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Synthesis of highly luminescent blue light perovskite
nanoplatelets with homogeneous-thickness for
optoelectronic applications

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2017

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A thesis/dissertation
submitted to the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
Master of Science

Taeyun Kim

12. 14. 2017

Approved by



Advisor

Jongnam Park

Synthesis of highly luminescent blue light
perovskite nanoplatelets with homogeneous-
thickness for optoelectronic applications

Taeyun Kim

This certifies that the thesis/dissertation of Taeyun Kim is approved.

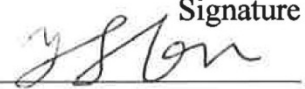
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Abstract

Colloidal semiconductor nanocrystals, also known as nanocrystal quantum dots(QDs), are being studied intensively as future optoelectronic materials due to its solution processing and outstanding optical properties. Among them, perovskite quantum dots(PeQDs) have a wide emission range from near-infrared to ultraviolet by controlling its composition, and are highly luminescent with narrow FWHM by easier synthesise process. Therefore, perovskite nanocrystals are receiving attention as a high-quality optoelectric device material.

However, there is a drop of quantum yield at specific composition includes chloride anion, which are covering blue to ultraviolet emission range. Due to the drop of quantum yield, high-quality blue LED with perovskite still not reported.

In this work, I report the highly luminescent chlorine-free blue perovskite nanoplatelets(PeNPLs) as pure bromide halide composition, which was synthesized by supporting of saturated amine ligand. The thickness of PeNPLs was controlled by reaction parameters such as reaction time and reaction temperature. Also, thickness homogeneity was secured by ligand assisted solubility adjustment method after synthesis. Through this two-step thickness control, photoluminescence properties of the synthesized PeNPLs could be easily concentrated on specific wavelength emission while the full width half maximum (FWHM) could be decreased under 22 nm. Furthermore, the time dependent stability of nanoplatelets increase through close-packed ligands which are less steric hindered. Lastly, blue light emitting diodes (LED) with surface-treated perovskite nanoplatelets could have higher efficiency than mixed-halide perovskite nanocrystal. It was possible by emitting material's property improvement and close-stacked nanoplatelets arrange. I strongly believe that this work would be the basic approach of perovskite nanoplatelet device.

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ChI. Introduction of perovskite QDs and light emitting diode

1.1 Introduction of perovskite QDs

1.1.1 The definition of QDs

Quantum dots (QD) are very small semiconductor particles with nanoscale size. It has been a central theme in nanotechnology since they were first discovered at 1980s.^[1] When particles of a specific inorganic compound enter nanoscale size, the energy level is differentiated due to the interaction between the atoms and the molecules, and the energy level slightly differs from the original bulk energy level. Those discontinuous energy levels which look like a continuous region of energy called energy band. QDs are the material which are able to control the gap of band between the band of energy occupied by the electrons (valence band) and empty energy band (conduction band) by controlling its size. This phenomenon is called quantum confinement effect.

When the size of semiconductor nanoparticle is larger than the exciton bohr radius, the electrons and holes are trapped in discontinuous energy levels quantum dot.^[2] The band gap between two bands is related to the size of nanoparticles, which follow particle in a box theory. As represented at following equation (1), the energy level (E_n) of trapped area is inversely proportional to the distance (L), which means a size of nanoparticles.

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (n = 1, 2, 3, \dots)(1)$$

Figure 1 shows absorption and emission plot of quantum dots with different size. Due to the quantum confinement effect, it is possible to control the optical properties without any composition control.

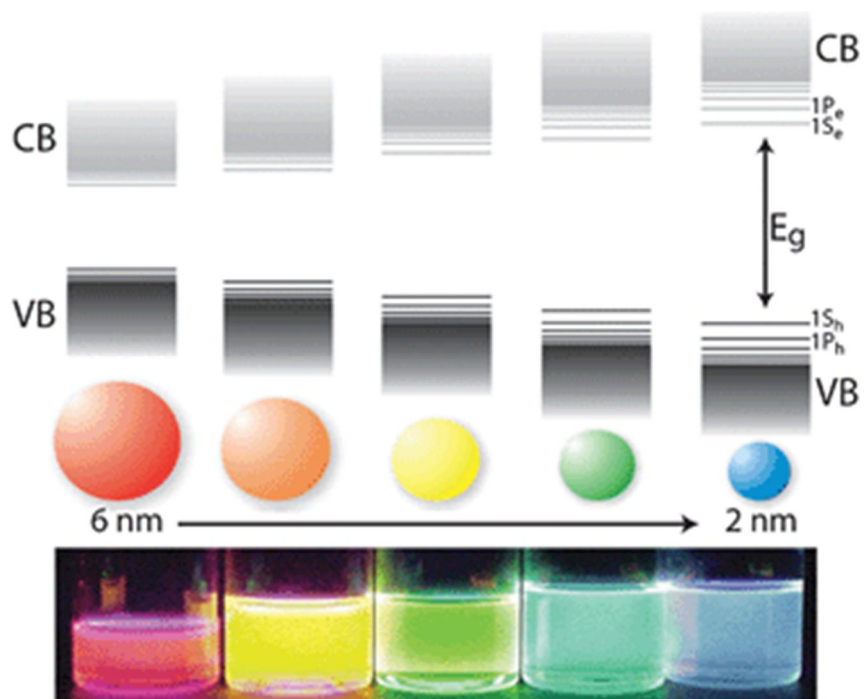


Figure 1. Concept of quantum confinement effect.

1.2 Dimension control of semicon QDs

For 0-dimension Quantum Dot, adjusting the size was the most common way to control the characteristics. However, as many studies of nanoparticles have been conducted, nanocrystals with various dimension were reported by utilizing binding of ligands or concentration of monomers.^[3-5] Also, these dimension controlled nanocrystals showed different properties for each. Accordingly, nanoparticles of various dimensions are synthesized according to necessity.

1.2.1 1-D Nanorod, Nanowire

One-dimensional semiconductor nanostructure have nanoscale cross-section. Nanorod have a ratio of a width to a length of under 10, and nanowire have a ratio more than 1000. Unlike quantum dot, which is a zero-dimensional material that must pass through a ligand in order to transfer heat or electrons, the one-dimensional material has a long continuous structure and is easy to transfer electricity and heat.^[6] Therefore, it is widely used in many electronic devices. A representative example is a nanowire laser, at figure 2, which is a nanoscale laser made in III-V.

1.2.2 2-D Nanoplatelet, Nanosheet

2D nano-structure, which is called quantum wells, has been recognized as an important class of quantum structures.^[7] In the 2D quantum wells, photogenerated excitons undergo strong 1D spatial confinement within a finite thickness. These 2D quantum wells have been explored for various applications in optoelectronic devices such as laser diodes and light-emitting diodes. Molecular beam epitaxy (MBE) in the high vacuum has been used as a process to make 2D nanostructure. However, the cost is expensive, and production cost can be greatly reduced in a solution process.

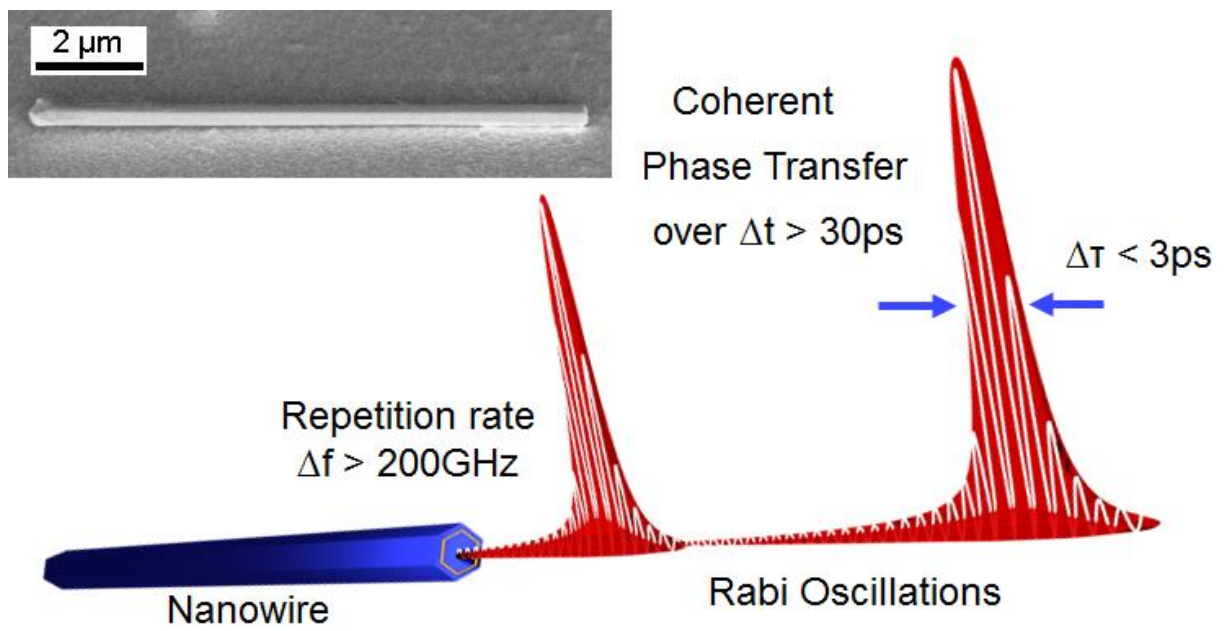


Figure 2. Concept of nanowire laser.

1.3 Perovskite and Perovskite nanocrystal

1.3.1 Properties of Cesium lead halide perovskite QD

Perovskite possess the crystal structure ABX_3 , where A and B are cation bound to anion X like figure 3. Among them, lead halide-based perovskite semiconductor materials have excellent optoelectrical properties and manufacturing through solution processes.^[8] The bandgap of material is possible to control the visible light and the near infrared region through the chemical composition, so that the bulk material has been widely used as a solar cell material. The synthesis of nanoparticles from the perovskite with Quantum Dot was the first in 2015, and was possible to adjust the band gap of 410-700 nm by adjusting the chemical composition likewise.^[9] Perovskite quantum dot is possible to reproduce a wide range of colors due to the narrow PL peak position and the bandgap characteristic controlled in the visible light region, and this range is wider than National Television System Committee (NTSC) standard on a CRI diagram (Fig. 5). Also, it has much more simple procedure for synthesis due to its ~90 % efficiency without classical QDs' core-shell structure. Because of these properties, it is attracting attention as a display material

1.3.2. History of PeQDs

The perovskite material of the cesium lead halide composition was first reported 50 years ago, and its properties such as its synthesis method, crystal structure and band gap have already been reported. It was possible to make this by a simple method of annealing the cesium halide and the lead halide on the substrate. By this method, the bulk material was synthesized for a long time. The first synthesis as a colloidal nanomaterial of cesium lead halide composition was made by injecting separately synthesized lead halide and cesium oleate^[8]. Reaction was carried out at a temperature between 150-200 for 5 seconds. In this report, it was confirmed that the nanocubic crystal of perovskite structure was synthesized through Xrd and TEM. Like the bulk material, the composition of the halide in the lead halide precursor was adjusted to change the properties. In the composition containing only iodine, the light emission was observed at 700 nm, and in the composition containing only chlorine, the light emission was 410 nm. Bromide composition showed 510 nm emission. Also, it was possible to synthesize the whole range between 700 to 410 nm by mixing halide composition. At this time, the particle size was very uniform, and it was not necessary to perform the size selection commonly performed in other QDs, and the maximum quantum efficiency was 90%.

Since then, many researchers have conducted many experiments on existing QDs like ion exchange^[10,11], doping^[12-14], surface modification^[15-17], and various synthesis methods.^[18-21] Perovskite nanoparticles are also capable of regulating their shape through ligand control during synthesis as in

the case of conventional QDs. The structure of nanoplates, nanocubes, and nanowires can be controlled by controlling reaction time and ligand type, and their properties are reported.

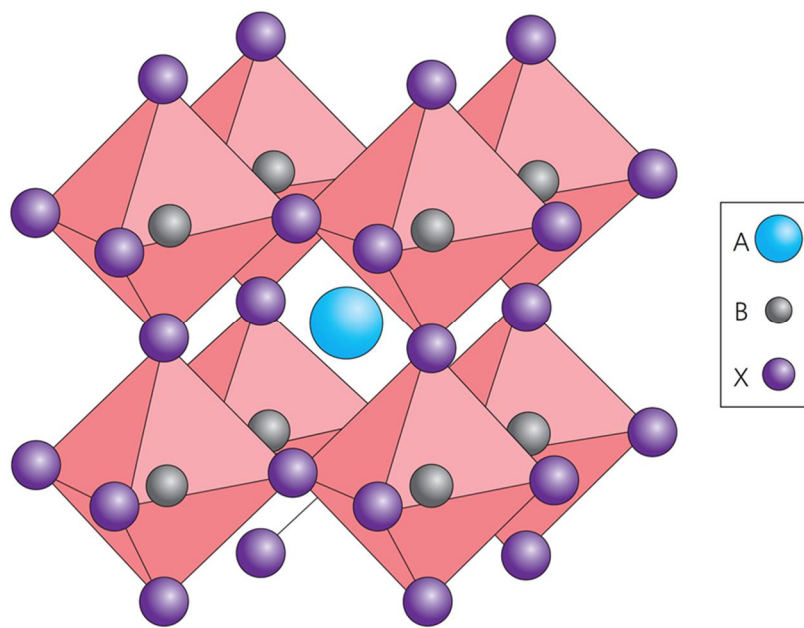


Figure 3. Perovskite structures with ABX₃ composition.

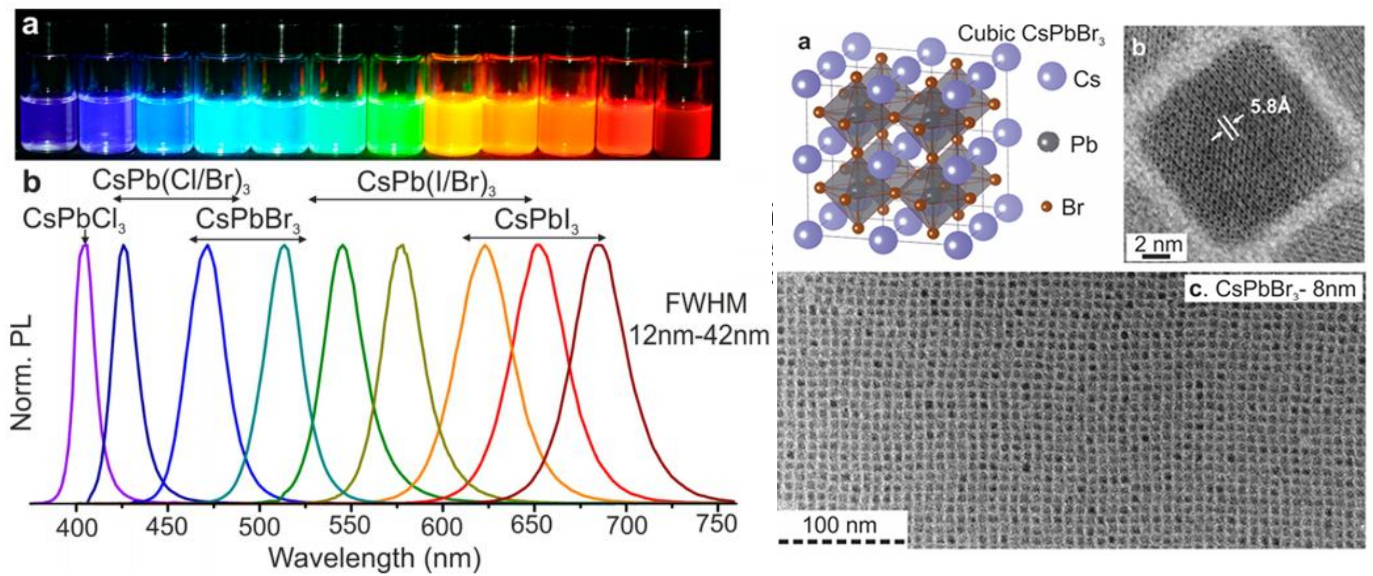


Figure 4. Optical property and TEM images of Cesium lead halide nanocrystals.

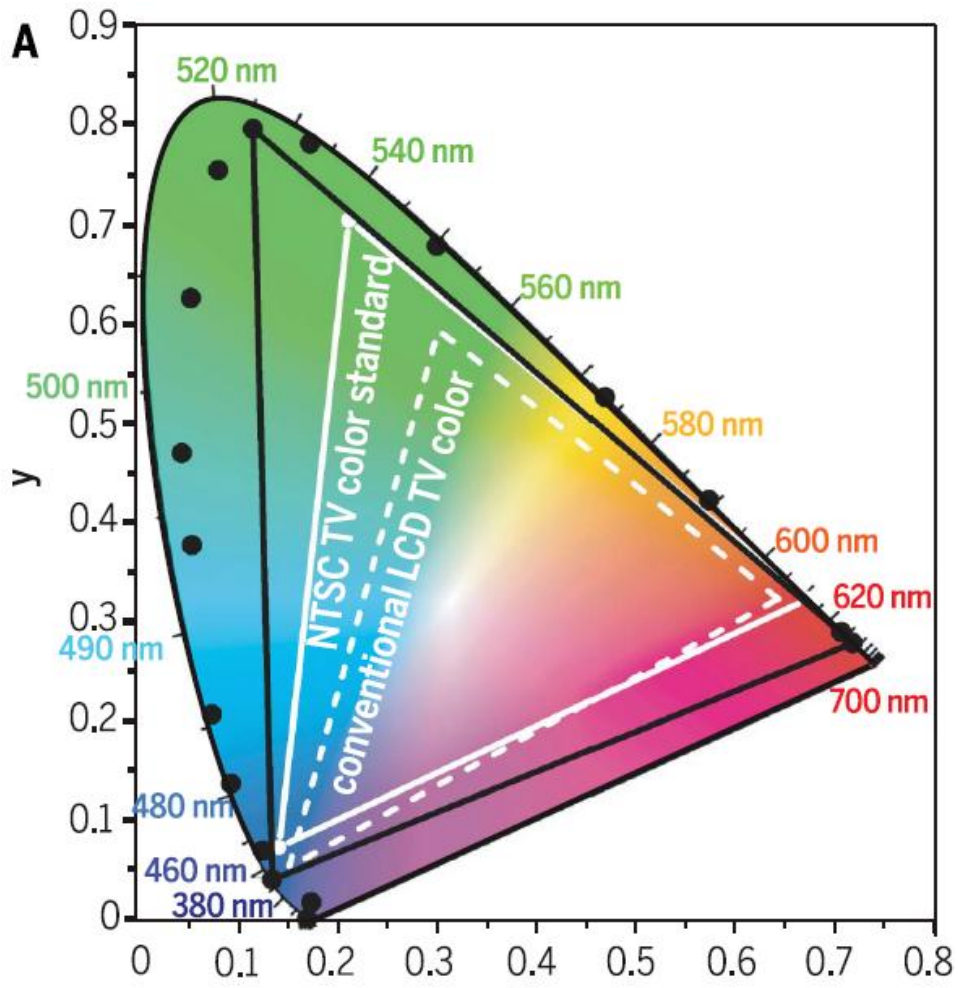


Figure 5. CRI diagram and NTSC color standard.

1.2 Light emitting diode of QDs

1.2.1 Introduction of light emitting diode

A light emitting diode (LED) is a light emitting device that uses the principle that electrons and holes are injected into a semiconductor light emitting material, recombine in the light emitting material layer, and the energy is emitted to light. This effect is called electroluminescence(EL).

The EL effect was found in silicon carbide in 1907 HJ round in England,^[22] and Oleg losev reported the first LED.^[23] Since then, various semiconductor luminescent materials have been reported, and LEDs such as red^[24], green^[25], blue^[26], white^[27], and ultraviolet light^[28], which are the luminescent colors of the materials, have been realized.

1.2.2 Principle of LED

The P-N junction can convert the absorbed light energy into current. Solar cells are made using this principle. In the case of an LED, the opposite process occurs, which is EL described above. At the junction, electrons move through the N-region to the emission layer emitting light, and recombine with holes existing in the P-region. The movement of holes and electrons travels through the conduction band of each layer in case of free electron, and the hole moves through the valence band. Semiconductor materials used in general diodes are mostly non-radiative recombination, which has an indirect band gap and does not optically diverge when recombining holes and electrons. In contrast, the semiconductor material used for LEDs has a direct band gap, causing the light to emit. The color of light changes according to the size of the band gap, and it can emit light in the NIR, visible, and NUV regions by controlling the band gap.

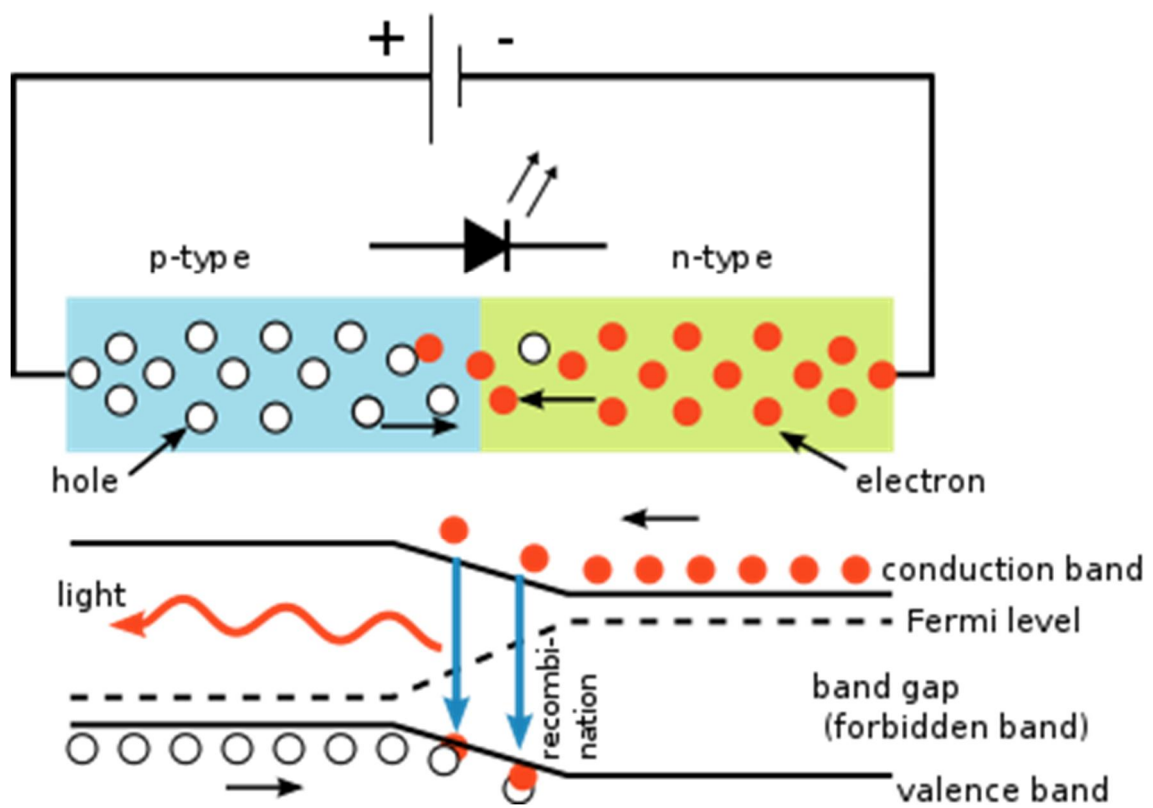


Figure 6. Concept of electroluminescence at P-N junction.

1.2 Quantum dot LED

QD is a material that perfectly matches an LED that need luminescent semiconductor material. Also, most of the colors on the CIE diagram can be realized because of the nature of the QD that can adjust the emission region to the visible region and the near-infrared region through the quantum confinement effect. Compared with the organic dye used as the material of the OLED, emission light of QD is much narrower than the organic dye having the red tail due to the vibrational state of the molecule, and the spectrum of the LED can be made much narrower so that a better color can be realized. In addition, the QD in the colloidal state has an advantage that a spin coating process can be performed and a large-area low-cost process can be performed.

There are two types of QD LEDs. First type is to pass the light of the primary light source to the QD to make the color, and the other is to generate the EL by directly generating the QD exciton electrically. When the color is adjusted by passing the light of the light source, the QD at this time is used as a color converting layer, not directly used as an LED. It was first reported by Michael Bowers^[29]. Using EL effect of QD in LED is a concept similar to that of OLED, in which QD layer is between electron transporting layer and hole transporting layer, and holes and electrons can be injected. The applied electric field generates holes and electrons, which is injected into the QD layer to cause recombination of excitons to produce light. QD display using QD LED of this principle is commercialized as II-VI series CdSe QD or III-V series InP QD.

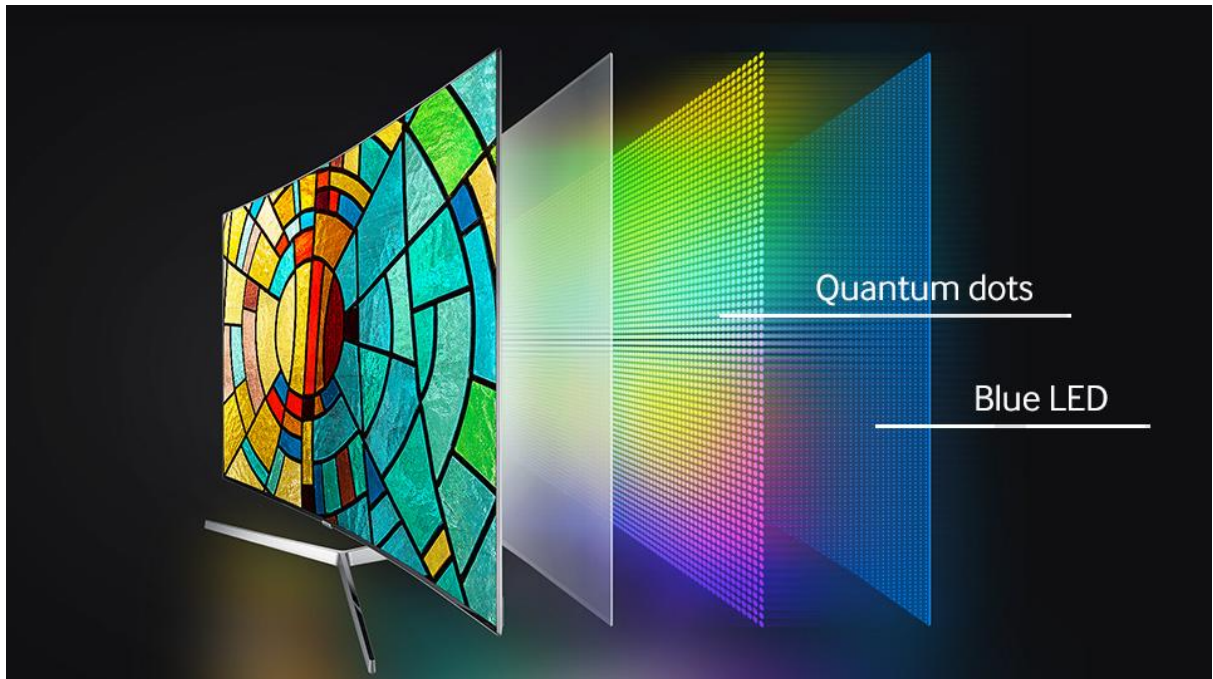


Figure 7. Commercialized quantum dot display.

1.2.3 LED using PeQD

InP QDs, which is mainly used for the conventional QD display, the full-width half maximum (FWHM) of 38-40 nm is reported as the best property in the red-green region because of difficulty in controlling its own composition.^[32] This is worse figure than that of PeQD or CdSe, which has a half-width of 20-35 nm in the same region. In addition, PeQD has a water process performance that has a simple process and high luminous efficiency when compared to QDs of other compositions. Figure 8 show that kinds of trend in display.

Another advantage of PeQD is that commercialization is easier than other types of QDs. In order to commercialize semiconductor QD, it is required to pass the international standard at table 1, RoHS(Restriction of Hazardous Substances), which is an international standard for regulating the content of heavy metals in electronic devices. In this standard, the content of heavy metals per product is limited to Cd <100 ppm and Pb <1000 ppm. Due to this regulation, backlighting films using Cd-based QDs are difficult to enter the market. As a result, there is only one Cd-based QD display that has been commercialized through this regulation which is a backlight made in Nanosys that contain 95 ppm of CdSePeQD is relatively free from these regulations because of the much higher 1000 ppm limit compared to Cd. Actually, there is a lead in the battery, solder, and piezoelectric element, which is not against the range of RoHS. Also, when using PeQD as a display, it is enough to make a 40-50 inch normal-driven display by using a positive lead that does not exceed the regulation. Due to these properties, PeQD is the subject of interest in display using QD recently.

RoHS Restricted Substances and Limits		
Lead	(Pb):	<1000 ppm
Mercury	(Hg):	<1000 ppm
Cadmium	(Cd):	<100 ppm
Hexavalent Chromium:	(Cr VI)	<1000 ppm
Polybrominated Biphenyls	(PBB):	<1000 ppm
Polybrominated Diphenyl Ethers	(PBDE):	<1000 ppm

Table 1. RoHS limits of chemicals.

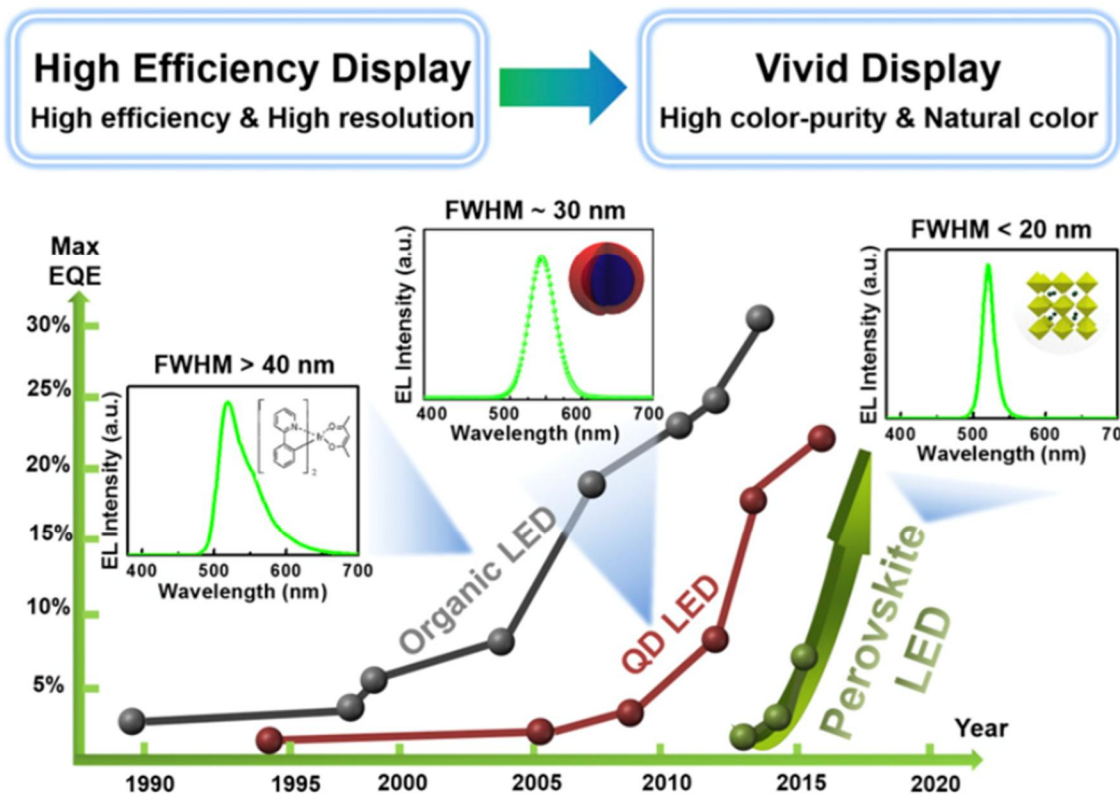


Figure 8. Trend of LED materials.

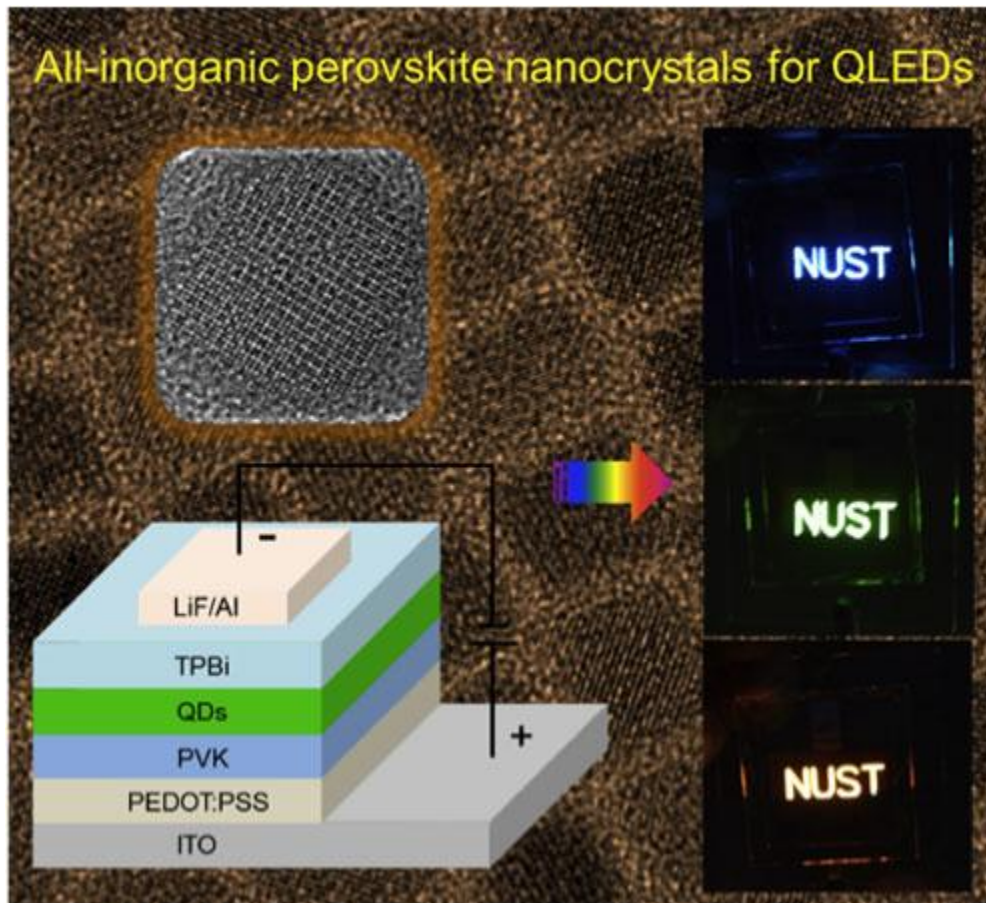


Figure 9. LED using perovskite quantum dots.

Ch2 Synthesis of PeNPLs and its application

2.1 Introduction of PeNPLs and its application

The colloidal semiconductor quantum dot has received a lot of attention due to its particular optoelectrical characteristic changes depending on its size and shape. Especially, it is being used as a new light emitting material in LED, laser, biological imaging related technologies due to the characteristic of regulating the region of light emanating through the quantum confinement effect. Today, semiconductor light emitting nanoparticles of various compositions (II-VI group, III-V group, Silicon) have been reported. Among them, the inorganic lead halide perovskite quantum dot of CsPbX₃ composition is more advanced than other quantum dots with properties suitable for use in devices. Perovskite Quantum Dot has an easy synthesis method, bright and narrow-band PL (from NUV to NIR) with well-tuned by halide composition control and size control in two ways. These properties are very suitable for commercializing LED. The reported PeQD LEDs already show high efficiencies like (green LEDs that contain cube-shaped CsPbBr₃ NCs, showing external quantum efficiencies (EQEs) of up to 6 to 9% and peak luminance of up to >15,000 cd/m².^[33,34] Red LEDs containing CsPbI₃ NCs have exhibited an EQE of 5.7% at 698 nm^[35] and an EQE of 7.25%, with a peak luminance of 435 cd/m² at 688 nm^[36]). However, the PeQD LEDs that exhibit this efficiency are those that use the perovskite QD in the red-green region.

However, the maximum efficiency of blue LED is reported at the bluegreen (cyan) region, a maximum EQE of 1.9% was observed for CsPbBr_xCl_{3-x} NCs showing a rather low peak luminance of 35 cd/m² at 490 nm^[37]. This is lower efficiency than the above two colors, and the emission was showed at a cyan blue wavelength band of 490 nm. Blue color is an essential color to serve as a display that implements all the colors in a color coordinate. The blue has to be a deep blue region with 460-470 nm wavelength to reproduce a wide area color. Blue Perovskite QD should have a higher chloride content in order to show its luminescence, but the QY will decrease as the chloride content. For this reason, in the above cyan blue LED report, cyan blue material with a relatively low chlorine content is used in order to secure the luminous efficiency of the material itself and obtain higher electrical efficiency. Making such an efficient deep blue color LED with PeQD is more challenging.

To retain brighter blue LED from perovskite nanocrystal, blue color emitting perovskite with higher efficiency was needed. A method of making blue color using the quantum confinement effect in the cesium lead bromide composition has been proposed, which became possible with the perovskite nanoplatelet of the CsPbBr₃ composition synthesized by introducing the strongly binding amine ligand^[38]. This perovskite nanoplatelet exhibits a quantum confinement effect according to one-

dimension size, the thickness. This makes a big difference from the existing size effect. In the case of the conventional QD which continuously changes in size, the band gap change due to the confinement effect also appears continuously. On the contrary, the thickness of perovskite QD can be expressed by the number of PbX_6 octahedron layers, which causes a confinement effect different from that of the conventional QD, in which the wavelength capable of emitting light by the platelet is also quantized like figure 10. Due to these properties, crude PeNPLs after synthesis are not a clear single peak but a mixture of several peaks, which is caused by the presence of NPL of various thicknesses shown at figure 11. As a result, a problem of single peak purification of perovskite NPL has been proposed and size selection process has been required to use it as a device material. However, this is a very sensitive process, so there is no report yet on the separation of single peak deep blue nanoplatelet.

In this study, a synthesis method of single-peak emission deep blue perovskite nanoplatelet was proposed. It consists of two steps: an induced growth step with increased reaction time and a ligand-assisted size selection step to select the desired size or smaller by using ligand-assisted solubility adjustment in the generated particles. This is a process to remove the side-peak emitting thickness (under 2 unit cell, above 4 unit cell) platelets which emit light of less than 440 nm and light of more than 480 nm respectively. The thinner plate was removed at longer reaction time through the induced growth step. The solubility was controlled by adding a certain amount of ligand to the platelet, and only the thicker plate was maintained in the precipitate state and removed with a centrifuge. Through these two steps, a high yield (54 %) emission peak of 21 nm at FWHM was obtained at 465 nm. A blue emitting device was fabricated using this platelet. The efficiency of the above measured nanoplatelet is three times higher than that of the synthesized Chloride containing blue perovskite nanocube. Maximum EL was 349 cd/m^2 and it was 2 times higher value than mixed halide device.

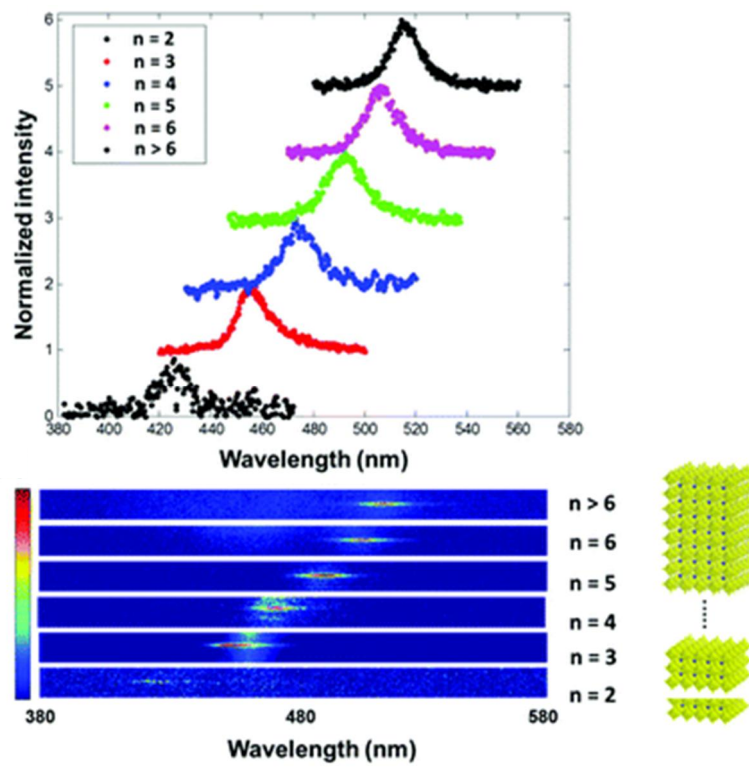


Figure 10. Quantize emission of perovskite nanoplatlets.

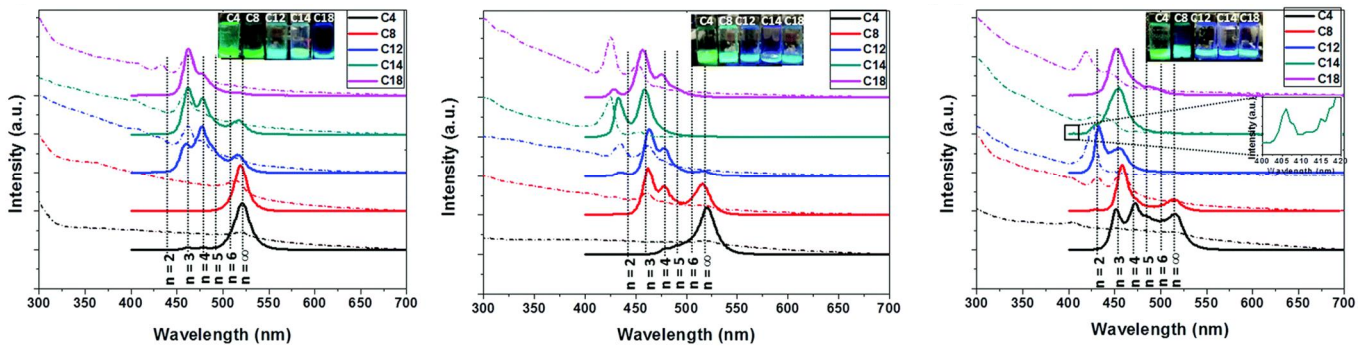


Figure 11. Emission of synthesized nanoplatelets without purification.

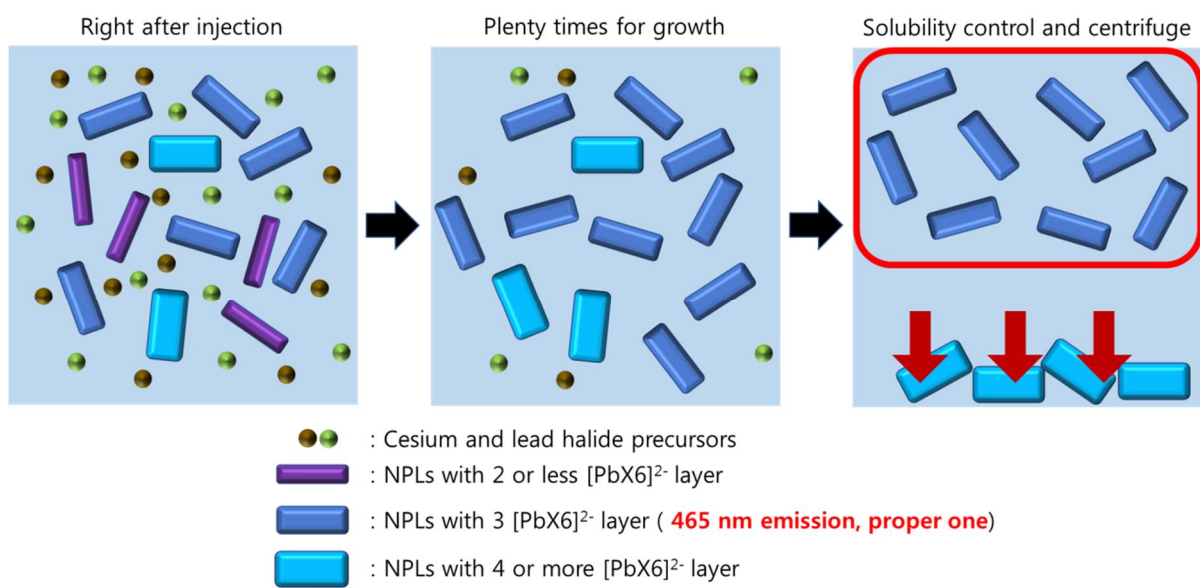


Figure 12. Schematic illustration of research.

2.2 Experimental session

2.2.1 Materials

Lead bromide(99.99%), Lead chloride(99.99 %), Cesium carbonate(99%), Oleic acid(90%), Oleylamine(70%), octadecylamine(99%),1-Octadecene(ODE, tech grade, 90 %), Benzene(99 %), Acetonitrile(99%) LiF(99%), were purchased from sigma Aldrich. Al, TPBi(OSM), PEDOT:PSS

2.2.2 Synthesis of Perovsite nanoplatelets

Cesium oleate stock solution was prepared by loading 0.032 g of Cs_2CO_3 into 50 mL 3-neck round bottomed flask with 10 ml OAc, dried under vacuum for 1 h at 120 °C. In parallel, 0.015 g of PbBr_2 and 0.22 g of octadecylamine was loaded in 5 mL ODE in a three-neck round bottomed flask, dried under vacuum for 30 min at 120 °C. 0.250 ml of OAc was injected in the batch for the complete dissolution of lead halide with lead oleate form. After additional 30 min drying, 1 mL of as-prepared Cs-OA solution was rapidly. The reaction mixture was maintained for 2 min and immediately quenched at Ice bath.

2.2.3 Purification of Perovskite nanoplatelets

In a typical steps, solubility controlling ligand stock solution was prepared by mixing 0.032 g of ODA and 0.1 ml benzoic acid solution(0.1 g of benzoic acid at 2 ml benzene) at 2.5 ml benzene. The crude solution was centrifuged at 7800 rpm for 5 min. The precipitate was dissolved in 1ml of benzene and would form pale yellow opaque solution. 0.3 ml of as-prepared ligand solution was injected, and centrifuged at 7800 rpm for 5 min. After centrifuge, precipitate was dropped and clear supernatant was used for removing thicker layered(more than 4 layer) nanoplatelets. 1 ml of acetonitrile was added for anti-solvent, and the solution was centrifuged 7800 rpm for 5 min. The precipitate was re-dissolved at 1 ml benzene, and 0.3 ml ligand solution was injected. Addition of anti-solvents and centrifuge step was done again with same quantities. Lastly, the precipitate was re-dissolved at 1 ml. For long-time storage, freeze-dried NPLs solid was stored under vacuum.

2.2.4 Synthesis of green emitting CsPbBr_3 perovskite nanocubes

For typical cubic synthesis, cesium oleate stock solution was prepared by loading 0.163 g of Cs_2CO_3 into 50 mL 3-neck round bottomed flask with 0.5 ml OAc and 8 ml 1-octadecene, dried under vacuum for 1 h at 120 °C. In parallel, 0.069 g of PbBr_2 and 0.5 ml of OA and OAm was loaded in 5 mL ODE in a three-neck round bottomed flask, dried under vacuum for 1 h at 120 °C. The temperature of batch was raised to 170 °C under Ar flow. 0.4 mL of as-prepared Cs-OA solution was

rapidly injected. The reaction mixture was maintained for 10 sec and immediately quenched at Ice bath. The purification was done with benzene solvent and acetonitrile anti-solvent.

2.2.5 Synthesis of blue emitting CsPbBr_{1.7}Cl_{1.3} perovskite nanocubes

In parallel, 0.038 g of PbBr₂, 0.29 g of PbCl₂, 0.5 ml of OA and OAm was loaded in 5 mL ODE in a three-neck round bottomed flask, dried under vacuum for 1 h at 120 °C. The temperature of batch was raised to 170 °C under Ar flow. 0.4 mL of as-prepared Cs-OA solution was rapidly injected. The reaction mixture was maintained for 10 sec and immediately quenched at Ice bath. The purification was done with benzene solvent and acetonitrile anti-solvent.

2.2.6 Optical properties

Absorption spectra were measured with a Shimadzu UV-1800 UV-Vis spectrometer. Photoluminescence (PL) spectra were recorded with an Agilent FL 1004 M008. PL QY of perovskite nanocrystals were performed with a quantum efficiency measurement system Phtal QE-2000. Time resolved PL(TRPL) were taken with a time-correlated single-photon counting setup(FluoTime 300, PicoQuant).

2.2.7 Transmission electron microscopy

Transmission electron microscopy (TEM) images were taken with a JEOL JEM02199 microscope with an 200 kV acceleration voltage using copper grids (Ted Pella, USA). The solutions of perovskite nanocrystals at benzene solvent were deposited on the grids.

2.2.8 X-ray powder diffraction

X-ray powder diffraction (XRD) measurements were performed with a Rigaku Ultimate-IV X-ray diffractometer operated at 40 kV/200 mA. Samples were placed onto glass substrates after purified solution's freeze drying.

2.2.9 Ultraviolet photoelectron spectroscopy

Ultraviolet photoelectron spectroscopy(UPS) were measured with a ESCALAB 250XI and ultraviolet source was He1, He2. Samples were prepared with spin coating of nanocrystal solutions on the ITO coated glass substrate.

2.2.10 LED fabrication

Device were built in a 1.5 cm x 1.5 cm glass substrate pre-coated with 140 nm thickness layer of

ITO. The ITO glass substrates are cleaned in an ultrasonic bath with acetone followed by ethanol and di water withalconox for 15 min each, and then dry-cleaned for 30 min by exposure to an UV-ozone ambient. PEDOT:PSS solution(filtered through a 0.45 um filter) were spin-coated onto the ITO-coated glass substrates at 2500 rpm for 20s and baked at 15 °C for 15 min. Perovskite layers were deposited by spin-coating at 4000 rpm for 20 s. TPBi(40 nm), LiF(1 nm), and Al electrode(100 nm) were deposited using a thermal evaporation system through a shadow mask under a vacuum of 2×10^{-7} torr.

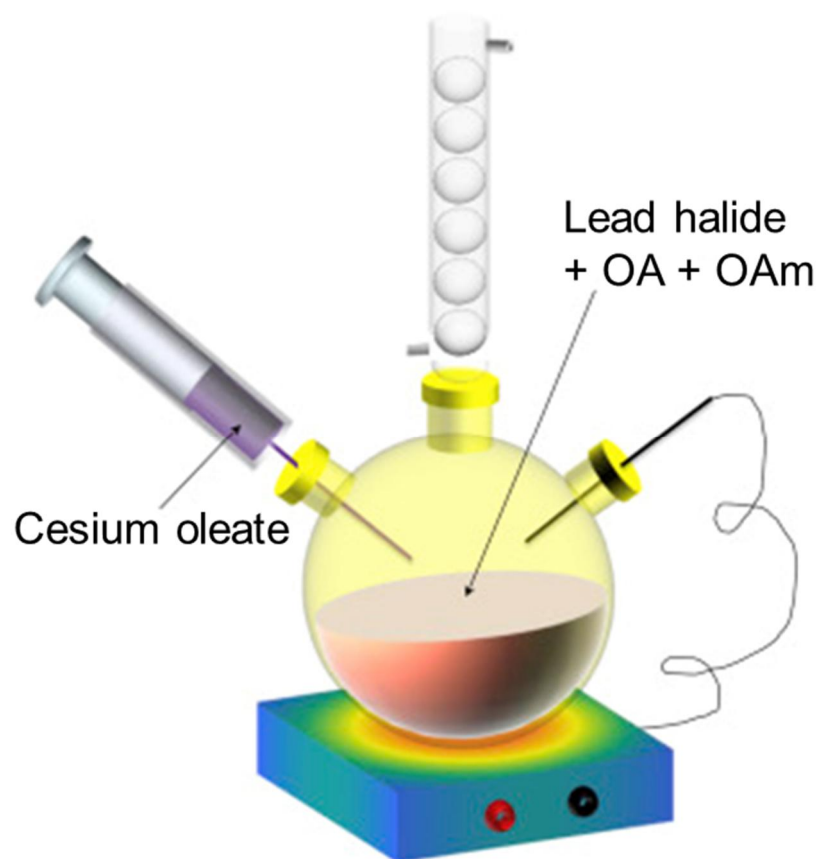


Figure 13. Illustration of synthetic method for perovskite nanocrystals.

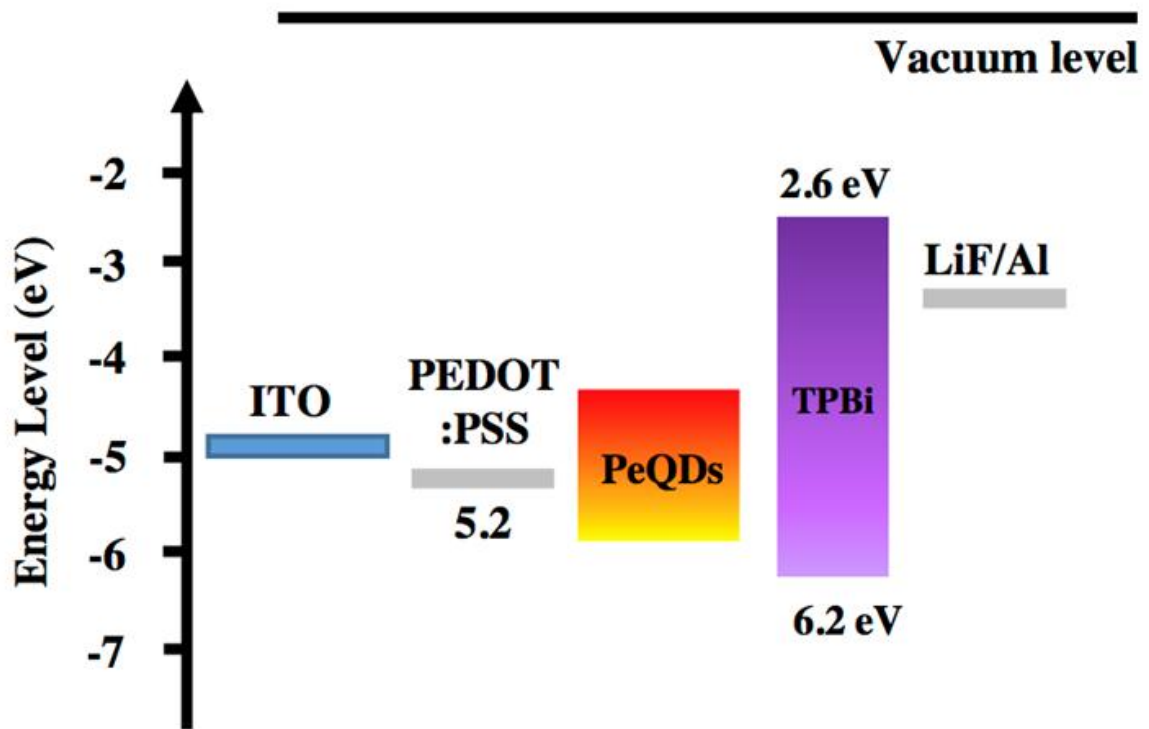


Figure 14. Structure of light emitting diode.

2.3 Result & Discussion

2.3.1 Synthesis of single-peak blue emitting cesium lead bromide nanoplatelet and its optical properties

Perovskite nanoplatelets were synthesized from precursors with saturated amine ligand. At the classical procedure of CsPbBr₃ nanocube lead halide precursor, Lead bromide powder was dissolved at ODE with Oleic acid and Oleylamine. It is well-known that amine ligands effectively control the growth of <100> direction by controlling carbon chain length, thus control the surface passivation ratio of (100) perovskite lattice plane. To synthesize CsPbBr₃ NPLs, octadecylamine which is a saturated amine that contain same number of carbon with Oleylamine was used to limit the growth of <100> direction with higher surface binding ratio than Oleylamine. The replacement of amine significantly shifts the emission peak to blue range. However, the PL spectra indicate that thickness of platelet is not homogeneous at figure 15a. To get rid of the left side peak, reaction time was increased for enough growth. As a result, PL spectra peak at 440-450 nm which means thinner size distribution was gone. Demanded thickness platelet was extracted by ligand assisted solubility adjustment method. By adding optimized amount of ligand solution, demanded size platelet completely dissolved in the benzene solvent during thicker platelet still remain the precipitate form so that the extraction was possible through centrifuge. The spectrum of nanoplatelets with extracted thickness show single peak shape at 465 nm like figure 15b.

Optical properties of blue emitting cesium lead bromide nanoplatelets were compared with the mixed halide nanocubic with same emission (465 nm, CsPbBr_{1.7}Cl_{1.3}). The absorption and PL spectra were measured for synthesized CsPbBr₃ nanoplatelets and CsPbBr_{1.7}Cl_{1.3} nanocubes over the visible range under 550 nm. FWHM of nanoplatelet was similar with the mixed halide cubic's fwhm as 21 nm as shown in figure 15 and Table 2. QY of nanoplatelet was 51 % and this value was 4 times higher than mixed halide nanocubes with same emission.

TRPL measurements were performed for CsPbBr₃ nanoplatelets, CsPbBr_{1.7}Cl_{1.3} nanocubes to investigate the PL decay kinetics at figure 16. The nanoplatelets' decay time was 3.4 ns which is a lower value than both nanocubes (Table). This result was induced at the difference of binding energy between nanocube and nanoplatelet.^[39,40] Decay time became shorter if when binding energy is strong. References show that binding energy of nanoplatelets is much stronger than that of nanocube.

UPS measurement were performed for blue perovskite nanocrystals (mixed halide nanocubes, nanoplatelet) to investigate HOMO levels at figure 17. In contrast, the HOMO level of perovskite nanoplatelet was existed at 0.3 eV lower than the HOMO level of nanocubes since the band gap of

both blue nanocrystals were same at figure 15. This phenomenon may originate from the difference between halide-based band gap tuning and size-based band gap tuning. The quantum confinement effect at the nanocrystal controls both HOMO and LUMO level to control the band gap. However, band gap tuning from halide control mainly tune the LUMO levels to control the band gap mainly control the LUMO level. Due to this difference, the HOMO level of nanoplatelet became lower than mixed halide blue perovskite nanocubes.

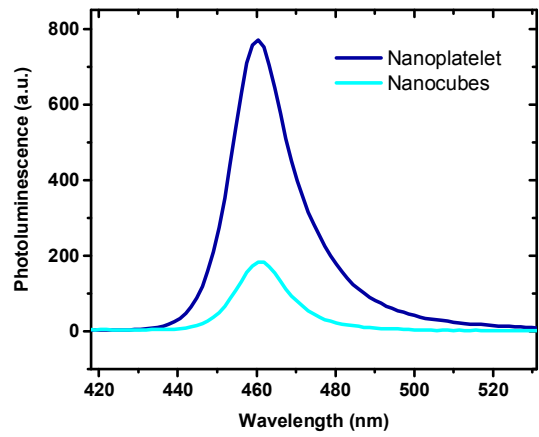
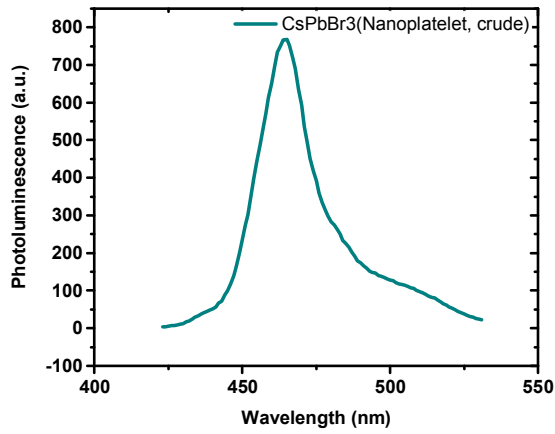


Figure 15. a) Photoluminescence of unpurified nanoplatelets. b) PL data of purified nanoplatelets and nanocubes with same emission. c) photograph showing PL of blue perovskite nanocrystal solution with different shape.

	Nanocube(NC)	Nanoplatelet(NPL)
Composition	CsPbBr_{1.7}Cl_{1.3}	CsPbBr₃
Quantum yield (%)	14	51
FWHM (nm)	21	21
Emission (nm)	463	465

Table 2. Quantum yield and FWHM of nanocube and nanoplatelet

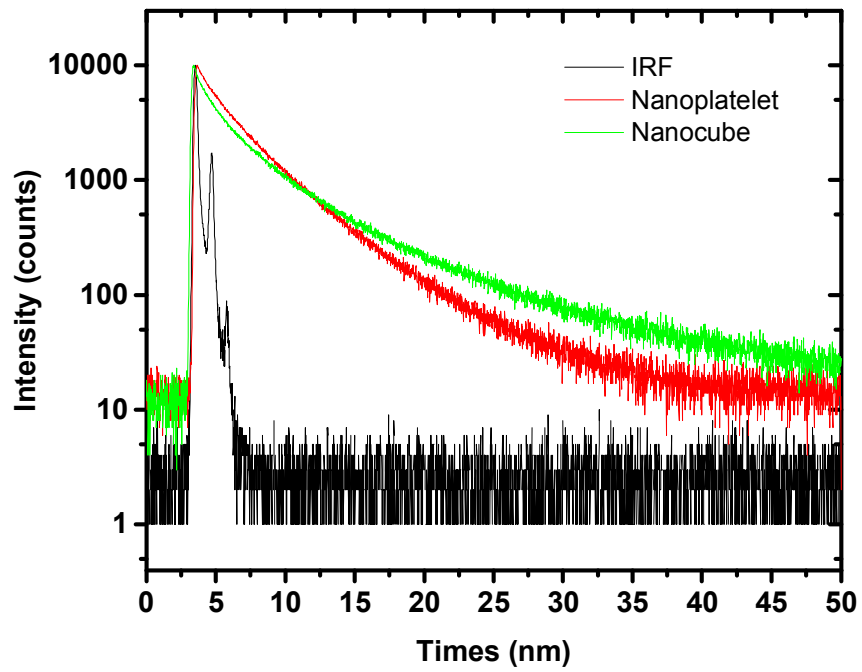


Figure 16. Time resolved PL decay of nanoplatelet and nanocube

	Nanocube(NC)	Nanoplatelet(NPL)
Composition	CsPbBr_{1.7}Cl_{1.3}	CsPbBr₃
PL lifetime (ns)	4.3	3.4
Exciton binding energy (meV)	50 meV	120 meV

Table 3. PL lifetime and exciton binding energy of nanoplatelet and nanocube

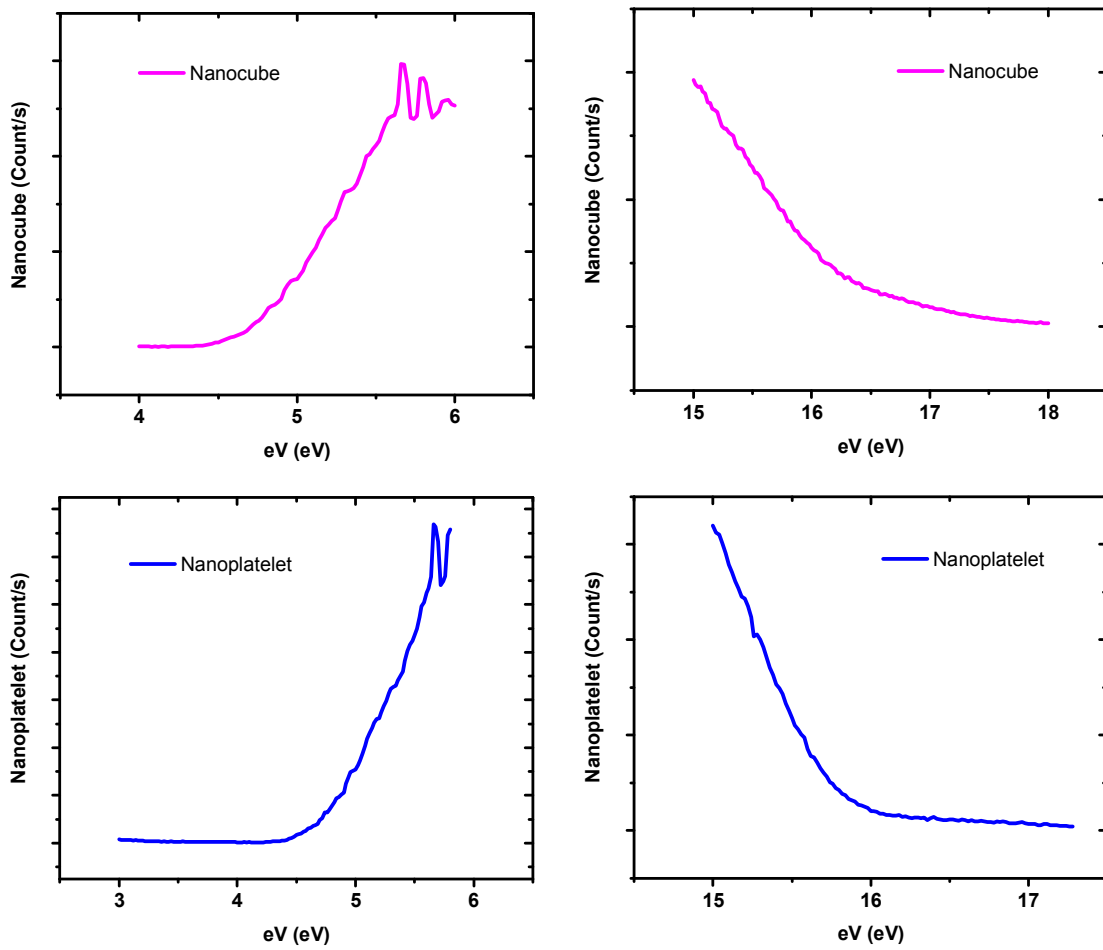


Figure 17. UPS data of nanoplatelet and nanocube

2.3.2 Structural comparison with cesium lead bromide nanoplatelets

Structural characteristics of CsPbBr₃ nanoplatelets were investigated with TEM and XRD analysis. TEM images of unpurified nanoplatelets and purified nanoplatelets are shown at Figure 18. It was possible to observe various size and shape of nanocrystals at unpurified one. However, the thickness of nanoplatelets was homogeneous after purified.

Synthesized cesium lead bromide nanocubes and nanoplatelets show monodisperse nanocrystals with the size of 10 nm for the cubic ones and 10 nm width and 3 nm thickness for platelets as shown at figure 19.

The XRD pattern of perovskite nanocrystals (CsPbBr₃ nanoplatelets, CsPbBr₃ nanocubes) shows peak position relation between the samples at figure 20. CsPbBr₃ nanoplatelets and nanocubes shows same peak position of CsPbBr₃ perovskite. However, there were relatively enhanced peak at (200) plane. It can be explained that the (200) signal enhancement due to the higher surface ratio than nanocubes'. As you can see at the right figure, surface of perovskite is a plane of 200, and this is the reason why only 200 peak enhanced relatively.

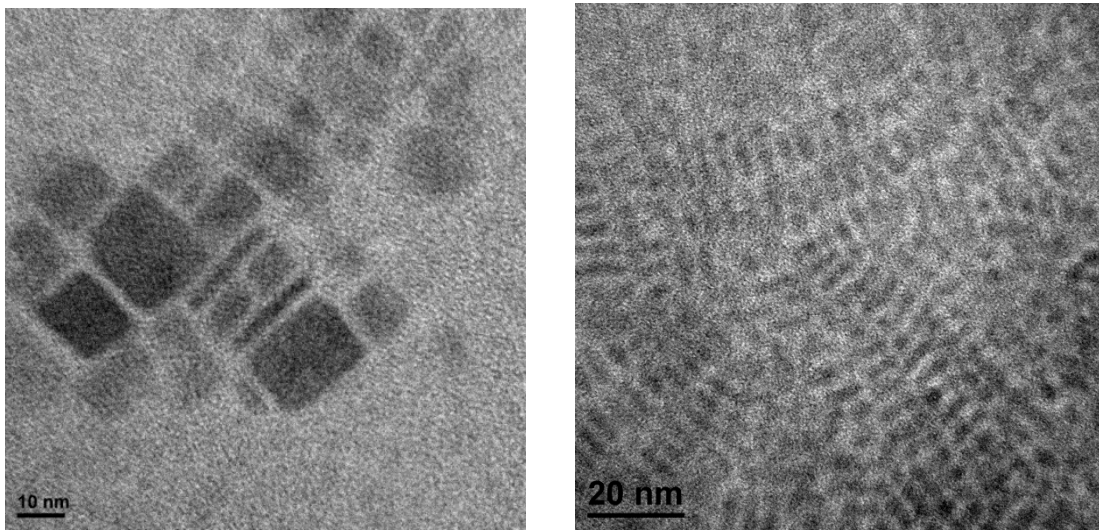


Figure 18. TEM image of unpurified nanoplatelet and purified nanoplatelet.

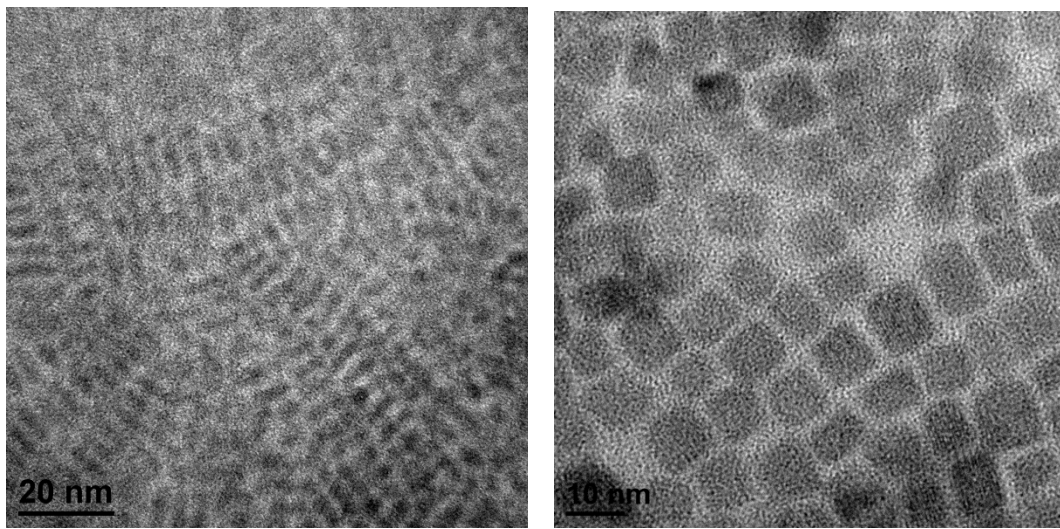


Figure 19. TEM images of CsPbBr₃ nanoplatforms and nanocubes.

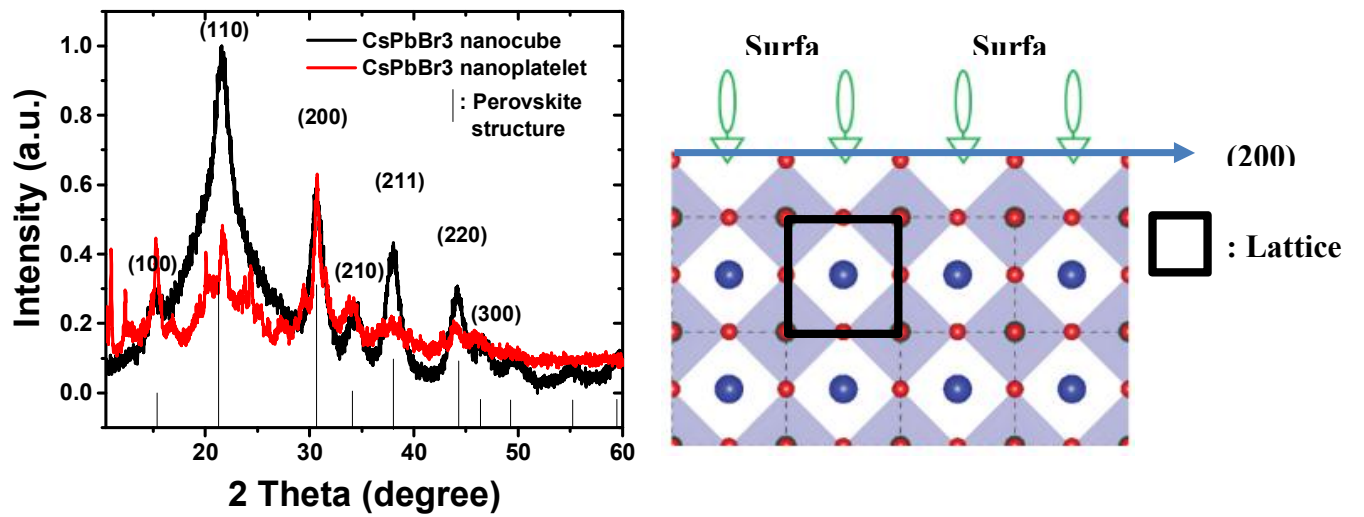


Figure 20. a) XRD pattern of CsPbBr₃ nanoplatelets and nanocubes. b) illustration of perovskite nanocrystal surface.

2.3.3 Blue light emitting device of perovskite nanoplatelet

The described synthesis of CsPbBr₃ nanoplatelets, including its relatively strong quantum yield and narrow emission without side peaks, can offer the possibility of high-performance light emitting diode using blue color nanoplatelets. Recently, blue LED using perovskite nanocubes has critical issue of low yield of light from chlorine component. CsPbBr₃ nanoplatelets with blue emission can be a substitute to solve above problem as long as the color purity was retained. Previously synthesized perovskite nanoplatelet is a completely corresponding material for blue perovskite nanocrystal LED. Thus, light emitting diode with ITO/Pedot:PSS/Perovskite/TPBi/LiF/Al structure was fabricated like the figure 14. Compared with the fabricated LED in parallel using 465 nm emitting CsPbBr_{1.7}Cl_{1.3}, current efficiency was 0.153 cd/A and maximum luminescence was 349 cd/m²(Figure). Furthermore, the EL spectrum of nanoplatelet device occurred at 467 nm without any side peak which is a same emission position with PL. This result is meaningful cause nanoplatelets as a device material in this structure contain more disadvantage than the cubic nanocrystals. According to UPS results, HOMO level of nanoplatelet is 0.3 eV lower than the CsPbBr_{1.7}Cl_{1.3} nanocubes. These level difference become the energy barrier for hole to transport. Even though there exists more energy gap, values of nanoplatelet device result was better than nanocube device. This result show the potential of nanoplatelet as a high quality blue LED emitter material.

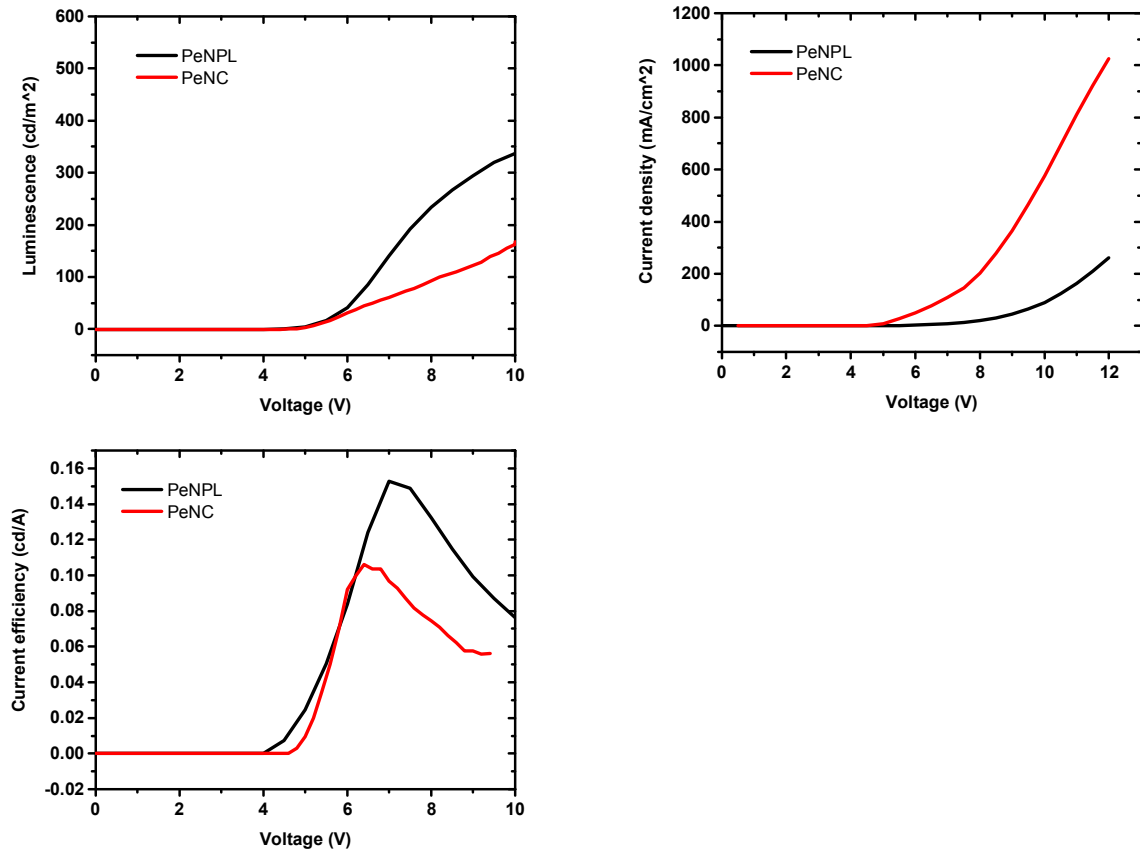


Figure 21. a) EL brightness of fabricated devices. b) current density of fabricated devices. c) current efficiency of devices

	Nanocube(NC)	Nanoplatelet(NPL)
E_g (nm)	462	467
C. Eff. (cd/A)	0.106	0.153
L_{max} (cd/m²)	162	349

Table 4. Table of values from fabricated devices

Conclusion

In summary, I developed synthesise method of blue emitting CsPbBr₃ perovskite nanoplatelets with pure deep blue color at 465 nm. The method was designed to select nanoplatelets with proper thickness, which is three layers of PbX₆ octahedral unit cell. Thinner nanoplatelets grow to proper thickness by increasing reaction time. Thicker particles were removed by controlling solubility of nanocrystals to precipitate thicker nanoplatelets through centrifuge.

The purified nanoplatelets show 260 % inhenced quantum yield than mixed halide nanocubes that emit same wavelength of light. Also, it was possible to evaluate perovskite nanoplatelets' suitability for LED device by time-resolve photoluminescence data. The exciton decay time of nanoplatelets was 3.4 ns, which is a 25 % lower value than nanocubes.

Fabricated LED using PeNPLs was worked and emitted electroluminescence light at same wavelength with photoluminescence. The brightness was 349 cd / m² , and other values show better result than mixed halide blue perovskite nanocube device. I strongly believe that this research can be based on perovskite nanoplatelet device research.

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