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Recent advances in synthesis of water-stable metal halide perovskites and photocatalytic applications†

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Solar-driven photocatalytic reactions have attracted wide interest as a viable method to generate green energy and alleviate environmental challenges posed by fossil fuels. Although, various classes of photocatalysts have been explored during the past decades, the pursuit towards even more efficient ones is still ongoing. Metal halide perovskites (MHPs) have been recently proposed as novel photocatalysts owing to their wide light absorption range and excellent optoelectronic properties. However, the instability of MHPs in water is the main obstacle that impedes their applications in practice and prompts stabilization strategies to be developed. This review focuses on the recent approaches for stabilizing MHPs in water, including surface engineering, common-ion effect, and intrinsic water stability. The photocatalytic applications of water-stable MHPs are summarized and an outlook with perspectives over the current challenges are provided.

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1 Introduction

During recent years, the exploration of greener energy sources has become of utmost importance to alleviate the inordinate reliance on non-renewable fossil fuel reserves and the

consequent serious energy shortage and environmental pollution.¹ Specifically, solar radiation, as an abundant, virtually endless, and green source of energy, has been seen as a promising option for the replacement of fossil fuels.² In this context, the question of how to convert solar energy into fuels and value-added chemicals in an efficient and economic manner is a pivotal issue. So far, diverse solar-to-chemical energy conversion systems, including conventional heterogeneous photocatalysis, photoelectrochemical and combined photovoltaic-electrocatalytic systems have been proven to meet the requirements and developed for practical use.³ Compared with other reported systems, photocatalytic routes are probably the

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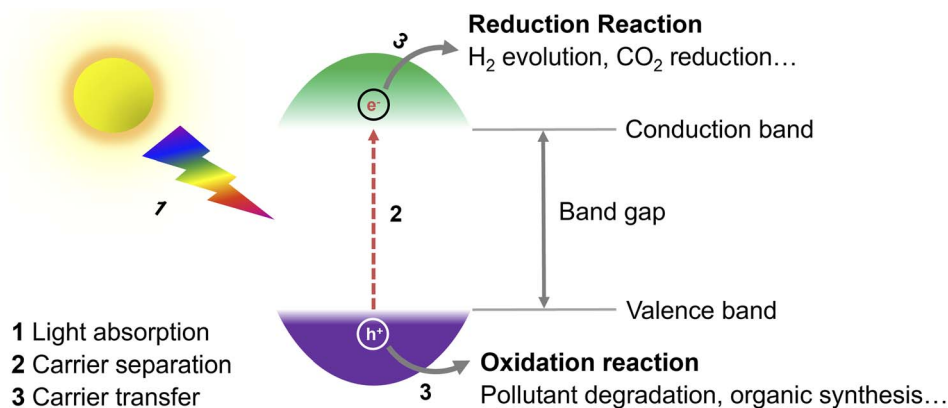


Fig. 1 Basic mechanism of heterogeneous photocatalysis.

simplest ones and easiest to implement. For example, Domen's group has already designed a 100 m² array of panel reactors to demonstrate hydrogen evolution from water over several months safely, with a maximum solar-to-hydrogen (STH) energy conversion efficiency of 0.76%.⁴ In a recent work of Zhou *et al.*, the efficiency has been improved significantly to 9.2%,⁵ which is close to the proposed target for commercialization according to techno-economic analysis.⁶ However, compared with the latest 47.6% solar-to-electricity conversion efficiency of the state-of-the-art four-junction solar cells,⁷ there is still a long road ahead to achieve such values in photocatalytic systems.

Exploring efficient, stable photocatalysts is thus one vital research field. In photocatalysis, the key component of the process is the photocatalyst (Fig. 1), whose role is to transform solar energy to charge carriers (electrons and holes) after light absorption, which then drift to the surface of the photocatalyst and participate in reduction/oxidation reactions.⁸ To date, several different photocatalysts either homogenous or heterogeneous have been proposed,⁹ including *e.g.*, transition metal complexes,¹⁰ organic photoredox catalysts,⁹ titanium

dioxide,^{11,12} carbon nitride,^{13,14} and perovskites.¹⁵ As most of the so far explored photocatalytic materials suffer from (i) limited photostability, high cost and potential toxicity,¹⁶ (ii) narrow utilizable solar spectral absorption range,¹⁷ (iii) sluggish charge carrier transport from the bulk of a photocatalyst to the surface and/or (iv) fast charge carrier recombination,¹¹ there is a room to improve conversion efficiencies.^{18,19}

The family of metal halide perovskites (MHPs) appears to offer features that tackle the aforementioned issues simultaneously. Organolead trihalide perovskites (*e.g.*, $\text{CH}_3\text{NH}_3\text{PbI}_3$) have emerged as novel high-performance photoactive absorbers with rocketing power conversion efficiency from 3.8% to certified 25.5% in just a few years.^{20,21} In general, the remarkable photovoltaic performance of MHPs originates from their high absorption coefficients,^{22,23} wide absorption window,²⁰ long electron-hole diffusion lengths^{22,24} and high carrier mobility.²⁵ All these excellent optical and charge-transport characteristics predestinate MHPs as ideal candidates for photocatalytic processes.²⁶ However, every coin has two sides, and unfortunately MHPs are not exceptions either. The ionic nature of MHPs imparts their vulnerability toward moisture and polar solvents (especially water), which severely restricts their photocatalytic applications,²⁷ and remains to be resolved. In 2016, Park *et al.* reported the pioneering work concerning the stabilization of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) in aqueous HI solution by exploiting the common-ion effect; however, this happens under harsh conditions, at $\text{pH} < -0.5$ and $-\log[\text{I}^-] < -0.4$.²⁸ Nevertheless, environmental concerns, costs, and the demand for practical conditions necessitate photocatalytic processes to be performed preferably in aqueous systems having less extreme chemistries.²⁹ While MHP-based photocatalysts have been reviewed from different perspectives, such as photoredox organic synthesis,³⁰⁻³³ CO_2 reduction,³⁴⁻³⁹ and H_2 generation,⁴⁰⁻⁴⁷ strategies to synthesize water stable MHPs or their photocatalytic applications are not yet adequately summarized. Therefore, in this review, we survey and overview the recent progress in stabilizing MHPs against water, and discuss the encountered challenges and potential limitations of their applications, with the goal of providing new ideas and inspiration to advance the design new generations of efficient MHP-based photocatalytic systems.



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field of research is Environmental Engineering, especially heterogeneous catalytic processes in gas and liquid phases. She has a special interest in *in situ* and *operando* spectroscopy applied in catalysis research.



2 Stabilization methods

Conventional lead-based MHPs are prone to decompose when exposed to moisture. It is reported that the perovskite solar cells lose more than 80% of their initial efficiency after one-day storage in ambient air, and only 5% is retained after 6 days.⁴⁸ Encapsulation of the MHP films using materials having diffusion barrier properties have been proposed to protect the MHP solar cells from moisture hence maintaining more than 90% of their initial performance for almost 2 months.⁴⁹ This is still far from the commercial long-term stability expected (25 years is typical for silicon solar cells),⁵⁰ thus the challenge in the MHP development remains to be solved.

To improve the water stability of MHPs, the role of water in the degradation of MHPs needs to be elucidated. The published results indicate that the MHPs adsorb water molecules quickly with a time scale of seconds⁵¹ and a single water molecule can accelerate the degradation of perovskite *via* acid-base reaction.⁵² What is even more troublesome, is that the water intake is not limited only to surface adsorption, but the water molecules also diffuse and penetrate the bulk and even infiltrate the MAPbI₃ unit cells (Fig. 2). However, some studies claim that MHPs have a minor tolerance to water. For example, MAPbI₃ was reported to remain intact when exposed to below 2×10^{10} Langmuir of H₂O (one Langmuir equals to an exposure of about 1.33×10^{-4} Pa for one second).⁵³ Only ~1% volume expansion of the crystal structure is observed although water incorporated in the perovskite.⁵⁴ These results are consistent with previous reports of a reversible process between the hydration and dehydration stages of MAPbI₃.^{55,56} To figure out the detailed degradation mechanism under moist conditions, the dependence of spatially resolved external quantum efficiency (EQE) under various humidity exposure conditions has been investigated by using laser beam induced current mapping, and a four-stage degradation process has been proposed.⁵⁷ When a tiny amount of water (1.6% H₂O in N₂) is introduced and kept for a short time (6 min), EQE increases marginally and reaches a maximum, which is caused by the solvation of CH₃NH₃⁺ (MA⁺)

and I⁻ ions,⁵⁸ that heals some defects, reduces the trap density, and thus improves the uniformity of perovskite films (Stage 1). As the time increases, a slow drop in EQE is observed due to the change of the electronic structure and carrier mobility of hole-transporting materials (Stage 2). In the next stage (Stage 3), a sharp decrease of EQE indicates the breakdown of 3D structure, while monohydrated 1-dimensional (1D) chains of CH₃NH₃PbI₃·H₂O or 0-dimensional (0D) dots of dihydrates (CH₃NH₃)₄PbI₆·2H₂O are formed (Stage 3). Finally, the degradation of MHPs results in the formation of CH₃NH₃I (MAI), PbI₂ and water (Stage 4). In general, the decomposition starts at the surface, especially at the MAI-terminations.⁵⁴ The loss of MA⁺ results in an open inorganic framework to form vacancies inside the crystal lattice that finally leads to a rapid deterioration or decomposition of the perovskite structure.⁵⁹ The dissolution of I⁻ ions in water is easier than that of MA⁺ ions since the hydrophobicity of -CH₃ group in MA⁺ requires higher dissolution energy.⁶⁰ These studies indicate that water molecules penetrate easily into the bulk of MHPs and the removal of ions (especially the I⁻ ions due to the lower energy barrier) is the main cause of the degradation. Based on the observations above, thus, the main strategies to obtain water stable MHPs are: (i) preventing the structure from the contact of water, (ii) compensating for the depletion of ions from the surrounding, and (iii) reducing the solubility of organic cations. In these efforts, three different strategies have been proposed, including surface engineering, utilization of the common-ion effect, and enhancement of the intrinsic stability of perovskites.

2.1 Surface engineering

Surface engineering has been explored to generate protecting layers on the MHPs, thus avoiding the direct contact of water with MHPs. In this section, six surface passivation methods are discussed: (1) organic ligands, (2) organic polymers, (3) inorganic materials, (4) metal-organic frameworks (MOFs), (5) phase engineering, and (6) water-assisted engineering.

2.1.1 Organic ligands. The application of organic ligands is a well-established strategy to manipulate the shape and size of

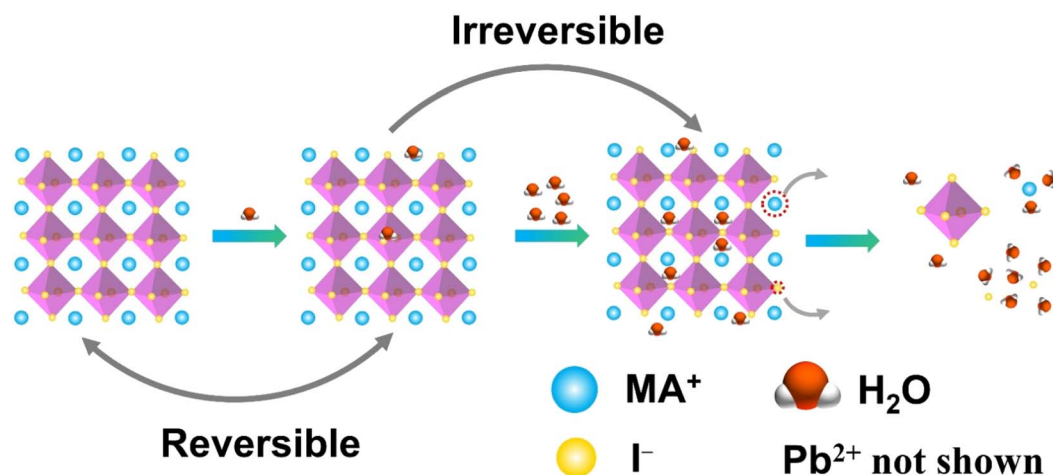


Fig. 2 Schematic illustration of MAPbI₃ decomposition in water.



MHP nanocrystals (NCs),⁶¹ and also to stabilize MHPs.⁶² Normally, frequently used ligands in synthesis of MHP NCs are oleic acid (OA) and oleylamine (OAm), which improve the dispersion of MHP NCs in nonpolar solvents, such as toluene and hexane. However, the dynamic adsorption-desorption process between the ligands and MHP NCs render the easy detachment⁶³ and removal of ligands in proton-donating solvents, causing the degradation of MHP NCs,⁶⁴ and consequent deterioration of their luminescent properties (including the electron density of states of emission bands, and the photoluminescence quantum yield).

The introduction of hydrophobic ligands on the surface of MHPs is one of the most efficient and convenient approaches to stabilize MHPs. A post-surface functionalization with hydrophobic cations *via* simple ligand exchange process can substitute surface methylammonium (MA⁺) ions and enhance the stability of MHPs. Many studies have indicated that the presence of hydrophobic quaternary ammonium cations, such as tetra-methyl ammonium, (CH₃)₄N⁺;^{65–67} tetra-ethyl ammonium, (C₂H₅)₄N⁺;⁶⁸ tetra-butyl ammonium, (C₄H₉)₄N⁺;^{69,70} and tetra-hexyl ammonium, (C₆H₁₃)₄N⁺;⁷¹ have a vital influence on the moisture-stability of MHPs. These quaternary ammonium cations adsorb chemically on the surface of MHPs, and inhibit the water intake of the lattice thus keeping the perovskite films stable under 90 ± 5% relative humidity (RH) for more than 30 days without a photovoltaic loss. This happens because the

bulky organic cations shift the surface Pb_{5c}-I_{1c} (I_{1c} represents the surface I atom coordinated with one Pb atom) bonds owing to the steric effects and impede the water adsorption on the five-coordinated surface Pb atoms (Pb_{5c}).⁷¹ In addition, these molecules can also suppress the iodide migration,⁷² evidenced by the shortened Pb–I bond (from 3.17 Å to 3.07 Å, Fig. 3a). Besides these factors, the formation of water-stable quaternary ammonium lead iodide shell may also contribute to the enhanced stability.^{66,73,74} For example, with (C₄H₉)₄NI post-treatment over CsPbI₃, the (C₄H₉)₄N⁺ cations can intercalate the inorganic framework of MHP and exchange Cs⁺ ions, forming a one-dimensional (C₄H₉)₄NPbI₃ layer⁷⁵ exhibiting intrinsic water stability (Fig. 3b).⁷⁶

Sufficient interactions between MHPs and ligands should also be considered because the instability MHP NCs partly originates from the easy detachment of ligands as described above.⁷⁷ Clearly, introducing reactive groups in the capping ligands and forming a covalent or ionic bonding between ligands and MHPs are deemed to improve the water stability of MHPs. For example, polyhedral oligomeric silsesquioxane (POSS) having a mercaptopropyl anchor group attaches to the surface of MHP NCs and forms a cage-like structure. Such POSS-protected CsPbX₃ (X = Br and/or I) NCs were shown to maintain the original green light emission and stability in water for 10 weeks.⁷⁸ Unlike the physical encapsulation strategy with hydrocarbons,^{79,80} the impressive enhancement of water

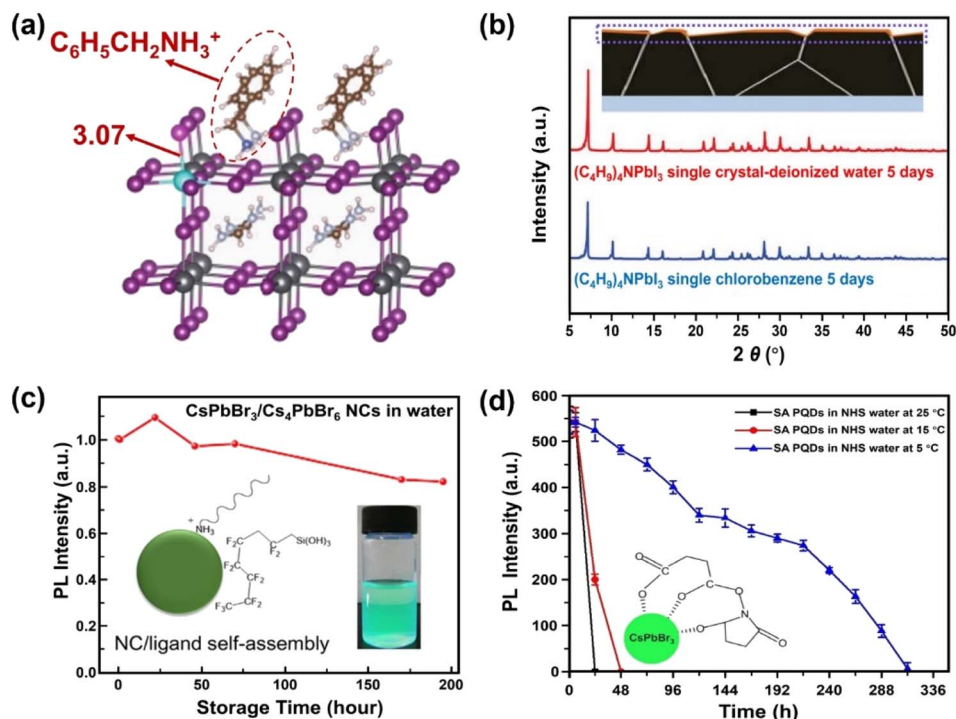


Fig. 3 Ligand engineering for water-stable MHPs. (a) Length of Pb–I bond over FA_{0.83}Cs_{0.17}PbI₃ after adding phenylmethylammonium ions. Adapted from ref. 72. (b) Formation of (C₄H₉)₄NPbI₃ layers over MHP from a (C₄H₉)₄NI post-treatment and XRD patterns of (C₄H₉)₄NPbI₃ single crystals after 5 days immersion in water and toluene. Adapted from ref. 76. Copyright 2021 John Wiley and Sons. (c) Variations of PL intensity over fluorocarbon-coating CsPbBr₃/Cs₄PbBr₆ NCs in water. Adapted from ref. 86. Copyright 2018 American Chemical Society. (d) PL intensity evolution of succinic acid-capping CsPbBr₃ QDs in *N*-hydroxy succinimide water and the formation of tridentate ligands over QDs. Adapted from ref. 93. Copyright 2021 Elsevier.





Fig. 4 Polymer encapsulation over MHPs. (a) Fluorescent photos of polystyrene, polycarbonate, acrylonitrile butadiene styrene, cellulose acetate and poly(methyl methacrylate)–MAPbBr₃ composites at different periods. Adapted from ref. 129. Copyright 2016 John Wiley and Sons. (b) Comparison of PL spectra over MAPbBr₃ NC–V18 composites before and after a 90 days immersion in water. Adapted from ref. 133. Copyright 2017 John Wiley and Sons. (c) TEM image and photos of CsPbBr₃/Cs₄PbBr₆ NCs protected by fluoropolymer shell. Adapted from ref. 138. Copyright 2022 American Chemical Society. (d) Visible light photopolymerization synthesis of CsPbBr₃/polypyrrole composites and XRD patterns after 30 days water immersion. Adapted from ref. 145. Copyright 2020 Elsevier.

examined as hosts, including polystyrene (PS), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), cellulose acetate (CA), polyvinyl chloride (PVC), poly(methyl methacrylate) (PMMA) and poly(styrene/acrylamide).¹²⁹ Among those, PS, PC, PVC and ABS can protect MHP NCs from being attacked by water for periods of months, while the CA loses stability after two days, and PMMA-protected MHP NCs fail instantly (Fig. 4a). The failure of CA originates from its hydrophilic character and thus its high-water permeability, whereas the reason of PMMA is likely stemming from its low swelling ratio of PMMA in DMF solvent and weak bonding interaction with MHPs. Specifically, the MAPbBr₃–PS and MAPbBr₃–PC composite films can survive in boiling water for 30 min with less than 15% and 7% of decay in PLQY, respectively.¹²⁹ The protecting effect of crosslinked PS is much better than other uncross-linked polymers because it cannot swell in polar solvents. For instance, the CsPbBr₃@PS composites maintain 65.7% of the absolute PLQYs after stirring in water for 3 days, and still exhibit strong green luminescence after 9 months storage.¹³⁰ Note that the composites have a good stability in acid/alkali aqueous solution, and even biologic buffers, showing advantages in monitoring pH, urea, and urease.¹³¹

Usually, the dissolution or swelling of polymers is time-consuming, especially for those of high-molecular-weight. Hence, the MHPs need to be prepared prior to coupling; however, serious degradation or aggregation may occur during the storage of MHP NCs or QDs. Through adding crosslinkable monomers into the MHP's precursor solution, polymer–MHPs composites can be achieved in a one-pot reaction assisted by heating or UV irradiation.¹³² For example, a crosslinked 4-

vinylbenzyl-dimethyloctadecylammonium chloride (V18)-MAPbBr₃ NC composite has been prepared *via in situ* polymerization under 90 °C for 30 min by employing azobisisobutyronitrile (AIBN) as an initiator.¹³³ The crosslinked MAPbBr₃ NC–V18 retains about 85% of PL intensity after immersion in water for 120 min. After copolymerization with methyl methacrylate, the water-resistance extends to 90 days without the change of its PL (Fig. 4b). However, the decomposition products of remaining photo-initiator may have an unintended consequence on the property of polymers and MHPs.¹⁴⁷ The alternative approach is to utilize polymers (for example, copolymer micelles) as nanoreactors and grow the MHPs inside the polymers. In contrast to random growth of MHPs during swelling-deswelling process, block copolymer micelles are highly ordered structures, featuring superior size uniformity and high stability of individual micellar building blocks, which are often employed as templates and scaffolds for producing arrays and ordered structures of nanomaterials.^{134,148,149} One good example is employing polystyrene-poly(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymer micelles as nanoreactors to prepare monodisperse polymer–MHP NCs. The resultant composites display strong stability against water over 75 days.¹³⁴

Similar to the strategies with ligands, improving the interface interactions between MHPs and polymers by introducing anchoring groups, such as –COOH groups^{139,150} and –CF₂ groups,¹³⁶ can enhance the stability of polymer–MHPs.¹⁵¹ For example, PMMA has been widely used as passivation to protect solar cells from oxygen and moisture.^{152–154} On the other hand, it fails to stabilize MHPs in water owing to the too weak interaction between those. Jiang *et al.* found that partially hydrolyzing



Table 2 Water-stable MHPs obtained from polymer coatings^a

Water-stable MHPs		Stability					
Materials	Methods	Medium	Characterizations	Retained PL intensity	PLQY before (after)	Observed durability	Ref.
NOA61/CH ₃ NH ₃ PbBr ₃ /glass	Photocuring	Water (washing)	PL	~100%	—	Four cycles	7
CsPbBr ₃ /PMSR (1.13 wt%)	Photocuring	Water (immersion)	PL	91%	43% (—)	24 h	122
MAPbBr ₃ /PMSR (1.13 wt%)	Physical blending	Water (immersion)	PL	93%	53% (—)	576 h	124
MAPbBr ₃ /PMSR (1.13 wt%)	Physical blending	Water (immersion, 70 °C)	PL	91%	53% (—)	50 min	124
MAPbBr ₃ /PMSR (1.13 wt%)	Physical blending	Water (immersion, 100 °C)	PL	77%	53% (—)	20 min	124
MAPbBr ₃ /SSDC (1.13 wt%)	Physical blending	Water	PL	77%	62% (—)	36 h	124
MAPbBr ₃ /SSDC (1.13 wt%)	Physical blending	Water (immersion, 70 °C)	PL	52%	62% (—)	10 min	124
MAPbBr ₃ /SSDC (1.13 wt%)	Physical blending	Water (immersion, 100 °C)	PL	44%	62% (—)	10 min	124
CsPbBr ₃ NCs-PMA (<i>R</i> _{pol} /area of 1500)	Physical blending	Water (immersion)	PL	—	—	>8 months	128
MAPbBr ₃ -polystyrene	Swelling-deswelling microencapsulation	Water (immersion)	PL	—	34% (32%)	2 months	129
MAPbBr ₃ -polycarbonate	Swelling-deswelling microencapsulation	Water (immersion)	PL	—	31% (31%)	2 months	129
MAPbBr ₃ -acrylonitrile butadiene	Swelling-deswelling microencapsulation	Water (immersion)	PL	—	48% (45%)	2 months	129
MAPbBr ₃ -polyvinyl chloride	Swelling-deswelling microencapsulation	Water (immersion)	PL	—	16% (15%)	2 months	129
MAPbBr ₃ -cellulose acetate	Swelling-deswelling microencapsulation	Water (immersion)	PL	—	47% (—)	2 months	129
MAPbBr ₃ -cellulose acetate	Swelling-deswelling microencapsulation	Water (immersion)	PL	5%	—	48 h	129
MAPbBr ₃ -poly(methyl methacrylate)	Swelling-deswelling microencapsulation	Water (immersion)	PL	—	14% (—)	2 months	129
MAPbBr ₃ -polystyrene	Swelling-deswelling microencapsulation	Boiling water (immersion)	PL	—	34% (29%)	30 min	129
MAPbBr ₃ -polyvinyl chloride	Swelling-deswelling microencapsulation	Boiling water (immersion)	PL	—	31% (29%)	30 min	129
CsPbBr ₃ QDs@polystyrene	Swelling-shrinking	Water (immersion, stirring)	PL	—	68% (64.7%)	3 days	130
CsPbBr ₃ QDs@polystyrene	Swelling-shrinking	Water (immersion, stirring)	PL	20–30%	68% (—)	30 days	130
CsPbBr ₃ -poly(methyl methacrylate)	One-pot thermal and UV polymerization	Water (immersion)	PL	54%	54.6% (—)	48 h (30 days)	132
CsPbBr ₃ -poly(butyl methacrylate)	One-pot thermal and UV polymerization	Water (immersion)	PL	56%	62.2% (—)	48 h (30 days)	132
MAPbX ₃ NCs-polystyrene-poly(2-vinylpyridine) (PS- <i>b</i> -P2VP)	<i>In situ</i> growth	Water (immersion)	PL	—	—	75 days	134
Polyimide-coated CsPbBr ₃ NCs	<i>In situ</i> growth	Water (immersion)	PL	~80%	88.1% (—)	60 min	135
MAPbBr ₃ (8 wt%) NCs/polyvinylidene fluoride	<i>In situ</i> growth	Water (immersion)	PL	—	94.6 ± 1% (68.1 ± 1%)	400 h	136

Table 2 (Contd.)

Water-stable MHPs		Stability					
Materials	Methods	Medium	Characterizations	Retained PL intensity	PLQY before (after)	Observed durability	Ref.
Hydrolyzed poly(methyl methacrylate)-coated $\text{CH}_3\text{NH}_3\text{PbBr}_3$	Mechanical grinding	Water (suspension)	PL	~80%	—	40 days	137
$\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ NCs-Hyflon-DFTHS/OLA	Physical blending	Water (suspension)	PL	68%	73% (—)	31 days	138
CsPbBr_3 /octylamine-modified polyacrylic acid + OAm NCs	Ligand engineering	Water (suspension)	PL	80.13%	—	15 days	139
PVP-capped CsPbX_3 NCs@polystyrene microhemispheres	Self-assembly	Water (washing)	PL	—	—	3 times	140
Silicone resin/PVP- CsPbBr_3 nanofibrous membranes	One-step electrospun	Water (immersion)	PL	—	—	Several hours	141
PS-PEB-PS and PEG-PPG-PEG coated CsPbBr_3 QDs	Physical blending	Water (immersion)	PL	60%	88% (86%)	1 month	142
CsPbBr_3 QDs-poly(styrene-ethylene-butylene-styrene) films	Physical blending	Water (immersion)	PL	—	—	122 days	143
V18-MAPBBr ₃ NCs	Thermal polymerization	Water (immersion)	PL	85%	—	120 min	133
V18-co-MMA-MAPBBr ₃ NCs	Thermal polymerization	Water (immersion)	PL	—	—	90 days	133
Crosslinked PETA-G/ $\text{FA}_{0.92}\text{MA}_{0.08}\text{PbI}_3$ films	Spin-coating and thermal polymerization	Water (immersion)	Photograph evolution	—	—	420 s	144
CsPbBr_3 /polypyrrole	Visible light polymerization	Water (immersion)	PXRD	—	—	30 days	145
CsPbBr_3 /polyaniline	Visible light polymerization	Water (immersion)	PL PXRD TEM	~93%	—	4 weeks	146

^a NOA61: Norland Optical Adhesives 61; Ergo: Ergo® optical adhesive 8500; PMSR: phenyl methyl silicon resin; SSDC: Silicone Sealant Dow Corning® 937; PMA: poly(isobutylene-*alt*-maleic anhydride)-*graft*-dodecyl; $R_{\text{pol/area}}$: the number of monomers of polymer per NP area [nm^{-2}]; Hyflo: Hyflon AD 60; DFTHS: dodecafluoroheptyl-trihydroxysilane; V18: 4-vinylbenzyl-dimethyloctadecylammonium chloride.



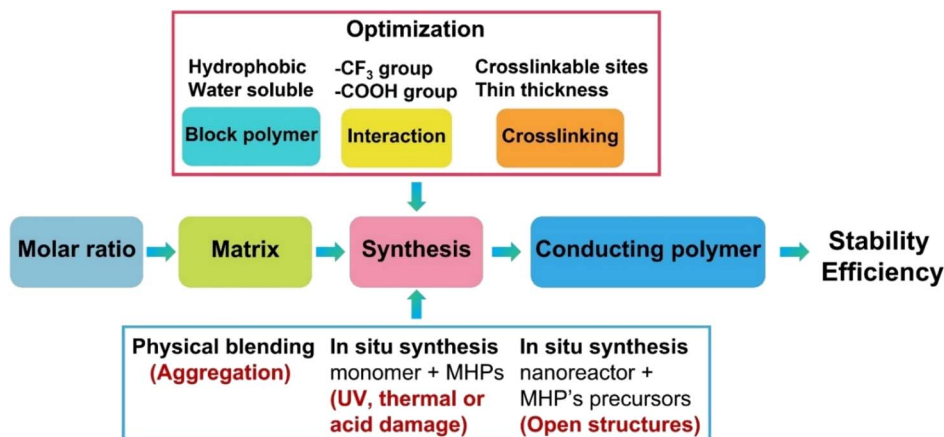


Fig. 5 Scheme of suggested strategies for the synthesis of polymer–MHPs composites.

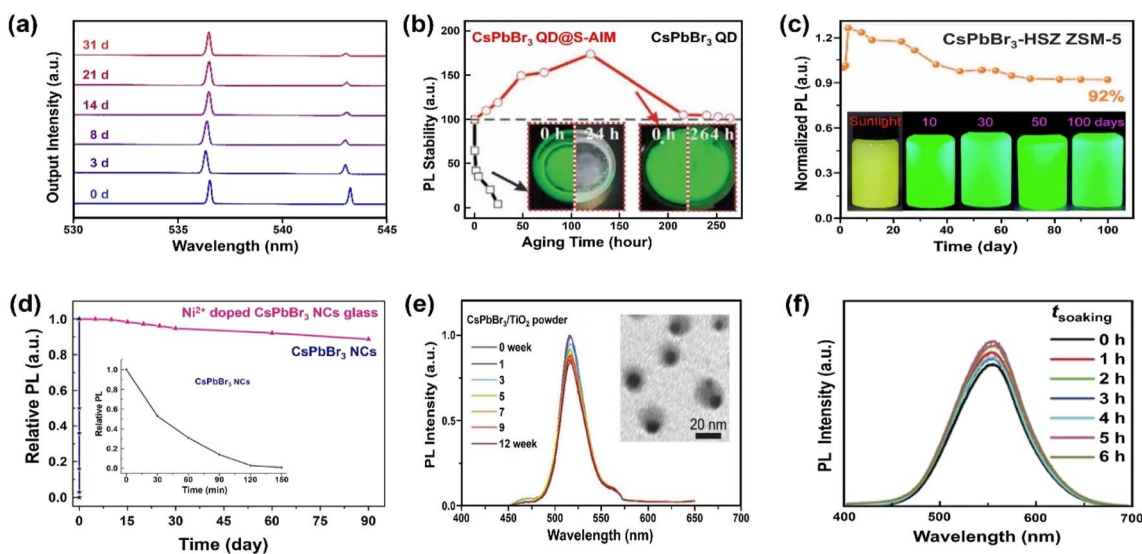


Fig. 6 Stabilizing MHPs by using inorganic materials. (a) Time-dependent normalized lasing spectra of the ALD Al₂O₃ coated CsPbBr₃ nanoplate after being immersed in water for 1 month. Adapted from ref. 158. Copyright 2020 American Chemical Society. (b) PL intensity evolution over CsPbBr₃ QDs and CsPbBr₃ QDs@superhydrophobic aerogel inorganic matrix (S-AIM) completely immersed in water with time. Adapted from ref. 163. Copyright 2020 John Wiley and Sons. (c) PL stability of CsPbBr₃-HSZ ZSM-5-700 composites when exposed in water and luminescent photographs of CsPbBr₃-HSZ ZSM-5-700 composite immersed in water for various time (5 mg mL⁻¹). Adapted from ref. 175. Copyright 2022 Elsevier. (d) The change in relative PL of Ni²⁺ doped CsPbBr₃ NCs glass and CsPbBr₃ NCs in water (inset: enlarged the change of PL with CsPbBr₃ NCs in water). Adapted from ref. 177. Copyright 2019 Elsevier. (e) The relative PL intensity of CsPbBr₃/TiO₂ NCs after immersing in Milli-Q water (0–12 weeks), inset shows a TEM image of CsPbBr₃/TiO₂ NCs after immersing in Milli-Q water for 12 weeks. Adapted from ref. 181. Copyright 2017 John Wiley and Sons. (f) Normalized PL spectra of Cs₂Sn_{0.89}Te_{0.11}Cl₆ versus different soaking time. Adapted from ref. 180. Copyright 2020 John Wiley and Sons.

from rough surface,¹⁹⁶ and the hydrophobic functional groups from the AGs.¹⁶³

However, the open shell after impregnation is still a threat to long-term stability. Thus, a second coating is normally needed. For this purpose, ALD grown compact AlO_x,¹⁶⁸ polymers^{169,170} and biomedical phospholipids^{171,172} have been reported. The mSiO₂-CsPbBr₃@AlO_x obtained with 100 ALD cycles keeps up to 95% of PL intensity after 8 h in water dispersion under stirring, and the stability extends to 90 days under static conditions.¹⁶⁸ He *et al.* embedded Mn-doped CsPbCl₃ QDs into SiO₂/Al₂O₃ monolith through a facile sol-gel process, followed by

a physical grinding. The obtained Mn-doped CsPbCl₃ QDs-SiO₂/Al₂O₃ monolith sample maintained around 92% of the initial PL intensity after 7 days under accelerated aging condition (85 °C and 85% RH).¹⁷³ For polymers, this strategy can trigger the formation of micro/nano structured SiO₂ surface, which is one essential feature needed for super-hydrophobicity.^{197,198} The coating of biomedical phospholipid can also further improve the stability over SiO₂ coated MHPs and broaden their applications in bioimaging and biosensing.^{171,172}

Another issue is the aggregation during the synthesis, which may cause quenching and instability.^{124,199} In conjunction with



polymer-type coatings, most of the studies focus on multiple MHP NCs. However, the synthesis of monodisperse MHP NCs at atomic-level is more desirable in LEDs, bio- or catalysis-related fields. Through a fast hydrolysis of highly reactive silica precursor (for example, tetramethoxysilane, TMOS) with a small amount of water, the MHP NCs or QDs can be wrapped by silica at the interface of water/nonpolar solvent *via* a simple sol-gel method to synthesize monodisperse CsPbX₃/SiO₂ nanoparticles.¹⁵⁹ The CsPbBr₃/SiO₂ Janus NCs suspension showed bright PL and remained 80% of the PL intensity after placing in water 7 days.¹⁵⁹ This method can be extended to other oxides, such as Ta₂O₅, ZrO₂.¹⁶⁰ However, the Janus structure means that part of the surfaces of MHPs are exposed to the environment simultaneously and would suffer from degradation. Subsequent work by Zhang's group has achieved monodisperse CsPbBr₃@-SiO₂ core-shell nanoparticles with the aid of ammonia *via* a modified supersaturated recrystallization method. They also found that ammonia is not mandatory for hydrolysis, but influences the morphology, size of the products and the formation rates of SiO₂. Under a harsh condition (ultrasound irradiation in water for 40 min), CsPbBr₃@SiO₂ core-shell nanoparticles still exhibited bright emission.¹⁶¹

SiO₂ is usually synthesized by the hydrolysis of Si precursor *via* a sol-gel method. Note that the choice of precursor and synthetic methods will also impact the water stability of MHP-SiO₂ composites. Owing to the fast hydrolysis rate of TMOS, it is widely used in synthesis of highly stable MHP-SiO₂ composites.^{159,161} However, it is reported that the MHP-SiO₂ composites synthesized *via* a modified ligand-assisted reprecipitation (LARP) method showed a lower stability in water, probably caused by the amorphous and porous structure.¹⁶⁴ Generally, tetraethoxysilane (TEOS) has been regarded as an inefficient precursor to envelop MHP NCs owing to its slower hydrolysis rate, which would form separate MHP NCs or big aggregates. However, monodisperse CsPbBr₃@SiO₂ NCs has been reported by using TEOS *via* one-pot hot-injection strategy.¹⁶⁵ By introducing the hydrophobic and multibranched trioctylphosphine oxide (TOPO) as ligands, the TOPO would anchor on the surface of NCs, and effectively tune the hydrolysis rate of TEOS and surface property of NCs resulting in the formation of core@-shell NCs at a nanoscale-particle level. The CsPbBr₃@SiO₂ NCs retained more than 70% of their initial fluorescence intensity within 8 days immersion in hexane-water (1/1.5, v/v) mixture. Accordingly, based on these results, we may conclude that the quality of SiO₂ and hence its barrier properties strongly depend on the synthetic routes applied.

Besides the choice of suitable precursors, the interaction of SiO₂ and MHPs would also influence the final water stability. It is found that coatings produced from phenyltriethoxysilane (phTEOS) could not envelope the MHP NCs because of the weak adsorption of intermediate silsesquioxanes over MHPs.²⁰⁰ Only combining TMOS with phTEOS (especially equimolar amount), the MHPs can be covered by 3D silica grafting with hydrophobic phenyl group, showing an improved water-resistance (at least for 24 hours).¹⁶⁴ The interaction can be strengthened by the addition of interfacial ligands (such as PVP¹⁶⁶) or the introduction of bonding interactions.¹⁶⁷ For example, Li *et al.* have

introduced a Pb-S bonding by directly using (3-mercaptopropyl) trimethoxysilane (C₆H₁₅O₃Si-SH, MPTMS) as SiO₂ precursor.¹⁶⁷ The strong bonding makes the perovskite@silica nanodots stable in water for over six weeks.

Zeolites represent a large family of inorganic porous crystalline materials, in which the anions of [AlO₄]⁵⁻ and [SiO₄]⁴⁻ tetrahedra are linked with oxo-bridges forming networks of 3D cages or channels.²⁰¹ The pore structure makes them vastly used in catalysis, separation, gas adsorption and ion-exchange.^{202,203} Cation exchange property of zeolite can activate the introduction of A site ions from MHPs, and the CsPbBr₃ QDs can grow into the zeolite structure *via in situ* crystallization. Such composites exhibit excellent photostability²⁰⁴ and water resistance.¹⁷⁴ Contrary to the commonly recognized CsPbBr₃ QDs, new species of [Na₄Cs₆PbBr₄]⁸⁺ QDs have been confirmed in the zeolite's super cage, in which the tetrahedral PbBr₄²⁻ ions are surrounded by Na⁺ and Cs⁺ ions. A recent study has shown that the high water-resistance (for 100 days) of CsPbBr₃ QDs-HSZ ZSM-5 (Fig. 6c) is attributed to the interconnected micro-mesoporous network in hierarchically structured zeolite (HSZ). The micropores act as a shielding wall to isolate MHPs from the external environment and mesopores promote the diffusivity of precursors towards the successful space-confinement of CsPbX₃ (X = Cl and Br) QDs.¹⁷⁵

As an alternative, inorganic glass matrices (silicate, soda-lime, lead-oxide *etc.*) have been proven as another effective way to stabilize MHPs. The glass matrixes feature excellent mechanical, thermal and chemical stability. Up to now, mostly CsPbX₃ NCs have been successfully incorporated into glass matrices, demonstrating dramatic enhancement of water stability, up to 90 days (Fig. 6d).^{176,177} This solution needs high processing temperature, which would unavoidable to engender the volatilization of halides precursor (*e.g.*, CsBr and PbBr₂).²⁰⁵ It has been reported that embedding CsPbBr₃ QDs into TeO₂-based inorganic glass can lower the temperature (from 1100 °C to 630 °C). However, the water stability decreases to 120 hours correspondingly.¹⁷⁸ However, the glass matrix is only studied in all-inorganic MHPs because of their higher thermal stability and structure integrity during the formation process of glass.

Although the encapsulation with AlO_x, SiO₂, zeolites and glassy materials can solve the instability issue of MHPs, similar to the non-conductive organic polymers or ligands, these insulating materials restrain charge extraction across the coating shell and thus greatly disable applications in catalysis. Therefore, instead, application of semiconducting inorganic coating materials such as SnO₂ and TiO₂ can be a more viable option. Apart from enabled carrier transport, another benefit of semiconducting coatings is a possibility to have electron-hole rectification across the interfacial junctions (depending on the band structures of the core and shell materials), which can eventually inhibit/delay recombination.²⁰⁶ Stable CsPbBr₃/TiO₂ core/shell NCs have been reported by calcination of CsPbBr₃ NCs and titanium butoxide at 300 °C for 2 h.¹⁸¹ The tight TiO₂ shell over CsPbBr₃ core ensures the stability of PL peak position and intensity (≈ 80%) for over three months (Fig. 6e). To obtain a robust protecting layer, crystalline TiO₂ is favored over an amorphous phase.²⁰⁷ However, the poor thermal stability of



Table 3 Inorganic materials used for synthesis of water-stable MHPs

Water-stable MHPs		Stability					
Materials	Methods	Medium	Characterizations	Retained PL intensity	PLQY before (after)	Observed durability	Ref.
CsPbX ₃ QDs/AlO _x films	ALD	Water (immersion)	PL	100%	—	>1 h	157
Al ₂ O ₃ -coated CsPbBr ₃ nanoplate	ALD	Water (immersion)	Lasing spectra	—	—	31 days	158
CsPbBr ₃ /SiO ₂	Water-triggered transformation and sol-gel method	Hexane/water (floating)	PL	80%	80% (—)	7 days	159
CsPbBr ₃ /ZrO ₂ -10	Water-triggered transformation and sol-gel method	Hexane/water (floating)	PL	80%	90% (—)	8 days	160
CsPbBr ₃ @SiO ₂ NPs	Modified supersaturated recrystallization	Water (ultrasonication, suspension)	PL	—	—	40 min	161
CsPbBr ₃ QDs/mesoporous silica AGs	Physical blending	Water (immersion)	PL	50%	—	14 days	162
Green-S-AIM/CsPbBr ₃ QDs	Postadsorption	Water (immersion)	PL	100%	75.6% (50.5%)	11 days	163
Green-S-AIM/CsPbBr ₃ QDs	Postadsorption	Hexane/water (floating)	PL	—	75.6% (77.6%)	4.5 months	163
phTEOS-TMOS@CsPbBr ₃ NCs	Hydrolysis-condensation	Water (immersion)	PL PXRD FTIR	—	—	24 h	164
CsPbBr ₃ QDs@SiO ₂	Nonpolar solvent	Hexane/water (floating)	PL	70%	~87% (—)	8 days	165
PVP-CsPbBr ₃ QD@SiO ₂ -octadecyl trimethoxysilane- lecithin core-shell nanoparticles	Physical blending, hydrolysis-condensation and self-assembly	Water (immersion)	PL	98%	41.6% (—)	10 days	166
CsPbBr ₃ QDs-Pb-S-SiO ₂ -SH nanodots	Hydrolysis-condensation	Water (suspension)	PL	50%	78% (—)	20 days	167
CsPbBr ₃ QDs-Pb-S-SiO ₂ -SH nanodots	Hydrolysis-condensation	Water (suspension)	PL	—	—	6 weeks	167
Mesoporous SiO ₂ -CsPbBr ₃ @AlO _x	Modified template-assisted formation and ALD	Water (suspension)	PL	95%	—	8 h	168
Mesoporous SiO ₂ -CsPbBr ₃ @AlO _x	Modified template-assisted formation and ALD	Water (suspension)	PL	20%	—	90 days	168
MAPbBr ₃ @SiO ₂ /PVDF nanoparticles	Impregnation and physical blending	Water (floating)	PL	—	85.5% (—)	1 month	169
MAPbBr ₃ @SiO ₂ /PVDF films	Impregnation and C	Water (immersion)	PL	83%	85.5% (—)	20 min	169
MAPbBr ₃ @SiO ₂ /PVDF films	Impregnation and physical blending	Water (immersion)	PL	55%	85.5% (—)	2 h	169
CsPbI ₃ @polystyrene@SiO ₂	Confined condensation	Water (boiling)	PL	97.8%	86% (—)	48 h	170



Table 3 (Contd.)

Water-stable MHPs		Stability					
Materials	Methods	Medium	Characterizations	Retained PL intensity	PLQY before (after)	Observed durability	Ref.
CsPbBr ₃ /SiO ₂ /PEGylated phospholipid	Hydrolysis-condensation and physical blending	Water (suspension)	PL	80%	—	2 weeks	171 and 172
Mn-doped CsPbCl ₃ QDs-SiO ₂ /Al ₂ O ₃ monolith	One-pot synthesis	85 °C and 85% RH	PL	~92%	—	7 days	173
[Na ₄ Cs ₈ PbBr ₄] ¹⁸⁻ zeolite	Ion-exchange and <i>in situ</i> growth	Water (immersion)	PL PXRD	100%	35% (—)	40 days	174
CsPbBr ₃ QDs-HSZ ZSM-5	Grinding-calcination	Water (immersion)	PL	92%	62% (—)	100 days	175
CsPbBr _{1.2} /I ₁₋₈ NCs@P-Si-Zn glass	Melt-quenching and subsequent heat-treatment	Water (immersion)	PL	~90%	—	40 days	176
Ni ²⁺ -doped CsPbBr ₃ NCs@B-Si-Zn glass	Melt-quenching	Water (immersion)	PL	88.2%	84.3% (—)	90 days	177
CsPbBr ₃ QDs@TeO ₂ -based glass	<i>In situ</i> nanocrystallization	Water (immersion)	PL	~90%	70% (—)	120 h	178
CsPbBr ₃ QDs@TeO ₂ -based glass	<i>In situ</i> nanocrystallization	Water (immersion)	PL	~60%	70% (—)	45 days	178
CsPbBr ₃ @ZnO nanoparticles	Physical blending	Water (ultrasonication)	PL	—	—	30 min	179
CsPbBr ₃ @NaF ₄ nanoparticles	Physical blending	Water (ultrasonication)	PL	—	—	30 min	179
Cs ₂ Sn _{0.85} Te _{0.11} Cl ₆	Hydrothermal method	Water (immersion)	PL PXRD	100%	95.42% (—)	360 min	180
CsPbBr ₃ /TiO ₂	Hydrolysis-drying	Water (immersion)	FTIR	—	—	1 week	181
CsPbBr ₃ /TiO ₂ core/shell NCs	Hydrolysis-calcination	Water (immersion)	XPS PL TEM PXRD	~85%	—	3 months	181



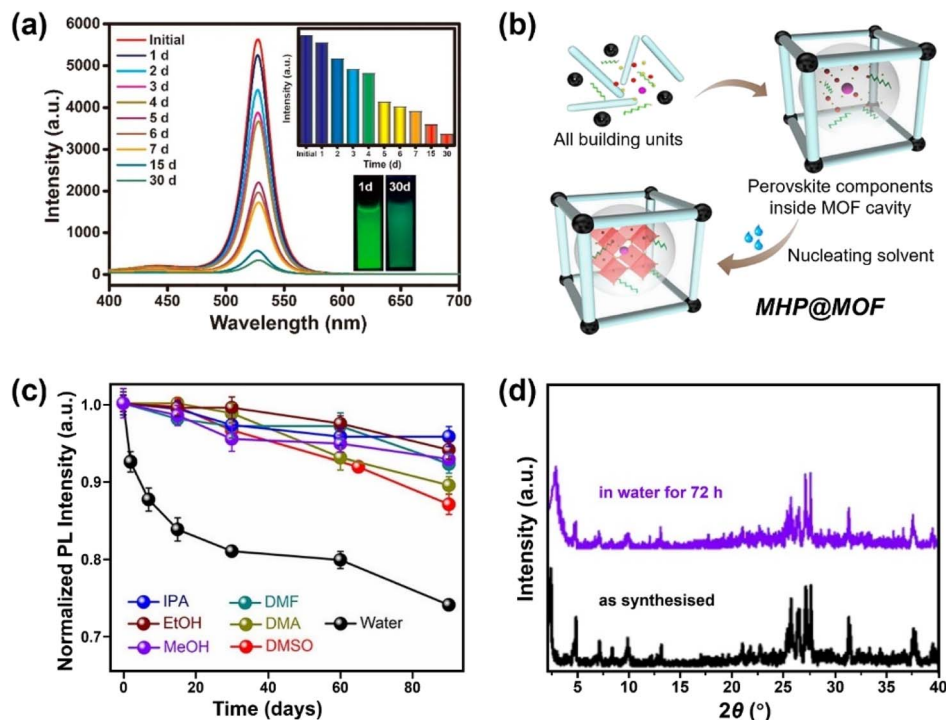


Fig. 7 MHPs encapsulated by MOF. (a) Time-dependent PL spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ @MOF-5 composites in water for different days (inset: the evolution of PL intensity and the images of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ @MOF-5 composites under 365 nm light after 1 and 30 days). Reproduced with permission from ref. 213. Copyright 2018 American Chemical Society. (b) Scheme for preparing MHP@MOF composites and (c) normalized PL intensity as a function of time in different polar solvents over a period of 90 days. Adapted from ref. 215. Copyright 2019 American Chemical Society. (d) XRD patterns of CsPbI_3 @PCN-222(20%) before and after immersion in water for 72 h. Adapted from ref. 218. Copyright 2022 John Wiley and Sons.

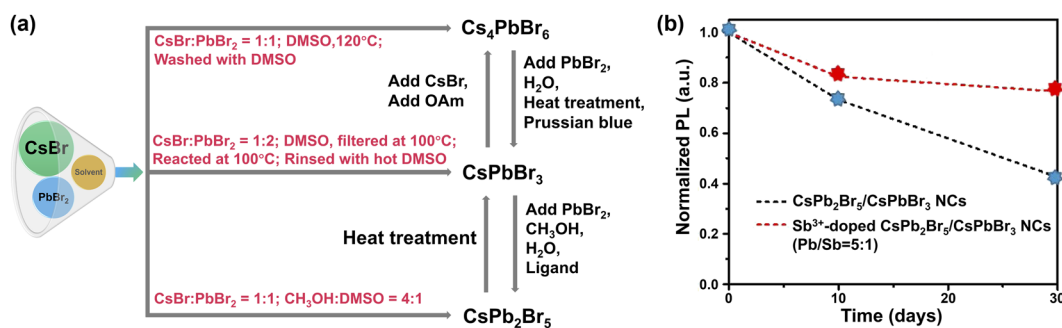


Fig. 8 Phase engineering. (a) Schematic diagram illustrating the synthesis of pure $\text{Cs}_x\text{Pb}_y\text{Br}_z$ -based MHPs and their potential transformations. (b) PL intensity of $\text{CsPbBr}_3/\text{CsPb}_2\text{Br}_5$ NCs and Sb^{3+} -doped dual phase $\text{CsPbBr}_3/\text{CsPb}_2\text{Br}_5$ NCs ($\text{Pb}/\text{Sb} = 5:1$) as a function of time. Adapted from ref. 237. Copyright 2021 Elsevier.

36 h storage.²⁴⁴ This strategy was further extended to exfoliate 0D Cs_4PbX_6 NCs into water-stable quasi-2D CsPbBr_3 nano-sheets,²⁴⁵ 1D CsPbBr_3 nanowires, 2D CsPbBr_3 nanoplatelets, and 3D CsPbBr_3 nanocubes.²⁴⁶

The reasons for the enhanced stability are manifold. As depicted in Fig. 9a, one is the dissolution of the defective surface and thus the formation of near to ideal stoichiometry (CsPbBr_3) having high stability.^{247,248} Benefiting from improved crystal quality of MHP NCs and the immiscibility of hexane with water, further dissolution of CsPbBr_3 NCs would not happen temporarily. Another explanation is the concurrent passivation

and the formation of halide-rich surface upon CsX -stripping.²⁴⁹ The origin of this passivation results from the dissolution of surface layers of MHP NCs during the CsX -stripping process and subsequently the formation of non-stoichiometric MHP surface (Fig. 9b).^{250,251} For example, with Cs_4PbBr_6 NCs as starting materials, the following water treatment engenders a phase transformation into CsPbBr_3 , accompanied by a passivation effect from the CsBr salt in water. The resultant CsPbBr_3 NCs display ultra-stability (over 200 days with $\sim 20\%$ decrease in the initial PL value, Fig. 9d).²⁵⁰ A third potential mechanism is based on the attached isomorphous hydroxyl (OH)



2.2 Common-ion effect

It is well-known that a salt can be precipitated by adding other soluble salts having common ions to the solution. Inspired by this, Nam's group have proposed the idea of common-ion effect to prepare water-stable MHPs in aqueous solution.²⁸ Although the MHPs are stabilized, it is a difficult-to-implement strategy in the practice due to the highly corrosive nature of the solution ($\text{pH} < -0.5$ and $[\text{I}^-] > 2.5 \text{ mol L}^{-1}$). Clearly, a more practical medium is needed. Later, Geng *et al.* found that $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}$ or Cl/Br) nanocrystals could be synthesized in aqueous solution when the pH value was in the range of 0–5.²⁶⁷ In this aqueous solution, the $[\text{PbX}_6]^{4-}$ ions would adsorb on NCs, facilitating the formation of halide-rich surface of NCs, thus preventing the dissolution of MHP NCs in water. However, they would decompose in neutral solution.

To realize the water stability of MHPs, our group explored to employ the bismuth halide perovskites as photocatalysts owing to their better stability in solar cells and photocatalysis.^{268–270} We found that the tri(dimethylammonium) hexaiodobismuthate (DA_3BiI_6) could be stabilized in aqueous solution using dimethylammonium iodide (DAI) without addition of acids.²⁷¹ We noted that a stepwise transformation of $\text{BiI}_3 \rightarrow [\text{BiI}_4]^- \rightarrow [\text{BiI}_6]^{3-}$ as the increase of DAI concentration and only $[\text{BiI}_6]^{3-}$ ions existed when the concentration of DAI was higher than 0.15 M (Fig. 10a and b). The structural integrity of DA_3BiI_6 could be preserved for more than two weeks (Fig. 10c and d). Similarly,

a series of 2D MHPs, including $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{PbI}_4$, $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3\text{PbI}_4$ and $\text{C}_6\text{H}_5(\text{CH}_2)_3\text{NH}_3\text{Pb}_2\text{I}_7$ have been stabilized in iodide salt aqueous solutions.²⁷²

2.3 Intrinsic water stability

Besides the strategies developed based on surface engineering and common-ion effect discussed above, exploring intrinsically water-stable MHPs are potentially advantageous because they can bypass the obstacles of water instability in aqueous media.

A few 3D MHPs have exhibited an intrinsic stability in water. As far as we know, the first reported intrinsically water-stable MHPs were hydroxyl ammonium lead iodo chloride ($\text{OHNH}_3\text{-PbI}_2\text{Cl}$) and hydroxyl ammonium lead chloride ($\text{OHNH}_3\text{-PbCl}_3$).²⁷³ After stirring in deionized water for 1 h, no leaching of Pb^{2+} was detected. In addition, no color change of the solids was observed after a 45 days immersion in water, suggesting outstanding water-stability. It is speculated that strong hydrogen bonding interactions among MHPs contribute to the water stability. However, it is worth noting that their crystal structures are still under debate.^{274,275} Also, $\text{C}_6\text{H}_4\text{NH}_2\text{CuBr}_2\text{I}$ with ABX_3 structure has exhibited no structure change after water immersion for 4 h.^{276,277} Currently, another widely studied water-stable MHPs are dimethylammonium tin halide perovskites,^{278,279} which feature no decomposition after 20 h in deionized water (see Fig. 11a). Based on DFT calculations (Fig. 11b), the intrinsic water-stability originates from higher

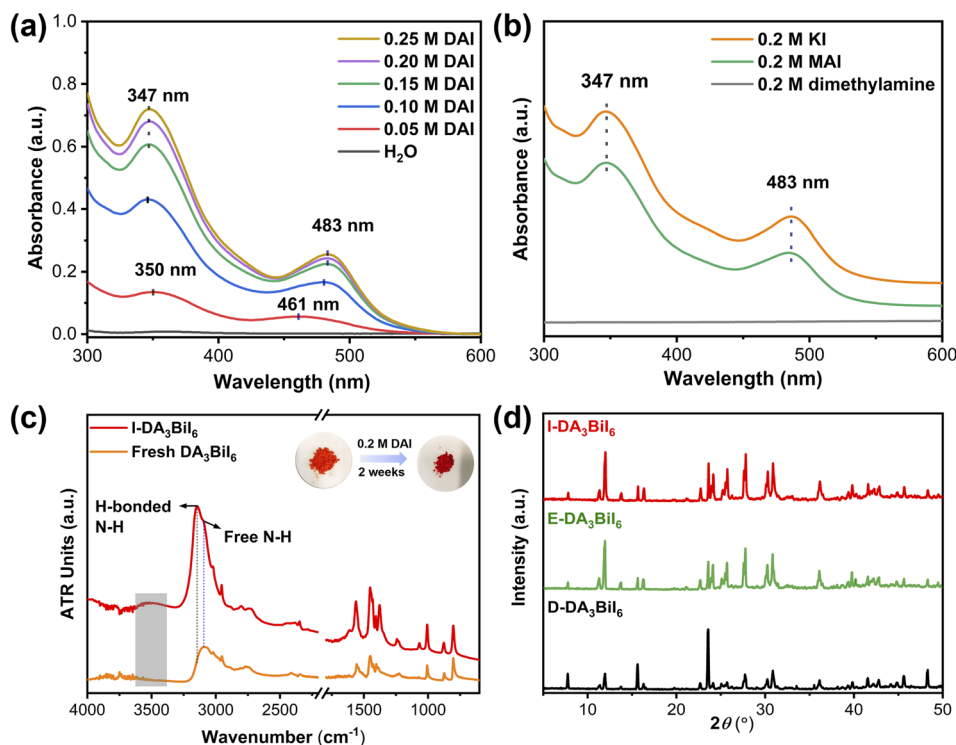


Fig. 10 Common-ion effect. (a) UV-vis absorption spectra of DAI aqueous solutions after immersing DA_3BiI_6 for 1 day. (b) UV-vis absorption spectra of 0.2 M aqueous dimethylamine, KI, and MAI solutions after immersing DA_3BiI_6 for 5 min. (c) ATR-FTIR spectra and color change of DA_3BiI_6 and immersed- DA_3BiI_6 powder. (d) XRD patterns of DA_3BiI_6 after immersion in water, ethanol and DA_3BiI_6 synthesized from DAI. Reproduced from ref. 271.



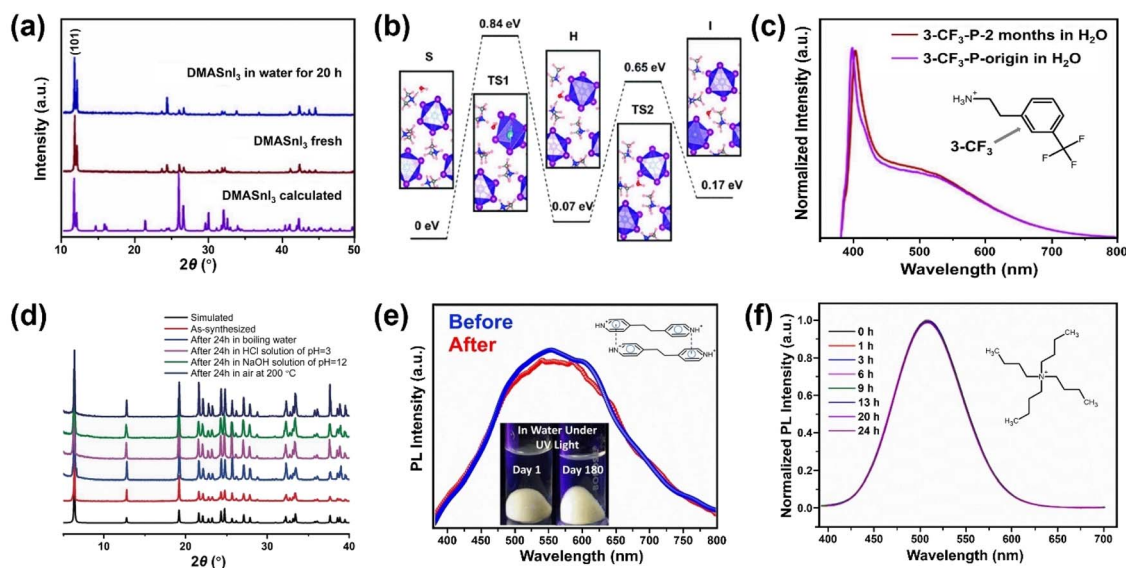


Fig. 11 Intrinsic water-stable MHPs. (a) The powder XRD (PXRD) patterns of DMASnI₃ before and after water treatment. Adapted from ref. 279. Copyright 2020 John Wiley and Sons. (b) Relative energy profile for water infiltration into (101) surface of DMASnI₃ crystal. Adapted from ref. 279. Copyright 2020 John Wiley and Sons. (c) PL spectra of 3-CF₃-MHP before and after being kept in water for 2 months. Adapted from ref. 285. Copyright 2022 American Chemical Society. (d) PXRD patterns of [Pb₂Cl₂]²⁺ [O₂C(CH₂)₂CO₂]⁻ before and after chemical treatment for 24 h. Adapted from ref. 288. Copyright 2017 John Wiley and Sons. (e) PL spectra of fresh and immersed (4,4'-EDP)Pb₂Br₆ for 180 days. Adapted from ref. 294. Copyright 2021 John Wiley and Sons. (f) Normalized PL spectra evolution of (C₄H₉)₄NCuCl₂ after water immersion for different periods. Adapted from ref. 296. Copyright 2021 American Chemical Society.

water surface adsorption energy, higher water osmotic energy barrier, and smaller intralayer spacing inside DMASnI₃ structure compared with the Pb-based counterpart.²⁷⁹

In contrast to 3D MHPs, low-dimensional (2D, 1D and 0D) perovskites have shown better environmental stability.^{280–282} A typical 2D perovskite can be regarded as interdigitating bulky organic bilayers intercalated by inorganic layers. The replacement of MA⁺ with bulkier alkylammonium cations results in enhanced stability.²⁵⁵ Inspired by this, several (quasi-) 2D perovskites having a bulky organic cation, *e.g.*, phenylethylammonium (C₈H₉NH₃⁺, PEA⁺),^{283–285} 1-hexadecylammonium (CH₃(CH₂)₁₅NH₃⁺, HDA⁺),²⁸⁶ have been developed (Fig. 11c). Among them, PEA-based MHPs have been widely investigated and proven that increased van der Waal's interactions²⁵⁵ and reduced water adsorption energy are the key factors for the improved stability.²⁸³ Another possibility is to have a better interaction between the A site (such as cysteamine,²⁸⁷ α,ω -alkanedicarboxylates [O₂C(CH₂)₄CO₂]⁻,^{288,289} bipyridine²⁹⁰) and inorganic framework (Fig. 11d).²⁸⁸ As supported by DFT calculations, the strong coordination between Pb atoms and adipate dianions increases the energy cost of surface hydrolysis and limits the penetration of water molecules.²⁸⁹

Meanwhile, a series of 1D and 0D MHPs with intrinsic water stability have been reported including 1D [N-methyldabconium]PbI₃,²⁹¹ [(AD)Pb₂Cl₅],²⁹² (DAO)Sn₂I₆ (DAO = 1,8-octyldiammonium),²⁹³ (4,4'-TMDP)Pb₂Br₆ (TMDP = trimethylenedipyridinium),²⁹⁴ (4,4'-EDP)Pb₂Br₆ (EDP = ethylenedipyridinium),²⁹⁴ and 0D (3-ethylbenzo[d]thiazol-3-ium)₄Bi₂I₁₀,²⁹⁵ (C₄H₉)₄NCuCl₂.²⁹⁶ The cations are summarized in Fig. 12, and the details of stability are listed in Table 4. The molecular design strategies aim to increase the ionization energy,²⁹¹ introduce

cation- π interaction (Fig. 11e),²⁹⁴ enhance steric hindrance effect (Fig. 11f),^{292,296} or utilize hydrogen-bond-free A sites.²⁹⁵ Among them, one report introduced the concept of long-range intermolecular cation- π interactions among A-site cations (4,4'-TMDP or 4,4'-EDP) of hybrid perovskites and facilitate the formation of polymer-like network, imparting water stability up to 180 days (Fig. 11e). Cation- π interaction is originated from the noncovalent interaction between the π face of aromatic ring and cation (such as alkali cations, ammonium ions),²⁹⁷ which is stronger than the cation-water interactions during the decomposition of MHPs.²⁹⁸ Undoubtedly, the development of intrinsic stability of MHPs in water may provide new directions and opportunities to advance the photocatalytic applications.

Besides the selection of A cations, substitution of the B sites with smaller divalent metals could reduce the lattice parameter and increase the cohesive energy, which has been reported to improve the MHP stability.^{299–301} Substitution of Pb²⁺ with smaller divalent metals would also favor the formation of vacancy-ordered A₂BX₆ double perovskites with improved stability. Hamdan *et al.* synthesized a vacancy ordered halide perovskite Cs₂PtI₆ exhibiting extraordinary stability up to 1 year under ambient condition and showing stability under high temperature (350 °C), extremely acidic (pH 1) and basic (pH 13) solutions.³⁰² DFT calculations suggest that the improved stability is due to the strong covalent interaction of the B-X bonds in the isolated [BX₆]²⁻ clusters.³⁰³

Halogen anion substitution is another approach. A partial replacement of iodide with bromide was found to enhance stability and water tolerance in mixed iodide-bromide MHP compositions.³⁰⁴ This is related to the suppression of oxygen incorporation and the presence of stronger hydrogen bonds



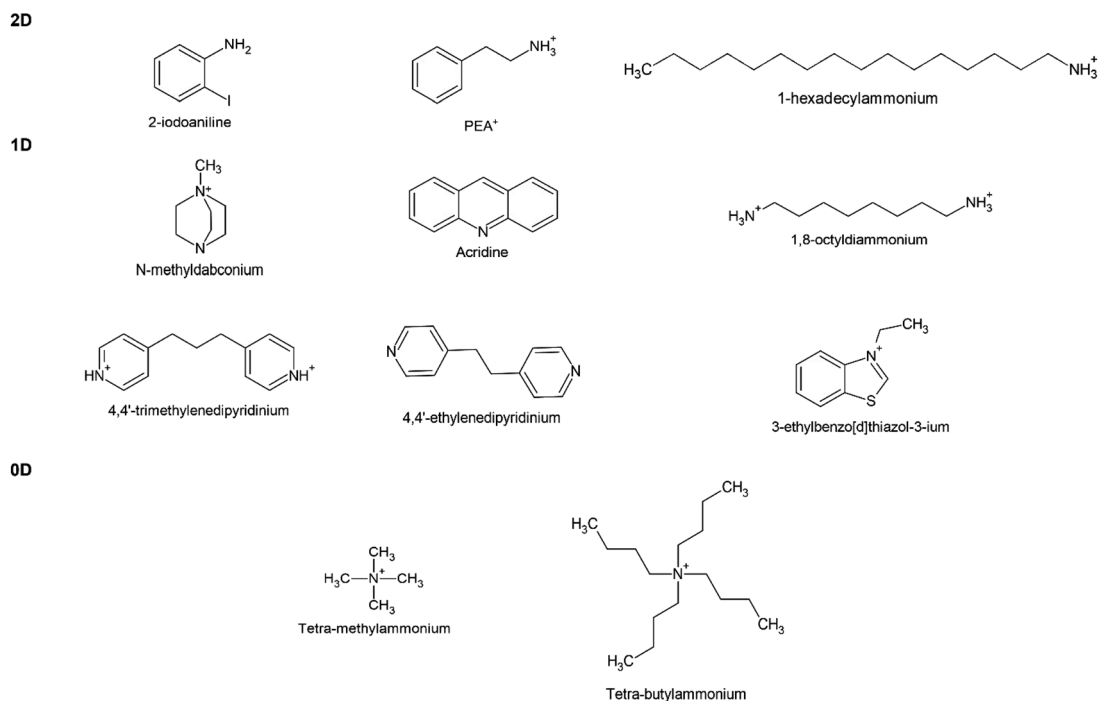


Fig. 12 Chemical structures of organic cations used for fabricating water-stable MHPs.

between the MA⁺ cation and Br⁻ ions as the bromide content increases³⁰⁵ as well as the weaker interaction of water with bromide.³⁰⁶ Apart from halogen ions, pseudohalides (cyanide, cyanate, thiocyanate, selenocyanate, azide, BF₄⁻, PF₆⁻, BH₄⁻, N₃⁻ and HCOO⁻) have shown significant stability enhancement of MHPs.³⁰⁷ For instance, thiocyanate (SCN)-substituted CH₃-NH₃Pb(SCN)₂I was shown to be more stable than pristine CH₃NH₃PbI₃ (for 4 h vs. <1.5 h) under 95% humidity.³⁰⁹

3 Photocatalytic applications

In the past seven years, water-stable MHPs have attracted much attention for numerous potential applications (Table S1 and Fig. S1†) owing to their enhanced stability and improved performance. Very recently, it has been exploited as potential photocatalysts in different reactions. In this section, we will provide an overview of these photocatalytic applications and will show lots of nice and encouraging studies for pollutant degradation, H₂ generation, CO₂ reduction and organic synthesis over water-stable MHP photocatalysts.

3.1 Pollutant degradation

Photocatalytic degradation is an attractive way to remove pollutants from wastewater and thus a great amount of work has been devoted to exploring effective photocatalysts. Aamir *et al.* firstly reported on water-stable OHNH₃PbI₂Cl and OHNH₃PbCl₃ for photocatalytic dye degradation of Direct Yellow 27 dye under sunlight with a degree of degradation of 93.98% within 20 min and almost 100% after 55 min, respectively.²⁷³ However, both catalysts are only UV-responsive. On the other hand, Ghosh and co-workers reported that the water-

stable MAPbBr₃@ZIF-8 composites could degrade different pollutants (methyl orange, methyl red and nitrofurazone) under visible light (60 W LED lamp, λ_{max} ~ 530 nm) or sunlight. The composite exhibited a higher degradation for methyl orange and could degrade methyl orange up to 90% in 100 min (degradation rate constant: 0.02723 min⁻¹), shown in Fig. 13a.²¹⁵ Although the degradation rate is not high enough compared to the other materials, it can be improved by using photoactive MOFs.³¹⁰

To alleviate the toxicity associated with Pb, some lead-free MHPs have been explored. Wu *et al.* prepared a C₆H₄NH₂CuCl₂I film to degrade rhodamine B (RhB) under visible light irradiation. Degradation of 18% of RhB in 60 min was achieved (degradation rate constant: 0.003 min⁻¹). They found that the sluggish transfer rate of holes restrains photocatalytic performance of this catalyst. After coupling the photocatalyst with a hole-transporting material (CuO), the charge separation was enhanced, resulting in a degradation rate of 0.005 min⁻¹.³¹¹ As also suggested by the study, one may enhance the overall photocatalytic activity by constructing heterojunctions that rectify electron-hole transport at the interface of two semiconductors to facilitate better charge separation and to limit photocharge recombination. A good example is a nanocomposite of PEA₂SnBr₄/g-C₃N₄ prepared *via* ball milling of the constituents. Compared with pristine g-C₃N₄, the heterojunction decreased the degradation time of methylene blue (10⁻⁵ M) from 90 min to 45 min (degradation rate constant: 0.078 min⁻¹) under solar light.²⁸⁴ Among the so far reported photocatalysts, DMASnI₃ seems to show the best photocatalytic performance with a complete conversion of methyl orange (100 mg L⁻¹) in 12–15 min (degradation constant rate: ~0.13 min⁻¹) under visible light.²⁷⁹



Table 4 Summary of intrinsically water-stable MHPs^a

Water-stable MHPs		Stability					
Materials	Methods	Medium	Characterizations	Retained PL intensity	PLQY before (after)	Observed durability	Ref.
(C ₄ H ₉) ₄ NPbI ₃ NBCAnPbI ₃ (CH ₃ NH ₂ PbI ₃)	Solvent evaporation	Water (immersion)	PXRD	—	—	5 days	76
	<i>In situ</i> synthesis	Water (immersion)	UV-vis absorption spectroscopy PXRD	—	—	30 min	73
Rb _{0.05} Cs _{2.95} Bi ₂ I ₉ single crystals	Temperature lowering method	Water (immersion)	PL, PXRD, XPS and UV-vis absorption spectroscopy	~100%	17.63% (—)	24 h	308
OHNH ₃ PbI ₂ Cl crystals	Solution method	Water (stirring)	UV-vis absorption spectroscopy	—	—	45 days	273
	Solution method	Water (stirring)	UV-vis absorption spectroscopy	—	—	45 days	273
C ₆ H ₄ NH ₂ CuBr ₂ I thin film	Grinding and spin-coating	Water (immersion)	PXRD	—	—	4 h	276
C ₆ H ₄ NH ₂ CuBr ₂ I thin film	—	Water (immersion)	PXRD	—	—	2 h	277
(CH ₃) ₂ NH ₂ SnI ₃ (DMASnI ₃) single crystals	Temperature lowering method	Water (immersion)	UV-vis absorption spectroscopy PXRD	—	—	16 h	278
	Temperature lowering method	Water (immersion)	PXRD	—	—	20 h	279
DMASnI _x Br _{3-x} crystals	—	Water (immersion)	PXRD XPS FTIR	—	—	—	—
Mn-doped (PEA) ₂ PbBr ₄ crystals	Lewis base-assisted precipitated method	Water (immersion)	UV-vis diffuse reflectance spectroscopy High-power XRD	—	>45% (—)	45 days	283
	Wet-chemistry (solvent evaporation)	Water (stirring)	PXRD ICP-OES	—	—	4 h	284
Trifluoromethyl-modified PEA ₂ PbBr ₄ (HDA) ₂ PbI ₄ (HDA ⁺ = CH ₃ (CH ₂) ₁₅ NH ₃ ⁺) (HCya) ₂ PbI ₄ (Cya = HS(CH ₂) ₂ NH ₂) crystals [Pb ₂ X ₂ ²⁺] [O ₂ C(CH ₂) ₄ CO ₂ ⁻] crystals	Temperature lowering method	Water (immersion)	UV-vis absorption spectroscopy XPS PL	~100%	18.11% (—)	74 days	285
	Modified ligand-assisted reprecipitation	Water (immersion)	PXRD PL	—	—	30 min	286
	Temperature lowering method	50% isopropanol-water (immersion)	—	—	—	>30 s	287
	Hydrothermal method	Boiling water, HCl solution (pH 3), and NaOH solution (pH 12)	—	PXRD	—	—	24 h



Table 4 (Contd.)

Water-stable MHPs		Stability					
Materials	Methods	Medium	Characterizations	Retained PL intensity	PLQY before (after)	Observed durability	Ref.
$[\text{Pb}_2\text{X}_2^{2-}]$ $[\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2^-]$ crystals	Hydrothermal method	HCl solution (pH 3–6), pure water (pH 7) NaOH solution (pH 8–11) and boiling water Water (immersion)	PXRD	—	—	24 h	289
APbX_2 (A = bipyridine) crystals	Ligand-assisted reprecipitation	Water (immersion)	PXRD XPS SEM	—	—	24 h	290
$[\text{N-Methyl(dabconium)]PbI}_3$ crystals	Solvent evaporation	Water (immersion)	PXRD Dielectric permittivity	—	—	15 h	291
$[\text{AD}]\text{Pb}_2\text{Cl}_5$ (AD = acridine) micro-belts	Precipitation	Water (immersion)	PL PXRD SEM	~100%	7.45% (58.79%)	60 days	292
$(\text{DAO})\text{Sn}_2\text{I}_6$ (DAO = 1,8-octyldiammonium) crystals	Temperature lowering method	Water (immersion)	XPS UV-vis absorption and Raman spectra, PXRD	—	20.3% (—)	>15 h	293
4,4'-Trimethylenedipyridinium lead bromide crystals $[(4,4'\text{-TMDP})\text{Pb}_2\text{Br}_6]$	Temperature lowering method	Water (immersion)	PL UV-vis absorption, PXRD	~100%	3.7% (—)	180 days	294
4,4'-Ethylenedipyridinium lead bromide crystals $[(4,4'\text{-EDP})\text{Pb}_2\text{Br}_6]$	Temperature lowering method	Water (immersion)	PL UV-vis absorption, PXRD	~100%	4% (—)	180 days	294
(3-Ethylbenzo[d]thiazol-3-ium) $_4$ Bi $_2$ I $_{10}$ (EtbtBi_{10}) single crystals	Solvent evaporation	Water (immersion)	PL XPS	98.6%	82% (—)	24 h	296
$(\text{C}_4\text{H}_9)_4\text{NCuCl}_2$ single crystals	Solvent evaporation	Water (immersion)	PXRD	—	—	4 h	302
Cs_2PtI_6 $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_3\text{I}$	Hydrothermal method Solvent evaporation	Water (immersion) 95% RH	UV-vis absorption spectra	—	—	4 h 4 h	309

^a NBCAnPbI₃: 4-[(N-3-butylne)carboxyamido]anilinium lead(II) iodide; ICP-OES: inductively coupled plasma optical emission spectrometry.

3.2 H₂ evolution reaction (HER)

MHPs have also been regarded as a promising family of materials for photocatalytic HER. However, due to the constraint of water stability, previous works in MHP photocatalysts mainly focused on hydrogen generation from concentrated halide acids as summarized before.^{40–47} Here, the results related to MHP-based photocatalysts for H₂ production from water are presented. The first results of H₂ evolution from water with MHPs was reported by Tao's group²⁷⁸ using DMASnI₃, H₂ evolution from water under 300 W Xe-lamp was explored and H₂ evolution rate of 3.2 μmol g⁻¹ h⁻¹ was obtained. One year later, Malavasi's group observed that DMASnBr₃ is also highly air-resistant.³¹² They proved that bare DMASnBr₃ photocatalyst exhibited a HER rate of 6 μmol g⁻¹ h⁻¹ (50 mW cm⁻², 1500 W Xenon lamp with UV filter), which was further improved to 11 μmol g⁻¹ h⁻¹ after introducing triethanolamine (TEOA) as sacrificial agent and 1 wt% Pt as co-catalyst. Later, g-C₃N₄ was introduced to further improve the HER performance by constructing heterojunctions. As shown in Fig. 13b, the DMASnBr₃@g-C₃N₄ (33 wt% DMASnBr₃) exhibited stable HER activities and reached an impressive H₂ production of 1730 μmol g⁻¹ h⁻¹ with an apparent quantum yield (AQY) of 6.6% (50 mW cm⁻², 1500 W Xenon lamp with UV filter).³¹³ The enhancement of photocatalytic activity is closely tied to the suitable bandgap and matched band alignment. Same strategy was extended to PEA₂SnBr₄/g-C₃N₄ and Cs₃Bi₂Br₉/g-C₃N₄ systems and the maximum HER rates of 1600 μmol g⁻¹ h⁻¹ (50 mW cm⁻²,

1500 W Xenon lamp with UV filter) and 1050 μmol g⁻¹ h⁻¹ (50 mW cm⁻², 1500 W Xenon lamp with UV filter) were achieved, respectively.^{284,314} Apart from hydrid MHPs, inorganic MHPs have also been employed as photocatalysts for HER due to their better stability in humid air.³¹⁵ Yin *et al.* prepared a series of inorganic Cs₂Pt_xSn_{1-x}Cl₆ (0 ≤ x ≤ 1) crystals *via* a hydrothermal method. The Cs₂Pt_{0.05}Sn_{0.95}Cl₆ catalyst exhibited good phase stability in water for at least 4 hours and obtained a rate of 16.11 μmol g⁻¹ h⁻¹ (300 W Xe lamp) for hydrogen evolution from water using TEOA as the sacrificial agent.²⁰⁹ Encouragingly, Fei's group reported the first organolead iodide layered crystalline material [Pb₈I₈(H₂O)₃]⁸⁺[⁻O₂C(CH₂)₄CO₂]⁻⁴ (TJU-16) with overall photocatalytic water splitting characteristics few years ago. Combing Rh as co-catalysts, the TJU-16-Rh_{0.22} exhibited a hydrogen evolution rate of 31 μmol g⁻¹ h⁻¹ (300 W Xenon lamp with an AM1.5 G filter) with AQY of 0.13% at 320 nm.²⁸⁹

3.3 CO₂ reduction

To alleviate environmental issues related to ever-increasing levels of CO₂ concentration in the atmosphere, photocatalytic valorization of CO₂ to useful compounds such as CO, methane, formic acid and alike have been placed in the focus of research for decades. Recently, Chen *et al.* combined water-stable perovskite-like organolead iodide [Pb₈I₈(H₂O)₃]⁸⁺[⁻O₂C(CH₂)₄CO₂]⁻⁴ (TJU-16) with Au co-catalyst (Au_{0.19}/TJU-16) for photocatalytic CO₂ reduction in aqueous solution.³¹⁶ Without using any sacrificial agent, the Au_{0.19}/TJU-16 with loading of 0.19 wt% of Au

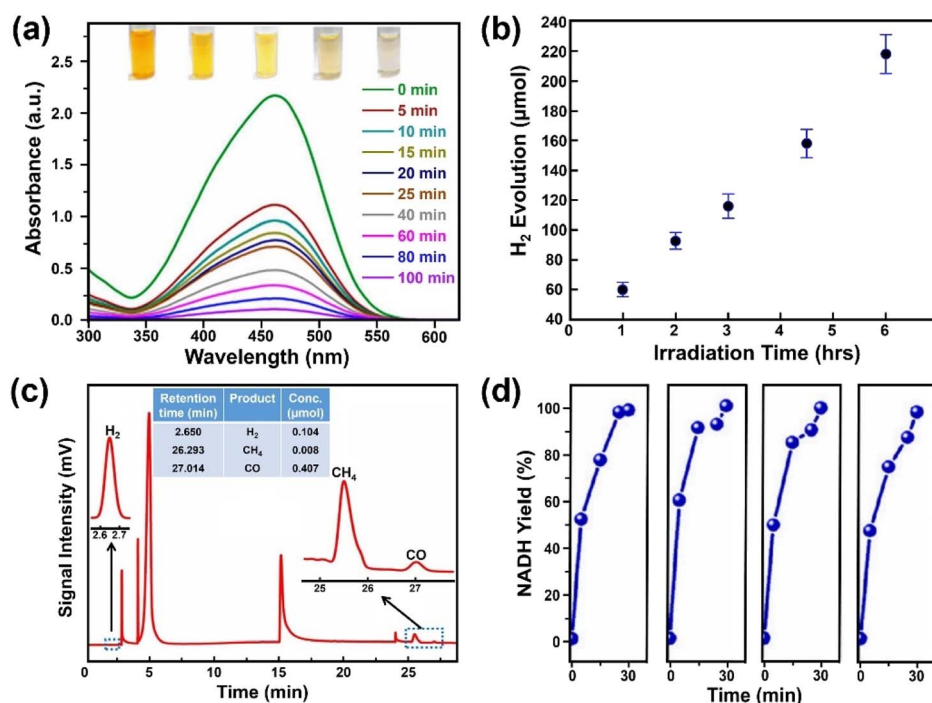


Fig. 13 Photocatalytic applications over water-stable MHPs. (a) Absorption spectra evolution of methyl orange solution degraded by MAPbBr₃@ZIF-8 under visible light irradiation. Adapted from ref. 215. Copyright 2019 American Chemical Society. (b) Hydrogen evolution over 33 wt% DMASnBr₃@g-C₃N₄ composite (1 g L⁻¹, 10% v/v triethanolamine, 3 wt% Pt) under simulated solar light. Adapted from ref. 313. Copyright 2020 John Wiley and Sons. (c) CO₂ reduction products over CsPbBr₃@g-C₃N₄ composite under AM1.5 G simulated sunlight. Adapted from ref. 317. Copyright 2022 Elsevier. (d) Nicotinamide adenine dinucleotide (NADH) yields over DMASnI₃ irradiated by blue LED lamp (wavelength of 450 nm) with four independent tests. Adapted from ref. 279. Copyright 2020 John Wiley and Sons.



nanoparticles showed the highest photocatalytic CO production rate of $2.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ and CH_4 production rate of $10.1 \mu\text{mol g}^{-1} \text{h}^{-1}$ in water under AM 1.5 G simulated irradiation, achieving a solar-to-fuel conversion efficiency of 0.034%. In addition, the consumption of electrons calculated from CO and CH_4 of $\text{Au}_{0.19}/\text{TJU-16}$ is 2.2-fold of individual TJU-16. It was concluded that the improvement in the activity originated from the spatial charge accumulation and enhanced interfacial charge transfer when applying the Au co-catalyst. In another study, photocatalyst film of CsPbBr_3 nanoparticles coated with monolayered C_3N_4 ($\text{CsPbBr}_3@g\text{-C}_3\text{N}_4$) was found to be capable of transforming CO_2 to CO, CH_4 and H_2 (0.407 , 0.104 and $0.008 \mu\text{mol cm}_{\text{cat}}^{-2}$, respectively) in the presence of water vapor under AM1.5 G solar without using scavengers.³¹⁷ Nanoparticles of the individual phases (*i.e.*, $g\text{-C}_3\text{N}_4$ or CsPbBr_3) alone did not produce any reduction species of CO_2 (Fig. 13c). Isotopic labeling experiments confirmed the origin of products from CO_2 reduction. The improved performance was ascribed to the enhanced stability of CsPbBr_3 coated with the $g\text{-C}_3\text{N}_4$ shell as well as by the promoted separation of photocarriers at the heterojunction interface.

Doping of the photocatalyst with ionic impurities offers a further strategy to improve their optical absorption, catalytic behavior as well as carrier transport properties.^{87,251} For example, Co-doped $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ NCs was demonstrated to be superior compared to its pristine counterpart for water-assisted CO_2 photoreduction with a conversion of $247 \mu\text{mol g}^{-1}$ under visible light irradiation (with CO and CH_4 as the main products). The Co-dopant is assumed to provide not only additional active sites, but it is also believed to be responsible for altering the adsorption energies of reactants and intermediates thus influencing the reaction pathways.

3.4 Organic synthesis

Photocatalytic synthesis of organic compounds is another fascinating field to offer environmentally benign and cost-effective routes. Although numerous works have been done with MHPs for organic synthesis, such as C–X (X = C, N, O, P) formation, carbon–carbon cleavage and carbon–hydrogen activation, all these photocatalytic reactions are limited to nonpolar solvent systems.^{30–33} To broaden their applications in aqueous system, a prerequisite factor is to utilize water-stable MHPs. Ju *et al.* firstly extended the organic synthesis to aqueous solution with $\text{DMASnI}_x\text{Br}_{3-x}$ for photoenzyme catalysis.²⁷⁹ The nicotinamide adenine dinucleotide (NADH) yield was nearly 100% within only 30 min and exhibited stable reproducibility in four tests under blue LED irradiation (Fig. 13d). $320 \mu\text{M}$ formic acid can be obtained over a period of 60 min in the photoenzymatic reaction, suggesting an efficient photocatalytic process in artificial photosynthesis.

4 Challenges and prospects

In this review, we summarize the significant advances in the development and applications of water-stable MHPs. To date, the water stability of MHPs has been achieved by surface engineering, common-ion effect and intrinsically stable MHPs. As

an emerging class of photocatalysts, the photocatalytic study of water-stable MHPs is still in their infancy. Several challenges and future research directions related to water-stable MHPs are identified as follows:

(1) Although various strategies have been proposed to obtain water stability of MHPs, to realize their photocatalytic applications, studies should be further focused on the charge carrier transport properties by exploring novel MHPs with intrinsic water compatibility (quasi-3D and 2D MHPs) and/or employing surface passivation that can protect MHPs from water while preserving good carrier transport features.^{318–323} For example, constructing a MHP@shell core–shell heterostructure is a highly promising way to hit two birds with one stone. By bringing MHPs with semiconducting/conductive shell, not only new catalytically active sites³²⁴ or protective coatings³²⁵ can be introduced by the second phase, but more importantly rectifying interfaces may be obtained.

(2) While some water-stable MHP based photocatalytic systems have shown good photocatalytic activity in the degradation of organic dyes, more challenging and highly relevant fields such as hydrogen evolution and activation/valorization of CO_2 are still in their early stages of development, and catalysts exhibit lower photocatalytic performance compared to traditional photocatalysts.³²⁶ One possibility for the inferior activity might lie in the severe surface charge recombination.³²⁷ In this regard, constructing a close-contact interface among MHP-based composites, which benefits the sufficient transfer and rectification of photogenerated charges, is highly desirable.^{328–330} It has been proven that chemical modification or *in situ* synthesis can result in an intimate heterointerface.^{151,325,330,331} Therefore, in the future, it is plausible to expect new avenues in this direction as well.

(3) Another vital direction of research is towards an in-depth understanding of reaction mechanisms over MHP-based photocatalysts, as the contemporary results are not entirely coherent and conclusive. Taking CO_2 reduction reaction as an example, there are debates over the CO_2 adsorption sites on bismuth-based $\text{A}_3\text{Bi}_2\text{I}_9$ (A = Rb^+ , Cs^+ or MA^+)^{332–335} and the origin of products (photocatalysis³¹⁷ or photolysis^{336,337}). The photocatalytic HER reaction mechanism over DMASnBr_3 is also not exhaustive. It is reported that the binding energy of electron polarons over DMASnBr_3 surface dominates the HER activity, but the specific role of electron polarons, as driving force or trapping charges, needs further investigation.³³⁸ In this regard, combining analytics, such as *in situ* Fourier-transform infrared spectroscopy, *in situ* Raman, *etc.*, with theoretical investigations, will provide new insights in understanding the mechanisms involved and thereby to the design of water-stable and efficient MHPs.

Author contributions

H. Z.: conceptualization, formal analysis, investigation, writing – original draft; K. K.: supervision, funding acquisition, resources, writing – review & editing; S. O.: supervision, funding acquisition, resources, writing – review & editing.



Conflicts of interest

There are no conflicts to declare.

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