Metal halide perovskite nanocrystals (PeNCs) have ionic crystal structures, and their optical properties are greatly affected by polar solvents owing to the formation of cation- and anion-defects. Herein, we fabricated low driving voltage and high efficiency NC light emitting devices (LEDs) using gel permeation chromatography (GPC) with nonpolar solvents to remove impurities such as excess ligands and reaction solvents. We confirmed that these impurities may be removed completely via the one-cycle GPC purification process in contrast to the conventional reprecipitation purification process having two-cycles. In addition, we demonstrated the effect of interfacial engineering between the hole transport layer and PeNC layer using alkyl ammonium salts containing Br anion, i.e., oleylamine bromide (OAm-Br), to passivate both cation- and anion-defects in PeNCs. The LEDs based on PeNCs with GPC purification achieved the maximum external quantum efficiency of 4.3% with OAm-Br layer.

Keywords: Perovskite nanocrystal, Light-emitting device, GPC purification process, Interfacial engineering, Alkyl ammonium layer

1. Introduction

Lead halide perovskite materials have been utilized in various applications, such as, photovoltaic devices [1,2], light-emitting devices (LEDs) [3-8], photodetectors [9,10], and lasers [11]. In particular, lead halide perovskite nanocrystal (PeNCs) exhibit high potential for LED application owing to their narrow full width at half maximum (FWHM), color turnability in the visible range, and high photoluminescence quantum yield (PLQY) [12,13]. External quantum efficiency (EQE) of the LEDs based on inorganic PeNCs (CsPbX3, X = Cl, Br, I) rapidly increased from 0.12% [14] to 16.5% [15] by surface modification [15], control of the ligand density [6], and ligand exchange [4,5]. In general, the synthesized PeNCs were purified by a reprecipitation (RP) method using polar solvents to remove impurities such as excess ligands, unreacted precursors, and reaction solvents. However, the ionic PeNCs were easily damaged in the polar solvents and decreased the PLQY owing to the occurrence of surface defects. We previously demonstrated that low-dielectric-constant ester solvents were used as anti-solvents in the RP method to prevent damage during purification [5,16]. Herein, we demonstrate gel permeation chromatography (GPC) [17] with a nonpolar solvent, toluene, that can completely remove impurities via a one-cycle purification process in contrast to the conventional RP process. In addition, we demonstrated the effect of the interfacial layer between the hole transport layer and PeNC layer using alkyl ammonium salts containing Br anion, i.e., oleylamine bromide (OAm-Br), to passivate cation- and anion-defects [18]. The PeNC LED with an OAm-Br layer exhibited a higher EQE of 4.3% than that of the LED without the OAm-Br layer (EQE 0.7%) owing to the effective suppression of interfacial...
cation- and anion-defects.

2. Experimental
2.1. Materials
Cesium carbonate (99.99%), octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAm, 90%), and lead bromide(II) (PbBr₂, 99.99%) were purchased from Sigma-Aldrich; PEDOT: PSS was purchased from Clevios; poly-TPD was purchased from American Dye Source; and TPBi and Liq were purchased from e-Ray Optoelectronics Technology Co., and were used as received. Bio-beads were purchased from BIO-RAD. All other materials and solvents were purchased from Sigma-Aldrich and were used as received.

2.2. Synthesis of CsPbBr₃-NCs
CsPbBr₃-NCs were synthesized using a hot-injection method [12,13]. Cesium carbonate (271 mg) and oleic acid (OA, 833 mL) were dissolved in ODE (10 mL) with a three-neck flask at 120 °C for 1 h in vacuum to synthesize Cs-oleate. Then, PbBr₂ (1.38 g), OA (10 mL), and oleylamine (OAm, 10 mL) were dissolved in dried ODE (100 mL) with three-neck flasks at 120 °C for 1 h under vacuum conditions. Subsequently, the temperature of the synthesized Cs-oleate increased to 160 °C, and then the Cs-oleate solution (8 mL) at 160 °C was quickly injected into the precursor mixture at 185 °C under a nitrogen atmosphere. After 5 s, the reaction mixture was rapidly cooled in an ice-water bath to room temperature and collected.

2.3. Synthesis of OAm-Br
OAm-Br was synthesized using the method mentioned in [13]. OAm (0.038 mol) was added in ethanol (100 mL) with a three-neck flask and stirred. The reaction mixture was cooled in an ice-water bath and then hydrogen bromide was added. Next, the reaction mixture was reacted overnight in a nitrogen atmosphere. After the reaction, the reaction mixture was dried in vacuum overnight to remove the solvent and the purified product was collected through multiple rinses with diethyl ether. Finally, the product was dried in vacuum overnight at 80 °C and white powder of OAm-Br was obtained.

2.4. RP washing process
The synthesized CsPbBr₃-NCs was centrifuged to remove the supernatant and collect the precipitate. The precipitate was dispersed in toluene and centrifuged to collect the stably dispersed supernatant. Next, 1-butanol was added into the toluene dispersion with a volume ratio of 1.5:1. The mixture was centrifuged to collect the precipitate and dispersed in octane.

2.5. GPC washing process
The bio-beads were swelled overnight in toluene to pack the column. Next, the swollen beads were packed into the column with a height of approximately 60 cm. To remove the free polystyrene in the column, pure toluene continued to flow overnight into the column. The synthesized CsPbBr₃-NCs were centrifuged and the precipitate was collected. The precipitate was dispersed in toluene and centrifuged to collect the stably dispersed supernatant. The NC dispersion and toluene were sequentially injected into the packed GPC.

2.6. Fabrication and characterization of PeNC-LEDs
The indium tin oxide (ITO)-coated glass substrates were cleaned with deionized water by ultrasonic spin cleaning and subsequent UV–ozone treatment. After treatment, PEDOT:PSS (40 nm, AI4083) with 55 wt% Nafion was spin-coated (2000 rpm/30 s) onto the ITO-coated glass substrates and baked at 150 °C for 10 min under atmospheric conditions. Next, poly-TPD (40 nm) was prepared by spin-coating (1000 rpm/30 s) with 4 mg mL⁻¹ poly-TPD in chlorobenzene onto modified PEDOT:PSS and baked at 100 °C for 10 min under a nitrogen atmosphere. Subsequently, washed CsPbBr₃-NCs (10 mg mL⁻¹ in octane) were spin-coated (2000 rpm/30 s) onto poly-TPD in nitrogen condition. Finally, TPBi (50 nm), Liq (1 nm), and Al cathode (100 nm) were stacked via thermal evaporation with an active area of 2 mm². The PeNC LEDs were characterized after encapsulation using a glass cover with epoxy glue. Electroluminescence spectra and current density–luminance–voltage characteristics were measured using Hamamatsu PMA-11, Keithley SMU 2400, and Minolta CS200.

3. Results and discussion
CsPbBr₃-NCs were synthesized according to the methods described in [12,13], that use Cs-oleate and PbBr₂ precursor with long alkyl ligands (OA and OAm). As-synthesized PeNCs were collected by centrifugation and dispersed toluene. Then, the toluene dispersion was introduced into the GPC that was filled with swelled bio-beads. In this process, the small size of molecules such as unbound ligands and ODEs are passed through at slow rates PeNCs. Therefore, we collected the
sample until 2/3 of the total volume on GPC, which is pure PeNCs without impurities. In addition, we further used the RP method with 1-butanol for the as-synthesized PeNCs to investigate the effect of the purification process.

Figure 1 shows UV–Vis absorption, photoluminescence (PL), and PLQY measurements of washed PeNC films onto the quartz substrate. The PL peak and FWHM of PeNC films with both purification methods were 507 nm and 19 nm, respectively, indicating that purification had no effect on emission wavelength and FWHM. However, the PeNC films exhibited low PLQY, 22% for RP method and 19% for GPC, owing to the formation of cation- and anion-defects. Therefore, we demonstrated the application of OAm-Br as an interfacial passivation layer of PeNCs to prevent surface defects. The PL peak and FWHM of OAm-Br/PeNCs films were nearly unchanged (507 nm and 20 nm, respectively), but the PLQY of PeNC film was significantly improved by up to 47%. This result indicated that interfacial engineering using OAm-Br was an excellent approach to effectively prevent surface defects [18].

Fourier transform infrared spectroscopy (FT-IR) spectra of PeNC films on Si substrate that were purified by RP or GPC method were measured to investigate the purification effect of surface ligands as shown in Fig. 2. The PeNCs with both purification methods showed the resonance of group (COO⁻) at 1530 cm⁻¹ and 1405 cm⁻¹ and amine group(N-H₃⁺) at 3000–3200 cm⁻¹, suggesting the presence of OA and OAm ligands on the PeNC surface [19]. The ¹H-NMR analysis was also performed to observe impurities such as excess ligands and ODE (Fig. 3). The PeNCs purified with the RP method exhibited the terminal alkene resonance peaks of the reaction solvent ODE at 4.9 ppm and 5.8 ppm. On the other hand, PeNCs with the GPC method did not exhibit those peaks owing to the complete removal of the impurities. The OA and OAm desorbed rapidly in the solution by mutual equilibrium between the protonated...
and unprotonated forms of these ligands (OAm$^+$ + OA$^-$ ⇌ OA + OAm) [20]. Therefore, desorbed ligands at 5.5 ppm can be observed in the PeNCs purified by both methods [21]. In addition, $^1$H-NMR analysis was also investigated to determine the density of surface ligands using ferrocene as the reference material. The integrated values (alkene resonance/ferrocene resonance) of capped ligand (5.5–5.6 ppm) concentrations were 0.15 for RP method and 0.05 for GPC, suggesting that surface ligand density of PeNCs for GPC was lower than that for RP method.

We fabricated the CsPbBr$_3$-NC LEDs with the following structure: ITO (130 nm) / poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) with Nafion (20 nm) / poly (bis-4butylphenyl-N,N-bisphenyl) benzidine) (polyTPD) (20 nm) / OAm-Br / CsPbBr$_3$ NCs / 1,3,5-tris(N-phenylbenzimidazol-2-yl) benzene (TPBi) (50 nm) / Liq (1 nm) / Al anode (100 nm), as shown in Fig. 4(a). The exhibited electroluminescence (EL) spectra of the PeNCs for the RP method was 511 nm, for GPC without OAm-Br layer was 509 nm, and for GPC with OAm-Br was 510 nm, respectively (Fig. 4(b)). The current density–voltage–luminance curves and the current density EQE curves of the PeNC-LEDs are shown in Fig. 4 (c) and (d). The PeNC-LEDs based on the GPC method showed a slightly higher current-density of 3.6 mA cm$^{-2}$ (at 4 V) than those with LED with the RP method of 2.4 mA cm$^{-2}$ (at 4 V). This result may occur owing to the reduction in ligand density on the PeNC surface and the removal of impurities. The PeNC-LED based on RP method showed a turn-on voltage of 3.8 V and maximum luminance of 329 cd m$^{-2}$, while PeNC-LED based on the GPC method achieved a lower turn-on voltage of 3.2 V and the higher maximum luminance of 554 cd m$^{-2}$. The maximum EQE was 0.2% for RP method and 0.7% for GPC, indicating that GPC is an effective purification process to obtain high quality PeNCs as compared to the RP method. In addition, the LED with OAm-Br exhibited a low turn-on voltage of 3.0 V,
higher luminance of 731 cd m\(^{-2}\), and EQE of 4.3%. This result suggests that the use of OAm-Br passivation layer can improve both PLQY and LED efficiency owing to the suppression of surface defects.

4. Conclusion
In summary, we have demonstrated that GPC with nonpolar solvent toluene is an effective new purification process for PeNCs. The GPC method completely removed the impurities with a one-cycle purification process in contrast to the conventional RP process. In addition, we demonstrated that the OAm-Br interfacial layer was effective in passivating cation- and anion-defects. The PeNC LEDs with OAm-Br exhibited a higher EQE of 4.3% than that of the LED without the OAm-Br layer (EQE 0.7%) owing to the suppression of surface defects.

References
1. Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin, and J. You, Nat. Photonics, 13 (2019) 460.
2. E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T-Y. Yang, J. H. Noh, and J. Seo, Nature, 567 (2019) 511.
3. L. Zhang, X. Yang, Q. Jiang, P. Wang, Z. Yin, X. Zhang, H. Tan, Y. Yang, M. Wei, B. R. Sutherland, E. H. Sargent, and J. You, Nat. Commun., 8 (2017) 15640.
4. J. Pan, L. N. Quan, Y. Zhao, W. Peng, B. Murali, S. P. Sarmah, M. Yuan, L. Sinatra, N. M. Alyami, J. Liu, E. Yassitepe, Z. Yang, O. Voznyy, R. Comin, M. N. Hedhili, O. F. Mohammed, Z. H. Lu, D. H. Kim, E. H. Sargent, and O. M. Bakr, Adv. Mater., 28 (2016) 8718.
5. T. Chiba, K. Hoshi, Y-J. Pu, Y. Takeda, Y. Hayashi, S.Ohisa, S. Kawata, and J. Kido, ACS Appl. Mater. Interfaces, 9 (2017) 18054.
6. T. Chiba, Y. Hayashi, H. Ebe, K. Hoshi, J. Sato, S. Sato, Y-J. Pu, S. Ohisa, and J. Kido, Nat. Photonics, 12 (2018) 681.
7. K. Lin, J. Xing, L. N. Quan, F. P. G. d. Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. Xiong, and Z. Wei, Nature, 562 (2018) 245.
8. Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang, and W. Huang, Nature, 562 (2018) 249.
9. L. Dou, Y. Yang, J. You, Z. Hong, W-H. Chang, G. Li, and Y. Yang, Nat. Commun., 5 (2014) 5404.
10. F. Cao, L. Meng, M. Wang, W. Tian, and L. Li, Adv. Mater., 31 (2019) 1806725.
11. G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabha, M. Grätzel, S. Mhaisalkar, and T. C. Sum, Nat. Mater., 13 (2014) 476.
12. L. Proteescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, and M. V. Kovalenko, Nano Lett., 15 (2015) 3692.
13. G. Nedelcu, L. Proteescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent, and M. V. Kovalenko, Nat. Lett., 15 (2015) 5635.
14. J. Song, J. Li, X. Li, L. Xu, Y. Dong, and H. Zeng, Adv. Mater., 27 (2015) 7162.
15. J. Song, T. Fang, J. Li, L. Xu, F. Zhang, B. Han, Q. Shan, and H. Zeng, Adv. Mater., 30 (2018) 1805409.
16. K. Hoshi, T. Chiba, J. Sato, Y. Hayashi, Y. Takahashi, H. Ebe, S. Ohisa, and J. Kido, J. Am. Chem. Soc., 140 (2018) 10504.
17. L. M. Wheeler, E. M. Sanehira, A. R. Marshall, P. Schulz, M Suri, N. C. Anderson, J. A. Christians, D. Nordlund, D. Sokaras, T. Kroll, S. P. Harvey, J. J. Berry, L. Y. Lin, and J. M. Luther, Adv. Mater., 30 (2018) 24607.
18. H. Ebe, Y. Takahashi, J. Sato, T. Chiba, S. Ohisa, and J. Kido, J. Am. Chem. Soc., 140 (2018) 329.
19. J. D. Roo, M. Ibañez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. V. Driessche, M. V. Kovalenko, and Z. Hens, ACS Nano, 10 (2016) 2071.
20. B. Fritzinger, R. K. Capek, K. Lambert, J. C. Martins, and Z. Hens, J. Am. Chem. Soc., 132 (2010) 10.