Recent advances in the development of perovskite@metal-organic frameworks composites

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Received 28 November 2022; Revised 4 February 2023; Accepted 12 February 2023; Published online 6 May 2023

Abstract: Metal-organic frameworks (MOFs) have received considerable attention because of their advantages of adjustable structure, high porosity, and rich active centers. Meanwhile, perovskite has attracted research interest due to its unique high-emission quantum yield and excellent optoelectronic properties. However, the instability of perovskites under certain conditions hinders their more comprehensive development. A novel strategy encapsulates perovskite in the pores of MOFs to protect it from external interference and increase the active centers, thus improving the performance of perovskite@MOF composites. In this review, the latest research progress in the synthesis strategy, function, and application of perovskite@MOF composites is systematically summarized. Additionally, the challenges of further developing perovskite@MOF composites are discussed. Hopefully, this review provides creative inspiration to advance future studies on perovskite@MOF composites in this emerging field.

Keywords: MOFs, perovskite, composites, synthesis, function, application

Introduction

Metal-organic frameworks (MOFs) are porous crystalline materials constructed by metal ions and organic ligands through coordination bonds [1–13]. In recent decades, the study of MOFs has gathered considerable attention in fields ranging from energy storage/conversion, sensing, anti-counterfeiting, light-emitting diodes, gas separation and sorption, and biomedicine [14–34], because of their high porosity, flexible and controllable structure, and simple synthesis method. Because of these excellent characteristics, MOFs are considered extremely promising materials.

Along with their unique structure and excellent properties, MOFs can be combined with other materials to mitigate their performance deficiencies [35,36]. First, the self-stability of MOFs can effectively be enhanced by encapsulating some materials in them. For instance, Gkaniatsou et al. [37] immobilized Microperoxidase-8 (MP8) in MIL-101 (Cr) to protect MP8 under acidic or oxidative conditions by confining it within a MOF matrix; the synthesized MP8@nanoMIL-101 retained long-term stability when stored at 4°C for 1 month. Moreover, Ye et al. [38] combined H3PW12O40 with UiO-66 (Zr) and successfully obtained PW/UiO-66 (Zr)-green samples, which exhibited excellent catalytic performance due to the increased active sites of MOFs.

The general formula of hybrid perovskite materials is ABX3, where A is a monovalent organic cation (such
as CH$_3$(NH$_2$)$_2^+$ or FA$^+$; CH$_3$NH$_3^+$ or MA$^+$), B is a divalent metal cation (such as Pb$^{2+}$, Ge$^{2+}$, or Mn$^{2+}$), and X is a monovalent halogen anion (Cl$^-$, Br$^-$, or I$^-$) [39–42]. Perovskite is an attractive system for applications such as photocatalysis, sensors, solar cells, and lasing because of its excellent charge-carrier transport performance, simple manufacturing process, and low cost [43–60]. Nevertheless, decomposition and aggregation occur when lead perovskite is exposed to moisture, oxygen, illumination, and particularly high temperatures due to the unique structures of perovskites [61,62]. Encapsulation is a feasible strategy that can form a host-guest structure with perovskite and provide an effective protective barrier for discrete perovskites [63,64]. To date, several encapsulation strategies for immobilizing and coating perovskites on porous supports have been explored to improve the stability of perovskites. One strategy involves coating the perovskite with protective layers of polymers, which can isolate the perovskite from contact with polar solvents and water, enhancing its stability [65]. Unfortunately, this strategy prevents the access of reactants, reduces the contact between reactants and perovskite, and adversely affects performance. Another strategy is to use porous materials such as Al$_2$O$_3$ and TiO$_2$ to improve the stability of perovskites. Nevertheless, the one-dimensional channel of these porous supports is inconsistent with the geometry or size of perovskite, which results in partial perovskite spilling out of the pores [66,67]. Therefore, materials with porous scaffolds and cage structures are needed to match the size and shape of perovskite to achieve efficient stability and expand its application in numerous fields.

In light of the discussion thus far, MOFs with porous structures and accommodation for various guest species can be used to encapsulate perovskites and improve their various defects, including poor stability, and the synergistic effect between components can further improve their performance [68]. Herein, we focus on the latest advances in developing perovskite@MOF composites and systematically summarize the strategies for synthesizing them. In particular, the roles of MOFs in perovskite@MOF composites are summarized, including encapsulation of perovskite, the improvement of stability, and the provision of extra active sites. Moreover, the application of perovskite@MOF composites in sensing, CO$_2$ reduction, the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), light-emitting diodes (LEDs), information security and anti-counterfeiting, and other areas are summarized. Finally, research directions that can be pursued to further improve the performance of this type of material are proposed (Figure 1).

**Strategies for synthesizing perovskite@MOF composites**

To date, the synthetic strategies of perovskite@MOF composites were identical to that of other guest species encapsulated in MOFs, which can be classified into bottle-around-ship and ship-in-bottle strategies according to the priority synthesis order of MOFs and perovskite matrices. The performance of the synthesized perovskite@MOF composites will be improved.

**Bottle-around-ship**

The bottle-around-ship strategy involves adding pre-synthesized metal nanoparticles (NPs) into the synthesis system of MOFs and obtaining metal NP@MOF composites through *in-situ* assembly and growth of MOFs around metal NPs (Figure 2A) [69]. This strategy can effectively avoid the formation of metal NPs on the
outer surface of MOFs, which ensures that the metal NPs are completely coated inside the MOFs. Simultaneously, the size, composition, and shape of metal NPs embedded in MOFs are effectively controlled to enable full contact [70]. The major drawback of the bottle-around-ship strategy is preserving the stability of perovskite under MOF synthesis conditions (polar solvents, high temperature, and high humidity). Applying the bottle-around-ship strategy to synthesize perovskite@MOF must overcome this difficulty.

Stone and co-workers [71] synthesized CdSe/CdS-PVP@ZIF-8 composites by mixing CdSe/CdS PVP, 2-methylimidazole, and Zn(NO$_3$)$_2$·6H$_2$O in methanolic solution using the bottle-around-ship strategy (Figure 3A). Meanwhile, Wang et al. [72] selected LaCoO$_{3-\delta}$ (LC) as the template perovskite owing to its excellent conductivity (Figure 3B). During the Co-MOF/LC interface synthesis, partial cobalt ions extracted from LC uniformly disperse over the LC surface and coordinate with controllable 2,5-dihydroxyterephthalic acid (H$_4$DOBDC), confining the growth of Co-MOF. Meanwhile, the cobalt ions in LC can sufficiently support the extraction of Co to form Co-MOF, which is conducive to maintaining the stability of the material. Furthermore, according to conjecture, perovskite can be encapsulated by MOF deposition technology, such as the chemical vapor deposition method, which can avoid the aforementioned problem [73].

**Ship-in-bottle**

*In situ* deposition

*In situ* deposition method is a common strategy employed in perovskite@MOF composite synthesis (Figure 2B). Generally, the precursors of synthetic MOFs and perovskites are mixed under certain conditions. Then, the added nucleation solvent promotes the nucleation and growth of perovskite in MOF pores. Simultaneously, the MOFs control the perovskite dimension and inhibit its aggregation [74]. In particular, the advantages of the *in situ* deposition method, with its easy control and high yield, ensure that...
perovskite@MOF composites can be applied in more fields.

Mollick et al. [75] reported metal-organic gel (MOG) as a protective matrix to protect perovskite from aerial or chemical degradation (Figure 3C). The EAPbBr\(_3\)@MOG composite was fabricated by premixing the precursors of MOG and EAPbBr\(_3\), such as trimesic acid, \(N,N\)-dimethylformamide (DMF), Al(NO\(_3\))\(_3\)·9H\(_2\)O, triethylamine, PbBr\(_2\), EABr, and OABr, which were added to the reaction system. During this process, the EAPbBr\(_3\) will be trapped in the MOG. Finally, the nucleating solvent toluene was added to obtain EAPbBr\(_3\)@MOG composites under ambient conditions. The encapsulation of EAPbBr\(_3\) by MOG offers dual benefits; namely, it enables the EAPbBr\(_3\) to exhibit impressive stability in air, water, and ultraviolet light while substantially enhancing the luminescence performance of white light-emitting diodes (WLEDs).

Sequential deposition

The sequential deposition method refers to the addition of a perovskite precursor to pre-synthesized MOFs during synthesis, which leads to the formation of perovskite in MOF pores and results in closer combinations with MOFs (Figure 2C) [76–78].

Xie et al. [79] reported the unique strategy of using porous UiO-66 as a porous matrix for the confined growth of MAPbBr\(_3\) PeQDs (QD=quantum dot) in situ. First, several concentrations of Pb\(^{2+}\) were immersed in UiO-66 synthesized by the solvothermal method to prepare precursors for Pb\(^{2+}\)@UiO-66. Second, the obtained Pb\(^{2+}\)@UiO-66 precursor was immersed in a MABr IPA solution and stirred for 12 h, and MAPbBr\(_3\) PeQDs were grown in the pores of UiO-66 by centrifugation and washed with DMF and IPA for several
times. Notably, according to the different concentrations of Pb\(^{2+}\) precursors, the author designed an *in situ* grown ultra-small MAPbBr\(_3\) PeQDs with the dimensions of 3.3–6.4 nm in UiO-66 (Figure 3D). Transmission electron microscopy (TEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) show that MAPbBr\(_3\)@UiO-66 composites still retain the octahedral morphology of UiO-66 and a uniform distribution of MAPbBr\(_3\) PeQDs. Qiao et al. [80] chose PCN-333(Fe) with mesoporous and microporous cages to combine with CsPbBr\(_3\) QDs and synthesized CsPbBr\(_3\)@PCN-333(Fe) composites, where the mesoporous cage was used to encapsulate CsPbBr\(_3\) QDs, and the microporous cage facilitated the diffusion of the catalytic reactants. Similar to other sequential deposition methods, this method first added the
pre-synthesized PCN-333(Fe) to a dimethyl sulfoxide (DMSO) solution containing PbBr$_2$, immersing PbBr$_2$ in a mesoporous medium (Figure 3E). Then, DMSO/ethanol was used to wash away PbBr$_2$ attached to the surface of PCN-333(Fe). The obtained PbBr$_2$@PCN-333(Fe) was subsequently immersed in a DMSO solution of CsBr for 1 h. In addition, experimental data and theoretical calculations prove that the electrons of CsPbBr$_3$ QDs can be transferred to the framework of PCN-333(Fe) inside the cage. In 2022, Wu et al. [81] reported a new sequential deposition strategy for encapsulating CsPbX$_3$ NCs in ZJU-28 without any atmospheric protection and synthesized ZJU-28@CsPbX$_3$ composites (Figure 3F). In particular, the authors sequentially deposited Pb$^{2+}$ and CsX into the channels of ZJU-28, enabling the growth of CsPbX$_3$ in situ under mild conditions. Moreover, a series of ZJU-28@CsPbX$_3$ composites were synthesized by adjusting the halide stoichiometry of CsX during deposition. The experimental results show a vast improvement in the stability of ZJU-28@CsPbX$_3$ because ZJU-28 provides surface passivation and protection for ZJU-28@CsPbX$_3$.

**Physical mixing**

Physical mixing refers to the simple mixing of MOFs and pre-synthesized perovskite by an ultrasonic or stirring method (Figure 2D) [82]. Additionally, this method requires MOFs to have appropriate pores to encapsulate perovskites or expand the pore size through the template. Unfortunately, it is difficult to control the structure of perovskite@MOF composites using this technique.

Ren et al. [83] synthesized MOF-5 with a mesoporous structure to encapsulate CsPbX$_3$ PeQDs and prepare CsPbX$_3$/MOF-5 composites (Figure 3G). In particular, Zn$^{2+}$, PTA, and template agents were selected to synthesize MOF-5 with a certain porosity, and MOF-5 with a mesoscopic structure was obtained after removing the templating agents. Mesoporous MOF-5 was deaerated, stirred with the pre-synthesized CsPbX$_3$ PeQDs for 10 min, and dried under a vacuum to obtain CsPbX$_3$/MOF-5 composites. The perfect encapsulation of CsPbX$_3$ PeQDs by MOF-5 provides a protective shell that prevents interference from the surrounding environment. Moreover, CsPbX$_3$/MOF-5 composites exhibit excellent thermal, optical, and long-term stability and satisfactory high luminous efficiency. This work was the first to encapsulate perovskite in mesoporous MOF-5, and the unique and facile encapsulation method guides the synthesis of perovskite@MOF composites. Moreover, Bhattacharyya et al. [84] synthesized CsPbX$_3$@AMOF-1 composites by the solvent-free mechanochemical method (Figure 3H). Using synthetic Pb$^{4+}$@AMOF-1 as the template and then grinding Pb$^{4+}$@AMOF-1 with CsX, CsPbX$_3$ PQDs were formed on the surface of AMOF-1. The synthesized CsPbX$_3$@AMOF-1 composites were characterized by PXRD and TEM, which proved that the size of CsPbX$_3$ PQDs formed was limited by AMOF-1. Meanwhile, the encapsulation of CsPbX$_3$ PQDs by AMOF-1 substantially improved the stability and processability of CsPbX$_3$@AMOF-1 composites.

**Direct conversion**

The direct conversion used a synthesized MOF matrix with Pb as the metal node, and halide salts were introduced so that Pb-MOF underwent a direct conversion reaction. The perovskite grows in the MOF pores to synthesize perovskite@MOF composites (Figure 2E) [85]. By comparison, the direct conversion effectively alleviates the diffusion resistance of perovskite into MOFs and is an extremely convenient method for
fixing perovskites in MOF pores. For instance, Tsai et al. \[86\] synthesized PeMOF via direct conversion (Figure 3I). First, the 1,3,5-H$_3$BTC solution was slowly added to Pb$^{2+}$ to obtain Pb-MOF solution after orderly ultrasonic, washing, and drying operations. Then, PeMOF was obtained by spinning CsX on a Pb-MOF film. TEM shows that a single CsPbX$_3$ nanocrystal with a size of 10–20 nm is present in the MOFs instead of Br$^-$ and Cl$^-$ alloyed into a single particle, demonstrating the successful preparation of the composites.

**The function of MOFs in perovskite@MOF composites**

As an emerging porous material with well-defined cages, MOFs have shown great potential as hosts for the immobilization and stabilization of active phases with various properties \[87–89\]. The advantage of being able to structurally and chemically tune the internal pores endows MOFs with distinct advantages over typical porous materials (zeolites, mesoporous SiO$_2$). These advantages make MOF channels unique nanoscale-confined spaces for encapsulating perovskites. Notably, the function of MOFs in perovskite@MOF composites is not only to encapsulate perovskites but also to improve their stability and conductivity. From this perspective, the function of MOFs in perovskite@MOF composites needs to be summarized.

**Encapsulation of perovskites**

By confining perovskites within the internal pores of MOFs to form host-guest composites, the size of perovskites is limited by the pore size of MOFs to form extremely small and uniform crystals \[90\]. Furthermore, by selecting different metal lattice points and organic chains during synthesis, the MOFs can be used to regulate the pore size of the cage. Moreover, because of the limitation of the cage size of the MOFs, when the perovskite reaches the maximum size, the trend of the infinite growth of perovskite will be restricted by the MOFs, and it cannot continue to grow into a larger size (Figure 4) \[91–94\]. Therefore, the synthesized perovskite@MOF composites can isolate perovskites from each other without aggregation, protect perovskites from exterior environmental stimulation, and realize new functions and wider practical applications \[95\].

Notably, the researchers discovered that perovskites in perovskite@MOF composites may be larger than...
MOF pores. For example, Mollick et al. [96] synthesized MAPbBr$_3$@ZIF-8 composites by uniformly growing spherical perovskite in sizes ranging from 6–8 nm in the pores of ZIF-8 (theoretical cavity of 1.16 nm) (Figure 5A). The larger MAPbBr$_3$ NCs in MAPbBr$_3$@ZIF-8 composites occupy the narrow cavity of ZIF-8 and have certain structural defects. This phenomenon can be attributed to missing linkers in the framework, a well-known observed characteristic of MOF materials [97,98]. TEM analysis indicates that ZIF-8 encapsulated MAPbBr$_3$ NCs, and the elements Zn, N, Pb, and Br appear in HAADF-STEM images, proving the successful preparation of MAPbBr$_3$@ZIF-8 composites (Figures 5B and 5C). Simultaneously, this situation is disadvantageous because it may destroy the MOF structure because of the growth of perovskite, and the perovskite produces partial aggregation, which will adversely affect the performance of perovskite@MOF composites.

**Improvement in stability**

Poor stability has long been a critical issue for perovskites, limiting their further practical applications in numerous fields [99–101]. This challenge has aroused the strong interest of researchers in the synthesis of stable perovskites. MOFs have shown great advantages as hosts for the immobilization and stabilization of the active phases of various properties, and thus were chosen to improve the stability of perovskites without the use of additional stabilizing agents.

Tang et al. [102] proposed a facile strategy for synthesizing MAPbBr$_3$@PbBr(OH) composites based on the hydrolysis reaction of PbBr$_2$ triggered by a MOF combined with the confining synthesis of perovskite crystals inside the MOF cavity. The MAPbBr$_3$@PbBr(OH) composites exhibited excellent stability to various polar solvents, light, and heat. Particularly, the photoluminescence (PL) intensity of MAPbBr$_3$@PbBr(OH) composites dipped in water, DMF, and acetone for 60 days only decreased by approximately 2%. Meanwhile, compared with the PL intensity of the MAPbBr and MAPbBr$_3$@PbBr(OH) composites under a 365-nm ultraviolet (UV) lamp, the PL intensity dropped rapidly for MAPbBr$_3$ and reduced by 80% after the 3
days of illumination, and the intensity of the MAPbBr$_3$@PbBr(OH) composites maintained at 40% of the original intensity even after the 5 days of illumination. Notably, the MAPbBr$_3$@PbBr(OH) composites were heated to 100°C, and the PL intensity was maintained at 40%. In contrast, the pure MAPbBr$_3$ disappeared at 90°C (Figure 6A). The above experiments verify that MOFs can improve the stability of perovskites. He et al. [103] reported a sequential deposition to generate crystalline MAPbBr$_3$ within the channels of ZJU-28, and ZJU-28@MAPbBr$_3$ composites were synthesized. Further, the ZJU-28 and ZJU-28@MAPbBr$_3$ composites were dispersed in toluene, and the time-dependent luminescence spectrum was tested in the air. The experimental results showed that MAPbBr$_3$ had no luminescence after 120 s of solvent evaporation, while ZJU-28@MAPbBr$_3$ composites maintained excellent luminous intensity after 100 min. Even after 7 days, the luminous intensity remained at 89% (Figures 6B and 6C). This result is obtained because ZJU-28 can provide effective surface passivation and enhanced MAPbBr$_3$ stability, which allows for the total exploitation of the unique luminescence properties of perovskites. Similarly, the PL intensity of MA-PeMOF thin films prepared by Tsai et al. [85] remained stable for over 200 h of irradiation, proving that the crystal structure of the perovskite was preserved. In contrast, the PL intensity of MAPbBr$_3$ thin films was almost completely attenuated within 6 h (Figure 6D). Simultaneously, Cs-PeMOF devices still maintained 50% of the original brightness after 50 h of continuous operation under a low current (Figure 6E). Through the above examples, perovskites are proven to be readily encapsulated and confined into different types of nanopore MOF materials to improve their stability, thus developing a path for the development of perovskite@MOF composites.

Figure 6 (A) PL retention of the composite versus heating temperature. Luminescence intensity spectra of composites (B) illumination-time-dependent and (C) in the air for 7 d. (D) PL intensity of composites versus time. (E) LED stability test of a Cs-PeMOF device. Panel (A): Reproduced with permission from [102]. Copyright©2022, The Royal Society of Chemistry. Panels (B and C): Reproduced with permission from [103]. Copyright©2019, Wiley-VCH. Panels (D and E): Reproduced with permission from [85]. Copyright©2021, Nature.
Providing extra active sites

Traditional perovskites are disadvantageous because they lack effective catalytic sites. An approach to addressing this issue is to encapsulate perovskite in MOFs and use the metal sites in MOFs to provide more catalytic active centers, thus improving the efficiency of the perovskite [104, 105].

For example, Wu et al. [106] encapsulated MAPbI₃ in the pores of the Fe-porphyrin-based MOFs of PCN-221(Feₓ) by sequential deposition. The close contact between MAPbI₃ and the highly efficient catalytic activity center of Fe in PCN-221(Feₓ) can shorten the distance of charge transfer, and the photogenerated electrons in MAPbI₃ QDs can quickly transfer to the catalytic site of Fe, thus improving the charge separation efficiency of MAPbI₃ QDs and the catalytic activity of PCN-221(Feₓ). As expected, compared with the blank MAPbI₃ QDs, the MAPbI₃@PCN-221(Feₓ) composites exhibited substantially improved photocatalytic stability and CO₂ reduction activity, with excellent stability and yield for the production of CO and CH₄ (Figure 7).

Application of perovskite@MOF composites

This section introduces the application of perovskite@MOF composites in the fields of sensing, CO₂ reduction, HER, OER, LEDs, information security and anti-counterfeiting, and others (Table 1 and Figure 8).

Sensing

MOFs have been widely used to boost biosensing sensitivity because their high specific surface area is conducive to the fixation of signal probes, which is the advantage required by perovskites.

In 2022, Liu et al. [118] selected Ag⁺@UiO-66-NH₂ with a high specific surface area and structural stability to improve the loading capacity of CsPbBr₃ NPs, and the synthesized Ag⁺@UiO-66-NH₂/CsPbBr₃ composites achieved excellent results for nitrofurazone (NFZ) detection. Particularly, the linear range of Ag⁺@UiO-66-NH₂/CsPbBr₃ composites for detecting NFZ under optimal conditions is

![Figure 7](image-url) Yields for CO₂ reduction with composites as photocatalysts after (A) 25 h and (B) 80 h of irradiation under a 300-W Xe lamp. Reproduced with permission from [106]. Copyright © 2019, Wiley-VCH.
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<td>MAPbBr₃</td>
<td>2020</td>
<td>Encapsulation perovskite</td>
<td>Others</td>
<td>[79]</td>
</tr>
<tr>
<td>CdSe/CdS-PVP@ZIF-8</td>
<td>Bottle-around-ship</td>
<td>ZIF-8</td>
<td>1.16</td>
<td>CdSe/CdS</td>
<td>2022</td>
<td>Encapsulation perovskite</td>
<td>Others</td>
<td>[71]</td>
</tr>
</tbody>
</table>
0.5 nmol L$^{-1}$–100 μmol L$^{-1}$, and the limit of detection (LOD) is 0.09 nm, which is better than most sensors that detect NFZ (Figure 9A). Meanwhile, the Ag$^+$/UiO-66-NH$_2$/CsPbBr$_3$ composites have excellent selectivity and stability for NFZ detection (Figure 9B). Interestingly, the system used a smartphone camera, neural network, and self-designed software to collect, process, and analyze the image, respectively, and the $R^2$ value of the sensor prepared was 0.9936. Therefore, the developed portable device provides a feasible and on-site strategy for NFZ detection.

Similarly, Shu and co-workers [119] prepared CsPbBr$_3$@Eu-BTC composites that can quickly and visually detect Hg$^{2+}$ in an aqueous solution and have excellent stability. After Hg$^{2+}$ was added to the reaction system, the green fluorescence of CsPbBr$_3$ at 520 nm turned red. In comparison, the red fluorescence of Eu-BTC at 616 nm remained unchanged, thus providing a new fluorescence sensor for detecting Hg$^{2+}$. The detection of Hg$^{2+}$ by CsPbBr$_3$@Eu-BTC composites can be observed by a fluorescence color change from green to red, the linear range is 0–1 μmol L$^{-1}$, and the LOD is 0.116 nmol L$^{-1}$ (Figures 9C and 9D). In addition, the CsPbBr$_3$@Eu-BTC composites were used to detect Hg$^{2+}$ in lake water and domestic sewage, with a qualified recovery rate. One highlight of the study is that the fluorescence sensors made the CsPbBr$_3$@Eu-BTC composite ratio a metric for the visual detection of Hg$^{2+}$, enabling the development of an instant detection of Hg$^{2+}$. Furthermore, the CH$_3$NH$_3$PbBr$_3$@MOF-5 composites synthesized by Zhang et al. [120] can maintain excellent moisture resistance after 30 days of exposure to water and have adaptability in the pH range of 1–13 (Figures 9E and 9F). Additionally, the CH$_3$NH$_3$PbBr$_3$@MOF-5 composites are stable fluorescence probes for detecting some ions in an aqueous solution. The excellent stability of CH$_3$NH$_3$PbBr$_3$@MOF-5 composites gives it unique advantages in sensors.

**CO$_2$ reduction**

Unmodified perovskites were rarely reported for photocatalysts because of their insufficient stability in the presence of moisture or polar solvents. Coincidentally, MOF materials have received tremendous attention as...
sustainable clean energy [121–123]. Compared with other materials, the narrow MOFs could anchor the monodisperse photoactive species, enhancing catalytic activity [124]. Moreover, the combination of MOFs and perovskite can provide redundant pathways for the migration of photogenerated electrons, facilitating charge carrier separation, and thus improving photocatalytic performance. Therefore, perovskite@MOF composites can be designed and synthesized to expand the photocatalytic applications of perovskites.

On the basis of the above studies, Wan et al. [108] encapsulated CsPbBr$_3$ QDs in the pores of UiO-66(NH$_2$) and synthesized CsPbBr$_3$ QDs/UiO-66(NH$_2$) composites that combined the advantages of both catalysts,

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Figure 9  (A) ECL sensor of Ag$^+$/UiO-66-NH$_2$ and (B) selectivity. (C) CsPbBr$_3$@Eu-BTC responding to Hg$^{2+}$ and (D) the fitting curve. (E) CH$_3$NH$_2$PbBr$_3$@MOF-5 composites and (F) different pH values. Panels (A and B): Reproduced with permission from [118]. Copyright©2022, Elsevier. Panels (C and D): Reproduced with permission from [119]. Copyright©2022, Elsevier. Panels (E and F): Reproduced with permission from [120]. Copyright©2018, American Chemical Society.
demonstrating a considerably enhanced CO$_2$ reduction photocatalytic activity in visible light. In detail, the yields of CH$_4$ and CO of 15%-CsPbBr$_3$ QDs/UiO-66(NH$_2$) composites in the photocatalytic reaction gradually increased, and the total yields were 3.08 and 98.57 μmol g$^{-1}$, respectively. The ultrahigh performance of CsPbBr$_3$ QDs/UiO-66(NH$_2$) composites was attributed to the following three reasons: (1) rapid electron transfer between UiO-66(NH$_2$) and CsPbBr$_3$ QDs; (2) the large specific surface area of UiO-66(NH$_2$); and (3) enhanced absorption capacity for visible light. Moreover, the CsPbBr$_3$ QDs/UiO-66(NH$_2$) composites can maintain excellent photocatalytic performance after three cycles and high thermal stability (Figure 10A). In the same example, Chen and co-workers [109] selected BIF-122-Co as a suitable host to temporarily coordinate with Pb$^{2+}$ in the perovskite precursor and then synthesized CsPbBr$_3$/BIF-122-Co composites by a

![Figure 10](image-url)
sequential deposition strategy. BIF-122-Co provides a protective barrier for CsPbBr$_3$ to enhance its stability. More importantly, the electrons in CsPbBr$_3$ can be transferred to BIF-122-Co, improving the performance of photocatalytic CO$_2$ reduction. After photocatalytic CO$_2$ reduction for 3 h, the electron consumption yield of CsPbBr$_3$/BIF-122-Co composites was 156.5 μmol g$^{-1}$, higher than most reported photocatalytic materials (Figure 10B). Furthermore, CsPbBr$_3$/BIF-122-Co composites still have excellent photocatalytic activity after three cycles (Figure 10C).

**HER**

MOFs have been widely applied to the HER [125,126]. Nevertheless, the visible light response of MOF-based composite applications is very rare. Thus, this challenge needs to be solved. The synthesis of MOFs with a broadband spectral response is a feasible and effective approach. In light of these considerations, Wang et al. [110] loaded Cs$_8$Bi$_2$I$_9$ (CBI) QDs into the inner pores of NH$_2$-Uio-66 (U6N) with excellent stability and low cost to synthesize CBI@U6N composites. Excitingly, the excellent photoelectric response of CBI QDs enabled the CBI@U6N composites to enhance the HER efficiency under visible light irradiation. The HER efficiency of the CBI@U6N composites was 32.21 μmol g$^{-1}$ h$^{-1}$ under certain conditions, and this excellent performance was attributed to the synergistic effect between U6N and CBI QDs. Additionally, the synthetic CP@U6N composites can improve the HER efficiency to 141.87 μmol g$^{-1}$ h$^{-1}$ (Figure 10D). As described in this paper, this work is the first application of CBI QDs to the HER, providing a theoretical basis for wider applications in the field of perovskites.

**OER**

Researchers have long been committed to solving the challenges of poor electrocatalytic activity, low catalytic activity utilization, and small specific surface area of perovskites [127]. To address these issues, Li et al. [128] prepared La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (LSCF) NF material with a porous structure by electrospinning and heat treatment. Then, LSCF NFs and Ni$_3$(HITP)$_2$ were compounded to fabricate LSCF@Ni$_3$(HITP)$_2$ NFs. As expected, the LSCF@Ni$_3$(HITP)$_2$ NFs have an extremely low resistance, an excellent OER performance (272 mV at 10 mA cm$^{-2}$), and the Tafel slope was 95 mV dec$^{-1}$ (Figures 10E and 10F). The excellent OER performance can be explained as follows: (1) the porous structure of LSCF NFs; (2) the high specific surface area of Ni$_3$(HITP)$_2$ contributed to the catalytic activity; and (3) the enhanced conductivity of LSCF@Ni$_3$(HITP)$_2$ NFs. The successful synthesis and excellent performance of LSCF@Ni$_3$(HITP)$_2$ NFs provide a feasible scheme for applying perovskite in the OER field.

**LEDs**

The world is currently facing an energy shortage crisis that urgently needs to be solved, and lighting accounts for 20% of global energy consumption. LEDs convert electrical energy into light energy by luminescent semiconductors and have the characteristics of high luminous efficiency and strong security. Notably, perovskites have been widely used in the LED field [129–131]. However, the poor stability and low lifetime of perovskites cannot be ignored. Therefore, the perovskite@MOF composites can encapsulate various types of
perovskites in the holes of MOFs to resolve the disadvantage of perovskite stability.

Cuan et al. [93] synthesized CsPbX$_3$@MOF composites using the bottle-around-ship strategy. The HP-Uio-66 material with a hierarchical porous structure is conducive to the diffusion of reactants and performance improvement. Meanwhile, HP-Uio-66 restricts the uniform growth of CsPbX$_3$ PNCs in the pores and enhances the stability of CsPbX$_3$@MOF composites (Figure 11A). The CsPbX$_3$@MOF composites showed a high PL emission intensity when exposed to humid air for 4 days and continuous UV light irradiation for 2 h. Meanwhile, the two composites were integrated with an InGaN LED chip to successfully prepare WLEDs, which outperformed other perovskite materials (Figure 11B). In another work, Hou et al. selected CsPbX$_3$ and a$_2$ZIF-62 to synthesize (CsPbX$_3$)$_{0.25}$(a$_2$ZIF-62)$_{0.75}$ for application in WLED fields [132]. The (CsPbX$_3$)$_{0.25}$(a$_2$ZIF-62)$_{0.75}$ material retained excellent PL strength after being soaked in water for 10,000 h (Figure 11C). Notably, (CsPbX$_3$)$_{0.25}$(a$_2$ZIF-62)$_{0.75}$ showed a wide color gamut and processability, making it an excellent candidate in the WLED fields (Figures 11D–11F).

**Information security and anti-counterfeiting**

Research on information security and anti-counterfeiting has always been a universal and worldwide concern. Researchers favor perovskites because of their strong, intensive PL intensity, and relatively high PL quantum yields [133,134]. Unfortunately, perovskites are impracticable for direct use in anti-counterfeiting applications because of their poor stability. On this basis, increasing the stability of perovskites by combining them with MOFs is feasible.

Zhang and co-workers [135] encapsulated CH$_3$NH$_3$PbBr$_3$ NCs in Eu-MOFs, and the synthesized CH$_3$NH$_3$PbBr$_3$@EuBTC composites have anti-counterfeiting behavior. Particularly, the PL strength of CH$_3$NH$_3$PbBr$_3$@EuBTC composites will be quenched when heated to a certain temperature. Simultaneously, the CH$_3$NH$_3$PbBr$_3$@EuBTC composites can be used as anti-counterfeit ink to write on paper, achieving
controllable quenching and reversible switching between two colors, which is due to the emission between Eu-MOFs and CH$_3$NH$_3$PbBr$_3$ (Figure 12A). In addition, Wang et al. [136] used the pre-synthesized Pb/Eu-MOF as the lead source and sacrificial template to prepare the MAPbBr$_3$@Pb/Eu-MOF@PFs paper by a direct conversion strategy and used it as anti-counterfeiting materials. The MAPbBr$_3$@Pb/Eu-MOF@PFs paper can emit green and red fluorescence under different wavelengths of UV excitation. The structure of MAPbBr$_3$ was destroyed after the addition of polar solvent, thus achieving a controlled luminescence signal (Figure 12B). Moreover, the MAPbBr$_3$ NC@Pb-MOF synthesized by Zhang et al. [113] could be quenched after adding a polar solvent; the luminescence was restored after introducing MABr. This controllable luminescence signal opens up a potential way to develop information security (Figures 12C–12E).

**Others**

The future of perovskites largely depends on their stability. MOFs with well-defined pore structures can arrange perovskites in multiple dimensions and adjust the spacing between perovskites.

Protesescu et al. [117] selected Cr-MIL-101 as a host to encapsulate CsPbBr$_3$, whose holes can rapidly diffuse CsPbBr$_3$ precursors to form ultra-small CsPbBr$_3$. An optimization using density functional theory demonstrated the occurrence of strong interfacial interactions between Cr-MIL-101 and CsPbBr$_3$, which is presumed to be responsible for the enhanced stability of CsPbBr$_3$ (Figures 13A–13C). Similarly, Cha et al. [116] selected MIL-101 as the protective container and nano-reactor, adjusted the size of the perovskite by adding different amounts of PbX$_2$, and synthesized CsPbX$_3$@MIL-101 composites. Meanwhile,
CsPbX₃@MIL-101 composites establish a blueprint for the practical application of optoelectronic devices (Figure 13D).

Conclusions and outlook

In summary, perovskite@MOF composites are receiving more attention due to their structural diversity and enormous potential for application in numerous fields. Therefore, this review summarizes the advances in perovskite@MOF composites. The encapsulation strategies between MOFs and perovskites, namely the bottle-around-ship and ship-in-bottle strategies, were highlighted. The ship-in-bottle strategy was further subdivided into in situ deposition, sequential deposition, physical mixing, and direct conversion to guide the encapsulation synthesis of perovskite@MOF composites. Furthermore, the MOFs in perovskite@MOF composites function to encapsulate perovskites and protect them from external factors. Importantly, MOFs can improve stability, provide active sites for perovskites, and substantially improve their performance. Excellent performance makes perovskite@MOF composites widely applicable in sensors, CO₂ reduction, HER, OER, LEDs, information security, and anti-counterfeiting, among other areas.
Despite the great effort and tremendous headway made in this field, some difficult problems remain unresolved. In general, possible future challenges can be summarized as follows.

1. The pore size of MOFs should be sufficiently considered in perovskite@MOF composite synthesis to avoid a mismatch between MOF pores and perovskite nanoparticle size/geometry, which results in insufficient interactions and considerable escape by perovskite nanoparticles. Therefore, selecting MOFs with sufficient pore size helps improve the capacity to accommodate and increase the loading of perovskite. Moreover, the MOFs preferably have cages with small window apertures to encapsulate perovskite and prevent leakage.

2. Stability is a vital factor that frustrates the application of perovskites in various fields. According to the current research, MOFs have been selected as the protective shell to encapsulate the perovskite to improve its stability. However, except for the well-known ZIFs and Zr-MOFs, the stability of most MOFs is difficult to predict, and the stability of MOFs themselves is easily compromised or destroyed under harsh conditions (low pH). Therefore, higher stability MOFs must be further explored, which is conducive to the practical application of perovskite@MOF composites.

3. Perovskites contain heavy metals, particularly Pb, which can cause severe environmental pollution even in trace amounts. Notably, in perovskite@MOF composites, the porous structure of MOFs has excellent potential for Pb fixation, thus reducing heavy metal ion pollution in the environment. However, effectively designing and synthesizing perovskites without Pb, such as Cs$_2$AgBiBr$_6$ and CsEuCl$_3$ [137,138], develops clean energy.

4. The application of traditional perovskites in photocatalysis is unsatisfactory, and their performance cannot be sufficiently improved by compounding with MOFs. On the basis of this report, 2D perovskites have excellent stability against humidity, and they can be used to synthesize perovskite@MOF composites with MOFs for more diverse applications in photocatalysis fields.

Overall, perovskite@MOF composite research remains in the developmental stage and has a large room for innovation. With the joint efforts of experts in various fields, perovskite@MOF composites may soon achieve multi-functional and multi-disciplinary practical applications.

Acknowledgements
We acknowledge the Priority Academic Program Development of Jiangsu Higher Education Institutions and the technical support we received at the Testing Center of Yangzhou University.

Funding
This work was supported by the National Natural Science Foundation of China (NSFC-U1904215), the Natural Science Foundation of Jiangsu Province (BK20200044), and the Program for Young Changjiang Scholars of the Ministry of Education, China (Q2018270).

Author contributions
Q.L. collated and summarized the literature and wrote the article. Y.Z. summarized the literature and wrote the article. G.Z. and Y.W. collated the literature. H.P. guided the article.

Conflict of interest
The authors declare no conflict of interest.
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