

Perspective

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Emerging microporous materials as novel templates for quantum dots

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How to cite this article: Lee J, Wang L, Hou J. Emerging microporous materials as novel templates for quantum dots. *Microstructures* 2023;3:2023021. <https://dx.doi.org/10.20517/microstructures.2023.08>

Received: 3 Feb 2023 **First Decision:** 27 Feb 2023 **Revised:** 11 Mar 2023 **Accepted:** 17 Apr 2023 **Published:** 26 Apr 2023

Academic Editors: Shujun Zhang, Zibin Chen **Copy Editor:** Fangling Lan **Production Editor:** Fangling Lan

Abstract

Microporous structures have attracted significant attention in recent years. In particular, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have received considerable attention due to their tailorable structures that offer a wide range of choices in terms of molecular building blocks. Due to their high tunability, these materials are considered as ideal host matrices for templating and encapsulating guest materials, particularly quantum dots (QDs). QDs are investigated heavily for various applications such as light-emitting diodes (LED), biosensors, catalysts, and solar cells due to their unique properties from the quantum confinement effect. However, one of the drawbacks of QDs is their tendency to aggregate and exhibit low stability due to their small size and kinetic trapping in nanoparticle form. This perspective highlights promising approaches to enhance the performance and stability of QDs by using microporous materials as an encapsulation layer. Additionally, potential mitigating strategies are discussed to overcome current challenges and improve the practicality of QDs embedded in microporous nanocomposites.

Keywords: Metal-organic frameworks, covalent organic frameworks, zeolites, microstructures, QD encapsulation

INTRODUCTION

Quantum dots (QDs) are nanocrystals that behave similarly to an atom as a result of quantum physics. When the size of nanomaterials reaches a level comparable to or even smaller than the Bohr radius, the



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materials will experience the quantum confinement effect. This phenomenon relates to the exciton and electronic energy level, which is continuous in bulk but becomes discrete in nanocrystals as the electron movement is confined to a specific energy level. An exciton is a bound state between an electron hole in valence band (VB) and an electron through Coulomb interaction. When a photon interacts with a semiconductor material and the energy of the photon exceeds or equals the bandgap (E_g), an electron in the VB is excited to the conduction band (CB), resulting in the formation of a positively charged hole referred to as an electron hole. As the excited electron and electron hole are confined within a limited space, more energy is required to excite them, which results in size-dependent band gaps and light emission. When a material is confined in one dimension, it forms a quantum well structure. Similarly, two-dimensional confinement results in a quantum wire, while three-dimensional confinement leads to a quantum dot, which is a material that is confined in all three dimensions^[1-8]. This energy state results in unique characteristics, including long fluorescence lifetime, narrow and symmetrical photoluminescence emission, wide absorption, and high photoluminescence quantum yield (PLQY). Furthermore, the photoluminescence emission band gap can be tuned by varying the size of QDs. Traditionally, combinations of 0D core-shell structure materials and group 12-16 elements have been investigated as promising quantum dot materials, such as ZnSe, ZnO, InP, InAs, and CdSe^[9-11]. Recently, organic-inorganic metal halide perovskites have been noticed as promising QD materials due to the recent successful development of photovoltaic (PV) cells, LEDs, and sensors based on perovskite QDs^[12-17]. However, in light of increasing concerns about the potential toxicity of some materials, there is growing interest in developing alternatives that are more biocompatible and environmentally friendly. For instance, carbon quantum dots (CQDs) and graphene quantum dots (GQDs) are emerging as promising candidates^[18-20]. Graphene Quantum Dots (GQDs) exhibit remarkable size-dependent luminescence properties that are attributed to their quantum confinement and edge effects. These properties make GQDs highly attractive for optoelectronic and photodetector applications, including LEDs and electroluminescent devices. However, GQDs often suffer from reduced fluorescence, which hampers their ability to function as optoelectronic devices due to phase separation and agglomeration in organic or inorganic solvents. Furthermore, the non-stoichiometric nature of GQDs makes it particularly challenging to achieve precise control over their chemical structure, size, shape, and structural defects, which are directly related to their optoelectronic properties. Therefore, there have been numerous attempts to incorporate GQDs into matrices such as polymer films or mesoporous solids in order to control the size of the nanoparticles and stabilise them. However, since many of the current fabrication methods are complicated and difficult to control, there is a need to investigate more reproducible and simpler methods to fully utilise the great fluorescence properties of GQDs^[21-25].

Despite the promising potential of quantum dots (QDs) in various applications and the significant progress achieved in material sciences, several challenges continue to hinder their widespread implementation. These challenges include issues such as agglomeration, precise size control, and operational stability, which demand further research and development to mitigate effectively. Generally, QDs show a strong tendency to aggregate into larger particles due to their high surface energy, which leads to the loss of their unique characteristics. Several recent studies have tried to mitigate the limitations of QDs through solvent engineering, surface passivation using semiconducting film, encapsulation with polymers, or embedment of QDs within porous nanomaterials^[26-29]. However, most of these strategies require complex fabrication processes, and it remains difficult to control the outcomes, which may reduce the efficacy of these methods.

Traditional nanomaterials with microporosity, such as mesoporous silica, zeolites, and porous carbon, have been investigated for various applications, including drug delivery, biosensing, separation, and catalysts^[30,31]. Despite their great advantages, i.e., high surface area, tunable porosity, and biocompatibility, they tend to have limited chemical tunability. This limitation inspired scientists to develop microporous functional

materials that can be readily tailored. In recent years, covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) have received tremendous attention from the materials science community as they can form tailored microstructures with metal-organic linker coordination bonds or covalent bonds^[32-34]. In addition, the material itself can be chemically active and biocompatible, as some types of COFs are studied for cancer diagnosis and therapy^[35-37]. Thanks to their high surface area, tunable structure, biocompatibility and diverse topology, these materials have been recognised as a promising functioning host matrix to mitigate some of the issues that quantum dots had. In view of this prosperous research area, we have outlined the quantum dots encapsulation in these emerging microporous materials and their potential applications. We believe that this Perspective will guide the potential future research directions in emerging QDs embedding in functional porous materials. The purpose of this Perspective is not to provide a comprehensive review and summary of these composite materials, but instead to give a brief history of the field, a summary of current progress, and, more importantly, highlight and discuss unsolved questions that are worth further investigation.

A HISTORICAL OVERVIEW OF QUANTUM DOTS WITHIN MICROPOROUS STRUCTURE

Quantum dots (QDs) are nanocrystals that exhibit quantum confinement effects due to their small size, leading to unique optical and electronic properties. These properties arise from the confinement of electrons and holes in a three-dimensional space, resulting in a behaviour similar to an atom because of quantum physics. It is generally agreed that the first QDs were discovered by Russian physicist Alexei Ekimov in the early 1980s. He synthesised copper chloride (CuCl_2) and cadmium selenide (CdSe) nanocrystals embedded in a glass matrix and observed a gradient of colours in the fluorescence emission spectra, which was dependent on the size of the nanocrystals^[38]. Ever since their discovery, much of the research on QDs has focused on improving size control to reduce size variation, producing high-quality nanocrystals, and achieving tunable fluorescence colours. Recently, significant improvements have been made in the quality and tunability of QDs, as well as in their photovoltaic applications such as in solar cells. However, QDs have a tendency to aggregate into larger particles due to their high surface energy, which can lead to the loss of their unique characteristics and efficiency. To mitigate this drawback, there have been attempts to fabricate QDs within microporous matrices in order to not only control the size of the QDs but also provide a protective layer that prevents their aggregation and loss of unique characteristics.

Mesoporous silica, zeolites, and porous carbon have conventionally been studied as templates for the growth of QDs. Among these, zeolites have received extensive attention due to their unique tunable characteristics and excellent stability. Zeolites are crystalline aluminosilicate polymers with an inorganic framework consisting of SiO_4 and AlO_4 tetrahedra. They possess a three-dimensional nanometre-sized structure with uniform windows, channels, and cavities, and have been extensively studied. While this family of materials may not be considered as “emerging” compared to other types of microporous materials, they can still offer valuable insights into regulating the structure, interface, and chemistry between the microporous template and guest QDs. Therefore, this Perspective will first provide a brief summary of early studies on using zeolite templates for encapsulating QDs. The unique properties of zeolites that combine features of both ionic and covalent crystals arise from the covalent network structures formed by sharing oxygen atoms between SiO_4 and AlO_4 tetrahedra, which depends on the Si/Al ratio^[39,40]. Materials exhibiting a ratio greater than 3 are categorised as high silica zeolites or zeolite Y. These high silica zeolites have good physical and chemical stability as well as hydrophobicity^[41]. When the ratio is less than 3, it is called zeolite X or low-silica zeolites. These zeolites display high ion exchange capacity, which makes them good candidates as ion exchange agents^[42]. Furthermore, pore size can also be tuned by changing the ratio and number of oxygen atoms connections to tetrahedra structure, or more directly through different synthetic conditions such as the use of surfactants. Their three-dimensional porous structure, along with their

tunability and uniformity, make these materials good candidates as host scaffolds for QDs.

An interesting topic in the field of synthesizing QDs in zeolites is the use of cadmium sulphide (CdS) QDs in zeolite Y. While this concept was established and researched in the 1980s, it continues to provide new insights for the next generation of researchers. CdS quantum dots are one of the most studied II-IV binary semiconductor materials due to their narrow band gap of 2.42 eV^[43]. However, the performance of the material highly depends on its size and three-dimensional structure. Thus, much research effort has been dedicated to avoiding aggregation, size control and stabilisation of QD structure. Herron *et al.* introduced the idea of cadmium sulphide quantum dots (CdS QDs) in zeolite Y to improve their stability and optoelectronic properties^[44]. In this work, CdS semiconductor clusters were synthesized using an aqueous solution process which involves cadmium ion exchange followed by hydrogen sulphide (H₂S) gas flowing to create CdS cluster within the zeolite pores. It was reported that during synthesis, QDs are formed in sodalite cages (5 Å) instead of supercage pores (13 Å) of zeolite Y structure through a percolative process [Figure 1A]^[45]. However, a recent study showed that CdS QDs exist in supercages rather than sodalite cages. The author found that the migrated Cd²⁺ ions in sodalite cage during drying process diffused back to supercage in later reaction process with H₂S to form QDs, showing the highly dynamic nature of the QD even in their condensed phase. The isolated CdS nanoclusters form interconnection through supercage window in [CdS]₄ unit, as shown in Figure 1B^[46]. This example demonstrates the templated growth methodology to form QDs within the micropores, and it also clearly shows that the QDs in the template are still preserving their dynamic properties.

Another important guest material is lead sulphide (PbS) QD which has a narrow band gap and size-dependent optical properties due to its large exciton Bohr radius which makes it a good candidate for third-order nonlinear optical (3NLO) applications^[47-49]. High 3NLO responses are enabled by smaller-size QDs and increased material density in the same matrix volume. However, the increased population of QDs in a small volume introduces aggregations and reduces the efficacy of the composite. Kim *et al.* demonstrated a significant increase in the third-order nonlinear optical (3NLO) activity of PbS quantum dots (QDs) by embedding them within the nanopores of zeolite Y^[50]. This work also highlighted the interplay between the host and guest materials. By replacing of H⁺ cation in the zeolite Y matrix with cations of different sizes, such as NH₄⁺, Li⁺, Na⁺, K⁺ and Rb⁺, the stability and 3NLO activity of the composite were noticeably enhanced^[50]. Considering it is difficult to tailor the chemical functionality or structure properties of zeolites based on guest materials, like other evolving porous materials, metal-organic frameworks (MOFs) or covalent organic frameworks (COFs), systematic replacement of zeolite's counter cations to guest material is one of the viable options to control pore volume, framework donor strength, cation acceptor strength, and electric field strength. This work shows a promising new approach to improve 3NLO activity within the zeolite matrix and the potential guest QDs.

In recent years, CsPbX₃ (X = Cl, Br, or I) perovskites QDs are receiving great attention as PVs or LEDs as they have a narrow emission band and high PLQY^[51,52]. They can be easily processed in liquid form, making them particularly suitable for templated growth within zeolites^[53]. Kim *et al.* used zeolite X as a host matrix for Na₄Cs₆PbBr₄ QDs, benefiting from its hydrophilic nature and relatively high aluminium content, which resulted in an increased number of extra framework cations (Na⁺) that effectively enhanced the stability of the quantum dots when compared to zeolite Y^[54]. This work was initially designed to create CsPbBr₃ QDs within zeolite X based on the previous research that encapsulates CsPbX₃ QDs within zeolite Y matrix. However, the author found out that the Cs⁺ cations interact with counter cations (Na⁺), forming new types of QDs, Na₄Cs₆PbBr₄. Those QDs are placed within the supercage of zeolite structure and interconnected through the window, as shown in Figure 2. The composite showed a much narrower light emission band

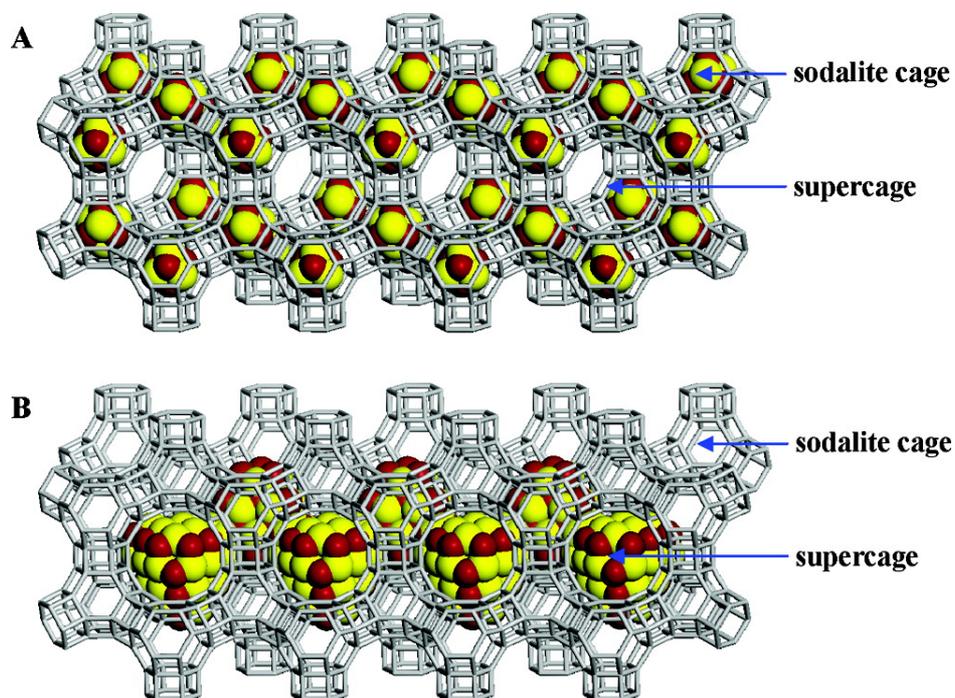


Figure 1. (A) Illustration of the zeolite-Y incorporating one $(\text{CdS})_4$ unit in each sodalite cage and (B) the zeolite-Y incorporating a larger CdS QD in each supercage. Reprinted with permission^[46]. Copyright © 2007 American Chemical Society.

and improved stability in water compared with unprotected CsPbBr_3 QDs, due to uniform distribution and interconnection of QDs within supercage of zeolite X structure^[54]. This work suggests that counter cations of zeolite structures are important to improve stability and sensitivity while also forming more direct interaction with guest material to create new types of QDs. The discovery of this interaction opens a whole set of new research directions for the selection of QDs and cations of zeolite structure.

QUANTUM DOTS IN COVALENT ORGANIC FRAMEWORKS

Compared to zeolites, COFs are porous materials formed through chemical bonds between organic-organic moieties. These building blocks consist of organic molecules that are covalently linked to form a porous crystalline structure. The resulting chemical bonds between organic building blocks create a flexible and tunable framework structure that enables precise control over the size, shape, and chemical properties of the pores and channels within the material. This flexibility and tunability make COFs highly versatile and suitable for a wide range of applications, such as gas storage, separation, catalysis, and sensing. Additionally, zeolites are composed of rigid inorganic frameworks, which limits their flexibility and tunability, though they are still widely used in applications such as catalysis and adsorption.

Considering the dynamic interaction observed between zeolites and QDs, it is anticipated that COFs, in addition to their inherent structure, can provide further tunability to improve the performance of the resulting composites. The dynamic nature of COFs presents both opportunities and challenges for the generation of QDs within their pores. Obtaining a well-ordered three-dimensional crystalline COF structure and preserving its integrity during QD synthesis are among the most critical challenges that need to be overcome in the development of QD-COF composites. COFs can form two- or three-dimensional structures through covalent bonds between organic monomers composed of light elements such as C, H, N, B, and O^[55,56]. In natural systems, covalent and noncovalent interactions play crucial roles in the formation

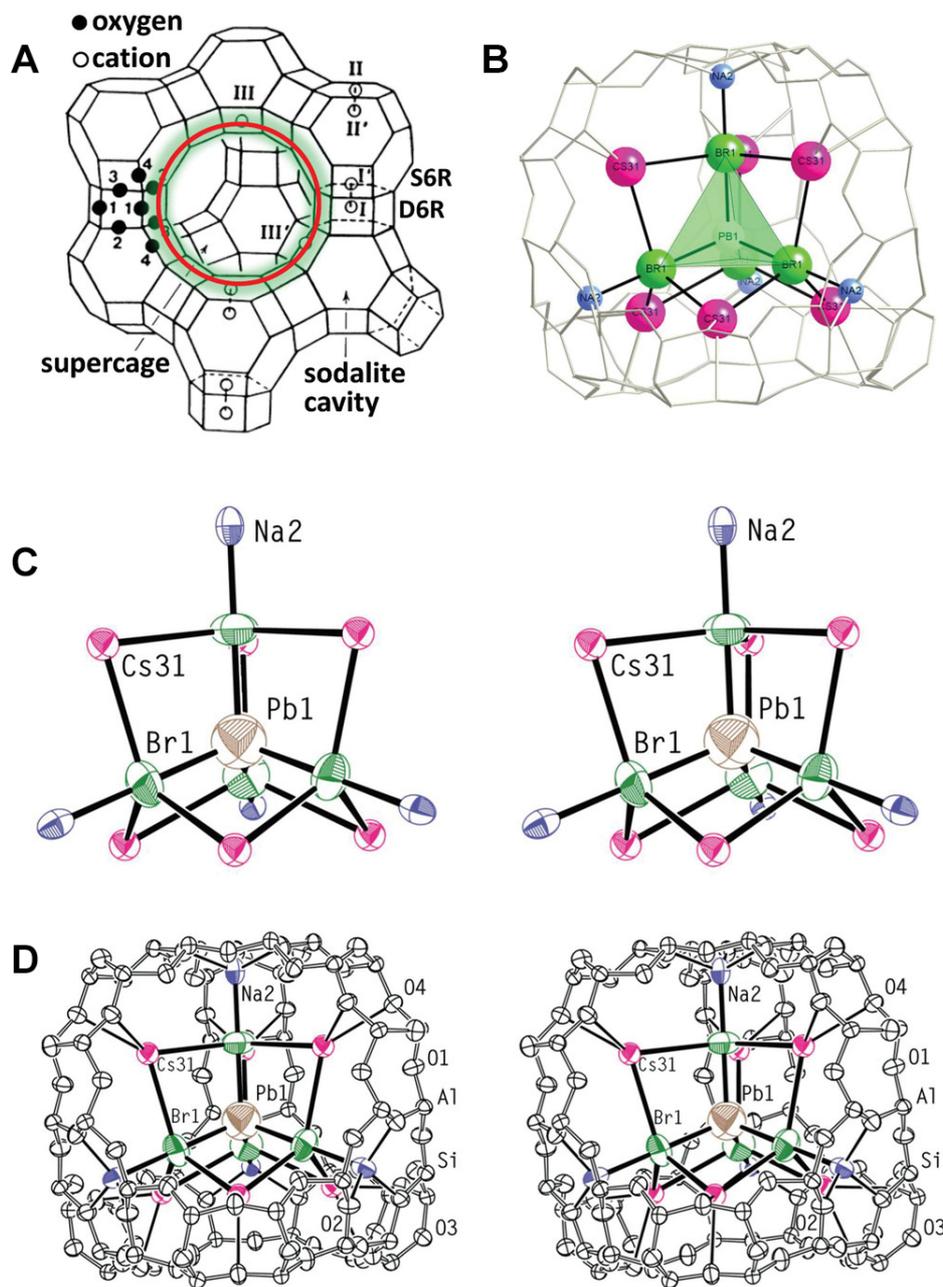


Figure 2. (A) Schematics of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1-4. The common extraframework cation positions are labeled with Roman numerals. One of the four entrances to the supercage is highlighted in red. (B) The $[\text{Na}_4\text{Cs}_6\text{PbBr}_4]^{8+}$ quantum dot (QD) in a supercage of zeolite X. (C) Stereoview of the $[\text{Na}_4\text{Cs}_6\text{PbBr}_4]^{8+}$ QD. (D) Stereoview of the $[\text{Na}_4\text{Cs}_6\text{PbBr}_4]^{8+}$ QD in a Pb, Br, H, Cs, Na-X supercage. This structure may be viewed as a series of concentric spheres of alternating charge (48 O^{2-} ions of the zeolite framework, 10 Cs^+ and Na^+ ions, and 4 Br^- ions) with a Pb^{2+} ion at its center. The two water molecules (at O5 that bond to each Cs^+ ion at Cs31 are not shown. Reprinted with permission^[54] © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

of pre-designed protein structures. For example, DNA and RNA utilise covalent bonds to regulate the sequence of their primary-order chain structure, while noncovalent interactions control their high-order morphology. Although biological polymer systems already use covalent interactions to form high-order structures, synthesising precise microporous organic coordination polymer structures was once considered

particularly challenging until Yaghi's team reported the first COFs in 2005^[55]. To obtain well-ordered crystalline three-dimensional organic structures held together by strong covalent bonds between each block, it is crucial to carefully design the covalent and noncovalent interaction sites in the primary structure. In the absence of a proper guiding system, the organic chains may grow randomly on a two-dimensional plane, resulting in either an amorphous structure or a packed one-dimensional (linear) crystalline structure^[57]. To address this issue, researchers have been studying different types of linkers, organic blocks, and fabrication conditions to tailor the COFs with diverse structures, as depicted in [Figure 3](#)^[58]. These explorations opened new opportunities for COFs to be considered as porous host materials due to their high specific surface area, tailorable pores and structure, and low density.

Mn-ZnS QDs are considered as one of the promising materials for chemical contamination fluorescent detectors as ZnS has low toxicity and a wide band gap of 3.7 eV^[59]. Furthermore, it has been broadly studied for metal ions, small molecules, and biopolymers detections. However, pure Mn-ZnS QDs have the limitation of low stability in a complex medium as the selectivity and sensitivity of the material reduce significantly over time^[60]. To overcome these issues, molecularly imprinted polymers (MIPs) methods have been investigated. MIP is a procedure to generate specifically tailored cavities in polymers that works like antibody-antigen systems in our bodies to select precisely aimed molecules in the matrix^[61]. This hybrid material showed great selectivity from shaped polymer and high sensitivity from QD material. However, achieving a uniform distribution and increasing the active material volume density remain challenging issues to address. Zhang *et al.* reported a new hybrid composite consisting of Mn-ZnS QDs embedded in TpPa-1 COFs with molecularly imprinted polymer (MIP) to improve the detection limit and stability of the composite in water^[62]. This technique was further developed to fabricate fluorescent probes for ferulic acid with high selectivity and sensitivity, as demonstrated in [Figure 4](#)^[63]. The fabricated composite demonstrated improved stability at room temperature, as well as a high photoluminescence quantum yield (PLQY) of 37%. In these applications, the COF serves not only as a passive protective framework but also as a platform for achieving even distribution and minimising aggregation of QDs.

Carbon quantum dots (CQDs) have been studied widely as a new type of fluorescent nanomaterials primarily due to their favourable characteristics such as environmental friendliness, functionalisability, excellent stability, biocompatibility, solubility, and low toxicity. These properties have rendered CQDs an ideal candidate for various applications such as sensing cellular copper, glucose, nucleic acids, and cancer detection and treatment. As a result, the investigation and exploration of CQDs continue to grow significantly^[64,65]. Despite significant advantages, the limited size control, uniformity, and low quantum yield of carbon quantum dots present major challenges. To address these issues, researchers have attempted to improve synthesis methods using various techniques such as solvent engineering, electrochemical fabrication, and laser ablation, as well as fabricating hybrid composites that include encapsulating CQDs with polymers and embedding them within porous matrices. Recent progress in encapsulating carbon quantum dots (CQDs) involves surface functionalization by coating them with amphiphilic monomers or polymers. Amphiphilic molecules contain both hydrophilic and hydrophobic components, which allows them to interact with both water and the CQDs surface. This method can provide a protective layer around CQDs which can improve their stability, reduce aggregation, and provide other desirable properties such as solubility in different solvents^[66-68]. Encapsulating CQDs within micro to mesoporous matrices such as mesoporous silica is a common approach to improve their stability and efficacy. Mesoporous silica, in particular, has attracted significant interest due to its large specific surface area, low toxicity, and good biocompatibility.

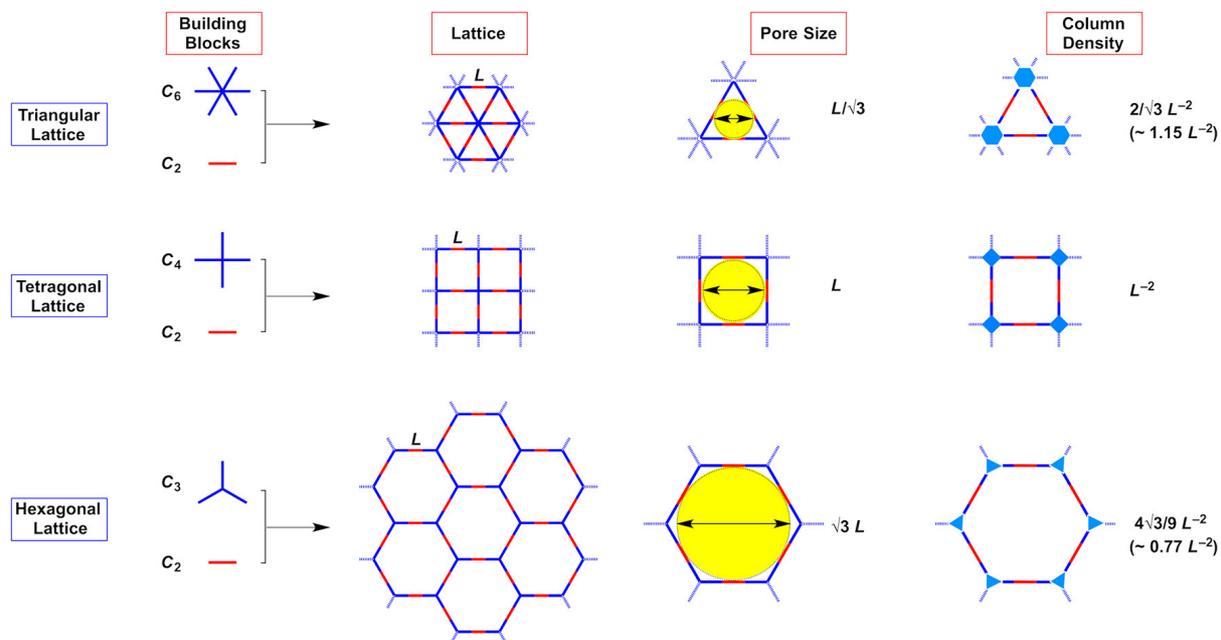


Figure 3. Dependency of pore size and column π -density of 2D COFs on topologies. Reprinted with permission^[58]. Copyright © 2020 American Chemical Society.

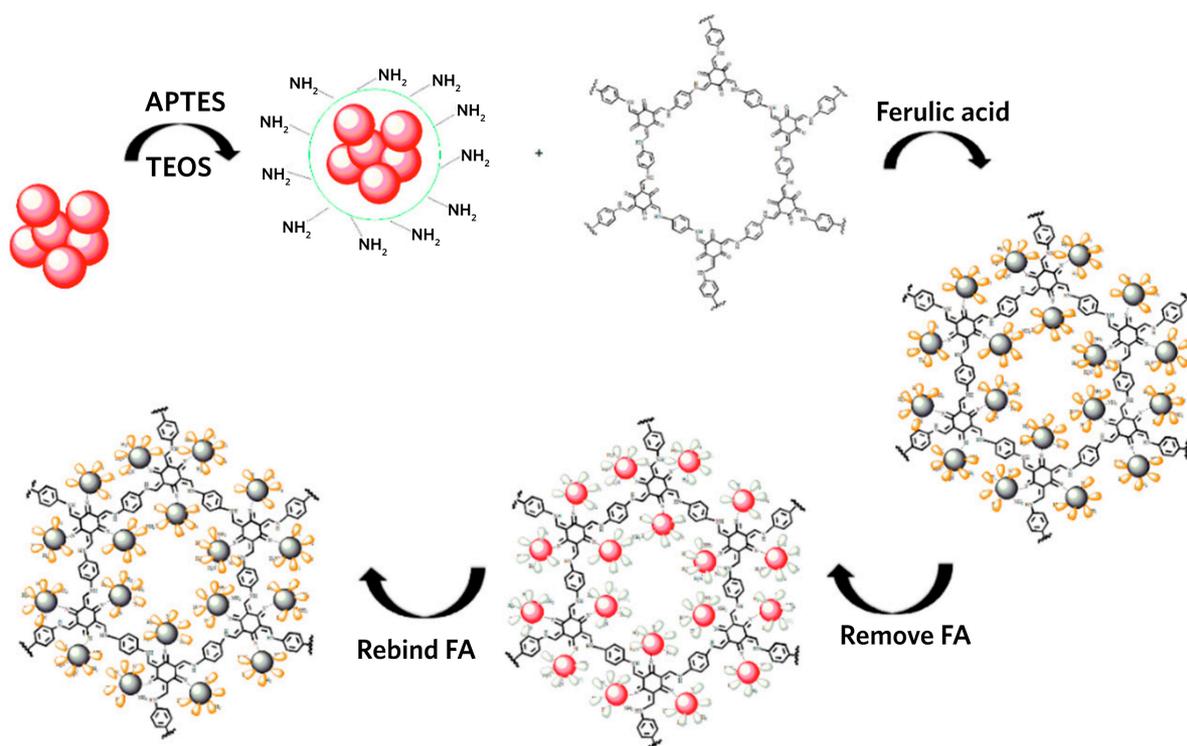


Figure 4. A schematic representation of the synthesis of molecularly imprinted polymers (MIPs) based on quantum dot-grafted covalent organic frameworks (QD-grafted COFs) for optosensing of ferulic acid (FA). Tetraethyl orthosilicate (TEOS) and (3-aminopropyl) triethoxysilane (APTES) are used as cross-linker and functional monomer, respectively, in MIP fabrication process. Reprinted with permission^[63].

Recently, covalent organic frameworks have emerged as a promising alternative for encapsulating CQDs in microporous structures, offering advantages such as high stability, excellent control over pore size and shape, and the ability to tune the chemical and physical properties of the framework for specific applications. The presence of a large number of conjugated structures for both CQDs and COFs enables a unique opportunity to engineer their interfacial properties. Generally, CQDs have a size between 3 and 5 nm, which can be considered as a big molecular block within a typical COFs structure. Chen *et al.* formed, for the first time, two COFs consisting of carbon quantum dots which were generated through the Schiff base reactions with CQDs and phenylenediamine (pPDA) and BODIPY with two amino groups, as shown in Figure 5^[69]. In this study, solvothermal methods were utilised to synthesise spherical CQDs with a size of ca. 5 nm. The synthesised CQDs were then dispersed in ethyl alcohol along with pPDA (p-phenylenediamine), and in a mixed solvent of ethyl alcohol and acetic acid with BODIPY, to form novel types of carbon dot-based covalent organic frameworks (CCOFs).

These newly synthesised CCOFs exhibit a bulk, spherical nanoparticle morphology, ranging in size from 200 to 500 nanometres. These structures are composed of carbon quantum dots, which are covalently bonded to organic ligands. Subsequently, the surfaces of these CCOFs are modified with polyethylene glycol (PEG) to further enhance their stability and dispersibility in aqueous environments. Following modification, the composite demonstrates no signs of aggregation for up to 24 h when exposed to a 10% fetal bovine serum (FBS) solution in water. By contrast, unmodified CCOFs exhibit aggregation under the same conditions. In addition, blood compatibility was evaluated by administering a dose of 10 mg/kg of modified CCOFs to mice, demonstrating no adverse effects on biosafety at that concentration. Furthermore, under green LED laser irradiation, the composite exhibited marked inhibition of tumour growth and size reduction. This carbon quantum dot-based covalent organic framework exhibits highly desirable characteristics, including excellent physiological stability, biocompatibility, and remarkable reactivity in oxygen generation, positioning them as a promising contender for cancer treatment^[69].

QUANTUM DOTS IN METAL-ORGANIC FRAMEWORKS

Compared to zeolites and COFs, MOFs are a highly versatile family of microporous materials with a hybrid organic-inorganic continuous porous structure. They are formed by the coordination of metal ions with organic ligands, creating a three-dimensional network of pores and channels with high surface area and tunable properties. This material was introduced by Tomic in 1965 as a porous coordination framework. More than 80,000 types of MOFs have been reported so far, due to the wide selection of metal ions and organic ligands used to form a structure [Figure 6]^[70-73]. The presence of inorganic and organic coordination is a distinguishing factor of MOFs compared to covalent organic COFs, which are composed solely of light organic elements such as carbon, nitrogen, hydrogen, boron, and oxygen. High surface area, uniform structure, flexible choice of metal and organic ligands, structure tunability, and chemical functionality make this material unique and ideal for various applications such as separation, catalysis, sensing, and as a protective host matrix. One of the most extensively studied topics in the field of MOFs is hybrid nanocomposite materials. Due to the strong coordination between metal nodes and organic ligands, MOFs exhibit good chemical resistance to a wide range of solvents, including polar, nonpolar, and apolar solvents. Furthermore, porous structures can be tailored to a given requirement. These advantageous characteristics make this material a strong candidate as the protective host matrix for hybrid nanocomposites^[74-77].

Organic-inorganic metal halide perovskites have been a trending subject in material science as a semiconducting light-harvesting material for various applications due to their outstanding properties, such as high light absorption coefficient, high defect tolerances and long charge carrier diffusion distances^[78,79]. However, relatively low stability to moisture, heat and most common polar solvents limits the applicable

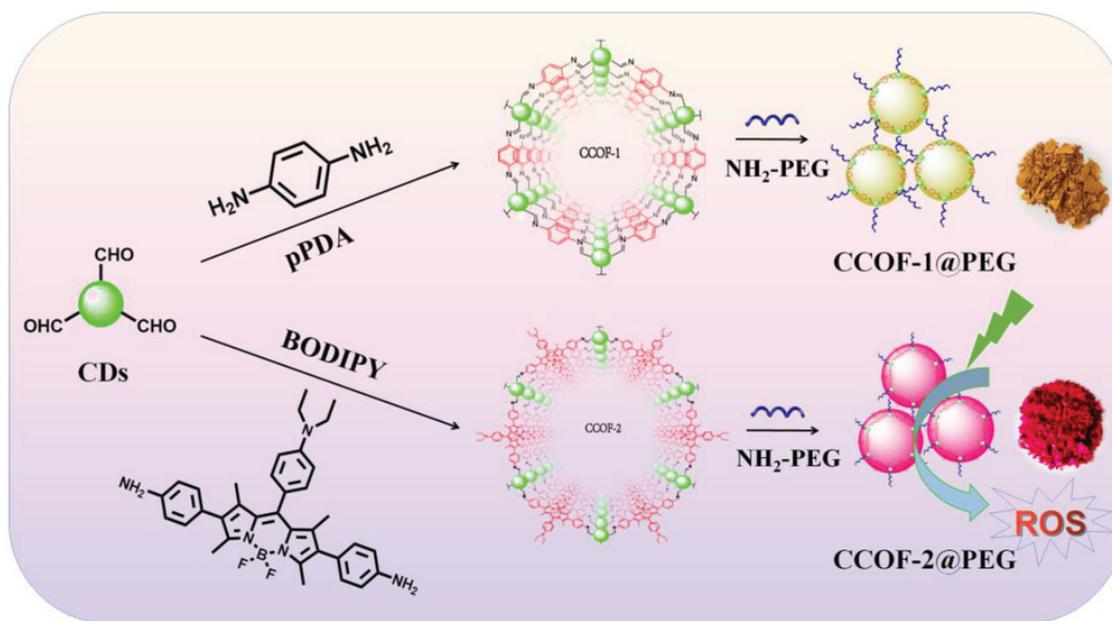


Figure 5. Schematic illustration of the synthesis of CCOF-1@PEG and CCOF-2@PEG and the application of CCOF-2@PEG for photodynamic therapy as reactive oxygen species (ROS). Carbon dots (CDs) and phenylenediamine (pPDA) and BODIPY are forming CCOF1 and CCOF2 respectively. Reprinted with permission^[69] © 2020 Wiley-VCH GmbH

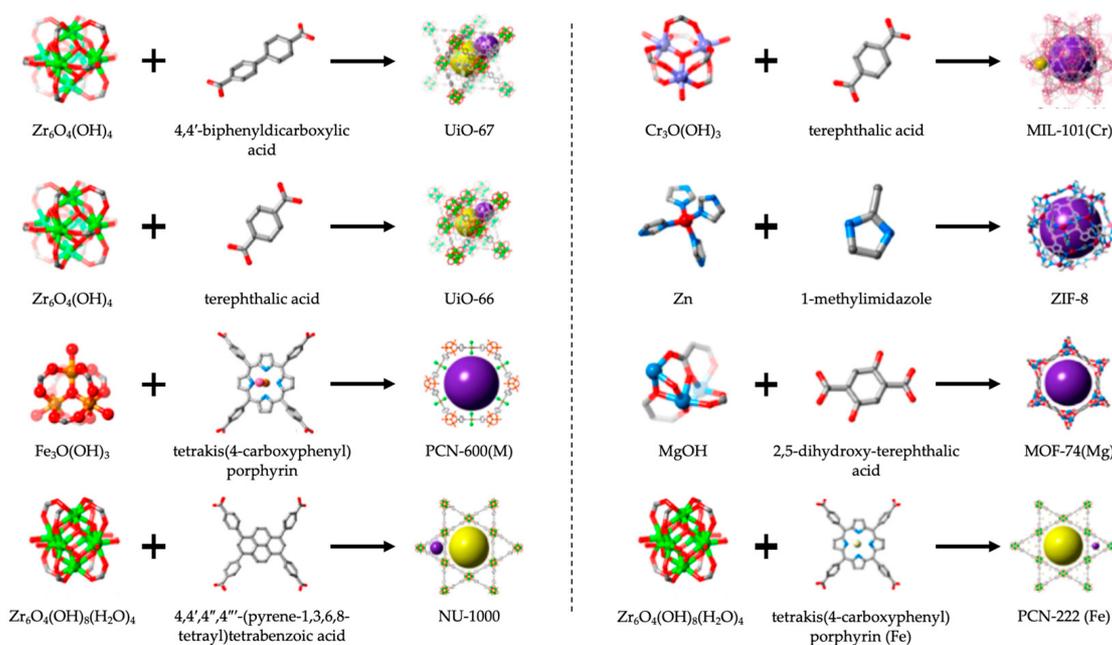


Figure 6. Representations of MOF structures and the corresponding node and linker constituents. Reprinted with permission^[73,74]. Copyright © 2016 American Chemical Society.

devices and shortens the life expectancy of the application^[80-82]. There have been various attempts to mitigate this major drawback of perovskite materials, such as compositional and interfacial engineering, surface passivation, and encapsulation^[83]. Especially in the encapsulation process, the efficacy of the active material can often be reduced. Therefore, using a porous structure is crucial to minimise the unwanted sacrifices. In

this sense, MOFs are strong candidates as a protective layer since they can provide a hydrophobic surface and a uniformly tailored porous structure. A cesium lead bromide (CsPbBr_3), an inorganic halide perovskite, has garnered interest as a viable photocatalyst for CO_2 reduction. However, it shares similar limitations with other perovskites. Recently, researchers have made significant progress by employing zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs, as a host matrix for CsPbBr_3 quantum dots. [Figure 7](#) illustrates the successful coating of CsPbBr_3 QDs with ZIFs through a “building a bottle around a ship” approach. The mild synthesis conditions of MOFs enable the fabrication of QD-MOF composites in this manner, providing reliable protection. The coated composite exhibits an improved CO_2 reduction efficiency due to its superior capturing ability and charge separation efficiency, as well as enhanced stability against moisture, compared to naked CsPbBr_3 . However, this method may pose challenges in controlling QD particle size as the size is no longer restricted by the inherent pore structure of the template. Moreover, the synthesis solvent may cause partial dissolution/decomposition of QDs, which can adversely affect the overall efficiency. Thus, it is crucial to exercise caution in regulating the final solvent removal and nucleation process^[84].

Typically, the pores in MOFs are considered too small to accommodate QDs, as most reported MOFs have microporous structures with pore diameters less than 2 nm. While this size range is suitable for the adsorption and separation of small molecules, such as gases, it is not ideal for QDs which are typically between 2 and 10 nm in size^[85,86]. Synthesising QDs within the MOF cavity offers significant advantages in controlling QD crystal size through MOF pores and limiting aggregation during fabrication. However, the primary challenge lies in fabricating large-pore MOFs, as they can result in pore interpenetration and blockage. A meticulous design of the pore structure is also crucial, with an ideal cavity having a narrow entry to suppress the dissolution or dissociation of the encapsulated QDs^[87]. To address this limitation, various efforts have been made to modify the pore sizes of MOFs to accommodate larger molecules such as QDs. One such approach involves introducing larger functional groups into the organic ligands or metal nodes, thereby expanding the pore size. Another approach is to employ post-synthesis modification techniques, including solvent or ligand exchange, to adjust the pore size of the MOF. These strategies have demonstrated promising outcomes in enlarging the pore size of MOFs, facilitating the integration of larger guest molecules like QDs^[88-90].

In a recent advance, Qiao *et al.* reported the successful fabrication of CsPbBr_3 quantum dots within the PCN-33 MOF pores through a sequential deposition method^[91]. PCN-333(Fe) possesses an extraordinary hierarchically porous structure with mesoporous cages ranging from ca. 4 to 5 nm and microporous cages with a diameter of around 1 nm, as well as excellent chemical stability. Its large mesoporous cages enable the accommodation of perovskite nanoparticles, while its microporous cages facilitate the diffusion of reactants for catalysis. In this study, PbBr_2 was positioned within the PCN-333(Fe) cavity, followed by the diffusion of CsBr into the pores to form CsPbBr_3 QDs within the mesoporous cage^[91]. This composite showed green fluorescence under ultraviolet (UV) light, which confirms the formation of CsPbBr_3 QDs. Also, the resultant shows excellent stability, oxygen reduction, and evolving catalytic reaction in an aprotic medium. As these photoelectrochemical characteristics are desired for photocathodes in lithium-oxygen batteries, the material was tested as a cathode without any carbon support. The round-trip efficiency of the battery under illumination was 92.7%, which was comparably higher than that of pure CsPbBr_3 (82.8%) or PCN-333(Fe) (85.2%). Furthermore, it improved stability noticeably compared with pure CsPbBr_3 as the MOF provides the protective aspect. This work shows the potential compatibility of perovskite QDs and MOFs and also offers new promising directions and insights for photo-rechargeable batteries [[Figure 8](#)]^[91].

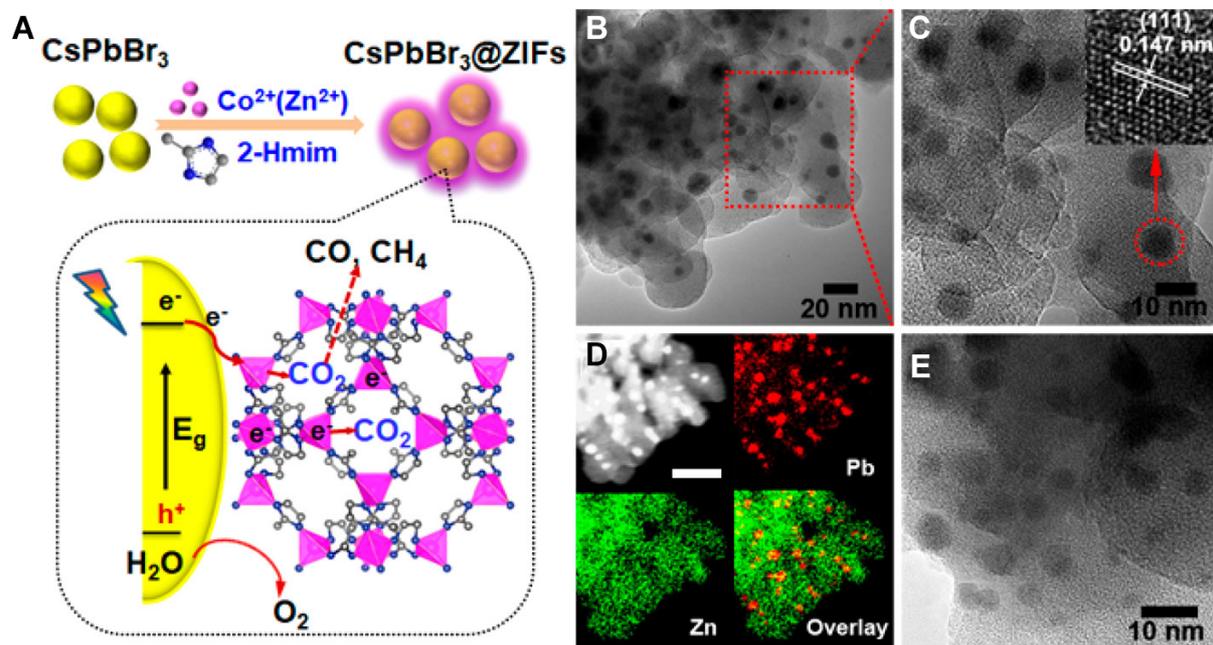


Figure 7. (A) Schematic illustration of the fabrication process and CO_2 photoreduction process of $\text{CsPbBr}_3/\text{ZIFs}$. (B and C) Low- and high-magnification TEM images of $\text{CsPbBr}_3@\text{ZIF-8}$. The inset of (C) is the high-resolution image of a single CsPbBr_3 QD marked with a red circle. (D) High-angle annular dark-field STEM image and elemental mapping of $\text{CsPbBr}_3@\text{ZIF-8}$. Scale bar: 50 nm. (E) TEM image of $\text{CsPbBr}_3@\text{ZIF-67}$. Reprinted with permission^[84]. Copyright © 2018 American Chemical Society.

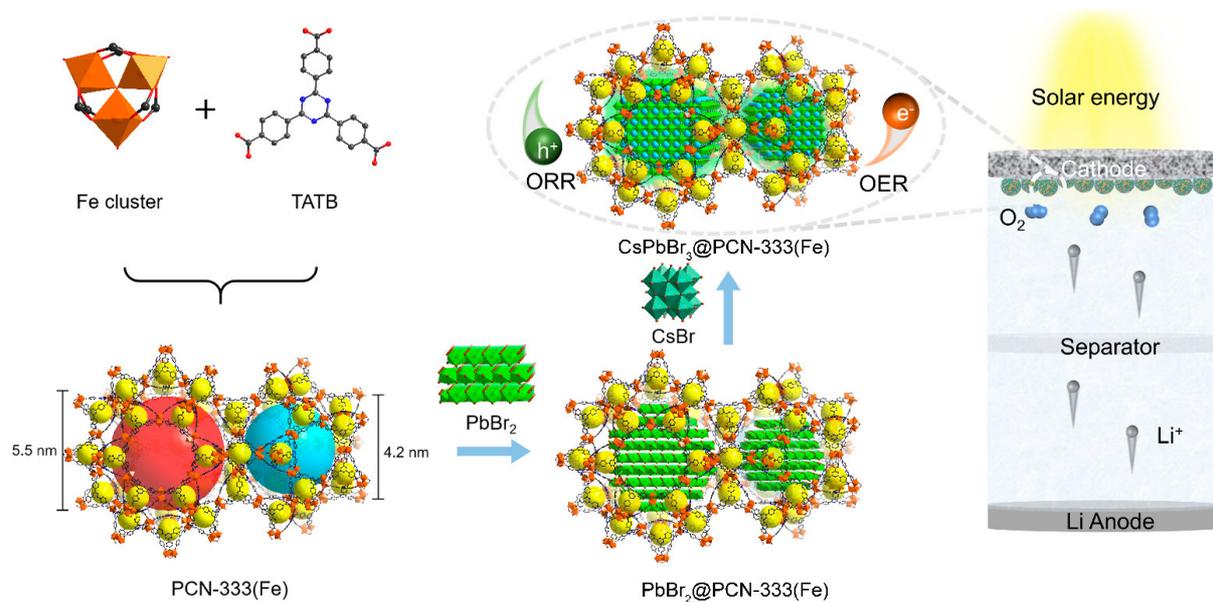


Figure 8. Schematic illustration of the Preparation of PCN-333(Fe) and $\text{CsPbBr}_3@\text{PCN-333(Fe)}$ Composite $\text{CsPbBr}_3@\text{PCN-333(Fe)}$ can be used as a photoelectric cathode material for light-assisted Li-O₂ batteries. Reprinted with permission^[91]. Copyright © 2021 American Chemical Society

So far, most research works on MOFs have focused on crystalline forms. However, limited processability and deprived interfacial bonding between host and guest materials have motivated the synthesis of non-crystalline structures. Recent studies showed that some of the MOFs, especially some of ZIFs, can form

amorphous structures via temperature-induced amorphisation through melting upon heating followed by a fast cooling (quenching) process at ambient pressure^[92,93]. These ZIF glasses form a continuous random network similar to the amorphous structure of silica glass. Also, these emerging new types of glasses show structural diversity and unique properties compared to inorganic, organic and metallic glasses^[94]. Recently, our group further developed this idea and successfully fabricated embedded perovskites within the ZIF glass matrix. This nanocomposite not only showed significantly improved photoluminescence under UV light in ambient conditions, but the stability also improved noticeably in most solvents. [Figure 9](#) shows how CsPbI₃ perovskite is encapsulated within the ZIF-62 glass matrix after the sintering process and the phase distribution based on ADF and SED-STEM spectroscopy^[95].

SUMMARY AND OUTLOOK

In conclusion, the embedment of various quantum dots into microporous materials has shown enormous potential for applications due to its ability to enhance long-term stability, reduce aggregation, improve efficiency, increase active material density, provide protective layers, and achieve uniform distribution. However, some of the methods are complicated and challenging to control during the fabrication process, which makes upscaling difficult. Although most of the studies are still in their early stages, especially QDs in COFs and MOFs, they have proved significant functionalities and potential. Based on above mentioned strategies, we hope this Perspective has highlighted the promising future research directions related to QDs in microporous structure.

(1) Biocompatible nanocomposite of QDs within microporous frameworks: The demand for biocompatible quantum dots and microporous templates is rapidly increasing for a wide range of applications, including disease detection, drug delivery, molecule detection, and cancer treatment. Currently, most of the research on biocompatible QDs is focused on surface engineering, including surface organic ligand exchange, polymer encapsulation and conjugation of biomolecules on the surface of QDs. However, those approaches still experience several issues such as size uniformity, aggregation, and stability in the biological environment. Furthermore, although there are numerous ongoing explorations for biocompatible and biodegradable MOFs and COFs for biomedicine applications, there have been limited investigations to combine biocompatible framework matrixes and QDs. Thus, by intermarriage of two biocompatible materials, QDs and specifically tailored frameworks matrix, can improve the selectivity of QDs and enable biological targeting of small molecules and antigens, as well as providing uniformity and stability to the composite.

(2) MOF glasses: one of the most recent and significant progress in porous materials is the development of MOF glasses. MOF glasses are new types of glasses that have unique characteristics compared with traditional glass materials. As these emerging materials have only been studied for less than 10 years, there are still many research gaps to investigate. We demonstrated a MOF glass with perovskite QD nanocomposites that greatly improved interfacial connectivity, which MOF crystals have not been able to achieve^[95]. Furthermore, MOF glasses can be obtained through mechanical vitrification or direct synthesis as glass^[96]. Thus, researching various types of MOFs and QDs hybrid materials as well as alternative fabrication routes of MOFs glass could open more new possibilities for QDs and MOF glasses nanocomposite.

(3) Fundamental study of QDs within microporous structure: Although great efforts have been made to fabricate QDs in microporous structures and improve their efficacy, there are remaining questions for a deeper understanding of the nanocomposite due to its set of rich physiochemical properties and dynamic interaction between two materials. In particular, x-ray-based techniques such as small-angle X-ray

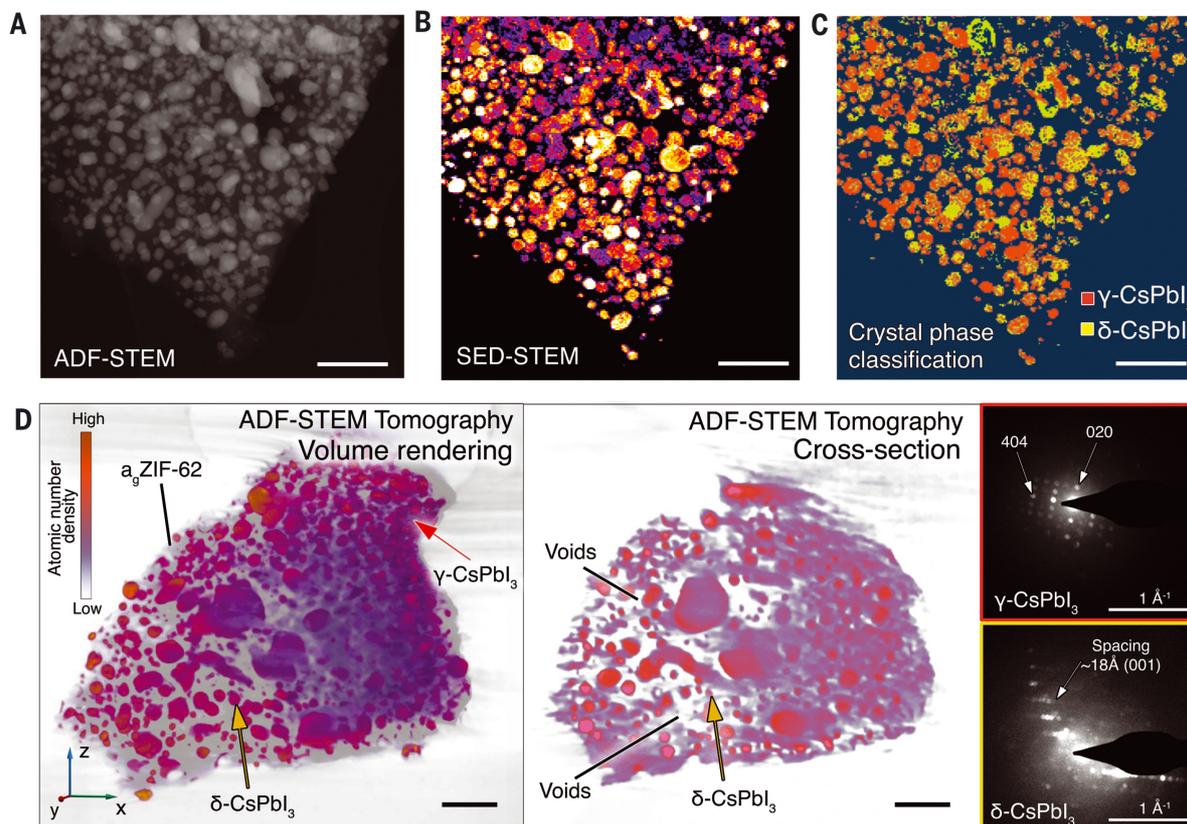


Figure 9. Phase distribution for the $(\text{CsPbI}_3)_{0.25}(\text{a}_8\text{ZIF-62})_{0.75}$ composite fabricated with 300 °C sintering. (A) ADF-STEM image, (B) SED-STEM mapping, and (C) CsPbI_3 crystal phase classification results for $(\text{CsPbI}_3)_{0.25}(\text{a}_8\text{ZIF-62})_{0.75}$ composite. (D) Volume rendering of tomographic reconstruction of $(\text{CsPbI}_3)_{0.25}(\text{a}_8\text{ZIF-62})_{0.75}$ and a single cross-sectional plane extracted from the volume. Color-coded arrows indicate the regions where electron diffraction data were collected. Scale bars, (A-D) 250 nm. Reprinted with permission^[95]. Copyright © 2021 American Chemical Society

scattering (SAXS) and wide-angle X-ray scattering (WAXS) could show the micro to atomic scale structures and interactions of the composite materials. Recently, our group revealed the nanoparticle size, homogeneity, and internal structure behaviour during the liquid phase sintering process of pure MOF to MOF-glass and hybrid nanocomposite with perovskite, and MOF-glass using WAXS and SAXS analysis^[92,94]. Furthermore, pair distribution functions (PDFs) from the X-ray diffraction pattern could explain the atomic structure formation, especially for composites with an amorphous matrix, as it can reveal information that X-ray diffraction is unable to obtain.

Terahertz/far-infrared (THz/far-IR) spectroscopy is another powerful technique that should be considered for investigating the dynamic properties of localised features within the composite. When paired with in-situ investigation capabilities, THz/far-IR spectroscopy can effectively identify the dynamic structural behaviour and emerging new chemical bonding between the guest and host materials. Hou *et al.* successfully integrated this technique to identify halogenation reactions during the melting process of MOF glass^[95]. Combined with thermal behaviour analysis and X-ray-based techniques, this spectroscopy can reveal additional dynamic properties of QDs embedded in the microporous matrix and how they interface internally.

Overall, despite the significant and rapid progress in quantum dots (QDs) and tailorable microporous structures, they remain relatively immature technologies that have not yet been fully integrated into real-life applications, leaving significant space for exploration. A deeper and more fundamental understanding of complicated properties, such as interfacial bonding, conductivity, and structural and functional diversity, is expected to unlock new opportunities in the areas of light emission, biomedicine, catalysts, and energy storage.

DECLARATIONS

Authors' contributions

Conceptual design and manuscript draft: Lee J

Manuscript Revision and Project supervision: Wang L, Hou JW

Availability of data and materials

Not applicable.

Financial support and sponsorship

This research was partially financially supported by the Australian Research Council (ARC) through Future Fellowship, Laureate Fellowship programs (FT210100589 and FL190100139) and an Australian Government Research Training Program (RTP) Scholarship.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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