Effect of Washing Solvents on the Properties of Air-Synthesized Perovskite CsPbBr$_3$ Quantum Dots for Quantum Dot-Based Light-Emitting Devices

LUNG-CHIEN CHEN$^{1,}$ (Member, IEEE), CHING-HO TIEN$^1$, PO-WEI TSENG$^1$, ZONG-LIANG TSENG$^2$, WEI-LUN HUANG$^2$, YOU-XUN XU$^2$, and HAO-CHUNG KUO$^{3,4}$, (Fellow, IEEE)

$^1$Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan
$^2$Department of Electronics Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan
$^3$Department of Photonics, National Chiao Tung University, Hsinchu 30010, Taiwan
$^4$Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

Corresponding authors: Lung-Chien Chen (ocean@ntut.edu.tw) and Zong-Liang Tseng (zltseng@mail.mcut.edu.tw)

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ABSTRACT In order to improve the stability and cost of perovskite CsPbBr$_3$ and establish a preparation process for quantum dot materials with excellent luminescence properties, CsPbBr$_3$ quantum dots were synthesized by the hot injection method and the ice bath method in air ambient. Then, a proprietary purification system was used to improve the properties of the quantum dots and prepare high-quality perovskite quantum dot films. Optimal material and light characteristics were exhibited with ethyl acetate:hexane as the purification solvent. In the solution form, the photoluminescence wavelength could be maintained at 508 nm with almost no shift compared with other conditions, and the quantum yield could reach 99%; however, superior performance was obtained in the thin-film form, which exhibited little to no shift in the photoluminescence wavelength and, surprisingly, achieved a quantum yield of 91.6% with a narrow PL emission with a full width at half-maximum of 28 nm. In addition, exceptional thin-film uniformity was observed from scanning electron microscopy image analyses. The CsPbBr$_3$ quantum dot light-emitting diode purified with ethyl acetate:hexane demonstrated an open-circuit voltage of 4 V, a maximum luminous brightness of 488 cd m$^{-2}$, and a maximum external quantum efficiency of 0.14%.

INDEX TERMS Optoelectronic devices, light emitting diodes, quantum dots, perovskite, CsPbBr$_3$.

I. INTRODUCTION

Perovskite quantum dots (QDs), due to their advantages of low cost, narrow full width at half-maximum (FWHM), high photoluminescence (PL) quantum yield, tunable emission wavelengths, and easy surface modification, have attracted widespread attention [1]–[5]. These excellent properties have made QDs one of the most potentially useful light-emitting materials currently applied in light-emitting diodes (LEDs) [6]–[8], lasers [9], [10], photodetectors [11], [12], displays [13], [14], and visible light communication [15], [16]; they are very attractive in the optoelectronic field. Compared with organic-inorganic hybrid perovskite materials (such as MAPbX$_3$ and FAPbX$_3$ (X = Cl, Br, I)), all inorganic CsPbX$_3$ (X = Cl, Br, I) perovskite materials have excellent optical properties and high stability [17]–[20]. Kovalenko et al. first reported a simple synthesis method for CsPbX$_3$ (X = Cl, Br, I) QDs in 2015, with adjustable emission over the entire visible spectral region of 410–700 nm under nitrogen protection and high temperature along with high PL quantum yield values of up to 90% and narrow emission line-widths of 12–42 nm [21]. In 2016, Zeng et al. proposed a method for synthesizing CsPbX$_3$ QDs in air at room temperature [22]. The above two methods have become the main synthesis methods for CsPbX$_3$ QDs. Both of these methods require a purification procedure of the QD crude solution. During the purification process, a polar solvent must be added to promote the precipitation of the QDs followed by
centrifugal purification. The commonly used polar solvents include ethyl acetate, acetone, and isopropanol. However, the choice of polar solvents has an important influence on the optical properties of the QDs obtained by purification. Jonathan et al. synthesized CsPbX3 QDs using acetone purification and a hot injection method to obtain a quantum yield of 83% [23]. Zeng et al. synthesized CsPbX3 QDs based on a room-temperature supersaturated recrystallization method and purified the product with acetone to obtain perovskite QDs with a quantum yield of 95% [22]. Takayuki et al. investigated the effects of three washing solvents, butanol, ethyl acetate, and butyl acetate, on PL quantum yield, PL lifetime, QD size, and the surface roughness of CsPbBr3 QD films. It was found that the butyl acetate two-step wash can effectively remove excess ligands of CsPbBr3 QDs, and the sample exhibited a high PL quantum yield of 42% in films [24]. Mei et al. [25] prepared CsPbBr3 QDs via a hot-injection approach and then combined them with ZIF-8 to obtain brightly luminescent CsPbBr3/ZIF-8 composites, which exhibits high quantum yield of 41.2%, narrow-band emission of 20 nm, and enhanced stability in comparison to bare QDs. In recent years, perovskite QDs have been actively studied in the field of optics, especially in the application of QD-LED devices. Yantara et al. used CsPbBr3 QDs to prepare QD-LED devices with lower excitation voltage (3 V), a narrower emission spectrum (18 nm), and higher emission intensity (407 cd m\(^{-2}\)) [26]. Li [6] demonstrated that the performance of the QD-LED could be further optimized by using different washing solvents and numbers of wash cycles. The ligand density in CsPbBr3 QDs was adjusted with a hexane/ethyl acetate mixed solvent to improve surface passivation and carrier injection. Consequently, the device achieved a maximum brightness of 15185 cd m\(^{-2}\) and a high external quantum efficiency (EQE) of 6.27%. Chiba et al. [24] used butyl acetate to remove the excess ligands in CsPbBr3 QDs, which obtained an EQE of 8.73% and a maximum power efficiency of 31.7 lm W\(^{-1}\) for the CsPbBr3 QD-LED. Therefore, the fabrication of perovskite QDs-LEDs with better light emitting performance and higher stability has been a research hotspot in this field. Typically, the synthesis method of perovskite QDs mainly employs the hot injection method; the capping ligands used are trioctylphosphine, trioctylphosphine oxide, oleic acid, oleylamine or didodecyl dimethyl ammonium bromide. After the reaction is completed, the QDs are obtained by a centrifugal purification process in the subsequent preparation of LED devices; excessive ligands will block the transmission of electrons and holes, affecting the light-emitting efficiency of the device [24], [27]–[29]. Therefore, purification procedures and elution ligands have become key factors that must be preprocessed to obtain high-quality and high-PL-quantum-yield perovskite QDs to achieve high-efficiency QD-LED devices. The purpose of this study is to improve the purification process technology for air-synthesized perovskite QDs by performing purification steps with varied numbers of wash cycles and various nonpolar purification solvents (such as ethyl acetate (EA), ethyl acetate:hexane (EA:H), acetone (ACE), acetone:hexane (ACE:H) to remove excess ligands on the surface of QDs, improve the air-synthesized perovskite CsPbBr3 QDs quality and prepare QDs for use as the emission layer in QD-LED devices.

II. METHODS

A. MATERIALS

Cesium carbonate (Cs\(_2\)CO\(_3\), 99.995%), lead (II) bromide (PbBr\(_2\), 99.999%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAM, 90%), and chlorobenzene (99.8%) were purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, AI4083) was purchased from Uni-Onward. Poly(4-butylphenyl-diphenyl-amine) (poly-TPD) and 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi, 99.5%) were purchased from Lumtec. Ethyl acetate (EA), n-hexane, and acetone were purchased from Echo Chemical.

B. SYNTHESIS AND PURIFICATION OF PEROVSKITE CsPbBr\(_3\) QDs

The perovskite CsPbBr3 QDs were synthesized using hot-injection and ice-water bath methods. The reaction flowchart of QD crude product is shown in Fig. 1. Cs\(_2\)CO\(_3\) (0.07 M) was loaded into a 7-mL flask along with ODE (3 mL) and OA (0.25 mL), then the solution was stirred at 200 °C until it became transparent to obtain Cs-oleate. PbBr\(_2\) (0.03 M), ODE (100 mL), OA (10 mL), and OAM (10 mL) were loaded into a 50-mL flask, which was stirred at 140 °C until the mixture was dissolved, and the flask was heated at 200 °C for 5 min. The Cs-oleate was then quickly injected. Five seconds later, a yellow cloudy reaction mixture was obtained. The reaction mixture was cooled using an ice-water bath for 40 s to stop the reaction and complete the CsPbBr3 QD crude solution. To elute the surface ligands of the CsPbBr3 QDs, we tested the addition of various nonpolar solvents for the purification process, such as EA, EA:H, ACE, and ACE:H, for which the purification process flowchart is shown in Fig. 2. The CsPbBr3 QD crude solution was centrifuged at 6000 rpm for 15 min, and the precipitate was collected. EA was added into the collected CsPbBr3 QD precipitate with a volume ratio of 3:1; the precipitate was collected separately.
after centrifugation at 6000 rpm for 10 min. This process needs to be repeated 3 times for CsPbBr$_3$ QDs. Subsequently, the final collected CsPbBr$_3$ QD precipitate was dispersed in 2 mL of n-hexane and then vortexed with an ultrasonic oscillator for 1 min to uniformly disperse the QDs to produce the purified perovskite CsPbBr$_3$ QDs. In the case of the sample purified with EA:H$_3$=3:2, ACE, and ACE:H$_3$=3:2, the same process was repeated. If it was an unpurified CsPbBr$_3$ QD sample (defined as normal), the CsPbBr$_3$ QD crude solution can be dispersed in 2 mL of n-hexane after centrifugation. All synthesis process was performed in ambient.

C. DEVICE FABRICATION

The patterned ITO-coated glass substrates were produced through a lithography process and then sequentially washed in an ultrasonic cleaner with deionized water, acetone, and isopropyl alcohol for 30 min. After that step, the patterned ITO-coated glass substrates were treated with oxygen plasma for 3 min. The PEDOT:PSS solution was deposited onto the patterned ITO-coated glass substrate by spin coating at 1000 rpm for 30 s and baked at 100 °C for 10 min. The 40-nm-thick TPBi electron transport layer and LiF/Al were used as the anode, the hole injection layer, hole transport layer, the electron transport layer, and the cathode, respectively. This device architecture presents both electron transport layer, the electron transport layer, and the cathode, respectively. This device architecture presents both electron and hole injection to the perovskite QD light-emitting layer for radiation recombination.

D. CHARACTERIZATION AND DEVICE MEASUREMENTS

The photoluminescence (PL) spectra, PL quantum yield, and time-resolved PL decay were detected using a FluoroMax spectrofluorometer (Horiba Jobin Yvon, Longjumeau, France) with an integrating sphere. The X-ray diffraction (XRD) patterns were recorded with a X’Pert PRO MRD system (PANalytical, Almelo, Netherlands). The perovskite QD size, surface morphology and chemical composition were observed using a JEM-2100F transmission electron microscope (TEM) (JEOL, Tokyo, Japan) and a ZEISS Sigma field emission scanning electron microscope (FESEM) (ZEISS, Munich, Germany), respectively. The PR-655 spectrascan spectroradiometer (Photo Research Inc., Syracuse, NY, USA) with a Keithley 2400 source meter was used to measure the current density–voltage–luminance ($J-V-L$), current efficiency (CE), power efficiency (PE), EQE, and electroluminescence (EL) spectra of the perovskite CsPbBr$_3$ QD-LEDs.

III. RESULTS AND DISCUSSION

Fig. 4a shows the luminescence images of 355-nm ultraviolet (UV) light excited and unexcited perovskite CsPbBr$_3$ QD solutions using different purification solvents for the purification process. From left to right, the solvents are as follows: unpurified (normal), ethyl acetate (EA), ethyl acetate:hexane (EA:H$_3$=3:2), acetone (ACE), and ace-ton:hexane (ACE:H$_3$=3:2); the dispersion solvent was hexane. The perovskite CsPbBr$_3$ QD solutions were visually comparable under ambient light or UV light; thus, the results are discussed in other measurement analyses. The PL spectrum of the perovskite CsPbBr$_3$ QD solution in Fig. 4b illustrates that the emission wavelength of the un purified QD solution was 507 nm, and the FWHM was $\sim$20 nm. After EA purification, it was observed that EA eroded the QDs during purification, reducing the size of the QDs. The wavelength also blueshifted to 505 nm. Following ACE and ACE:H purifications, because of the high polarity of ACE, the ligands of the QDs were damaged during the purification process, which led to agglomeration and resulted in a redshift in the wavelength to 509 nm and an increased FWHM to 33.5 nm. Additionally, the excitation waveform of the QD solution with the ACE:H purification solvent...
was disrupted and deformed, and the FWHM was 43 nm. Among the solvents, the wavelength of 508 nm and FWHM of 24 nm of EA:H purification were comparable with the unpurified sample, demonstrating that it was the optimal purification condition. Furthermore, the quantum yield of the unpurified perovskite CsPbBr$_3$ QD solution reached 68%, and an 83% quantum yield could be maintained with EA and EA:H purifications, respectively. Although the quantum yield of ACE purification was also close to 73%, ACE:H purification was inferior, with a quantum yield of only 49%.

The PL spectral analyses, FWHMs, and quantum yields of the QD solutions are listed in Table 1 and Fig. S1. In theory, because the perovskite CsPbBr$_3$ QD solution is a type of fluorescent material, the decay time of the photons should be short. Fig. 4c shows that the decay time of the unpurified QD solution was $\sim$43.0 ns. Following the purification process, the decay time of all QD solutions was significantly reduced, which was more in line with the characteristics of fluorescent materials; in particular, the decay time of the solution after EA:H purification was only 33.8 ns. It is speculated from this phenomenon that because the unpurified QD solution was protected by ligands, the excited photons were bound to the ligands and could not undergo extinction freely; however, purified QD solutions had fewer ligands and, thereby shortening the decay time. The detailed time-resolved PL analyses of the QD solutions are listed in Table 2.

Fig. 5 shows the TEM images and the size distribution chart of perovskite CsPbBr$_3$ QD solutions using different purification solvents for the purification process. Figure 6 shows the elemental distributions and energy dispersive X-ray spectroscopy (EDS) results of the QD solutions,
and Table S1 gives the results of the element ratio analyses of the QDs solutions. Fig. 5a shows the TEM image of the unpurified perovskite CsPbBr$_3$ QD solution. It was discovered that the unpurified QDs solution could be fully organized in a checkerboard arrangement because of the presence of ligands, and the size distribution was $\sim$11 nm. The distribution chart from the elemental analysis illustrates that the distribution of the elements was largely uniform. Although the Br content was slightly lower, this did not affect the QDs structure, as shown in Fig. S2a. Fig. 5b shows the EA-purified perovskite CsPbBr$_3$ QD solution. Because of the loss of protection from the ligands, the QDs under this condition could not form an ordered arrangement and were instead scattered. The shape of the CsPbBr$_3$ QDs transformed from square to spherical, and the size distribution also changed to $\sim$9 nm because of the erosion of the solvent. This verified the blueshift phenomenon of the excitation wavelength. The distribution chart from the elemental analysis illustrates that the elements remained evenly distributed. The element ratio of Cs and Br changed significantly, and the element ratio after purification was also similar to the standard ratio.

The distribution chart from the elemental analysis illustrates that the elements remained evenly distributed. The element ratio of Cs and Br changed significantly, and the characteristics of the QDs also altered slightly, as shown in Fig. S2b. Fig. 5c shows the EA:H-purified perovskite CsPbBr$_3$ QD solution. Similarly, the protection from the ligands was lost, and the QDs under this condition could not form an ordered arrangement and were instead scattered. Nevertheless, the QDs maintained a square shape, and the size distribution varied. Compared with the unpurified QDs, the excitation wavelength had a redshift of only 1 nm. For the elemental analysis, although the QDs were scattered, the element content of the QDs remained uniform, and the element ratio after purification was also similar to the standard ratio. This finding is evidence that the EA:H mixed purification solvent is conducive to the purification of QDs, as shown in Fig. S2c. Fig. 5d is the ACE-purified perovskite CsPbBr$_3$ QD solution. Even though the number of ligands was reduced, the QDs maintained a weakly ordered arrangement under this condition. Nevertheless, although the shape of the QDs could be maintained as a square and the size distribution was $\sim$12 nm, a small number of QDs clearly agglomerated, resulting in a nonuniform distribution. For the elemental analysis, the elements were concentrated in larger QDs, resulting in a notably poor uniformity in the element distribution. The element ratio also altered slightly, as shown in Fig. S2d. The use of this solvent for purification significantly affected the structure of the QDs and added multiple uncertainty factors. Fig. 5e shows the ACE:H-purified perovskite CsPbBr$_3$ QD solution. Because the number of ligands was limited, not only were the QDs unable to form an ordered arrangement, but they also started to agglomerate severely. The size distribution of a single QD was $\sim$10 nm, but the size difference between the dots was substantial. Both agglomeration and excessive size were the causes of waveform distortion. The elemental analysis shows that because of the agglomeration phenomenon, the elements concentrated in agglomerated blocks. The element ratio was fragmented and diverged from the ratio of conventional perovskite, as shown in Fig. S2e. The results demonstrate that this solvent is not suitable for the purification of QDs.

Fig. 6a shows the luminescence images of 355-nm UV light excited and unexcited perovskite CsPbBr$_3$ QD films using different purification solvents for the purification process. Under ambient light, the unpurified QD film appeared fluorescent green because the QD solution was not sufficiently dried after coating; hence, the thin film exhibited a color similar to that of the solution. In contrast, the purified QD films were not overly damp, and they appeared yellow-green after coating. Under the 355-nm UV light, the unpurified QD film appeared fluorescent green with high brightness. Except for the green ACE:H-purified QD film, while other conditions were also fluorescent green, the brightness, in comparison, was not as high. The PL spectra in Fig. 6b show that the excitation wavelength of the unpurified QDs film was 507 nm, and the FWHM was $\sim$25 nm. After EA and EA:H purifications and coatings, the wavelength of the QD films did not shift, and the wavelength remained at 507 nm; however, the FWHMs widened. After ACE and ACE:H purifications and coatings, because the solution had agglomerated, redshifts in the excitation wavelength were pronounced, and the FWHMs also slightly increased. For the quantum yield, the unpurified QDs film also had a quantum yield reaching 67% as the unpurified solvent. After EA purification and coating, the quantum yield decreased significantly; after ACE:H purification and coating, the quantum yield was notably poor, reaching only 36%. The quantum yield after EA:H and ACE purifications and coatings could reach around 60%, which demonstrates that EA:H purification solvent is favorable to the optimization of QD films. The PL spectral analyses, FWHMs, and quantum yields of the QD films are listed in Table 3. Because of the possibility of red-shift the wavelength with ACE purification, the subsequent application of the devices may be affected. The time-resolved PL analyses suggested that a two-piece piecewise fitting function could not fully express the trend of the time-resolved PL. Therefore, a three-piece piecewise fitting function was attempted, and the results showed that the $\tau_2$ decay time was notably long [30], [31]. The appearance of $\tau_2$ also suggested the occurrence of fluorescence resonance energy transfer in the QDs. Because the QDs were very densely stacked on each other after being formed into a film, the light energy of the QDs was exchanged after being excited, which resulted in this phenomenon. The phenomenon was also exceptionally pronounced because

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The decay time of the QDs after film formation was very short, as shown in Table 4. Fig. 6c illustrates that although the QD films and QD solutions showing similar downward trends under different conditions, the decay times of the QD films increased significantly by approximately threefold. The decay time of the thin film purified with EA:H was as short as 9.9 ns, and the 21.9 ns change compared with the unpurified thin film was substantial. This demonstrates that the purification process is imperative to the quality improvement of the QD films.

The X-ray diffraction analyses of CsPbBr$_3$ QD films purified with various nonpolar purification solvents in Fig. 7. Obviously, through purification steps with varied numbers of wash cycles and various nonpolar purification solvents, this study showed the presence of hybrid rhombohedral Cs$_4$PbBr$_6$ (PDF#73-2478) and monoclinic CsPbBr$_3$ (PDF# 18-0364). The Cs$_4$PbBr$_6$ nanocrystals exhibit a superior quantum yield than that of CsPbBr$_3$ nanocrystals [32], [33]. The diffraction peaks of the unpurified QDs film were not pronounced. This finding was observed because the QDs were still protected by the ligands, which weakened the measured signals. Although the signals were not improved with EA purification, the standard phase of perovskite CsPbBr$_3$ QDs appeared after the purification with EA:H, ACE, and ACE:H solvents. The XRD patterns of the d(200) crystal plane were used to calculate the lattice constant of the QDs for comparison. The lattice constant of the unpurified QDs was ~5.91 nm, which slightly differed from the standard value of 6.01 nm. The lattice constants of the EA and EA:H purified QDs were clearly closer to the standard value; in particular, the lattice constant after EA purification was 5.96 nm with an error of less than 1% and was comparable to the standard value, as shown in Table S2.

Fig. 8 shows the scanning electron microscopy images of the perovskite CsPbBr$_3$ QDs films using different purification solvents for the purification process. The unpurified perovskite CsPbBr$_3$ QD film contained ligands; consequently, the image appeared blurred, because the thin film was not dried completely. Nonetheless, QDs could still be observed at high magnification, as shown in Fig. 8a. Fig. 8b shows the EA-purified perovskite CsPbBr$_3$ QD film. The QDs remained insufficiently dried; nevertheless, some surface morphology could be identified, and the shape of the QDs could also be observed. Fig. 8c is the EA:H-purified perovskite CsPbBr$_3$ QD film, and the purified thin film had excellent uniformity. In addition, QDs could be observed distinctively. Although the size of the QDs varied slightly because of a small degree of agglomeration, it was not sufficient to affect the optical characteristics. Fig. 8d shows the ACE-purified perovskite CsPbBr$_3$ QD film. It was observed that the QD film had poor uniformity, and there were small clusters scattered on the surface. The high-magnification image illustrates that the size distribution of the QDs was consistent; however, the agglomeration phenomenon was detrimental and slightly changed the optical characteristics of the QD film under this condition. Fig. 8e shows the ACE:H-purified perovskite CsPbBr$_3$ QD film. The QDs could not be wholly coated under this condition because the degree of agglomeration was severe, which was one
of the reasons why the optical properties of this condition deteriorated.

Based on the LED devices fabricated from the QDs under the above conditions, only the device using EA:H as the purification condition was successful. Fig. 9a shows a typical EL spectrum of the EA:H-purified CsPbBr$_3$ QD-LED device with an emission peak at 512 nm. The FWHM of the EL was only 25 nm, which was slightly widened by ∼1 nm, indicating that this QD-LED inherited the PL color purity of CsPbBr$_3$ QDs. The inset of Fig. 9a is the luminescence image at an operating voltage of 5 V. Uniform green light was emitted, and the brightness was sufficient to be seen in a normal light environment. Compared with the PL spectrum of the QDs solution, the EL peak of the QDs-LED displayed a slightly redshifted wavelength of ∼4 nm. This effect may result from the dielectric dispersion effect of the solvents [34], [35], or the Stark effect and particle interaction caused by the electric field [35]–[37]. Fig. 9b shows the characteristic curves of the brightness and current density of the QD-LED device versus the operating voltage. The device began to operate at 4 V, and the current density was 0.04 mA cm$^{-2}$. The maximum brightness was 487.8 cd m$^{-2}$ at 8 V, and the current density could reach 362 mA cm$^{-2}$. Fig. 9c shows the curves of current efficiency and power efficiency versus brightness. The device had a maximum efficiency of 0.432 cd A$^{-1}$ and 0.246 lm W$^{-1}$ at a brightness of 13.15 cd m$^{-2}$; later, the efficiency decreased as the brightness increased. Fig. 9d is a graph of the EQE versus brightness. When the brightness was 13.15 cd m$^{-2}$, the maximum EQE was 0.14%, that is, the maximum EQE was highest when the efficiency was the highest.

IV. CONCLUSION

In this study, air-synthesized perovskite CsPbBr$_3$ QD solutions were purified with a proprietary purification system and various purification solvents, and the thin-film quality was successfully improved. A blueshift phenomenon was observed with EA as the purification condition because the size of the QDs was reduced, regardless of solution or thin-film form. QDs readily agglomerated with ACE and ACE:H purification; the degree of agglomeration was more severe with ACE:H purification. EA:H purification was shown to be beneficial in all aspects; notably, the quantum yield of the thin film reached 90%. In addition, fluorescence resonance energy transfer was observed in the QDs from the time-resolved PL analyses. The LED device of the EA:H-purified CsPbBr$_3$ QD film displayed a narrow EL spectrum and a high color purity with an FWHM of 25 nm. The maximum luminous brightness, maximum current efficiency, maximum power efficiency, and maximum EQE reached 487.8 cd m$^{-2}$, 0.432 cd A$^{-1}$, 0.246 lm W$^{-1}$, and 0.14%, respectively. In addition, the present work demonstrates to use the most effective purification solvent to obtain the high-quality and high PL quantum yield perovskite QDs. However, the optoelectronic performance of the device as the active layer has not been greatly improved. This will help to further improve and solve the performances of perovskite films and devices by tuning the number of washing cycles of the QD or using Lewis base and acid to reduce defect density.

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LUNG-CHIEN CHEN (Member, IEEE) received the B.S. degree in electrical engineering from the National Taiwan University of Science and Technology, Taipei, Taiwan, in 1991, and the Ph.D. degree in electrical engineering from National Tsing Hwa University, Hsinchu, Taiwan, in 1999. In 2002, he joined the Institute of Electro-Optical Engineering, National Taiwan University of Technology, Taipei, as a Faculty Member. He has authored or coauthored more than 145 SCI technical papers in 60 international conferences, and 180 conference papers. He holds more than 21 patents in his fields of expertise. His current research interests include the MOCVD, LPE, and solution CVD epitaxial growth techniques, fabrication and analysis of III–V compound semiconductor/oxide devices, fabrication and characterization of nanomaterials, light-emitting diodes (LEDs), sensors, solar cells, perovskite quantum dots, and perovskite optoelectronic devices.

CHING-HO TIEN received the B.S. degree in electrical engineering from Dayeh University, Changhua, Taiwan, in 2006, and the M.S. and Ph.D. degrees from the Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei, Taiwan, in 2012. From 2012 to 2017, he was a Postdoctoral Fellow of the Department of Materials Science and Engineering, National Chung Hsing University, Taichung, Taiwan. He is currently a Research Assistant Professor with the Department of Electro-Optical Engineering, National Taipei University of Technology. His current research interests include the growth of III-nitride-based optoelectronic devices, UVC/white LED package design, oxide semiconductor devices, perovskite quantum dots, and perovskite optoelectronic devices.
PO-WEI TSENG received the B.S. degree from the Department of Electronics Engineering, National United University, Miaoli, Taiwan, in 2017, and the M.S. degree from the Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei, Taiwan, in 2019. His major research interests include perovskite quantum dot synthesis techniques, especially in perovskite quantum dot LED applications.

ZONG-LIANG TSENG received the B.S. and Ph.D. degrees in electrical engineering from National Cheng Kung University (NCKU), Tainan, Taiwan, in 2007 and 2013, respectively. In 2018, he joined the Ming Chi University of Technology (MCUT), New Taipei City, Taiwan, as a Faculty Member of the Department of Electronics Engineering and a member of the Organic Electronics Research Center. He has authored more than 60 SCI technical articles. His current research interests include solution-processed hybrid perovskite devices such as perovskite solar cells, perovskite light-emitting diodes, perovskite quantum-dot light-emitting diodes, and perovskite photodetectors.

WEI-LUN HUANG is currently pursuing the bachelor’s degree with the Department of Electronics Engineering, Ming Chi University of Technology, New Taipei City, Taiwan. His major research interests include perovskite quantum dot synthesis techniques, especially in CsPbBr$_3$.

YOU-XUN XU is currently pursuing the bachelor’s degree with the Department of Electronics Engineering, Ming Chi University of Technology, New Taipei City, Taiwan. His major research interests include solution-process devices, especially in perovskite QLED.

HAO-CHUNG KUO (Fellow, IEEE) received the B.S. degree in physics from National Taiwan University, Taipei, Taiwan, the M.S. degree in electrical and computer engineering from Rutgers University, New Brunswick, NJ, USA, in 1995, and the Ph.D. degree from the University of Illinois at Urbana-Champaign, Urbana, IL, USA, in 1999. He has an extensive professional career both in academic research and industrial research institutions, which include a Research Assistant at Lucent Technologies and Bell Laboratories, from 1993 to 1995, and a Senior Research and Development Engineer of the Fiber-Optics Division, Agilent Technologies, from 1999 to 2001, and LuxNet Corporation, from 2001 to 2002. Since October 2002, he has been a Faculty Member with the Institute of Electro-Optical Engineering, National Chiao Tung University (NCTU), Hsinchu, Taiwan. He is currently the Associate Dean of the Office of International Affairs, NCTU. He has authored or coauthored 300 international journal articles and two invited book chapters, and holds six granted and 12 pending patents. His current research interests include semiconductor lasers, VCSELs, blue and UV LED lasers, quantum-confined optoelectronic structures, optoelectronic materials, and solar cells. He was elected as an OSA Fellow and the SPIE Fellow in 2012. He was a recipient of the Ta-YouWu Young Scholar Award from the National Science Council Taiwan in 2007 and the Young Photonics Researcher Award from the OSA/ SPIE Taipei Chapter in 2007. He is an Associate Editor of the IEEE/OSA JOURNAL OF LIGHTWAVE TECHNOLOGY and was a Guest Editor of the of the Special Issue on Solid-State Lighting of the IEEE JOURNAL OF SELECTED TOPICS IN QUANTUM ELECTRONICS in 2009.