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Surface-Passivated Pb-free Double-Perovskite Halide Quantum Dots for Electrically Driven Efficient White Light-Emitting Diodes

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ABSTRACT: Sel- wavelength emissi	ected double-perovskite hal on owing to the effectiveness perovskite halide quantur	ides have demonstrated broad of self-trapped excitons. Herein, n dots (ODs) composed of		AI LIF	

wavelength emission owing to the effectiveness of self-trapped excitons. Herein, specific double-perovskite halide quantum dots (QDs) composed of $Cs_2AgIn_{0.9}Bi_{0.1}Cl_6$ are proposed as the active layer in a rare example of electrically driven white light-emitting diodes (LEDs). The QDs are modified by substituting Na at the Ag site and post-treating the surface of QDs to control carrier transport for efficient emission. Compared with QDs without Na, an optimal QD composition of $Cs_2Ag_{0.6}Na_{0.4}In_{0.9}Bi_{0.1}Cl_6$ exhibited a higher photoluminescence quantum yield of 19.31% and a longer lifetime of 1.4 μ s. Additional post-treatment with an inorganic salt, KCl, further improved the luminance performance, attaining



a notable peak luminance of 80.3 cd m⁻² at a low bias of 6 V and a device half-lifetime of 36.5 min. These achievements are assumed to be primarily due to the combined effects of favorable band alignment, effective recombination, and defect passivation.

KEYWORDS: double perovskite, quantum dot, electroluminescence, white light-emitting diode, surface passivation

INTRODUCTION

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Lead halide perovskites, APbX₃, where A is a cation and X is a halogen, have been actively studied for use in light-emitting diodes (LEDs) owing to their suitable optoelectronic characteristics, such as high color purity, tunable emission wavelength, and high photoluminescence quantum yields.¹⁻³ Recently, Pb-based halide perovskites have emerged as excellent candidates for broadband emission, which is associated with the presence of self-trapped excitons (STEs), which can produce white luminescence.⁴⁻⁶ However, typical halide perovskites have some drawbacks, including the toxicity of Pb and their poor chemical stability against oxygen and humidity, as well as their limited compositional flexibility for controlling luminescence.^{7,8} Double perovskites with the general formula A2M+M3+X6, wherein Pb2+ ions are replaced with mixed ions, typically monovalent M1+ and trivalent M3+ ions, have been studied as Pb-free alternatives while maintaining broadband emission and chemical stability.^{9,10} Popular mixed ions are based on the combination of Ag¹⁺ or Na¹⁺ with Bi³⁺ or In³⁺ in Cs-based double perovskites, such as Cs₂AgBiCl₆^{,11} Cs₂AgInCl₆^{,12} Cs₂NaBiCl₆^{,13} and Cs₂NaInCl₆^{,14} in which the emission wavelengths strongly depend on the Bsite cation chemistry.

In particular, $Cs_2AgInCl_6$ has recently been reported as an active layer for quantum dot (QD)-based electroluminescence (EL) white LED devices with extensive emission coverage in the visible wavelength range.^{15–17} Notably, incorporating organic materials as guest components within the emitting layer has been shown to further enhance the device structure.¹⁸ However, the photoluminescence quantum yield (PLQY) of

Cs₂AgInCl₆ QDs must be increased through suitable compositional engineering to improve their performance. The incorporation of Mn and Bi cations has been reported to effectively enhance the PLQY by ~16% and 11%, respectively, in Cs₂AgInCl₆ QDs.^{19,20} Moreover, incorporating lanthanide elements into Cs2AgInCl6 perovskite extends the emission spectrum from the visible range to the near-infrared region.²¹ Concerning the EL characteristics of double-perovskite QDs, the surface defects of the QDs must be minimized because they can reduce the EL efficiency.^{22,23} Surface treatment with an appropriate inorganic salt may be an effective method to inactivate surface defects. For example, K⁺ ions introduced into CsPbCl₃ QDs were reported to act as a metal ligand to suppress nonradiative pathways and thus improve carrier transport.²⁴ As another example, a KBr treatment suppressed halide segregation by passivating the defects of perovskite QDs.²⁵ However, the passivation effects of surface treatments have not been reported for double perovskites in EL devices.

Herein, we present a successful approach for enhancing the emission characteristics of white LEDs in double-perovskite QDs using both compositional and surface manipulations. The selected double perovskite, $Cs_2AgInCl_{6}$, was modified by substitutions with Na and Bi to enhance the carrier lifetime

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Figure 1. (a) Schematic of the double-perovskite $Cs_2Ag_{In}Cl_6$ structures modified by substituting Na and Bi at the Ag and In sites, respectively, (b) XRD patterns of the $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ (x = 0, 0.2, 0.4, 0.6, and 0.8) QDs with the highlighted pattern of (022) peaks, (c) high-resolution TEM images of the synthesized x = 0 and 0.4 QDs (insets: lattice fringe images for the (022) plane), and (d) TEM image of $Cs_2Ag_{0.6}Na_{0.4}In_{0.9}Bi_{0.1}Cl_6$ QDs with the elemental mapping images.

with efficient STE emission. After an additional KCl surface treatment, the optimal $Cs_2Ag_{0.6}Na_{0.4}In_{0.9}Bi_{0.1}Cl_6$ QD LED demonstrated impressive performance metrics, namely, a maximum luminance of 80.3 cd m⁻², a peak external quantum efficiency (EQE) of 0.05%, a lifetime of 36.5 min, and a driven voltage of 6 V. These results provide insight into the practical utilization of double perovskites in white LED applications.

EXPERIMENTAL SECTION

 $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ (x = 0, 0.2, 0.4, 0.6, and 0.8) QDs were prepared using the hot-injection method, and different compositions were prepared by changing the stoichiometric ratio of Na/Ag in the precursors. For example, for the Na-incorporated QDs with x = 0.4, the precursors were 1 mmol of cesium acetate [CH₃CO₂Cs, Cs(OAc), 99.9%], 0.3 mmol of sliver acetate [CH₃CO₂Ag, Ag(OAc), 99.9%], 0.2 mmol of sodium acetate [CH₃CO₂Na, Na(OAc), 99.99%], 0.45 mmol of indium(III) acetate [(CH₃CO₂)₃In, In-(OAc)₃, 99.99%], and 0.05 mmol of bismuth(III) acetate $[(CH_3CO_2)_3Bi, Bi(OAc)_3, 99.99\%]$. These amounts were mixed with 10 mL of octadecene ($C_{18}H_{36}$, 90%), 2.5 mL of oleic acid (C₁₈H₃₄O₂, 90%), and 0.66 mL of oleylamine (C₁₈H₃₇N, 70%) and stirred at 110 °C for 40 min under vacuum. The mixed precursor solution was heated to 180 °C in a N₂ atmosphere, and then, 0.5 mL TMSCl (chlorotrimethylsilane, 99.9%) was injected into the solution to precipitate the QDs. After a holding time of 30 s, the reaction solution was rapidly cooled to room temperature in an ice-water bath. The reaction mixture was then centrifuged at 10,000 rpm for 12 min, and the obtained precipitates were dispersed via sonication after immersion in 5 mL of *n*-hexane (CH₃(CH₂)₄CH₃, 95%). Following a second centrifugation at 8000 rpm for 15 min, the resulting supernatant was transferred to another centrifuge tube. As an antisolvent, 2.5 mL of ethyl acetate (CH₃COOC₂H₅, 99.5%) was added for purification. For the KCl treatment of the QD surfaces, the supernatant was added to ethyl acetate with 10 mg/mL potassium chloride (KCl, 99%) and then sonicated for 10 min. The mixture was centrifuged again at 8000 rpm for 15 min. The final precipitate was redispersed in n-hexane for further use, and each obtained QD dispersion was stored at 4 °C. All of the above-mentioned precursors and reagents were acquired from Sigma-Aldrich.

Indium tin oxide (ITO)-coated glass was washed consecutively in deionized water, acetone, and ethanol for 30 min and then treated

with oxygen plasma for 10 min. As a hole injection layer, poly(3,4ethylenedioxythiophene) polystyrenesulfonate (PEDOT/PSS, AI 4083, Heraeus) was spin-coated onto the substrate at 4000 rpm for 40 s and dried at 120 °C for 20 min. Next, poly(N,N'-bis-4butylphenyl-N,N'-bisphenyl) benzidine (poly-TPD) diluted in chlorobenzene (C₆H₅Cl, 99.8%) at a concentration of 5.5 mg/mL was spin-coated onto the PEDOT/PSS-coated glass at 5000 rpm for 40 s and annealed at 100 °C for 40 min. QDs were diluted to 1.5 mg mL⁻¹, redispersed via sonication for 30 min, and then filtered through a 0.22 μ m polytetrafluoroethylene (PTFE) membrane prior to deposition on the poly-TPD layer via spin-coating at 5000 rpm for 30 s in an Ar-filled glovebox. The deposited QDs were annealed at 150 °C for 10 min. Next, 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (C45H30N6, TPBi; 30 nm thick) and LiF (1 nm) were thermally evaporated on the QDs. Finally, a 100 nm-thick Al electrode was deposited by thermal evaporation using a shadow mask. The active area of the device was 9 mm², which was the overlapping area of the patterned ITO and Al electrodes.

The morphology of the perovskite QDs was investigated by transmission electron microscopy (TEM: JEM-ARM 200F, JEOL) equipped with energy-dispersive spectrometry (EDS). The surface microstructure of the QD films was observed by field-emission scanning electron microscopy (SEM: JSM-7800F, JEOL). The crystalline phase was identified by an X-ray diffractometer (Ultima IV, Rigaku) using Cu–K radiation in the range of 10° to 60°. The absorption and emission spectra were obtained using an ultraviolet (UV)–visible absorption spectrophotometer (Shimadzu, UV-2450) and a photoluminescence (PL) spectrophotometer (FS5, Edinburgh Instruments). Time-resolved PL spectra of the QDs were fitted using the following relationship, considering double exponential decays

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$
(1)

where A_1 and A_2 are the amplitudes, and τ_1 and τ_2 represent the fast and slow decay lifetimes, respectively. The average lifetime τ_{avg} was calculated using the following equation

$$\tau_{\rm avg} = \left(\frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}\right) \tag{2}$$

The PLQY of the QDs was assessed in an integrating hemisphere using an absolute PLQY measurement system (QE-2000, Otsuka). Fourier-transform infrared (FT-IR) spectra were obtained using a

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Figure 2. (a) Absorption spectra of $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ (x = 0, 0.2, 0.4, 0.6, and 0.8), (b) PL spectra (excited at 365 nm) of $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ QDs, (c) PLQY (excited at 365 nm) of the $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ QDs, (d) time-resolved PL spectra of the $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ QDs with the fitted curves, (e) temperature-dependent fwhm of the PL peaks of the x = 0.4 QDs, and (f) the schematic illustration of the emission by STEs through the energy gap formed between the Fermi energy (FE) and ground state (GS), along with the QD structure.

VERTEX 10 FT-IR spectrometer. X-ray photoelectron spectra (XPS) and UV photoelectron spectra (UPS) were recorded by an X-ray photoelectron spectrometer (AXIS Supra, Kratos Analytical Ltd.). The EL spectra and luminance-current density-voltage characteristics of the device were collected by a spectroradiometer (CS-2000A, Konica Minolta) fitted with a Keithley 2400 voltage-current source unit.

RESULTS AND DISSCUSSION

Figure 1a demonstrates the change in the crystal structure of Cs₂AgInCl₆ with the accommodation of Na¹⁺ and Bi³⁺ ions at the BI and BIII sites, respectively, in the double perovskite of $A_2(B^I, B^{III})X_6$. The substituted Na¹⁺ and Bi³⁺ ions were positioned at the center of the halogen octahedra (thus forming octahedral $[NaCl_6]^{5-}$ and $[BiCl_6]^{5-}$, respectively) in the apex-to-apex octahedral network. Figure 1b shows the Xray diffraction (XRD) patterns of the as-synthesized $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ QDs with different Na contents (x = 0-0.8) before the surface treatment. All patterns exhibited a phase-pure cubic perovskite structure with the space group Fm $\overline{3}$ m. By contrast, after Na was added, the (111) peak appeared at an angle of $\sim 14.8^{\circ}$, which increased in intensity as more Na was incorporated. This increasing peak intensity indicated that B-site cationic ordering proceeded with the gradual occupancy of Na at the B site.²⁶ The enlarged view of the (022) peak in Figure 1b highlights how the peak shifted toward lower 2θ angles with increasing Na. Although Na¹⁺ has a smaller radius (1.02 Å) than Ag¹⁺ (1.15 Å), the Na–Cl bonds have a weaker covalency than Ag–Cl bonds, possibly making them longer,^{27,28} which may have been responsible for the peak shift and thus the lattice extension.

Figure 1c shows TEM images of the synthesized $Cs_2AgIn_{0.9}Bi_{0.1}Cl_6$ (x = 0) and $Cs_2Ag_{0.6}Na_{0.4}In_{0.9}Bi_{0.1}Cl_6$ (x = 0.4) QDs. Discrete, well-defined crystals are observed in the

QDs. The average particle size of ~ 12.7 nm for x = 0.4 was slightly larger than ~ 12.2 nm for x = 0. The lattice spacing between the (022) planes was 0.377 and 0.379 nm for QDs with x = 0 and x = 0.4, respectively, confirming that Na extended the lattice in the perovskite structure.²⁹ As shown in Figure S1 of Supporting Information, the (004) lattice spacing for x = 0.4 (0.267 nm) was also larger than that for x = 0(0.264 nm). Figure 1d shows EDS images with selected elemental distributions for the x = 0.4 QDs, which demonstrate quite consistent distributions of the elements over the surface of the QDs. Figure S2 shows the XPS spectra of the x = 0 and 0.4 QDs. As expected, the chemical states of Cs 3d, Ag 3d, In 3d, Bi 4f, and Cl 2p could be distinguished, with no changes in the chemical states after adding Na. A distinct 1s Na peak at 1071.4 eV for x = 0.4 confirmed that Na was accommodated by the perovskite structure.

Figure 2a shows the optical absorption spectra of Cs₂Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl₆ QDs with different Na contents up to x = 0.8. Upon increasing the Na fraction from 0 to 0.8, the absorption behavior tended to retard toward higher energy levels, suggesting that Na increased the optical bandgap of the double perovskite. The bandgap was obtained from the intercepts of the extrapolated spectra curves onto the x-axis, which increased from 3.17 to 3.37 eV as x increased from 0 to 0.8. Figure 2b shows the PL spectra of the Na-substituted QDs, which were measured under a 365 nm ultraviolet irradiation. All the QDs featured a broad PL band with peak positions ranging from 650 to 700 nm. This indicates that the PL did not originate from the emission of band-edge carriers but from STE recombination through the trapped emission between the localized states in the BiCl₆ and AgCl₆ octahedra. A broad PL peak is a feature of double-perovskite QDs owing to their extensive STEs.³⁰ Figure S3 shows the normalized PL spectra,

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Figure 3. (a) XPS, (b) FT-IR, and (c) PL spectra of the untreated and surface-treated x = 0.4 QDs, (d) current density-voltage curves of the untreated and surface-treated samples in the dark, and (e) schematic illustration of potassium passivation.

where a slight redshift is clearly observed as the Na content increases. This shift may result from a reduction in excitedstate energy caused by enhanced electron-phonon coupling. In addition, the PLQY of $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ QDs was characterized, as shown in Figure 2c. The PLQY reached an optimal value of 19.31% at x = 0.4, which increased from 6.19% for x = 0. The decrease beyond x = 0.4 was attributed to nonradiative loss due to the excessive incorporation of Na. In addition, the strong orbital overlap between electrons and holes with excess Na reduced the transition dipole moment.^{31,32}

Figure 2d shows the time-resolved PL spectra of the $Cs_2Ag_{1-x}Na_xIn_{0.9}Bi_{0.1}Cl_6$ QDs. The resultant τ_{avg} obtained from the fitted PL spectra for the QDs was approximately 1.4 μ s at x = 0.4, which is approximately five times longer than 0.27 μ s at x = 0. All relevant values are listed in Table S1. The enhanced lifetime with Na incorporation indicates a reduction in nonradiative recombination, which also increases the PLQY.³³ The temperature-dependent PL of the x = 0.4 QDs was measured to understand the STE behavior as shown in Figure S4. As the temperature decreases, the PL peak exhibits a slight redshift due to increased localization of excitons. The reduced phonon activity lowers the energy of exciton-lattice interactions, allowing excitons to localize more easily in specific lattice regions. This facilitates the formation of stable selftrapped exciton states, which emit at lower energy levels, resulting in the observed redshift in PL intensity. In addition, the PL spectrum narrows with the decrease in temperature, which is attributed to the reduction in the strength of electron-phonon coupling at low temperatures. The STE formation associated with strong electron-phonon coupling can be estimated using the Huang-Rhys factor s.³⁴ The s factor was obtained from the following relation between the full width at half-maximum (fwhm) of the PL peak and temperature³⁵

$$FWHM = 2.36\sqrt{s}\,\hbar\omega_{\rm phonon}\sqrt{\coth\frac{\hbar\omega_{\rm phonon}}{2k_{\rm B}T}} \tag{3}$$

where \hbar is the reduced Planck constant, ω_{phonon} is the phonon frequency, *T* is the temperature, and k_{B} is the Boltzmann constant. The *s* factor was determined to be 37.4, which was obtained by fitting the temperature-dependent fwhm of the PL peaks, as shown in Figure 2e. The *s* factor has been reported to be 3.2 for typical inorganic halide CsPbBr₃³⁶ and 79.5 for STEcontributed Cs₃Bi₂I₉.³⁷ Balancing the electron–phonon coupling with excited-state energy dissipation leads to efficient STE emissions.^{38,39} Our moderate *s* factor suggests that Na incorporation achieved strong STE emission owing to improved radiative recombination, as illustrated by the schematic of the energy bands in Figure 2f.

Although their promising optical properties make doubleperovskite QDs suitable as light-emitting layers, the existence of surface defects may hinder their practical application.⁴⁰ Therefore, as a second step, the surfaces of the synthesized QDs were treated with an inorganic KCl salt. This surface treatment with inorganic salts was reported to passivate $CsPb(I_xBr_{1-x})_3$ nanocrystals by minimizing surface defects.^{41,42} Despite the reported effectiveness of KCl in passivating the surface defects of perovskite nanocrystals, 43,44 surface-defect passivation with inorganic salts in double-perovskite QDs has never been reported in the literature. Thus, surface passivation was performed in this study by adding KCl to the antisolvent used to purify the QDs. Figure 3a shows the XPS spectra of the surface-treated x = 0.4 QDs. The two main peaks of K $2p_{3/2}$ and $2p_{1/2}$ in the range of 290–298 eV clearly appeared after the surface treatment, indicating the existence of K⁺ ions on the surface of the QDs as evidence of the presence of an inorganic salt.



Figure 4. (a) Device structure of Al/LiF/TPBi/QDs/poly-TPD/PEDOT/PSS/ITO glass, (b) energy band alignments of the layers in contact with the three QD cases (x = 0, x = 0.4, and surface-treated x = 0.4), (c) variations in luminance with applied voltage for the x = 0.4 QD device before and after the surface treatment (with the x = 0 device for comparison), and (d) current density versus voltage for the three devices. (e) EQE curves as a function of current density for the three devices, and (f) changes in the EL intensity with the increasing applied voltage for the untreated and surface-treated x = 0.4 devices.

In addition, FT-IR spectra were obtained to investigate the evolution of the organic ligands after the introduction of K⁺ ions, as shown in Figure 3b. Notably, the peak intensities of organic ligands at ~ 1375 and ~ 2950 cm⁻¹, which can be attributed to CH₃ vibrations, were reduced by the introduction of K⁺, suggesting fewer organic ligands on the surface of the perovskite QDs. In the PL spectra in Figure 3c, the KCl-treated QDs show higher PL intensities than the untreated QDs, confirming the effective defect passivation of the surface treatment. The current-voltage curves were also compared for the two types of QDs, as shown in Figure 3d, and a higher current was evident for the surface-treated QDs. A device structure of Al/TPBi/QDs/[6,6]-Phenyl C₆₁ butyric acid methyl ester (PCBM)/ITO was separately prepared for the space charge-limited current measurement of Figure 3d. Using the trap-filed limit voltage in Figure 3d, the trap state density $N_{\rm trap}$ was calculated using the following equation^{45,40}

$$N_{\rm trap} = \frac{2\varepsilon_0 \varepsilon V_{\rm TFL}}{eL^2} \tag{4}$$

where V_{TFL} is the trap-filed limit voltage, ε_0 is the zero permittivity, ε is the relative permittivity, ε is the electric charge, and L is the thickness of QD layer. The resulting trap state density was found to decrease from 1.06×10^8 to 6.9×10^7 cm⁻¹ after the KCl treatment. The analytical result indicates that the KCl treatment limited the surface defects and improved the conductivity by favorably modifying the organic ligands on the QD surface. It is assumed that K⁺ ions bond with halide ions to form metal ligands anchored on the surface of QDs, reducing the amount of organic ligands and passivating the surface defects, as schematically shown in Figure 3e.

An EL device with a structure of Al/LiF/TPBi/QDs/poly-TPD/PEDOT/PSS/ITO glass (Figure 4a) was fabricated to characterize the luminescence behavior of the QDs. TPBi and poly-TPD layers were used as electron and hole injection layers, respectively, as reported previously.47,48 The crosssectional SEM image (Figure S5) of the device with the optimal x = 0.4 QD shows the discrete layers. Figure S6 shows surface SEM images of the QD films before and after the surface treatment. As anticipated from the literature,^{21,49,50} agglomerated QDs are visible on the surface of the films. After the KCl-treatment, however, the film surface showed less agglomeration, which indicates that the surface modification impedes intimate contacts among the QD nanoparticles. The PL intensity and PLQY were also compared in the form of QD solution and film as seen in Figure S7. The prepared film exhibited weaker PL intensity compared to that for the solution, primarily due to the agglomeration effect of QDs in the film. However, the surface treatment improved the quantum yield of both the solution and film by reducing agglomerates and surface defects.

The relative positions of the energy levels of the halide layers were obtained from the Tauc plots and UPS results (Figure S8). The resulting energy band alignments of the layers are schematically illustrated in Figure 4b, wherein the energy levels of the active layers composed of the x = 0 and 0.4 QDs are projected along with the case of the surface-treated x = 0.4QDs. The x = 0 QDs showed an optical bandgap of 3.17 eV, which is similar to the reported value of 3.18 eV.⁵¹ The inorganic salt treatment decreased E_g slightly from 3.25 to 3.24 eV. The Fermi level E_F and valence band maximum E_V for the QDs were directly evaluated from the secondary cutoff and low-binding-energy regions of the UPS spectra, and the conduction band minimum $E_{\rm C}$ was determined by adding $E_{\rm g}$ to $E_{\rm V}$. The $E_{\rm C}$ of the pristine and Na-incorporated QDs were estimated to be -4.92 and -4.84 eV, respectively. The incorporation of Na decreased the energy offset with the TPBi layer, which facilitated electron injection from TPBi to the QDs. In addition, the KCl treatment improved the band alignment between the charge injection layer and QDs because it increased the magnitude of $E_{\rm V}$ to -8.04 eV and that of $E_{\rm C}$ to -4.80 eV. More efficient charge transport across the interface from the charge injection layer into the QDs is expected to enhance device performance.

Figure 4c presents the voltage-luminance characteristics of the QD devices with x = 0 and 0.4 along with the case of the surface-treated x = 0.4 QDs. As expected, the luminance increased with the increasing voltage in the range of 5-10 V but tended to saturate at higher voltages. After incorporating Na (x = 0.4), the luminance increased from 29.7 to 65.8 cd m⁻² at 10 V. Incorporating Na enhances the charge injection efficiency with an improved carrier lifetime and thus reduces nonradiative recombination by Na. With an appropriate incorporation of Na, the electron-phonon coupling is optimized by altering phonon vibration modes. This facilitates the formation of stable self-trapped exciton states, thereby enhancing radiative recombination. Incorporating metal ions into perovskite nanocrystals has had similar effects on their photoelectric properties. 52,53 The surface-treated device with x = 0.4 exhibited the highest brightness of 80.3 cd m^{-2} and the lowest turn-on voltage of 6 V. With the introduction of K⁺ ions, which can strongly bond with halogen anions to form inorganic ligands on the surface of QDs, the excess amount of insulating organic ligands was reduced, the conductivity of QDs increased. In addition, surface-treated QDs showed lower nonradiative recombination because of the passivation effect of the defects caused by the desorption of organic ligands and the protonation between acids and amines.^{54,5}

The variations in the current density with increasing voltage are plotted for the three main cases under investigation (x = 0, x = 0.4, and surface-treated x = 0.4) in Figure 4d. A higher current density was achieved over the voltage range because of the Na and surface treatment. As their combined effect, the increment in current density from 189 to 366 mA $\rm cm^{-2}$ at 10 V can be ascribed to more favorable energy alignments between the charge transport and QDs layers. The current densityvoltage curves also indicated that the combination of Na incorporation and surface treatment could reduce the chargeinjection barrier by modifying the energy levels. The EQE values were plotted against the changes in the current density for the three cases, as shown in Figure 4e. The highest EQE of 0.05% was achieved for the surface-treated x = 0.4 device, which indicates that the radiative efficiency was improved by the enhanced carrier lifetime and defect passivation. Na incorporation alone prolonged the lifetime, indicating a reduction in nonradiative recombination. The successful passivation of surface defects by K⁺ ions also inhibited nonradiative recombination. These processes enhanced the QD efficiency by reducing defects that act as sites for nonradiative pathways. Consequently, more charge carriers underwent radiative recombination.

Figure 4f presents the emission spectra of the x = 0.4 devices under various forward biases before and after the surface treatment. The emission spectrum confirms that the devices exhibit significant white EL during operation, characterized by dual emission peaks around 430 and 610 nm. Based on the PL

and EL spectra of poly-TPD,⁵⁶⁻⁵⁸ it can be concluded that the low-energy emission peak originates from the STE recombination of QDs while the high-energy emission peak is attributed to the contribution by poly-TPD. When the voltage was increased from 6 to 9 V, the EL spectra of the untreated QD device shifted from 615 to 644 nm, whereas the emission peak of the treated QD devices shifted less, from 613 to 622 nm, indicating that the phase segregation caused by ion migration was suppressed by K⁺ passivation.⁵⁹ K⁺ and halide ions can form halide-sequestering species at the grain boundaries in QD films, fixing the halide ions and thereby inhibiting ion migration.⁶⁰ Therefore, the surface-treated device demonstrated spectral stability with increasing voltage. Similarly, stable emission spectra have been reported for CsPbI_{3-r}Br_r nanocrystals surface-treated by KBr, which was assumed to originate from the suppression of halide ion migration.⁶¹ It should be mentioned that the EL spectra exhibit a slight blue shift with the surface treatment, opposing the red shift in the PL spectra. This can be attributed to different excitation mechanism for EL with the imbalanced carrier injection causing recombination at higher energy levels. As seen in Figure S9, surface-treated x = 0.4 device exhibited color coordinates of (0.36, 0.36), with a color temperature of 4132 K and a color-rendering index of 75 at 10 V, which are close to the ideal pure white light coordinate set by the Commission Internationale de l'Eclairage. The lifetimes of the devices were estimated from the plots of luminance versus time, as shown in Figure S10. The device fabricated with x = 0 QDs exhibited a rapid drop in luminance, with a half-life of only 13.7 min. The half-life was greatly increased by Na to 21.6 min for the device with x = 0.4 QDs and further extended to 36.5 min for the surface-treated x = 0.4 QDs, indicating the KCl-passivated QDs were the most stable. The improved stability was due to both Na incorporation and KCl surface treatment, which reduced nonradiative recombination in the QDs and consequently decreased thermal energy generation.

CONCLUSIONS

As a rare case of EL devices with halide perovskites, the whiteluminance performance of electrically driven double-perovskite QD LEDs was enhanced by adopting combined compositional and surface engineering. A Cs2AgIn0.9Bi0.1Cl6 double perovskite was specifically selected as the active layer for the substitution of Na at the Ag site. After optimizing the Na content in the perovskite, the resultant QD displayed a higher PLQY of 19.31% and a longer lifetime of 1.4 μ s than the case without Na because of enhanced radiative recombination and effective STE emission. When the QDs were additionally treated by KCl for surface passivation, the luminance performance further improved, as supported by the current density and lifetime of the device. As the optimal material, the surface-treated Cs2Ag06Na04In09Bi01Cl6 QDs demonstrated a luminance maximum of 80.3 cd m⁻², EQE of 0.05%, and halflifetime of 36.5 min, which are very promising when compared with reported values. In particular, a low turn-on voltage of 6 V is meaningful for double-perovskite devices.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.4c06194.

Additional figures of TEM images, XPS spectra, SEM image, Tauc plots, UPS spectra, PL spectra, PLQY, color coordinates, and luminance with time; a table on decay parameters (PDF)

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Notes

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