

# **Electrically-Driven Violet Light-Emitting Devices Based on Highly Stable Lead-Free** Perovskite Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> Quantum Dots

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Supporting Information

ABSTRACT: Recently, substantial progress has been made in perovskite-based light-emitting devices (LEDs) with near-infrared, red, green, and blue emissions. However, short-wavelength perovskite LEDs targeted at violet emission remain a great challenge. Moreover, the majority of previously reported devices were focused on the conventional lead halide perovskites. In this study, for the first time, electrically driven violet emission (408 nm) from lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> quantum dots (QDs) was demonstrated at room temperature, the shortest wavelength for perovskite LEDs as far as we know, and an external quantum efficiency of ~0.206% was achieved. The device demonstrated an excellent working stability. After a long-term running for 6 h, almost 90% of the initial electroluminescence performance was retained, and no current density rising occurred with the running



time. The results obtained suggest that the lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs are potentially attractive candidates for the preparation of environment-friendly and stable violet LEDs, making practical applications of them a real possibility.

ecently, the newly emerging halide perovskites (CsPbX<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, X = Cl, Br, and I) have attracted worldwide attention because of their tremendous potential in low-cost display and lighting applications.<sup>1-9</sup> The attractive properties of such perovskites that may enable superiorities in luminescent devices are the tunable emission color, high photoluminescence quantum yield (PLQY), rather high color purity, and the facile processing technique.<sup>10-14</sup> Since the first demonstration of perovskite light-emitting devices (LEDs) based on CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> by Friend and co-workers,<sup>15</sup> the external quantum efficiency (EQE) of perovskite LEDs has shown a high-speed rise over the past four years. Currently, the EQE of green-, red-, and near-infrared-emitting perovskite LEDs has been dramatically boosted to over 20%.4,9 A recent report on blue electroluminescence (EL, 483 nm) based on quasi-two-dimensional perovskites has achieved a high EQE of up to 9.5%.<sup>16</sup> However, short-wavelength perovskite LEDs targeted at violet

emission (<435 nm) remain a great challenge. As a key optoelectronic component, violet LEDs can enable widegamut, full-color displays, fluorescence-based biological and chemical sensors, and optical detectors.<sup>17,18</sup> Although many efforts have been paid, there is still a lack of important breakthroughs. On the one hand, the conventional lead halide perovskites with violet emission were always featured by a poor stability against heat and environment moisture/oxygen.<sup>19,20</sup> On the other hand, owing to a relatively large bandgap for violet emitter, higher requirements are put forward for the device structure design to establish an effective carrier injection and confinement to fully utilize its exciton luminescent properties.

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Figure 1. Low-resolution TEM images of the as-prepared  $Cs_3Sb_2X_9$  QDs. (a)  $Cs_3Sb_2Cl_9$ , (b)  $Cs_3Sb_2Cl_{4,5}Br_{4,5}$ , (c)  $Cs_3Sb_2Br_9$ , (d)  $Cs_3Sb_2Br_{4,5}I_{4,5}$ , and (e)  $Cs_3Sb_2I_9$ . (f-j) High-resolution TEM images of the  $Cs_3Sb_2X_9$  QDs. (insets) The photographs of the  $Cs_3Sb_2X_9$  QDs colloidal solution under sunlight and UV light excitation. (k) PL and (l) absorption spectra of  $Cs_3Sb_2X_9$  QDs (X =  $Cl_xBr_yI_{1-x-y}$ ,  $0 \le x, y \le 1$ ).

Another important factor is that the majority of previously reported perovskite LEDs were focused on the conventional lead halide perovskites, in which the heavy metal Pb is toxic to both the environment and humans. Also, the operation stability of such device has always been plagued; these are the major obstacles seriously hindering their practical applications and mass production in the future.<sup>21-25</sup> These issues have motivated researchers to develop strategies to search environmentally stable and lead-free perovskites for LED preparation. In this regard, there are many representative works. For instance, Zhang et al. reported the synthesis of twodimensional Ruddlesden-Popper-type (C<sub>18</sub>H<sub>35</sub>NH<sub>3</sub>)<sub>2</sub>SnBr<sub>4</sub> perovskites, and a bright orange EL at 620 nm with an EQE of 0.1% was achieved by designing an inverted LED structure.<sup>26</sup> On the basis of the vapor-phase-processed CsSnBr<sub>3</sub> thin films, Wu et al. fabricated a small-sized (0.01 mm<sup>2</sup>) perovskite LED with a relatively large turn-on voltage of 5.0 V. The device demonstrated a red emission at 672 nm and a maximum EQE of ~0.34%.<sup>27</sup> More recently, Tang's group proposed a Na-alloying strategy to promote the emission performance of lead-free double perovskite Cs<sub>2</sub>AgInCl<sub>6</sub>, which displays an efficient and stable warm white emission. At a current density of 50 mA/cm<sup>2</sup> (~14.0 V), a broadband emission at 560 nm was achieved with an operation lifetime of 10 min.<sup>28</sup> Despite these efforts and progresses, violet-colored

LEDs based on lead-free perovskites are quite rare. For wider application in technologies from information to optoelectronic fields, researches of electrically driven violet LEDs based on lead-free and stable perovskites are urgently needed and necessary to be improved.

Following this line of thought, violet-emissive lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> quantum dots (QDs) were synthesized by a modified supersaturated recrystallization method in the present case, which were characterized by a high PLQY of 51.2% and an outstanding stability toward heat, ultraviolet (UV) light, and environmental moisture/oxygen. With the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs as the light emitter, electrically driven violet EL at 408 nm was achieved, which is the shortest wavelength for perovskite LEDs as far as we know. Moreover, an EQE of 0.206% was achieved for such devices. More importantly, in a continuous current mode the fabricated device demonstrated an excellent operation stability. After 6 h of operation, almost 90% of the initial EL performance was retained, and no current density rising occurred with the running time, greatly superior to other lead halide perovskite counterparts. Together with the ecofriendly properties and facile processing technique, the leadfree Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs can therefore be regarded as a promising candidate as reliable light emitter for violet LED applications.

In this work, lead-free  $Cs_3Sb_2X_9$  QDs were prepared according to the reported solution supersaturated recrystalliza-



Figure 2. (a) Seven heating/cooling cycling measurements of the  $Cs_3Sb_2Br_9$  QDs. (b) Comparison of the decomposition enthalpy of  $Cs_3Sb_2Br_9$  and lead halide perovskites. (insets) The structure of (left) cubic  $CsPbBr_3$  and (right) trigonal  $Cs_3Sb_2Br_9$ , respectively. (c) Photostability test of the  $Cs_3Sb_2Br_9$  and  $CsPbBr_3$  QDs under UV lamp (365 nm, 30 W) illumination. (d) Photographs of the  $Cs_3Sb_2Br_9$  and  $CsPbBr_3$  QDs (0.5 mL of deionized water was added to 2 mL of  $Cs_3Sb_2Br_9$  QDs solution). (f) Evolution of the XRD patterns of the  $Cs_3Sb_2Br_9$  QDs after water treatment.

tion approach with some modifications at a relatively low processing temperature of 50 °C,<sup>29,30</sup> and the detailed synthesis procedures can be found in the Experimental Section and Figure S1 (Supporting Information). Figure 1a-e displays the transmission electron microscopy (TEM) images of the prepared Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs, which are featured by uniformly distributed nanoparticles with a quasi-spherical shape. Note that the average diameter of the QDs increases slightly from 5.01 nm (chloride) to 5.79 nm (iodide), which can be attributed to the lattice contraction/expansion of QDs, because the radius of these halogen ions are different (Figure S2, Supporting Information). Figure 1f-j displays the highresolution TEM images of single Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QD, in which clear and well-resolved lattice fringes were observed, corresponding to the trigonal Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> structure. Take Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs as an example (Figure 1h), an interplanar distance of 2.28 Å can be easily observed, corresponding to the (212) crystal plane of trigonal Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>.

We further studied the optical properties of the assynthesized  $Cs_3Sb_2Br_9$  QDs by UV–visible absorption and PL spectra measurements. As shown in Figure S3 (Supporting Information), the absorption curve (blue) displays an obvious band-edge absorption peak at ~368 nm. With UV lamp (365 nm) irradiation, the QDs solution shows a bright violet emission (inset of Figure S3). The red line displays the corresponding PL spectrum of the  $Cs_3Sb_2Br_9$  QDs, which characterizes an intense emission peak at ~409 nm. Note that no significant sub-bandgap emissions typically involved with the defects in perovskites were detected, which makes the material suitable as an effective and pure-color emitter in LEDs. We then measured the absolute PLQY of the  $Cs_3Sb_2Br_9$ 

QDs, and a typical value of 51.2% can be obtained, much higher than the values obtained from other reported lead-free perovskite QDs, such as CsSnX<sub>3</sub>, Cs<sub>2</sub>PdX<sub>6</sub>, Cs<sub>2</sub>AgBiBr<sub>6</sub>, and Cs<sub>3</sub>Bi<sub>2</sub>X<sub>9</sub> systems,<sup>25,31,32</sup> and comparable with the conventional CsPbCl<sub>3</sub> QDs with the same emission wavelength.<sup>30</sup> The statistical PLQY data (Figure S4, Supporting Information) shows that the average PLQY of the QDs is 49.3% with an error deviation of  $\sim 10.2\%$ , manifesting a good reproducibility for QDs synthesis. In addition, to better examine the exciton dynamics of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs, PL measurements at different temperatures were conducted. Figure S5a (Supporting Information) presents a pseudocolor map of the temperature-dependent PL spectra. One can see that the emission intensity decreases monotonically with the increase of temperature, which could be ascribed to the thermally activated nonradiative recombination. By plotting the integrated PL intensity versus measured temperature, the exciton binding energy  $(E_{\rm B})$  of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs was estimated as  $39.8 \pm 4.9$  meV (Figure S5b, Supporting Information). It is worth noting that the fitted data are much larger than the thermal ionization energy ( $\sim 26 \text{ meV}$ ) at room temperature (RT), ensuring the exciton's survival wellabove RT and highlighting the potential of such materials in exciton-related optoelectronic devices.<sup>33</sup>

Our facile supersaturated recrystallization method for synthesizing  $Cs_3Sb_2X_9$  QDs can be readily available to tune the absorption and emission spectra of the products by varying the halide composition. Figure S6 (Supporting Information) presents the optical images of the colloidal  $Cs_3Sb_2X_9$  QDs solution with different halide compositions under UV lamp, and a regular color change from violet to red can be observed,

covering a broad wavelength range of 385-640 nm, as seen in Figure 1k. Note that the spectral tunability in our case is obviously superior to other studies on lead-free perovskite QDs.<sup>24,25,34,35</sup> The detailed data of the spectra (peak position, line width, PLOY, and Stokes shift) were summarized in Table S1 (Supporting Information). An additional observation is that the Cs<sub>3</sub>Sb<sub>2</sub>BryI<sub>9-v</sub> QDs with mixed halide ions display a broadened PL spectra, which may result from the undesirable Br or I vacancy formed in the  $Sb(Br/I)_6$  octahedron. This is because the halogen compounds (CsBr, and CsI) have different solubilities in the solvent dimethyl sulfoxide (DMSO). Analogously, the light absorption edge of the  $Cs_3Sb_2X_9$  QDs was observed to shift from 350 ( $Cs_3Sb_2Cl_9$ ) to 600 (Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub>) nm, as presented in Figure 11. Figure S7 (Supporting Information) shows the X-ray diffraction (XRD) results of Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs with different halide composition. All Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs samples, irrespective of halide composition, belong to the trigonal phase structure. Besides, time-resolved PL measurements for different Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs samples were performed (Figure S8a, Supporting Information), and the obtained average PL lifetime  $(\tau_{ave})$  are summarized in Figure S8b. One can see that the  $\tau_{ave}$  increases monotonously from 1.88 to 260.69 ns as the halide component changes from Cl to I; in other words, the shorter lifetime for QDs samples with a larger bandgap, which is analogous to the properties of traditional lead halide perovskite QDs.<sup>36,37</sup>

As we all know, the environmental stability of perovskite materials has been plagued, which has been a major obstacle hindering their practical applications.<sup>38,39</sup> In this work, the environmental stability of the lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs was evaluated by investigating the influence of heat, UV lamp irradiation, and water on the optical and structural characteristics of these QDs. We first performed seven successive heating/cooling cycling PL measurements (293-393 K) to assess the thermal stability of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs. As plotted in Figure 2a, the relative PL intensity of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs decreased with the increase of temperature, which can be ascribed to the added nonradiative recombination induced by the well-known heating effect.<sup>40</sup> In detail, a slight decay of ~6.5% appears after the first cooling process, and the decay magnitude gradually decreases in the following cycles. After the seventh cooling process was performed, the PL intensity shows a 16% decay together. Figure S9 (Supporting Information) presents the normalized PL spectra of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs in the first heating cycle and the seventh cooling cycle. Except for the changed peak intensity, the spectral shape and line width of the PL spectra change almost not at all. In sharp contrast, the relative PL intensity of conventional CsPbBr<sub>3</sub> QDs was decreased by more than 90% after seven heating/cooling measurement cycles, as seen in Figure S10 (Supporting Information). The above observation indicates the remarkable thermal tolerance and temporal stability of the lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs. Here, we consider that the significantly different thermal stability of Cs3Sb2Br9 and CsPbBr3 QDs is closely related with their different material dimensions. Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> is characterized by a two-dimensional layer phase, while that for CsPbBr<sub>3</sub> is a three-dimensional cubic phase. As shown in the insets of Figure 2b, the average bond length of Sb-Br is shorter than that of Pb-Br, thus increasing the stiffness of SbBr<sub>6</sub> octahedron. Meanwhile, the distortion angle of the Br-Sb-Br in SbBr<sub>6</sub> octahedron was calculated to be 174°, as summarized in Table S2 (Supporting Information). The distortion of the SbBr<sub>6</sub> octahedron reduces the total

energy of the system, thereby enhancing the intrinsic structural stability of  $Cs_3Sb_2Br_9$ . Moreover, theoretical calculations show that the decomposition energy of  $Cs_3Sb_2Br_9$  is much larger than that of  $CsPbBr_3$  (Figure 2b), which also demonstrates that the  $Cs_3Sb_2Br_9$  is more stable than  $CsPbBr_3$ .

Further, the photostability of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs was studied by continuously illuminating the sample with a UV lamp. As depicted in Figure 2c, an undesirable emission decay of ~17.5% for Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs was observed after 73 h of continuous irradiation, which may be caused by the photooxidation effect.<sup>41</sup> In contrast, the PL intensity of the CsPbBr<sub>3</sub> QDs decreased to 9% of the initial value even with a much shorter irradiation time of 12 h. Therefore, a better photostability was demonstrated for such Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs. More details can be found from the corresponding PL spectra of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> and CsPbBr<sub>3</sub> QDs recorded at different time intervals (Figure S11, Supporting Information). Figure 2d displays the photographs of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs (upper, 73 h) and CsPbBr<sub>3</sub> QDs (bottom, 12 h) solutions before and after UV light irradiation. One can observe that a bright violet emission can still be maintained for Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs after 73 h of continuous irradiation, while the CsPbBr<sub>3</sub> QDs lost most of the brightness, corresponding to the above discussions. This significantly different photostability may be caused by the photoinduced regrowth of CsPbBr<sub>3</sub> QDs,<sup>41</sup> while that for Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs is not apparent, which has been confirmed by additional experiments (Figures S12 and S13, Supporting Information). We herein consider that such improvements benefit from the self-formed SbBr<sub>x</sub>-rich surface for Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs, as observed in Zhang's report.<sup>35</sup> Additional experiments were performed to confirm this point (Figure S14, Supporting Information). Because of the special morphology configuration, the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs are separated from each other, and the regrowth possibility of QDs was inhibited by the SbBr<sub>r</sub> shell. Therefore, the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs demonstrate an outstanding photostability without quick PL degradation.

Besides, the moisture stability of the as-synthesized Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs was evaluated through monitoring the change of PL intensity with time after adding a certain amount of deionized water (0.5 mL) into the QDs colloidal solution (2 mL, toluene). As shown in Figure 2e, ~80% of the initial emission intensity of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs was retained after a continuous test for 45 h, while, for the reference sample (CsPbBr<sub>3</sub> QDs), the fluorescence quenching is very fast, retaining only ~9% of the original performance even with a much shorter test time (4 h). The above results are evidence of a better moisture stability of such lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs. For two types of QDs, the distinct degradation performances can be attributed to their different chemical reaction processes after water invasion. In detail, after exposed to water, the CsPbBr<sub>3</sub> will decompose quickly in a three-step process (Figure S15, Supporting Information), including (1) formation of CsPbBr<sub>3</sub>·H<sub>2</sub>O by CsPbBr<sub>3</sub> + H<sub>2</sub>O  $\rightarrow$  CsPbBr<sub>3</sub>·H<sub>2</sub>O, (2) partial degradation into CsPb<sub>2</sub>Br<sub>5</sub>·H<sub>2</sub>O and CsBr by 2CsPbBr<sub>3</sub>·  $H_2O \rightarrow CsPb_2Br_s \cdot H_2O + H_2O + CsBr_s$  and (3) complete degradation into CsBr and PbBr<sub>2</sub> with release of H<sub>2</sub>O molecules by  $CsPb_2Br_5 H_2O \rightarrow CsBr + H_2O + 2PbBr_2$ while, for Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs, owing to the existence of SbBr<sub>x</sub> shell, the inner Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> core can be protected to a certain extent, because the  $SbBr_x$  shell can serve as a strong diffusion barrier against  $H_2O$ . Of course, the chemical reaction of  $SbBr_r$ with  $H_2O$  also occurs (take SbBr<sub>3</sub> as an example):

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Figure 3. (a) Schematic device structure of the  $Cs_3Sb_2Br_9$  QDs-based LEDs. (b) Cross-sectional SEM image of the Al/MoO<sub>3</sub>/TCTA/  $Cs_3Sb_2Br_9$ /PEI/ZnO/ITO heterostructured device. (c) A photograph of the fabricated device.



Figure 4. (a) UPS data of the  $Cs_3Sb_2Br_9$  active layer. (b) Simplified energy levels of each layer of the heterostructure. (c) I-V and luminance-voltage curves of the device. (inset) The photograph of the emitting unit operated at 7.0 V. (d) EL spectra of the device under forward bias voltages of 5.0, 6.0, and 7.0 V, respectively. (e) EQE of the device at different bias voltages. (f) Histogram of the peak EQE obtained from 32 LEDs prepared with the same conditions.

$$4SbBr_3 + 5H_2O \rightarrow Sb_4O_5Br_2 + 10HBr$$
(1)

Combined with the experimental PL results above, one can recognize that the formation of  $Sb_4O_5Br_2$  product could slow the degradation rate of inner  $Cs_3Sb_2Br_9$  core. By using the XRD measurements, we confirmed the above reaction processes after water invasion, as displayed in Figure 2f.

From an application point of view, it is meaningful to fabricate electrically driven LEDs with  $Cs_3Sb_2X_9$  QDs as the active layer. Fortunately, violet LEDs based on  $Cs_3Sb_2Br_9$  QDs have been successfully realized by constructing the indium tin oxide (ITO)/ZnO/poly(ethylenimine) (PEI)/Cs\_3Sb\_2Br\_9/tris-(4-carbazoyl-9-ylphenyl)amine (TCTA)/MoO\_3/Al multilay-ered structure (Figure 3a). The detailed fabrication processes

can be found in the Experimental Section. Figure 3b shows the corresponding cross-sectional scanning electron microscopy (SEM) image of the heterostructure grown on ITO-coated substrate, showing a uniform and compact framework and well-defined heterointerfaces. The thickness of each layer can be easily estimated based on this architecture, because all deposited layers are clearly highlighted:  $MoO_3/Al$  (70 nm, pink), TCTA (50 nm, green),  $Cs_3Sb_2Br_9$  (40 nm, purple), ZnO (80 nm, yellow), and ITO (110 nm, cyan). Figure 3c displays a typical photograph of the fabricated LED with four working units, and the device-emitting area was 4 mm<sup>2</sup> as defined by the overlapping area of the Al electrode and patterned ITO.

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Figure 5. (a) The EL intensity and current density of the LEDs as a function of running time under a fixed applied voltage of 7.0 V. (b) Two EL spectra of the device detected before aging and after 6 h operation. (c) Comparison on the diffusion barrier of  $V_{Br}^+$  in trigonal Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> and cubic CsPbBr<sub>3</sub>.

To verify the structural rationality of the fabricated perovskite LEDs, UV photoelectron spectroscopy (UPS) measurements of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs active layer were therefore conducted to illustrate the energy band alignment of the heterostructure. As shown in Figure 4a, the valence band maximum (VBM) of  $Cs_3Sb_2Br_9$  was determined to be -6.24eV. An electron affinity of  $\sim$ 3.1 eV was derived by combining the bandgap of  $Cs_3Sb_2Br_0$  (~3.14 eV) from the above UVvisible absorption. Figure 4b displays the schematic band diagram of the heterostructure with respect to the vacuum level. In the present case, the ITO and MoO<sub>2</sub>/Al layers were selected as cathode and anode, respectively, due to their Ohmic carrier injection characteristics.<sup>42</sup> The ZnO nanoparticle layer could be regarded as the electron-injection/holeblocking layer due to its low valence-band energy level and electron affinity matching with the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> layer.<sup>43</sup> The PEI interlayer could lower the work function of cathode contacts, favoring a better carrier injection.<sup>17</sup> The TCTA was selected as a hole-transporting layer and meanwhile electron-blocking layer thanks to its favorable VBM (-5.7 eV) and small electron affinity (-2.3 eV).<sup>44</sup> The suitable energy-level structure enables the carrier injection and radiative recombination in Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> active layer effectively, generating the light emission corresponding to the bandgap of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>. The corresponding current-voltage (I-V) curve of the device was shown in Figure 4c (dotted red line), in which a turn-on voltage of  $\sim$ 4.0 V can be observed. The dotted blue line presents the dependence of luminance of the device on bias voltage. At  $\sim$ 8.0 V, the device reaches a maximum luminance value of 29.6  $cd/m^2$ . Figure 4d displays the measured EL spectra under the forward biases of 5.0, 6.0, and 7.0 V, respectively. One can see that the EL intensity increases monotonously with the bias voltage, and the spectral shape and peak position are almost unchanged. By comparing the EL spectra with the PL

performance of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs, we confirm that the EL comes from the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> active layer. Note that no parasitical emission from the TCTA function layer was detected, as seen in Figure S16 (Supporting Information), indicating that the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs active layer acts as the primary exciton generation and recombination zone. The inset of Figure 4c presents a typical emission image of one device unit taken from the back side under a bias of 7.0 V. The overall emission shows violet and is uniform throughout the whole active area  $(2 \times 2)$ mm<sup>2</sup>). Moreover, the EQE of the fabricated perovskite LEDs as a function of operating voltage was measured and shown in Figure 4e. One can observe that the value of EQE initially rises with the increasing voltage and then decreases, similar to the trends observed in lead halide perovskite-based LEDs, <sup>5,14,30,45,46</sup> and a maximum EQE of ~0.206% was achieved at 8.0 V. It is worth noting that the above results were obtained with current injection of  $\sim 1/10$  lower than that in other reports, which means that small energy losses were caused by charge injection and transport. Additionly, the reproducibility of the fabricated devices was also evaluated by processing 32 devices for identical measurement. As presented in Figure 4f, the statistics data indicate an average value of 0.197%, suggesting a good reproducibility of the fabricated devices. However, at other wavelengths, such as violet light (Cs<sub>3</sub>Sb<sub>2</sub>Cl<sub>9</sub> QDs), yellow light (Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>4.5</sub>I<sub>4.5</sub> QDs), and red light (Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub> QDs), electrically driven multicolor LEDs have not been achieved yet. Here, we think that further improvement of PLQY at other wavelengths is the key to device fabrication. Besides, the surface coverage and crystallinity integrity of Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs thin films, and also the device structure design for more sophisticated charge injection and transport configurations should be further optimized.

As is well known, the working stability of perovskite optoelectronic devices remains a challenge. In this study, the

Table 1. Summary of the Performance of the Perovskite-Based LEDs

emitter materials	lead-free (yes/no)	EL $\lambda_{\max}^{a}$ (nm)	max EQE (%)	$t_{\rm R}^{\ b}$ (min)	emission decay	ref
MAPbBr <sub>3</sub> films	no	513	9.3	45	50%	14
MAPbBr <sub>3</sub> films	no	535		48	58%	47
MAPbBr <sub>3</sub> films	no	533	0.065	4	75%	48
MAPbBr <sub>3</sub> QDs	no	520	3.8	0.5	50%	49
MAPbBr <sub>3</sub> QDs	no	520	1.2	600	90%	50
Cs <sub>0.7</sub> FA <sub>0.3</sub> PbBr <sub>3</sub> NPs <sup>c</sup>	no	483	9.5	4.2	50%	16
CsPbBr <sub>3</sub> films	no	527	0.008	20	50%	51
CsPbBr <sub>3</sub> films	no	525	20.3	10.4	50%	9
CsPbBr <sub>3</sub> films	no	512	15.17	72	50%	45
CsPbCl <sub>0.9</sub> Br <sub>2.1</sub> films	no	480	5.7	10	50%	19
CsPbBr <sub>3</sub> QDs	no	516	0.06	10	50%	52
CsPbBr <sub>3</sub> QDs	no	516	0.11	105	30%	53
CsSnBr <sub>3</sub> films	yes	670	0.34	60	90%	27
Cs <sub>2</sub> Ag <sub>0.6</sub> Na <sub>0.4</sub> InCl <sub>6</sub> films	yes	552		10	50%	28
Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> QDs	yes	408	0.206	360	10%	this work
$a\lambda$ · peak position $b_{t_{n}}$ · ru	nning time <sup>c</sup> NPs, nanor	particles				

preliminary stability study of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs-based violet LEDs was performed by using "single point versus time" measurements. The applied voltage of the device was fixed at 7.0 V, and the EL intensity was recorded in real-time at a constant wavelength of 408 nm. As shown in Figure 5a, the studied perovskite violet LED can continuously work for 6 h with a slight intensity decay of  $\sim 10\%$ , which is much better than other reported perovskite LEDs fabricated with conventional lead halide perovskites (Table 1). Figure 5b presents the EL spectra of the device detected before aging and after running for 6 h operated at 7.0 V, and a small emission degradation is consistent with the above discussions. Also, we can observe that the central position of the EL spectra remains unchanged after continuous operation for 6 h, excluding the possibility of the emission decay induced by the discrepancy between the detected wavelength and the actual emission wavelength over running time. In addition, another important observation is that the current density of the studied violet LED at a fixed bias (7.0 V) keeps almost unchanged with the running time, which is obviously different from the lead halide perovskite-based LEDs. Some recent studies have reported that the current density in CsPbBr<sub>3</sub>-/CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>-based LEDs would rise slightly with operating time.<sup>14,54,55</sup> Since there is no phase transition or chemical reaction in the device, they considered that the increased current density is presumably due to the reduced device resistance or interface contact improvement caused by the ineluctable joule heating. Moreover, the ion migration induced by electrical field in perovskite active layer was also taken into account, because it can destroy the crystal lattice, producing halide vacancy defects in perovskites and forming charge-accumulated interfaces.<sup>56-58</sup> As a result, after a long-term running for the LEDs, the perovskite active layer will become more conducting. Moreover, this process is not reversible, even if the fabricated LED is relaxed or cooled. However, the above two aspects are not applicable to our device constructed with Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs active layer. On the one hand, the injection current density is very low  $(65-70 \text{ mA/cm}^2)$ , not so large as to induce heating effect. Experimentally, we monitored the device temperature in real time over the entire running period, and there is no significant fluctuation of the measured temperature value. On the other hand, we further extended the theoretical study into the migration of inherent defects (i.e., Br vacancy,  $V_{\rm Br}^{+}$ ) in

trigonal Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>. As presented in Figure 5c, the theoretical calculations suggest the diffusion barrier of  $V_{\rm Br}^+$  in trigonal Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> is much higher than that in cubic CsPbBr<sub>3</sub> in two diffusion paths (*ab* plane and *c* axis). Therefore, the nondiffusion behavior of dominate defects also increased the chemical stability of Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>. Maybe this is the essential reason for a remarkable long-term stability and constant current density of such Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub>-based LEDs, compared with the lead halide perovskite counterparts.

In conclusion, we have successfully synthesized the lead-free Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs by using a modified supersaturated recrystallization method with a broad spectral tunability region of 385-640 nm. Typically, the as-synthesized Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs exhibit a bright violet emission with a high PLQY of 51.2%, and outstanding stability toward heat, UV light, and environmental moisture/oxygen was demonstrated, greatly superior to that of conventional CsPbX<sub>3</sub> QDs, and the differences of degradation mechanisms between them were detailedly explained. Further, for the first time, electrically driven violet LEDs (408 nm) based on Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs were successfully realized with an EQE of ~0.206%. More importantly, the fabricated device demonstrates a remarkable working stability, and only a small emission decay of ~10% occurs after a continuous running for 6 h. Also, there is no current density rising over the entire operation stage at a fixed bias. By combining with the theoretical calculation results on the diffusion barrier of  $V_{\rm Br}^{+}$  in perovskites, the possibility of electrical-field-induced ion migration in Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> was excluded. The obtained results highlight the great potential of lead-free Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs as an environmental-friendly and stable violet emitter for the LEDs compatible for practical applications.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.9b02096.

Experimental section, lifetime calculation from timeresolved PL decay curves, synthesis procedures of the  $Cs_3Sb_2X_9$  QDs, size distribution of the  $Cs_3Sb_2X_9$  QDs, optical properties of the  $Cs_3Sb_2Br_9$  QDs, reproducibility of the PLQY of the  $Cs_3Sb_2Br_9$  QDs, temperaturedependent PL measurements of  $Cs_3Sb_2Br_9$  QDs, optical images of the  $Cs_3Sb_2X_9$  QDs solutions (X =  $Cl_xBr_yI_{1-x-y}$   $0 \le x, y \le 1$ ), investigations on the XRD patterns of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs, comparison on the PL decay behavior of the Cs<sub>3</sub>Sb<sub>2</sub>X<sub>9</sub> QDs, investigation on the thermal stability of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs, evaluation on the thermal stability of the CsPbBr<sub>3</sub> QDs, comparison on the photostability of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> and CsPbBr<sub>3</sub> QDs, morphology and structure evolution of the CsPbBr<sub>3</sub> QDs after 12 h of UV light irradiation, morphology and structure evolution of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> QDs after different UV light irradiation periods, dependence of the PL spectra on the UV-ozone treating and Ar<sup>+</sup> etching times, evolution of the XRD patterns of the CsPbBr<sub>3</sub> QDs after water treatment, indication of no parasitical emission from the TCTA function layer, summary of the optical performances of as-synthesized Cs<sub>2</sub>Sb<sub>2</sub>X<sub>9</sub> QDs, summary of the bond length and distortion angle of  $CsPbBr_3$  and  $Cs_3Sb_2Br_9$  (PDF)

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#### **Author Contributions**

Z.S., L.Z., and C.S. conceived the idea for detailed experiments. Z.M. and F.Z. performed the material preparation experiments. Z.M., S.L., and D.W. carried out the XRD, PL, and SEM measurements. L.W. and Z.S. performed the TEM analysis. Y.Z., X.L., and Y.Z. conducted the device measurement and analyzed the data. D.Y., G.N., and L.Z. performed the firstprinciples calculations and analyzed the results. The paper was cowritten by Z.M. and Z.S.; L.Z. and C.S. guided the whole project.

#### Notes

The authors declare no competing financial interest.

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