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Colloidal Metal Halide Perovskite Nanocrystals: Synthesis, Characterizations, and Applications

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Abstract

Colloidal metal halide perovskite nanocrystals (NCs) have emerged as promising materials for optoelectronic devices and received considerable attention recently. Their superior photoluminescence (PL) properties provide significant advantages for lighting and display applications. In this highlight, we discuss recent developments on the design and chemical synthesis of colloidal perovskite NCs, including both organic-inorganic hybrid and all inorganic perovskite NCs. We review excellent PL properties and current optoelectronic applications of these perovskite NCs. In addition, critical challenges that currently limit perovskite NCs are discussed, and prospects for future directions are proposed.

1. Introduction

A recent breakthrough in the family of low temperature solution-processed semiconductors is metal halide perovskites. This class of perovskites can be generally described using the chemical formula of ABX_3 , where A is an organic (*e.g.* methylammonium, short as MA) or alkali metal (*e.g.* cesium) cation, B is a divalent metal cation (*e.g.* lead, tin), and X is a halide anion binding to both cations (as shown in Fig. 1).^{1, 2} These perovskites exhibit strong light absorption, small exciton binding energies, high charge carrier mobilities, as well as long and balanced charge diffusion lengths.³⁻⁶ In addition, their absorption could be conveniently tuned from visible to near infrared (NIR) region by changing cationic or anionic components.^{7, 8} As a result, great success has been made in photovoltaic technologies based on metal halide perovskites light harvesters. The power conversion efficiencies of perovskite solar cells have rocketed from 3.8% to over 20% within only a few years.⁹⁻¹³ In addition to photovoltaics, metal halide perovskites also show great potential in other optoelectronic devices, such as light-emitting diodes (LEDs), lasers, photodetectors and transistors, *etc.*¹⁴⁻¹⁸

Along with the rapid development of bulk perovskites deposited from precursor solutions, the research into colloidal perovskite nanocrystals (NCs) has also emerged very recently.¹⁹⁻²¹ Nanosized perovskites provide additional means for tailoring electronic and optical properties via effects of quantum confinement and wave function engineering.²² A highlight for perovskite NCs is that they exhibit superior photoluminescence (PL) properties, making them especially attractive for lighting and display technology. The PL quantum yield (PLQY) of perovskite colloidal solutions could reach 80% for methylammonium lead bromide ($MAPbBr_3$) NCs,²³ and could be as high as 90% for all inorganic cesium lead bromide ($CsPbBr_3$) NCs.¹⁹

In this article, we highlight recent developments in the design and synthesis of colloidal perovskites NCs, including both organic-inorganic and all inorganic perovskite NCs. We also discuss current optoelectronic applications of perovskite NCs and associated challenges, with prospects for future directions being proposed.

2. Organic- inorganic hybrid perovskite NCs

2.1 Chemical synthesis and characterizations of organic-inorganic perovskite NCs

Pérez-Prieto and co-workers pioneered the wet chemistry colloidal synthesis of free-standing hybrid perovskite NCs (MAPbBr₃ in their case).²¹ They employed a simple one-step approach: a mixture of ammonium bromide with short methyl chain and longer alkyl chains (*e.g.* octadecyl or octyl) was reacted with PbBr₂ in the presence of oleic acid (OA) and octadecene (ODE). The MA cations are embedded in the middle part of the crystal to connect neighbouring [PbBr₆]⁻ octahedra, while the longer alkyl ammonium cations occupy the outer space, terminating the growth of NCs. Thus, these longer alkyl ammonium cations work as the capping ligands of the NCs, and keep the NCs dispersible in a wide range of organic solvents. The obtained perovskite nanodots could be stable in concentrated solutions as well as solid states for several months.

A closer look at the transmission electron microscopy (TEM) images of these organic-inorganic perovskite NCs reveals that these NCs are a mixture of nanodots and nanoplatelets, as shown in Fig. 2a. Tisdale and co-workers separated nanodots from the nearby nanoplatelets, and were able to obtain ‘purified’ nanoplatelets.²⁴ They found that the absorption of these nanoplatelets is dominated by a single sharp excitonic absorption peak at 431 nm, which is significantly blue shifted compared with the absorption of bulk MAPbBr₃ (525 nm). They argued that these nanoplatelets belong to the family of layered perovskites, which can be described by the formula of (RNH₃)₂[MAPbX₃]_{n-1}PbX₄, where R is a long alkyl chain, and n is the number of metal cation monolayer sheets within the two organic insulating layers (note

that we use a slightly different formula compared with the Tisdale's paper to include the case of 2D perovskites ($(\text{RNH}_3)_2\text{PbX}_4$). They claimed that $n=2$ nanoplatelets dominate the purified nanoplatelets with traces amount of $n>2$ perovskites, as shown in their absorption spectra. However, the PL mainly origins from perovskites with $n=\infty$ (*i.e.*, 3D perovskites), implying ultrafast energy transfer from high energy nanoplatelets with small n values to low energy nanoplatelets with larger n values.

Interestingly, Sichert and co-workers claimed that these nanodots are most likely not initially present in the colloidal solutions.²² The energy dispersive spectroscopy (EDS) measurements from their work revealed a molar content of Pb to Br between 1:1.3 and 1:0.75 of these nanodots, rather than 1:3 expected from 3D perovskites or 1:4 expected from 2D perovskites. Based on the results, the authors argued that the nanodots were actually not perovskites. Instead, they were caused by degradation of perovskite nanoplatelets under strong electron beams and laser illumination, and were composed of a mixture of PbBr_2 , pure Pb, and potentially other phases. However, Zhong and co-workers reported totally different EDS results of these nanodots, which were prepared through a ligand assisted reprecipitation technique.²⁵ They found a Br/Pb ratio of 3.5 for the nanodots with an average diameter of 3.3 nm, and proposed that a Br/Pb ratio larger than 3 is caused by Br-rich surfaces in the perovskite nanodots. In addition, both of their X-ray photoelectron spectroscopy (XPS) results and simple modelling indicated that surface Br ions significantly increase for the nanodots, supporting their EDS measurements. Considering the discrepant results from these two groups, further investigations are required to clearly understand the composition stoichiometry of the organic-inorganic perovskite NCs.

In addition to the one-step synthesis method, which produced a mixture of nanodots and nanoplatelets, Scholes and co-workers recently developed a novel two-step synthesis approach to prepare homogeneous organic-inorganic perovskite spherical nanodots (Fig.

2b).²⁶ In their method, spherical PbX_2 NCs were firstly synthesized based on the popular method used for lead chalcogenide semiconductor NCs. These PbX_2 seeds were then reacted with MAX, long-chain alkyl ammonium halide, or a mixture both halides, producing organic-inorganic perovskite NCs. The reaction takes place by intercalation of the organic MAX moiety between the Pb-X-Pb layers of the crystalline PbX_2 host, resulting in the formation of layered perovskites with the formula of $(\text{RNH}_3)_2[\text{MAPbX}_3]_{n-1}\text{PbX}_4$. By changing the alkyl chains and mixing ratios between them, the authors were able to obtain different layered structure perovskite nanodots with $n=1, 2, 3$, which show excitonic gap (Fig. 2c).

Organic-inorganic perovskite NC solutions exhibit excellent PL emission with a narrow full width at the half-maximum (FWHM) and high PLQY. It has been reported that PLQY of perovskite NCs can be optimized by changing the ratios of the precursor compounds (especially the ammonium). For example, Snaith and co-workers observed a maximum PLQY of ~36% at a medium ratio of 0.6 octylammonium/ 0.4 MA (Fig. 2d).²⁷ A similar trend was demonstrated by Sichert *et. al.*, who observed a maximum PLQY of ~30% at 0.7 octylammonium / 0.3 MA.²² By fine-tuning the molar ratio of all the reaction precursors, the perovskite NC solution with a superior PLQY up to 83% was achieved by Pérez-Prieto and co-workers.²³

2.2 Applications of organic-inorganic perovskite NCs

Similar to bulk perovskites, the emission colour of organic-inorganic hybrid perovskite NCs can be easily tuned by varying the halide compositions, providing opportunities for white-light emission. Snaith and co-workers prepared perovskite NCs with PL emission continuously tuned from 385 to 770 nm.²⁷ They further aimed for white light emission by mixing perovskites with different emission colours. The challenge is that significant halide exchanges happen in the solution. For example, pure Br perovskite and pure I perovskite NCs have individual PL emission peaks at 520 and 753 nm, respectively. When mixed in the

solution, PL emission appears at 551 and 704 nm, with the original PL peaks disappearing. This result indicates that halide exchanges automatically happen in the solution, being detrimental for stable and controlled white light emission. To solve this problem, the authors blended perovskite NCs with different colours in an insulating and transparent polymer (*e.g.* polystyrene; PS/poly methyl methacrylate; PMMA). In this way, halide exchange is inhibited, and the emission wavelength could be stabilised at desired wavelengths (Fig. 3a). Based on this technique, broad PL emission covering the entire visible spectral region was obtained from a mixture of blue, green, red and intermediate emitting perovskite NCs in a polymer matrix (Fig. 3b).²¹ Another way to obtain white-light emission is to combine green emissive MAPbBr₃ NCs and red emissive rare-earth phosphor in phosphor-converted white-light-emitting diodes (pc-WLEDs). Based on this idea, Zhang *et al.* demonstrated wide-colour gamut prototype white-light emitting devices by combining green emissive MAPbBr₃ NCs and red emissive rare-earth phosphor K₂SiF₆:Mn⁴⁺ (KSF) with blue emissive GaN chips.²⁵

Compared with the bulk perovskite films deposited from precursor solutions, organic-inorganic perovskite NCs exhibit significantly improved PL emission, making them promising candidates for LEDs. The first LEDs (with luminance lower than 1 cd m⁻²) based on organic-inorganic MAPbBr₃ perovskite NCs was demonstrated by Pérez-Prieto and co-workers.²¹ As shown in Fig. 3c and 3d, Ling *et al.* recently dramatically improved the luminance to 10590 cd m⁻² (at 12 V).²⁸ In their report, single crystalline MAPbBr₃ nanoplatelets with PLQY up to 85% were used as the light emitters. However, the strong interaction of capping ligands causes rough film morphology with aggregated perovskite stacks and pinholes in the directly deposited perovskite layers, being detrimental for the device performance. In order to optimize the film morphology and the charge injection balance, a blend of hole-transport matrix and the electron transport materials of poly(9-vinylcarbazole):2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PVK:PBD) was introduced as

host materials for perovskite NC emitters. Although the device performance is still moderate, the bright LEDs using organic-inorganic perovskite NCs open up a new pathway towards low-cost solution-processed optoelectronic devices based on this new class of materials.

3. All inorganic cesium lead halide perovskite NCs

3.1 Colloidal synthesis of CsPbX₃ NCs

In addition to organic-inorganic perovskite NCs, colloidal synthesis routes of all inorganic cesium lead halide perovskite NCs (CsPbX₃, X=Cl, Br, I or mixed Cl/Br, Br/I systems) have also been developed. Following the traditional hot-injection method which is commonly used for the synthesis of metal chalcogenide NCs, Kovalenko and co-workers successfully synthesized monodisperse CsPbX₃ colloidal nanocubes.¹⁹ The hot-injection method used in their report involves rapid injection of Cs precursors (*e.g.* Cs-oleate) into lead halide precursors containing hot, high boiling point solvents (*e.g.* ODE). A mixture of oleylamine and oleic acid was used to dissolve PbX₂ and stabilize the NCs. Based on *in situ* PL measurements, it was found that the growth of the majority of NCs could be finished within several seconds after the injection of Cs precursors. In such a quick process, reaction temperature is critical for the size of perovskite NCs. With the reaction temperature carefully controlled between 140 and 200 °C, the size of perovskite NCs can be tuned from 4 to 15 nm. As shown in Fig. 4a and 4b, the obtained CsPbX₃ NCs exhibit continuously tunable PL emission with narrow FWHM of 12-42 nm and superior PLQY of up to 90%. Such an excellent PL property is amazing, considering the facile synthesis route which involves neither core-shell structures nor surface modifications.

As shown in Fig. 4c, the emission wavelength of CsPbX₃ NCs could also be conveniently tuned by varying the halide compositions via post-synthetic halide anion exchange reaction, which is similar to their organic-inorganic counterparts.²⁹ Akkerman *et al.* and Nedelcu *et al.* independently reported the fast halide anion exchange of CsPbX₃ NCs using different

compounds capable of delivering halide ions.^{20, 30} The investigated halide ions sources include organometallic Grignard reagents (MeMgX), oleylammonium halides (OAmX), octadecylammonium halides (ODAX), tetrabutylammonium halides (TBAX) and simple PbX₂ salts. They noticed that the anion exchange reaction is very fast (within seconds) and that most of halide sources could initiate efficient anion exchange reaction either to a blue shift (both Br⁻ to Cl⁻ and I⁻ to Br⁻ routes) or to a red shift (Br⁻ to I⁻ and Cl⁻ to Br⁻ routes). It was also pointed out that anion exchange reaction could be realized by directly mixing perovskite NCs with different halide compositions, even without any additional halide sources. Although there is a little size change after the anion exchange, the shape and crystal structure of obtained NCs are identical to their parent NCs. In addition, the reaction does not introduce any remarkable lattice/surface defects. As a result, the PL properties (including the FWHM and the PLQYs) of the anion-exchanged CsPbX₃ NCs are comparable with those directly synthesized through the hot injection method.

3.2 Characterizations and applications of all inorganic CsPbX₃ NCs

Nag and co-workers compared the PL properties between CsPbBr₃ NCs and traditional CdSe quantum dots (QDs) in details.³¹ In addition to the superior colour purity mentioned previously, the comparison demonstrated that the CsPbBr₃ NCs exhibit excellent photostability. PL emission from the ensemble of CsPbBr₃ NCs is quite stable even under prolonged exposure to UV light. It was also demonstrated that the increased temperature (from 25 °C to 100 °C) has no obvious effect on the PL peak position of CsPbBr₃ NCs. The origin of the thermal stable PL property is still unclear and further studies need to be done for a better understanding of this behavior. Moreover, unlike the red shift and reduced PL emission of thin films based on CdSe-based QDs, both peak position and PL intensity of CsPbBr₃ NCs remain almost identical for closely-packed films. This feature indicates less

influence of the self-absorption and Förster resonance energy transfer (FRET) on the PL of CsPbBr₃ NC films compared to CdSe QD films.

In addition to the ensemble CsPbX₃ NCs, the PL emission of individual NCs has also been investigated. Single photon emission at room temperature for CsPbX₃ NCs has been demonstrated by two recent papers.^{32, 33} Both reports demonstrated that the second-order PL intensity correlation function, $g^{(2)}$, is in the range of 0.05-0.06 at time $t = 0$ and then increases to unity at longer times with both continuous-wave and with pulsed excitation (Fig. 5a and 5b). This indicates strong photon antibunching, which confirms that single CsPbX₃ NCs can serve perfectly as a single photon source at room temperature. This observation is explained by efficient Auger recombination of multiexcitons, resulting in complete suppression of the photon coincidence signal in the $g^{(2)}$ measurements and a pure single photon stream without random interruptions of multiphoton events. This working mechanism is similar to the single photon emission observed in traditional metal-chalcogenide NCs.

Though promising as an effective single photon emission source, the materials quality of CsPbX₃ NCs need to be carefully optimized for practical applications, because they may exhibit strong emission intermittency (PL blinking). The paper from Nag and co-workers claimed that approximately 90% of the individual NCs remain emissive (on-time >85%) for high quality CsPbBr₃NCs with a PLQY ~90%.³¹ However, both reports from Hu et al. and Park et al. observed obvious PL blinking behavior of single CsPbBr₃ NCs.^{32, 33} PL blinking has been also reported in organic-inorganic hybrid perovskites, where several different explanations (*e.g.* spatially localized quenchers/emitters, Auger recombination of photogenerated carriers with surface/interface traps, *etc.*) were proposed to explain the reasons behind the PL blinking.³⁴⁻³⁷ Fortunately, the discussions on the reason for PL blinking in inorganic CsPbX₃ NCs is much less scattered, and the PL blinking in this case is generally believed to be caused by fast nonradiative Auger decay of charged excitons. And hence vast

amount of previous work on colloidal NCs could provide useful insights into tackling the PL blinking in perovskite NCs.³⁸⁻⁴¹

Encouraged by the highly efficient PL of CsPbX₃ NCs, the possibility of using these NCs as inexpensive optical gain medium has been explored. As demonstrated in a recent report from Kovalenko and co-workers, thin films based on monodisperse CsPbX₃ NCs exhibit room temperature amplified spontaneous emission (ASE) with low pump thresholds in a range of 5 -22 $\mu\text{J cm}^{-2}$ and high values of model net gain of at least $450 \pm 30 \text{ cm}^{-1}$ (Fig. 5c and 5d).⁴² Wang et al. also reported a similar pump threshold of $\sim 22 \mu\text{J cm}^{-2}$ in the CsPbBr₃ system.⁴³ In comparison, such a low threshold was still impossible on precisely engineered core-shell colloidal CdSe QDs after intensive study for decades.⁴⁴ Only until recently, comparable ASE thresholds for inorganic colloidal NCs (6 $\mu\text{J cm}^{-2}$ at 520 nm and 8 $\mu\text{J cm}^{-2}$ at 635 nm) were achieved based on 2D atomically flat CdSe nanoplatelets.^{45, 46} Given the superb optical gain of CsPbX₃ NCs, whispering-gallery-mode lasing was successfully achieved in the CsPbBr₃ system by introducing a high quality cavity resonator. Moreover, random lasing mediated by light scattering on CsPbBr₃ NC aggregates was also observed.

The outstanding PL properties of CsPbX₃ perovskite NCs also make them promising candidates for low-cost solution-processed lighting sources. Zeng and co-workers reported LEDs using light emitters based on CsPbX₃ NCs.⁴⁷ As shown in Fig. 5e, in their device the poly (ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and poly (9-vinylcarbazole) (PVK) were used as the hole injection layers, and thin films of 2, 2', 2'' - (1,3,5-benzinetriyl)tris(1-phenyl- 1-*H*-benzimidazole) (TPBi) was vacuum deposited on top of the perovskite NC films, serving as the electron injection layer. The LEDs based on CsPbBr₃ NCs exhibited a maximum current efficiency of 0.43 ca A^{-1} and a champion external quantum efficiency (EQE) of 0.12% at a luminance of 100 cd m^{-2} (Fig. 5f). The electroluminescence of these devices can be easily tuned by changing the halide compositions in CsPbX₃ NCs, and

all the devices with different colours exhibited pure colours with the FWHM of ~ 20 nm. Although the device performance is much lower than what is expected from the high PLQY of CsPbX₃ NCs (50% to 90%), this work demonstrates great potential of CsPbX₃ NCs on LED applications.

4. Conclusions and outlook

These recent developments on perovskite NCs, as highlighted in this article, not only provide novel properties and applications for semiconducting metal halide perovskites, but also add a new class of members to the family of the colloidal NCs. These perovskite NCs, prepared through facile synthesis procedures, possess excellent emission properties, including easy tunability of the emission colour, narrow FWHM, and extremely high PLQY. As a result, in spite of a short development of only two years, perovskite NCs have shown great potential in applications of lasers, LEDs, single photon emitters, etc.

Along with these rapid developments, there are also serious challenges to be solved in order to push forward practical applications of perovskite NCs. For example, similar to traditional metal-chalcogenide NCs, novel approaches are needed to tailor the surface ligands and enhance the NC stability. For inorganic CsPbX₃ NCs, the PL blinking complicates their applications as single photon emitters. Furthermore, in spite of high PLQY, the LEDs based on both hybrid and inorganic perovskite NCs show very poor performance. Either novel modification of perovskite NCs or new device structures are required to make a step change in the device performance. Despite these challenges, we believe that the development of perovskite NCs has a bright future, especially considering that a vast amount of previous work on both perovskites and colloidal NCs may provide useful insights to tackle these challenges, helping to advance this field in the direction of practical technologies.

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Notes:

After submission of our manuscript, we noticed that a recent paper had improved the EQE of LEDs based on green emissive MAPbBr₃ QDs to a high value over 1%, demonstrating quick development of this promising area.⁴⁸ In this work, Zhong and co-workers employed a nonaqueous emulsion synthesis technique to prepare size tunable MAPbBr₃ QDs, which were then purified into solid-state powder for the fabrication of efficient perovskite LEDs.

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Figures:

Fig. 1 Schematic perovskite ABX_3 structure, where A (blue) is usually an organic MA (*e.g.* $CH_3NH_3^+$) or alkali metal (*e.g.* Cs^+) cation, the B cation (red) is usually Pb^{2+} or Sn^{2+} , and the anion X (yellow) is a halogen ion (Cl^- , Br^- , I^- or mixtures thereof) forming corner-shared BX_6 octahedra with the B cation.

Fig. 2 (a) The TEM image of one-step synthesized organic-inorganic MAPbBr₃ perovskite NCs with a mixture of nanodots and nanoplatelets. Reprinted with permission from ref. 24 Copyright 2015 American Chemical Society. (b) The TEM image of two-step synthesized organic-inorganic lead iodide perovskite spherical NCs, and (c) absorption and steady-state PL spectra of the 2D organic-inorganic lead iodide perovskites with $n=1$, 2 and 3. The PL was measured with an excitation wavelength of 480 nm. Reprinted with permission from ref. 26 Copyright 2015 Willey-VCH. (d) PLQE results of the perovskite NCs prepared with varying the ratio between methylammonium and octylammonium. Reprinted with permission from ref. 27 Copyright 2015 American Chemical Society.

Fig. 3 (a) Image of the perovskite crystal/polymer composite films emitting blue, green and red light under the UV lamp (365 nm) and (b) white light emission from the stacked perovskite crystal/polymer composite films on a blue LED (450 nm emission). Reprinted with permission from ref. 27 Copyright 2015 American Chemical Society. (c) The device structure for an LED device based on PVK:PBD hosted perovskite nanoplatelet light emitters and (d) current-voltage and brightness-voltage characteristics for devices based on perovskite nanoplatelets with varying PVK:PBD ratio. Reprinted with permission from ref. 28 Copyright 2015 Willey-VCH.

Fig. 4 (a) The image of all inorganic CsPbX₃ perovskite NC colloidal solutions in toluene under UV (365 nm) lamp and (b) the representative PL spectra (excited by 400 nm light but 350 nm for CsPbCl₃). Reprinted with permission from ref. 19 Copyright 2015 American Chemical Society. (c) Schematic of the halide anion-exchange process and suitable reagents used for the reaction. Reprinted with permission from ref. 30 Copyright 2015 American Chemical Society.

Fig. 5 Second-order PL intensity correlation functions measured from a single CsPbI₃ NC under (a) continuous-wave (7.9 W/cm² intensity) and (b) pulsed excitation. Reprinted with permission from ref. 32 Copyright 2015 American Chemical Society. (c) Threshold behavior for the intensity of the ASE band of the CsPbBr₃ NC film and (d) Variable stripe-length experiment for estimation of modal net gain for the CsPbBr₃ NC film. All spectra were excited at 400 nm with 100 fs laser pulses. Reprinted with permission from ref. 42 Copyright 2015 Nature Publish Group. (e) The schematic device architecture of LED devices based on inorganic CsPbX₃ perovskite NC emitters and (f) and current density and external quantum efficiency as a function of luminance for the fabricated CsPbBr₃ LEDs. Reprinted with permission from ref. 47 Copyright 2015 Willey-VCH.