INTRODUCTION

Metal halide perovskite materials have attracted great scientific and technological interest in recent years, due to their attractive optical and electronic properties combined with low cost and solution processability, which greatly contribute to their high potential for photovoltaic and light-emitting devices (LEDs). The earliest scientific work on perovskites was conducted in the late 70s by Weber, who characterized these materials in detail. Significant advances were made in the 90s and 2000s by Mitzi et al., leading to the first implementation of perovskites in devices. Interest seemed to subside for a while until the first reports on the utilization of organic–inorganic lead halide perovskites as sensitizers in solar cells in 2009 (Kojima et al.) and the demonstration of their light emission in 2012. Since then, many studies have contributed toward the fundamental understanding of this fascinating material and to its various technological applications as well. Halide perovskites have a general formula of ABX$_3$, where A and B are monovalent and divalent cations, respectively, and X is a monovalent halide (Cl, Br, I) anion. The three-dimensional (3D) crystal structure of lead halide perovskites is shown in Figure 1a, where the B cation, commonly Pb, but also Sn, is coordinated to six halide ions in an octahedral configuration. The octahedra are corner-sharing, with the A cation located in between those octahedra. Lead halide perovskites are further classified into either organic–inorganic (hybrid) or all-inorganic, depending on whether the A cation is an organic molecule, most commonly methylammonium (MA, CH$_3$NH$_3$), or an inorganic cation (commonly Cs$^+$), respectively. The optical and electronic properties of perovskites are tunable by varying the composition of constituted halide ions and to a smaller degree of the cations. In addition, the size and dimensionality of perovskites can also be used to tune their optical properties, similar to conventional metal chalcogenide semiconductors. Although perovskites can be obtained with dimensionality ranging from the 3D to 2D by varying the synthetic conditions used (Figure 1b), they have a strong tendency to form layered two-dimensional (2D) and quasi-2D structures (Figure 1c). Recent studies have shown that colloidal perovskite nanocrystals (NCs) can exhibit very high photoluminescence quantum yields (PL QYs) and strong quantum confinement effects when their dimensionality changes from 3D to 2D, offering additional tunability of optical properties. Perovskite NCs have already shown great promise in many applications such as lasers, LEDs and photovoltaic devices. Even though the research on perovskite NCs is still in its starting stage, they are expected to have a significant role in the development of modern nanoscience and nanotechnology in the near future. This review provides an overview of the up-to-date developments in the synthesis of hybrid organic–inorganic and all-inorganic perovskite NCs, their attractive optical properties and related emerging applications. After considering different synthetic approaches for the preparation of perovskite NCs with tunable optical properties (both direct synthesis and ion exchange-based routes), we follow up with a discussion of quantum confinement effects, single-particle emission and lasing studies. We
summarize recent developments on perovskite NCs employed as active materials in several applications such as LEDs, solar cells and photodetectors, and provide a critical outlook into the existing and future challenges.

**SYNTHESIS OF PEROVSKITE NCs**

**Direct synthesis of hybrid organic–inorganic perovskite NCs**

MA lead halide perovskite (MAPbX_3) nanoparticles were first explored as components of mesoporous titania-based dye-sensitized solar cells in 2009. By spin-coating a precursor solution containing MA halide and PbX_2 onto a TiO_2 thin film, perovskite NCs of 2–3 nm in size were formed. In 2012, a strong PL from such nanoparticles was observed, again in a mesoporous material, in this case synthesized by a template method. The two methods were similar, with a precursor solution spin-coated onto a porous Al_2O_3 film and a rapid crystallization of the perovskite on evaporation of the solvent in the latter case. This also constituted the first report on the preparation of luminescent perovskite NCs.

The first solution-based synthesis of colloidal MAPbBr_3 NCs was carried out by the Pérez-Prieto and colleagues, who employed medium-length alkyl chain organic ammonium cations, octylammonium bromide and octadecylammonium bromide as capping ligands to obtain luminescent NCs via the solvent-induced reprecipitation method. The role of these ligands was to provide a self-termination of the crystal growth on binding to the perovskite, however predominantly in one direction. The researchers were able to assign individual PL peaks to different crystal planes, and thus the size and shape of the NCs could be controlled. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3, indicating that the dispersions were not phase pure, but rather comprised of NCs of different sizes and shapes.

This approach was further refined by other groups, leading, for example, to the demonstration of efficient perovskite-based chemical sensors. Luo et al. used either octylammonium bromide or octadecylammonium bromide to produce perovskite NCs of 3.9 or 6.5 nm size, respectively, by means of the reprecipitation method. Although no mechanism for the size control was provided, we anticipate that the difference in size of NCs with different ligands was caused by their difference in ligand binding kinetics. The high solubility of longer hydrophobic chain ligands facilitates the increase of NC size compared with the size of NCs obtained by using short hydrophobic chain ligands. However, an in-depth study of the mechanism behind the size/shape-controlled growth of perovskite NCs would be highly valuable. Tyagi et al. employed a similar approach, synthesizing colloidal nanoplatelets of MAPbBr_3. They claimed that the excitonic-like features previously attributed to quantum confinement in spherical MAPbBr_3 nanoplatelets were in fact a property of the nanoplatelets with decremental thickness, down to a single unit cell. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3.

**Future challenges.**

This synthetic approach was subsequently adopted by several groups, leading, for example, to the demonstration of efficient perovskite-based chemical sensors. Luo et al. used either octylammonium bromide or octadecylammonium bromide to produce perovskite NCs of 3.9 or 6.5 nm size, respectively, by means of the reprecipitation method. Although no mechanism for the size control was provided, we anticipate that the difference in size of NCs with different ligands was caused by their difference in ligand binding kinetics. The high solubility of longer hydrophobic chain ligands facilitates the increase of NC size compared with the size of NCs obtained by using short hydrophobic chain ligands. However, an in-depth study of the mechanism behind the size/shape-controlled growth of perovskite NCs would be highly valuable. Tyagi et al. employed a similar approach, synthesizing colloidal nanoplatelets of MAPbBr_3. They claimed that the excitonic-like features previously attributed to quantum confinement in spherical MAPbBr_3 nanoplatelets were in fact a property of the nanoplatelets with decremental thickness, down to a single unit cell. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3.

This synthetic approach was subsequently adopted by several groups, leading, for example, to the demonstration of efficient perovskite-based chemical sensors. Luo et al. used either octylammonium bromide or octadecylammonium bromide to produce perovskite NCs of 3.9 or 6.5 nm size, respectively, by means of the reprecipitation method. Although no mechanism for the size control was provided, we anticipate that the difference in size of NCs with different ligands was caused by their difference in ligand binding kinetics. The high solubility of longer hydrophobic chain ligands facilitates the increase of NC size compared with the size of NCs obtained by using short hydrophobic chain ligands. However, an in-depth study of the mechanism behind the size/shape-controlled growth of perovskite NCs would be highly valuable. Tyagi et al. employed a similar approach, synthesizing colloidal nanoplatelets of MAPbBr_3. They claimed that the excitonic-like features previously attributed to quantum confinement in spherical MAPbBr_3 nanoplatelets were in fact a property of the nanoplatelets with decremental thickness, down to a single unit cell. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3.

This synthetic approach was subsequently adopted by several groups, leading, for example, to the demonstration of efficient perovskite-based chemical sensors. Luo et al. used either octylammonium bromide or octadecylammonium bromide to produce perovskite NCs of 3.9 or 6.5 nm size, respectively, by means of the reprecipitation method. Although no mechanism for the size control was provided, we anticipate that the difference in size of NCs with different ligands was caused by their difference in ligand binding kinetics. The high solubility of longer hydrophobic chain ligands facilitates the increase of NC size compared with the size of NCs obtained by using short hydrophobic chain ligands. However, an in-depth study of the mechanism behind the size/shape-controlled growth of perovskite NCs would be highly valuable. Tyagi et al. employed a similar approach, synthesizing colloidal nanoplatelets of MAPbBr_3. They claimed that the excitonic-like features previously attributed to quantum confinement in spherical MAPbBr_3 nanoplatelets were in fact a property of the nanoplatelets with decremental thickness, down to a single unit cell. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3.

This synthetic approach was subsequently adopted by several groups, leading, for example, to the demonstration of efficient perovskite-based chemical sensors. Luo et al. used either octylammonium bromide or octadecylammonium bromide to produce perovskite NCs of 3.9 or 6.5 nm size, respectively, by means of the reprecipitation method. Although no mechanism for the size control was provided, we anticipate that the difference in size of NCs with different ligands was caused by their difference in ligand binding kinetics. The high solubility of longer hydrophobic chain ligands facilitates the increase of NC size compared with the size of NCs obtained by using short hydrophobic chain ligands. However, an in-depth study of the mechanism behind the size/shape-controlled growth of perovskite NCs would be highly valuable. Tyagi et al. employed a similar approach, synthesizing colloidal nanoplatelets of MAPbBr_3. They claimed that the excitonic-like features previously attributed to quantum confinement in spherical MAPbBr_3 nanoplatelets were in fact a property of the nanoplatelets with decremental thickness, down to a single unit cell. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3.

This synthetic approach was subsequently adopted by several groups, leading, for example, to the demonstration of efficient perovskite-based chemical sensors. Luo et al. used either octylammonium bromide or octadecylammonium bromide to produce perovskite NCs of 3.9 or 6.5 nm size, respectively, by means of the reprecipitation method. Although no mechanism for the size control was provided, we anticipate that the difference in size of NCs with different ligands was caused by their difference in ligand binding kinetics. The high solubility of longer hydrophobic chain ligands facilitates the increase of NC size compared with the size of NCs obtained by using short hydrophobic chain ligands. However, an in-depth study of the mechanism behind the size/shape-controlled growth of perovskite NCs would be highly valuable. Tyagi et al. employed a similar approach, synthesizing colloidal nanoplatelets of MAPbBr_3. They claimed that the excitonic-like features previously attributed to quantum confinement in spherical MAPbBr_3 nanoplatelets were in fact a property of the nanoplatelets with decremental thickness, down to a single unit cell. They found that the absorption peak of their perovskite NC dispersion was blue-shifted by 0.5 eV with respect to the absorption onset of the bulk MAPbBr_3.
they choose a reverse way of the reagent mixing: the nanoparticles were formed with n-octylamine and oleic acid as ligands through addition of the perovskite precursors in a good solvent, for example, dimethylformamide or γ-butyrolactone, into a bad solvent, for example, toluene or acetone, as shown in Figure 3a. It was assumed that n-octylamine controls the kinetics of crystallization and mainly contributes to the size control of NCs formed, whereas oleic acid suppresses aggregation effects and ensures their colloidal stability. From transmission electron microscope (TEM) studies, MAPbBr₃ NCs were quasi-spherical and had an average diameter of 3.3 ± 0.7 nm (Figure 3b). The authors reasoned that the increased PLQY of the NCs with respect to micrometer-sized bulk perovskite particles resulted from higher excitonic binding energies of up to nearly 400 meV, when the size of the NCs approached the Bohr radius of the respective perovskite, on the order of 13–30 Å, depending on the material.²⁵,⁴⁷,⁴⁸ By replacing the bromide anion with chloride or iodide, or by using mixtures of the three anions, the authors were able to obtain perovskite NC dispersions emitting throughout the full range of the visible spectrum (Figure 3c). The average PL lifetimes of these NCs were considerably shorter than for the respective bulk films.

Signs of strong 3D quantum confinement in 0D perovskite NCs were recently observed in the work by Huang et al.²⁹ (Figure 3d). Herein, the re-precipitation technique was used to prepare MAPbBr₃ NCs with tunable emission by altering the temperature of the bad solvent. A certain amount of the perovskite precursor solution with oleylamine as the organic ligand was quickly injected under vigorous stirring into the toluene, which had been pre-cooled or heated to specific temperatures between 0 and 60 °C. The PL emission wavelength of the resulting NCs ranged from 475–520 nm, with a high PLQY of 74 to 93%, and short radiative lifetimes of only 13–27 ns in comparison with non-radiative lifetimes of 100 ns and longer.

Methods such as emulsion synthesis⁴⁹ and electrospray technique coupled antisolvent–solvent extraction⁵⁰ have been used for the synthesis of perovskite NCs of different morphologies, mostly yielding rather polydisperse nanoparticles. It has been shown that nearly
monodisperse blue-emitting nanoplatelets and green-emitting nanorods can be prepared in 1-octadecene at high temperature. Micro-crystals and NCs comprising layered quasi-2D perovskites in the form of $A_2PbX_4$, $A_4PbX_6$ and $A(A')_2Pb_2X_7$ were also reported to be luminescent. Chen et al. synthesized nano- and micro-sized MAPbI$_3$ perovskite crystals by using mild heating of MAI and PbI$_2$ in different polar solvents. By using solvents with different polarities, MAPbI$_3$ NCs of different shapes (cubes, rods and hexagons) were obtained. Zhu et al. reported different morphologies for MAPbX$_3$ NCs with shape-correlated PL by varying the solvents and using different capping ligands. The same group were also the first to report on the instability of perovskite nanostructures under the electron beam in TEM measurements, warning on the correlation of the morphology observed in the TEM with the actual shape of nanoparticles in colloidal dispersions. This was further corroborated by studies of Sichert et al. who showed that the electron beam could degrade the perovskite nanoplatelets, producing small spherical particles comprising metallic lead or lead bromide.

Several fabrication techniques have been developed for the growth of organic–inorganic perovskite nanowires (NWs) directly.
on substrates. Spina et al.\textsuperscript{57} have shown that NW arrays can be grown in open nanofluidic channels; using this approach, the size, aspect ratio, cross-sectional shape and orientation of NWs could be controlled. Solution processed perovskite films grown on substrates could be converted into NWs via dissolution and recrystallization, as demonstrated by Zhu et al.\textsuperscript{58} Yuan et al.\textsuperscript{59} reported deep blue-luminescent layered lead bromide perovskite microdisks, a few micrometers in size laterally and 15–100 nm-thick with a PLQY reaching 50%. The same group also reported nanoscale quasi-2D layered perovskites with tunable emissions from 403 to 530 nm by changing the organic cations used.\textsuperscript{60}

**Direct synthesis of all-inorganic perovskite NCs**

Perovskite NCs with all-inorganic cations have been receiving significant attention, partly due to their higher stability compared with the hybrid organic–inorganic perovskites. Kovalenko and colleagues\textsuperscript{24} were first to report on caesium lead halide perovskite NCs (CsPbX\textsubscript{3}, X = Cl, Br and I), with a high degree of compositional bandgap engineering. They were produced as monodisperse nanocubes with edge lengths of 4–15 nm using the arrested precipitation of Cs-oleate and Pb(II)-halide precursors in octadecene. It was found that the size of the NCs decreases by decreasing the reaction temperature. Mixed-halide perovskite NCs could be conveniently produced by varying the ratios of precursor salts (PbCl\textsubscript{2}/PbBr\textsubscript{2} or PbBr\textsubscript{2}/PbI\textsubscript{2}). CsPbX\textsubscript{3} NCs crystallized in the cubic phase rather than the orthorhombic or tetragonal phases at high temperatures (Figures 4a and b). The bandgap energies and emission spectra of these NCs were tuneable over the entire visible spectral region of 410–700 nm by varying the halide composition and the size of the NCs (Figures 4c and d). The PL of CsPbX\textsubscript{3} NCs was characterized by narrow emission linewidths of 12–42 nm, a wide colour gamut covering up to 140% of the National Television System Committee color standard, high PLQYs of up to 90% and PL lifetimes in the range of 1–29 ns (Figure 4e). Later on, by means of a droplet-based microfluidic platform, allowing for online absorption/PL measurements, the same group explored the formation mechanism of these perovskite NCs.\textsuperscript{61} Koolyk et al.\textsuperscript{62} investigated the growth process of caesium lead halide perovskite NCs by time-dependent TEM characterization. They found that the growth kinetics are different for CsPbBr\textsubscript{3} and CsPbI\textsubscript{3}, providing a model for each growth process. From the full width at half maximum (FWHM) of the PL spectra, it was observed that CsPbI\textsubscript{3} NCs exhibited size focusing during the first 20 s of growth, followed by a subsequent size de-focusing (the FWHM increased due to the broadening size distribution). On the contrary, CsPbBr\textsubscript{3} NCs exhibited a de-focusing of the size distribution from the beginning of the reaction and no size focusing occurred within the full reaction time of 40 s. However, a prolonged reaction at higher temperatures leads to the formation of light-emitting single-crystalline CsPbX\textsubscript{3} NWs that crystallize in the orthorhombic phase as reported by Yang and colleagues\textsuperscript{63} (Figures 4f–h). The initially formed cubic NCs transformed into NWs with a few percent of nanosheets as a side product for the prolonged reaction time.

In addition to the hot-injection technique, room-temperature reprecipitation methods have also been used for the synthesis of CsPbX\textsubscript{3} NCs of different morphologies. For instance, Huang et al.\textsuperscript{49} reported the emulsion-based synthesis of perovskite NCs (both hybrid and all-inorganic) at room temperature. In a recent report Li et al.\textsuperscript{64} reported the emulsion-based synthesis of perovskite NCs (both hybrid and all-inorganic) at room temperature. In a recent report Li et al.\textsuperscript{64} reported the emulsion-based synthesis of perovskite NCs (both hybrid and all-inorganic) at room temperature.
showed that CsPbX₃ NCs can be synthesized at room temperature, similar to the LARP method used for the MAPbX₃ system. Manna and colleagues⁶⁵ have demonstrated the synthesis of quantum-confined CsPbBr₃ nanoplatelets at room temperature. They have shown that anisotropic growth leads to the formation of nanoplatelets at room temperature through the injection of acetone in a mixture of precursor. The low growth temperature facilitates the control of the plate thickness down to three monolayers. In addition, it was shown by Sun et al.,⁶⁶ that the shape of the NCs could be controlled using different ligand molecules. In this regard, CsPbX₃ NCs of different shapes such as spherical dots, nanocubes, nanorods and nanoplatelets were prepared by using different organic acids and amine ligands; however, the growth mechanism was not discussed. The room-temperature solution-phase synthesis of nanoplatelets can be easily scaled up as shown by Yu and colleagues.⁶⁶ Driven by the wish to replace the toxic lead, Lelioce et al. synthesized CsSnX₃ perovskite NCs, with optical properties tunable both by quantum confinement and halide composition.⁶⁷ The overview of reported studies clearly demonstrates that reaction temperature and the choice of ligands play a vital role in determining the dimensionality and size of colloidal metal halide perovskite NCs. In general, low reaction temperatures and high ligand concentrations favor anisotropic growth, mainly producing nanoplatelets with controlled thickness and lateral sizes.

**Synthesis of perovskite NCs through halide ion exchange reactions**

A post-preparative halide ion exchange on perovskite NCs provides an additional means to modify their composition and thus the optical properties, while preserving their size and morphology. Kovalenko and colleagues⁶⁸ and Manna and colleagues⁶⁹ have almost simultaneously reported this approach for CsPbX₃ (X = Cl, Br, I) NC systems, tuning their emission over the spectral range of 410 – 700 nm with high PLQYs of 20 – 80% (Figures 5a and b). Such anion exchange was also reported for hybrid MAPbBr₃ NCs, which were synthesized in an approach similar to that of Pérez-Prieto and colleagues,⁷⁰ and subsequently mixed with methyl ammonium halide (Cl or I) to produce MAPbBrₓ−ₓClₓ or MAPbBrₓ−ₓIₓ NCs (Figure 5c).⁷¹ The UV-visible absorption and PL emission of both colloidal solutions and films confirmed the composition control of the exchange reaction, demonstrating band gap tuning over the whole visible range (Figure 5d). The anion exchange is also possible in the solid phase as demonstrated by Yang and colleagues.⁷¹ Following a solution-phase growth of MAPbBr₃ nanorod arrays, they were subsequently converted to MAPbI₃ of similar morphology via annealing at 140–150 °C in MAI vapour. The MAPbBr₃ nanorod array exhibited a green electro-luminescence at 533 nm with a FWHM of 26 nm, whereas the MAPbI₃ emitted at 782 nm.

**OPTICAL PROPERTIES OF PEROVSKITE NCs**

Metal halide perovskite NCs exhibit intriguing optical properties, such as high PLQYs and a narrow emission spectrum, which is tunable as high PLQYs and a narrow emission spectrum, which is tunable values for bulk layered perovskites.⁴³,⁸⁸,⁸⁹ Thus, it is possible to tune the optical properties of perovskite nanoplatelets by controlling the number of layers. Similar effects have been also reported by other groups.⁴²,⁴⁶,⁵¹,⁵⁹ For instance, Snait and colleagues⁸⁶ used the same approach to demonstrate tunable PL from MAPbI₃ NCs. The increase of octylammonium content in the reaction medium resulted similarly in the formation of nanoplatelets.

Friend and colleagues⁸⁸ observed size-dependent photon emission from MAPbBr₃ NCs embedded in an organic matrix, where the NC size and thus their PL peak could be tuned by varying the concentration of the precursors. The PL peak gradually shifted to higher energies with decreasing particle size. Hassan et al.⁸⁶ showed tunable PL from metal halide perovskite NCs by varying the number of layers, starting...
from pre-synthesized NC seeds by a controlled addition of alkyl ammonium halide. As shown in Figure 7a, the resulting MAPbI3 NCs emit green, orange and red colors for 1, 2 and 3 layers, respectively. Sapori et al.87 performed a theoretical study on the quantum confinement in 2D perovskite NCs composed of different cations and halide ions. Their results, showing an increase of the band gap with the number of layers in the nanoplatelets decreases, are in good agreement with the experimental results discussed above (Figure 7b).

In addition to solution-based colloidal synthesis, NCs of different sizes were grown on solid substrates.85 Yang and colleagues91 have shown that atomically thin single-crystalline 2D organic–inorganic perovskites of square-shaped morphology can be directly grown on silicon substrates by drop casting a very dilute precursor solution followed by mild heating (Figures 7c–e). AFM images showed that the prepared 2D (C6H5NH3)2PbBr4 sheets exhibit single to few unit cell thicknesses due to the stacking of layers through van der Waals interactions between ligands (Figure 7e). The stacking effect had only a minor effect on the optical properties as stacks of varying thicknesses due to the stacking of layers through van der Waals interactions between ligands (Figure 7e). The stacking effect had only a minor effect on the optical properties as stacks of varying thicknesses due to the stacking of layers through van der Waals interactions between ligands (Figure 7e). This emission was still considerably blue shifted with respect to the PL peak of the bulk perovskite due to the quantum confinement effect.

Quantum confinement effects have also been reported for all-inorganic CsPbX3 NCs. Kovalenko and colleagues24 reported size-dependent PL emission from square-shaped CsPbBr3 NCs, in which the PL peak gradually blue shifted from 512 to 460 nm as the edge size decreased from 11.8 to 3.8 nm. Alivisatos and colleagues92 reported the synthesis of quantum-confined highly fluorescent (PLQY 84%) CsPbX3 perovskite nanoplatelets (Figures 6c–e). They showed that the thickness of CsPbBr3 nanoplatelets can be tuned from 1 to 5 unit cells thick by changing the reaction temperature, with the monolayer platelets emitting at 400 nm (Figure 6c), whereas the bulk-like crystals emitted at 520 nm (Figure 6d). Similarly, Manna and colleagues65 have shown that the thickness of CsPbBr3 platelets could be precisely tuned between 3 and 5 monolayers, keeping a narrow emission and a strong blue shift of the PL peak compared with that of bulk CsPbBr3. In addition, they have also shown that the lateral size of the quantum-confined CsPbBr3 nanoplatelets (thickness ~ 3 nm) can be controlled up to the micrometer range by varying the ratio of shorter ligands (octanoic acid and octylamine) to longer ligands (oleic acid and oleylamine), while maintaining their thickness and, to a large degree, the optical properties.93

**Single-particle emission of perovskite NCs**

Most of the studies discussed above have been performed on ensembles of perovskite NCs. However, single-particle measurements are sometimes necessary, in order to obtain accurate correlations between their optical properties and size/morphology.27,71,94–99 Tian et al.100 provided direct visualization of the photogenerated carrier diffusion in single MAPbBr3 and MAPbI3 NWs and nanoplatelets using time-resolved PL-scanning microscopy (Figures 8a–e). This technique is based on the photoexcitation of a single particle at one specific position and subsequently scanning the substrate at different positions by time-resolved PL as a function of delay time. The diffusion lengths, averaged for holes and electrons, for MAPbI3 and MAPbBr3 were found to be 14.0 ± 3.1 and 6.0 ± 1.6 μm, respectively. Another interesting phenomenon that has been addressed by single-particle studies of perovskite NCs is emission blinking.96–98 Fluorescence intermittency (blinking) has been widely observed in metal-chalcogenide quantum dots, which can remain in so-called ‘dark states’ for significant times, ranging from microseconds up to several minutes.101,102 Blinking is generally thought to result from light-driven charging (or ionization) and discharging of the colloidal NC core or of surface electron traps on photoexcitation. The neutral semiconductor NCs appear bright when photoexcited electron-hole pairs recombine, emitting photons. However, charging of NCs can promote Auger recombination and trap states can bind charge.
carriers, preventing recombination, all of which has been considered to contribute to blinking.\textsuperscript{102–104} Tian \textit{et al}.\textsuperscript{98} observed PL blinking from MAPbI\textsubscript{3} nanorods (Figures 8h–j) and attributed it to photo-induced activation and de-activation of PL quenching sites, presumably present at the ends of the rods where formation of geometrical and chemical defects are most likely to occur. Similarly, blinking was also observed in single perovskite MAPbBr\textsubscript{3} NCs and attributed to the presence of charge trapping surface states.\textsuperscript{97} Blinking was also seen in all-inorganic CsPbX\textsubscript{3} perovskite NCs (Figure 8f).\textsuperscript{94–96} It was observed that the FWHM of the PL of single CsPbBr\textsubscript{3} NCs is nearly the same as that of the ensemble PL spectrum, indicating that the size distribution does not alter their optical properties significantly. This was ascribed to the fact that the charge carriers are only weakly Bohr radius confined for the particle size studied (11 nm), which exceeds the exciton of CsPbBr\textsubscript{3}.\textsuperscript{36} As shown in Figure 8g, individual CsPbBr\textsubscript{3} NCs show fast recovery times from the off- to on-state, with the on-states dominating. However, eliminating the blinking behaviour in perovskite NCs is crucial for advancing their applications for LEDs and in biosystems. Over the years, various strategies have been proposed to eliminate the blinking in conventional semiconductor NCs. One of the most widely employed solutions is based on suppression of ionization by growing a thick semiconductor shell on the NC surface. Being a relatively new field, there have not been any studies yet on reducing blinking in perovskites. Some studies have shown that CsPbX\textsubscript{3} (where X = Cl/Br) NCs seem to be less prone to blinking and display stable emission at low temperatures.\textsuperscript{105} Nevertheless, it seems as the problems associated with photostability and blinking of perovskite NCs are largely similar to those of conventional semiconductor quantum dots. Therefore, resolving the issue by applying the methodologies developed over the years for semiconductor NCs is of a great relevance.

Amplified spontaneous emission and lasing with perovskite NCs
Perovskites are considered an attractive class of materials for lasing, owing to their large absorption coefficients, slow Auger recombination and high optical gain.\textsuperscript{10,37} Xing \textit{et al}.\textsuperscript{10} observed a stable amplified spontaneous emission (ASE) at low thresholds from solution processed thin films comprising MA-based perovskites. The wavelength of ASE could be tuned across the whole visible and near-IR spectral range by varying the halide ion content of perovskites, as for the regular PL emission.\textsuperscript{10} Despite the ease of fabrication of bulk perovskite films by solution processing, they exhibit relatively low PLQYs, limiting further applications in this respect. High PLQY is one of the main advantages of the colloidal perovskite NCs, prompting researchers to perform intensive investigations for their use as optical gain media for lasing.\textsuperscript{13,34,36,37,106–108} Zhu \textit{et al}.\textsuperscript{13} have demonstrated wavelength-tunable lasing from single-crystalline organic–inorganic lead perovskite NWs with low thresholds (\textasciitilde 220 nJ cm\textsuperscript{−2}) and high quality factors of $Q \sim 3600$ (Figures 9a–c). The narrowing of the FWHM in the PL spectra by two orders of magnitude above an excitation fluence threshold presented a clear sign of lasing (Figure 9b). Time-resolved fluorescence analysis indicated that charge carrier trapping was
**Figure 8** (a) Schematic illustration of fluorescence scanning confocal microscopy set-up for visualizations of the charge carrier diffusion in perovskite plates. (b) Schematic representation of the charge carrier excitation and probing the diffusion, and recombination processes. (c) Optical (the red spot indicates the laser excitation spot) and (d) PL intensity images of a CH₃NH₃PbI₃ plate ('A' indicates the position where the PL kinetics is probed with respect to time delay). Scale bar: 5 μm. (e) PL kinetics obtained from the position 'A' (blue squares). Solid green curve is PL decay collected from the entire plate, which was used to estimate the wave-guided component for subtraction. Red curve represents the net kinetics at position A after subtracting the wave-guided contribution. The inset shows the PL kinetics collected from excitation site. Reproduced from Tian et al.100 (f) PL image and intensity line profiles of individual CsPbBr₃ NCs. (g) PL intensity fluctuation versus time for three typical single NCs marked in the part (f). Reproduced from Swarnkar et al.96 (h) PL image of individual CH₃NH₃PbI₃ NCs. (i) PL intensity fluctuation of a typical CH₃NH₃PbI₃ NC vs time and (j) the positions of corresponding emission localization. Reproduced from Tian et al.98

**Figure 9** (a) Illustration of a single CH₃NH₃PbI₃ NW on SiO₂ substrate pumped under a laser excitation: (i) optical image (ii) and PL image of this NW below (iii) and above (iv) threshold (scale bar: 10 μm). (b) PL spectra of a CH₃NH₃PbI₃ NW at different pump fluences. The inset shows the integrated PL intensity and FWHM as a function of pump fluences. (c) Tunable lasing emission wavelengths from MA-based perovskite NWs made of mixed lead halides. Reproduced from Zhu et al.13 (d) PL spectra of CsPbBr₃ NCs at different pump fluences, showing ASE at higher fluences. (e) Tunable ASE from caesium lead mixed halide perovskite NCs. (f) Stripe-length-dependent ASE measurement for the estimation of net gain for CsPbBr₃ NC film. (g) Lasing from CsPbBr₃ NC film: Evolution of PL spectra into whispering-gallery-mode lasing with increasing pump fluence in a film covered on top of microsphere resonator. Reproduced from Yakunin et al.37
minimal, with a lasing QY of nearly 100%. Interestingly, the NWs emitted nearly uniformly across their whole length at low pump fluences (Figure 9a (iii)), whereas the emission predominantly came from the ends when excited above the lasing threshold (Figure 9a (iv)). The stability of NWs was low, as they degraded under continuous illumination after a few tens of minutes, likely to be due to a build-up of heat. Fu et al.\textsuperscript{106} have found that formamidinium lead halide perovskite NWs exhibit higher thermal stability under continuous pulsed excitation compared with MA-based perovskite NWs. Xing et al.\textsuperscript{108} reported lasing from hybrid perovskite NWs produced by vapour-phase synthesis. Two-photon excitation can also lead to lasing in perovskite wires at low thresholds (674 $\mu$J cm$^{-2}$), with quality factors of $Q \sim 682$. Other morphologies of hybrid perovskites such as microdisks have also been shown to produce efficient optical gain.\textsuperscript{107,109}

All-inorganic perovskite NCs, with high PLQYs and greater stability, have also been explored as a potential optical gain medium. Kovalenko and colleagues\textsuperscript{37} demonstrated wavelength tunable low-threshold ASE and lasing from colloidal caesium lead halide perovskite NCs at room temperature (Figures 9d–g). The lasing threshold and the modal net gain (estimated from the variable stripe-length experiment shown in Figure 9f) were found to be $5 \pm 1 \mu$J cm$^{-2}$ and $450 \pm 30$ cm$^{-1}$, respectively. The authors also reported whispering-gallery-mode lasing on silica microsphere resonators coated with CsPbBr$_3$ NCs (Figure 9g), whereas thin films of the NCs showed random lasing.\textsuperscript{37} Suspensions of such NCs showed ASE and lasing when infiltrated into a capillary tube.\textsuperscript{110} Wang et al.\textsuperscript{36} demonstrated low-threshold one-, two- and multi-photon pumped ASE from 9 nm CsPbBr$_3$ NCs with large two-photon absorption cross-sections. These studies indicate that both hybrid and inorganic perovskite NCs are promising for low-threshold laser devices.

**APPLICATIONS OF PEROVSKITE NCs**

**Perovskite NCs in LEDs**

Tunable emission with high PLQY, low cost and solution processability of perovskite NCs make them attractive for use in LEDs.\textsuperscript{9} Metal halide perovskite-based LEDs have been fabricated both by solution processing and chemical vapor deposition methods. Perovskite materials were incorporated into LEDs functioning at liquid nitrogen temperature back in 90s\textsuperscript{111} and room temperature-working bright LEDs were fabricated by solution processing of hybrid perovskites by Tan et al.\textsuperscript{9} In this device, emitting in the IR, a solution-processed CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$ perovskite layer was sandwiched between TiO$_2$ and poly(9,9-dioctylfluorene) (F8) layers for effective radiative recombination of electrons and holes in the perovskite layer. The device produced a radiance of 13.2 W sr$^{-1}$ m$^{-2}$ at a current density of 363 mA cm$^{-2}$, with internal and external quantum efficiencies of 3.4% and 0.76%, respectively. Using the bromide perovskite, an LED operating in the green was fabricated with an architecture of ITO/PEDOT:PSS/CH$_3$NH$_3$PbBr$_3$/F8/Ca/Ag, producing a luminance of 364 cd m$^{-2}$ at a current density of 123 mA cm$^{-2}$. LEDs based on perovskite NCs, which have significantly higher quantum efficiencies than bulk perovskite films, are expected to exhibit far superior performance.\textsuperscript{32,38} Gao and colleagues\textsuperscript{32} reported bright green LEDs using MAPbBr$_3$ nanocrystals in a device made of glass/ITO/ PEDOT: PSS/CH$_3$NH$_3$PbBr$_3$/F8/Ca/Ag, producing a luminance of 647 cd m$^{-2}$ at a current density of 170 mA cm$^{-2}$. LEDs based on perovskite NCs, which have significantly higher quantum efficiencies than bulk perovskite films, are expected to exhibit far superior performance.\textsuperscript{32,38}
electron transport and hole/exciton blocking layer. Integration of a bipolar host layer PVK:PBD (poly(9-vinylcarbazole):2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole) improved the film morphology, charge transport and recombination, resulting in a luminance of 10 590 cd m\(^{-2}\) with a maximum power conversion efficiency of 1 l mW\(^{-1}\). The performance of LEDs depends on the radiative recombination of electrons and holes in the active layer, where the film morphology has a vital role.\(^{32,112}\) Incorporation of perovskite NCs into a dielectric polymer matrix may help to reduce non-radiative current losses, as demonstrated by Di et al.\(^{85}\) Perovskite NW arrays have also been used for the fabrication of LEDs with a device structure of glass/ITO/PEDOT:PSS/CH\(_3\)NH\(_3\)PbBr\(_3\)-NWs/F8/Ca/Ag, as demonstrated by Yang and colleagues.\(^{71}\)

Recently, LEDs based on all-inorganic perovskite NCs have also been demonstrated. Song et al.\(^{35}\) reported on wavelength tunable LEDs with sharp emission spectra based on CsPbX\(_3\) NCs. For the device structure of ITO/PEDOT:PSS/CH\(_3\)NH\(_3\)PbBr\(_3\)-NWs/F8/Ca/Ag, as demonstrated by Yang and colleagues.\(^{71}\)

Perovskite NCs in solar cells and photodiodes
Perovskite-based solar cells have become one of the hottest research fields since the report published by Miyasaka and colleagues.\(^{6}\) Intense research efforts have led to a rapid increase in power conversion efficiencies to over 20% within a span of only 5 years, with the current certified record being listed at over 22% by Sang Il Seok’s group.\(^{115,116}\) Although most of the reported efficient solar cell devices are based on perovskite films, there have been several recent attempts in employing perovskite NCs as active materials, too. Im et al.\(^{117}\) reported the fabrication of solar cells using MAPbI\(_3\) NWs (Figure 11a) prepared by an aprotic solvent-assisted two-step spin coating process. The maximum power conversion efficiency of these solar cells reached 14.7% using the device architecture of FTO/compact TiO\(_2\)/mesoporous TiO\(_2\)+MAPbI\(_3\)-NW-MAPbI\(_3\)+Spiro-MeOTAD/Au (Figure 11a). It was also found that 1D NWs exhibited faster carrier and higher lateral conductivity compared with bulk 3D perovskites. Mali et al.\(^{33}\) fabricated MAPbBr\(_3\) NC-based solar cells with a power conversion efficiency of 11.4% using FTO/Bi-TiO\(_2\)/mp-TiO\(_2\)+MAPbBr\(_3\) (~2 nm NCs)/PTAA/Au as a device configuration (Figure 11b). In this fabrication method, MAPbBr\(_3\) NCs were prepared by spin coating a dimethyl sulfoxide solution of MA bromide and PbBr\(_2\) onto a
mesoporous TiO$_2$ layer followed by annealing on a hot plate. These devices were found to be stable for up to 4 months. Solar cells comprising all-inorganic perovskite NCs (CsPbI$_3$) have reached efficiencies of 9.8%, still significantly lower than solar cells made of hybrid perovskite NCs.$^{118}$

Most of the semiconductor materials displaying high photoconversion efficiencies can act as efficient photodetectors. In light of this, perovskite NCs have also been employed as broadband photodetectors, even though this research field is rather new.$^{119,120}$ Yang and colleagues$^{121}$ reported solution-processed photodetectors based on MAPbI$_3$$_{x}$Cl$_{1-x}$ films with an inverted device configuration made of glass/ITO/PEDOT:PSS/MAPbI$_3$-CN/meso-PCBM ([6,6]-Phenyl-C61-butyric acid methyl ester)/PPN poly[(9,9-bis(30-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioclylfluorene)] (hole blocking layer)/Al. The photodetector operating at room temperature showed excellent detection sensitivity approaching $10^{14}$ Jones with a fast photoresponse and a linear dynamic range over 100 dB. Perovskite NWs have also been used for the fabrication of visible-light photodetectors, as reported by Zhang and colleagues$^{120}$ (Figures 11c–e). Their device was made by depositing perovskite NWs on a gold interdigital electrode comprising 14 pairs of fingers with adjacent intervals of ~150 μm. MAPbBr$_3$ NWs were prepared via self-templated directed approach, in which Pb-containing precursor NWs were first synthesized and then transformed into perovskite wires by reacting with an isopropanol solution containing CH$_3$NH$_2$Br and HBr. Porous MAPbBr$_3$ NWs employed in these cells exhibited superior optoelectronic activity with a fast photo-response and decay times. In spite of these early demonstrations, there is a lot of scope for improving their device performances by controlling the NC morphology and device architectures.

**SUMMARY AND OUTLOOK**

During the last few years, perovskite materials have received great attention; first, in the form of thin films and most recently as colloidal NCs. Our review introduces the common synthetic strategies for the fabrication and control over the size and morphology of both hybrid organic/inorganic and all-inorganic perovskite NCs. Their fascinating optical properties were investigated, both in the ensemble and on the single-particle level. These properties have inspired the use of perovskite NCs in lasers and LEDs, solar cells and photodetectors.

In spite of the impressive progress in all the areas related to perovskite NCs, there are still several challenges to be addressed. Similar to their thin film counterparts, the stability of perovskite NCs is an important issue, as they tend to degrade rapidly. Degradation can happen due to several external factors, for example, moisture, oxygen, high temperature and UV light. The related mechanisms are not yet completely understood, limiting the possibilities of preventing degradation from happening. In terms of degradation due to moisture, this is inherent to the metal halide perovskites, which are easily dissolled in polar solvents, in particular water. UV light possibly enhances ion migration in the perovskite or leads to the formation of free radicals. In the immediate future, researchers need to focus on either encapsulating NCs to prevent degradation or changing their chemical composition to obtain an intrinsic stability, especially to high temperatures and water. In addition, the halide ion exchange in between perovskite NCs made of different halides has been detrimental to the fabrication of white LEDs. This problem requires immediate attention for advancing the field of perovskite LEDs. Very recently, we and others have demonstrated that the encapsulation of perovskite NCs in a polyhedral oligomeric silsesquioxane matrix or a mesoporous silica shell not only prevents this halide exchange, but also enhances the water resistivity of the NCs.$^{122–125}$ In addition, perovskite NCs are extremely sensitive and tend to degrade or transform in to other compounds (such as metallic lead) under exposure to electron beams.$^{25}$ The exact mechanisms of these transformations need to be investigated, as TEM studies are crucial for unambiguous characterization of the morphology of perovskite NCs. A recent study by Milosavljević et al.$^{126}$ showed that even a low-energy electron beam can induce structural and chemical transformations in MAPbI$_3$. The transformations were attributed to the decomposition of perovskites through the interaction of the electrons with the organic cation of perovskites, leading to the formation of PbI$_2$ and polymer hydrocarbon residue (–CH$_2$–) on the surface. On the other hand, inorganic metal halide perovskites seem to be more stable under low-energy electron illumination, enabling high-resolution TEM characterization. Nevertheless, they can still degrade under a high-energy electron beam, similarly leading to the formation of small dots on the NC surface. An accurate characterization of the elemental composition after degradation of particles would provide better understanding of degradation mechanism; however, it is likely to be metallic lead or lead halide, as observed in previous studies.$^{25}$

Apart from the stability issues, there are a number of other challenges related to perovskite NCs. Foremost is the desire to eliminate toxic lead from both hybrid and all-inorganic perovskites, either produced in nanoparticle form or as thin films. This is especially necessary for upscaling the perovskite fabrication for widespread photovoltaic use. There have been some attempts to use tin instead of Pb, but this element is also not non-toxic and very unstable, as Sn (II) can easily be oxidized, transforming to the Sn(IV) state. CsSnX$_3$ NCs have been prepared using synthesis methods developed for their lead-containing counterparts; however, the particles degrade within a few hours after preparation. Finding methods for enhancing the viability of lead-free perovskites deserves more attention in the future.

A better control over dimensionality and size of perovskite NCs during synthesis is one of the critical issues for understanding structure–property relationships, as well as advancing their applications. The formation of perovskites occurs extremely rapidly, making a study of the intermediate particles difficult, which could aid in understanding the growth mechanisms. Although there have been some studies showing an ability to control the shape of the perovskite particles to some degree, a full understanding of their nucleation and growth mechanisms is still lacking. Hybrid perovskite NCs seem especially difficult to control, often yielding rather polydisperse NCs, whereas inorganic NS tend to be more monodisperse with better control over size and dimensionality. Syntheses of nanoplatelets often produce mixtures of nanoplatelets with different thickness, which have proven to be difficult to separate, limiting studies aiming to understand the thickness-dependent optical properties of perovskite nanoplatelets.$^{25,52}$ In spite of these difficulties, theoretical models have been developed to understand the quantum size effects of perovskite NCs and, with some improvement, experimental studies will be able to confirm or refute these results.$^{25,87}$

In spite of the recent advances in synthesis, not many studies exist concerning the photophysics of perovskite NCs; this area will definitely become more active and studies exploring carrier relaxation and charge transfer processes will follow. Such studies will help us to better understand and control not only the optical properties of perovskite NCs but also their electronic character, which is necessary to maximize the efficiency in many device types. Although the recombination mechanisms of photoexcited charge carriers in perovskite bulk films are generally known, there are not many studies that have shed light on the processes occurring in perovskite NCs.
Although bimolecular recombination is attributed to direct band-to-band electron–hole recombination, mono-molecular charge recombination originates from trap states and excitonic recombination.\(^2\) With increased exciton binding energy, it is expected that excitonic recombination will dominate in NCs, whose dimensions are reduced enough to exhibit quantum confinement effect. High-quality mono-disperse NCs are needed, in order to attain an unambiguous understanding of their photophysics. This will constitute an important step in advancing the utilization of perovskite NCs in modern optoelectronic devices.

An ability to perform controlled exchange of ligands to promote charge transfer in perovskite NC films is also highly desirable. Another aspect that has to be thoroughly addressed is the influence of ligands on the interfacial contacts in devices fabricated using perovskite NCs, something that is not present in the case of devices based on thin perovskite films. There have already been several studies on the development of various layers for removing or minimizing the interfacial barriers, in order to enhance device performance.\(^3\) Ligands or other specific surface coatings could potentially also help to prevent ion migration between NCs, a process limiting the use of these materials for energy transfer applications so far. Based on the optical properties and applications discussed in this review, it is obvious that metal halide perovskite NCs resemble conventional semiconductors in certain aspects, while also displaying unique properties such as ion conductivity and ease of synthesis. Therefore, much of the knowledge on conventional II–VI semiconductor NCs can be applied to perovskite analogs helping to overcome some of the challenges and advancing their device applications. For example, optimized device architectures and materials (electron and hole transport layers and electrodes) that have been widely employed for semiconductor devices can be directly tested on perovskite-based devices.\(^5\)\(^9\) Despite all of the challenges remaining, perovskites have rapidly advanced as one of the premier materials for a plethora of applications. With the vast amount of research being conducted in this field, it is to be expected that many of these challenges can be overcome rapidly, enabling consumer-friendly device applications.

**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

**ACKNOWLEDGEMENTS**

This work was supported by the grant from the Research Grants Council of the Hong Kong SAR, China (project CityU 11337616), by Bavarian State Ministry of Science, Research and Arts through the grant ‘Solar Technologies go Hybrid (SolTech)’ and by the Alexander von Humboldt-Stiftung (LP).
Colloidal lead halide perovskite nanocrystals

H Huang et al.

33 Mai, S. S., Shim, C. S. & Hong, C. K. Highly stable and efficient solid-state solar cells based on methylammonium lead bromide (CH3NH3PbBr3) perovskite quantum dots. *NPG Asia Mater.* 7, e208 (2015).

34 Pan, J., Samah, S. P., Murali, B., Dursun, I., Peng, W., Pandi, M. R., Liu, J., Sinha, L., Aiyani, N., Zhao, C., Alarousu, E., Ng, T. K., Ooi, B. S., Bak, D. M. & Mohammed, Q. F. Robust surface-passivated perovskite quantum dot solar cells for ultra-rapid, single- and two-photon-induced spontaneous emission. *J. Phys. Chem. Lett.* 6, 5027–5033 (2015).

35 Song, J., Li, J., Li, X., Xu, L., Dong, Y. & Zeng, H. Quantum dot light-emitting diodes based on inorganic perovskite cesium lead halides (CsPbX3). *Adv. Mater.* 27, 7162–7176 (2015).

36 Wang, Y., Li, X., Xiao, X., Leng, S. & Sun, H. Nonlinear absorption and stimulated emission from CH3NH3PbBr3 perovskite nanocrystals. *Nanoscale* 16, 448–453 (2016).

37 Yakunin, S., Protosevich, L., Krieg, F., Bodnarchuk, M. I., Nedelcu, G., Hummer, M. De Luca, G., Fiebig, M., Heiss, W. & Kovalenko, M. V. Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskite nanodisks. *Nat. Commun.* 6, 8056 (2015).

38 Zhang, X., Lin, H., Huang, H., Reckmeier, C., Zhang, Y., Choy, W. C. & Rogach, A. L. Enhancing the brightness of cesium lead halide perovskite nanocrystals based green light-emitting devices through the interface engineering with perfluorinated ionomer. *Adv. Mater.* 28, 1713–1714 (2016).

39 Ishiara, T., Takahashi, J. & Goto, T. Optical properties due to electronic transitions in two-dimensional semiconductor (CH3NH3)2PbI3 films. *Phys. Rev. B* 42, 11099–11107 (1990).

40 Calleja, J., Jones, N. L., Harlow, R. L., Herron, N., Thorn, D. L. & Wang, Y. Preparation and characterization of layered lead halide compounds. *J. Am. Chem. Soc.* 113, 2328–2330 (1991).

41 Papavasiliou, G. C., Koutselis, I. B., Lagoudaros, D. J., Kapoutsis, J., Terzis, A. & Papaioannou, G. J. Optical and related properties of some 3-dimensional and lower-dimensional semiconductor systems. *Mater. Chem. Phys.* A 252, 395–404 (1994).

42 Papavasiliou, G. C. & Koutselis, I. B. Structural, optical and related properties of some natural three- and lower-dimensional semiconductor systems. *Synth. Metals* 71, 1713–1714 (1995).

43 Koutselis, I. B., Ducasse, L. & Papavasiliou, G. C. Electronic properties of three- and low-dimensional semiconductor materials with Pb halide and Sn halide units. *J. Phys.Condens. Matter* 8, 1217–1227 (1996).

44 Muthu, C., Nagamma, S. R. & Nair, V. C. Luminescent hybrid perovskite nanoparticles as a new platform for selective detection of 2,4,6-trinitrophenol. *RSC Adv.* 4, 55908–55911 (2014).

45 Luo, B., Pu, Y.-C., Yang, Y., Lindley, S. A., Abdelmageed, A., Ashry, H., Li, Y. L., Li, X. & Zhang, J. Synthesis, optical properties, and exciton dynamics of organolead bromide perovskite nanocrystals. *J. Phys. Chem. C* 119, 26672–26682 (2015).

46 Tyagi, P., Arveson, S. M. & Tsisda, W. A. Colloidal organohalide perovskite nanoplatelets exhibiting quantum confinement. *J. Phys. Chem. Lett.* 6, 1911–1916 (2015).

47 Nolte, R., Prato, M. & Manna, L. Tuning the optical properties of cesium lead halide perovskite nanoplatelets with monolayer-level thickness control. *J. Am. Chem. Soc.* 138, 1010–1016 (2016).

48 Wang, K.-H., Wu, L., Li, L., Yao, H.-B., Qian, H.-S. & Yu, S.-H. Large-scale synthesis of highly luminescent perovskite-related cspb2br5 nanoplatelets and their fast anion exchange. *Org. Chem. Ind. Ed.* 55, 8328–8332 (2016).

49 Jang, D. M., Park, K., Kim, D. H., Park, J., Shojaei, F., Kang, H. S., Ahn, J. P., Lee, J. & Song, J. K. Reversible halide exchange reaction of organometal trihalide perovskite colloidal nanocrystals for full-range band gap tuning. *Nat. Nano* 15, 5191–5199 (2016).

50 Wang, A. B., Lai, M., Maiti, S. W., Wu, Y., Lin, E., Dou, L. F., Fu, A. & Yang, P. Growth and anion exchange conversion of CH3NH3PbI3 nanocrystals for highly luminescent PbI2 quantum dots. *Adv. Mater.* 28, 5132–5138 (2016).

51 Lignos, I., Stavrakis, S., Nedelcu, G., Protosevich, L., deMello, A. J. & Kovalenko, M. V. Synthesis of cesium lead halide perovskite nanocrystals in a droplet-based microfluidic platform: fast parametric space mapping. *Nano Lett.* 16, 1869–1877 (2016).

52 Kooly, M., Amgar, D., Aharon, S. & Elgar, L. Kinetics of cesium lead halide perovskite nanocrystal growth; focusing and de-focusing of size distribution. *NanoScale* 8, 6403–6409 (2016).

53 Zhang, D., Eaton, S. W., Yu, Y., Dou, L. & Yang, P. Solution-phase synthesis of cesium lead halide perovskite nanowires. *J. Am. Chem. Soc.* 137, 9230–9233 (2015).

54 Li, X., Wu, Y., Zhang, S., Cai, B., G., Song, J. & Zeng, H. Controlled growth of PbS quantum dots for lighting and displays: room-temperature synthesis, photoluminescence superiorities, underlying origins and white-light emitting diodes. *Adv. Funct. Mater.* 26, 2435–244510 (2016).

55 Akkerman, Q. A., Mott, S. G., Srinath Kandada, A. R., Mosconi, E. D’Innocenzo, V., Bertoni, G., Marris, M., Kaminou, B. A., Miranda, L. De Angelis, F., Petrozza, A., Prato, M. & Manna, L. Towards synthesis approach to colloidal cesium lead halide perovskite nanoplatelets with monolayer-level thickness control. *J. Am. Chem. Soc.* 138, 1010–1016 (2016).

56 Zhu, F., Men, L., Guo, Y., Zhu, Q., Bhattacharjee, U., Goodwin, P. M., Petrich, J. W., D., Spina, M., Bonvin, E., Sienkiewicz, A., Forro, L. & Horvath, E. Controlled growth of CH3NH3PbI3 nanowires in arrays of open nanofluidic channels. *Sci. Rep.* 6, 19834 (2016).
Sapori, D., Kepenekian, M., Pedesseau, L., Katan, C. & Even, J. Quantum con
Fu, Y., Zhu, H., Schrader, A. W., Liang, D., Ding, Q., Joshi, P., Hwang, L., Zhu, X. Y. &
Tachikawa, T., Karimata, I. & Kobori, Y. Surface charge trapping in organolead halide
Galland, C., Ghosh, Y., Steinbruck, A., Sykora, M., Hollingsworth, J. A., Klimov, V. I. &
Tian, Y., Merdasa, A., Peter, M., Abdellah, M., Zheng, K., Ponseca, C. S. Jr,
Xing, J., Liu, X. F., Zhang, Q., Ha, S. T., Yuan, Y. W., Shen, C., Sum, T. C. & Xiong, Q.
89 Kitazawa, N. Excitons in two-dimensional layered perovskite compounds:
97 Tachikawa, T., Karimata, I. & Kobori, Y. Surface charge trapping in organolead halide
98 Tian, Y., Merdasa, A., Peter, M., Abdellah, M., Zheng, K., Ponseca, C. S. Jr,
94 Hu, F., Zhang, H., Sun, C., Yin, C., Lv, B., Zhang, C., Yu, W. W., Wang, X., Zhang, Y. &
91 Dou, L., Wong, A. B., Yu, Y., Lai, M. L., MacManus-Driscoll, J. L., Greenham, N. C. & Friend, R. H. Size-dependent
Htoon, H. Two types of luminescence blinking revealed by spectroelectrochemistry of
96 Swarnkar, A., Chulliyil, R., Ravi, V. K., Irfanullah, M., Chowdhury, A. & Nag, A.
95 Zheng, K., Zhu, Q., Abdellah, M., Messing, M. E., Zhang, W., Generalov, A., Niu, Y.,
92 Dou, L., Yang, Y. M., You, J., Hong, Z., Chang, W. H., Li, G. & Yang, Y.
104 Xing, J., Liu, X. F., Zhang, Q., Ha, S. T., Yuan, Y. W., Shen, C., Sum, T. C. & Xiong, Q.
90 Kitazawa, N. Excitons in two-dimensional layered perovskite compounds:
87 Sapori, D., Kepenekian, M., Pedesseau, L., Katan, C. & Even, J. Quantum con
88 Hassan, Y. Song, Y., Pensack, R. D., Abdelrahman, A. I., Kobayashi, Y., Winnik, M. A. &
86 Hassan, Y., Song, Y., Pensack, R. D., Abdelrahman, A. I., Kobayashi, Y., Winnik, M. A. &
93 Pullerits, T., Yartsev, A., Sundstrom, V. & Scheblykin, I. G. Giant photoluminescence
656–573 (2016).
203,2 0 6 6–6964 (1992).
3 4 9, 1 5 1 8–1521 (2015).
3 2 9, 1 9 5 5–1958 (2015).
3 2 8, 7 9 2 3–7926 (2015).
3 2 4, 5 6 9 4 (1992).
6 9 6 4 (1992).
3 1 8, 8 9 6 8 (2016).
1 4 6, 8 0 6 6 (2015).
1 1 8, 1 0 0 8 7 (2016).
1 1 6, 1 5 1 8–1521 (2015).
1 1 5, 1 5 1 8–1521 (2015).
1 1 4, 2 9 6 9–2975 (2015).
1 1 3, 2 9 5 4–2969 (2015).
1 1 2, 2 9 5 4–2969 (2015).
1 1 1, 2 9 5 4–2969 (2015).
1 1 0, 2 9 5 4–2969 (2015).
1 0 9, 2 9 5 4–2969 (2015).
1 0 8, 2 9 5 4–2969 (2015).
1 0 7, 2 9 5 4–2969 (2015).
1 0 6, 2 9 5 4–2969 (2015).
1 0 5, 2 9 5 4–2969 (2015).
This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.
The Author(s) 2016