Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Reprecipitation Synthesis of Luminescent $CH_3NH_3PbBr_3/NaNO_3$ Nanocomposites with Enhanced Stability

Gaoling Yang,‡[a] Qingsong Fan,‡[a] Bingkun Chen,[b] Qingchao Zhou,[a] Haizheng Zhong*[a]

a. Beijing Key Laboratory of Nanophotonics and Ultrafine Optoelectronic Systems, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China.

b. Beijing Engineering Research Center of Mixed Reality and Advanced Display, School of Optoelectronics, Beijing Institute of Technology, Beijing 100081, China.

‡ These authors contributed equally to the work.

* E-mail: hzzhong@bit.edu.cn

CONTENTS:

Fig. S7 Photographs of fabricated white LED before (a, d) and after (b) the application of a forward current of 20 mA. (c) Schematic illustrating of a down-conversion white LED.

Fig. S8 PL spectra of the green-emitting LED measured at different working time.

4. Tables:

Table S1. Summary of the XRD analyses including miller index, 2θ degree and lattice spaces.

1. Experimental Section

1.1 Materials

All reagents were used as received without further purification: lead(II) bromide ($PbBr_2$, 99%, Aladdin), methylamine (CH_3NH_2, 33 wt % in absolute ethanol, Aladdin), n-octylamine (99%, Aladdin), oleic acid (90%, Alfa Aesar), N,N-dimethylformamide (ana-lytical grade, Beijing Chemical Reagent Co., Ltd., China), sodium nitrate ($NaNO_3$, Beijing Chemical Reagent Co., Ltd., China), toluene (analytical grade, Beijing Chemical Reagent Co., Ltd., China), $K_2SiF_6:Mn^{4+}$ (KSF, Beijing Yuji Science & Tech-nology Co., Ltd., China).

1.2 Synthesis of CH_3NH_3Br

CH_3NH_3Br was synthesized by reaction of the methylamine with hydrobromic acid (HBr). First, methylamine in absolute ethanol was stirred and cooled to 0 °C with the addition of acid. The reaction solution was stirred for 2 h. Then rotary evaporation was applied to evaporate the solvent with a pressure of -0.1 MPa at 45 °C. The precipitate was washed three times with diethyl ether and dried under vacuum (60 °C, 5 h) for future use.

1.3 Synthesis of $CH_3NH_3PbBr_3/NaNO_3$ nanocomposites

First, 73.4 mg (0.2 mmol) lead bromide ($PbBr_2$), 17.9 mg (0.16 mmol) methylammonium bromide (CH_3NH_3Br), 20 μL *n*-octylamine, 0.5 mL oleic acid (OA), 5 mL DMF and 0.1 g (1.18 mmol) $NaNO_3$ are mixed to form a precursor solution, then poured into 30 mL toluene under vigorous stirring at room temperature. The yellow precipitates were collected and air-dried after centrifugation at 6000 rpm for 3 min.

1.4 Synthesis of $CH_3NH_3PbBr_3$ nanocrystals

Controlled $CH_3NH_3PbBr_3$ nanocrystals (NCs) were fabricated following our previous technique.[1] Simply, a mixture of 17.9 mg (0.16 mmol) CH_3NH_3Br and 73.4 mg (0.2 mmol) was dissolved in 5 mL of DMF with 20 μL of n-octylamine and 0.5 mL of oleic acid to form a precursor solution. 2 mL precursor solution was dropped into 10 mL of toluene with vigorous stirring. Along with the mixing, strong green PL emission was observed. After centrifugation at 7000 rpm for 10min to discard the precipitates, a bright yellow-green colloidal solution was obtained.

1.5 Fabrication of LED devices

A fixed amount of $CH_3NH_3PbBr_3/NaNO_3$ nanocomposite powder and $K_2SiF_6:Mn^{4+}$ powders were mixed with 100 mg of thermal-curable silicone resin OE-6551A (Dow Corning Co.) under vigorous stirring for 30 min. Subsequently, 200 mg of the hardener OE-6551B was added. In order to eliminate the air bubbles, the mixture was placed into a vacuum oven for 30 min at 50 °C to form a composite sol, which deposited by drop casting on top of an InGaN blue-emitting LED chip (455 nm S-16CBMUP-A, Sanan optoelectronics, China) to form the down-conversion layer.

2. Characterization

2.1 X-ray Diffraction (XRD)

The XRD measurements were measured on a Bruker/D8 FOCUS X-ray diffractometer, using a Cu KR radiation source (wavelength at 1.5405 Å). The samples were scanned from $3° < 2\theta < 60°$ at an increment of 2°/min.

2.2 UV-vis Absorption Spectroscopy and Photoluminescence (PL) Spectroscopy

UV-vis absorption spectra were measured on a UV-6100 UV-vis spectrophotometer (Shanghai Mapada Instruments Co., Ltd., China). PL spectra were taken using a F-380 fluorescence spectrometer (Tianjin Gangdong Sci. & Tech. Development Co., Ltd., China).

2.3 Field Emission Scanning Electron Microscopy (FE-SEM)

The morphology and corresponding compositional analysis were characterized by Field Emission Scanning Electron Microscope (FESEM) (HITACHIS-4800) equipped with Energy Dispersive X-Ray spectroscopy (EDX). The $CH_3NH_3PbBr_3/NaNO_3$

nanocomposites powder was embedded into histological resin (Kulzer) by initiating the cross-linking process using a 254 nm UV light (15 min, 80 ℃). After 8 hours, sheets were cut into thin sheets for SEM measurements.

2.4 Absolute PL quantum yields measurements

The absolute PLQYs were determined using a fluorescence spectrometer with an integrated sphere (C9920-02, Hamamatsu Photonics, Japan) excited at a wavelength of 450 nm using a blue LED light source.

2.5 Time-resolved PLmeasurements

Time-resolved PL measurement was collected using a fluorescence lifetime measurement system (C11367-11, Hamamatsu Photonics, Japan).

2.6 Solvent/thermal/photo stability measurement

To test the thermal stability of $CH_3NH_3PbBr_3$ NCs and $CH_3NH_3PbBr_3/NaNO_3$ nanocomposite, we dropped a certain amount of NCs/toluene and nanocomposite/toluene mixture onto a piece of quartz glass to form a thin film. The thermal stability test was carried out by measuring the PL spectra of the samples at different temperature. For photostability test, continuous UV lamp (365 nm, 6 W) irradiation was implemented at room temperature. The test period was set from 1 h to 14 h, and the corresponding PL spectra were recorded. We choose chloroform as the solvent to test their solvent resistance. We poured the same quality of $CH_3NH_3PbBr_3$ NCs and $CH_3NH_3PbBr_3/NaNO_3$ nanocomposite powders into the same chloroform solvent, the mixtures were stored in the dark air at room temperature. The PL intensity of the precipitates in chloroform is recorded using fluorescence spectrometer.

3. Figures:

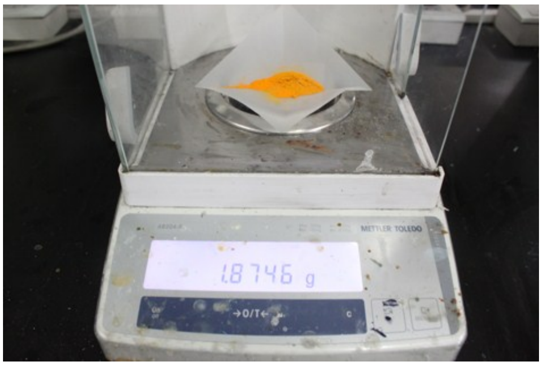

Fig. S1 Optical picture of the sample (around 1.9 g) obtained from large-scale synthesis.

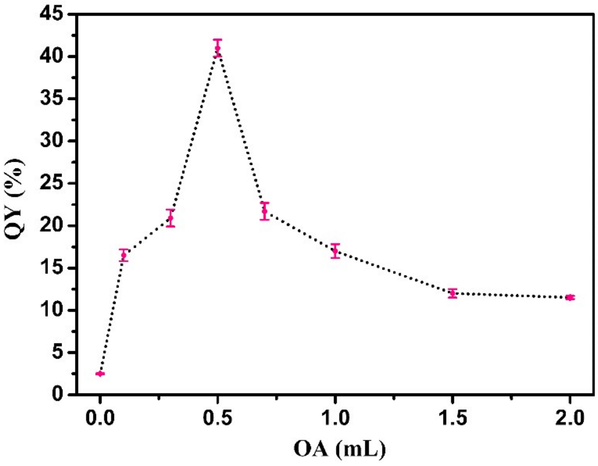

Fig. S2 PL QYs of $CH_3NH_3PbBr_3/NaNO_3$ nanocomposite as a function of the amount of oleic acid.

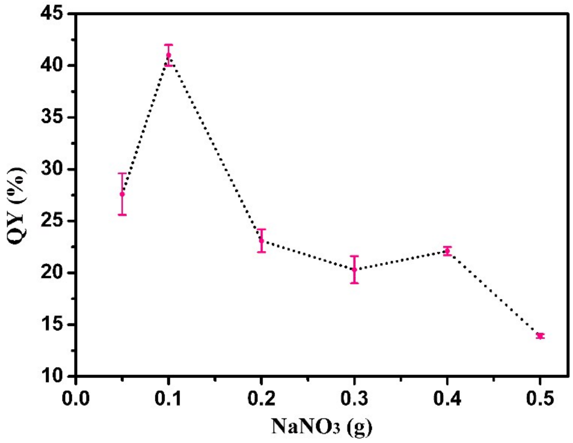

Fig. S3 PL QYs of $CH_3NH_3PbBr_3/NaNO_3$ nanocomposites as a function of the amount of $NaNO_3$.

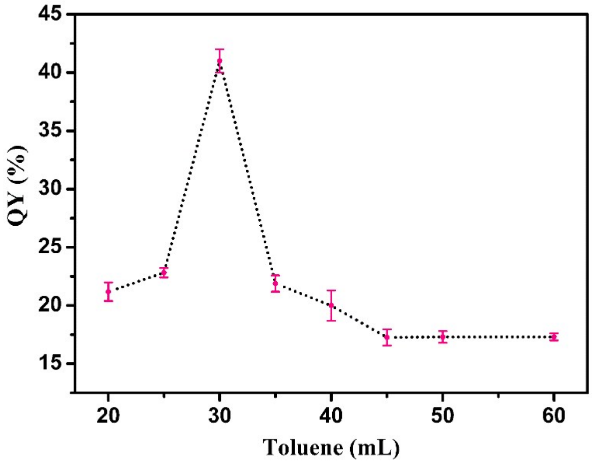

Fig. S4 PL QYs of $CH_3NH_3PbBr_3/NaNO_3$ nanocomposites as a function of the amount of toluene.

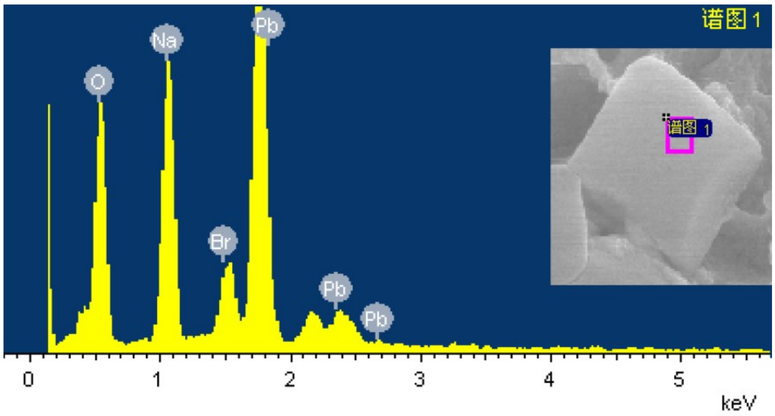

Fig. S5 EDS spectrum and corresponding SEM image (inset) of as-fabricated $CH_3NH_3PbBr_3/NaNO_3$ nanocomposites.

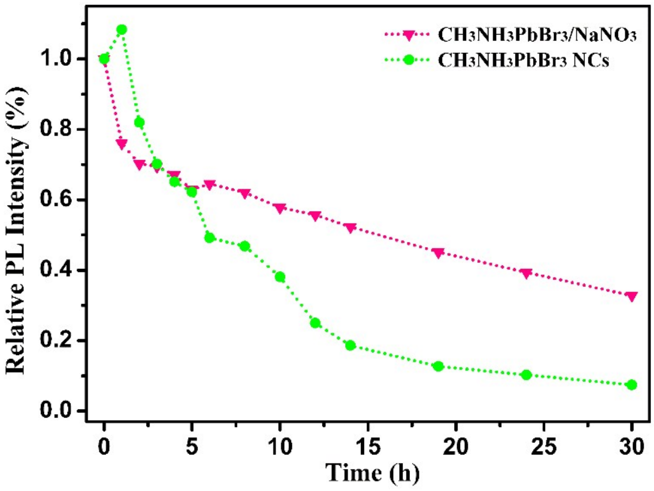

Fig. S6 Solvent stability test of $CH_3NH_3PbBr_3$ NCs and $CH_3NH_3PbBr_3/NaNO_3$ nanocomposites in chloroform.

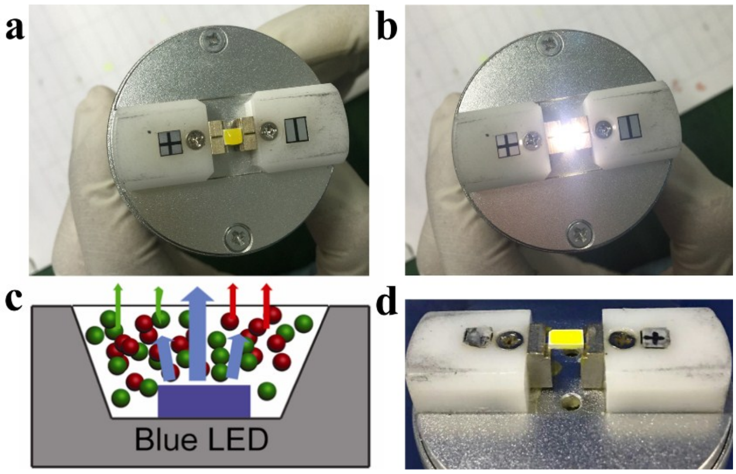

Fig. S7 Photographs of fabricated white LED before (a, d) and after (b) the application of a forward current of 20 mA. (c) Schematic illustrating of a down-conversion white LED.

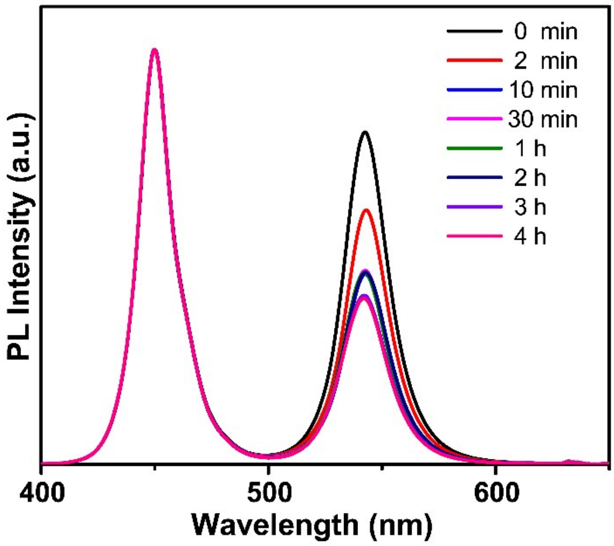

Fig. S8 PL spectra of the green-emitting LED measured at different working time.

4. Tables:

Table S1. Summary of the XRD analyses including miller index, 2θ degree and lattice spaces.

(h k l)	2-theta	d (nm)
(100)	15.1°	22.8
(200)	30.3°	30.2
(210)	34°	21.9
(211)	37.3°	25.0
(300)	46°	27.9
(222)	53.6°	31.1
(321)	58.3°	23.2

Reference

1. F. Zhang, H. Z. Zhong, C. Chen, X. G. Wu, X. M. Hu, H. L. Huang, J. B. Han, B. S. Zou, Y. P. Dong, ACS Nano, 2015, 9, 4533.