# Cite This: ACS Nano 2018, 12, 1462–1472

www.acsnano.org

## Strategy of Solution-Processed All-Inorganic Heterostructure for Humidity/Temperature-Stable Perovskite Quantum Dot Light-Emitting **Diodes**

Zhifeng Shi,<sup>†</sup><sup>©</sup> Sen Li,<sup>†</sup> Ying Li,<sup>†</sup> Huifang Ji,<sup>†</sup> Xinjian Li,<sup>\*,†</sup> Di Wu,<sup>†</sup> Tingting Xu,<sup>†</sup> Yongsheng Chen,<sup>†</sup> Yongtao Tian,<sup>†</sup> Yuantao Zhang,<sup>‡</sup> Chongxin Shan,<sup>\*,†,§</sup> and Guotong Du<sup>‡</sup>

<sup>†</sup>Key Laboratory of Materials Physics of Ministry of Education, Department of Physics and Engineering, Zhengzhou University, Daxue Road 75, Zhengzhou 450052, China

<sup>‡</sup>State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Oianjin Street 2699, Changchun 130012, China

<sup>§</sup>State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

#### Supporting Information

ABSTRACT: Recently, a pressing requirement of solidstate lighting sources with high performance and low cost has motivated increasing research in metal halide perovskites. However, the relatively low emission efficiency and poor operation stability of perovskite light-emitting diodes (LEDs) are still critical drawbacks. In this study, a strategy of solution-processed all-inorganic heterostructure was proposed to overcome the emission efficiency and operation stability issues facing the challenges of perovskite LEDs. Solution-processed n-ZnO nanoparticles and p-NiO are used as the carrier injectors to fabricate all-inorganic heterostructured CsPbBr<sub>3</sub> quantum dot LEDs, and a high-



efficiency green emission is achieved with maximum luminance of  $6093.2 \text{ cd/m}^2$ , external quantum efficiency of 3.79%, and current efficiency of 7.96 cd/A. More importantly, the studied perovskite LEDs possess a good operation stability after a long test time in air ambient. Typically, the devices can endure a high humidity (75%, 12 h) and a high working temperature (393 K, three heating/cooling cycles) even without encapsulation, and the operation stability is better than any previous reports. It is anticipated that this work will provide an effective strategy for the fabrication of highperformance perovskite LEDs with good stability under ambient and harsh conditions, making practical applications of such LEDs a real possibility.

**KEYWORDS:** perovskite, light-emitting diodes, CsPbBr<sub>3</sub>, humidity tolerance, temperature tolerance

ecently, newly emerging perovskite light-emitting diodes (LEDs) have attracted worldwide attention due to their application potentials in low-cost lighting and display fields.<sup>1-4</sup> This benefits from the good optical properties of perovskite materials, such as high photoluminescence (PL) emission efficiency, tunable emission region, narrow emission line width, and ambipolar carrier transport. Since the demonstration of perovskite LEDs by Friend's group in 2014,<sup>5</sup> the external quantum efficiency (EQE) of this kind of LED has achieved a rapid rise, and the highest EQE ever reported has reached 9.3%.<sup>6</sup> Despite the rapid rise in EQE, the current perovskite LEDs are subjected to an unsatisfactory stability operable in ambient or harsh conditions

(e.g., high-humidity or high-temperature environments). It is mainly because the mostly studied hybrid halide perovskites (CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, MAPbX<sub>3</sub>) are characterized by a poor stability against environment oxygen/moisture and heat. More recently, some studies have confirmed that the inorganic cesium lead halide (CsPbX<sub>3</sub>) system possesses a relatively higher thermal stability (~500 °C) compared to that of MAPbX<sub>3</sub>,<sup>7</sup> but the instability of perovskite LEDs remains unresolved effectively

Received: November 5, 2017 Accepted: January 11, 2018 Published: January 11, 2018



Figure 1. (a) Low- and high-resolution TEM images of the CsPbBr<sub>3</sub> QDs. (b) Histogram for the diameter statistics of the CsPbBr<sub>3</sub> QDs. (c) XRD spectra of the CsPbBr<sub>3</sub> QDs at different storage time in air. (d) Absorption and PL spectrum of the CsPbBr<sub>3</sub> QDs. The insets show the photographs of the as-obtained CsPbBr<sub>3</sub> QDs under ambient conditions and the UV lamp (365 nm) irradiation, respectively. (e) PL QY evolution of the CsPbBr<sub>3</sub> qDs after different storage periods at the same measurement conditions. (f) Time-resolved PL decay and fitting curve of the CsPbBr<sub>3</sub> QDs.

yet. In general, a standard perovskite LED structure includes an intrinsic perovskite emissive layer, a n-type electron-providing layer, and a p-type hole-providing layer. In addition to the crucial perovskite active layer, the n-/p-type carrier-providing layers are also important objects, not only for a well-balanced charge transport but also to achieve a high device stability. Although various organic small molecules and conducting polymers have been previously used as carrier-providing layers in perovskite LEDs, <sup>1,2,5,8-13</sup> recent studies have shown that inorganic carrier injectors (e.g., ZnO and NiO) may be a better choice. On the one hand, the inorganic carrier injectors can be synthesized by simple solution methods. On the other hand, such inorganic oxides are more stable against environment moisture/oxygen and heat, and thus the device could survive for a long running time even at harsh environments.<sup>14–16</sup> Also, their tunable band gaps could form a desirable band alignment with perovskite active layer, supporting the carrier injection and confinement processes. More importantly, these metal oxide materials could serve as a diffusion barrier against moisture/ oxygen to protect the sandwiched perovskite emitter because of their desirable scavenging effect.<sup>17</sup> In reality, there are some reports that used ZnO and NiO as the carrier injectors for quantum dot (QDs) LED fabrication, such as CdSe/ZnS QDs and silicon QDs.<sup>18-21</sup> The proposed all-inorganic device structure has taken better place in low-cost processing and long-term stability of the QD LEDs and has been approved to be effective for high-efficiency and air-stable device fabrication.<sup>21</sup> Therefore, solution-processed metal oxide carrier injectors are of particular interest in perovskite LED fabrication

due to the simplicity and scalability to large-size substrates. However, no report on combining the concepts of a solutionprocessed approach and all-inorganic heterostructure into the fabrication of perovskite LEDs can be found to the best of our knowledge. To be used more widely in practical light sources and displays, development of solution-processed all-inorganic heterostructures for future applications of perovskite LEDs is highly desired.

In this study, we designed and fabricated an all-inorganic heterostructured CsPbBr<sub>3</sub> QD perovskite LED, in which solution-processed n-ZnO nanoparticles (NPs) and p-NiO were used as the carrier injectors, without any less-stable or labile organic components. The best-performing device can achieve a high luminance of 6093.2  $cd/m^2$ , an EQE of 3.79%, a current efficiency of 7.96 cd/A, and a power efficiency of 4.26 lm/W. More importantly, the all-inorganic heterostructured perovskite LEDs possess a good operation stability in ambient conditions (20 °C, 30-40% humidity) over the aging test and can endure a high humidity (75%, 12 h) and a high working temperature (393 K, three heating/cooling cycles) even without encapsulation. Our results obtained here may push forward the development of high-efficiency and stable perovskite LED compatibility for practical applications under harsh conditions.

#### **RESULTS AND DISCUSSION**

Figure 1a presents the transmission electron microscopy (TEM) images of the synthesized CsPbBr<sub>3</sub> QDs, and a spherical shape with an average size of  $\sim$ 4.5 nm can be

**ACS Nano** 



Figure 2. (a) Temperature-dependent PL spectra of the CsPbBr<sub>3</sub> QDs at the temperature range of 10–300 K. (b) Dependence of the photon energy of the CsPbBr<sub>3</sub> QDs on measured temperature. (c) Integrated PL intensity of CsPbBr<sub>3</sub> QDs *versus* inverse temperature and the Arrhenius fit (solid line). Thermal cycling measurements showing the thermal stability of the CsPbBr<sub>3</sub> QDs: (d) cycle 1; (e) cycle 2; (f) cycle 3. (g) PL decays of the CsPbBr<sub>3</sub> QDs at different temperature, and the inset shows the changing trend of the  $\tau_{ave}$ .

observed (Figure 1b). Note that the spherical CsPbBr<sub>3</sub> QDs in our case are different from previous studies, which may be caused by the different capping agents. Their diameters can be tuned in a range of 3.7-5.0 nm, corresponding to an emission range of 493-516 nm (Figure S1, Supporting Information). From the high-resolution TEM image shown in Figure 1a, an interplanar distance of 2.96 Å can be identified, corresponding to the (200) crystal planes of cubic perovskite CsPbBr<sub>3</sub>. The energy-dispersive X-ray spectroscopy (EDS) spectrum of the spherical CsPbBr<sub>3</sub> QDs is shown in Figure S2 (Supporting Information), and the incorporated Cs, Pb, and Br elements have an atom ratio of 1.00:1.05:3.19, confirming the presence of a Br-rich surface, in good agreement with other studies.<sup>18</sup> The X-ray diffraction (XRD) patterns of the synthesized products are displayed in Figure 1c, where the characteristic peaks at  $2\theta = 15.11$ , 21.45, 30.47, 33.93, 37.67, and  $43.51^{\circ}$ correspond, respectively, to (100), (110), (200), (210), (211), and (202) diffractions of cubic CsPbBr<sub>3</sub> (JCPDS No. 54-0752). More importantly, the as-prepared CsPbBr<sub>3</sub> QDs possess a good chemical stability, which preserves their structural properties under ambient air conditions for 30 days without the appearance of other additional diffractions. Further, we investigated the optical properties of the CsPbBr<sub>3</sub> QDs by ultraviolet-visible absorption and PL spectra measurements, and an obvious excitonic absorption peak (~503 nm) was observed (red line, Figure 1d), similar to other observations.<sup>2,4,22,23</sup> With UV lamp (365 nm) irradiation, the QD colloidal solution exhibits a bright green emission (inset of Figure 1d), and the PL spectrum (dotted blue line) of the CsPbBr<sub>3</sub> QDs displays a green emission ( $\sim$ 513 nm) with a line

width of 18.2 nm. We then investigated the absolute PL quantum yield (QY) of the as-prepared CsPbBr<sub>3</sub> QDs, and a value range of 79.7-83.6% can be obtained. Moreover, the CsPbBr<sub>3</sub> QD solution exhibits a higher stability in contrast to that of the organic-inorganic hybrid MAPbBr<sub>3</sub> QDs. As shown in Figure 1e, after a storage of 30 days in ambient conditions, the CsPbBr<sub>3</sub> QD solution displays a 6.2% drop in the PL QY, whereas that for MAPbBr<sub>3</sub> QDs is >85% even with a shorter storage time (7 days), which indicates that the as-synthesized CsPbBr<sub>3</sub> QDs can work as suitable building blocks for highefficiency LED applications. In addition, time-resolved PL measurements were carried out to reveal their exciton recombination dynamics. As shown in Figure 1f, the PL decay spectrum of CsPbBr<sub>3</sub> QDs is nearly biexponential, giving an average PL decay lifetime of 9.72 ns. Further, we estimated the radiative  $(k_r)$  and nonradiative  $(k_{nr})$  decay rates of the CsPbBr3 QDs based on the obtained PL QY and average lifetime by the following equations:<sup>24</sup>  $k_{\rm r} = \phi / \tau_{\rm ave.}$  and  $k_{\rm nr} = (1 - t_{\rm ave.})$  $\phi)/ au_{
m ave.}$  where  $\phi$  is the PL QY, and  $au_{
m ave.}$  is the average PL lifetime. Finally,  $k_r = 0.085 \text{ ns}^{-1}$  and  $k_{nr} = 0.018 \text{ ns}^{-1}$  were calculated. Compared with the methylammonium lead bromide perovskite crystals ( $k_r = 0.010 \text{ ns}^{-1}$  and  $k_{nr} = 0.247 \text{ ns}^{-1}$ ), the produced CsPbBr3 QDs in our case possess much slower nonradiative decay rate and faster radiative decay rate, explaining the short radiative lifetime and high PL QY of asprepared CsPbBr<sub>3</sub> QDs.<sup>25-27</sup>

To better investigate the optical recombination mechanisms of the CsPbBr<sub>3</sub> QDs, we further performed the temperaturedependent PL measurements (10-300 K). As seen in Figure 2a, with the increase of temperature, the emission intensity of



Figure 3. (a) Coating solutions of  $C_{10}H_{14}NiO_4$  in acetonitrile, CsPbBr<sub>3</sub> QDs in hexane, and ZnO NPs in chlorobenzene. (b) Schematic illustration of solution-processed perovskite LEDs with a multilayered structure of Al/n-ZnO NPs/CsPbBr<sub>3</sub> QDs/p-NiO/ITO. (c) Photograph of the resulting device consisting of six emitting units with an area of  $2 \times 2 \text{ mm}^2$ . Top-view SEM images of the device after each processing step: (d) NiO, (e) CsPbBr<sub>3</sub> QDs, and (f) ZnO NPs. (g) Cross-sectional SEM image of the n-ZnO NPs/CsPbBr<sub>3</sub> QDs/p-NiO/ITO heterostructure. The right panel is the elemental (Zn, Br, Ni, and Sn) mapping results of the heterostructure. (h) XRD patterns and (i) normalized absorption spectra of the NiO and ZnO NPs. (j) Simplified energy band diagram of the LED heterostructure.

the CsPbBr<sub>3</sub> QDs exhibits a decreasing trend, accompanied by a continuous blue shift of the emission peak, and Figure 2b plots the corresponding photon energy of the CsPbBr<sub>3</sub> QDs versus measured temperature. This counterintuitive blue-shift phenomenon is uncommon and may be related to the thermal expansion of the crystal lattice over the temperature-increasing process and the electron-phonon renormalization.<sup>28</sup> In addition, the line width broadening behavior of the emission peak with increasing temperature was also studied to inspect the exciton-phonon interaction during the carrier recombination process (Figure S3, Supporting Information). The corresponding optical phonon energy was calculated to be  $29.6 \pm 3.2$  meV, implying a strong exciton-phonon interaction, which agrees well with the desired thermal antiquenching action of CsPbBr<sub>3</sub> QDs, and so the device operation under harsh environments could be expected. Excitation powerdependent PL measurements were also performed to verify the excitonic emission characteristics of the CsPbBr<sub>3</sub> QDs (Figure S4, Supporting Information). Because the cubic phase of CsPbBr<sub>3</sub> QDs is stable over the temperature-dependent PL measurements, we further investigated the exciton binding

energy of CsPbBr<sub>3</sub> QDs by plotting their integrated PL intensity as a function of measured temperature. As shown in Figure 2c, the PL emission intensity at 10 K is about 4 times stronger than that at 300 K, which can be attributed to the thermally activated channels contributing for nonradiative recombination. The integrated PL emission intensity could be fitted well by the following equation:<sup>29</sup>

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{E_{\rm B}}{KT}\right)} \tag{1}$$

in which  $I_0$  is the emission intensity at 0 K and A is a proportional constant. The fitting presented in Figure 2c exports a value of  $E_{\rm B} = 49.1 \pm 3.8$  meV, which is well consistent with other previously reported data.<sup>11,22,30</sup>

As shown in Figure 2d, we further carried out the thermal cycling measurements in the temperature range of 300–393 K to understand the thermal stability of the as-synthesized CsPbBr<sub>3</sub> QDs. One can observe that the relative PL intensity of the CsPbBr<sub>3</sub> QDs gradually reduces with the increase of temperature (heating process). After the cooling process was



Figure 4. (a) Dependence of current density (dotted red line) and luminance (dotted blue line) on applied voltage of the LED. (b) EL spectra measured at different voltages, together with a typical emission photograph of the LED with an active area of  $2 \times 2 \text{ mm}^2$  (at 5.0 V). (c) EQE, current efficiency, and power efficiency *versus* voltage of the LED. (d) Histogram of the peak EQE measured from 30 devices with the same device structure. (e) EQE of the LEDs structured with different size of ZnO NPs. (f) Change in the EQE and current efficiency with different Mg content in  $Zn_{1-x}Mg_xO$  NPs.

administered, a slight emission decay appears and ~85.5% of the original PL intensity remains. The unrecoverable behavior of emission intensity implies an undesired thermal degradation of PL performance, and the loss of ligands on the QD surface should be responsible for these phenomena.<sup>31,32</sup> Even so, an acceptable thermal stability of the CsPbBr<sub>3</sub> QDs opens opportunities for making high-performance LEDs with a good temperature tolerance. Figure 2e,f shows the successive heating/cooling cycles for PL measurements, and a  $\sim 22\%$ emission decay was produced after three cycles, similar as the observation in Pan's study.<sup>33</sup> Furthermore, time-resolved PL measurements at high temperatures were performed to investigate the decay kinetics of the CsPbBr<sub>3</sub> QDs. At five representative temperature points (300, 323, 343, 363, and 393 K), PL decay spectra were measured and fitted, and the obtained PL decay lifetimes of the CsPbBr<sub>3</sub> QDs are summarized in the inset of Figure 2g. As mentioned above, the PL emission decays from CsPbBr<sub>3</sub> QDs can be fitted with biexponential decay, exhibiting a short lifetime  $(\tau_1)$  and a long lifetime ( $\tau_2$ ). The  $\tau_1$  could be ascribed to the recombination of initially generated excitons with light absorption, and the  $\tau_2$ may correspond to the bimolecular radiative recombination or exciton recombination involving the surface states.<sup>34</sup> Note that, as the temperature is  $\leq$ 160 K, the obtained PL decay curve can be fitted by a single-exponential function, and as the temperature is  $\geq 180$  K, the emission decay is biexponential (Figure S5, Supporting Information). For instance, the PL decay curve at 100 K was fitted by a single-exponential function (Figure S5b), which can be assigned to the exciton-related emission. This suggests that the exciton emission dominates the emission decay at low temperature. In other words, the lower energy emission at low temperature might be the exciton emission that stabilizes. At the high-temperature region (180 K and above), two different radiative mechanisms are involved. The component proportion of  $\tau_1$  gradually decreases with the

increasing temperature, whereas the opposite is the case for  $\tau_2$ . Therefore, the  $\tau_{ave.}$  increases gradually with increasing temperature (shown in the inset of Figure 2g). The subsequent decline of  $\tau_{ave.}$  above 343 K may be due to the thermal degradation of CsPbBr<sub>3</sub> QDs at high temperature, such as the loss of ligands on the surface of QDs.<sup>34</sup>

Figure 3a-c illustrates the fabrication procedures of the perovskite LEDs. The solutions of C<sub>10</sub>H<sub>14</sub>NiO<sub>4</sub> in acetonitrile, CsPbBr<sub>3</sub> QDs in hexane, and ZnO NPs in chlorobenzene were spin-coated sequentially on a patterned ITO-coated glass with a sheet resistance of 8  $\Omega$ /sq. The schematic illustration of the solution-processed, all-inorganic heterostructured LEDs is displayed in Figure 3b, consisting of a multilayer structure of Al/n-ZnO NPs/CsPbBr<sub>3</sub> QDs/p-NiO/ITO. A typical photograph of the resulting device with an emitting unit area of  $2 \times 2$ mm<sup>2</sup> is displayed in Figure 3c. We monitored the corresponding surface morphologies after each processing step (Figure 3d-f), and three spin-coated layers are all uniformly and compactly formed. Figure 3g presents the cross-sectional scanning electron microscope (SEM) image of the device structure, and a well-defined multilayered configuration can be found, from which the thickness of each functional layer can be estimated: ZnO (65 nm, purple), CsPbBr<sub>3</sub> (52 nm, green), NiO (90.5 nm, cyan), and ITO (120 nm, brown). Further, EDS elemental mapping measurements (right panel) were performed on the ZnO/CsPbBr<sub>3</sub>/NiO/ITO structure using Zn, Br, Ni, and Sn as the detection signals, and these elements distribute regularly following the well-defined heterointerfaces. In addition, the structural characteristics of solution-processed NiO and ZnO NP layers were examined by XRD. As seen in Figure 3h, three diffraction peaks typical to cubic NiO structure (JCPDS No. 47-1049) can be observed (top panel).<sup>14</sup> The diffractions from ZnO NPs (bottom panel) could be indexed to wurtzite ZnO.35,36 Figure 3i shows the normalized absorption spectra of NiO and ZnO NPs, and the

Tabl	e 1.	Summary	of	the	Device	Perf	ormances	of	the	Prepared	l Perovskite	e LEDs
------	------	---------	----	-----	--------	------	----------	----	-----	----------	--------------	--------

emission materials	EL $\lambda_{\max}^{a}$ (nm)	line width (nm)	max $Lu^{b}$ (cd/m <sup>2</sup> )	max $CE^c$ (cd/A)	max EQE (%)	max $PE^d$ (lm/W)	ref
CsPbBr <sub>3</sub> QDs	519	19	6093.2	7.96	3.79	4.26	this work
CsPbBr <sub>3</sub> QDs	516	18	1377	0.19	0.06		38
CsPbBr <sub>3</sub> QDs	523	19	2335		0.19		7
CsPbBr <sub>3</sub> QDs	527	24	3753	8.98	2.21	3.40	45
CsPbBr <sub>3</sub> QDs	516	23	946	0.43	0.12	0.18	2
CsPbBr <sub>3</sub> QDs	512	20	>10000	13.3	6.27	5.24	46
CsPbBr <sub>3</sub> films	527	18	407	0.035	0.008		47
MAPbBr <sub>3</sub> QDs	524	24	2503	4.5	1.1	3.50	48
MAPbBr <sub>3</sub> QDs	520	20	2398	3.72	1.06		37
MAPbBr <sub>3</sub> QDs	534	19	~3000		1.20		49
MAPbBr <sub>3</sub> QDs	545		>10000	4.91	1.1		50
MAPbBr <sub>3</sub> QDs	522	22		15.5	5.09	12.17	51
MAPbBr <sub>3</sub> films	517	≥30	364	0.3	0.24		5
MAPbBr <sub>3</sub> films	513		2900	17.1	9.3	13.0	6
MAPbBr <sub>3</sub> films	543	~20	417	0.577	0.125		9
MAPbBr <sub>3</sub> films	530	~41	~545	0.22	0.051	0.11	52
MAPbBr <sub>3</sub> films	540	20	>10000	42.9	8.53		1
MAPbBr <sub>3</sub> films	540	~25	3490	0.43	0.10	0.31	53
MAPbBr <sub>3</sub> films	535		7263	9.45	2.28		54
<i><sup>a</sup>λ</i> <sub>max</sub> : peak position	. <sup>b</sup> Lu: luminance.	<sup>c</sup> CE: current effic	iency. <sup>d</sup> PE: power e	fficiency.			

band gap of NiO (ZnO) is approximately 3.71 eV (3.58 eV). As An

shown in Figure 3j, the energy band alignment of the proposed heterostructure was drawn, and all the values are indexed to the vacuum level. In our case, the bottom p-type NiO layer can play the roles of hole-injection/electron-blocking layer owing to the large ionization energy and small electron affinity. The n-type ZnO NP layer acts as the hole-blocking/electron-injection layer thanks to the matched electron affinity with the CsPbBr<sub>3</sub> active layer and a low valence-band energy level. Note that there exists a relatively small electron injection barrier at the ZnO/CsPbBr<sub>3</sub> interface, but such an undesirable energy barrier could be compensated effectively by a slightly small bias. Thus, electron injection or transport from the top ZnO NPs to the CsPbBr<sub>3</sub> QD emissive layer take effect, and the recombination of electron and hole carriers confined in the CsPbBr<sub>3</sub> layer can be expected.

To assess the device performance, the studied LEDs (Al/n-ZnO NPs/CsPbBr<sub>3</sub> QDs/p-NiO/ITO) were electrically driven in the DC mode, and the light emission was detected from the back side of the ITO/glass substrates. Figure 4a shows the dependence of measured current density (dotted red line) and luminescence (dotted blue line) on applied voltage, and a turnon voltage of  $\sim$ 2.8 V can be achieved, much smaller than many reported perovskite QD LEDs.<sup>2,37,38</sup> The relatively low turn-on voltage suggests that an efficient charge injection process has been established. At 9.0 V, the device reaches a luminance of 5863.5  $cd/m^2$ , corresponding to a current density of 87.7 mA/ cm<sup>2</sup>. Figure 4b shows the electroluminescence (EL) spectra of the device generated at different bias voltages (3.0-8.0 V), displaying a bright green emission (~519 nm). The Commission International de l'Eclairage (CIE) color of the green emission is measured with the coordinates of (0.105,0.705), as seen in Figure S6 (Supporting Information). Also, we confirmed the Lambertian emission feature of the perovskite LEDs by performing the angle-dependent EL spectra (Figure S7, Supporting Information). At different viewing angles, no noticeable spectra shape change or peak shift can be observed. The inset of Figure 4b displays a typical emission photograph of the LED from the back side using a digital camera (at 5.0 V).

An enlarged view of the emission photo captured by an optical microscope is also displayed in Figure S8 (Supporting Information) to demonstrate the emission uniformity and color of the device unit. As shown in Figure S8, the emission is uniform throughout the whole active area except for the border area of the metal area, where some emission dark spots exist. As the bias voltage is increased, the EL intensity gradually increases, and meanwhile, the corresponding line width of the EL spectra broadens slightly from 18.5 to 19.6 nm, which could be attributed to an enhanced longitudinal optical-phonon interaction at high electric field.<sup>39</sup> Nevertheless, such a low line width makes it possible to be used as a component in highdefinition display. Note that there is no parasitic emission from the carrier injectors in the electrically driven process of the device (Figure S9, Supporting Information), which implies that the injected electrons and holes are well confined within the CsPbBr<sub>3</sub> QDs active layer, and the recombination zone (CsPbBr<sub>3</sub> QDs) does not shift under operation. As shown in Figure 4c, other key parameters (EQE, current efficiency, and power efficiency) of the perovskite LEDs were also measured, and the values of the above three parameters rise rapidly with the increase of the bias voltage, which indicates that the radiative bimolecular recombination dominates at high excitation densities.<sup>5</sup> Consequently, the device demonstrates a maximum EQE of ~3.53%, a current efficiency of 7.76 cd/A, and a power efficiency of 4.06 lm/W. Note that these data were obtained at an injection current density of  $\sim 1/10$  lower than that in the other reports,<sup>7,40</sup> implying a small energy loss from charge injection and transport. In addition, the internal quantum efficiency (IQE) of the device was further estimated by using the empirical formulas of IQE =  $2n^2 EQE^{41}$  and an IQE = 15.9% was calculated finally. The reproducibility of the device to practical LED applications was assessed, and 30 devices were measured for comparison on their performances by using EQE as the evaluation criterion. As shown in Figure 4d, both the average EQE of 3.50% and a relative deviation of 16.5% indicate a good reproducibility of the studied devices.

Furthermore, we investigated the dependence of device performances on the size of ZnO NPs, and the obtained results



Figure 5. (a) Emission intensity of the perovskite LED versus running time under continuous bias voltages (4.0, 6.0, and 8.0 V). (b) EL spectra of the LED measured before aging, after operation for 12 h, and after a relaxation time of 20 min. (c) Normalized emission intensity of the perovskite LED after different running periods under different humidity conditions. (d) Temperature-dependent EL spectra of the device at a fixed driving current density of 50 mA/cm<sup>2</sup>. The insets show the corresponding photographs of an emitting unit of the LED acquired at different working temperature. (d) Three thermal cycling measurements of the perovskite LEDs at a fixed driving current density of 50 mA/cm<sup>2</sup>.

are summarized in Figure 4e. Herein, we employ the EQE as the evaluation criterion, and three typical ZnO NPs with different sizes were used for device preparation. One can observe that the devices perform best when the size of ZnO NPs is  $\sim$ 3.5 nm. Two possible reasons were thereby proposed for discussion: (1) For the ZnO NPs with a smaller size, a more favorable energy level alignment at the ZnO/CsPbBr<sub>3</sub> interface can be achieved. From the absorption and PL spectra shown in Figure S10 (Supporting Information), one can see that the band gap of ZnO NPs increases with the decrease of NP size because of the quantum confinement effect. Accordingly, the conduction (valence)-band edge of ZnO would ascend (descend).<sup>42</sup> Therefore, a favorable electron injection process from ZnO NPs to an adjacent CsPbBr<sub>3</sub> QD active layer can be expected due to a reduced interfacial energy barrier. Also, the valence-band offset at the ZnO/CsPbBr<sub>3</sub> interface becomes

larger for a smaller size of ZnO NPs, which implies an improved hole-blocking effect and effective leakage suppression, thereby promoting the carrier recombination efficiency of the device. (2) It can be generally accepted that the ZnO NPs with a smaller size possess a higher conductivity,43 which is in accordance with their effective electron mobility (Table S1, Supporting Information), and similar behavior has been observed in other oxide NP systems.<sup>44</sup> Therefore, higher electron mobility in ZnO NPs with a smaller size will facilitate efficient electron transport to the CsPbBr<sub>3</sub> QD emissive layer, increasing the efficiency of carrier injection and recombination. Moreover, the carrier injection and confinement behavior can be further improved by incorporation Mg into ZnO NPs to produce Zn1-xMgxO injectors, which will induce a decreased electron affinity and a descending valence band. Therefore, a more favorable energy level alignment at the Zn<sub>1-r</sub>Mg<sub>r</sub>O/ CsPbBr<sub>3</sub> interface can be expected. Even so, the  $Zn_{1-r}Mg_rO$ injector made from NPs suffers from a high density of surface defects, so the exciton quenching may also occur at the  $Zn_{1-r}Mg_rO/CsPbBr_3$  interface. Figure 4e shows the change in the EQE and current efficiency with different Mg content in  $Zn_{1-r}Mg_rO$  NPs. The maximum values for EQE (3.79%) and current efficiency (7.96 cd/A) were obtained when the Mg content is 0.2, and a summary of the detailed device characteristics is given in Table 1. However, above the critical content of 0.2, the device performance shows an obvious degradation. We herein consider that the  $Zn_{1-x}Mg_xO$  NPs with higher Mg content have the advantages for carrier injection and a confinement process, but the compromised electron concentration goes against an efficient electron injection to the CsPbBr<sub>3</sub> QD active layer. Thus, it seems reasonable that the carrier recombination emission efficiency is reduced for  $Zn_{1-x}Mg_xO$  NPs with a relatively high Mg content.

It is well-known that the operation stability for perovskite LEDs has always been a challenge. In this work, we performed the stability study on the unencapsulated perovskite LEDs through the "single point versus time" measurements under ambient conditions (20 °C, 30-40% humidity). Figure 5a plots the EL intensity of the device versus running time under continuous bias voltages (4.0, 6.0, and 8.0 V). At 4.0 V, a slight decay (~10.2%) in the emission intensity was observed over the whole aging test (12 h). As the bias voltage is elevated to 6.0 V and above, the decay magnitude of emission intensity increases gradually. Specifically, the emission decays at 6.0 and 8.0 V were ~13.5 and ~18.2%, respectively. Despite this, the operation stability herein is still better than that in previous studies (Table S2, Supporting Information). The corresponding demonstrative experiment (20 min at 8.0 V) on operation stability of the device can be found in Movie S1 (Supporting Information). For the undesired emission decay, the possible reason can be attributed to the inevitable heating effect, which increases with the bias voltage and the running time of the device.55 Generally, the heating effect would induce the generation of additional nonradiative recombination centers, substantially decreasing the carrier recombination efficiency of the device. Figure 5b demonstrates the EL spectra of the LED measured before aging (blue curve) and after operation for 12 h (green curve), and the significantly reduced emission intensity is consistent with the above discussions. An additional observation is that such an emission decay is recoverable; after a non-operating state (~20 min), its emission performance (red curve) almost recovers to the initial level.

In real life, the functional LEDs have to work in the open air with inconsistent humidity conditions. Therefore, the longterm operation stability of the perovskite LEDs was further investigated in humid air (25-75% humidity) without encapsulation. In this measurement, we monitored the emission decay of the perovskite LEDs at different running periods under five humidity points (25, 40, 55, 65, and 75%), in which the applied bias was fixed at 8.0 V and the time interval for signal acquisition was 1 h. As shown in Figure 5c, the studied perovskite LEDs exhibit a slight emission decay of <20% even after 12 h running in humid air (25-55% humidity). As the humidity is increased to 65% and above, the increment of emission decay shows an increasing trend. Specifically, the emission decays at 65 and 75% humidity are ~23.7 and  $\sim$ 29.1%, respectively. Despite this, the humidity tolerance of the perovskite LEDs in our case is greatly superior to that of other perovskite-based optoelectronic devices.56,57 It has been generally accepted that the metal oxide semiconductors could function as effective moisture barriers that prevent H<sub>2</sub>O from penetrating into the sandwiched perovskite active layer.<sup>58</sup> For the larger emission decay at higher environmental humidity, it could be ascribed to the slight degradation of the CsPbBr<sub>3</sub> emitter.

To evaluate the temperature tolerance of the proposed perovskite LEDs further, temperature-dependent EL measurements were performed. As shown in Figure 5d, at a fixed driving current density of 50 mA/cm<sup>2</sup>, the EL performances demonstrate a regular change, and the EL intensity reduces gradually with increasing working temperature. At 343 K, the integrated EL intensity decreases to 35%, and at 393 K, only <5% of the emission intensity remains, as seen in Figure 5e (blue plotted line). The insets of Figure 5d illustrate the corresponding photographs of an emitting unit of the perovskite LED acquired at different working temperature, and an obvious weakening trend on the emission intensity can be distinguished, which results from the increasing probability of heating-induced nonradiative recombination. Although the emission peak of the solution-processed perovskite LEDs is observed to diminish with increasing temperature, the effective EL emission can be sustained at a high level up to  $\sim$ 393 K. Such a high operation temperature indicates a good temperature tolerance of the proposed perovskite LEDs and is also evident of the rational device design with an all-inorganic heterostructure.

For a better understanding on the temperature tolerance of the perovskite LEDs, three successive thermal cycling EL measurements were performed, and the injection current density was fixed at 50 mA/cm<sup>2</sup>. For cycle 1, after the cooling process, a relatively low emission decay of ~9.6% was observed. Therefore, we consider that the emission degradation at high temperature is recoverable, but it could not recover to its original state, which is consistent with the experimental results in thermal cycling PL measurements shown in Figure 2d-f. An additional observation is that the decay magnitude of emission intensity is slightly increased after the cooling processes of cycles 2 and 3. After three measurement cycles, the EL emission intensity shows a 15.1% decay. The above observations indicate the stable and reproducible characteristics of the proposed perovskite LEDs and also their excellent temperature tolerance, promoting the existing applications and indicating additional potentials.

#### CONCLUSIONS

In conclusion, we have demonstrated a solution-processed approach to fabricate all-inorganic heterostructured perovskite LEDs, in which solution-processed n-ZnO NPs and p-NiO are used as the carrier injectors and inorganic CsPbBr<sub>3</sub> QDs are employed as the active layer. Through the size optimization and band gap adjustment of the ZnO NP injector, the proposed perovskite LEDs demonstrate a high-efficiency green emission with a luminance of 6093.2  $cd/m^2$ , an EQE of 3.79%, and a current efficiency of 7.96 cd/A. Note that the studied perovskite LEDs, even without encapsulation, present a good operation stability after a long running time in ambient air conditions. More importantly, the EL emission of the devices can be efficiently sustained at a high humidity (75%, 12 h) and a high temperature ( $\sim$ 393 K, three heating/cooling cycles), indicating high humidity/temperature tolerances and a desired compatibility for practical applications under harsh conditions. It is anticipated that the results obtained may push forward the development and practical deployment of high-efficiency and stable perovskite LEDs.

#### **EXPERIMENTAL SECTION**

**Materials.** Cs<sub>2</sub>CO<sub>3</sub> ( $\geq$ 99.9%), PbBr<sub>2</sub> ( $\geq$ 99.9%), octadecene (ODE, 90%), oleic acid (OA, 90%), octylamine (90%), hexanoic acid (90%), and zinc acetate dehydrate ( $\geq$ 99%) were purchased from Aladdin. *N*,*N*-Dimethylformamide (DMF), chlorobenzene, hexane, KOH, and acetonitrile were purchased from Beijing Chemical Reagent Co., Ltd., China.

**Preparation of Cs-Oleate Solution.**  $Cs_2CO_3$  (0.65 g) and OA (2.5 mL) were loaded in a three-neck round-bottom flask along with 18 mL of ODE. The mixture was heated to 120 °C for 60 min. Then, the temperature was increased to 150 °C under nitrogen conditions until the reaction was completed fully.

Synthesis of CsPbBr<sub>3</sub> QDs. PbBr<sub>2</sub> (0.272 mmol) and DMF (5 mL) were added in a three-neck round-bottom flask. Then, octylamine (0.6 mmol) and hexanoic acid (0.1 mmol) were loaded. Thereafter, the temperature of the mixture was increased to 150 °C. At this temperature, 2.5 mL of Cs-oleate solution was added quickly. Five seconds later, an ice–water bath was used to cool the reaction mixture. By using the centrifugal process (5000 rpm, 6 min), the resultant solution was extracted. Finally, by the addition of hexane into the resulting solution, the CsPbBr<sub>3</sub> QD solution was obtained.

**Preparation of ZnO NPs.** The ZnO NPs were synthesized according to ref 59. First, 2.95 g of zinc acetate dehydrate dissolved in methanol was stirred vigorously at 60 °C. Then, 1.48 g of KOH dissolved in methanol was added into the zinc acetate dehydrate solution dropwise (~10 min). The obtained mixture was stirred for 135 min (60 °C). After the temperature was cooled to room temperature, the precipitate was extracted and washed with methanol. By adjusting the concentration of precursor, three different sizes of ZnO NPs were synthesized. For use of electron-providing layer in perovskite LEDs, the methanol solvent was removed to minimize the negative effect on the underlying CsPbBr<sub>3</sub> layer. After the drying process, the resulting ZnO NP solution with the concentration of 3%.

**Device Preparation.** First, densely packed NiO films were prepared on the precleaned ITO glass substrates by using the spraying technique, in which the solution of  $C_{10}H_{14}NiO_4$  in acetonitrile was employed as the precursors and the substrates were mounted on a hot template (450 °C). Following that, the CsPbBr<sub>3</sub> QD solution (hexane, 10 mg/mL) was spin-coated (1500 rpm, 20 s) to produce a compact layer. The ZnO NP solution (chlorobenzene, 3%) was then spin-coated at 2000 rpm for 30 s, followed by an annealing treatment at 100 °C for 10 min. Finally, a Au electrode (~40 nm) was thermally evaporated on the ZnO layer using a shadow mask, and the active area of the device was 4 mm<sup>2</sup>.

Characterizations. Materials. The microstructures of the assynthesized perovskite QDs were characterized using a high-resolution TEM (JEOL, JEM-3010). The crystallinity characterizations of CsPbBr<sub>3</sub> QDs, NiO, and ZnO NPs were analyzed by XRD (Panalytical X'Pert Pro). The morphologies and chemical compositions of the products were analyzed by SEM (JEOL, JSM-7500F) and EDS. The optical properties of the products were measured using a Shimadzu UV-3150 spectrophotometer and steady-state PL spectra (Horiba; Fluorolog-3) with an excitation line of 395 nm. A closed-cycle helium cryostat (Jannis; CCS-100) was used to carry out the PL measurement at different temperatures. The absolute PL QY of the CsPbBr<sub>3</sub> QD solution was measured using a fluorescence spectrometer (Horiba; FluoroMax-4) with an integrated sphere (Horiba; Quanta- $\varphi$ ) with the excitation wavelength of 360 nm. A pulsed NanoLED (Horiba; 371 nm) was used to conduct the transient PL measurement. Note that the measured absorption/PL spectra and QY of the CsPbBr<sub>3</sub> QDs at room temperature were performed with the colloidal solution (hexane). Excitation power/temperature-dependent PL were conducted with the perovskite films by spin-coating the CsPbBr<sub>3</sub> QD solution on SiO<sub>2</sub>/Si substrates.

*Devices.* The current–voltage curve of the perovskite LEDs was analyzed using a Keithley 2400 source. A spectra acquisition system including lock-in amplifier (Stanford; SR830-DSP) and photomultiplier tube (PMTH-S1-R1527) was used for EL spectra collection. For high-temperature EL measurement, the device was placed on a copper heat sink, the temperature of which can be controlled by a heating pane with a heating area of 40 mm  $\times$  40 mm. The luminance–voltage characterization was measured by using a PR650 SpectraScan spectrophotometer, a calibrated luminance meter, and a Keithley 2400 source. A silicon photodetector (THORLABS; S120VC) and a digital optical power meter (THORLABS; PM100D) were used to record the output optical power.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b07856.

Lifetime calculation from time-resolved PL decay results, size-dependent PL emission of the CsPbBr<sub>3</sub> QD, analysis of the chemical composition of the CsPbBr<sub>3</sub> QDs, dependence of the fwhm of the PL emission on the measured temperature, power-dependent PL measurements verifying the excitonic emission characteristics, comparison on the PL decay behavior of the CsPbBr<sub>3</sub> QDs, CIE coordinates of the LED, angle-dependent EL spectra of the LED, emission uniformity and color of the device unit, indication of no parasitic emissions from the carrier-providing layers, optical properties of ZnO NPs with different sizes, Table S1 mobility characterization of ZnO NPs films, Table S2 comparison of the operation stability between our work and the previously reported perovskite LEDs (PDF)

Movie S1 (AVI)

#### **AUTHOR INFORMATION**

#### **Corresponding Authors**

\*E-mail: lixj@zzu.edu.cn.

\*E-mail: cxshan@zzu.edu.cn.

### ORCID 🔍

Zhifeng Shi: 0000-0002-9416-3948

#### **Author Contributions**

Z.S., X.L., and C.S. conceived the idea for detailed experiments. Z.S., S.L., and Y.L. performed the material preparation experiments. D.W. and H.J. carried out the XRD, PL, and SEM measurements. T.X. and Y.T. performed the TEM analysis. Y.C., Z.S., and X.L. conducted the device measurement and analyzed the data. The paper was co-written by Z.S. and C.S. G.D. guided the whole project.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors acknowledge the financial support from National Natural Science Foundation of China (Nos. 11774318, 11604302, 11504331, and 61176044), Henan Province Postdoctoral Research Sponsorship (2015008), Postdoctoral Science Foundation of China (2017T100535 and 2015M582193), Henan Province Science and Technology Research Project (162300410229), Outstanding Young Talent Research Foundation (1521317001), and Startup Research Foundation (1512317003) of Zhengzhou University.

#### REFERENCES

(1) Cho, H.; Jeong, S. H.; Park, M. H.; Kim, Y. H.; Wolf, C.; Lee, C. L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T. W. Overcoming the Electroluminescence Efficiency Limitations of Perovskite Light-Emitting Diodes. *Science* **2015**, *350*, 1222–1225.

(2) Song, J. Z.; Li, J. H.; Li, X. M.; Xu, L. M.; Dong, Y. H.; Zeng, H. B. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX<sub>3</sub>). *Adv. Mater.* **2015**, *27*, 7162–7167.

(3) Sutherland, B. R.; Sargent, E. H. Perovskite Photonic Sources. *Nat. Photonics* 2016, *10*, 295–302.

(4) Zhang, F.; Zhong, H. Z.; Chen, C.; Wu, X. G.; Hu, X.; Huang, H. L.; Han, J. B.; Zou, B. S.; Dong, Y. P. Brightly Luminescent and Color-Tunable Colloidal  $CH_3NH_3PbX_3$  (X = Br, I, Cl) Quantum Dots: Potential Alternatives for Display Technology. *ACS Nano* **2015**, *9*, 4533–4542.

(5) Tan, Z. K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nat. Nanotechnol.* **2014**, *9*, 687–692.

(6) Xiao, Z.; Kerner, R. A.; Zhao, L. F.; Tran, N. L.; Lee, K. M.; Koh, T. W.; Scholes, G. D.; Rand, B. P. Efficient Perovskite Light-Emitting Diodes Featuring Nanometer-Sized Crystallites. *Nat. Photonics* **2017**, *11*, 108–115.

(7) Li, G. R.; Rivarola, F. W. R.; Davis, N. J. L. K.; Bai, S.; Jellicoe, T. C.; de la Pena, F.; Hou, S. C.; Ducati, C.; Gao, F.; Friend, R. H.; Greenham, N. C.; Tan, Z. K. Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes Enabled by a Universal Crosslinking Method. *Adv. Mater.* **2016**, *28*, 3528–3534.

(8) Xing, J.; Yan, F.; Zhao, Y.; Chen, S.; Yu, H.; Zhang, Q.; Zeng, R. G.; Demir, H. V.; Sun, X. W.; Huan, A.; Xiong, Q. H. High-Efficiency Light-Emitting Diodes of Organometal Halide Perovskite Amorphous Nanoparticles. *ACS Nano* **2016**, *10*, 6623–6630.

(9) Kim, Y. H.; Cho, H.; Heo, J. H.; Kim, T. S.; Myoung, N.; Lee, C. L.; Im, S. H.; Lee, T. W. Multicolored Organic/Inorganic Hybrid Perovskite Light-Emitting Diodes. *Adv. Mater.* **2015**, *27*, 1248–1254.

(10) Liang, D.; Peng, Y.; Fu, Y.; Shearer, M. J.; Zhang, J. J.; Zhai, J. Y.; Zhang, Y.; Hamers, R. J.; Andrew, T. L.; Jin, S. Color-Pure Violet-Light-Emitting Diodes Based on Layered Lead Halide Perovskite Nanoplates. *ACS Nano* **2016**, *10*, 6897–6904.

(11) Perumal, A.; Shendre, S.; Li, M.; Tay, Y. K. E.; Sharma, V. K.; Chen, S.; Wei, Z.; Liu, Q.; Gao, Y.; Buenconsejo, P. J. S.; Tan, S. T.; Gan, C. L.; Xiong, Q. H.; Sum, T. C.; Demir, H. V. High Brightness Formamidinium Lead Bromide Perovskite Nanocrystal Light-Emitting Devices. *Sci. Rep.* **2016**, *6*, 36733.

(12) Kim, Y. H.; Cho, H.; Lee, T. W. Metal Halide Perovskite Light Emitters. Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 11694–11702. (13) Gil-Escrig, L.; Miquel-Sempere, A.; Sessolo, M.; Bolink, H. J. Mixed Iodide-Bromide Methylammonium Lead Perovskite-Based Diodes for Light Emission and Photovoltaics. *J. Phys. Chem. Lett.* **2015**, *6*, 3743–3748.

(14) Kim, H. P.; Kim, J.; Kim, B. S.; Kim, H. M.; Kim, J.; Yusoff, A. R. B. M.; Jang, J.; Nazeeruddin, M. K. High-Efficiency, Blue, Green, and Near-Infrared Light-Emitting Diodes Based on Triple Cation Perovskite. *Adv. Opt. Mater.* **201**7, *5*, 1600920.

(15) Fu, F.; Feurer, T.; Weiss, T. P.; Pisoni, S.; Avancini, E.; Andres, C.; Buecheler, S.; Tiwari, A. N. High-Efficiency Inverted Semi-Transparent Planar Perovskite Solar Cells in Substrate Configuration. *Nat. Energy* **2016**, *2*, 16190.

(16) Shi, Z.; Li, Y.; Zhang, Y.; Chen, Y.; Li, X.; Wu, D.; Xu, T.; Shan, C.; Du, G. High-Efficiency and Air-Stable Perovskite Quantum Dots Light-Emitting Diodes with an All-Inorganic Heterostructure. *Nano Lett.* **2017**, *17*, 313–321.

(17) Lee, K.; Kim, J. Y.; Park, S. H.; Kim, S. H.; Cho, S.; Heeger, A. J. Air-stable Polymer Electronic Devices. *Adv. Mater.* **2007**, *19*, 2445–2449.

(18) Mashford, B. S.; Nguyen, T. L.; Wilson, G. J.; Mulvaney, P. All-Inorganic Quantum-Dot Light-Emitting Devices Formed *via* Low-Cost, Wet-Chemical Processing. *J. Mater. Chem.* **2010**, *20*, 167–172. (19) Nguyen, H. T.; Nguyen, N. D.; Lee, S. Application of Solution-Processed Metal Oxide Layers as Charge Transport Layers for CdSe/ ZnS Quantum-Dot LEDs. *Nanotechnology* **2013**, *24*, 115201.

(20) Ji, W. Y.; Liu, S.; Zhang, H.; Wang, R.; Xie, W. F.; Zhang, H. Z. Ultrasonic Spray Processed, Highly Efficient All-Inorganic Quantum-Dot Light-Emitting Diodes. *ACS Photonics* **2017**, *4*, 1271–1278.

(21) Kumar, B.; Campbell, S. A.; Ruden, P. P. Modeling Charge Transport in Quantum Dot Light Emitting Devices with NiO and ZnO Transport Layers and Si Quantum Dots. *J. Appl. Phys.* **2013**, *114*, 044507.

(22) Li, X. M.; Wu, Y.; Zhang, S. L.; Cai, B.; Gu, Y.; Song, J. Z.; Zeng, H. B. CsPbX<sub>3</sub> Quantum Dots for Lighting and Display: Room-Temperature Synthesis, Photoluminescence Superiorities, Underlying Origins and White Light-Emitting Diodes. *Adv. Funct. Mater.* **2016**, *26*, 2435–2445.

(23) Kim, Y. H.; Lee, G. H.; Kim, Y. T.; Wolf, C.; Yun, H. J.; Kwon, W.; Park, C. G.; Lee, T. W. High Efficiency Perovskite Light-Emitting Diodes of Ligand-Engineered Colloidal Formamidinium Lead Bromide Nanoparticles. *Nano Energy* **2017**, *38*, 51–58.

(24) Yuan, Z.; Shu, Y.; Tian, Y.; Xin, Y.; Ma, B. W. A Facile One-Pot Synthesis of Deep Blue Luminescent Lead Bromide Perovskite Microdisks. *Chem. Commun.* **2015**, *51*, 16385–16388.

(25) Kawano, N.; Koshimizu, M.; Sun, Y.; Yahaba, N.; Fujimoto, Y.; Yanagida, T.; Asai, K. Effects of Organic Moieties on Luminescence Properties of Organic-Inorganic Layered Perovskite-Type Compounds. J. Phys. Chem. C 2014, 118, 9101–9106.

(26) Dai, J.; Zheng, H. G.; Zhu, C.; Lu, J. F.; Xu, C. X. Comparative Investigation on Temperature-Dependent Photoluminescence of  $CH_3NH_3PbBr_3$  and  $CH(NH_2)_2PbBr_3$  Microstructures. J. Mater. Chem. C 2016, 4, 4408–4413.

(27) Priante, D.; Dursun, I.; Alias, M. S.; Shi, D.; Melnikov, V. A.; Ng, T. K.; Mohammed, O. F.; Bakr, O. M.; Ooi, B. S. The Recombination Mechanisms Leading to Amplified Spontaneous Emission at the True-Green Wavelength in CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> Perovskite. *Appl. Phys. Lett.* **2015**, *106*, 081902.

(28) Dey, P.; Paul, J.; Bylsma, J.; Karaiskaj, D.; Luther, J. M.; Beard, M. C.; Romero, A. H. Origin of the Temperature Dependence of the Band Gap of PbS and PbSe Quantum Dots. *Solid State Commun.* **2013**, *165*, 49–54.

(29) Jiang, D. S.; Jung, H.; Ploog, K. Temperature Dependence of Photoluminescence from GaAs Single and Multiple Quantum-Well Heterostructures Grown by Molecular-Beam Epitaxy. *J. Appl. Phys.* **1988**, *64*, 1371–1377.

(30) Li, X. M.; Cao, F.; Yu, D. J.; Chen, J.; Sun, Z. G.; Shen, Y. L.; Zhu, Y.; Wang, L.; Wei, Y.; Wu, Y.; Zeng, H. B. All Inorganic Halide Perovskites Nanosystem: Synthesis, Structural Features, Optical Properties and Optoelectronic Applications. *Small* **2017**, *13*, 1603996. (31) Swarnkar, A.; Chulliyil, R.; Ravi, V. K.; Irfanullah, M.; Chowdhury, A.; Nag, A. Colloidal CsPbBr<sub>3</sub> Perovskite Nanocrystals: Luminescence Beyond Traditional Quantum Dots. *Angew. Chem.* **2015**, *127*, 15644–15648.

(32) Wang, H. C.; Lin, S. Y.; Tang, A. C.; Singh, B. P.; Tong, H. C.; Chen, C. Y.; Lee, Y. C.; Tsai, T. L.; Liu, R. S. Mesoporous Silica Particles Integrated with All-Inorganic CsPbBr<sub>3</sub> Perovskite Quantum-Dot Nanocomposites (MP-PQDs) with High Stability and Wide Color Gamut Used for Backlight Display. *Angew. Chem., Int. Ed.* **2016**, 55, 7924–7929.

(33) Wei, S.; Yang, Y. C.; Kang, X. J.; Wang, L.; Huang, L. J.; Pan, D. C. Room-Temperature and Gram-Scale Synthesis of  $CsPbX_3$  (X = Cl, Br, I) Perovskite Nanocrystals with 50-85% Photoluminescence Quantum Yields. *Chem. Commun.* **2016**, *52*, 7265–7268.

(34) Jones, M.; Lo, S. S.; Scholes, G. D. Signatures of Exciton Dynamics and Carrier Trapping in the Time-Resolved Photoluminescence of Colloidal CdSe Nanocrystals. *J. Phys. Chem. C* 2009, *113*, 18632–18642.

(35) Zeng, H. B.; Duan, G. T.; Li, Y.; Yang, S. K.; Xu, X. X.; Cai, W. P. Blue Luminescence of ZnO Nanoparticles Based on Non-Equilibrium Processes: Defect Origins and Emission Controls. *Adv. Funct. Mater.* **2010**, *20*, 561–572.

(36) Shi, Z. F.; Xia, X. C.; Yin, W.; Zhang, S. K.; Wang, H.; Wang, J.; Zhao, L.; Dong, X.; Zhang, B. L.; Du, G. T. Dominant Ultraviolet Electroluminescence from p-ZnO:As/n-SiC(6H) Heterojunction Light-Emitting Diodes. *Appl. Phys. Lett.* **2012**, *100*, 101112.

(37) Deng, W.; Xu, X.; Zhang, X. J.; Zhang, Y. D.; Jin, X. C.; Wang, L.; Lee, S. T.; Jie, J. S. Organometal Halide Perovskite Quantum Dot Light-Emitting Diodes. *Adv. Funct. Mater.* **2016**, *26*, 4797–4802.

(38) Zhang, X. Y.; Lin, H.; Huang, H.; Reckmeier, C.; Zhang, Y.; Choy, W. C. H.; Rogach, A. L. Enhancing the Brightness of Cesium Lead Halide Perovskite Nanocrystal Based Green Light-Emitting Devices Through the Interface Engineering with Perfluorinated Lonomer. *Nano Lett.* **2016**, *16*, 1415–1420.

(39) Wood, V.; Panzer, M. J.; Caruge, J. M.; Halpert, J. E.; Bawendi, M. G.; Bulovic, V. Air-Stable Operation of Transparent, Colloidal Quantum Dot Based LEDs with a Unipolar Device Architecture. *Nano Lett.* **2010**, *10*, 24–29.

(40) Ling, Y.; Tian, Y.; Wang, X.; Wang, J. C.; Knox, J. M.; Perez-Orive, F.; Du, Y.; Tan, L.; Hanson, K.; Ma, B. W.; Gao, H. Enhanced Optical and Electrical Properties of Polymer-Assisted All-Inorganic Perovskites for Light-Emitting Diodes. *Adv. Mater.* **2016**, *28*, 8983– 8989.

(41) Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D. H.; Sargent, E. H. Perovskite Energy Funnels for Efficient Light-Emitting Diodes. *Nat. Nanotechnol.* **2016**, *11*, 872.

(42) Stroyuk, O. L.; Dzhagan, V. M.; Shvalagin, V. V.; Kuchmiy, S. Y. Size-Dependent Optical Properties of Colloidal ZnO Nanoparticles Charged by Photoexcitation. J. Phys. Chem. C 2010, 114, 220–225.

(43) Pan, J.; Chen, J.; Huang, Q.; Khan, Q.; Liu, X.; Tao, Z.; Zhang, Z. C.; Lei, W.; Nathan, A. Size Tunable ZnO Nanoparticles to Enhance Electron Injection in Solution Processed QLEDs. *ACS Photonics* **2016**, *3*, 215–222.

(44) Biju, V.; Abdul Khadar, M. DC Conductivity of Consolidated Nanoparticles of NiO. *Mater. Res. Bull.* **2001**, *36*, 21–33.

(45) Zhang, X.; Xu, B.; Zhang, J. B.; Gao, Y.; Zheng, Y. J.; Wang, K.; Sun, X. W. All-Inorganic Perovskite Nanocrystals for High-Efficiency Light-Emitting Diodes: Dual-Phase CsPbBr<sub>3</sub>-CsPb<sub>2</sub>Br<sub>5</sub> Composites. *Adv. Funct. Mater.* **2016**, *26*, 4595–4600.

(46) Li, J. H.; Xu, L. M.; Wang, T.; Song, J. Z.; Chen, J. W.; Xu, J.; Dong, Y. H.; Cai, B.; Shan, Q. S.; Han, B.; Zeng, H. B. 50-fold EQE Improvement Up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr<sub>3</sub> QLEDs *via* Surface Ligand Density Control. *Adv. Mater.* **2017**, 29, 1603885.

(47) Yantara, N.; Bhaumik, S.; Yan, F.; Sabba, D.; Dewi, H. A.; Mathews, N.; Boix, P. P.; Demir, H. V.; Mhaisalkar, S. Inorganic Halide Perovskites for Efficient Light-Emitting Diodes. *J. Phys. Chem. Lett.* **2015**, *6*, 4360–4364. (48) Huang, H. L.; Zhao, F. C.; Liu, L.; Zhang, F.; Wu, X.; Shi, L. J.; Zou, B. S.; Pei, Q. B.; Zhong, H. Z. Emulsion Synthesis of Size-Tunable CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> Quantum Dots: An Alternative Route Toward Efficient Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2015**, 7, 28128–28133.

(49) Li, G. R.; Tan, Z. K.; Di, D.; Lai, M. L.; Jiang, L.; Lim, J. H. W.; Friend, R. H.; Greenham, N. C. Efficient Light-Emitting Diodes Based on Nanocrystalline Perovskite in a Dielectric Polymer Matrix. *Nano Lett.* **2015**, *15*, 2640–2644.

(50) Bade, S. G. R.; Li, J. Q.; Shan, X.; Ling, Y. C.; Tian, Y.; Dilbeck, T.; Besara, T.; Geske, T.; Gao, H.; Ma, B. W.; Hanson, K.; Siegrist, T.; Xu, C.; Yu, Z. B. Fully Printed Halide Perovskite Light-Emitting Diodes with Silver Nanowire Electrodes. *ACS Nano* **2016**, *10*, 1795–1801.

(51) Kim, Y. H.; Wolf, C.; Kim, Y. T.; Cho, H.; Kwon, W.; Do, S.; Sadhanala, A.; Park, C. G.; Rhee, S. W.; Im, S. H.; Friend, R. H.; Lee, T. W. Highly Efficient Light-Emitting Diodes of Colloidal Metal-Halide Perovskite Nanocrystals Beyond Quantum Size. *ACS Nano* 2017, *11*, 6586–6593.

(52) Yu, J. C.; Kim, D. B.; Baek, G.; Lee, B. R.; Jung, E. D.; Lee, S.; Chu, J. H.; Lee, D. K.; Choi, K. J.; Cho, S.; Song, M. H. High-Performance Planar Perovskite Optoelectronic Devices: A Morphological and Interfacial Control by Polar Solvent Treatment. *Adv. Mater.* **2015**, *27*, 3492–3500.

(53) Yu, J.; Kim, D. B.; Jung, E. D.; Lee, B. R.; Song, M. H. High-Performance Perovskite Light-Emitting Diodes *via* Morphological Control of Perovskite Films. *Nanoscale* **2016**, *8*, 7036–7042.

(54) Chen, P.; Xiong, Z. Y.; Wu, X. Y.; Shao, M.; Ma, X. J.; Xiong, Z. H.; Gao, C. H. Highly Efficient Perovskite Light-Emitting Diodes Incorporating Full Film Coverage and Bipolar Charge Injection. *J. Phys. Chem. Lett.* **2017**, *8*, 1810–1818.

(55) Jaramillo-Quintero, O. A.; Sanchez, R. S.; Rincon, M.; Mora-Sero, I. Bright Visible-Infrared Light Emitting Diodes Based on Hybrid Halide Perovskite with Spiro-OMeTAD as a Hole-Injecting Layer. *J. Phys. Chem. Lett.* **2015**, *6*, 1883–1890.

(56) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical Management for Colorful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells. *Nano Lett.* **2013**, *13*, 1764–1769.

(57) Tiep, N. H.; Ku, Z. L.; Fan, H. J. Recent Advances in Improving the Stability of Perovskite Solar Cells. *Adv. Energy Mater.* **2016**, *6*, 1501420.

(58) Hoye, R. L.; Chua, M. R.; Musselman, K. P.; Li, G.; Lai, M. L.; Tan, Z. K.; Greenham, N. C.; MacManus-Driscoll, J. L.; Friend, R. H.; Credgington, D. Enhanced Performance in Fluorene-Free Organometal Halide Perovskite Light-Emitting Diodes Using Tunable, Low electron Affinity Oxide Electron Injectors. *Adv. Mater.* **2015**, *27*, 1414–1419.

(59) Beek, W. J. E.; Wienk, M. M.; Kemerink, M.; Yang, X.; Janssen, R. A. Hybrid Zinc Oxide Conjugated Polymer Bulk Heterojunction Solar Cells. J. Phys. Chem. B 2005, 109, 9505–9516.