Inorganic and Hybrid Organo-Metal Perovskite Nanostructures: Synthesis, Properties, and Applications

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Hybrid perovskite and all-inorganic perovskite have attracted much attention in recent years owing to their successful use in the photovoltaic field. Usually the perovskite is used in its bulk form, although recently, perovskites’ nanocrystalline form has received increased attention. Recent developments in the evolving research field of nanomaterial-based perovskite are reviewed. Both hybrid organic-inorganic and all-inorganic perovskite nanostructures are discussed, as well as approaches to tune the optical properties by controlling the size and shape of perovskite nanostructures. In addition, chemical modifications can change the perovskite nanostructures’ band-gap, similar to their bulk counterpart. Several applications, including light-emitting diodes, lasers, and detectors, demonstrate the latent potential of perovskite nanostructures.

1. Introduction

Controlled size reduction of crystalline materials into nanometric dimensions is an important and challenging topic that the scientific community faces. This decrease in the nanoscale gives rise to new, distinct properties that have not yet been seen in the bulk form.[1,2] These properties open opportunities for new research directions and future applications. In parallel to nano-based perovskites, bulk hybrid organic-inorganic perovskite (HOIP) is one of the most promising materials in the photovoltaic (PV) field. HOIP has been investigated in just the last few years, and represents a tremendous increase in power conversion efficiency.[3-5] Next, perovskites will be characterized, highlighting their optical and electrical properties.

Perovskites are crystalline materials with the chemical formula ABX₃, where A and B are cations and X is an anion; therefore, the overall charge of the resulting crystal is zero (see Figure 1).[6] The cation A can be either organic or inorganic, for example, methylammonium (MA⁺) or formamidinium (FA⁺) for an organic cation and Cs⁺ for an inorganic cation. B is a bivalent metal cation, such as Pb⁺², and X is a halide, usually Cl⁻, Br⁻, or I⁻.[7,8] Clearly, perovskite’s composition is very versatile; thus, the optical and electrical properties of these materials can be controlled and optimized.[9] HOIP absorbs light in the spectral range of 400–800 nm, covering most of the visible region. Aside from its use in PV, it has been used in various optoelectronic applications, such as light-emitting diodes (LEDs) and lasers.[10-13] Moreover, a few recent reviews have discussed perovskite’s properties and its potential in optoelectronic applications, mainly in its bulk form.[14-16] Although it is an attractive bulk material, the properties of nanocrystalline perovskite remain ambiguous; however, some research has also been devoted to investigating the nanocrystalline form.

This evolving interest in perovskite nanostructures has led to studying the intrinsic and fundamental properties of this intriguing material. Understanding the basic characteristics of nanocrystalline perovskite is also relevant to its bulk form. Furthermore, synthesizing perovskite as nanostructures will pave the way to additional applications, some of which are discussed here.

In this review article, we summarize recent developments related to perovskite in its nanocrystalline form, covering both inorganic and hybrid perovskites. The routes used to synthesize both types of perovskite nanostructures are discussed, along with the differences between them. This includes the optical and electrical properties of these perovskite nanostructures, as well as their potential in a variety of applications, such as in optoelectronics.

2. Inorganic Perovskite Nanostructures Based on Cesium Lead Halide

2.1. Synthesis

Protesescue et al.[17] were the first to report a novel synthesis of CsPbX₃ (X = Cl, Br, I) inorganic perovskite nanoparticles (IPNPs). This synthesis was based on the hot-injection method; it was carried out by injecting the cesium precursor (Cs-oleate) into a hot solution containing lead halide salt (PbX₂), high-boiling point-solvent (e.g., 1-octadecene), and ligands needed for stabilizing the NPs and for dissolving PbX₂. De Roo and co-workers[18] investigated the dynamics of the ligands’ binding and studied its surface chemistry. Their work contributed to better understanding the photophysics and chemistry of these IPNPs. In addition, the quantitative absorption was measured.
to determine the absorption coefficient, and nuclear magnetic resonance spectroscopy was used to characterize the surface chemistry in detail. This study shed more light on the surface composition and reactivity of IPNPs, which can also influence the purification process in which a minimal excess of organic material is desired. The photoluminescence (PL) spectra of IPNPs exhibited narrow emission peaks and the photoluminescence quantum yield (PLQY) was 90%.\[^{17}\] Furthermore, it was reported that IPNPs can form mixed halide systems with proper ratios of different halide salts. Therefore, shifts in the absorption and the PL peak positions were observed, according to the exchanged perovskite compound.\[^{19,20}\] Figure 2a shows an example of the tunable optical properties in CsPbX\textsubscript{3} NPs. During the reaction, the halide precursors underwent rapid crystallization to form CsPbX\textsubscript{3} NPs. The kinetics of this synthesis is typical for a metathesis reaction, meaning that the reaction occurs within the first 1 to 3 seconds. The quantum size effect (QSE) and different halide compositions of the perovskite enabled us to tune the band-gap, which covered most of the visible region (410–700 nm). Transmission electron microscopy (TEM) images of the obtained IPNPs (Figure 2b) indicate that they have a cubic-like shape. In this context, IPNPs are known to crystalize in orthorhombic, tetragonal, and cubic crystal structures, depending on the reaction temperature.\[^{17}\] However, a recent work used XRD and PDF analysis and concluded that the CsPbBr\textsubscript{3} crystal structure is unequivocally orthorhombic (Pnma).\[^{21}\]

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Lioz Etgar obtained his Ph.D. (2009) at the Technion–Israel Institute of Technology. He completed his post-doctoral research with Prof. Michael Grätzel (2009–2012) at EPFL, Switzerland. Since 2012, he has been a senior lecturer in the Institute of Chemistry at the Hebrew University. Etgar’s research group focuses on the development of new excitonic solar cell structures/architectures, while designing and controlling the inorganic sensitizer structure and properties to improve the PV parameters. He was the first to demonstrate the possibility to work without hole conductor in perovskite based solar cells.

Figure 1. Perovskite crystalline structure – ABX\textsubscript{3} – A is represented by the beige spheres, B by the dark-orange sphere, and X by the white spheres.

Figure 2. (a) Colloidal perovskite CsPbX\textsubscript{3} in toluene under UV lamp (\(\lambda = 365\) nm). (b) Typical TEM images of CsPbBr\textsubscript{3} NPs. Reproduced with permission.\(^{17}\) Copyright 2015, American Chemical Society.
In addition, several publications reported simplified syntheses of IPNPs that are more applicable for commercial use, occurring at room temperature (RT) and free from vacuum and an inert environment. Li et al. published RT synthesis based on supersaturated recrystallization (SR). In this synthesis the precursors $\text{Cs}^+$, $\text{Pb}^{2+}$, and $X^-$ are transferred into an insoluble solvent. This kind of synthesis was observed in natural minerals and ionic solutions. Ions precipitate into crystals when a soluble system is found in a non-equilibrium state; they are activated accidently by impurity or stirring, for example. The crystallization continues until the system reaches equilibrium. Even though crystallization takes place at RT, this method maintains the excellent optical properties of IPNPs, achieving 95% PLQY. Li et al. found that the exciton binding energy of $\text{CsPbBr}_3$ was much higher than the thermal disturbance energy; thus, it enables a radiative recombination of excitons at RT. Figure 3a illustrates the principles of the aforementioned RT-SR synthesis. Note that because of the smaller concentrations of the ion sources, their solubility is low compared with their solubility in dimethylformamide (DMF) and is much higher than in toluene, which is a very poor solvent for the ions. By activating stirring, the supersaturated system rapidly recrystallizes into $\text{CsPbBr}_3$ NPs. Figure 3b-f shows snapshots of four typical samples after adding precursor ion solutions. The potential of this RT synthesis, being both simple and optically efficient, led to the development of white LEDs.

It is known that information about the crystallization parameters when using conventional methods of synthesizing IPNPs is still lacking. As previously mentioned, the kinetics of this metathesis reaction is extremely fast and more information about it is required. Importantly, Lignos and co-workers reported a droplet-based microfluidic approach to synthesize IPNPs with better control of the reaction parameters, including the molar ratios of the ionic reactants, the reaction temperature, and the reaction time. In this work, ultrafast kinetic measurements, along with PL and absorption characterization in real time, were implemented. Such control can result in highly efficient synthesis as well as the saving of reagents. Interestingly, this microfluidic platform requires only small amounts of reagents and a few hours of reaction, and yields information equivalent to the information reached in 200–1000 conventional syntheses.

In addition, Koolyk et al. studied the kinetics of IPNPs’ growth by investigating the focusing and defocusing mechanism underlying the NPs’ size distribution. Here we describe the kinetic mechanism in the first seconds after the reaction by tracking the NP size at various sequential growth durations. High-resolution TEM and examination of the size distribution

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Figure 3: Schematic of RT formation of IPNPs ($\text{CsPbX}_3$ ($X = \text{Cl, Br, I}$)). (a) SR can finish within 10 seconds (s) by transferring the $\text{Cs}^+$, $\text{Pb}^{2+}$, and $X^-$ ions from the soluble to insoluble solvents at RT without any protecting atmosphere and heating. C: ion concentrations in different solvents. C$_0$: saturated solubility in DMF, toluene, or mixed solvents (DMF + toluene). Reproduced with permission. Copyright 2016, Wiley-VCH. (b) Clear toluene under UV light. Snapshots of four typical samples after adding precursor ion solutions for 3 s, blue (c, Cl:Br = 1), green (d, pure Br), yellow (e, I:Br = 1), and red (f, I:Br = 1.5), respectively. Reproduced with permission. Copyright 2016, Wiley-VCH.
were used in the analysis (see Figure 4a–h). The size distribution of both CsPbBr$_3$ and CsPbI$_3$ were examined at growth durations of 1 s, 4 s, 20 s, and 40 s, resulting in different tendencies. The size distribution of CsPbBr$_3$ NPs showed a trend of defocusing from the beginning, whereas with CsPbI$_3$, the size distribution exhibited a focusing step in the first 20 s of growth, followed by defocusing over longer growth periods. This study suggests using a kinetic model of the NPs' growth, as described in Figure 4i. Based on the kinetic model, the monomers in the CsPbBr$_3$ NP synthesis were depleted faster than the monomers in the CsPbI$_3$ synthesis. Accordingly, small particles of CsPbBr$_3$ never reach the critical radius of nucleation (owing to the faster diffusion of the bromide-based monomers), and therefore, they broaden the size distribution. On the other hand, the monomers of the CsPbI$_3$ NP synthesis are diffused more slowly and can nucleate, expressed as a focusing step. Better understanding the kinetics of IPNPs provides an efficient and simple path to generate uniform NPs with narrow size distributions.

Aside from studying the kinetics of this synthesis, it was interesting to investigate how QSEs influenced the shape and properties of IPNPs by producing asymmetric structures of them. The fascinating optical properties and relatively simple synthesis of CsPbX$_3$ NPs led to further examination in order to implement their optoelectronic application potential. Recently, a few groups reported on CsPbX$_3$ nanoplate (NPL) synthesis. Bekenstein et al. first reported highly luminescent NPLs with PLQY that reached 84%.[28] These NPLs tend to self-assemble into a stacked phase and also form thin sheets, depending on the synthesis conditions. Akkerman et al.[22] worked on CsPbBr$_3$ NPLs synthesized at room temperature, as shown in Figure 5e–h. These NPLs crystallized because of the injection of acetone into the precursors’ solution. The low temperature contributed to the controllable growth of the NPLs down to the number of monolayers formed. As expected, the quantum confinement of this morphology yielded narrow PL spectra, prominent exciton peaks,
Thus, Cl\textsuperscript{TBA} is a soft acid that prefers to bind to softer halide ions. For example, Cl\textsuperscript{TBA} cannot work owing to hard/soft acid/base reactions. For example, as seen in Figure 5a–d as well as nanosheets, with superior optical properties for use of optoelectronic mate-

2.2. Optical Properties

As mentioned previously, IPNPs are known for their efficient tunable optical properties. The band-gap tuning can result from compositional modifications or quantum confinement via size and shape modifications. For instance, substituting cations (FA instead of MA or Sn instead of Pb) was investigated for HOIPs.\cite{19} Recently, Akkerman and co-workers extensively studied halide-exchange reactions by using a variety of halide precursors, such as octadecylamine-halide (ODA-X) and PbX\textsubscript{2}, as seen in Figure 6a.\cite{19} The efficient exchangeable nature of the halides in this system derives from their high ion mobility and rapid diffusion in solution. The optical tuning across the visible, from green-emitting NPs to blue- or red-emitting NPs, was simply produced by mixing IPNPs with halide precursors (Figure 6b). The mixing reactions resulted in compositional homogenization, which led to intermediate optical features. Apparently, while using tetrabutylammonium-halides (TBA-X), the routes for halide exchange were restricted to specific directions, from Br\textsuperscript{−} to Cl\textsuperscript{−} and from I\textsuperscript{−} to Br\textsuperscript{−}. The reverse routes did not work owing to hard/soft acid/base reactions. For example, TBA is a soft acid that prefers to bind to softer halide ions. Thus, Cl\textsuperscript{TBA} from CsPbCl\textsubscript{3} will not be exchanged with Br\textsuperscript{−} from TBA-Br because Br\textsuperscript{−} is softer than Cl\textsuperscript{−} and prefers to remain bound to TBA. The halide-exchange reactions led to a blue or red shift in the optical features, verifying that the new halides were integrated into the crystal structure (Figure 6b). Figure 6c presents the change in the band-gap as a function of the molar ratio between the added halide and the starting Br, showing the gradual replacement of the halide content. Figure 6d shows PLQY throughout the exchange process and the approximate matching of exchanged NPs and the NPs from direct synthesis. Furthermore, it is important to note that methylammonium-halides (MA-X) constitute problematic halide sources because of the possibility of a cation exchange between the Cs\textsuperscript{+} and the MA\textsuperscript{+} ions.\cite{20} Halide-exchange processes were further demonstrated by other groups as well.\cite{20,34} Kamat et al. reported on sintered IPNP solids with tunable optical features through halide-exchange reactions. The significance of this work is highlighted by its offering a proper solution for the instability of cubic phase CsPbI\textsubscript{3} film, starting with a sintered CsPbBr\textsubscript{3} film and then converting it into stable CsPbI\textsubscript{3}.\cite{34}

Hu and co-workers investigated IPNPs as single photon emitters, demonstrating the superior optical properties of this material using absorption cross sections and lifetime measurements.\cite{35} The intriguing optical features of IPNPs stimulated the search for further knowledge about their intrinsic spectral and dynamic mechanisms. Makarov et al. investigated these aspects comprehensively, focusing on single and multiexciton states in IPNPs. This analysis included measurements of exciton radiative lifetimes, rates of intraband cooling, the strength of exciton-exciton coupling, and non-radiative Auger recombination. The latter proved to be very efficient in IPNPs; however, it was detrimental to potential applications involving emissive optoelectronics. This study emphasized significant similarities in the spectroscopic properties between IPNPs and known semiconducting quantum dots (QDs), such as PbS and CdSe. For instance, two similarities are the extremely short biexciton Auger lifetimes (trions), decaying by the Auger mechanism. Moreover, the measured binding energy of bieexcitons was stated as approximately 10 meV, again, similar to other QD systems.\cite{36} A few other groups have investigated related mechanisms.\cite{37–39}
An interesting work was reported by Seth et al.\(^{(40)}\); they revealed fluorescence blinking in the microsecond time scale and photoinduced emission enhancement for CsPbBr\(_3\) and CsPbBr\(_2\)I NPs, which provide insight into the radiative and nonradiative deactivation pathways. Moreover, Raino and co-workers\(^{(41)}\) described IPNPs’ highly stable narrow emissions with reduced blinking. The significance in this work lies in the outstanding single-photon radiative decay of 250 ps, which was highly accelerated compared with other emitting NPs. The PLQY of IPNPs reached exceptionally high values, ≈90%. Wu and co-workers\(^{(42)}\) investigated the origins of the outstanding PLQY values by studying the dynamics of the carriers’ trapping and recombination mechanisms within CsPbBr\(_3\) IPNPs using transient absorption (TA) spectroscopy. The charge transfer to charge acceptors was also investigated, as presented in Figure 8a. The main explanation for the high PLQY value is the negligible traps of electrons and holes, resulting in non-radiative decay. It was also attributed to the efficient dissociation of excitons in the presence of hole or electron acceptors, such as phenothiazine (PTZ) and benzoquinone (BQ), respectively. TEM analysis revealed that the IPNPs had a short edge of ≈6 nm, which is much smaller than the bulk Bohr exciton diameter (≈7.4 nm), thus creating quantum confinement. Therefore, discrete electron and hole levels are formed and the optically allowed charge transitions between them lead to discrete absorption bands in the absorption spectrum. The potentials of the lowest electron and hole levels were estimated to be ≈3.62 eV and 6.36 eV relative to the vacuum level, respectively. Using pump-probe TA measurements, CsPbBr\(_3\) NPs were excited and the induced changes were recorded versus wavelength and time. Figure 8b shows the exciton bleach (XB) feature, which can be attributed to the state-filling-induced bleach and exciton absorption (XA) feature, which in turn, can be attributed to the hot-exciton-induced red shift of the lowest energy excitonic band (X1). The transfer of electrons to an electron acceptor indicated that the state filling of the hole and electron levels were 32.8% and 67.2% of the XB feature, respectively. The valence band is more degenerated than the conduction band is, which may explain the larger contribution of the electrons to the XB feature. Figure 8c presents the kinetics of the transient features; the time constant of the XB feature was 4.5 ± 0.2 ns. Complexes of CsPbBr\(_3\)-BQ/PTZ were used to measure the rates of electron transfer (ET) and hole transfer (HT) from photoexcited CsPbBr\(_3\). For ET, the half-lives and recombination were found to be 65 ± 5 ps and 2.6 ± 0.4 ns, respectively.
respectively. For HT, it was $49 \pm 6$ ps and $1.0 \pm 0.2$ ns, respectively. The absence of trap states and rapid interfacial ET and HT represent the most logical explanation for the unique PLQY. These findings may also be the key for the required photophysical understanding related to the charge separation phenomenon in solar applications and for future development of emissive devices.

A later work, by Swarnkar and co-workers,[43] focusing on the abnormal luminescence of IPNPs, provided new insights about the intrinsic optical features, and emphasized the advantages of IPNPs beyond traditional semiconducting QDs. The intense optical features of traditional colloidal QDs are associated with quantum confinement of charge carriers, thus enhancing the probability for transition. However, this characteristic leads to a broad size distribution and to numerous trap state issues. Accordingly, light properties, such as PLQY, are affected by self-absorption and Förster resonance electron transfer (FRET) mechanisms; thus, they change with the concentration of the NPs. Another typical disadvantage of using common QDs with LED devices is their temperature instability. An increase in temperature can induce a reduction of the band-gap, which consequently can cause color changes in the LED devices. This work highlights the valuable optical advantages of IPNPs, both as ensembles and single-crystals, in overcoming the above deficiencies. The PLQY of IPNPs could reach 90%, showing suppressed PL blinking. Regarding the temperature challenge, the PL of IPNPs did not change with temperature, when measured in the range of 25 to 100 °C. In addition, a single and an ensemble of IPNPs exhibit almost the same spectral gap, indicating no additional PL broadening, self-absorption, and FRET issues, which were discussed before. Furthermore, polarized emission was observed for the first time,[44] with polarization values of 0.36 and 0.40, associated with CsPbI$_3$, in solution and as a film, respectively.

Energy transfer between colloidal CsPbBr$_3$ NPs was also recently demonstrated.[45] The energy transfer process was driven by concentration and by band-gap differences, moving from the smaller to the larger NP (Figure 9). The proximity of the colloidal NPs enabled energy transfer processes to occur, and enhancement of the ET was observed after a few hours, after which the NPs could settle in their positions. PL measurements revealed a shift, where the PL wavelength changed from the small NPs to the larger NPs. In addition, where mixing of sizes was present in the sample, a shoulder appeared, indicating different NP sizes in the sample. Next, various applications of IPNPs with regard to LEDs will be discussed.

2.3. Applications

2.3.1. CsPbX$_3$ NPs for Light-Emitting Diodes (LEDs)

The excellent optical properties of IPNPs, including sharp emissions and high PLQY values, revealed their huge potential as light-emitting materials in a variety of optoelectronic applications, such as LEDs and lasers. Song et al.[46] were the first to report CsPbX$_3$ NP-based LEDs that produced an external quantum efficiency (EQE) of 0.07%, 0.09%, and 0.12% for three LEDs with different halide contents (blue, orange, and green devices, respectively; NP-based LEDs are presented in Figure 10c–e, as well as the corresponding electroluminescence (EL) spectra). The devices have the following layered
structure: indium tin oxide (ITO)/poly(ethylenedioxythiophene): polystyrene (PEDOT:PSS)/poly(9-vinylcarbazole) (PVK)/CsPbX3 NPs/ 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi)/ LiF/Al. TPBi thin films were employed as an electron transporting layer and PVK served as the hole conductor and electron blocking layer, thus encouraging the electrons and holes to recombine in the NP layer. The device's structure and energy diagram are presented in Figure 10a,b.

Following this work, several other studies have been conducted in this direction. [47–53] In this context, Kim and co-workers reported on IPNP solids that can be utilized for LEDs and other optoelectronic applications. IPNPs were fabricated using a centrifugal casting process that combined both purification and deposition of IPNPs on a desired substrate. The obtained layer was highly homogenous and the thickness could be controlled by the ratio between the crude NPs and the anti-solvent in the centrifuge tube. This process may have potential in future optoelectronic applications, such as for forming a uniform layer of IPNP-based emitters. [54]

Palazon et al. [55] reported polymer-free films of CsPbX3 NPs as a UV-to-white color-conversion layer in LEDs, using X-ray treatment that inhibits halide exchange processes. The X-ray treatment enabled the formation of a bi-layer of CsPbBr3 and CsPbI3 with individual emissions, thus preventing their compositional homogenization. The effect of X-ray irradiation was further implemented for lithographic processes on IPNP films. [56]

A recent work by Huang and co-workers [57] described the synthesis of water-resistant IPNPs with a polyhedral oligomeric silsesquioxane (POSS) capping agent and the subsequent utilization of these stable NPs in white LEDs. This NP protection prevents the rapid halide exchange process in solution and in the solid state, which enables the desired optical characteristics to be preserved. Taking the color stability into account, down-conversion white LEDs were fabricated using Br- and I-based POSS-IPNPs as powders, achieving 14.1 lm W−1 luminance efficiency. For future development, QY must be increased from the present value of 45% up to 70% in order to achieve the commercial requirement of phosphors.  

2.3.2. CsPbX3 NPs as Lasers

CsPbX3 NPs have become appropriate candidates for optoelectronics thanks to their enhanced optical properties, such as high stability, low cost, simple synthesis, and tunable low excitation threshold emission. Eaton et al. [32] recently reported a new method of synthesizing CsPbX3 NWs and demonstrated their virtues as efficient lasers. This was the first time that surfactant-free CsPbX3 NWs were synthesized with diameters suitable for photonic NW lasing (higher than ≈180 nm). CsPbBr3 NW lasers have been shown to lase for more than 109 excitation cycles, presenting high stability while lasing even under ambient conditions. The NWs had the technical characteristics required to act as both a gain medium and a laser cavity. Furthermore, it was shown that above their threshold, the NWs stimulated emission that was increased with their excitation intensity, as demonstrated in Figure 11. Additional groups also studied the lasing potential of IPNPs. [58–60] Xu et al. [61] reported polymer-free films of CsPbX3 NPs as a UV-to-white color-conversion layer in LEDs, using X-ray treatment that inhibits halide exchange processes. The X-ray treatment enabled the formation of a bi-layer of CsPbBr3 and CsPbI3 with individual emissions, thus preventing their compositional homogenization. The effect of X-ray irradiation was further implemented for lithographic processes on IPNP films. [56]

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investigated CsPbBr$_3$ NPs that exhibit two-photon-pumped lasing with an exceptionally low threshold when coupled with microtubule resonators.

2.3.3. CsPbX$_3$ NPs as Photodetectors

Additional research introduced the use of IPNPs as spectrochemical probes and halide reservoirs in catalysis. As mentioned, the halide content in perovskite NPs can be altered by simple halide-exchange reactions. This exchangeable nature gave rise to possible applications in organo-halide chemistry, as shown in Figure 12. It was suggested that IPNPs react as a catalytic reservoir for a Finkelstein exchange reaction between IPNPs and organo-halides, which is of major importance in various synthetic reactions and in the colorimetric assay of free ions in solution. The IPNPs that participate in the reaction exist in high concentrations and have high solubility to enable the halides to directly catalyze the reaction. A PL test was performed to validate the halide reservoir role of the NPs, and indeed, a change in PL was observed, confirming the change in the halide content within the CsPbX$_3$ lattice. In general, the IPNP features controlled the reaction kinetics in real time, via a colorimetric response in a simple and efficient manner.[62]

One of the pioneering works that used CsPbI$_3$ as photodetectors was reported by Ramasamy et al.[63] In this work, the possibility of tuning the IPNPs’ optical properties by forward and reverse anion-exchange reactions was demonstrated. Red-emitting CsPbI$_3$ NPs were used in a photodetector device due to their relatively longer radiative lifetime than the green- and blue-emitting NPs. The photodetector structure...
is shown in Figure 13a, where CsPbI$_3$ NPs were drop casted on a Si substrate with pre-patterned gold electrodes and later annealed at 200 °C for 30 min in a N$_2$ atmosphere. The photocurrent was increased by several orders of magnitude of the light intensity (Figure 13b); therefore, the photosensitivity, which is defined as the ratio of photocurrent to dark current ($I_{ph}/I_{dark}$), was exceedingly good (105). The response of the photocurrent to the light intensity is shown in Figure 13c; the fitting of this response is consistent with different applied biases. Figure 13d shows the spectral response of the photocurrent, which closely follows the absorption spectrum of CsPbI$_3$. The photocurrent time, measured in the dark and under illumination, is presented in Figure 13e, exhibiting a reproducible response to ON–OFF cycles, whereas rapid rise and decay times can be seen in Figure 13f for this photodetector device.

An additional interesting work was reported by Li et al.\textsuperscript{[64]} using the IPNPs in planar photodetectors. A recyclable dissolution–recrystallization process was conducted on the IPNPs, creating crack-free surfaces made at room temperature. Using this strategy, planar photodetectors were fabricated, as can be seen in Figures 14a+b. The charge transport was difficult for the untreated film, as can be seen in Figure 14a, whereas it was much improved for the treated film (Figure 14b). Figure 14c+d...
show the increased response of more than sevenfold for the treated photodetectors compared with the untreated ones under 10 V bias. The EQE, which is an important factor, indicated that the efficiency of the photogenerated carriers was also improved, as can be seen in Figure 14 e,f, for the untreated and treated films, respectively. The maximum EQE value reached 41% at 10 V, which is much higher than that of the untreated device, which is less than 6%. The main reason for these differences is due to the loss of photogenerated carriers from scattering and recombination.

Next, hybrid organic-inorganic perovskite nanostructures will be discussed.

3. Hybrid Organic-Inorganic Lead Halide Perovskite Nanostructures

In parallel to works discussing IPNPs, a growing number of reports have discussed hybrid organic-inorganic perovskite nanostructures. Two main fundamental differences arise when discussing the synthesis and properties of all-inorganic perovskite nanostructures compared with hybrid perovskite nanostructures. First, when synthesizing hybrid perovskite with organic cations instead of inorganic ones, the possibility of band-gap tuning increases, reaching longer wavelengths of ~800 nm (compared with ~700 nm wavelength with the

Figure 14. Photoresponse of all-inorganic pervoskite films before and after RDR healing. Schematic diagram showing the device’s structure of CsPbBr3 NCs (a) before and (b) after treatment. (c,d) Response and (e,f) EQE spectra of the PDs based on untreated and treated CsPbBr3 films under different biases, respectively. Reproduced with permission.[64] Copyright 2016, American Chemical Society.
inorganic perovskite nanostructures). In addition, the organic cation limits the synthesis temperature, permits high precursors to be soluble, and allows a standard atmosphere of humidity and oxygen during the synthesis, as described next.

3.1. Synthesis of HOIP NPs

Pioneering work in this field was done by Schmidt et al., who demonstrated the synthesis of CH₃NH₃PbBr₃ NPs (see Figure 15) by injecting methyl ammonium bromide (MABr) and PbBr₂ solutions into a preheated reaction medium of oleic acid (OAc) and octyl ammonium bromide (OABr) dissolved in octadecene. In the next step, the particles were precipitated by adding acetone, followed by centrifugation. These particles (dispersed in toluene) exhibited a PLQY of ≈20% as well as good stability (longer than three months).

Following this work, Zhang et al. developed a ligand-assisted re-precipitation strategy for fabricating brightly luminescent and color-tunable colloidal CH₃NH₃PbX₃ (X = Cl−, Br−, I−) NPs. This synthesis included a dropwise injection of a solution of precursors in DMF (the precursors included PbX₂, MAX, and n-octylamine) into toluene while vigorously stirring the reaction medium. These NPs exhibited absolute PLQY up to 70%. The halides’ composition changed the optical properties as the PL wavelength was altered in the range of 405–730 nm for the various halide compositions (Figure 16). In this work the use of these NPs in white LEDs was also demonstrated.

One of the disadvantages of the HOIP NPs is their instability in polar solvents. In order to overcome this problem, Vybornyi et al. synthesized CH₃NH₃PbBr₃ NPs without using a polar solvent. The reaction between PbX₂ and the methylamine was conducted using a high boiling point, nonpolar solvent with the ligands present in the solution. A PLQY of 15–50% was demonstrated with amplified spontaneous emission from thin films of green-emitting CH₃NH₃PbBr₃ NWs.

3.2. Size and Shape Control of HOIP NPs

The synthetic routes of the HOIP NPs, as previously described, have two problematic aspects: (1) the size distribution of the NPs is wide and (2) the shape of the NPs is hard to define.

In HOIP the organic cation plays an important role. Using a long-chain organic cation that cannot be introduced into the perovskite structure will result in reduced dimensionality of the perovskite structure. Dou et al. synthesized a single crystalline 2D hybrid perovskite using C₄H₉NH₃ as the organic cation and Br as the halide. The long organic cation results in well-defined square shaped plates, which leads to a shift in the band-gap of the material. In another work, broad spectral tunability was achieved by changing the composition of the methyl and octylammonium cations in colloidal synthesis. By increasing the octylammonium cation, 2D perovskites were formed with a platelet nature; however, their emission was lower than the 3D perovskite.

Keeping in mind the role of the cation in these HOIP NPs, the synthesis of the solution-processed core-shell type mixed with methylammonium–octylammonium, leading to bromide perovskite NPs was demonstrated. The NPs’ size ranged between 5 and 12 nm with a spherical shape and tunable optical properties. The core-shell-type NPs exhibited PLQY up to 92%. The ratio of the cations in the precursor solution is the factor that controls the growth layer and the stability of these NPs. The reported core-shell-type structure, comprising a shell, consists of high band-gap 2D perovskite (C₄H₉NH₃)ₓ(CH₃NH₃)₁−ₓPbₓBr₃₊ₓ (x = 1, 2, 3,...) over a low band-gap MAPbBr₃ core, as shown in Figure 17a. Figures 17b+c present TEM images of the mixed organo-lead bromide NPs obtained from cation ratios of 8:2 and 3:7, respectively.

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Therefore, several attempts were made to find a synthetic route to make a narrow size distribution and a controlled shape of the HOIP nanostructures. Huang et al. showed that by changing the precipitation temperature during the synthesis, the size of the NPs can be defined, which results in better control over the optical properties of the NPs.\[72\] Hassan et al. synthesized two-dimensional perovskite NPs in two steps: first, PbI\(_2\) NPs were synthesized, then the PbI\(_2\) NPs were reacted with an alkyl ammonium iodide cation to produce perovskite NPs with a narrow size distribution and a controlled absorption range.\[73\] Another work demonstrated the synthesis of nano-platelets; when the octylamine content was gradually increased, the researchers managed to control the thickness of the final nano-platelets.\[74\] Jang et al. demonstrated a novel chemical treatment that utilizes the halides' particle composition; briefly, MAX was mixed with HOIP NPs having a specific halide content, where X is a different halide than the one present in the NPs. This reaction led to halide conversion between the particles and the MAX salt, and consequently, to the acquisition of highly controllable and simply prepared NPs having specific halide compositions.\[75\] Recently, Aharon et al. synthesized two-dimensional HOIP nano-rods (NRs) with varying halide compositions (Br\(^{-}\)/I\(^{-}\)), see Figure 18. The band-gap energy of the NRs was defined by the halide content (Br/I), whereas the shape was dictated by the ligand’s content and type (oleic acid (OAc)/Octylammonium iodide (OAI)). The NRs’ structure is based on the two-dimensional perovskite, which shifts the band-gap energy of the NRs to shorter wavelengths (higher energy) owing to quantum confinement (relative to the same halide composition in the bulk form).\[76\]

### 3.3. Applications

As with their counterparts (the all-inorganic perovskite nanostructures), HOIP NPs can be used in several applications such as highly efficient LEDs,\[65,77,78\] as well as for detection and sensing.\[77,79,80\] Jang et al.\[75\] used HOIP NPs for fabricating photodetectors. The photodetectors had the structure of SiO\(_2\) substrate/Au/HOIP-NPs/Au. The photosensitivity of the HOIP-NP-based photodetectors (defined as the ratio of ΔI to the dark current (I\(_0\)), ΔI/I\(_0\)) was exceptionally good (10\(^5\)). The researchers found a strong correlation between the photocurrents and the PL decay times. For instance, the I-rich alloy of MAPbBrI\(_2\) exhibited both the highest photocurrent and the longest PL decay time (Figure 19). Moreover, future applications such as in solar cells and lasers that use these fascinating HOIP nanostructures are possible.

#### 3.3.1. Use of CH\(_3\)NH\(_3\)PbBr\(_3\) Perovskite NPs in EL Devices

CH\(_3\)NH\(_3\)PbBr\(_3\) perovskite NPs were synthesized and used in EL devices.\[77\] The EL devices have a structure as presented in Figure 20a; glass/indium–tin oxide (ITO)/PEDOT:PSS (40 nm)/CH\(_3\)NH\(_3\)PbBr\(_3\) QDs/QBPbI\(_2\) (40 nm)/CsF(1 nm)/Al (80 nm). The CH\(_3\)NH\(_3\)PbBr\(_3\) was spin coated on top of the PEDOT:PSS layer and served as a green emitter. The emission peak at 524 nm can be observed in Figure 20b, where the inset displays a lit QD EL device with 120 cd m\(^{-2}\) brightness. The turn on voltage of this device was 2.9V at 1 cd m\(^{-2}\), which is higher than typical thin film in LED. The reason might be due to a large band-gap and therefore a high injection barrier. The current density and brightness versus the voltage are presented in Figure 20c; Figure 20d shows a maximum current efficiency of 4.5 cd/A, a power efficiency of 3.5 lm W\(^{-1}\), and an EQE of 1.1% with the brightness of 410 cd m\(^{-2}\). These EL devices were stable for 10 days in air.

HOIPs have gained much interest as bulk light-harvesting materials in the field of perovskite-based solar cells. However, improvements in the active material are always required in order to enhance the cells’ performance. The work of Fu and co-workers demonstrated the use of HOIPs’ nanostructures for optoelectronic and PV applications. By modifying the shape of the HOIPs’ crystals into NWs, nanorods, and NPLs, they were able to fabricate a layer with a stronger PL and longer carrier...
lifetime, relative to the bulk form. The formation of the perovskite nanostructure-based layer was carried out using a dissolution-recrystallization platform over spin-coated PbI$_2$ (or lead acetate) film, shown in the scheme in Figure 21. The obtained single-crystal nanostructures were characterized via surface photovoltage measurements and identified as n-type semiconductors. Also reported was an interfacial conversion of the PbI$_2$ film into a highly crystalline MAPbI$_3$ layer (Figure 21) that can generate PV devices with high power conversion efficiency.

The nanocrystalline form of HOIPs was found to have many advantages for optoelectronic applications, as mentioned previously. In addition to LED, photodetection, and PV, HOIP nanostructures have another potential use as lasing materials. Zhu et al. utilized the attractive physical properties for HOIP

Figure 18. TEM images and inset FFTs of NRs having various halide compositions. Reproduced with permission. Copyright 2015, American Chemical Society.

Figure 19. (a) I–V characteristics of MAPbBr$_3$ film under 365 and 505 nm irradiation (60 mW cm$^{-2}$) and dark conditions. The SEM image shows the film deposited on Au electrodes with a 2 µm gap (inset). (b) I–t curves at a bias voltage of 2 V under chopped radiation. (c) I–V and (d) I–t curves of MAPbBr$_3$ film under 365 (60 mW cm$^{-2}$), 505 (60 mW cm$^{-2}$), and 617 nm (40 mW cm$^{-2}$) irradiation and dark conditions. reproduced with permission. Copyright 2015, Wiley-VCH.
NW-based lasers, synthesized by surface solution growth deposition at RT. The NWs' length reached \(\approx 20\ \mu m\) and the NWs' width reached a few hundred nm. The grown HOIP NWs had a RT tunable lasing with extremely low thresholds (220 nJ cm\(^{-2}\)), corresponding to a low charge carrier density of \(1.5 \times 10^{16}\ \text{cm}^{-3}\). The minimal trap states of the charge carrier can be translated to an estimated PLQY that can reach 100%.

4. Conclusions and Outlook

We have summarized the main important contributions to the field of perovskite-based nanostructures. Perovskite nanostructures have been recently reported and their outstanding optical and electronic properties have been under intense research as a result. We focused on IPNPs and on HOIP nanostructures, their interesting properties, and potential applications. We have discussed the synthetic methods of fabricating perovskite NPs (with inorganic and organic cations), as well as their optical and structural modification and characterization. Importantly, it was found that halide-exchange processes and QSEs are highly effective in both perovskites, enabling band-gap tuning across the visible spectrum, thus making them attractive for optoelectronic applications. Some reports demonstrated highly efficient LEDs and photodetectors based on perovskite NPs, whereas other reports described the sensing ability of these perovskite NPs. The utilization of CsPbX\(_3\) IPNPs was also found to be applicable for lasing applications. Extremely high PLQY values, narrow emission peaks in the visible region, a tunable band-gap, and an additional degree of stability were reported, showing the potential of these nanostructures.

Looking forward, there are still many fundamental open questions regarding these interesting perovskite nanostructures, in addition to new applications that have not yet been reported. Here, we discussed several key issues and challenges, which should receive more attention in the future. First, a few improvements were recommended regarding the purification process of the NPs, affecting PLQY, to generate high-quality perovskite NPs for electronic applications. Regarding this aspect, the stability (photo-stability, thermal stability, and chemical stability), especially related to HOIP NPs, needs to be improved in order to further utilize perovskite NPs in optoelectronic applications. Moreover, to date, there has been no efficient way to deposit these perovskite nanostructures as a conductive film with good transport properties. The organic ligands protecting the perovskite nanostructures pose difficulties in their transport through the deposited film; therefore, establishing an efficient ligands exchange method is essential. Second, the bulk form of perovskite attained a revolutionary success as a light-absorbing material in solar cells, encouraging further investigation of the electronic properties of the nano-form in terms of energy.
transfer and band-gap engineering. In addition, Kamat et al.\cite{34} suggested an approach to generate a bulk CsPbX₃ film, starting from CsPbX₃ NPs. This can pave additional pathways for solar applications. Third, water-soluble IPNPs and HOIP NPs constitute an interesting research direction, since they would open the possibility for biological applications. It is known that perovskite is not stable in water; therefore, on the one hand, this task is very challenging, but on the other hand, it can open directions for new applications. In addition, in seeking novel functional materials, one of the interesting directions can be composite structures, such as hybrid and core-shell nanostructures, taking into account the similarity of perovskite NPs to other semiconducting QDs (PbS, CdSe, and others). This will open the possibility to extend the absorbance wavelength of these materials. Another motivation for using such hybrid composites is hidden in the PL stability of traditional semiconducting QDs. For example, the need for core-shell structures is related to the enhancement of the optical properties, especially the radiative decays and lifetimes, which constitute a serious drawback of using traditional QDs. These optical parameters also influence the overall PLQY mostly affected by trap states at the surface. It was reported that perovskite nanostructures have negligible trapping at the surface due to rapid dissociation of the exciton in the presence of charge acceptors;\cite{42,82} therefore, perovskite nanostructures might contribute in this direction. Ning et al.\cite{83} reinforced the feasibility of fabricating the suggested hybrid nanostructures in terms of energetic considerations and crystallographic matching between the crystalline structure of PbS QDs and MAPbX₃. The possibility of generating ‘dots-in-a-matrix’ crystals via epitaxial growth was presented and discussed, accompanied by density functional theory (DFT) calculations. The authors claimed that the dots inherit the crystalline alignment of the perovskite. This work may inspire and open a new window to apply this system to core-shell nanocomposites of perovskite with known QDs. To do so, a better understanding and control of the surface chemistry of these NPs is required.

In summary, we think that a fundamental understanding and implementation of these novel IPNPs and HOIP NPs is still lacking. An in-depth physical and chemical understanding of the underlying exciton, recombination, and PL mechanisms is needed and their thorough investigation is the main factor necessary for facilitating the functionalization and implementation of these materials.

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