Review

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Stability Enhancements on Methylammonium Lead-Based Perovskite Nanoparticles: the Smart Use of Host Matrices

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Abstract: Despite the current advancements, yet improving the intrinsic structure and external environmental stability of hybrid metal halide perovskite nanomaterials is required for developing efficient perovskite-based devices. Up-to-date, a very attractive method is growing and/or embedding perovskite nanocrystals within organic polymeric matrices, or into porous inorganic and hybrid nano/micromaterials (e.g., metal-organic frameworks, mesoporous silica, zeolites, and others), favored through confinement effect within the pores. In this review, we highlighted the last two years of research progress on enhancing the stabilization of perovskite nanoparticles based on methylammonium cations. In the future generation of optoelectronic and photovoltaic devices along with other interesting applied fields, it is predicted that an effective way to trigger the widespread use of this type of perovskite nanocrystals may involve combining different functional host materials, acting as a smarter protection method for the guest nanocrystals.

Keywords: perovskite nanocrystals · methylammonium · stability · polymers · porous hybrid materials

1. Introduction

Over the last decade, metal halide perovskite-based materials[1] have emerged a promising future in the form of semiconducting nanoparticles (NP) and nanostructures due to their unique electrical and optical properties.[2] Enhancing the current synthetic strategies for diverse low-dimensional halide perovskite nanostructures including quantum dots (QD), nanocrystals (NC), nanowires, or nanocrystalline thin films have brought fruitful progress in optical and electronic applications, owing to their unique quantum confinement effect, high photoluminescence quantum yield (PLQY), large surface-to-volume ratio, and optical tenability. The nomenclature through emerged literature terms different types of perovskite nanostructures interchangeably. It is noticeable that the correct semantics has been lost in translation by the common usage of the nanometer length scale of all these particles, especially in the case of colloidal particles. In simple terms, in the case of metal and wide gap semiconductor nanocrystals, the common term used is NPs, or NCs if they are colloidally grown (whether covalent II–VI or ionic perovskites). Yet, if the size of the spherical nanoparticle is smaller or on the order of the excitonic Bohr radius, then these semiconductor nanocrystals become QDs. Hence, to avoid misleading discussions, in this review, we will use the same term selected for such nanosized particles reported by the provided cited research groups.[3]

In general, the main advantage of perovskites over classical inorganic semiconductors is their low-cost, low-temperature-based deposition on a large variety of substrates by coating or printing techniques. In addition, the high crystallization ability from precursor solutions allows obtaining a large variety of nanostructures, where the surface chemistry governs the formation of nanoparticles. In this sense, perovskite nanomaterials are of great interest as prospective active materials for many emerging applications, such as light-emitting diodes (LEDs), and lasers, among others.[4] Besides the utilization of these quantum dots in solar cells, also their application on photodetectors and resistive switching memory devices has been demonstrated.[5]

The synthesis of colloidal perovskite nanoparticles involves stabilizing the crystal growth by ligands and surfactants. In this regard, ligand-assisted reprecipitation (LARP) is a powerful ligand-engineering tool to fine-tune nanostructured perovskite features targeted for specific applications. This method is generally selected for preparing nanoparticles since it is cost-effective and easy to scale up synthetic pathways, which only requires affordable equipment and convenient operational temperatures. This method was reported in 2014 by Schmidt and collaborators to prepare colloidal methylammonium lead bromide ($MAPbBr_3$, MA stands for $CH_3NH_3^+$) NPs with a size of 6 nm, by using long-chain primary amines and long-chain carboxylic acids as organic ligands.[6] The as-prepared colloidal $MAPbBr_3$ NPs showed good stability for over three months and exhibited a low

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PLQY of 20%. One year later, this method was modified by Zhang *et al.*, resulting in brightly luminescent and color-tunable colloidal MAPbX$_3$ (X=Br, I, Cl) QDs prepared at room temperature and low excitation fluencies, exhibiting an enhanced PLQY$\approx$70%.[7] The optimization of this ligand-assisted precipitation approach can open a path towards numerous possible combinations of perovskite nanoparticles and tailored nature-inspired capping agents, envisioning a new generation of applied functional electronic materials.

In general, the physical properties of these semiconducting nanoparticles can be tuned not only by the chemical stoichiometry and by the confined size growing of the particles at the dimensional scale, but also by several other parameters. Therefore, it is necessary to precisely understand which synthetic parameters may influence the resulting optical properties of the final nanomaterials. In our recent work, we studied the influence of the choice of solvent system, capping agents, the temperature during precipitation, and the ratios of precursor chemicals were described, as well as the colloidal stability and stability of the precursor solution.[8] With the current advances in the fabrication of nanomaterials, the next step is to expand their field of applications through the utilization of functional and modifiable ligand chemistry to achieve highly luminescent perovskite nanoparticles with controllable sizes. In this regard, bio-inspired capping agents can be chosen to stabilize the MAPbBr$_3$ nanoparticles. As far as amino acids have been incorporated into the perovskite structure by their side chains, oligopeptides (e.g., containing L-Lysine or L-Arginine) or cyclic peptides located on the perovskite surface,[9] alongside various surfactants, can enhance the affinity to desired surfaces, therefore broadening the applicability of perovskite nanoparticles such as self-assembly properties and sensing abilities.[10] Another promising simple method reported recently for controlling the size of the perovskite NPs during preparation, is the use of water as an additive in the precursor solution.[11] This water addition results in the formation of highly mobile species, and thus, the enhancement of perovskite lattice growth. Hence, the exhibited chemical tunability of the structural composition of perovskite-based nanocrystals enables the control of their size, shape, and optical properties at will.

Fabricating perovskite nanomaterials with homogeneous morphologies, and thus properties is a current remaining challenge to be solved, with a critical effect on the

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optoelectronic performance. Additionally, nanoparticles' spontaneous aggregation tendency should not be underestimated, which reduces substantially their PLQY when processed, for example, as thin films. However, nanocrystalline films based on traditional colloidal nanocrystals suffer from the use of long insulating ligands, as well as low colloidal nanocrystal concentration, resulting in the impossibility of film formation, and significant aggregation during film formation.[12] One efficient way of ligand engineering is to use multifunctional materials, which would not only interrupt crystallization processes forming the nanoparticles, but also would bring functionality from the surface groups. Indeed, the inherent poor stability to oxygen, humidity, light, and heat, as well as ion migration issues, has been improved by integrating and encapsulating them into organics, such as solid polymer matrixes, and inorganic hybrid porous materials (e.g., mesoporous silica nanoparticles, metal – organic frameworks or zeolites), or another type of inorganic oxides (TiO_2 or Al_2O_3) (Figure 1). Despite the great advances done so far over the utilization of protective, functional, and modifiable host matrices, with different chemical synthetic nature, still some issues need to be addressed. To mention some: a) the low loading efficiency within the host matrix, due to precursors diffusion resistance or the formation of NCs on the external surface; b) reduced PLQYs of the NCs after being embedded within the host cavities; and c) possible compatibility issues between the pre-synthesized NCs and the host formation conditions. Yet, a future key point to take into consideration will be the stability of the host under real operational conditions and practical applications. Moreover, the high versatility and functionality of perovskite NC composites can be driven towards more efficient strategies to better adapt the interaction between the NC and the host, such as pre- or post-functional modifications of the host to improve such encapsulation/immobilization process. Along this field, in the past immense signs of progresses have been made in all-inorganic perovskite nanoparticles stability, in comparison to organic-inorganic counterparts, which have shown very attractive features in the optoelectronics field. Furthermore, while the fast advancing stretchable/wearable devices require apart from stability even flexibility, and scalability, current perovskites suffer from incompatible mechanical properties. Applying polymeric matrix to form stretchable films or gels offers a great opportunity to provide perovskites with suitable mechanical properties. According to the type of polymer matrix used, it is possible, apart from protecting the embedded perovskite NPs, to tune their mechanical properties from rigid structures suitable for 3D printing to highly elastic structures. Those advances could be of high interest due to the increased and urgent demand for highly stable and flexible new systems to be used in fabricating flexible or wearable optoelectronic devices, such as stretchable LEDs.[13]

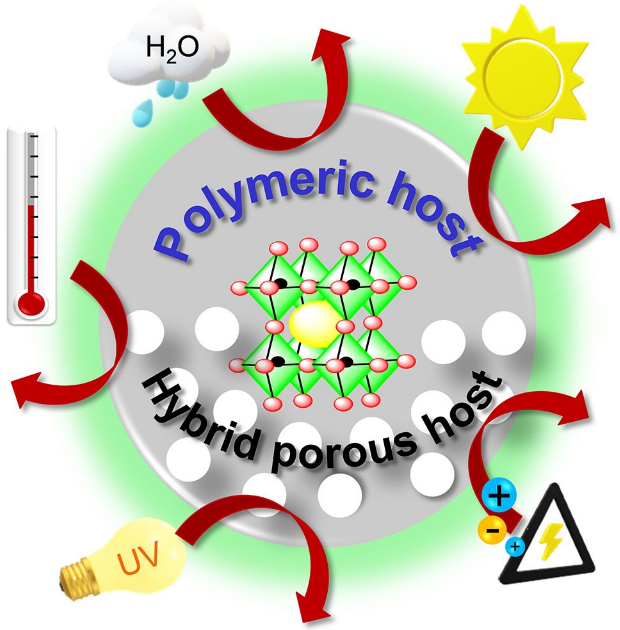


Figure 1. Schematic illustration of the enhanced stability of colloidal perovskite NCs against ambient conditions (water and oxygen), irradiation (UV and Visible light), temperature, and ion migration, by protection and integration into either polymeric matrices or porous organic-inorganic hybrid materials.

In this review, we will make emphasis on the last few years of research progress on the stability and mechanical properties improvement of methylammonium lead halide perovskites nanoparticles. Most of the excellent research work done before the year 2018 is not included here and mainly selected examples of recent work from 2019 up to date are highlighted. Among different possible strategies to increase their stability, here we will describe the matrix encapsulation of perovskite nanocrystals with solid polymers, inorganic, and hybrid porous matrices, together with promising applications as optoelectronic devices, battery storage, smart textiles, as well as flexible electronics.

2. Encapsulation within Solid Polymer Matrix

The stability of perovskites against moisture urgently needs to be studied and addressed wisely. The use of polymers as hosts to protect the perovskite NCs from fast degradation has been demonstrated to be the most efficient and easy route. However, to a certain degree, such polymer-encapsulation needs to be improved to avoid hindering the charge transport process and thus allowing possible photoelectrochemical applications. Hybrid organometallic halide perovskite-based optoelectronic devices possess a very negative factor, ionic movement. The movement of ions in the perovskite lattice has a big impact on device efficiency and stability. Ion movement is a common property of perovskite lead-halide materials and is considered as an undesirable behavior resulting in hysteresis in J–V measurements and affecting the stability of solar cell devices.[14] Though, with proper utilization of the ionic movement, it is possible to create devices with possession of both a solar cell and battery storage properties. Consequently, the encapsulation of NCs by polymeric shells is an advantageous strategy to avoid halide ion exchange, as well as to provide stability against degradation caused by water. Recently, two different groups employed diblock copolymer micelles as nanoreactors were recently reported, i.e., polystyrene-poly(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymers were prepared for the synthesis of highly monodispersed methylammonium lead-based perovskite NCs in the core of the micelles.[15] When comparing with the unprotected NCs, films made with $MAPbI_3$ and $MAPbBr_3$ NCs displayed >15-fold lifetime in ambient conditions, and remarkably, these films were able to survive for more than 75 days underwater.[15a] In the case of noble metal nanocrystals formation, sometimes an extra step is required for removing the polymer shell that is surrounding the final particles, either by chemical reduction or by plasma treatment. Though, depending on the final purpose, such a step might not be even needed. The ability of the NCs to self-assemble in films on substrates has the potential to enable integration into optoelectronic devices. By applying polymers as additives or layers it is possible to minimalize or control the ionic movement and produce devices with high power conversion efficiency and excellent energy storage properties. For controlling the ion movement in device fabrication, the sandwiched thin-film structure can be wisely selected. Following this approach, conductive indium tin oxide (ITO) layers are covered by PEDOT:PSS polymer layer, and on the other side of the perovskite layer, a conjugated P3HT polymer layer is placed.[16] In this work, MoO_3/Al was used as the counter electrode and $MAPbI_3$ as the active perovskite layer. At a steady-state, the energy distribution is symmetrical in the device, but after applying 3.0 V the balance is broken. Holes can enter the device from the counter electrode while iodine ions are present in the perovskite lattice. Normally, the holes can cross the layers and end in various kinds of recombination processes. However, in that case, iodine anions were locked in the device structure. After charging, the device behaved as a photovoltaic panel thanks to an imbalance of charge distribution, or as a power source while discharging like a battery. The authors then presented a multifunctional energy device with $MAPbI_3$ perovskite layer stabilized and modified by two conjugated polymers which express excellent properties as a solar cell and battery device.

Nevertheless, the desire for hybrid perovskite solar cells that possess hysteresis-free characteristics has been unfulfilled, and the ionic movement was only controlled or modulated. To overcome that, one-step self-assembled $MAPbI_3$ solar cells co-crystallized with poly(ethylene oxide), PEO, was reported by Zheng, Wang, and coworkers.[17] Prepared co-crystal layers with PEO provided high-quality thin films with significantly enlarged crystal grains due to weak hydrogen interactions between $MAPbI_3$ and polymer. The presence of these interactions resulted in the vanishing of photocurrent hysteresis and significant improvement in the stability. This one-step process used low boiling point solvents (i.e., acetonitrile) for the perovskite precursor solution to form films through spin coating. Here the precursor solution was prepared by exfoliation of single crystals, rather than mixing of precursors in solution. Some authors also demonstrated how the hybrid perovskite solar cells stabilized by PEO dramatically suppressed photocurrent hysteresis and significantly boosted stability.[17b] On one hand, exposure to ambient conditions with 50% relative humidity proved the extreme stability of the devices when basic $MAPbI_3$ devices without polymer protection showed a blue-shift of absorption spectra that means degradation after six days. On the other hand, these thin films were stable after 40 days, with no significant changes.

The essential characteristic with impact on the properties and stability of perovskite-based devices is the possibility of grain boundaries manipulation. The solution-processing method introduces defects and then low molecular passivating agents cannot suppress the defect completely because of low molecular substances volatility and diffusivity. However, the polymer intermediate phase can be produced with perovskite cross-linked composite material where the cross-linker part bridges the perovskite grains to minimize grain to grain electrical decoupling, producing excellent environmental stability and enhancing photovoltaic parameters. In this regard, poly(propylene carbonate) (PPC) as a polymeric Lewis base was used, because the repeating unit possesses a high molecular dipole moment resulting in good solubility in polar solvents.[18] Moreover, the PPC units exhibit strong interactions with Lewis acidic perovskite precursors of $MAPbI_3$. Accordingly, the interactions of the polymeric Lewis base modulated the NCs formation and provided high moisture stability (over 150 h with a relative humidity of the environment at 70%). Subsequently, the addition of the polymeric Lewis base enhanced all operational photovoltaic parameters in the prepared solar cells, as well as bringing excellent stability. The degradation was attributed probably to the intergrain cross-linking of the perovskite, induced by the macromolecular intermediate phase.

Besides thermal and environmental stability, the mechanical stability of devices for use in stretchable and flexible electronics is equally important. Reported fabrication of $MAPbBr_3$ perovskite/thermoplastic polyurethane (TPU) based multicolor luminescent core-shell nanofibers connect all properties (Figure 2a).[19] The TPU was applied as the stretchable polymeric shell, whereas the TPU acted as a hydrophobic matrix, protecting and stabilizing the perovskite part of nanofibers. According to the 31 days aging test, there occurred a negligible degradation, and PLQY remained at the same level for the whole time. Moreover, thanks to the TPU, nontoxicity and biocompatibility nanofibers are prepared, which are applicable in smart textiles and wearable electronics. Furthermore, the urethane group of TPU forms certain interactions with Pb atoms or methylammonium cations of perovskites, modulating the crystal growth. The second strategy to form stable perovskite polymer hybrid fibers is employing the emulsion electrospinning approach (Fig-

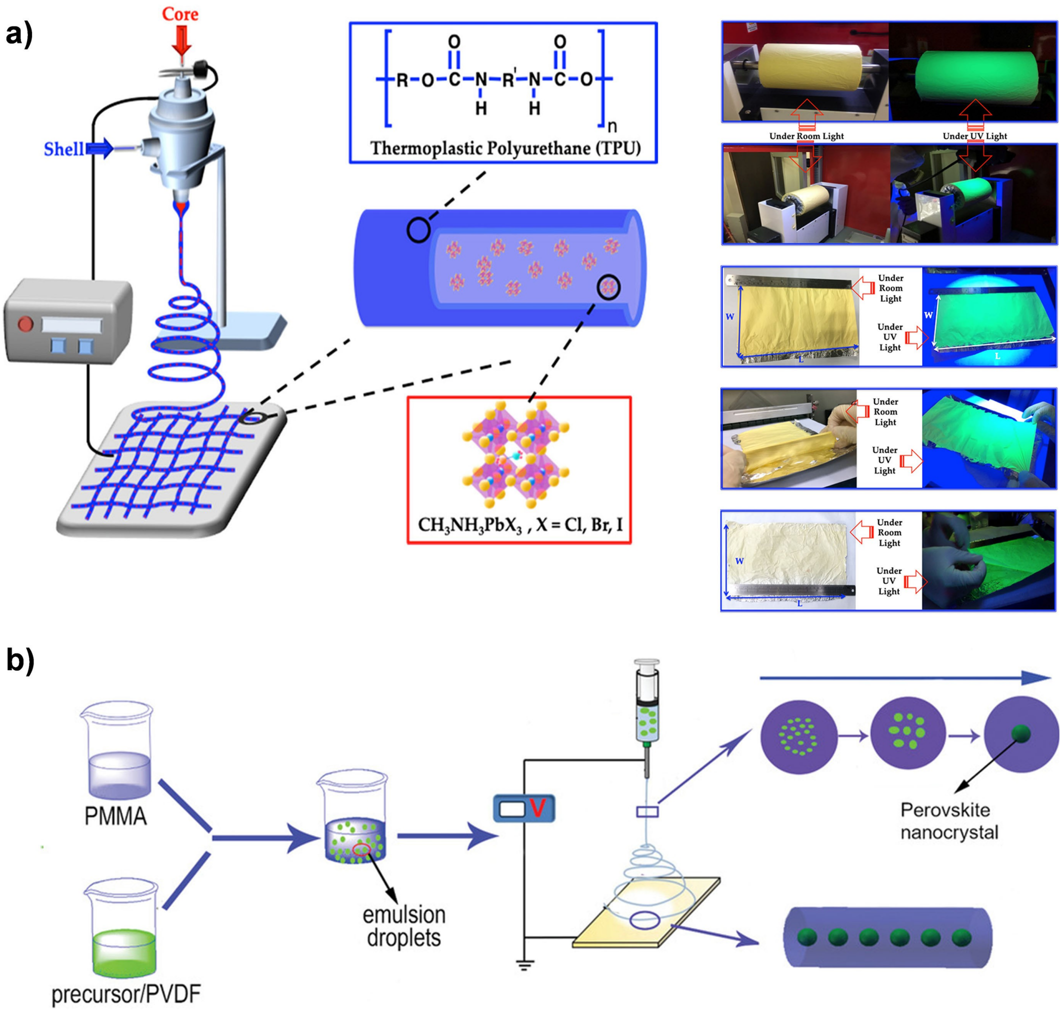


Figure 2. a) Schematically illustration of the coaxial electrospinning setup and the fabricated stretchable core–shell TPU/perovskite luminous nanofibers; right images: horizontal electrospinning system employed to prepare the large-scale luminous fiber mat and the real picture of the rotary drum after collecting uniaxial fibers under room light and UV light. Reproduced and adapted with permission from Ref. [19]. Copyright 2019, American Chemical Society.; b) Schematic of the emulsion electrospinning synthesis of $MAPbBr_3$ perovskite@polymer nanofibers, where emulsion droplets are pushed inward during solidification of the polymer fiber. Reproduced and adapted with permission from Ref. [20]. Copyright 2020, Wiley.

ure 2b).[20] During the process of fiber preparation, at the first point, the polymethyl methacrylate (PMMA) solidifies to create an outer shell cover. In the second step, emulsion drops of poly(vinylidene fluoride) (PVDF) with perovskite precursors are delivered inside to create perovskite nanocrystals, thus protected by PVDF. The smooth PMMA cover is beneficial due to light transport, and PVDF protects $MAPbBr_3$ nanocrystals against moisture. The prepared hybrid fibers exhibited intensive emission even after storage in water, and amplified spontaneous emission from the fiber network or waveguide lasing from chopped single fibers was obtained. Another protective polymer used for the $MAPbBr_3$ perovskite stabilization in the form of fibers is polystyrene (PS).[21] In this work, perovskite-PS composite fiber membranes, prepared by electrospinning technology, showed strong photoluminescence and excellent stability with 70 % of the PL intensity was preserved after soaking in water for 30 days and 85 % of the PL intensity preservation was obtained after long term heating up to 95 °C or even under irradiating with UV light. The next essential parameter of importance on perovskite-based devices is an easy and up-scalable fabrication. In this direction, printing techniques are the most used methods in this field. Quasi-two-dimensional (quasi-2D) perovskite structures stabilized by polymers have been recently prepared by different groups by injecting printing (see Figure 3.a), achieving superior lifetimes and highly luminescent composite materials.[22] Recently, Jia and coworkers prepared quasi-2D perovskite composite sheets by inject printing on the polymer sheets, where the ink preparations consisted of perovskite precursors (phenethylammonium bromide PEABr, methylammonium bromide MABr,

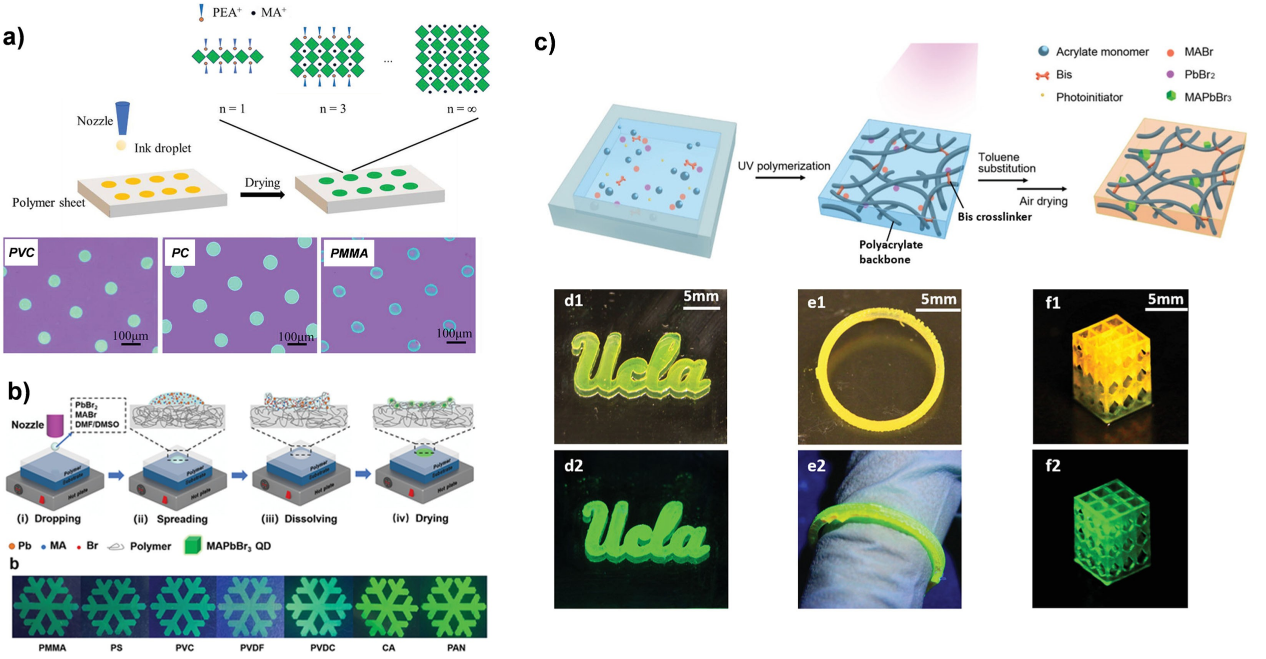


Figure 3. a) Schematic illustration of the preparation of quasi-two-dimensional (quasi-2D) perovskite composite sheets by inkjet printing. Images of printed patterns on different polymer sheets. Reprinted with permission of Ref. [22a]. Copyright 2020, Wiley; b) Schematic diagram of the in-situ inkjet printing strategy for fabricating $MAPbBr_3$ QD-based patterns by printing perovskite precursor solution onto a polymeric layer and the optical images of printed PQD patterns obtained on different polymer substrate under UV light. Reprinted with permission of Ref. [22b]. Copyright 2019, Wiley; c) Schematic of the preparation of perovskite nanoparticles gels, based on an on-site reprecipitation process, using poly(butyl acrylate) (PBA) gel containing $MAPbBr_3$ NPs; d1–f2) 2D patterns and 3D structures of $MAPbBr_3$ NPs gels printed by a digital light processing-based 3D printer, structure under white light (d1–f1), under UV light (d2–f2). Reprinted and adapted with permission of Ref. [13]. Copyright 2019, Wiley.

and lead bromide $PbBr_2$) in N,N-dimethylformamide (DMF) as a solution.[22a] When dropping ink with precursors onto the polymer sheets, the polymer partially dissolved and swelled thanks to the solvent, through the use of the swelling-deswelling microencapsulation method, like in other reported cases.[23] After both annealing and evaporating of the solvents, perovskite quasi-2D structures were formed. The polymer sheets consisted of commercially available polymers like polyvinyl chloride (PVC), as well as PMMA, polyvinyl pyrrolidone (PVP), or polycarbonate (PC). Remarkably, the prepared devices exhibited very strong stability against water, air, and light. In fact, the sheets maintained 80% PL intensity after 20 days in water or 50 days at ambient conditions. These PEA-based polymer samples exhibited improvement in PLQY due to the well self-organized structure, whereas the combination of PEA with PVC brought excellent optical properties and better homogeneity, in comparison with other polymers thanks to chlorine atoms in PVC, affecting the crystallinity and reducing defects in the lattice. This strategy avoids the use of polymer-containing inks and was further proven as a simple, yet general strategy to achieve ultrastable, highly luminescent $MAPbBr_3$–polymer composite films. Multiple polymers can be chosen, apart from the aforementioned, adding up PS, PVDF, polyvinylidene chloride (PVDC), cellulose acetate (CA), or polyacrylonitrile (PAN), compatible for colour tunability by using other perovskite QDs compositions, such as $CsPbBr_3$ and $FAPbBr_3$ (Figure 3.b).[22b] Particularly, using PVDC film the luminescence resistance to water dipping was above 100 days, in comparison with lower resistance behaviour to degradation of the samples prepared on PS, PMMA, PVC, PVDF, PAN and CA (which lasted 50, 20, 4, 1, 1.5, and 0.1 h respectively).

The two-step swelling–deswelling method may have limited the device efficiency by the resulting small fraction of the active perovskite nanoparticles layer in the final polymer film (normally, a thin layer is achieved which occupies less than 10% of the entire polymer film thickness). Therefore, strong competitors to the abovementioned 2D film structures are the 3D compact crosslinked polymerized structures, like organogels or hydrogels, which provide superior water stability.[24] Lately, perovskite organogels were prepared by photopolymerization at room temperature with in-situ perovskite precipitation which is a favorable low energy cost, one step scalable method of preparation.[13] These organogels with embedded, homogeneously distributed $MAPbBr_3$ nanoparticles throughout the entire 3D network of poly(butyl acrylate) (PBA) gel, were proved to have high stability at various pH values and temperatures, and to maintain their PLQY even after more than 110 days of immersing in water. The matrix consisted of crosslinked hydrophobic PBA organogel prepared by one-pot polymerization method, instead of using a hydrophilic network, hydrophobic polyacrylate was selected to protect the perovskites against moisture. Here, a solution of perovskites was created by mixing PBA, methylammonium bromide, and lead bromide in DMF with oleic acid and oleyl amine ligands. Another solution was prepared consisting of an acrylate monomer with a crosslinker (in this case, a commonly used N,N′-methylenebisacrylamide (BIS) was selected) and an adequate photo-initiator (Figure 3.c). After mixing those two solutions and forming the transparent gel system under UV, the gel was immersed in toluene for solvent substitution to start the perovskites nucleation. This group demonstrated the tunable and remarkable mechanical properties (from elastic to rigid), highly stretchable perovskite-based WLED device by fabricating several 3D-printed freestanding architectures (Figure 3.d1–f2), which displayed how this method successfully boosted the stability while maintaining the processability and scalability of the perovskites. Occasionally, it is impossible to dissolve the polymer matrix at ambient conditions, so it is necessary to use higher temperatures, pressure, or even aggressive solvents. For this case, the swelling-deswelling method was modified[25] by the deep-dyeing strategy.[26] With this method, it is possible to directly convert commercially available polymer matrices (for example, polyethylene terephthalate (PET)) into polymer-protected perovskite composites with excellent environmental stability.[27] The process starts with a high enough temperature that swells the polymer matrix to allow widening the polymer matrix with the precursor solution containing the perovskite precursors and surfactants in form of organic amine and organic acid. After cooling down, the deswelling process follows (annealing or antisolvent washing). Perovskite $MAPbBr_3$ nanoparticles are uniformly formed during the deswelling process in the PET polymer matrix, yielding to devices that exhibit quantum yields up to 78 %. Furthermore, the excellent stability in water showed no degradation and preservation over 87 % of their original PL after 3 years in water solution, even after several heating-cooling cycles up to 140 °C or 10 hours of permanent laser excitation.

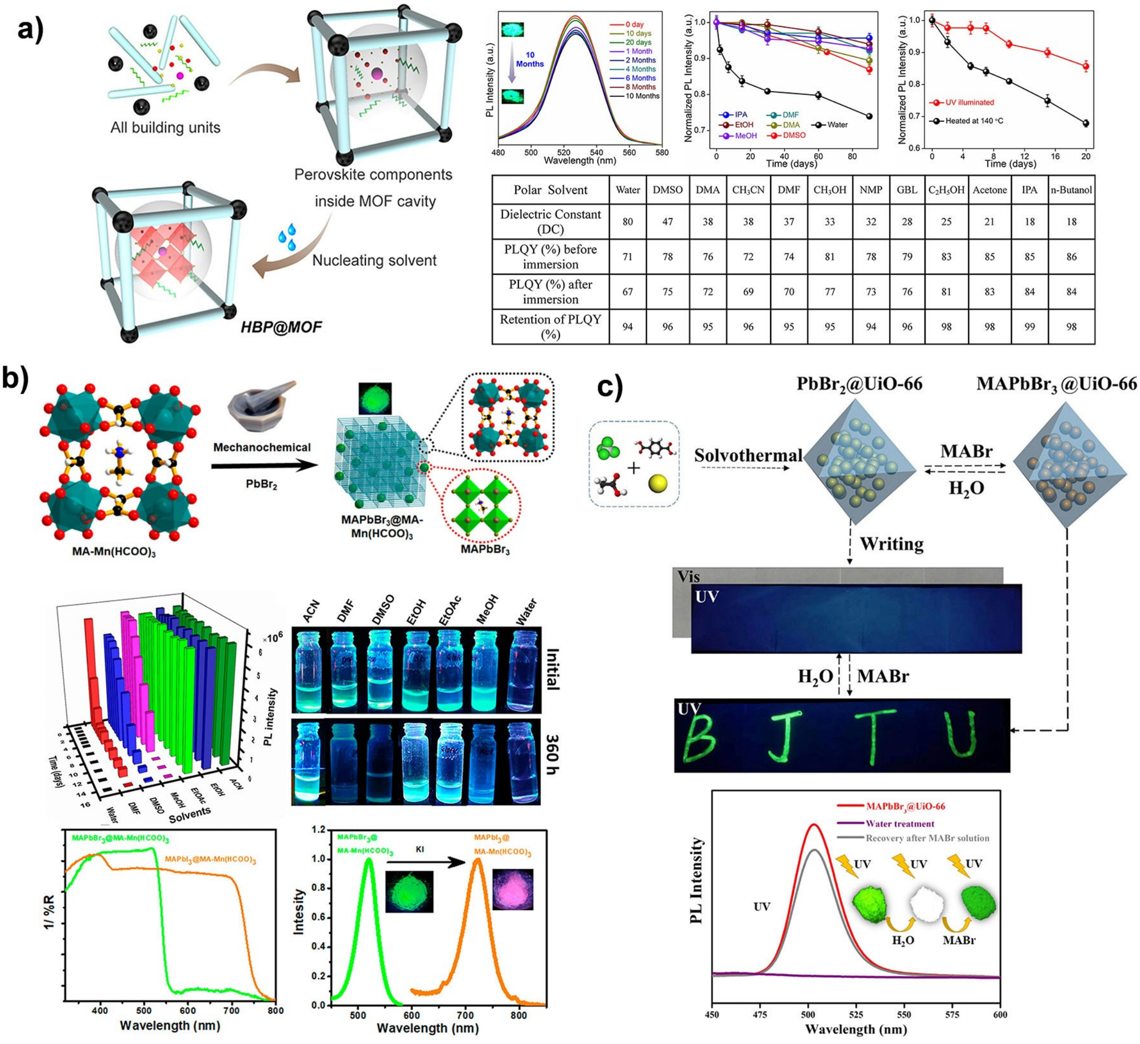
Still, the big challenge in perovskite polymer device production is its simplification. The latest research about scalable production of waterproof light-emitting perovskite polymer microparticles described the use of a continuous microfluidic reactor.[28] This method allowed $MAPbBr_3$ perovskite nanoparticles preparation by ligand-assisted precipitation and in situ UV induced cross-linking polymerization in the microfluidic channel. As polymer protection, PS was used to provide excellent air and water stability. However, the problem of this synthetic approach was the use of DMF, since on the one hand, it has to be used as a solvent for perovskite precursors, but on the other hand, it has undesirable effects such as suppression of photopolymerization and dissolving of PS. Substituting DMF by water lets the polymerization reaction unaffected. Hence, to minimize those above-mentioned drawbacks, an aqueous solution was used as a continuous phase in one-step continuous microfluidic reactor. This device enabled the in-situ production of metal halide perovskite nanoparticles by using the LARP method followed by encapsulation with UV cross-linking polymerization inside the microfluidic channel. The resultant perovskite–polymer composite microparticles exhibited narrow size distribution and extreme stability with no significant change after 168 days at ambient conditions, considered as a light-emitting waterproof composite.

3. Encapsulation within Hybrid Organic-Inorganic Porous Matrices

In comparison with organic matrices, the use of porous inorganic or hybrid materials to enhance the stability of perovskite nanocrystals while maintaining their excellent luminescent properties to enable luminescent devices could be of great interest due to the higher thermal stability, and precise control over the pore sizes of the host matrix. In general, there are two established approaches for immobilizing perovskite nanocrystals within porous matrices, independently of the type of host involved in the process: a) *ex-situ* process, which involves essentially the physical encapsulation of previously synthesized nanocrystals by adding them to a solution containing the host porous scaffold (here the size and optical properties of the colloidal NCs will be not predetermined by the matrix but from the ligands used and the synthetic conditions); and b) *in-situ* growing synthetic process, which exploits the use of the host pores from an already prepared framework as nanoreactors or ligands shells, where the perovskite precursors will be located and converted into desired perovskite nanoparticles. In this in-situ deposition method, also referred as “ship-in-bottle”, the pore size of the host will play a crucial role to achieve a fine control of the guest semiconductor size and monodispersity at the nanoscale, highly significant for their final integration into light emitting or photovoltaic devices.

3.1 Metal-Organic Frameworks (MOFs)

A very promising strategy to enhance the stability of perovskite quantum dots, to isolate them from one another while protecting them from degradation, is the immobilization within metal-organic frameworks (MOF). This porous type of material consists of inorganic metal centers and organic linkers connected by coordinating bonds. MOFs are very promising as porous hybrid host materials which pores can be adjusted in terms of size. This type of material present also has an unprecedented chemical tunability, and has extraordinarily large internal surface areas.[29] If the organic linker is modified or exchanged for another linker, the size of the pores can be controlled and also the MOF functionality. Thus, there is no doubt about their widely rich host-guest chemistry demonstrated in or diverse fields, such as gas separation,[30] catalysts,[31] biomedicine,[32] chemical sensing,[33] as well as for energy storage.[34] These matrices have recently allowed for the preparation of stable but functional perovskite solid composites, with great possibilities in optoelectronics.[35] Either inheriting from MOF counterparts or by the guest luminophores located within the MOFs pores, these materials may possess excellent luminescence properties.[36] In this regard, to achieve chemically stable composite luminescent systems, the right MOF choice will be a crucial step. In this track, Gosh and co-workers reported a series of ultrastable and luminescent $MAPbBr_3$ effectively encapsulated within MOFs following the "ship-in-bottle" synthetic strategy.[37] In this case, these nanocomposites were prepared via a pore-encapsulated solvent-directed approach which favored the loading of NCs, by their uniform and controlled growth inside the well-oriented pores of the selected host, zeolitic imidazolate framework (ZIF-8), see Figure 4.a. This $MAPbBr_3$@MOF nanocomposite exhibited interesting high stability in terms of photoluminescence and also morphology for over 10 months of storage (under ambient conditions), and under continuous heat treatment (140 °C) and prolonged UV light illumination (365 nm). The PLQYs were maintained after dipping the



Polar Solvent	Water	DMSO	DMA	CH_3CN	DMF	CH_3OH	NMP	GBL	C_2H_5OH	Acetone	IPA	n-Butanol
Dielectric Constant (DC)	80	47	38	38	37	33	32	28	25	21	18	18
PLQY (%) before immersion	71	78	76	72	74	81	78	79	83	85	85	86
PLQY (%) after immersion	67	75	72	69	70	77	73	76	81	83	84	84
Retention of PLQY (%)	94	96	95	96	95	95	94	96	98	98	99	98

Figure 4. a) Illustration of the procedure to prepare hybrid bromide perovskite@MOF nanocomposites (HBP@MOF); Stability study results of $MAPbBr_3$@MOF composite under time, and different conditions of illumination, heating and polar solvents. Reproduced and adapted from Ref. [37]. Copyright 2019, American Chemical Society; b) Strategy for synthesis of $MAPbBr_3$ QDs on a Perovskite MOF ($MAPbBr_3$@MA-Mn$(HCOO)_3$) via solvent-free mechanochemical grinding: PL intensity changes of the composite in different solvents with respect to time, photographs under UV light, UV–vis and PL spectra of $MAPbBr_3$@MA-Mn$(HCOO)_3$ and $MAPbI_3$@MA-Mn$(HCOO)_3$ (inset) photographs under UV light before and after iodide exchange. Reproduced and adapted from Ref. [38]. Copyright 2020, American Chemical Society; c) Promising application in optical information protection of $MAPbBr_3$@UiO-66 composites prepared in-situ growth, showing a significant reversible fluorescence switching with water. Reproduced and adapted from Ref. [45]. Copyright 2020, Elsevier.

nanocomposites in a wide range of polar solvents, including water for over 90 days (see inset table in Figure 4.a).

By following the in-situ synthetic route, Rambabu *et al.*, reported a one-step and solvent-free green approach.[38] The authors focus on the NC@MOF composite synthesis via a solid-state mechanochemical grinding process (Figure 4.b). Specifically, the competitive interactions between $PbBr_2$ and methyl ammonium cations were well distributed within a MOF framework[39], which acts as a template to assist the growing of $MAPbBr_3$ NCs. The preparation of MA-M-$(HCOO)_3$ [M=Mn and Co] was inspired by previous mechanochemically studies,[40] where simply grinding was enough to stabilize the NCs mechanochemically, demonstrating its cost-effectiveness and up-scalability since it avoids the use of solvents or harsh reaction conditions. Furthermore, this composite was more stable than the template-free oleic acid stabilized $MAPbBr_3$ QDs, during 15 days in different solvents, such as acetonitrile, ethyl acetate, or ethanol, excluding water, as seen in Figure 4.b. Furthermore, iodide ion exchange was achieved successfully, and its excellent processability.

One more potential avenue for the exploitation of high-performance multiphoton excited hybrid single microcrystals for future optoelectronic and micro- and nano-photonic integration applications was reported by Qian *et al.*[41] These authors showed the emerging potential of using MOFs for achieving highly luminescent crystalline $MAPbBr_3$ QDs in a high loading concentration, in this case, within the 1D channels of ZJU-28 ($[In_3(BTB)_4]$ $(Me_2NH_2)_3$) as a single crystal. The growing of NCs under this framework confinement allowed for a controlled size (8–11 nm) and narrow particle size distribution, while the aggregation-caused quenching effect was diminished. Moreover, the beneficial external protection against moisture atmosphere was demonstrated (together with effective surface passivation), since these NCs were photostable after storage in air without additional protection for 7 days (temperature = 27 °C, humidity = 60 %), in comparison with unprotected $MAPbBr_3$ QDs. One more example where the fluorescence characteristics of $MAPbBr_3$ QDs were well protected by the MOFs while bringing highly improved stability (90 days after exposure to oxygen in the air as powder) was reported by Chi and coworkers.[42] These authors fabricated three-color RGB and white light LEDs by combined the green fluorescence of the MOFs-protected perovskite QDs with the blue emission of parent MOF, together with the use of a red-emitting dopant (ruthenium(II) complex). The fluorescence quantum yields of the three materials were tested to be about 20 %. The authors chose Bio-MOF-1 as a protecting porous host for several reasons: this MOF was prepared as micro-sized crystals with abundant pores (enhancing the encapsulation efficiency of nanometric perovskites); the MOF could adsorb metal ions as Pb^{2+} for the inside in-situ growing of QD, and it has blue emission, of interest in blue light-emitting LEDs preparation. Additionally, this blue emission was demonstrated to be quenched by fluorescence resonance energy transfer (FRET) between the host MOFs and the guest luminophores. Alongside the improvement of poor resistance to moisture, polar solvents, high temperature, or UV light and oxygen exposure, another extreme challenge appears to be the production of ultra-small lead halide perovskite QDs. Thus far, the use of templating agents did not produce other but large $MAPbBr_3$ NCs. Indeed, the fast reactivity of the precursors hinders the production of ultra-small NCs by common colloidal synthetic approaches (such as the hot injection method or ligand-assisted reprecipitation method). Therefore, this technological interest in synthesizing stabile and highly monodisperse ultra-small lead bromide perovskite QDs (< 5 nm), was demonstrated by Protesescu *et al.*, through the use of nano-sized MOFs (specifically, Cr-MIL-101).[43] The perovskite precursors efficiently diffused through the large mesoporous cages of this MOF, whose pore size defined the QDs size. This simple and effective strategy, employing both host and guest in nanoparticle form, was successful for the formation and stabilization of $CsPbBr_3$, besides $MAPbBr_3$ and $FAPbBr_3$ QDs. Nanoparticles with sizes around 3 nm were promoted by interfacial interactions with the MOF pore walls, alongside minimizing aggregation of the entrapped species.

Among other technological applications including sensors, photocatalysis, light-emitting diodes, and solar cells, the possibility to control the luminescence of NC is very attractive for developing novel optical anti-counterfeiting, encryption/decryption technology, which may help to solve a worldwide problem within the field of information security protection. However, the use of $MAPbBr_3$ NCs is difficult for optical information protection, due to the instability of perovskite NCs and visibility under either ambient or UV light. In the last few years, through the NCs encapsulation by MOFs as host, it has been proved the possible off-on switching of the PL emission, via reversible formation-degradation with water and MABr solution treatments.[44] This smart and reversible phase change and luminescence of the perovskite NCs has allowed for multiple encryption-decryption, for example, by using MOFs based on Zr (UiO-66).[45] This matrix acted as a stable host for in-situ growth and encapsulating of $MAPbBr_3$ crystals by reacting a MABr solution with $PbBr_2$@UiO-66 MOF precursor (see Figure 4.c.). The quench-recovery of the luminescence could be controlled multiple times. Benefitting from the instability of $MAPbBr_3$ in polar solvents by converting the $PbBr_2$@UiO-66 from white powder exhibiting excellent stability and invisible under either ambient or UV light, to highly luminescent $MAPbBr_3$@UiO-66 through the assistance of MABr solution and water under 365nm UV light, the authors showed here the great potential of these composites in the next-generation of encryption-decryption devices (Figure 4.c).

Hybridization of MOFs with polymer matrix may become another way to adjust the optical properties of perovskite quantum dots while improving their stability. This method was provided recently by Yang *et al.*, who introduced $MAPbBr_3$ grown and encapsulated into a series of lanthanide-based metal-organic frameworks within a poly(methyl methacrylate) (PMMA) matrix.[46] This hybrid composite material showed an improved and maintained photoluminescence stability of the perovskite quantum dots (ca. 85 % of the original intensity) for a long time (after 30 days under air) avoiding their decomposition. Moreover, the PMMA films obtained by this process could achieve tunable emission from red to green light, interesting for practical applications.

To date, this research still is developing, but we can say that the encapsulation of perovskite quantum dots in metal-organic frameworks is a rising strategy to fabricate stable and functional perovskite-based solid composites with great potential for optoelectronics, catalysis, and luminescence applications. Yet in these applications, the exciton diffusion distance that determines the performance of these composites remains unknown. Bearing in mind that the group of Jin found that the exciton diffusion length is seven times longer in perovskite QDs embedded in a MOF matrix (MOF-5 = Zn_4O-$(BDC)_3$ and BDC is 1,4-benzenedicarboxylate) than solid films made of colloid $MAPbBr_3$ QDs containing long organic ligands.[47] The fast energy migration and long exciton diffusion length in QDs@MOF were attributed to the small particle size, the short dot-to-dot distance between neighboring perovskite QDs, and the surface passivation through encapsulation within the host matrix which allows for long carrier lifetimes. This investigated effect could establish the potential use of this type of QDs@MOF crystal composites for optoelectronic devices, in combination with an improved thermal and moisture resistance, as an alternative to perovskite QDs-solid film.

3.2 Silica-Based Host Materials

The confinement of luminescent perovskite nanocrystals within a porous host, which control over the pore network, can be offered promisingly by porous silica-based materials. Taking advantage of the remarkable properties of mesoporous silica nanoparticles (MSNs) and polyhedral oligomeric silsesquioxanes (POSS), recent examples of these types of porous materials will be revised and highlighted in this section.

3.2.1 Mesoporous Silica Nanoparticles (MSN)

Stabilizing perovskites with MSN have been successfully applied to bring monodispersity as well as stability. Specially, these materials have set a precedent in many areas (such as controlled drug delivery, catalysis, or sensing) due to their thermal and mechanical stability, biocompatibility, rigid framework, and homogeneous porous network, large pore volume to allow loading of various molecules and tunable pore sizes.[48] Moreover, the silica surface can be functionalized to adequate specific requirements towards real applications or to make it hydrophilic or hydrophobic, and it is inert and cheap. Overall, MSNs have great potential to solve the release toxicity issues of NCs into the environment. Along this line, many groups have reported in the last years the use of amino-containing organosilanes as capping agents for inorganic perovskite QDs, i. e., 3-aminopropyl)triethoxysilane (APTES) or (3-aminopropyl)trimethoxysilane (APTMS)).[49] Specially, APTES may favors the dissolving of PbX_2 and the stabilization of the QDs, while the amino group can effectively passivate the QD's surface keeping stable the high PLQY.[49b] However, the long-term stability (particularly against temperature) of the QDs was not improved dramatically, and hence, it is crucial to develop new methods that drive us efficiently towards the fabrication of high-performance devices, for example, LEDs. Besides, the silica walls present an easy possibility to attach chemically many different functional organic molecules (following either co-condensation or the simple post-grafting approach)[50] to allow for future more controllable designs and growth of perovskite nanocrystals, further stabilizing and improving their optical properties. According to previous works, there is a correlation between NC size and the PL maximum if using silica-based templates with pore sizes in the range of 2.5–7 nm, yet this effect is smaller for larger pores (especially for $MAPbI_3$).[51]

All these abovementioned features make them capable stand-out candidates as hosts for metal halide perovskite nanocrystals, as an efficient way to improve their stability. Very interestingly, the use of this kind of mesostructured particles has been shown by many works to enhance the stability of the guest semiconductor nanocrystals entrapped within the pores, together with a decrease in concentration defects, as well as versatility in terms of processing.[48] Yet, these powder-like materials can strongly diffuse the light and act as a barrier for charge transport, which requires further efforts and investigations towards their use for optical devices preparation, such as light-emitting displays or solar cells. Even most of the recent literature regarding the synthesis of perovskite NCs using silica templates was on $CsPbX_3$ (examples represented in Figure 5 a–b),[52] there is still a high need to continue improving the production of silica-based composites, which so far did not exhibit strong photoluminescence emission and, at the same time, high stability against moisture and temperature.

The adaptation of these previously reported methods to stabilize compositions, such as methylammonium or also formamidinium-based NCs, will be very promising for the field. During the last few years, several attempts reported the aim of improving the stability of perovskite NCs by embedding within different types of mesoporous silica materials, so far not completely achieved due to the inherent hydrophilicity and large specific surface area of the host.[53] For example, mesoporous silica powders with a different pore sizes (6–15 nm) were successfully used to prepare highly efficient and moisture-stable $MAPbBr_3$ perovskite nanocrystals (see Figure 5c).[54] Here, a ligand-free templated approach was selected to effectively grow perovskite nanocrystals within mesoporous silica. The results obtained in this work were related to a large excess of MABr, added to effectively passivating the surface traps and reduce the non-radiative recombination, rising the stability against moisture, and overall

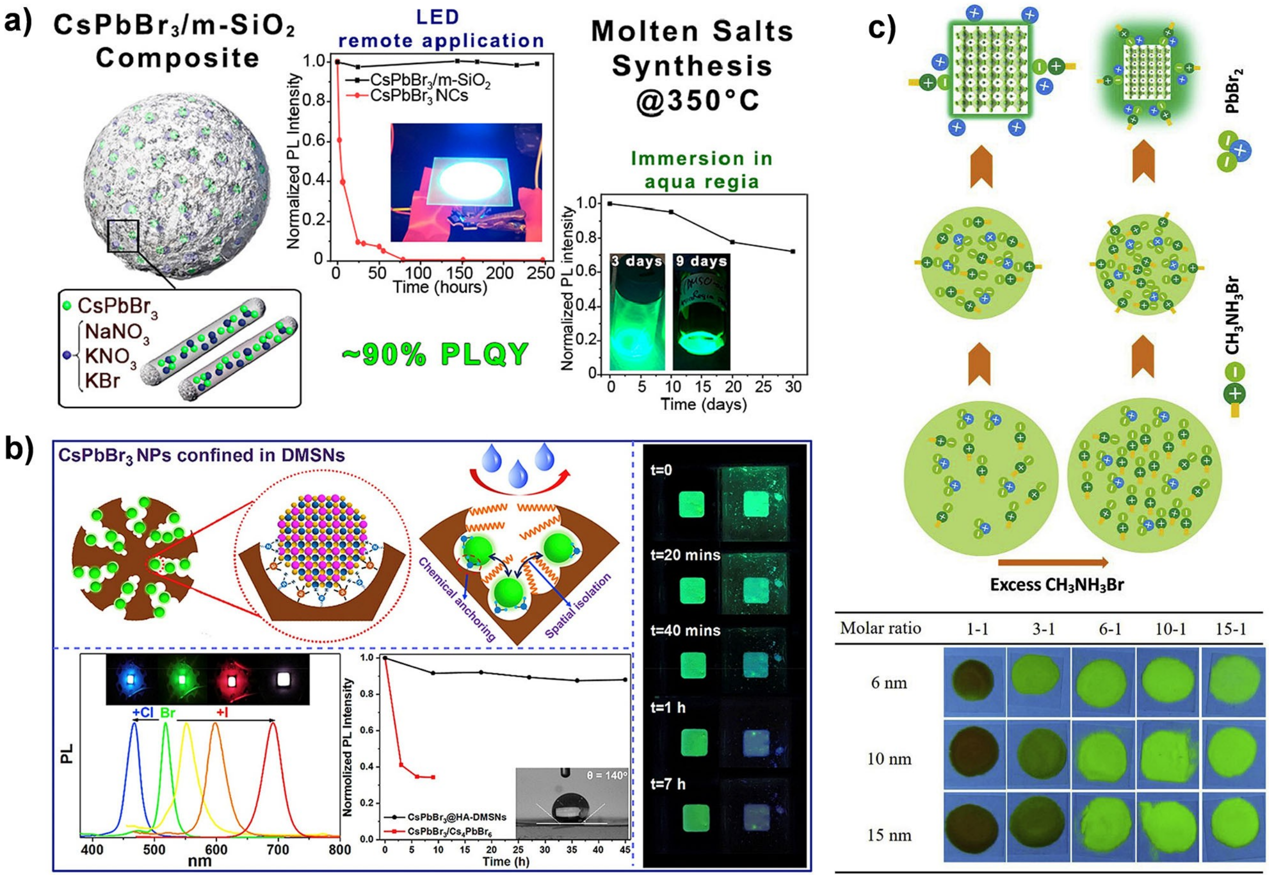


Figure 5. a) Molten-salts-based approach delivering $CsPbBr_3$/mesoporous-SiO_2 composites with high PLQY (ca. 90%) and high stability to heat, water, and aqua regia. Reproduced from Ref. [52d]. Copyright 2021, American Chemical Society; b) Spatial and chemical confined ultrasmall $CsPbBr_3$ perovskites NPs in dendritic mesoporous silica nanospheres with tuning emission colors and super water-resistant stability. Reproduced with permission of Ref. [52c]. Copyright 2020, Elsevier. c) Diagram for the impact of excess organic cations upon the nanocrystals size and particle surface and photographs of composite powders under the illumination of white light with different molar ratio of MABr:$PbBr_2$ and pore size of mesoporous silica. Reproduced and adapted with permission of Ref. [54]. Copyright 2018, Elsevier.

incrementing the PLQY (here about 75%, yet inferior to colloidal ones). The composite system kept high stability and luminescence after storage for 3 months in the air, at high humidity, and under UV illumination.

3.2.2 Polyhedral Oligomeric Silsesquioxane (POSS)

Further, overcome the poor water resistance of perovskite NCs together with unwelcome anion exchange reactions, perovskite NCs have been also embedded into polyhedral oligomeric silsesquioxane (POSS). POSS has a nanoscale Si–O cage-shaped structure (Si_8O_{12}) with organic functional groups that link to the Si atoms. This material has a length of the nanosized rigid cage structure from 1 to 3 nm, presents excellent mechanical and thermal properties, has good compatibility with polymers, and has optical transparency in the ultraviolet and visible spectra.[55] The unique organic-inorganic nature of POSS (inorganic siloxane cage and organic groups at the borders) makes them very interesting emerging candidates among hybrid materials science and engineering fields.[56] The use of these building blocks was reported to help to retain the emission of perovskite NCs for months, and the additional hole-blocking layer enhanced the performance of electroluminescent green LEDs based on $CsPbX_3$/POSS composite, as well as the stability of the device.[57] For encapsulating perovskites nanocrystals, this kind of matrix has shown the beneficial role of an insulator due to the hard and heat-insulating silica core, thus acting as a protective material for creating high-performance organic optoelectronic materials. POSS have been selected in the last years to prepare novel composites in nanosized,[58] with a great potential for optoelectronic applications and in emerging perovskite solar cells.[59]

3.3 Other Mesoporous Templates

Besides the ordered silica mesostructured used so far, for the controlled growth and improved stabilization of organometal halide perovskite NCs directed by mesoporous structures, the perovskite precursor solution can be also incorporated in other types of metal oxide mesoporous templates. For example, a promising synthetic route was reported to grow hybrid perovskite QDs of two compositions ($MAPbI_3$ and $MAPbBr_3$) in tunable sizes within pores in the range 1.7–5.1 nm of fluorine-doped TiO_2 mesoporous templates with 3D nanoflowers shape.[60] On one hand, again embedding QDs inside the porous template is a process that gives them the aimed PL stability for several hours under UV irradiation in the air promising for light-emitting diodes applications. Whereas on the other hand, the PL of the bulk film decreases, a tendency often observed in the past due to the natural aggregation of the perovskite when nanocrystals are processed as thin films.[61]

Alternatives for tailoring the photoluminescence and stability of the NCs formed inside one mesoporous structure through confined growth strategies seem of real application interest, but also their preparation at room temperature on flexible substrates which cannot stand high-temperature treatment. In this context, instead of silica, an alumina matrix with disordered and randomly interconnecting wormhole mesoporous structure was proved to be an advantageous template and insulating nature of the matrix. Highly emissive $CsPbBr_3$ NCs were formed in situ within the mesopores of Al_2O_3 as the template, at both high temperature[62] and at room temperature[63] towards thin-film configuration photovoltaic devices with the highest photoluminescence. Nevertheless, highly luminescent perovskite aluminum oxide composites with a composition like $MAPbX_3$ (X=I, Br, Cl) have not been much explored in the last few years.[64] But then again just recently, a feasible way to improve the stability of in-situ formation of ligand-free $MAPbBr_3$ perovskites was approached by the chemical functionalization of mesoporous alumina with sulfhydryl.[65] The sulfhydryl-protected NCs-composite material, aimed for fluorescence turn-on sensing of $Pb^{(II)}$ in water, showed excellent stability against the moisture and air over 30 days (see Figure 6.a).

Another promising host matrix worth to be highlighted for aiming stabilization improvement on perovskite nanocrystals is the zeolite. This kind of material has a regular pore structure, large specific surface area, and high thermal and chemical stability. For decades, the use of zeolites has shown its potential for encapsulating cations, complexes, and diverse metals and metal nanoparticles, or luminescent materials through their diverse interactions with guest species.[66] Like the other materials mentioned earlier, zeolites are another interesting host material for proper confinement of metal halide perovskite nanocrystals for limiting aggregation issues and providing them with improved stability and photophysical features.[67] Still, the understanding regarding the growth behavior of the perovskite nanocrystals within the zeolite pores, along with in what manner the interactions of the nanocrystals and the host may affect their final photophysical properties, is deficient. Recent developments have offered their preparation as microporous inorganic crystalline materials presenting ordered micropores arrangement, which considerably reduces the mean diffusion path of reactants. Zho *et al.* made perovskite–zeolite composite based on aluminophosphate AlPO-5 zeolite crystals, by following the strategy of in-situ passivation and encapsulation (Figure 6.b).[68] In this study, the growing of MA- and Cs-based perovskites benefited from ultrahigh and long-term stability under 15 months under ambient conditions and in water (for longer than 2 weeks). Likewise, the $MAPbBr_3$@AlPO-5 composite presented high thermal stability since the emission intensity retained 80 % of its initial intensity after several heating-cooling treatments. Here, the high stability, photoluminescence performance, and longer lifetimes obtained in comparison to bulk films came from the passivation effect of the perovskite's defects achieved by H-bonding interaction of the zeolite host matrix, and the strong emission of the composite was assigned to the nanoconfinement provided by the AlPO-5 template. The perovskites quantum-confinement-assisted emission agreed with previous results achieved from, for example, mesoporous silica templates,[53a] which pore size is near the exciton Bohr radius (r_B) of the perovskite nanocrystal. These perovskite-zeolite composites exhibited great potential for LEDs and backlight display developments.

4. Ion Liquids as Stabilizing Agents

Currently, ion liquids have been used to improve and stabilize perovskites. Ion liquids consist of cations and anions and possess excellent conductivity, thermal and electrochemical properties for application in the field of optoelectronic devices. It is possible to improve the properties of the electron transportation layer, or by use of ion liquids as interlayer, passivate interfacial defects between the electron transportation layer and the perovskite.

Ion liquids may contain multifunctional groups, providing interactions with the bulk perovskites.[69] For instance, tetrafluoro borate-based ion liquids may bring high-quality perovskite films with reduced defect density. By the introduction of 1-butyl-3-methylimidazolium tetra- fluoroborate into electron transportation layer results in n-type perovskite film with much lower trap density. As well, it is possible to add a small amount of 1-butyl-3-methylimidazolium tetra- fluoroborate right into the perovskite precursor resulting in device performance and stability improvement.[70]

5. Reported Data Compendium

We provide a summary of the different matrices employed to stabilize the guest $MAPbX_3$ nanoparticles in Table 1 (for polymeric matrices) and Table 2 (for porous organic-inorganic

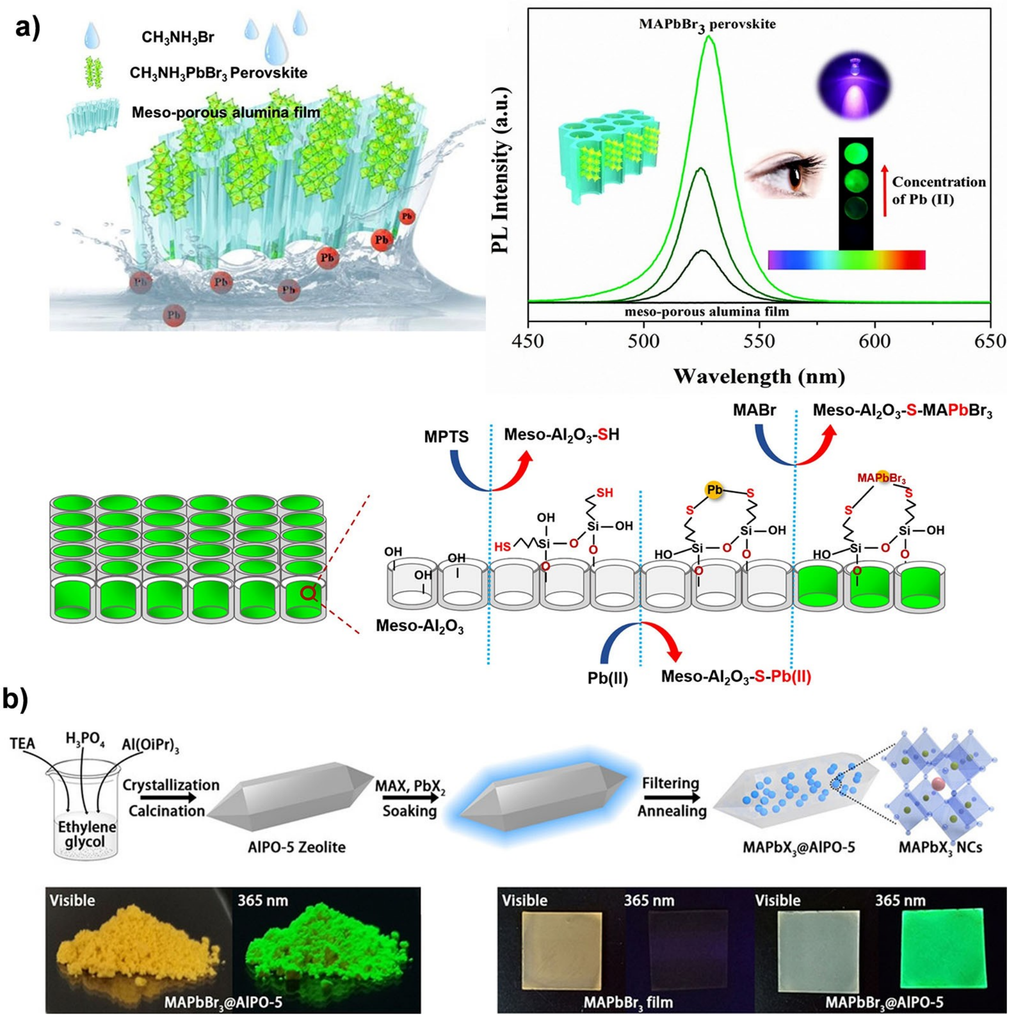


Figure 6. a) Schematic illustration of the template assisted in-situ Pb(II) extraction and formation of $MAPbBr_3$ perovskite with enhanced stability: schematic illustration of the fluorescence turn-on and visual determination of Pb(II) and illustration of the sulfhydryl functionalization, Pb(II) enrichment, and on-site conversion of Pb(II) to $MAPbBr_3$ perovskite. Reproduced from Ref. [65]. Copyright 2021, Elsevier; b) Illustration of the one-step synthesis of $MAPbX_3$@AlPO-5 composite, reached by impregnating perovskite precursor solution into AlPO-5 zeolite crystals: (left) photographs of the synthesized $MAPbBr_3$@AlPO-5 composite powder under visible illumination and UV illumination at 365 nm, and (right) photographs of $MAPbBr_3$ polycrystalline film and $MAPbBr_3$@AlPO-5 film under visible illumination and UV light at 365 nm. Reproduced from Ref. [68]. Copyright 2020, Wiley.

hybrid matrices), along with the process method used to obtain the final material and the stability characteristics reported.

6. Summary and Outlook

Metal halide perovskite materials have gained tremendous attention in the last few years mainly because of their highly interesting properties and promising applications in the fields including photovoltaic panels, light emitting diodes, solid state lasers, photodetectors, sensing, battery storage, smart wearable and stretchable devices.[71] In particular, the power conversion efficiency of perovskite solar cells has rapidly increased to 25.2 % from an initial value of 3.8 % within the past decade.[72] To date, the ligand-assisted re-precipitation method has been commonly selected for perovskite nanoparticles preparation, and it is still very promising due to its mild equipment requirements, moderate operating temperatures and easy scalability. In general, many of the recent methods and improvements have been done for all-inorganic perovskites,[73] whereas the optimal preparation and stabilization of highly luminescent organic-inorganic methylammonium lead-based perovskite nanoparticles has not been fully exploited. Nonetheless, despite all efforts done up to now, researchers still need to challenge the stability against water, oxygen, heat, or light, not yet achieved by those well-known and generally used perovskite stabilization methods. Additionally, it is very notable that this very fast-growing field of optoelectronics

Table 1. Summary of selected polymeric host-guest materials.

Stabilising matrix (Host)	Perovskite NPs (Guest)	Method	Stability features	Ref.
Polystyrene-poly(2-vinlypyridine) (PS-b-P2VP) micelles	$MAPbI_3$ $MAPbBr_3$	In-situ growing encapsulation	$>$75 days under water	[15]
P3HT + PEDOT:PSS	$MAPbI_3$	Sandwiched-thin-films	Against ion movement	[16]
Poly(ethyleneoxide) (PEO)	$MAPbI_3$	Thin layers deposition	$>$40 days ambient conditions	[17]
Popyl(propylene carbonate) (PPC)	$MAPbI_3$	Cross-linked polymerisation	$>$150 h in water; $>$2 h AM 1.5G sun illumination	[18]
Polyurethane (PU)	$MAPbBr_3$	Electrospinning; core-shell nanofibers	$>$31 days ambient conditions	[19]
Polymethyl methacrylate(PMMA); poly(vinylidene fluoride) (PVDF)	$MAPbBr_3$	Electrospinning	$>$30 days in water	[20]
Polystyrene (PS)	$MAPbBr_3$	Electrospinning	$>$30 days in water; heating; UV irradiating	[21]
Polyvinylchloride (PVC); polymethylmethacrylate (PMMA); polycarbonate (PC); polyvinyl pyrrolidone (PVP)	$MAPbBr_3$	In situ inkjet printing	$>$20 days in water; $>$50 days ambient conditions	[22a]
Polymethyl methacrylate (PMMA); polystyrene (PS); polyvinyl chloride (PVC); polyvinylidene fluoride (PVDF); polyvinylidene chloride (PVDC); cellulose acetate (CA); polyacrylonitrile (PAN)	$MAPbBr_3$ $FAPbBr_3$ $CsPbX_3$	In situ inkjet printing	$>$100 days in water (PVDC)	[22b]
Poly(butyl acrylate) (PBA)	$MAPbBr_3$	Photopolymerization; in-situ precipitation	$>$110 days in water	[13]
Polyethylene terephthalate (PET)	$MAPbBr_3$	Swelling-deswelling method	$>$3 years in water	[27]
Polystyrene (PS)	$MAPbBr_3$	UV-crosslinking polymerization in microfluidic reactor	$>$168 days ambient conditions	[28]

requires novel properties and functions, not possible to be achieved unless involving other types of materials. In fact, metal halide perovskites encapsulation has become a significant strategy to promote their application in optoelectronic fields. In this perspective, in this minireview we have provided to the reader with an overview of the very recent and available methods, technologies, and materials focusing mainly on MA-based perovskite stabilization, reported from end of 2018 and beginning of 2019 to our day, which at the same time yielded to properties improvement.

With the scope of enhancing dramatically the MA-based perovskite nanocrystals stabilization for their applications in devices, on the one hand, different polymers have been selected to prepare composite materials to encapsulate these perovskite nanocrystals. Among others, to choose from host matrices made from various commercially available and technologically good processable polymers, such as PVDF, PS, TPU, or PET provided excellent stability and aging results where perovskite composites survived even years in humidity or months in water environments. Except for water stability, which still is a limiting factor to overcome in the next years, many recent materials exhibited very strong durability in UV irradiation, thermal exposition, and other tests. Providing such excellent stability is necessary for real application in everyday life and industry, likewise the optical quality of the host, which is not always granted. On the other hand, polymeric matrices may have few drawbacks like changes in optical properties including absorbance and transmittance, non-homogenous distribution of nanoparticles in the polymer matrix in thin films or gels, causing unreproducible results. Inorganic and hybrid porous matrices were also able to provide similar stability improvements and bring vast advantages over the precise control of defined perovskite dimensions through the provided matrix pore size. Relevant factors need to be considered when choosing a specific porous scaffold, like if the pores are open or closed, the pore volume if those pores are interconnected or isolated from each other, and of course, the diameter of the pores. All these parameters will affect the amount and diffusion of the precursors within the host cavities (that act as nanoreactors), which at the end will have a correlation with the final morphology of the perovskites formed. Thus, the encapsulation of the nanocrystals aims to

Table 2. Summary of selected organic-inorganic porous materials.

Stabilising matrix (Host)	Perovskite NPs (Guest)	Method	Stability features	Ref.
Metal-organic frameworks (ZIF-8)	$MAPbBr_3$	In-situ encapsulation	> 10 months ambient conditions; heat; UV irradiation; > 90 days in water	[37]
Metal-organic frameworks (MA-Mn(HCOO)$_3$)	$MAPbI_3$ $MAPbBr_3$	Solvent-free mechanochemical encapsulation	> 15 days in different solvents	[38]
Metal-organic frameworks (ZJU-28)	$MAPbBr_3$	In-situ growth encapsulation	> 7 days ambient conditions	[41]
Metal-organic frameworks (Bio-MOF-1)	$MAPbBr_3$	In-situ growth encapsulation	> 90 days in air; High thermal, moisture, and UV stability	[42]
Metal-organic frameworks (Cr-MIL-101)	$MAPbBr_3$ $FAPbBr_3$ $CsPbX_3$	In-situ growth encapsulation	High thermal, moisture, UV stability	[43]
Metal-organic frameworks (Zr (UiO-66))	$MAPbBr_3$	In-situ growth encapsulation	High thermal, moisture, UV stability	[44–45]
Lanthanide-based MOFs within PMMA	$MAPbBr_3$	In-situ growth encapsulation	> 30 days ambient conditions	[46]
Metal-organic frameworks (MOF-5)	$MAPbBr_3$	In-situ growth encapsulation	Aqueous and thermal resistance	[47]
Mesoporous silica powder	$MAPbBr_3$	Passivation on silica host	> 3 months in air; at high humidity; UV illumination	[54]
Polyhedral oligomeric silsesquioxane (POSS)	$CsPbX_3$	In-situ growth encapsulation	High water resistance	[57]
Fluorine-doped TiO_2mesoporous nanoflowers	$MAPbI_3$ $MAPbBr_3$	In-situ growth encapsulation	Several hours at ambient conditions; UV irradiation	[60]
Mesoporous alumina (Al_2O_3)-SH	$CsPbX_3$	In-situ growth encapsulation	> 30 days in water; air	[65]
Aluminophosphate AlPO-5 zeolite crystals	$MAPbBr_3$ $CsPbX_3$	Passivation and encapsulation	15 months in ambient conditions; < 2 weeks in water	[68]

enhance their stability while keeping their highest photoluminescence. Even though the use of host matrices for stabilizing perovskite nanoparticles has tremendous advantages and is one of the best strategies, still some limitations remain unsolved. The host material might behave as an insulator hindering the charge transport-based applications. In contrast, the flexibility of such as matrices may influence the growing process and/or embedding of the perovskite nanocrystals, if comparing polymeric hosts which might suffer from inner possible deformations to more rigid scaffolds. Mesoporous silica materials in different forms, along with POSS, alumina, or various modified zeolite scaffolds are remarkable hosts with significant impact on the perovskite stability, yet in need of further explorations. Regardless, some limitations are present by using MSNs as hosts, highlighting for example the yet low diffusion of the perovskite precursors through the mesopores, influenced by capillarity effects, being affected by the compatibility matrix-solvents, where specific synthesis parameters are crucial for achieving aimed physicochemical and optoelectronic properties. Here, the specific pores characteristics and the anchoring of different functional organic groups could improve the emission properties of the perovskite nanocrystal guests and enhance their stabilization. However, this requires of either an extra reaction step if selecting external post-grafting or even more synthetic complications by following the co-condensation process to add specific functional groups within the inner walls of the porous network. Therefore, a careful selection of the perovskite nanocrystals and the functional groups may allow for a controlled enhanced design of the final host-guest composite material.

Among them, specific types of porous matrices with promising tunability over the properties of the final composite materials are the metal-organic frameworks. MOFs are emerging and promising porous hybrid materials in which chemical modification of the inorganic metal center or the organic linkers brings many possible adjusts, depending on the interactions expected towards the in-situ formation and protection of perovskite nanocrystals. It seems only a matter of time to apply these matrices for hosting and protecting hybrid organic-inorganic perovskites after well-achieved optimization. A proper external chemical modification of the host matrix may open new opportunities to boost the humidity stability of future lead halide perovskites fabrication, which is of great interest for light-emitting devices and photovoltaic devices preparation. Overall, the most common limitations observed by using MOFs as host materials are: a) the perovskites loading yield is yet relatively low, due to a large diffusion resistance within the pores (hence the NCs end up accumulated on the external surface); b) incompatibility and instability issues between the precursor solution and the perovskite NCs; and c) the PLQY of the perovskite NCs drops after being trapped within the MOF′s pores due to lack of surface passivation by extra organic ligands. Further research should pay attention not only to the stability of the NCs is important but also to the operation stability of the MOF host towards future applications working under long-term exposure to humidity and illumination.

Moreover, another future challenge to overcome is the leakage of the poisonous element Pb from optoelectronic devices, which minimization by using encapsulation methods can prevent the general public health and environmental concern. Nevertheless, for a future large-scale production of the next generation of optoelectronic devices involving the encapsulation methods, the processing costs need to be highly considered. Currently, the combination of both inorganic host encapsulation followed by a polymer coating is being adopted to develop the new generation of enhanced composite films. This novel two-step encapsulation strategy will replace the previous methods used to prepare perovskite films. The first inorganic encapsulation could reduce the agglomeration of NCs and improve the stability, while the second packaging method with organic polymers may add processability, low density, high flexibility, and transparency towards obtaining high-quality perovskite-based devices. As aforementioned in this review, the polymer coverage will passivate the NCs surface and avoid their contact directly with the environment. The overall results may lead to better optical performance if compared with the pure NCs/polymer composites.[74] Additionally, recent research in the application of ion liquid has shown great potential in the field of perovskite stabilization and efficiency improvement, but time will uncover its real benefit.[69] At this stage, we conclude that the precise stabilization of hybrid organic-inorganic perovskites nanocrystals is moving in the right direction, where the smart use of novel host materials has a fascinating open future for enhancing this field.

Authors Contribution

J. J and Y. S did the conceptualization, organization, and writing, contributing equally to this work. J. K. and O. B reviewed and edited it. All authors have read and agreed to the published version of the manuscript.

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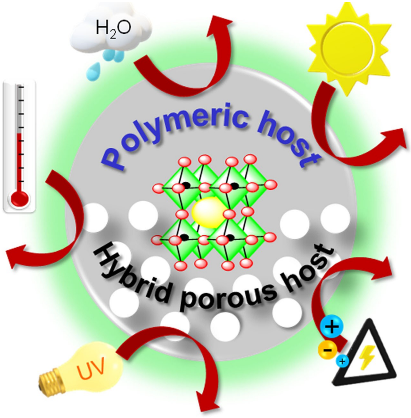

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Stability Enhancements on Methylammonium Lead-Based Perovskite Nanoparticles: the Smart Use of Host Matrices