Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information:

Single Component Mn-doped Perovskite-related $CsPb_2Cl_xBr_{5-x}$ Nanoplatelets with A Record White Light Quantum Yield of 49%: A New Single Layer Color Conversion Material for Light-emitting Diodes

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Supporting Information

Experimental Section

Materials and Chemicals: $PbBr_2$ (lead (II) bromide 99%, Aladdin), $PbCl_2$ (lead (II) chloride 99.99%, Aladdin), CsBr (cesium bromide 99.5%, Sinopharm Chemical Reagent Co.Ltd (SCRC)), CsAC (cesium acetate 99.9%, Aladdin), $MnCl_2.4H_2O$ (Mn (II) chloride 99%, SCRC), $MnBr_2$ (Mn (II) bromide 98%, Alfa Aesar), $Mn(AC)_2$ (Mn (II) acetate 99.99%, Alfa Aesar), HBr (AR, SCRC), $C_6H_{15}N$ (hexylamine 99%, Afla Aesar), toluene (C_7H_8 AR, SCRC), n-octylamine (≥99%, Aladdin), oleic acid (90%, Alfa Aesar), DMF (N,N-dimethylformamide 99.5%, Kelong), n-hexane (97%, Kelong), acetone (99.5%, SCRC), PS (polystyrene, Aladdin).

Preparation of $C_6H_{13}NH_3Br$: 25 mL of methanol and 10 mL of hexylamine were loaded into a 100 mL flask and maintained at 0 °C using an ice water bath, forming a mixture via vigorous stirring. Then 10 mL of HBr was added dropwise into the as-obtained mixture, removing the ice water bath and the mixture was stirred for 2 hours at room temperature. After that, a rotary evaporator was used to remove the solvent (50 °C, 60rpm). The material was washed by diethyl ether and finally recrystallized from diethyl ether and ethanol mixture. After suction filtration, the production was collected and dried in a vacuum oven for 24 h and then transferred into the glove box for storage and following synthesis (H_2O<0.1 ppm, O_2<0.1 ppm).

Synthesis of $CsPb_2Br_5$ nanoplatelets: 0.1835g of $PbBr_2$ and 0.060 g of HABr were dissolved in 10 mL DMF. Then the mixture was injected in 100 mL toluene under stirring and 5 mL CsBr (0.035g)/DMF suspension was added to the precursor solution by dropwise. Continuously stirring for 2 hours to guarantee the complete reaction. For the $CsPb_2Cl_xBr_{5-x}$ nanoplatelets, the Pb-precursor was modified as the mixture of $PbBr_2$ and $PbCl_2$ in a certain proportion.

Synthesis of Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets: 0.1835g of $PbBr_2$ and 0.060g of HABr were dissolved in 10 mL DMF forming a mixture. Then the mixture were injected in 100 mL toluene under stirring and $MnCl_2$ with specific molar ratio which was dissolved in 1mL DMF was added to the precursor solution by dropwise, after that, 0.035g of CsBr suspended in 5 mL DMF was added to the mixed solution by dropwise. After continue stirring for 2 hours to guarantee the complete reaction.

Purification: The resulting yellow precipitates of $CsPb_2Br_5$ and Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets were collected from the crude solution by centrifuging at 6500 rpm for 10 min to discard the supernatant containing unreacted precursor and byproducts. After that, 30 mL of toluene was added into the precipitates to disperse, followed by centrifugation at 6500 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitates were redispersed in toluene, forming a stable colloidal solution for further characterization.

Synthesis of Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets:PS： 2.0g PS were dissolved in 5 mL toluene， followed by heating at 70 °C and stirring for 4 hours. Then the purified yellow precipitates of Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets were added until completely redissolved.

Fabrication of LEDs from Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets: as-prepared nanoplatelets incorporating PS in toluene solution, was coated on the surface of a hemispheric lamp-chimney through its viscosity and plasticity. Then the chimney was baked at 60°C until completely cured. The UV LED fabricated with the obtained lamp-chimney emits bright white fluorescence when energized.

Synthesis of $CsPbBr_3$ nanocubes: 0.191g of Cs(AC) was dissolved in 1 mL DMF forming the

'aqueous phase' Cs-precursor, and 0.367g of $PbBr_2$ was dissolved in 1 mL DMF forming Pb-precursor, respectively. 6 mL oleic acid and 0.8 mL n-octylamine was mixed in 30 mL n- hexane under vigorous stirring forming the 'oil phase' solution. Then the Pb-precursor solution was added dropwise into the as-prepared 'oil phase' solution. Five minutes later, the 'aqueous phase' Cs-precursor solution was added into the above-mentioned solution. Along with the mixing, emulsion was formed and the color of solution turned from clear to slight white. The nanocrystals were precipitated with acetone and collected by centrifugation (6500 rpm, 15 min). For the $CsPbCl_xBr_{3-x}$ nanocubes, the $PbBr_2$ in Pb-precursor was partially substituted by the $PbCl_2$ in a certain proportion.

Synthesis of Mn-doped $CsPbCl_xBr_{3-x}$ nanocubes: The above $CsPbBr_3$ NCs were dissolved in 10 mL toluene. Then 1 M $MnCl_2$ DMF solution was dropped into the $CsPbBr_3$ toluene solution quickly with vigorous stirring. After the reaction, the NCs were separated by centrifugation and dispersed in n-hexane. the reaction can be accelerated by operating at a higher temperature (50 °C) using heating plate.

Characterization: UV-vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV- vis near-infrared spectrophotometer. Photoluminescence (PL) spectra were recorded with a Shimadzu RF-5301 PC spectrofluorometer. The excitation wavelength was set as 350 nm. The PL quantum yield (QY) of NCs was calculated by comparison to that of rhodamine 6G, which possessed known QY of 95%. All optical measurements were performed at room temperature under ambient conditions. Transmission electron microscopy (TEM) was recorded by a JEM-2100 electron microscope with an acceleration voltage of 200 kV. Chemical composition of the Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets were examined by X-ray photoelectron spectroscopy (XPS). X-ray powder diffraction (XRD) investigations were carried out using a thermos scientific escalab 250xi spectrometer with Al Kα as the X-ray source. For XRD, all samples used are purifies powder. Atomic force microscope (AFM) measurements were carried out by a Bruker bioscope in the peakforce mode. Single- NC PL Microscopy and Spectroscopy was performed with a Zeiss Elyra P.1 super-resolution microscope equipped with a 100×oil-immersion objective. The samples were prepared via dropping dilute NCs toluene solution on fluorescence microscope slides at 60 °C for 1 hour. The PL delay spectra probed 450 nm were recorded with a PluoroLog 3-TCSPC spectrophotometer. The excitation wavelength was set as 350 nm. The Mn/Pb ratio of Mn-doped $CsPbCl_xBr_{3-x}$ nanocubes were determined using a PE5300DV Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). The NCs were digested in a 10% HNO_3 solution in deionized water.

Tables and Figures

Table S1. Photoluminescence Quantum Yields of $CsPb_2Br_5$ and Mn-doped $CsPb_2Cl_xBr_{5-x}$ Perovskite

$MnCl_2$-to-$PbBr_2$ molar feed ratio	Exciton QY (%)	Mn QY (%)	Total QY (%)
undoped	84	-	84
1:1	53	6	59
2:1	26	23	49
5:1	17	30	47
6:1	13	27	40

Table S2. The PL lifetime fit results of Mn-doped/undoped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets and Mn doped/undoped $CsPbCl_xBr_{3-x}$ nanocubes with similar perovskite band-edge emission wavelength nearby 450 nm.

	y_0	x_0	A_1	τ_1	Adj. R-Square
$CsPb_2Cl_xBr_{5-x}$	4737.4	65.7	46103.8	6.6	0.99
Mn-doped $CsPb_2Cl_xBr_{5-x}$	3354.4	64.9	40981.2	1.6	0.99
$CsPbCl_xBr_{3-x}$	4302.8	65.4	22054.0	9.6	0.99
Mn-doped $CsPbCl_xBr_{3-x}$	3667.7	64.6	31789.9	6.7	0.99

Figure S1. PL specture of $CsPb_2Br_5$ nanoplatelets via adding different Mn precursors ($MnCl_2$, $MnBr_2$ or $Mn(AC)_2$).

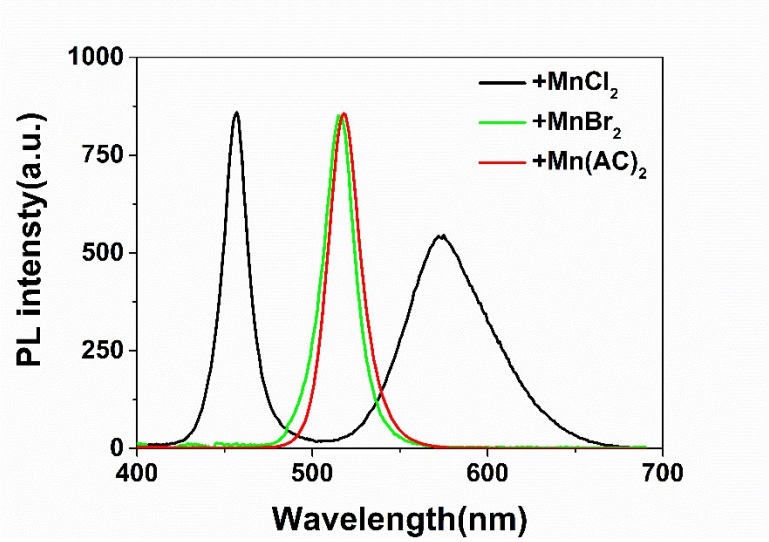

Figure S2. The plot of statistics size distribution of Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets.

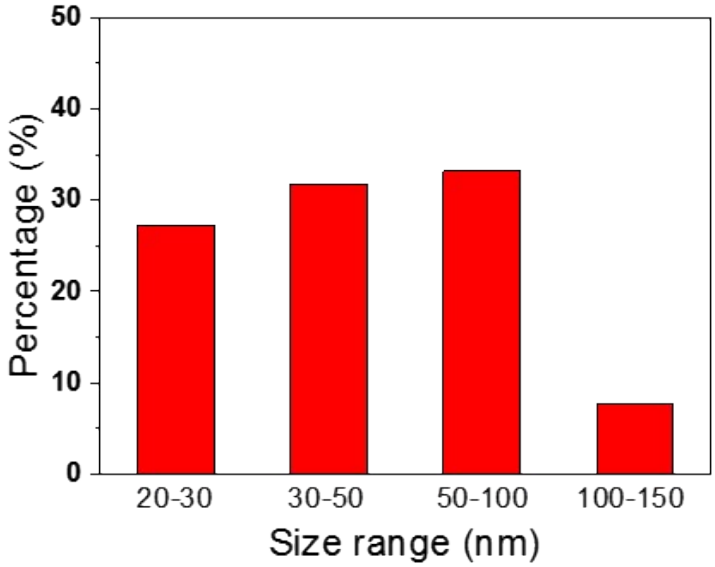

Figure S3. AFM image and thickness measurements of Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets.

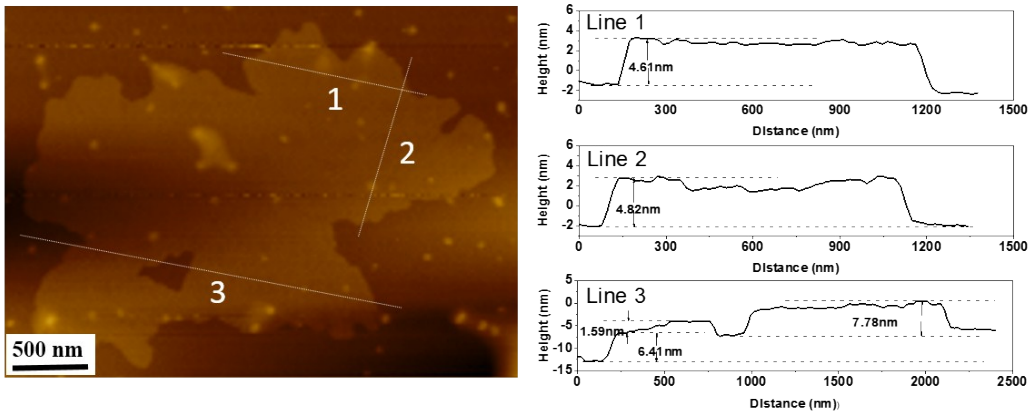

Figure S4. Narrow-scan XPS results for Mn, Cs, Pb, N and halides ions of Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets.

Note that the content of N in narrow scan results is used for calculating the composition of $C_6H_{13}NH_3$ in perovskite. According to the narrow-scan results for N, Cs, Pb, Mn, Cl and Br, the measured composition of perovskite should be $(C_6H_{13}NH_3)_{0.39}Cs_{0.61}Pb_{1.78}Mn_{0.22}Cl_{2.06}Br_{2.94}$.

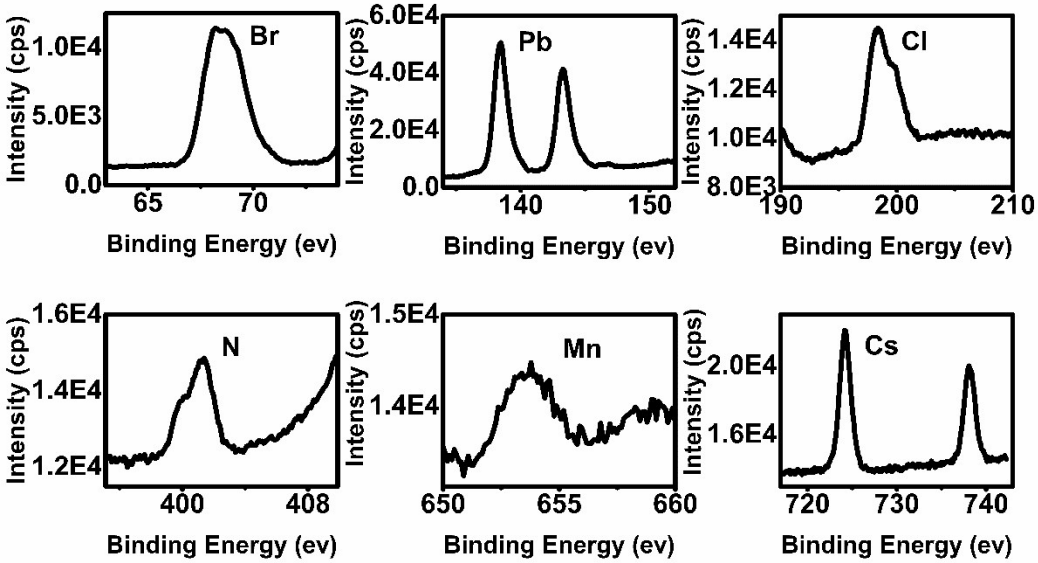

Figure S5. PL spectra for white emission Mn-doped $CsPb_2Cl_xBr_{5-x}$ nanoplatelets at same feed ratio and synthesis conditions prepared at four different batches.
Note that the PL spectra via four different batches exhibit two emission bands, with almost no change, demonstrating an impressive reproducibility.

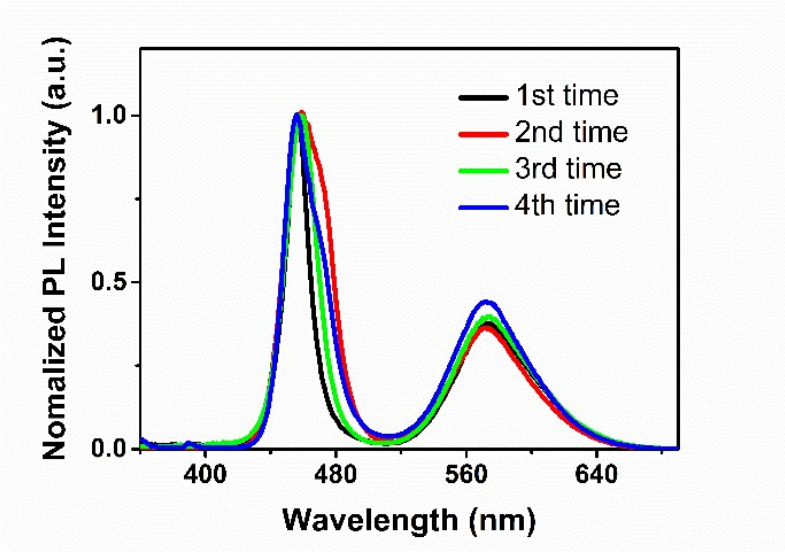

Figure S6. (a) The PL spectra of Mn-doped/undoped $CsPbCl_xBr_{3-x}$ nanocubes with similar perovskite band-edge emission wavelength nearby 450 nm. (b) PL decay spectra of Mn-doped/undoped $CsPbCl_xBr_{3-x}$ nanocubes.