A New Generation of Luminescent Materials Based on Low-Dimensional Perovskites

Jun Pan, Lutfan Sinatra, Marat Lutfullin, Ibrahim Dursun, and Osman M. Bakr
King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Abstract

Low-dimensional perovskites with high luminescence properties are promising materials for optoelectronic applications. In this article, properties of two emerging types of low-dimensional perovskites are discussed, including perovskite quantum dots CsPbX_3 ($X = \text{Cl}, \text{Br}$ or I) and zero-dimensional perovskite Cs_4PbBr_6 . Moreover, their application for light down conversion in LCD backlighting systems and in visible light communication are also presented. With their superior optical properties, we believe that further development of these materials will potentially open more prospective applications, especially for optoelectronics devices.

Author Keywords

Luminescence; Perovskites; Quantum Dots; Light down converter; LCD backlighting; Visible light communication.

1. Introduction

Nowadays, luminescent materials are an essential part of lighting technology, particularly in light emitting diodes (LEDs), liquid crystal displays (LCDs), and lasers. Industry requirements and demands for these materials have increased significantly. Higher brightness, ability to tune the emission wavelengths, narrower band emission, and compatibility with different materials are now essential requisites. Low-dimensional perovskites, such as perovskite quantum dots (QDs) and zero-dimensional (Zero-D) perovskite phases, are brand new luminescent materials that possess the aforementioned requirements.

Perovskite quantum dots are nanoparticles with diameters in the range of 2-12 nm and having the formula ABX_3 (where $A = \text{Cs}^+$, CH_3NH_3^+ , or $\text{HC}(\text{NH}_2)_2^+$ or other monovalent cations; $B = \text{Pb}^{2+}$, Sn^{2+} or other divalent cations; $X = \text{Cl}^-$, Br^- or I^-). They exhibit impressive luminescent properties in the visible spectral region. A unique feature of their luminescent properties is that the wavelengths of emission light can be precisely tuned by changing the nanoparticle's composition, sizes and shapes [1].

Recently, a new type of highly luminescent low-dimensional perovskites was proposed in powder form, so-called zero-dimensional perovskites. Zero-D perovskites have a common formula A_4BX_6 , where A could be Cs^+ or another monovalent cation, $B = \text{Pb}^{2+}$ or other divalent cations, and X is Cl^- , Br^- or I^- . They adopt the Bergerhoff-Schmitz-Dumont crystal type structure, in which the metal-anion octahedra are spatially confined. Zero-D perovskites also show outstandingly high photoluminescence even in solid form [2].

The present work is devoted to the recent progress in low-dimensional perovskites and their optical properties. These materials can be applied to optoelectronic applications, such as light down-converters for LCD backlighting, for white and horticultural LEDs, and for solar cells. Two case studies of using these materials for LCD backlighting and white lighting are presented.

2. CsPbX_3 Perovskite Quantum Dots

Among a wide range of perovskite QDs, all-inorganic CsPbX_3 QDs have received special attention due to their superior efficiency and stability that can be used as a promising material for solution-processed optoelectronics such as photovoltaics, lasing, light-emitting diodes, and photodetectors. They have high photoluminescence quantum yield (PLQY) up to 95 % and narrow full width at half maximum (FWHM) around 15-35 nm [3]. Despite the impressive metrics of the entire family of lead halide perovskites, however, poor stability, in particular with respect to air, moisture, and light exposure, remains a ubiquitous impediment for all perovskite materials and devices. The lack of stability has prevented the commercial application of perovskite optoelectronics.

One of the main approaches to increase the stability of perovskite QDs is surface engineering, through chemical modification or treatment. In our lab, we have developed a new passivation technique in which the surface of QDs is coated with an inorganic-organic hybrid ion pair. This novel approach yields high PLQY with high operational stability under ambient conditions ($60 \pm 5\%$ lab humidity), thus overcoming a major challenge impeding the development of perovskite-based applications.

Figure 1. a) Absorption and emission spectra of the untreated and the treated QD with various sulfur amounts. b) Corresponding PLQY. Reproduced with permission [4]. Copyright 2015, American Chemical Society.

For example, we introduced an inorganic–organic hybrid ion pair (didodecyl dimethylammonium sulfide, S^{2-} -DDA $^{+}$) to passivate the QDs, didodecyl dimethylammonium bromide (DDAB) was used as a source of DDA $^{+}$ to passivate the perovskite $CsPbBr_3$ QDs [4]. Fig. 1 shows the absorption and photoluminescence (PL) spectra of the QD films before and after surface passivation. QD films were prepared by spin-coating of untreated and treated QDs on a glass substrate. As seen, emission intensity and PLQY for treated film are increasing substantially with increasing of treatment agent amount reaching a maximum with its certain amount. It can be suggested that the passivation decreases defects on the surface thus increasing PL efficiency.

To confirm the air and photostability of the passivated $CsPbBr_3$ QDs films, we tested their propensity for amplified spontaneous emission (ASE) through one- and two-photon pumping under ambient conditions (room temperature, $60 \pm 5\%$ humidity). We observed that the untreated sample suffered from partial degradation within hours, displaying a sharp contrast in performance, whereas the passivated Quantum Dot film exhibited the same threshold and optical characteristics even after 4 months of open air storage and rounds of photostability testing.

The above-mentioned technique can be applied to all $CsPbX_3$ QDs to make them highly efficient and stable: emission wavelengths 450 – 660 nm with FWHM 15-35 nm and PLQY up to 90 % (Fig.2).

Figure 2. a) Photo of treated Quantum Dots under UV light. b) PL of treated Quantum Dots.

3. Cs_4PbBr_6 Zero-D Perovskite

Among Zero-D perovskites phases, Cs_4PbBr_6 is the most well studied. The crystal structure of Cs_4PbBr_6 consists of $PbBr_6^{4-}$ octahedra that are spatially confined with each other with Cs^{+} cations between them (Fig. 3). Zero-D perovskite shows an outstandingly high photoluminescence even in solid form. It has quantum yield (PLQY) of more than 45% with very narrow emission (FWHM < 20 nm) of green light with the peak at 520 nm. Cs_4PbBr_6 has also a strong and stable emission at excitation wavelengths of $\lambda > 340$ nm, while the absorption edge of pure Cs_4PbBr_6 is at 540 nm. A pure phase of Cs_4PbBr_6 powder was for the first time prepared by our group [2].

Figure 3. Crystal structure of (a) $CsPbBr_3$ and (b) Cs_4PbBr_6 depicting corner-shared and isolated $PbBr_6^{4-}$ octahedra, respectively. Reproduced with permission [2]. Copyright 2016. American Chemical Society.

The reason of such emission is not clear yet. Some researchers assume that emission comes from quantum confinement of isolated octahedra. Others assume that emission comes from defects in Cs_4PbBr_6 , like atom dislocations and so on. And finally, others suggest that emission comes from $CsPbBr_3$ nanoparticles embedded into the Cs_4PbBr_6 matrix.

One of the main advantages of this material is its superior optoelectronic properties combined with extreme stability. It can be stored at ambient conditions for at least a year without changing in emission wavelength, PLQY and FWHM.

While Cs_4PbBr_6 powder has promising luminescent properties, its nanocrystals (NCs) have even better efficiencies [5]. Cs_4PbBr_6 NCs were synthesized through a modified reverse microemulsion method, in which nanocrystals with narrow size distribution around 26 ± 4 nm can be obtained. The optical properties of Cs_4PbBr_6 NCs were investigated by absorption, photoluminescence, and reflectance spectroscopic techniques. The PL emission was centered at 515 nm with a standard Gaussian profile and an FWHM of 23 nm (Figure 4). The absorption spectrum of colloidal sample exhibits a strong peak at 315 nm with a long tail from 350 to 550 nm.

While Cs_4PbBr_6 in a bulk powder form has PLQY of 45%, Zero-D NCs has a relatively high PLQY of 65% (excitation at 480 nm) in colloidal form. This value is slightly lower than that (80–90%) of $CsPbBr_3$ QDs colloidal. However, it is more practical and important to compare their PLQY in thin-film form when considering their use in optoelectronic devices. For example, PLQY of $CsPbBr_3$ NCs dramatically decreased to 18% or even less when they are transformed from colloidal to thin-film due to the loss of ligands or aggregation [6]. Cs_4PbBr_6 NCs retained a record PLQY of 54% even after drop-casting into a thin film on a glass substrate (Fig.4, inset).

Figure 4. Absorption, excitation, photoluminescence spectra and bandgap alignment of Cs_4PbBr_6 NCs colloidal; insets show a photograph of a thin-film sample and a colloidal sample under the illumination of 365 nm UV light. Reproduced with permission [5]. Copyright 2017, American Chemical Society.

To investigate the dynamics of exciton recombination, we used streak camera to record the PL decay of thin film and colloidal samples of Cs_4PbBr_6 nanoparticles. The colloidal Cs_4PbBr_6 NCs sample shows a biexponential decay profile with a short lifetime of 1.6 ns and a long lifetime of 9.1 ns. The short and long components can be attributed to the excitons located on the surface and interior of the Cs_4PbBr_6 NCs, respectively. Importantly, time-resolved PL measurement of thin-film Cs_4PbBr_6 NCs sample reveals a slightly decreased lifetime with a short component ~ 1.4 ns and a long component ~ 8.6 ns, which is consistent with the slight decrease in PLQY from colloidal to thin film.

Using of stable colloidal Zero-D NPs can facilitate application of this material in the solution-processed fabrication of optoelectronics devices where the layers of luminescent materials are deposited by drop casting, blade casting or spin coating.

4. Application of low-dimensional perovskites for optoelectronics

Low-dimensional perovskites with high luminescence brightness and efficiency, tunable emission wavelengths, narrow band emission are promising materials for optoelectronic devices such as light down-converters for LCD backlighting, for white LEDs

and horticultural LEDs. Moreover, it can be used also as active materials for LEDs and solar cells etc. Here, application of low-dimensional perovskites for LCD backlighting and visible light communication are presented.

Light down-converters for LCD backlighting

The QDs backlighting system is an emerging technology for LCDs. In such LCD backlight, part of the blue light from a conventional LED is converted into pure green and red colors that results in a wider color gamut, brighter and higher contrast display images. Nowadays, several TV manufacturers, such as Sony, Samsung and LG, are adopting backlighting systems based on CdSe and InP QDs. Low-dimensional perovskites are also good candidates for use in a light converting material for LCDs.

As a proof of concept we fabricated and tested a prototype of PMMA film with Cs_4PbBr_6 powder and red CdSe/ZnS QDs as shown in Figure 5. This film is semi-transparent with green shades under ambient lighting and with green-yellow illumination under UV. It has a thickness of 200 μm and is laminated by two pure PMMA 100 μm films from two sides to prevent from degradation under air and moisture. PL spectrum of the film consists of two emission peaks with relative intensities 3:1. The higher one corresponds to Cs_4PbBr_6 with emission peak at 520 ± 1 nm and very narrow FWHM < 20 nm. The smaller one corresponds to CdSe/ZnS QDs with emission peak at 620 ± 1 nm and FWHM > 25 nm. CIE 1976 Chromaticity Diagram for this film is presented in Fig. 5. As we can see, it has a very pure green color and the color gamut area is 124 % of NTSC area. The big advantage of such film is that it is compliant with EU restriction of hazardous substances (RoHS) rather than films containing only CdSe QDs. The concentration of lead and cadmium are below 0.1 % and 0.01 % respectively. Also, we tested its photo stability by monitoring of PLQY for samples that was treated to continuous illumination under blue LED setup with power 10 W for 1000 hours. We observed no any decrease of PLQY and no change of FWHM during this test.

There are some optimizations should be done for commercial application of such material, like increasing PLQY from current 50 % to > 80 %. It can be done by fabrication of Zero-D NPs that have higher efficiency than bulk powder and/or provide surface treatment.

Green Cs_4PbBr_6 /red CdSe/ZnS QDs/ PMMA composite

Figure 5. A proof of concept of using Low-Dimensional Perovskite Cs_4PbBr_6 in polymer film for LCD backlighting.

Light down-converters for visible light communication

Light emitting diodes are becoming prevailing for indoor and outdoor illumination. Moreover, LEDs can be utilized as light sources not only for illumination but also for data transmission; the latter application is referred to as visible light communication (VLC). VLC has many advantages compared to lower frequency communications techniques (including Wi-Fi and Bluetooth), such as an unregulated communication spectrum, greater security, and no RF interferences. This technology allows data transmission with a potential rate as high as 10 Gbit/s, whereas the current WiFi technology is limited with up to average 100 Mbit/s. However, the conventional lighting phosphors for white lighting that are typically integrated with LEDs have limited modulation bandwidth and thus limit the data transmission rate (to a few 10s of Mbit/s).

Current white LEDs contain either yellow rare-earth phosphors material, for example cerium-doped yttrium aluminium garnet ($\text{Ce}^{3+}:\text{YAG}$), or the combination of green and red phosphors. Current phosphors have long PL decay time of microseconds, causing to limit of data transmission. On the other hand, CsPbX_3 QDs perovskites have very short lifetime of nanoseconds that can support a high speed of data transmission through white LEDs.

As a proof of concepts, we fabricated a polymer composite based on a green emissive perovskite CsPbBr_3 QDs in combination with red-emitting nitride phosphorus (LAM-R-6237, Dalian Luming Group) in PDMS. This composite with blue laser as a light source (Fig. 6) exhibits an unprecedented modulation bandwidth of 491 MHz that is ~ 40 times greater than that of conventional phosphors (3–12 MHz), and the capability to transmit a high data rate of up to 2 Gbit/s [7]. Moreover, this perovskite QDs-enhanced white light source exhibits a high color rendering index of 89 and a correlated color temperature of 3236 K, thereby enabling dual VLC and solid-state lighting functionalities.

Figure 6. A representation of perovskite enhanced device for white lighting and data transmission. Reproduced with permission [7]. Copyright 2016, American Chemical Society.

5. Conclusion and Perspective

Low-dimensional perovskites: perovskite quantum dots and Zero-D perovskites are very promising class of luminescent materials. We showed here some of their representatives, like CsPbX_3 QDs and Cs_4PbBr_6 Zero-D Perovskite that have high PLQY up to 90 %, tunable emission wavelengths through the entire visible region and narrow band emission of 15–35 nm. Still, it requires several efforts that should be done to commercialize this new generation of luminescent materials, like provide long term stability and performance tests, optimize synthesis procedures and so on. It should be noted that low-dimensional perovskites are the wide range of materials that are not fully explored yet. It is a big room to search luminescent materials with desired properties, like with higher efficiency and stability, or lead-free.

6. Impact of Our Research

The present work shows the possibilities and advantages of using recently discovered low-dimensional perovskites for applications as light down-converters for LCD displays, white-light communication, and potentially other optoelectronic devices. With further development, we expect this next generation of luminescent materials to play an important role in advanced display and lighting applications.

7. References

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