

Fabrication for formamidinium lead bromide perovskite for light emission

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Abstract. *Formamidinium bromide was synthesized by slowly mixing formamidinium acetate powder with hydrobromic acid for synthesizing FAPbBr₃. Photoluminescence of FAPbBr₃ has been studied, showing a PL peak at 562 nm. Spin-coating method was used to prepare FAPbBr₃ thin films and FTO/FAPbBr₃/FTO sandwich structures. These structures exhibited green luminescence with a center wavelength at 545 nm. The emission centers were observed for single crystals of FAPbBr₃ perovskite.*

Keywords: formamidinium lead bromide; perovskite light-emission; spin-coating; electroluminescence; PEDOT: PSS.

Classification numbers: 85.60.Jb; 81.07.Pr; 78.60.Fi; 81.16.-c; 68.55.ag; 85.60.-q.

1. Introduction

In the crystal structure of perovskite was described in 1926 by Victor Goldschmidt [1] and especially in recent decades, perovskite has garnered significant attention from scientists worldwide due to its remarkable advantages over conventional semiconductor materials, including simpler fabrication processes, greater flexibility, excellent absorption and emission coefficients, long diffusion lengths, high carrier mobility, high photoluminescence quantum yield, and a tunable optical band gap. As a result, substantial progress has been made in various research fields, particularly in photovoltaics.

In 2012, the first three-dimensional perovskite emitters were reported, which consisted of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanoparticles [2]. After that, research on perovskite emitters has grown exponentially and achieved high photoluminescence efficiency. Over a few years, more than 70 papers on perovskite emitters have been published, with some reporting a maximum external quantum efficiency (EQE) of 8.53% [3–5]. In 2014, the EQE of red perovskite light emission materials (PEM) at room temperature was initially reported to be as low as 0.76% [6]. However, there has been significant improvement in the following eight years, with the EQE increasing to 25.80% [7]. Similar progress has been made with other color LEDs during this period. For instance, green PeLEDs had an EQE of 0.10% [6], which has now increased to 28.10% [8]. Recently, Wan *et al.* successfully fabricated stable LEDs based on perovskite nanocrystals by coating a layer of NiO_x over CsPbBr_3 nanocrystals which reduced the thickness of the active layer to 10 nm and obtained EQE of 26.70% [9].

Besides, the power conversion efficiency (PCE) of the hybrid perovskites also increased from 2.20% [3] of methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) in 2006 by Miyasaka's group to 3.80% [10] of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) in 2009, achieved 6.50% [11] two years ago. In 2012, Kim *et al.* reported a large PCE of 9.70% [12] on solid-state mesoscopic heterojunction solar cells employing nanoparticles of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Only two years later, 20.10% [13] of PCE was published by Lee Jin-Wook and colleagues. Until 2022, the PCE was 25.50% [14]. Overall, research and development of PEMs have shown remarkable progress with impressive speed.

Formamidinium lead bromide (FAPbBr_3) perovskite has the ability to emit pure green luminescence and exhibit long stability in the atmosphere, making it a promising material for use in passive photoluminescence or optoelectronic devices [15]. Uniform FAPbBr_3 thin films achieved EQE as high as 16.30% [16] and 17.10% [17] in 2018 and 2020, respectively. However, in many reports, although PeLEDs were fabricated with a simple structure such as indium tin oxide (ITO)/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ /ITO, their external quantum efficiency was still low [18]. Thus, the aim of our work is to prepare FAPbBr_3 perovskite thin films for improving electroluminescent efficiency in the dependence of the charge injection in a multi-layer's structure of FTO/ FAPbBr_3 /FTO.

2. Experiment

2.1. Fabrication of perovskites

Formamidinium bromide (FABr) was synthesized by slowly mixing formamidinium acetate powder (FAAc, 99%, Aldrich) with hydrobromic acid (HBr, 48%, China) in a molar ratio of 1 : 1. The mixture was then stirred in a round bottom flask for 2 hours at 0°C under a nitrogen atmosphere. The rotary evaporator was utilized to evaporate the solvent. The solid self was washed

with diethyl ether until no yellow color was found. The white powder was then dried overnight for two days before using.

The precursor solution of FAPbBr₃ was performed by the one-step method. There, FABr and lead bromide (PbBr₂, 98%, USA) at a 1 : 1 molar ratio were dissolved in a mixture of two solvents: *N,N*-dimethylformamide (DMF, 99.9%, France) and anhydrous dimethyl sulfoxide (DMSO, 99.5%, China) with a 7:3 volume ratio in a concentration 1M. The solution was magnetically stirred at 60 °C for 2 hours prior to use.

2.2. Fabrication of sandwich FTO/PEM/FTO structure (FPeMF)

The fluorine-doped tin oxide (FTO)-coated glass substrates were thoroughly cleaned by subjecting them to ultra-sonication in deionized water, acetone, and isopropanol for 30 minutes each. After drying the substrates using N₂ gas, they were then treated with oxygen plasma for 15 minutes. Next, the FAPbBr₃ precursor solution was spin-coated onto the substrates at 4000rpm for 60 seconds. During the spin-coating process, the film was treated with a chlorobenzene solution after 40 seconds of spinning. The coated substrates were then annealed at 120°C for 30 minutes in an N₂ gas. Finally, the substrates were capped with another FTO-patterned substrate and held together using two paper clips.

2.3. Characterization

The structural and morphological characterization, as well as the electrical and optical performance of perovskite layers, were investigated using various techniques. X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer using Cu – K_α radiation with a wavelength of 1.5406Å to obtain structural information. The morphology was observed using scanning electron microscopy (SEM) on an FEI Nova NanoSEM 450 system. J-V characteristics were measured using a Keithley 2602 and controlled by Keithley LabTracer Software. Electroluminescence (EL) from PeLEDs was collected by a lens coupled with an optical fiber and characterized using an Avantes spectrometer with a charge-coupled detector. A 1064 nm Nd:YAG laser with a pulse width of 30 ± 3 ps and a maximum repetition rate of 50 Hz was used for excitation. The laser beam passed through a second harmonic generator to achieve an excitation wavelength of 532 nm. Photoluminescence (PL) signal was collected by a microscope objective and guided by an optical fiber to the same spectrometer. Ultraviolet-visible (UV-Vis) absorption measurements were conducted on a Shimadzu UV24500 system. Photoluminescence excitation (PLE) spectra were recorded on a Horiba FM4 system.

3. Results and discussion

Figure 1 indicated typical XRD patterns of the FAPbBr₃ thin film and powder. The diffraction peaks of both samples were coincident. Diffraction peaks at 14.62°, 20.92°, 29.65°, and 33.50° can be recognized to the (100), (110), (200), and (210) planes of the three-dimensional FAPbBr₃ crystal (Pm3 m), respectively, which is consistent with previous reports [19, 20].

The UV-Vis, PL and PLE spectra of the FAPbBr₃ thin film were superimposed in Fig. 2. We could observe that the PL peak at 562 nm overlapped with the absorption edge, indicating the recombination nature of the free carriers of this peak. On the other hand, the FAPbBr₃ shows intense green light emission, making it a promising material for LED and green laser applications. Compared to the emission of CH₃NH₃PbBr₃, it is evident that FAPbBr₃ emits an even stronger

green light [21]. Even though, the excitation wavelength is at the absorption edge, not at the maximum emission (at about 467 nm as observed from the PLE spectrum), the green emission is quite intense. We suggest that this green emission of FAPbBr₃ would correspond to extended states near the band edge of this material.

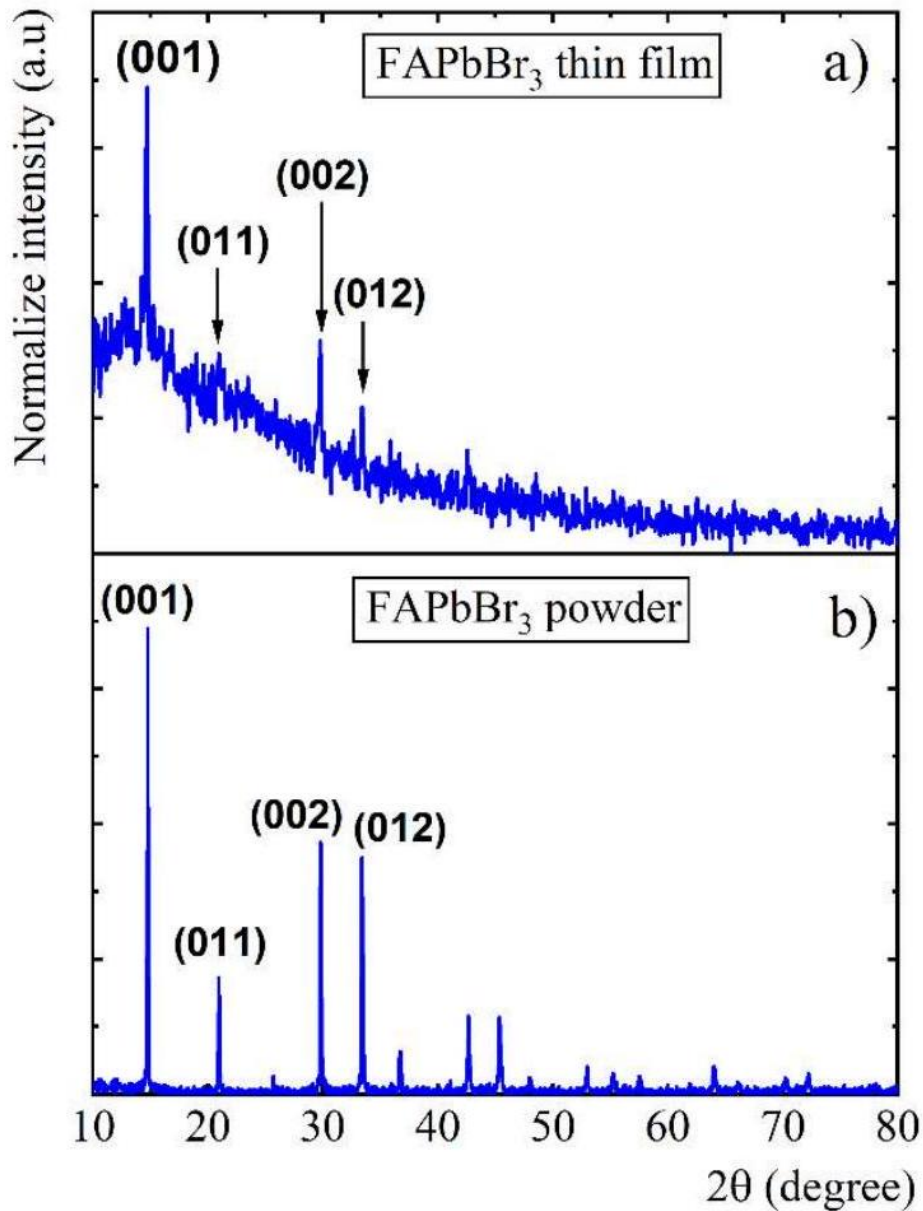


Fig. 1. XRD patterns of (a) FAPbBr₃ thin film and (b) FAPbBr₃ powder. These patterns match with JCPDS 87-0158.

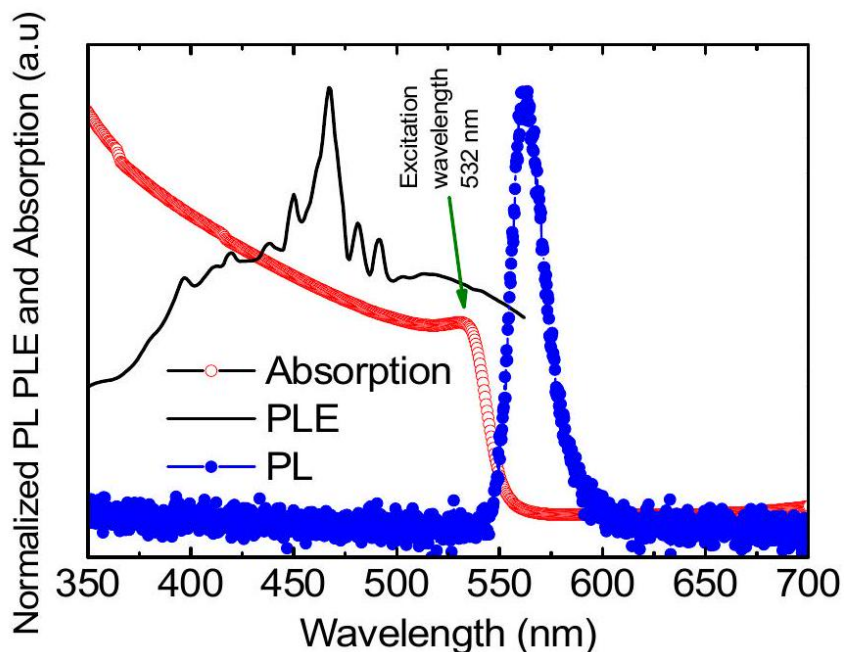


Fig. 2. (Color online) Normalized absorbance (red open circle), photoluminescence (blue filled circle) and excited photoluminescence (black line) measured at 562 nm spectra of FAPbBr₃ thin film.

In Fig. 3a, a FPeMF based on FAPbBr₃ is presented, with a thin film of FAPbBr₃ sandwiched between two FTO substrates. No green light is observed when there is no current injection (0 A) between the top and bottom FTO substrate. Figures 3b, 3c, and 3d illustrate the luminescence emission from the FAPbBr₃ under a specific current injection. Figure 3b shows an optical photograph of the FPeMF, revealing green light emission covering the entire PeLEDs under a current injection of 70 mA. Figures 3c and 3d show emission details of the FAPbBr₃ at different positions, with many visible green light points indicating the center of EL. These emission centers were observed where single crystals of FAPbBr₃ perovskite were present.

The EL spectra of the fabricated FPeMF are presented in Fig. 4. An increasing EL from single crystal FAPbBr₃ was observed when the injection current was increased from 40 mA to 50 mA. Notably, no green light was obtained when the injection current was smaller than 40 mA. However, the emission intensity decreased when the current was further increased from 50 mA to 110 mA. We suggest that the heat generated by the injection current may destroy the material sandwiched between the two electrodes, thus reducing the EL signal afterward. The peak of the EL spectra is observed at around 545 nm, which is smaller than the peak of PL. The red shift of all emission spectra can explain this observation due to the PL excitation wavelength of 532 nm. The peak intensity of the EL spectra increased with increasing injection current. In contrast, the peak position remained at around 545 nm, indicating the stability of the FAPbBr₃ perovskite material in the FPeMFs under different injection currents.

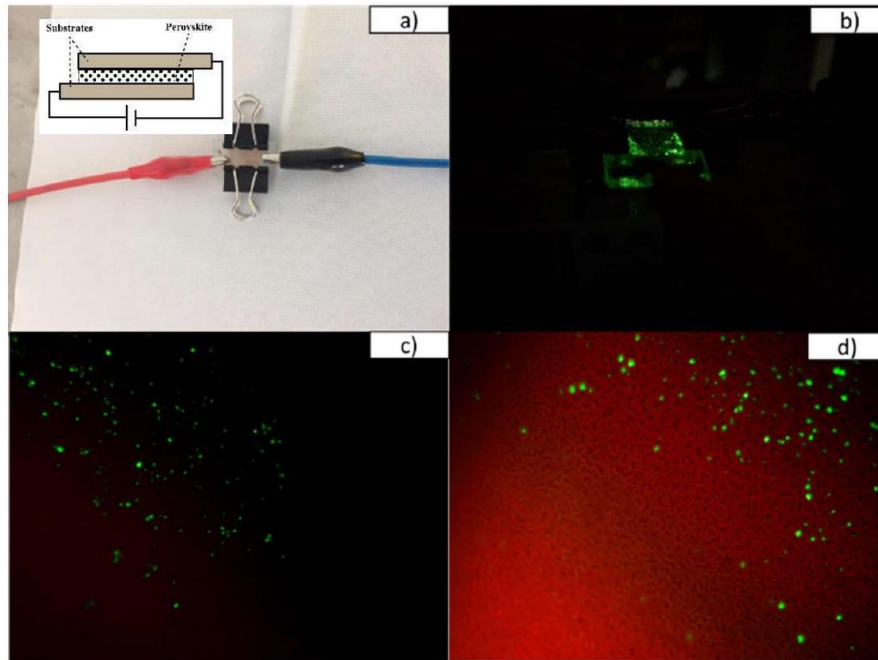


Fig. 3. Optical photographs of a FPeMF at (a) 0 mA, and (b) 70 mA of current injection. Optical microscope images of FPeMF (c, d) at a current injection of 50 mA.

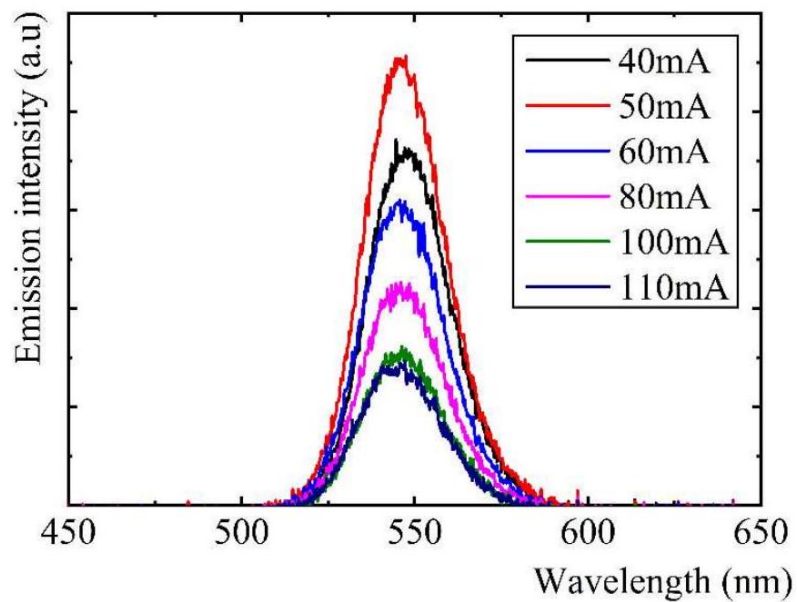


Fig. 4. EL spectra of a fabricated FPeMFs were measured under different injection currents.

Figure 5 illustrates the current (I) and versus voltage (V) of the fabricated FPeMFs. As the voltage rises from 0 V to 6 V, the current also increases, indicating that carriers are being injected into the single crystal. The decrease in current may be attributed to heating. Notably, the crystal structure was visibly disrupted at bias voltages exceeding 10 V, this would be due to the fact that FAPbBr₃ crystals were destroyed by high injection voltage.

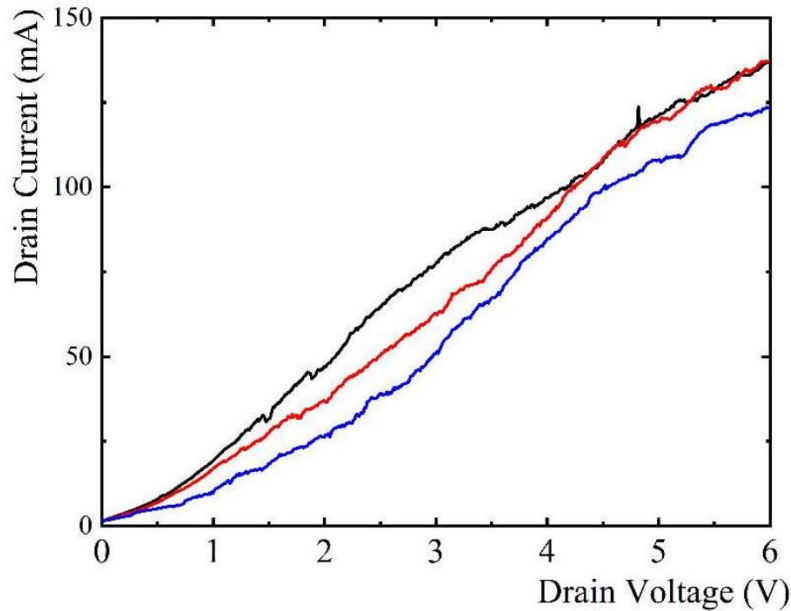


Fig. 5. I-V curves of a fabricated FPeMFs, measured in three cycles.

4. Conclusion

In summary, we have fabricated FABr by synthesizing slowly mixing formamidineum acetate powder with hydrobromic acid, then FAPbBr₃ thin films and FTO/FAPbBr₃/FTO sandwich structures were prepared by spin-coating method. Both the photoluminescence and electroluminescence of FAPbBr₃ have been observed. PL- and EL peaks of the spectra were revealed at 562 nm and 545 nm, respectively. The obtained results suggest potential applications of FAPbBr₃ in optoelectronic devices such as solar cells and light emitting diodes.

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References

- [1] V. M. Goldschmidt, *Die Gesetze der Krystallochemie*, *Naturwissenschaften* **14** (1926) 477.
- [2] A. Kojima, M. Ikegami, K. Teshima and T. Miyasaka, *Highly luminescent lead bromide perovskite nanoparticles synthesized with porous alumina media*, *Chem. Lett.* **41** (2012) 397.

- [3] Y.-H. Kim, H. Cho and T.-W. Lee, *Metal halide perovskite light emitters*, *Proc Natl Acad Sci U S A* **113** (2016) 1169411702.
- [4] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee *et al.*, *Overcoming the electroluminescence efficiency limitations of perovskite light-emitting diodes*, *Science* **350** (2015) 1222.
- [5] L. Protesescu, S. Yakunin, M.I. Bodnarchuk, F. Krieg, R. Caputo, C.H. Hendon *et al.*, *Nanocrystals of Cesium Lead halide perovskites (CsPbX₃ X = Cl, Br, and I): Novel optoelectronic materials showing bright emission with wide color gamut*, *Nano. Lett.* **15** (2015) 3692
- [6] Z.-K. Tan, R.S. Moghaddam, M.L. Lai, P. Docampo, R. Higler, F. Deschler *et al.*, *Bright light-emitting diodes based on organometal halide perovskite*, *Nat. Nanotechnol.* **9** (2014) 687.
- [7] J. Jiang, Z. Chu, Z. Yin, J. Li, Y. Yang, J. Chen *et al.*, *Red perovskite lightemitting diodes with efficiency exceeding 25% realized by co-spacer cations*, *Advanced Materials* **34** (2022) 2204460.
- [8] Z. Liu, W. Qiu, X. Peng, G. Sun, X. Liu, D. Liu *et al.*, *Perovskite lightemitting diodes with EQE exceeding 28% through a synergetic dualadditive strategy for defect passivation and nanostructure regulation*, *Adv. Mater.* **33** (2021) 2103268.
- [9] Q. Wan, W. Zheng, C. Zou, F. Carulli, C. Zhang, H. Song *et al.*, *Ultrathin light-emitting diodes with external efficiency over 26% based on resurfaced perovskite nanocrystals*, *ACS. Energy. Lett.* **8** (2023) 927.
- [10] A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *Organometal halide perovskites as visible-light sensitizers for photovoltaic cells*, *J. Am. Chem. Soc.* **131** (2009) 6050.
- [11] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, *6.5% efficient perovskite quantum-dot-sensitized solar cell*, *Nanoscale* **3** (2011) 4088.
- [12] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro *et al.*, *Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%*, *Sci. Rep.* **2** (2012) 591
- [13] J.-W. Lee and N.-G. Park, *Perovskite solar cell*, *Vacuum Magazine* **1** (2014) 10
- [14] D. I. Kim, J. W. Lee, R. H. Jeong and J.-H. Boo, *A high-efficiency and stable perovskite solar cell fabricated in ambient air using a polyaniline passivation layer*, *Sci. Rep.* **12** (2022) 697.
- [15] A. Perumal, S. Shendre, M. Li, Y. K. E. Tay, V. K. Sharma, S. Chen *et al.*, *High brightness formamidinium lead bromide perovskite nanocrystal light emitting devices*, *Sci. Rep.* **6** (2016) 36733.
- [16] D. Han, M. Imran, M. Zhang, S. Chang, X. Wu, X. Zhang *et al.*, *Efficient light-emitting diodes based on in Situ fabricated FAPbBr₃ nanocrystals: The enhancing role of the ligand-assisted reprecipitation process*, *ACS. Nano.* **12** (2018) 8808
- [17] H. Chen, L. Fan, R. Zhang, C. Bao, H. Zhao, W. Xiang *et al.*, *High efficiency formamidinium lead bromide perovskite nanocrystal-based lightemitting diodes fabricated via a surface defect self-passivation strategy*, *Adv. Opt. Mater.* **8** (2020) 1901390.
- [18] V.-C. Nguyen, H. Katsuki, F. Sasaki and H. Yanagi, *Single-crystal perovskite CH₃NH₃PbBr₃ prepared by cast capping method for lightemitting diodes*, *Jpn. J. Appl. Phys.* **57** (2018) 04FL10.
- [19] T. Nguyen-Tran, M. N. An, T. T. Luong, H. H. Nguyen and T. T. Truong, *Growth of single crystals of methylammonium lead mixedhalide perovskites*, *Comm. Phys.* **28** (2018) 237.
- [20] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Bertolotti, N. Masciocchi, A. Guagliardi *et al.*, *Monodisperse formamidinium lead bromide nanocrystals with bright and stable green photoluminescence*, *J. Am. Chem. Soc.* **138** (2016) 14202.
- [21] T. V. P. Vu, M. T. Nguyen, D. T. T. Nguyen, T. D. Vu, D. L. Nguyen, N. M. An *et al.*, *Three-photon absorption induced photoluminescence in organolead mixed halide perovskites*, *J. Electron. Mater.* **46** (2017) 3622.