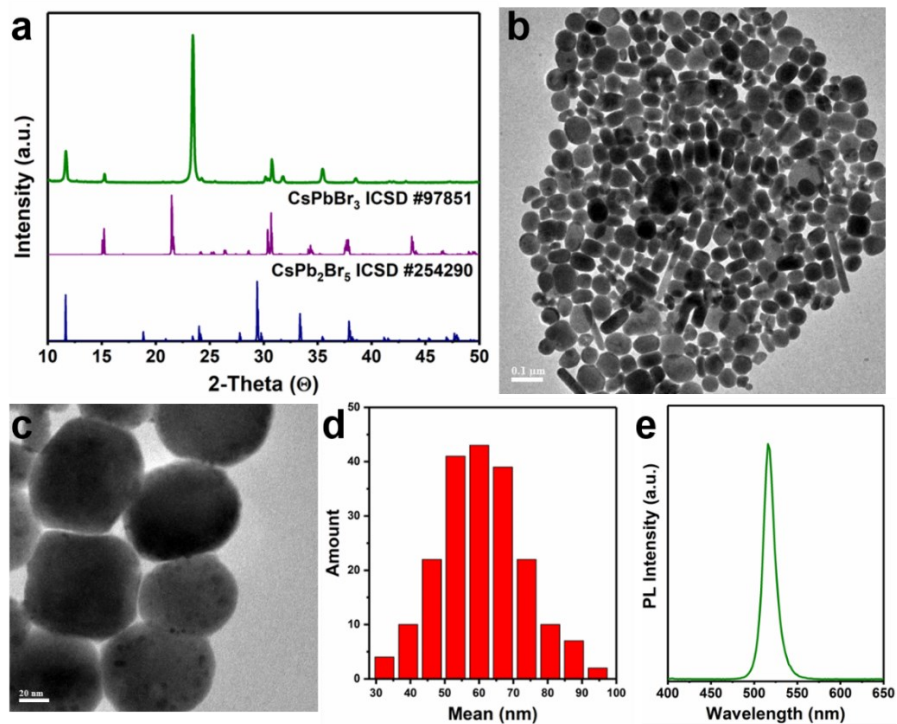


Figure S6. (a) XRD patterns of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. (b) TEM and HRTEM images of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. (d) The size distribution of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. (e) The PL emission spectrum of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs. The CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs were prepared without the treatment of HF.

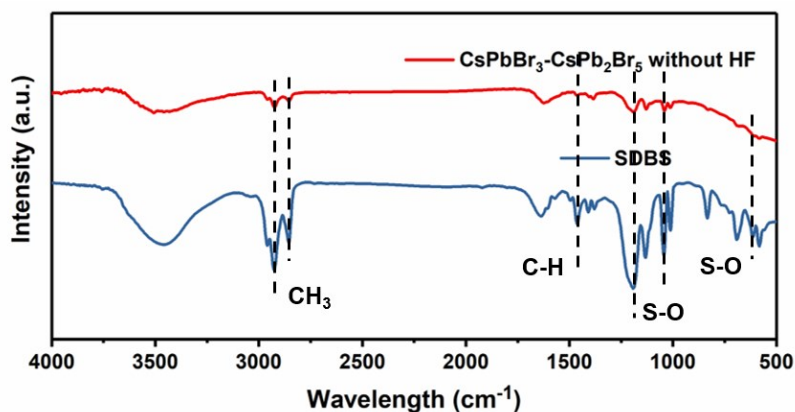


Figure S7. The FTIR spectra of the SDBS and CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs, which were without the treatment of HF.

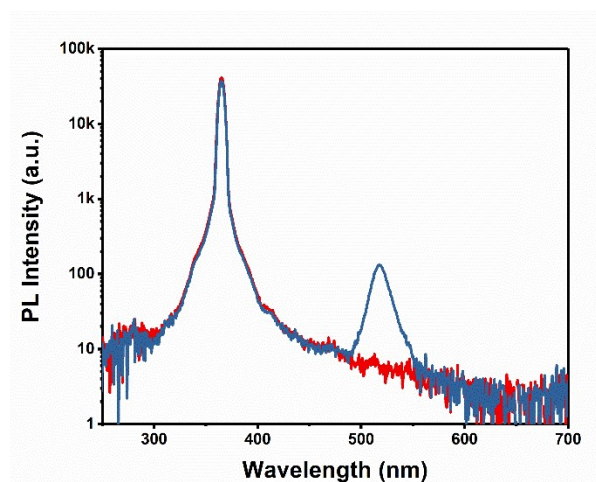


Figure S8. The PL QY spectra of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs without the treatment of the HF

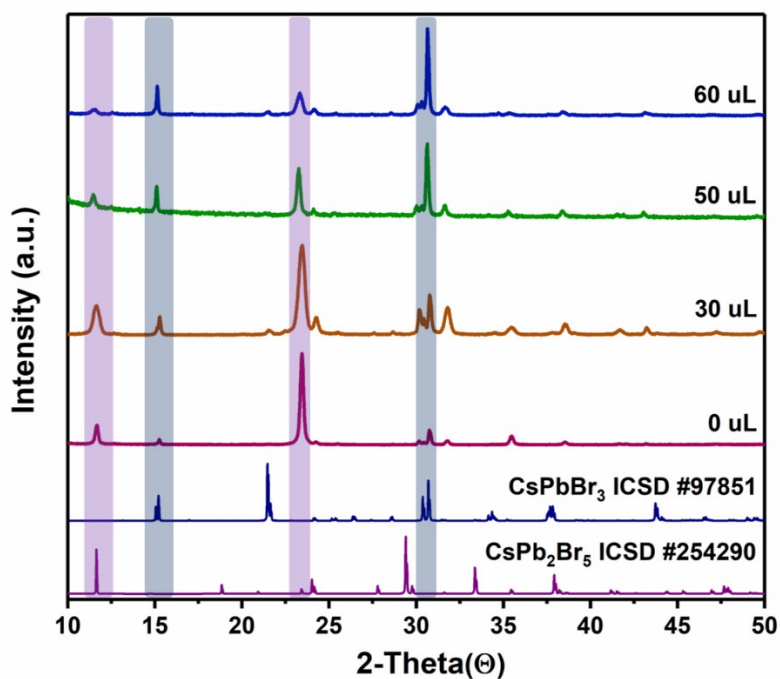


Figure S9. XRD patterns of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs by treatment with different amounts of HF.

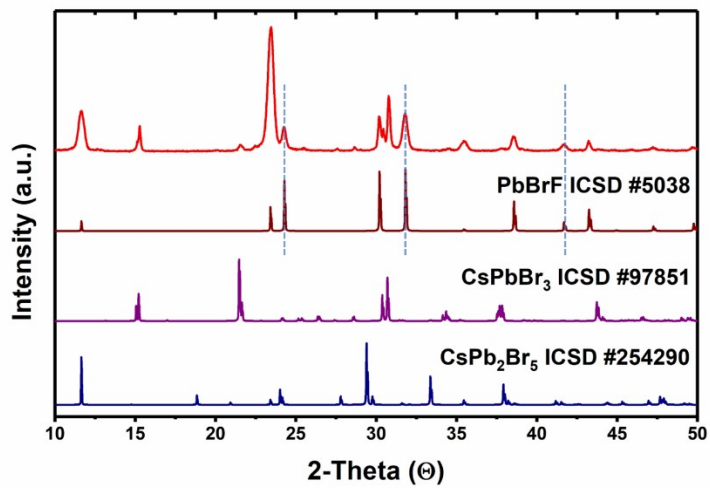


Figure S10. XRD patterns of the precipitate which was centrifuged for the first time (5000 rpm for 3.0 min) by treatment with HF.

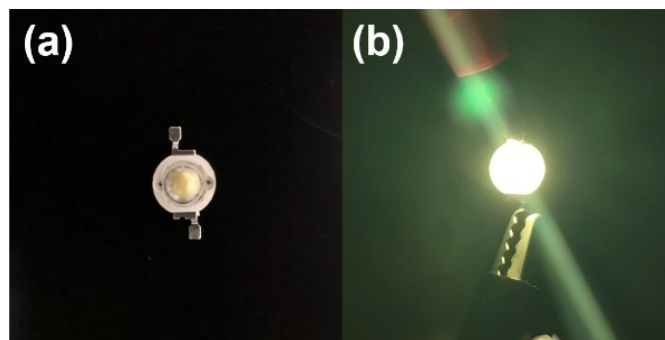


Figure S11. Photographs of the white LED based on as-prepared CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs and K<sub>2</sub>SiF<sub>6</sub>:Mn<sup>4+</sup>, off (a) and on (b) at 3.5 V and 50 mA.

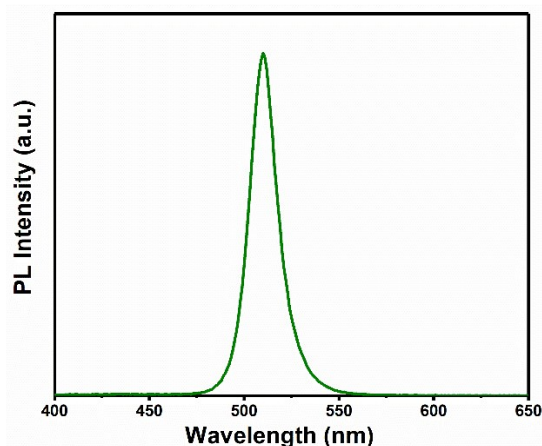


Figure S12. The PL emission spectrum of the CsPbBr<sub>3</sub> NCs.

The PL spectrum of CsPbBr<sub>3</sub> NCs centers at 511.0 nm with a full width at half maximum of 17.5 nm.

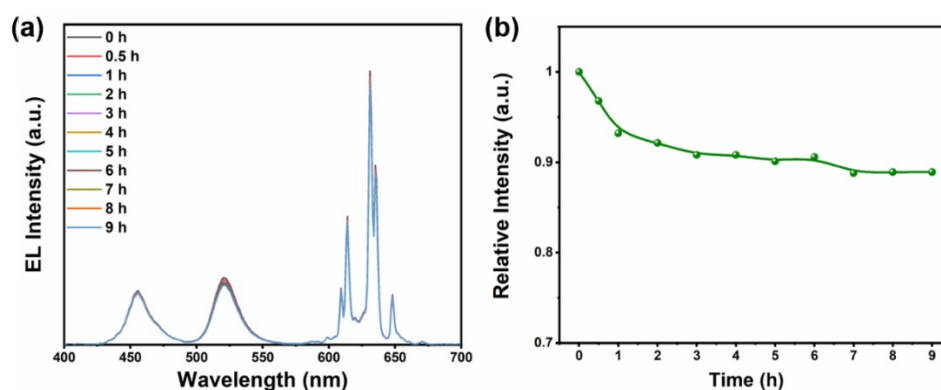


Figure S13. (a) EL spectra of the as-fabricated LED working at 3.5 V and 50 mA for a different time. (b) The dependence of the green EL emission intensity from CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs on working time.

To evaluate the stability of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs in the electroluminescent test, we have prolonged the work time of the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs based LED. Figure S13(a) and S13(b) show the EL spectra of the as-fabricated LED and the dependence of its green EL emission intensity from CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs on working time, respectively. Initially, the EL emission from the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs gradually decreases as the working time of the as-fabricated LED increases. After it works for 0.5 h and 7 h, the green EL emission intensities are about 96.8% and 89% of its original intensity, respectively. Thereafter, the green EL emission intensity does not further decrease. At 9 h, it still keeps 89% of the initial intensity. These results indicate that the CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> composite NCs has better stability in the electroluminescent test and demonstrate potential applications in white LEDs for wide color gamut display.