Supporting Information for

Space-Confined Growth of Large-Mismatch $CsPb(Br_xCI_{1-x})_3$/GaN Heterostructures with Tunable Band Alignments and Optical Properties

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Table S1 Experimental growth parameters for the synthesis of $CsPb(Br_xCl_{1-x})_3$ on *c*-GaN substrate with four different compositions, including molar ratio of precursors, temperature of Zone-1 (T_1) and Zone-1 (T_2), gas flow, the distance between the precursors and substrate (d), and growth time (τ_g).

Composition (x)	Precursor (molar ratio)				T_1 (°C)	T_2 (°C)	Gas flow (sccm)	d (cm)	τ_g (min)
	CsCl	$PbCl_2$	CsBr	$PbBr_2$					
0	1	1	0	0	700	430	110	19	25
0.29	0	1	1	0	700	440	110	19	25
0.49	4	1	0	3	700	440	110	19	25
0.73	1	0	0	1	700	460	110	19	25
1	0	0	1	1	700	480	110	19	25

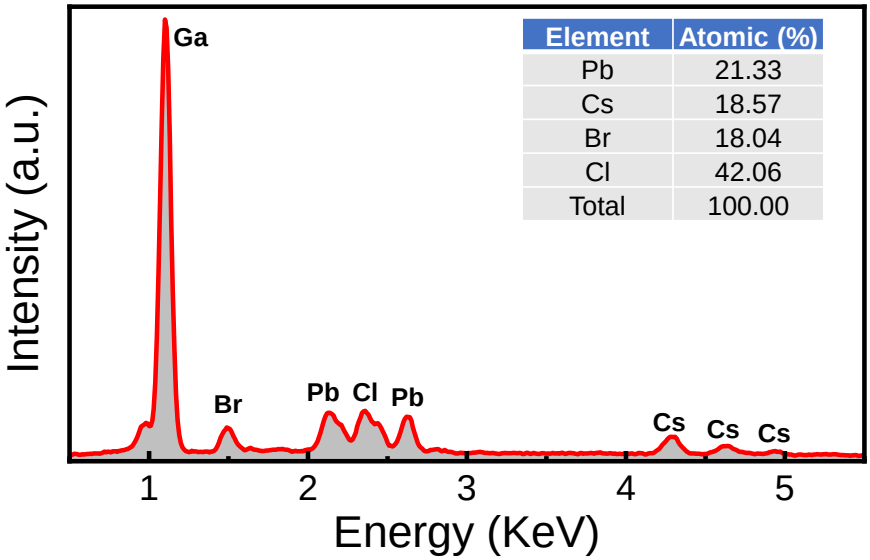

Fig. S1 EDS spectra of the as-grown $CsPbBr_{0.87}Cl_{2.13}$ NSCs on GaN substrate. The inset indicates the atomic ratio of Cs, Pb, Br, and Cl in the perovskite NSCs.

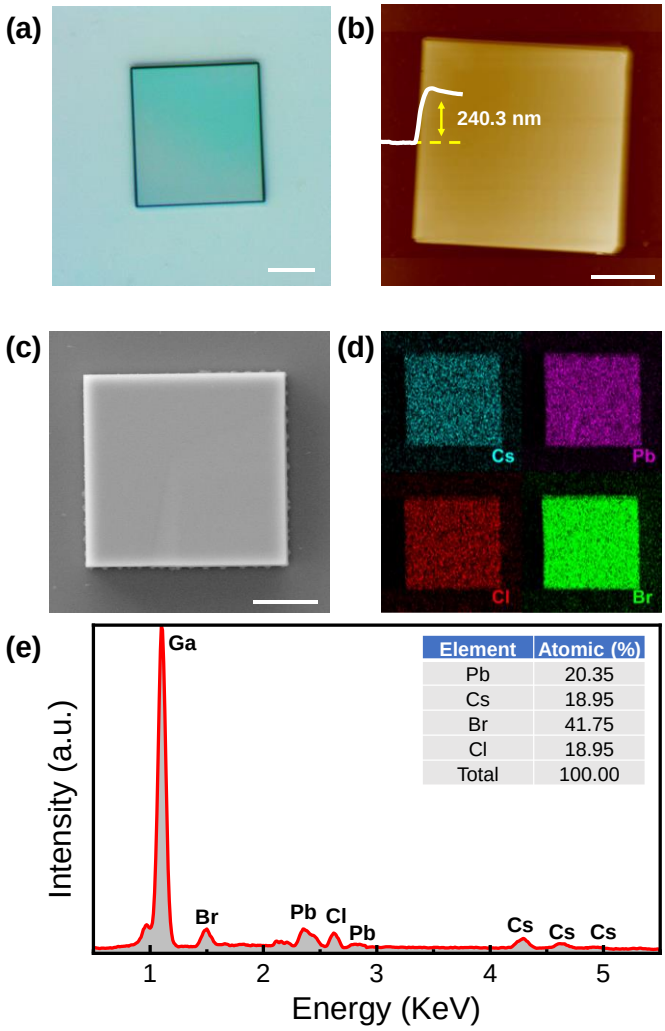

Fig. S2 Morphology and chemical composition of as-grown $CsPbCl_{0.81}B_{r2.19}$ NSCs on GaN substrate. (a) OM image, (b) AFM image and height profile, (c) SEM image, (d) EDS mappings, and (e) EDS spectra of as-grown $CsPbBr_{2.19}Cl_{0.81}$ on GaN substrate. The inset in (e) indicates the atomic ratio of Cs, Pb, Br, and Cl in the perovskite NSCs. The scale bar is 10 μm.

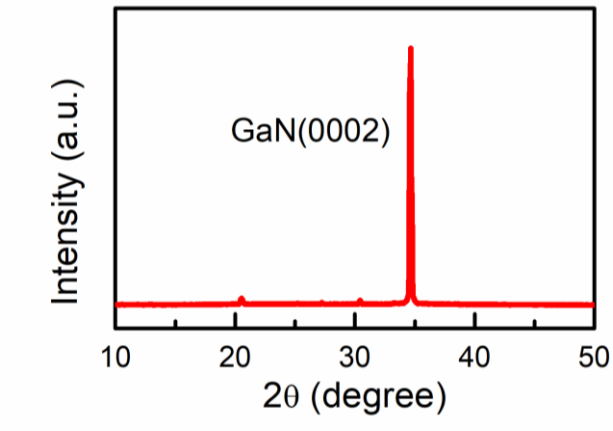

Fig. S3 XRD pattern of GaN substrate. The sharp diffraction peak located at 34.5° is well-indexed to the (0002) plane of GaN.

Fig. S4a shows the room-temperature PL spectra of the as-grown $CsPb(Br_xCl_{1-x})_3$ NSCs on GaN substrate. It can be seen that the PL emission peak continuously increases from 415 nm (~2.99 eV) to 528 nm (~2.35 eV) with the variation of Br content *x* from 0 to 1, which arises from composition-dependent band gap in these samples. Since the energy of PL emission peak corresponds to the band gap of the materials, we plot the band gap of $CsPb(Br_xCl_{1-x})_3$ NSCs obtained from the PL emission peak as a function of composition *x* in Fig. S4b. The band gap values show a nearly linear reduction with the increase of composition *x*, and they can be described by Vegard's Law with a bowing parameters *b* as follows,

$$E_g(x) = xE_{g(CsPbBr_3)} + (1-x)E_{g(CsPbCl_3)} - bx(1-x) \quad (1)$$

Fitting the data of Fig. S4b, we obtain the bowing parameter *b* = 0.05 eV. The ultrasmall bowing parameter implies highly uniform halide element distribution in the as-grown $CsPb(Br_xCl_{1-x})_3$ NSCs. The composition-dependent band gaps in the perovskite alloys can be understood by DFT calculations. We plot the band gaps of $CsPb(Br_xCl_{1-x})_3$ alloys as a function of Br composition *x* in Fig. S4b, and their band structures are presented in Fig. S5. The calculated band gap of $CsPbCl_3$ and $CsPbBr_3$ is 2.99 and 2.35 eV, which agrees well with the PL emission peak at *x* = 0 and *x* = 1, respectively. Moreover, the bowing parameter *b* (*b* = 0.05 eV) fitted by DFT band gaps is same to that obtained by PL data. The results suggest that the composition-tunable $CsPb(Br_xCl_{1-x})_3$ NSCs on GaN substrate without any phase transition and phase separation.

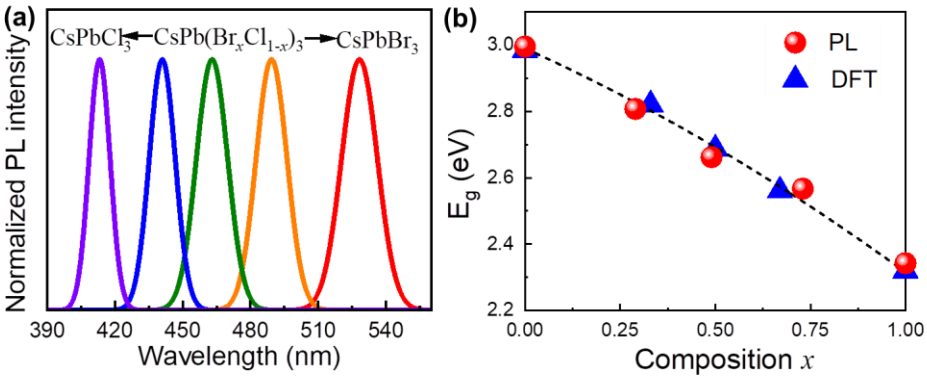

Fig. S4 Composition-dependent PL spectra and band gaps of $CsPb(Br_xCl_{1-x})_3$ grown on GaN substrate. (a) Normalized PL spectra of $CsPb(Br_xCl_{1-x})_3$ NSCs on GaN substrate with the composition *x* from 0 to 1. (b) Band gap (E_g) of $CsPb(Br_xCl_{1-x})_3$ NSCs grown on GaN substrate as a function of composition *x*. The balls and triangles denote the band gaps from the PL spectra and DFT calculations, respectively.

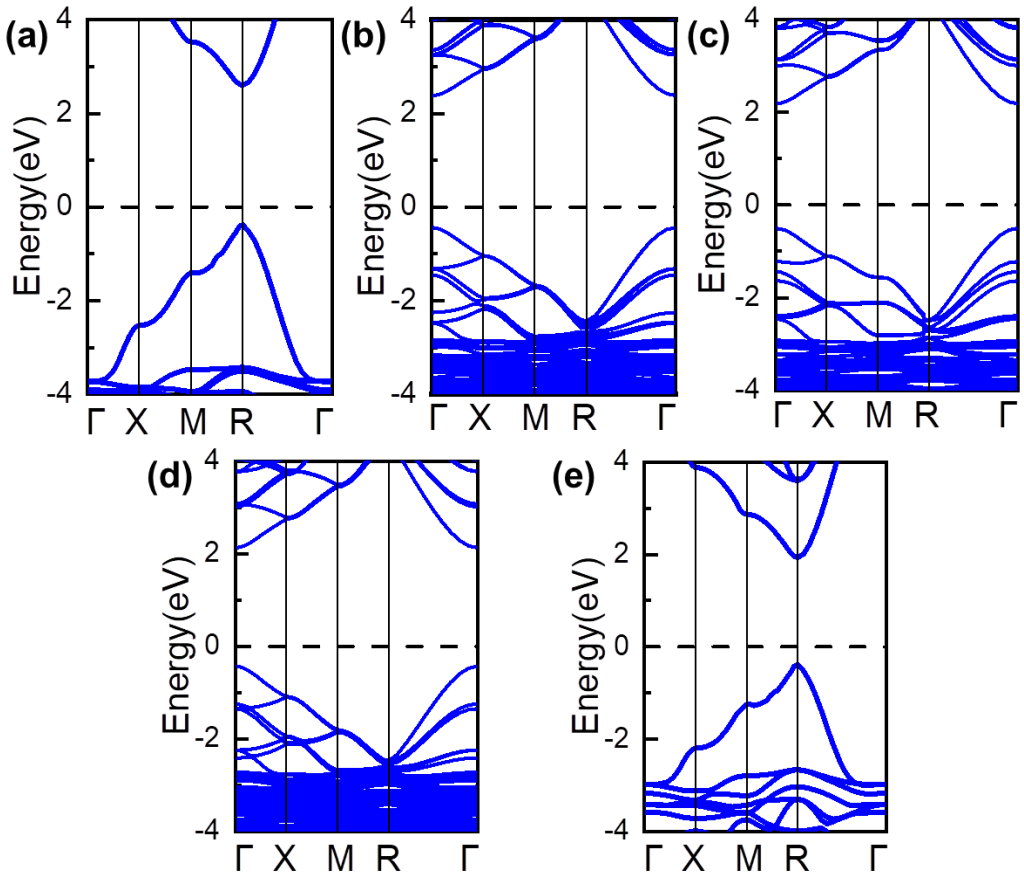

Fig. S5 Band structures of $CsPb(Br_xCl_{1-x})_3$ alloy perovskites calculated by the HSE06 functional. (a) The band structure of $CsPb(Br_xCl_{1-x})_3$ with the alloy composition of (a) x =0, (b) x = 0.25, (c) x = 0.5, (d) x = 0.75, and (e) x =1. The Fermi level is set to energy zero point. Here the band structures of $CsPbCl_3$ and $CsPbBr_3$ were calculated by using the (1×1×1) primitive cells and other alloy structures were calculated by using the (2×2×2) supercells.

Table S2 Lattice constant a (in Å) of cubic $CsPb(Br_xCl_{1-x})_3$ perovskites with the variation of alloy composition x from 0 to 1.

Composition x	0	0.29	0.49	0.73	1
Lattice constant a	5.604	5.639	5.681	5.740	5.830

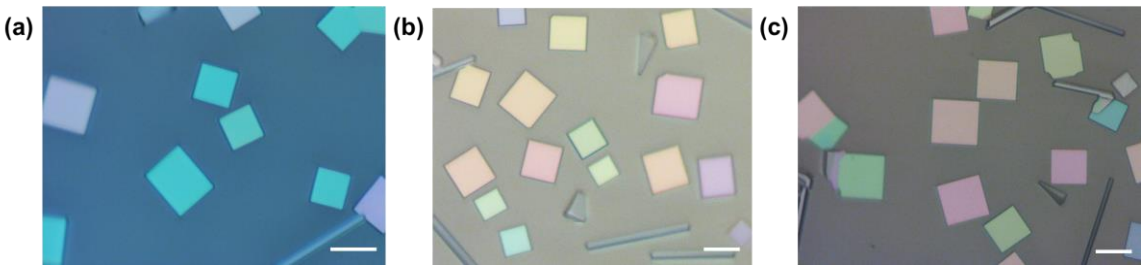

Fig. S6 OM image of (a) $CsPbBr_{0.87}Cl_{2.13}$, (b) $CsPbBr_{1.47}Cl_{1.53}$, and (c) $CsPbBr_{2.19}Cl_{0.81}$ NSCs grown on mica substrate. The scale bar is 20 μm.

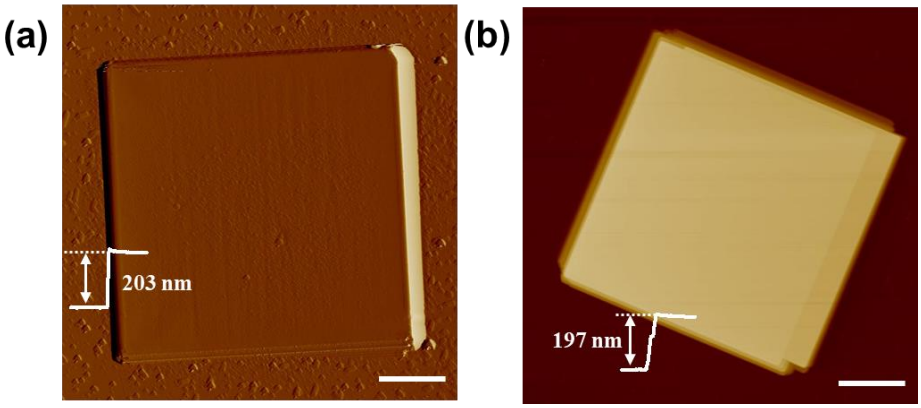

Fig. S7 AFM image and height profile of (a) $CsPbBr_{0.87}Cl_{2.13}$ and (b) $CsPbBr_{2.19}Cl_{0.81}$ crystal domains grown on mica substrate. The scale bar is 5 μm. The numbers in the height profiles show the thickness of the crystal domains.

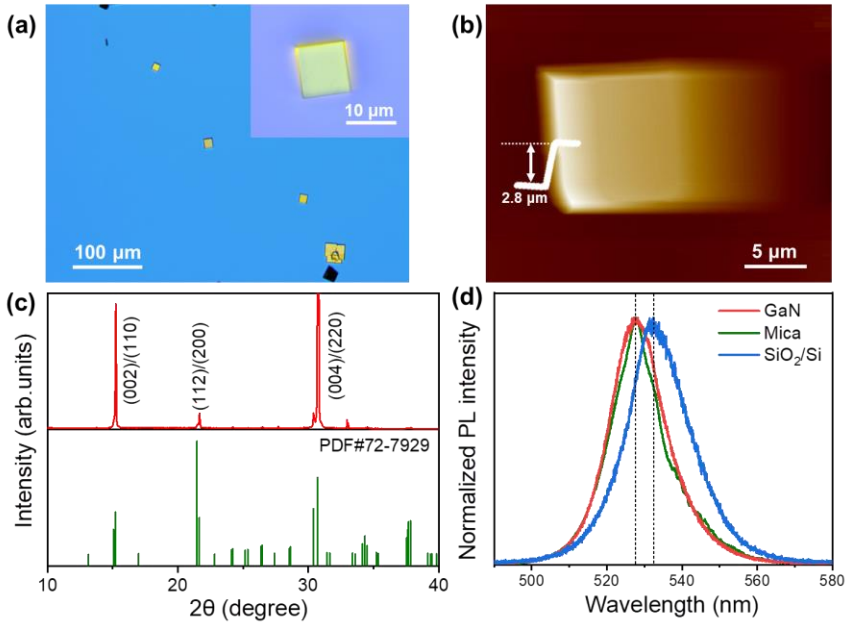

Fig. S8 Morphological and structural characterizations of $CsPbBr_3$ NSCs grown on SiO_2/Si substrate. (a) OM image, (b) AFM image, and XRD pattern of $CsPbBr_3$ grown on SiO_2/Si substrate. (d) The comparison of PL spectra of $CsPbBr_3$ grown on GaN, mica, and SiO_2/Si substrates.

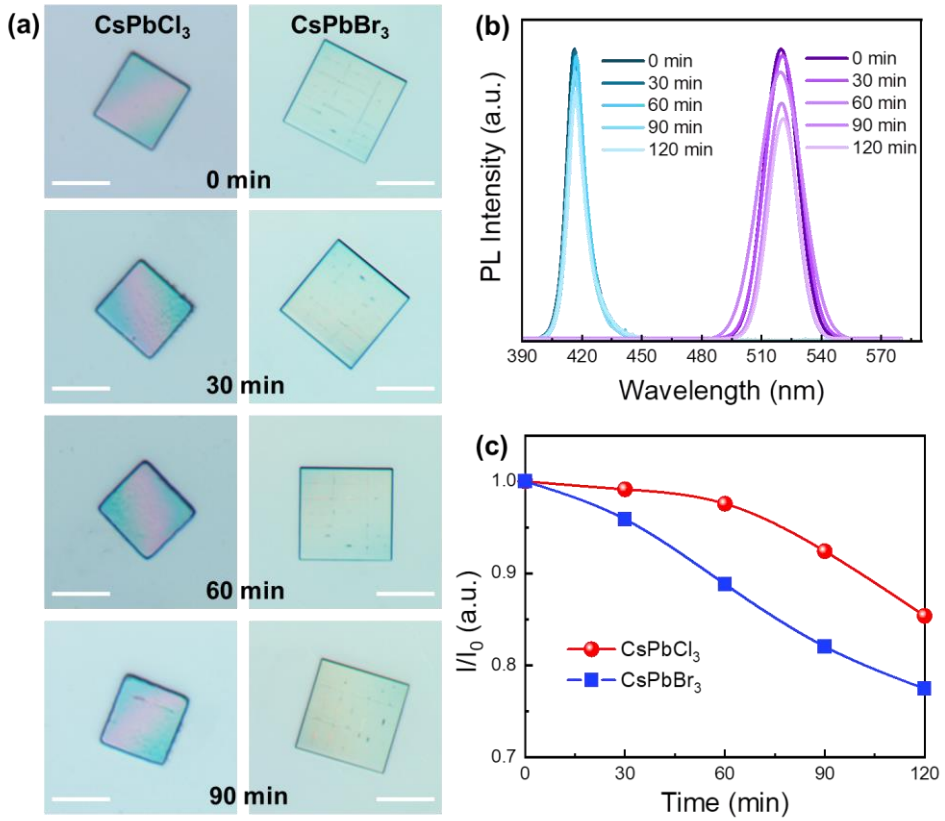

Fig. S9 Ambient stability comparison between the $CsPbCl_3$ and $CsPbBr_3$ grown on GaN substrate. (a) OM images, (b) PL spectra, (c) PL intensity ratio (I/I_0) of $CsPbCl_3$ and $CsPbBr_3$ grown on *c*-GaN substrate with the variation of exposure time from 0 to 120 min. The scale bar in OM images is 20 μm. I_0 and I denote the PL emission intensity of the pristine and etching perovskite samples, respectively

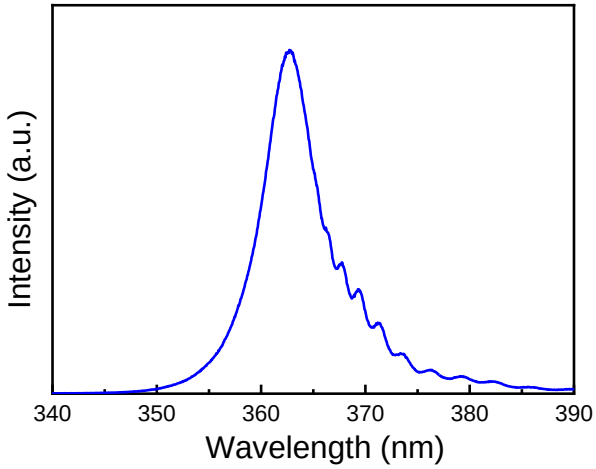

Fig. S10 PL spectra of GaN substrate. It was conducted under 325 nm laser excitation with the laser beam focused on a spot size of ~2 μm.

Table S3 The fitting parameters of TRPL spectra of $CsPb(Br_xCl_{1-x})_3$ NSCs grown on mica and GaN substrates.

Perovskite	Substrate	τ_1(ns)	τ_2(ns)	τ_3(ns)	A_1	ω_1	A_2	ω_2	A_3	ω_3
$CsPbCl_3$	Mica	1.53	8.87	/	0.64	0.671	0.32	0.329	/	/
	GaN	0.67	2.56	10.88	0.921	0.910	0.08	0.080	0.011	0.010
$CsPbBr_{0.87}Cl_{2.13}$	Mica	3.608	23.02	/	0.861	0.876	0.12	0.124	/	/
	GaN	4.829	4.83	17.21	0.594	0.595	0.252	0.252	0.153	0.153
$CsPbBr_{2.19}Cl_{0.81}$	Mica	6.56	33.95	/	0.207	0.259	0.593	0.741	/	/
	GaN	12.70	6.50	87.06	0.391	0.536	0.315	0.431	0.025	0.034
$CsPbBr_3$	Mica	12.05	59.83	/	0.155	0.156	0.840	0.844	/	/
	GaN	32.76	7.97	152.30	0.252	0.525	0.214	0.446	0.014	0.03