

## Dual Color Photoluminescence Emissions from All-Inorganic CsPbBr<sub>3</sub> Nanopillars

Md. Shafiul Islam<sup>1</sup>, A. Ahad<sup>2</sup>, M. Kamal Hossain<sup>2\*</sup>

<sup>1</sup>Department of Physics, Jahangirnagar University, Savar, Dhaka, Bangladesh

<sup>2</sup>Department of Physics, Comilla University, Kotbari, Cumilla 3506, Bangladesh

---

**Abstract:** The distinguishing optoelectronic properties of all-inorganic CsPbX<sub>3</sub> (X = Cl, Br, I) have attracted intense attention of the materials research community and therefore in the research focus today. Here, we report on the conventional single-step chemical vapor deposition (CVD) grown all-inorganic CsPbBr<sub>3</sub> nanopillars. These nanopillars have atomically smooth surfaces and truncated nano-cone like geometrical shape. The structural uniqueness of the halide nanopillars makes them excellent photoemitters. Ultraviolet He-Cd laser excitations ( $\lambda \sim 320$  nm) of the nanopillars exhibited dual color photoluminescence emissions respectively in the blue ( $\lambda \sim 460$  nm) and green ( $\lambda \sim 530$  nm) emission regions of the visible spectral range. Surface smoothness along with unique structural geometry make the all-inorganic CsPbBr<sub>3</sub> halide nanopillars potential for future optoelectronic devices especially for dual-wavelength mode laser applications.

**Background:** All-inorganic halide perovskites have many distinguishing optoelectronic properties. These properties can be controlled by tuning the composition as well as introducing size variations of the halide crystallites. Due to the above, a wide variety of structures have already been studied namely nanowires, nanorods, microwires, nanoplates, microplates, nanocubes, microcubes and nanosheets. As an extension of the previous works, here, the growth and photoluminescence property of the all-inorganic CsPbBr<sub>3</sub> halide nanopillars are discussed.

**Materials and Methods:** The CsPbBr<sub>3</sub> nanopillars are grown by the conventional single-step chemical vapor deposition (CVD) synthesis approach.

**Results:** The smooth nanopillars having truncated nano-cone like geometrical shape showed very good optical emission property. Steady state photoluminescence emissions spectra obtained for the nanopillars exhibited dual color emissions in the visible spectral range.

**Conclusion:** All-inorganic CsPbBr<sub>3</sub> halide nanopillars are good optical emitters with dual band photoluminescence emissions in the green and blue regions of the visible spectral range. They have potential for dual-mode lasing applications.

**Key Words:** All-inorganic halides; chemical vapor deposition; nanopillars; dual color photoluminescence emission.

---

Date of Submission: 03-10-2022

Date of Acceptance: 17-10-2022

---

### I. Introduction

The impressive trend of the increased photoconversion efficiency ( $\eta \sim 26\%$ ) of the hybrid halide perovskites (OHPs) within a very short period of time (2009 - 2022), have attracted immense interests of the materials research community<sup>1,2,3,4,30</sup>. Also, their earth abundancy as well as easy solution-deposited absorbing layers in photovoltaic solar cells helped them to explore quickly compared to the other contemporary photovoltaic materials<sup>5,6,7</sup>. These hybrid halide perovskite materials possess many distinguishing optoelectronic properties including strong optical absorption<sup>8</sup>, easy bandgap tunability<sup>2</sup>, and balanced electron-hole mobility<sup>9</sup>. All these characteristic features make them suitable for many outstanding performance device applications including high efficiency solar cells<sup>10,11</sup>, light manipulation and detection related multiphoton absorbers<sup>12,13</sup>, single- and multi-mode lasers<sup>6,14</sup>, photodetectors<sup>2</sup>, and sensors<sup>15</sup>. Though there is an excellent research progress with a proven potentiality of the organic-inorganic hybrid halide perovskite-based materials, the hygroscopic nature along with severe thermal decomposition of the organic component made them to suffer from poor ambient air and thermal stability<sup>6,16</sup>. Also, the typical lithography which is an essential part of the fabrication of any sophisticated optoelectronic device, is not supported by this hybrid halide perovskites materials system<sup>6</sup>. All of the above restrict the viability of the wide range commercial applications of this novel materials system. In this regard, all-inorganic halide perovskites (IHPs) because of their inherent structural and compositional stability are considered to be the competent alternative of the organic-inorganic hybrid halide perovskites (OHPs), and therefore, in the research spotlight today<sup>2,17</sup>.

As because of the comparable optoelectronic properties of IHPs as that of OHPs, a considerable number of literatures have been grown up around all-inorganic lead halide perovskite (IHPs) materials during the last few years<sup>2,7,18,19,20,21,22</sup>. Also, since different geometrical shapes are considered to be suitable for different types of device fabrications, to date, several efforts have been made to realize IHPs with controlled morphologies like quantum dots<sup>23</sup>, nanocrystals (NCs)<sup>17</sup>, nanowires<sup>3</sup>, nanorods<sup>3</sup>, 2D nanosheets, thin films<sup>12</sup> and microplates<sup>2</sup> depending on a variety of growth techniques<sup>7</sup>. In addition to the hydrothermal synthesis, co-evaporation, and spin coating, etc., are also used to grow IHPs where different unavoidable defect densities may be associated with the as-grown materials which may be ascribed to the polycrystalline nature of the final products<sup>6</sup>. Sometimes it is also claimed that solution chemistry is not viable for growing halide alloys. Consequently, the synthesis of single crystalline defect free IHPs suitable for high performance optoelectronic applications still remains a major challenge. Among many other issues, right choice of the synthesis technique could be a key contributing factor to this challenge<sup>6</sup>. Thanks to the chemical vapor deposition (CVD) growth technique for proving its uniqueness in growing high quality semiconductor materials using a simple setup including a furnace and a pumping system. It has a reputation in the mass production of almost defect free single crystalline materials allowing a strict control over the crystal structure and other geometrical parameters of the as grown materials<sup>26</sup>. Studies over the past decades have provided important information on different mechanisms of chemical vapor deposition (CVD) synthesis of micro-nano structured materials<sup>14</sup>.

Photoluminescence (PL) emission is an important optical property which provides various different information on the studied material including optical emission, defects in crystal, external quantum efficiency (EQE) and photoluminescence quantum yield (PLQY), etc<sup>24</sup>. All these information is vital to design an optoelectronic device. All-inorganic CsPbBr<sub>3</sub> halides are dedicatedly green emitting material compositions whereas CsPbCl<sub>3</sub> compositions are of blue emitting one. However, the comparatively poor photoluminescence quantum yield (PLQY) obtained for the all chloride based organic-hybrid or all-inorganic pure form of halide perovskites suggested the search for other alternative source of stable blue emitting halide perovskite compositions and structures<sup>25</sup>.

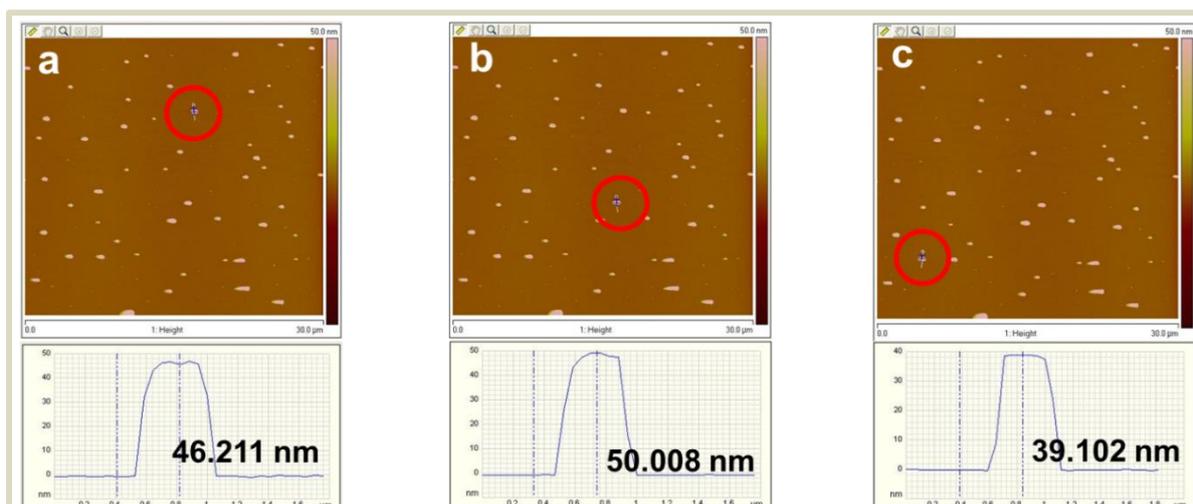
Here, we report on the conventional single-step chemical vapor deposition grown all-inorganic CsPbBr<sub>3</sub> halide nanopillars. The smooth nanopillars having truncated nano-cone like geometrical shape show very good optical emission property. Steady state photoluminescence emissions spectra obtained for the nanopillars exhibited dual color emissions respectively in the blue and green emission regions of the visible spectral range. In addition to the desired regular green color emission, the all-inorganic CsPbBr<sub>3</sub> halide nanopillars also emit blue colors. This result, therefore, suggests that all-inorganic bromide (CsPbBr<sub>3</sub>) composition is good as both green and blue emitting sources. Moreover, the dual color emissions from the nanopillars may further enhance their application prospects for devising the dual band lasers.

## **II. Materials and Methods**

The CsPbBr<sub>3</sub> nanopillars were grown by the conventional single-step chemical vapor deposition (CVD) synthesis approach. To grow the desired all-inorganic halide nanostructures, precursor materials, namely, CsBr and PbBr<sub>2</sub> with a molar ratio 1:1 were initially mixed together and introduced into the CVD chamber central heating zone using an alumina crucible. A few pieces of c-sapphire substrates were put in the downstream reactor zone. The CVD tube reactor was then pumped down to less than 50 mTorr and a high purity argon (Ar) gas was introduced into the reactor tube at a rate of 100 sccm for 20 mins to purge the residuals. The carrier gas flow was then readjusted to a value of 10 sccm and a stable optimized pressure of 5 Torr was attained. Growth was conducted for a period of 40 mins. The CVD chamber was then allowed to reach the room temperature value and the samples were collected to perform different necessary characterizations.

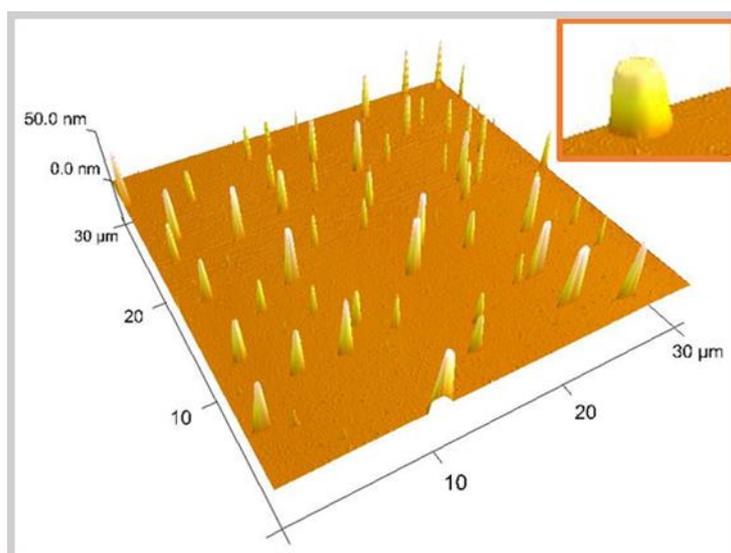
## **III. Results and Discussion**

To see the morphology of the as-grown CsPbBr<sub>3</sub> halide structures, high resolution atomic force microscopy (AFM) imaging was performed first. Figure 1 shows the AFM morphology scan of the as-grown all-inorganic CsPbBr<sub>3</sub> nanostructures. The AFM scans taken randomly on three different samples are shown in Figure 1 (a-c). The height profiles measured on three individually chosen CsPbBr<sub>3</sub> halide structures (marked on the scanning images a, b and c as 'red circle') are attached beneath the respective AFM scanning images shown in Figure 1. The length (vertical height) of the nanopillars ranges in between ~ ≤10 nm – 50 nm. The base and crest of the measured pillars are found ~500 nm and ~250 nm, respectively. The length, base, and the crest's proportions have given most of the nanopillars a truncated nano-cone like geometrical shape. Since different shapes and geometry of the all-inorganic halides have been studied for various suitable applications<sup>4,7,18,26</sup>, the nanopillars may, therefore, find their prospects for future optoelectronic device applications.



**Figure 1** High-resolution atomic force microscopy (AFM) scans of all-inorganic CsPbBr<sub>3</sub> truncated nano-cone shaped nanopillars. (a, b and c) The scanning image and the corresponding height, base and crest profiles of different nano-cones. Profiles are measured for randomly chosen nano-cone like nanopillars.

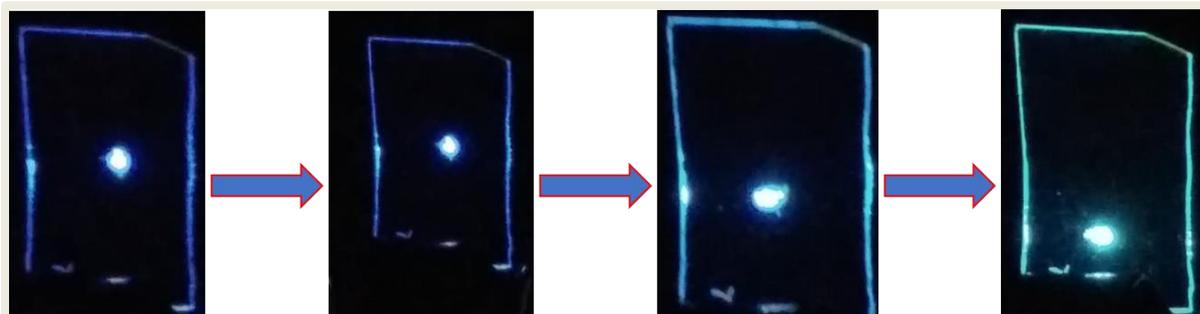
To visualize the true geometrical shape of the nanopillars, we further performed the spatial 3D atomic force microscopy (AFM) imaging of the nanostructures grown on the sapphire substrates. A di MultiModeV (Veeco) atomic force microscopy measurement system controlled by the NanoScopeV was used to perform the study. A spatial 3D image of the nanopillars is shown in Figure 2. It is clearly observed from the figure that the nanostructures are pillar-like. The high magnification image shown in the inset of the Figure 2 also confirms that the necessary geometrical configurations including the base to crest ratio along with the vertical height profile of the halide nanostructures gave them the perfect pillar like shapes. Further, the rational base - crest - height profiles of the nanopillars also gave them the structural stability to serve the purpose of a pillar during their device applications. The high magnification image shown in the inset of the Figure 2 demonstrates that the nanopillars have a truncated nano-cone like geometry which may facilitate and thereby enhance the device applications of these nanopillars.



**Figure 2** A spatially measured 3D AFM image showing the all-inorganic CsPbBr<sub>3</sub> nanopillars. Inset (in the top-right corner) represents the high magnification image of the truncated nano-cone like geometry of the nanopillars.

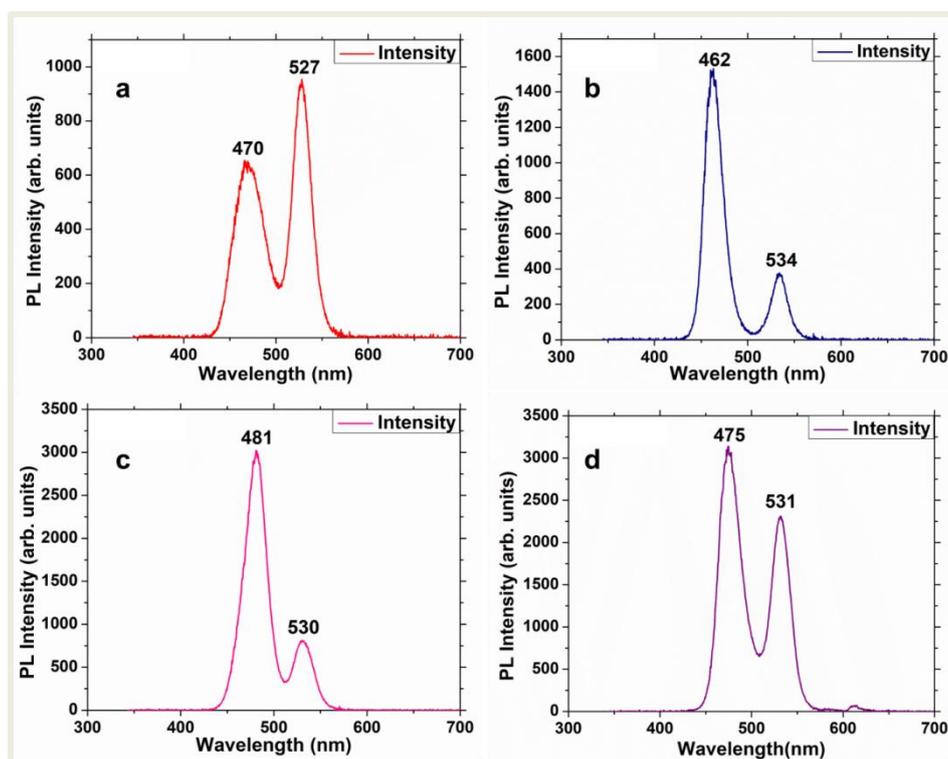
Since all-inorganic halides are well reported as highly absorbing and emissive materials<sup>5,23</sup>, we performed steady state photoluminescence (PL) measurements of the all-inorganic CsPbBr<sub>3</sub> nanopillar structures. A He-Cd laser working in the ultraviolet (UV) excitation region was used to optically excite the nanopillars. A laser power of 1.54 mW and an excitation time of 350 ms are used for the PL measurements. The real color emissions from the nanopillars obtained from a particular CsPbBr<sub>3</sub> sample is shown in Figure 3. It is

observed that at the beginning of the UV laser exposure, the emission from the nanopillars was mostly blue in color while with the increase in the laser exposure time, the emission gradually changed to mostly green in color. Here, it is seen that within a short period of excitation time, the nanopillars emit two different photoluminescence colors, i.e., the nanopillars have dual PL emission property. Figure 3 shows the transitions in the PL emission colors starting from the blue to the green.



**Figure 3** Real color photoluminescence (PL) emission images obtained for all-inorganic CsPbBr<sub>3</sub> truncated nano-cone like nanopillars. Arrow signs represent the continuous transitions from blue to green emissions.

The photoluminescence spectra obtained from the steady state PL measurements of the all-inorganic CsPbBr<sub>3</sub> halide nanopillars are shown in Figure 4. Almost similar observations are found for 4 different samples grown in the same CVD growth environment. Dual photoluminescence emissions observed in the emission wavelengths of (462 – 481) nm and (527 – 534) nm, respectively, correspond to the visible blue and visible green colors of the visible spectral range. The blue emission wavelength is found to be varied in between 462 to 481 nm while the green emission wavelength varied in between 527 to 534 nm. It should be noted here that the halide compositions and all other growth parameters were same for all 4 different samples' growth. The variation in the emission wavelengths for both blue and green emission colors may arise from the variation in the crystallite sizes of the nanopillars<sup>25,27</sup>. Comparatively larger nanopillars produce green emissions which is usual for the all-inorganic CsPbBr<sub>3</sub> halide compositions. However, the blue emissions may arise from the quantum size confinement effect of the inorganic halide nanopillars<sup>25,28,29</sup>. The quantum confinement effects occurred for the nanopillar structures may have the sizes  $\leq 10$  nm.



**Figure 4** Steady state photoluminescence (PL) emission spectra of CsPbBr<sub>3</sub> truncated nano-cone like nanopillars. (a, b, c, and d) PL emission spectra obtained for 4 different CsPbBr<sub>3</sub> nanopillar samples.

#### IV. Conclusion

In this work, we demonstrated the conventional single-step chemical vapor deposition growth of all-inorganic CsPbBr<sub>3</sub> halide nanopillars. The smooth nanopillars having truncated nano-cone like geometrical shapes showed very good optical emission property. Steady state photoluminescence (PL) emissions spectra obtained for the nanopillars exhibited dual color emissions in the visible spectral range. In addition to the desired regular green color emission, the all-inorganic CsPbBr<sub>3</sub> halide nanopillars also emit blue colors. This result, therefore, suggests that all-inorganic bromide composition (CsPbBr<sub>3</sub>) is good as both blue and green emitting sources. Moreover, the dual color emissions from the CsPbBr<sub>3</sub> nanopillars may further enhance their application prospects for devising dual band lasers.

#### References

- [1]. Li, X. *et al.* All Inorganic Halide Perovskites Nanosystem: Synthesis, Structural Features, Optical Properties and Optoelectronic Applications. *Small***13**, 1–24 (2017).
- [2]. Mo, X. *et al.* All-inorganic perovskite CsPbBr<sub>3</sub> microstructures growth: Via chemical vapor deposition for high-performance photodetectors. *Nanoscale***11**, 21386–21393 (2019).
- [3]. Qiu, T. *et al.* Recent advances in one-dimensional halide perovskites for optoelectronic applications. *Nanoscale***10**, 20963–20989 (2018).
- [4]. Mi, Y. *et al.* Fabry–Pérot Oscillation and Room Temperature Lasing in Perovskite Cube-Corner Pyramid Cavities. *Small***14**, 1–8 (2018).
- [5]. Edri, E., Kirmayer, S., Cahen, D. & Hodes, G. High open-circuit voltage solar cells based on organic-inorganic lead bromide perovskite. *J. Phys. Chem. Lett.***4**, 897–902 (2013).
- [6]. Wang, Y. *et al.* Chemical vapor deposition growth of single-crystalline cesium lead halide microplatelets and heterostructures for optoelectronic applications. *Nano Res.***10**, 1223–1233 (2017).
- [7]. Zhao, C. *et al.* Stable Two-Photon Pumped Amplified Spontaneous Emission from Millimeter-Sized CsPbBr<sub>3</sub> Single Crystals. *J. Phys. Chem. Lett.***10**, 2357–2362 (2019).
- [8]. Yin, W. J., Yan, Y. & Wei, S. H. Anomalous alloy properties in mixed halide perovskites. *J. Phys. Chem. Lett.***5**, 3625–3631 (2014).
- [9]. Li, Y. *et al.* Controllable Vapor-Phase Growth of Inorganic Perovskite Microwire Networks for High-Efficiency and Temperature-Stable Photodetectors. *ACS Photonics* **5**, 2524–2532 (2018).
- [10]. Jiang, Y. *et al.* Combination of Hybrid CVD and Cation Exchange for Upscaling Cs-Substituted Mixed Cation Perovskite Solar Cells with High Efficiency and Stability. *Adv. Funct. Mater.***28**, (2018).
- [11]. Barker, A. J. *et al.* Defect-Assisted Photoinduced Halide Segregation in Mixed-Halide Perovskite Thin Films. *ACS Energy Lett.***2**, 1416–1424 (2017).
- [12]. Krishnakanth, K. N., Seth, S., Samanta, A. & Venugopal Rao, S. Broadband ultrafast nonlinear optical studies revealing exciting multi-photon absorption coefficients in phase pure zero-dimensional Cs<sub>4</sub>PbBr<sub>6</sub> perovskite films. *Nanoscale***11**, 945–954 (2019).
- [13]. Tahara, H., Yamada, T., Handa, T. & Kanemitsu, Y. Nonlinear optical properties of lead halide perovskites. *AM-FPD 2018 - 25th Int. Work. Act. Flatpanel Displays Devices TFT Technol. FPD Mater. Proc.* 1–4 (2018) doi:10.23919/AM-FPD.2018.8437382.
- [14]. Gu, Z. *et al.* Controllable Growth of High-Quality Inorganic Perovskite Microplate Arrays for Functional Optoelectronics. *Adv. Mater.***32**, 1–6 (2020).
- [15]. Wei, H. & Huang, J. Halide lead perovskites for ionizing radiation detection. *Nat. Commun.***10**, 1–12 (2019).
- [16]. Beal, R. E. *et al.* Cesium Lead Halide Perovskites with Improved Stability for Tandem Solar Cells. *J. Phys. Chem. Lett.***7**, 746–751 (2016).
- [17]. Seth, S. & Samanta, A. A facile methodology for engineering the morphology of CsPbX<sub>3</sub> perovskite nanocrystals under ambient condition. *Sci. Rep.***6**, 1–7 (2016).
- [18]. Zhang, Q. *et al.* High-Quality Whispering-Gallery-Mode Lasing from Cesium Lead Halide Perovskite Nanoplatelets. *Advanced Functional Materials* vol. 26 6238–6245 (2016).
- [19]. Hoffman, J. B., Schleper, A. L. & Kamat, P. V. Transformation of Sintered CsPbBr<sub>3</sub> Nanocrystals to Cubic CsPbI<sub>3</sub> and Gradient CsPbBr<sub>3</sub>1-x through Halide Exchange. *J. Am. Chem. Soc.***138**, 8603–8611 (2016).
- [20]. Aamir, M. *et al.* Cesium Lead Halide Perovskite Nanostructures: Tunable Morphology and Halide Composition. *Chem. Rec.***18**, 230–238 (2018).
- [21]. Pramanik, A., Gates, K., Gao, Y., Begum, S. & Chandra Ray, P. Several Orders-of-Magnitude Enhancement of Multiphoton Absorption Property for CsPbX<sub>3</sub> Perovskite Quantum Dots by Manipulating Halide Stoichiometry. *J. Phys. Chem. C***123**, 5150–5156 (2019).
- [22]. Lin, C. K. *et al.* Two-Step Patterning of Scalable All-Inorganic Halide Perovskite Arrays. *ACS Nano***14**, 3500–3508 (2020).
- [23]. Song, J. *et al.* Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX<sub>3</sub>). *Adv. Mater.***27**, 7162–7167 (2015).
- [24]. Online, V. A. *et al.* Photoluminescence and Raman mapping characterization of WS<sub>2</sub> monolayers prepared using. (2015) doi:10.1039/c5tc00016e.
- [25]. Shi, H., Zhang, X., Sun, X. & Zhang, X. Deep Blue Emission of All-Bromide-Based Cesium Lead Perovskite Nanocrystals. *J. Phys. Chem. C***124**, 1617–1622 (2020).
- [26]. Shoaib, M. *et al.* Directional Growth of Ultralong CsPbBr<sub>3</sub> Perovskite Nanowires for High-Performance Photodetectors. *J. Am. Chem. Soc.***139**, 15592–15595 (2017).
- [27]. Shamsi, J. *et al.* Colloidal Synthesis of Quantum Confined Single Crystal CsPbBr<sub>3</sub> Nanosheets with Lateral Size Control up to the Micrometer Range. *J. Am. Chem. Soc.***138**, 7240–7243 (2016).
- [28]. Protesescu, L. *et al.* Nanocrystals of Cesium Lead Halide Perovskites (CsPbX<sub>3</sub>, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.***15**, 3692–3696 (2015).
- [29]. Zhang, Z. Y. *et al.* Size-dependent one-photon- and two-photon-pumped amplified spontaneous emission from organometal halide CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> perovskite cubic microcrystals. *Phys. Chem. Chem. Phys.***19**, 2217–2224 (2017).
- [30]. <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies-rev220630.pdf> (visited on 25 July 2022).