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REVIEW

MOF-based nanocomposites in polymer matrix: progress and prospects

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Abstract

Metal–organic frameworks (MOFs), an emerging class of crystalline microporous functional fillers, have garnered significant attention in materials science owing to their tunable pore architecture and abundant coordinatively unsaturated sites. However, MOF materials encounter substantial challenges in practical applications, including poor spatial dispersion, severe agglomeration, and insufficient interfacial compatibility with polymer matrix, which substantially impede their incorporation into polymer composite materials. Building upon the foundational research of our group in MOF surface modification and nanocomposite engineering, this work systematically investigates the hierarchical integration strategies of MOFs with dimensionally controlled nanomaterials (encompassing 0D nanoparticles, 1D nanofibers/nanotubes, 2D nanosheets, and 3D interconnected networks). Through precise modulation of interfacial chemistry and architectural design, we have successfully addressed the dispersion limitations of MOFs and significantly enhanced the synergistic effects within the composite matrix. Experimental results demonstrate that this novel integration approach effectively mitigates nanofiller aggregation and substantially enhances the flame retardancy, mechanical strength, and electrical conductivity of the resultant composites. A detailed examination has been conducted exploring how MOF-based nanocomposites integrate within the polymer matrix, encompassing fabrication approaches, physical and chemical properties, and prospective uses. Our investigation addresses existing obstacles while evaluating future directions within this expanding research domain. By offering both fundamental scientific understanding and concrete recommendations, this work aims to facilitate advances in developing advanced functional materials incorporating MOF-based nanomaterials. The findings presented serve as a foundation for researchers working toward innovative composite systems with enhanced capabilities and performance metrics.

Keywords Metal–organic framework · Polymer composites · Nanocomposites · Flame retardancy · Mechanical properties · Electrical performance

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1 Introduction

The development of functional polymer composites has garnered significant research attention to meet diverse industrial requirements and enhance product performance. Polymeric materials, known for their exceptional performance characteristics and versatility, have been widely applied in civil engineering, transportation, textiles, biomedical engineering, electronics, and aerospace industries [1–7]. The integration of metal–organic frameworks (MOFs) into these polymers offers innovative solutions for creating advanced composite materials. MOFs are innovative crystalline microporous fillers that enhance polymer composites through their adjustable pore structures and numerous coordinatively unsaturated sites (CUSs) [8–10]. By altering organic ligands and metal ions, their pore architecture can be finely tuned. UiO-66, a Zr-MOF, has two 5.0 Å "through-windows," making it effective for gas separation and storage. Its pore size can be modified via functionalization: o-TBA-UiO reduces to 4.4 Å, and m-TBA-UiO to 3.0 Å, significantly affecting gas molecule transport [11]. CUSs in MOFs enable strong interactions with gases like CO_2 and H_2, improving adsorption and separation. MIL-101's CUSs, when grafted with ethylenediamine, enhance gas adsorption and catalytic performance [12]. Moreover, HE-UiO-66's lattice distortion exposes metal nodes, creating abundant CUSs that boost catalytic transfer hydrogenation reactions [13]. Since the 1990 s, many MOFs, such as ZIFs, MILs, and UiOs, have been developed and named after their institutions of origin [14–17]. Their high adaptability stems from their large surface area and porosity, enabling diverse applications. UiO-66, with a surface area of up to 1326.5 m2/g, is particularly effective for capturing pollutants.

Characterization of MOFs is essential for understanding their structural and functional properties within nanocomposites. Specifically, X-ray diffraction (XRD) is employed to confirm crystalline phase purity and framework integrity. Scanning/transmission electron microscopy (SEM/TEM) serves as a valuable tool for observing morphology and dispersion, enabling assessment of agglomeration challenges in polymer matrix. Nitrogen adsorption–desorption testing analyzes specific surface area and pore size distribution. Fourier-transform infrared spectroscopy (FTIR) identifies functional groups and chemical bonds. Additionally, thermogravimetric analysis (TGA) investigates the thermal stability of MOFs, as well as structural changes and decomposition behavior during heating processes. These methods collectively validate MOF integrity before integration [18, 19], establishing a scientific foundation for the targeted design of MOF-based nanocomposites with integrated flame-retardant, mechanical-reinforcement, adsorption functionalities, and so on.

To address these challenges, researchers have explored innovative synthetic methods and modification strategies aimed at optimizing the incorporation of MOFs in polymer matrix. One effective approach is the hierarchical integration of MOFs with nanomaterials of various dimensions—zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanofibers/nanotubes, two-dimensional (2D) nanosheets, and three-dimensional (3D) interconnected networks. This multi-dimensional integration strategy enhances the functional properties of MOF-based composites by providing additional reactive sites, improving energy storage and conversion efficiency, enhancing mechanical strength and chemical stability, and facilitating better dispersion and interfacial interactions within the polymer Matrix. For instance, 0D nanomaterials like silica nanoparticles (SNPs) [20–22] and polyhedral oligomeric silsesquioxane (POSS) [23–25] enhance catalytic performance and gas adsorption by providing additional reaction sites and increasing surface area. Similarly, 1D nanomaterials such as halloysite nanotubes (HNTs) [26–28] and carbon nanotubes (CNTs) [29–31] improve energy storage and conversion efficiency by offering more active sites and shortening proton and electron transport paths. 2D nanomaterials such as MXenes [20, 32, 33], graphene [34–36], and boron nitride (BN) [37–39] contribute to the mechanical strength and chemical stability of composites, while 3D nanomaterials such as covalent organic frameworks (COFs) [40–42] and graphene oxide aerogel (GA) [43] enhance MOF dispersion and interfacial interactions.

Traditional materials, such as carbon materials, layered double hydroxides (LDHs), and silicon-based nanomaterials, have been extensively studied due to their unique properties. Compared to MOFs, carbon materials (such as graphene and CNTs) exhibit excellent electrical and thermal conductivity. For instance, graphene's elastic modulus can reach up to 1 ± 0.1 TPa [44], with outstanding electrical conductivity of approximately 7000 $cm^2/V \cdot s$ [45], whereas the conductivity of MOFs is generally poor, and their thermal conductivity is relatively low. Therefore, in applications requiring efficient energy transfer, carbon Materials often demonstrate superior advantages. Additionally, one-dimensional CNTs have a thermal conductivity of 6600 W/mk [46], significantly higher than that of Many MOF Materials. Two-dimensional carbon materials, such as MXene, have a tensile strength of around 15.4 GPa [47] and good electrical conductivity, effectively enhancing the electrical and thermal properties of composites. On the other hand, LDH and silicon-based nanomaterials have drawn attention for their good dispersibility and mechanical properties. LDH possesses high ionic conductivity and surface area, making it suitable for energy storage devices such as batteries and supercapacitors. Its layered structure provides good dispersibility, which helps to enhance the mechanical properties of composites. Silicon-based nanomaterials, due to their excellent stability and biocompatibility, have extensive applications in biomedicine and electronics. In contrast, while MOFs exhibit unique porous structures and a wealth of coordinatively unsaturated sites, they inherently have certain flammability and thermal stability limitations that may restrict their performance in specific applications [48, 49]. However, the designability and multifunctionality of MOFs allow them to be combined with the aforementioned materials to leverage the advantages of both and produce synergistic effects. For example, combining MOFs with CNTs can significantly enhance the electrical and thermal conductivities of MOFs [50], thereby broadening their applications in energy storage and conversion fields. Through this approach, not only can the deficiencies of single materials be compensated for, but the strengths of each material can also be harnessed, providing new ideas for the development of high-performance composite materials. Comparative analysis through Table 1 indicates that MOF-based nanocomposites not only match but often exceed the performance of state-of-the-art materials in various applications. Their multifunctionality, tunability, and potential for cost-effective production make them highly competitive candidates for future material development.

The review delves into the integration of MOFs with various nanomaterials, examining the impact on composite performance in key areas such as flame retardancy, mechanical reinforcement, energy storage, and water treatment. We provide a detailed analysis of how structural design and functional integration can effectively enhance critical performance indicators, including flame retardant efficiency, mechanical properties, electrical performance, and so on. By summarizing research progress and successful case studies, and addressing challenges, the review offers valuable insights for researchers aiming to advance the field of MOF-polymer composites.

2 Nanomaterials integrated with MOFs

The integration of specific MOFs with nanomaterials leverages their unique pore architectures and coordinatively unsaturated sites to significantly enhance composite performance. Notably, different MOFs, such as UiO-66, MIL-101, and ZIF-8, exhibit distinct pore architectures and chemical compositions, which significantly influence their performance in polymer composites. The integration of ZIF-8, a Zn-based MOF with a sodalite (SOD) topology, with CNTs has been shown to improve the electrical conductivity and mechanical strength of composites [57]. In contrast, the use of MIL-101(Cr), with its larger pore size and higher surface area, in combination with graphene oxide (GO), leads to enhanced adsorption capacity and catalytic activity in water treatment applications [58].

2.1 0D nanomaterials

2.1.1 POSS

As shown in Fig. 1a, POSS particles represent a distinctive category of caged inorganic–organic hybrid nanomaterials. These particles are composed of an inorganic core comprising a silicon-oxygen skeleton with alternating Si–O linkages and an outer perimeter encased in organic groups (hydrogen atoms, alkyl groups, alkenyl groups, amino groups, hydroxyl groups, etc.).

One of the distinguishing features of POSS particles is their highly regular cage structure and tunable surface properties. This structure endows POSS particles with excellent thermal and chemical stability and mechanical strength. At the same time, the organic functional groups on its surface can participate in a variety of chemical reactions, which makes POSS particles show great potential for application in material modification, functionalization, and preparation of composite materials. In addition, POSS particles have excellent optical transparency, a low refractive index, and good biocompatibility. These characteristics make them have

Table 1 Comparisons with state-of-the-art materials

Application	MOF-based composites	State-of-the-art materials	Performance comparison
Flame retardancy	ZIF-67@PZS in EP composites [51]	LDH@PZE-Fe in EP composites [52]	Comparable or lower smoke production; higher limiting oxygen index (LOI)
Mechanical properties	P-MOF [53]	Multi-walled carbon nanotubes (MWCNTs) [54]	Competitive strength enhancements with additional multifunctionality
Electrical performance	Mn-MOFs/CNT composite electrode [50]	CNT electrodes in supercapacitors [55]	Comparable specific capacitance and cycling stability
Environmental and cost considerations	Fe_3O_4-FeBTC MOF in water treatment [56]	Activated carbon	Comparable adsorption efficiency at a lower cost

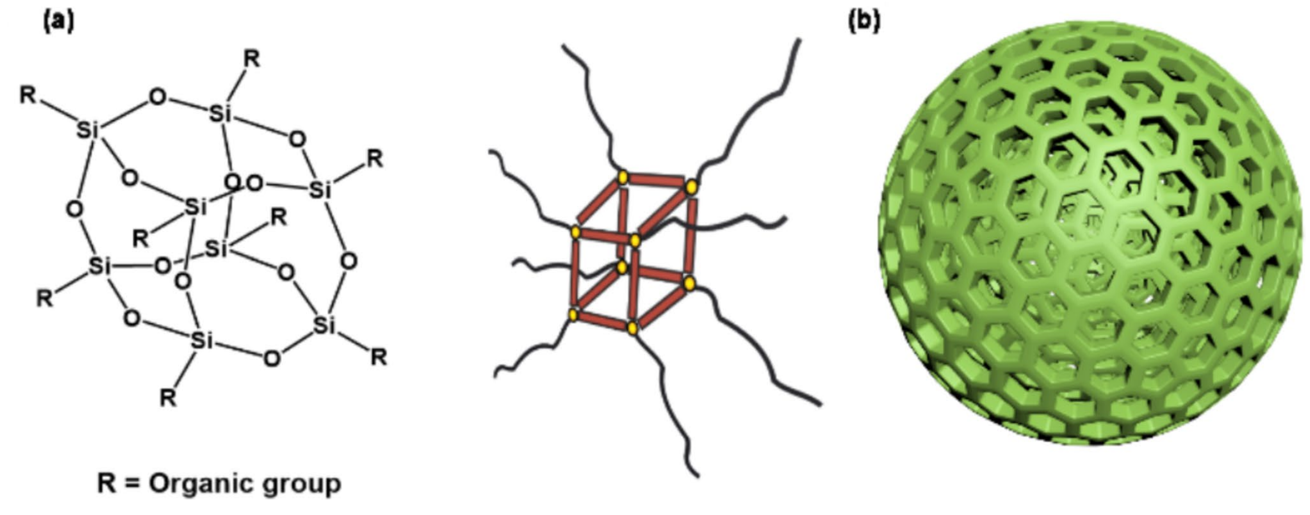

Fig. 1 **a** Schematic structure of POSS. Reproduced with permission from ref. [60]. **b** Schematic structure of SNPs

a wide range of applications in the fields of optical materials, biomedical materials, and advanced functional materials. For example, in optical materials, the introduction of POSS particles can improve the light transmittance and refractive index tunability of the materials; in biomedical materials, their good biocompatibility and degradability make POSS particles ideal for the preparation of bioactive materials and tissue engineering scaffolds.

It is noteworthy that POSS particles can be utilized not only as standalone materials but also as components in composite materials, where they can be combined with other materials, including polymers and inorganic nanoparticles, to create composites with exceptional properties. These composites have a wide range of applications in aerospace, automotive manufacturing, electronic packaging, and other fields. Similarly, the synthesis and preparation methods of POSS particles, surface functionalization strategies, and the design of nanoengineered structures provide a broad platform for their use in the preparation and application of advanced nanomaterials.

2.1.2 SNPs

As shown in Fig. 1b, silica nanoparticles (SNPs) are inorganic nanomaterials composed of the elements silicon and oxygen with a variety of crystals and nanostructures. The pioneering synthesis and study of SNPs were initiated by Werner Stöber in 1968, who developed the sol–gel chemistry method to produce solid, monodisperse SNPs with adjustable diameters ranging from 20 to 2000 nm [59]. Over the past 50 years, many different types of SNPs have been produced with different particle sizes and shapes, as well as a variety of pore structures, giving them multifunctional properties.

SNPs are now widely utilized in a multitude of applications, offering substantial advantages in polymer-based nanocomposites. These include enhanced mechanical properties, improved thermal stability, and flame retardancy. The high specific surface area and excellent compatibility of silica enable it to effectively enhance the overall properties of composites, particularly in terms of mechanical strength and thermal stability. Additionally, silica is environmentally friendly, making it an optimal choice for safety–critical applications such as food packaging and medical devices.

2.2 1D nanomaterials

2.2.1 CNTs

As shown in Fig. 2, CNTs are a significant one-dimensional carbon nanomaterial that have garnered considerable interest from the materials science community due to their distinctive physicochemical properties and extensive range of applications. CNTs exhibit a range of morphologies, including single-walled carbon nanotubes (SWCNTs) and MWCNTs, which impart distinct properties and applications to the nanotubes. SWCNTs possess an atomic-scale wall structure comprising carbon atoms arranged in a hexagonal honeycomb configuration, which enables the formation of stable conjugated π-bonds [61]. This structural feature endows CNTs with exceptional mechanical strength, electron transport properties, and thermal conductivity. These properties have enabled CNTs to demonstrate considerable potential in a number of fields, including electronics, composites, energy storage, and biomedicine. MWCNTs are composite structures comprising multiple layers of nested concentric circular tubes, which exhibit enhanced mechanical stability and a broader range of potential applications [62].

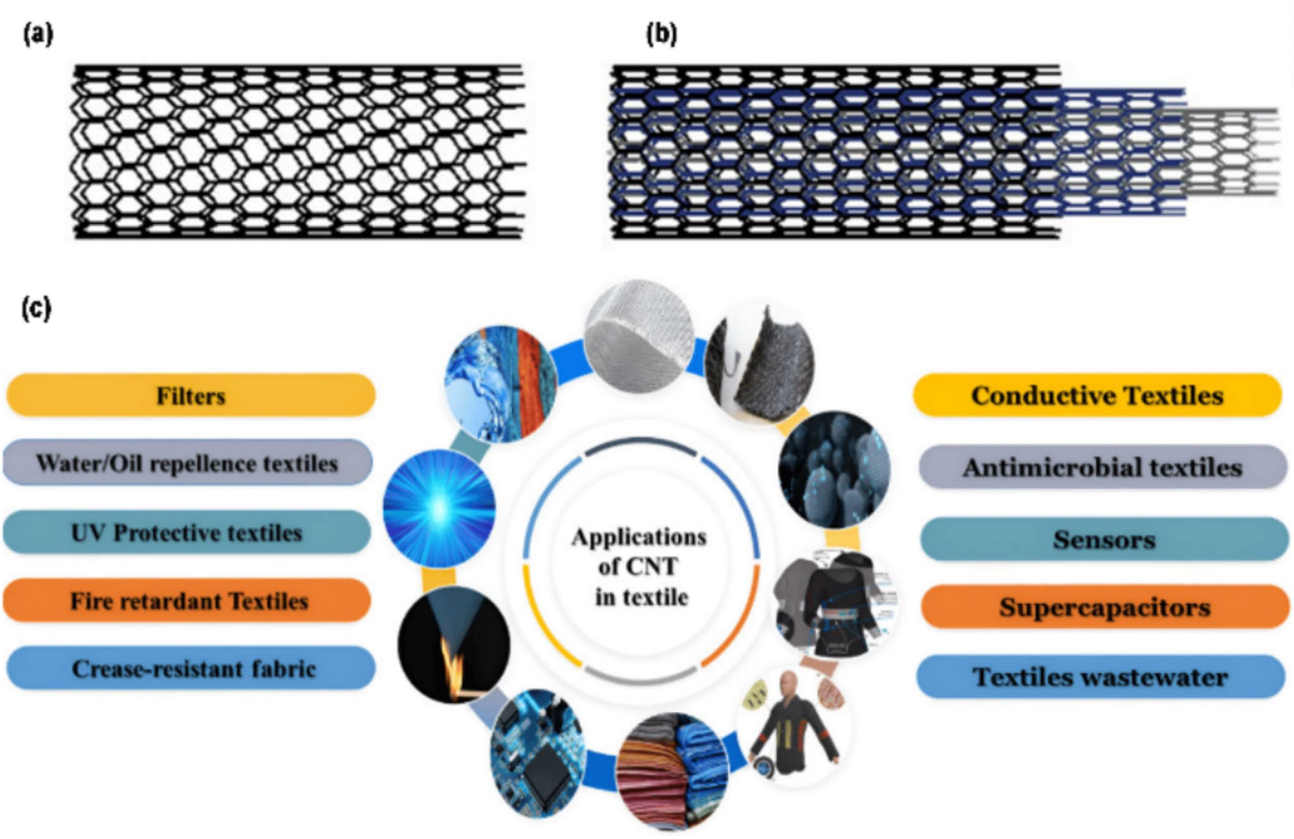

Fig. 2 **a** Schematic structure of SWCNT and **b** MWCNT. **c** Schematic illustration of multifunctional nanotubes in polymer textile applications. Reproduced with permission from ref. [63]

Additionally, CNTs possess favorable electrical properties and distinctive chemical functionalization capabilities, rendering them valuable in domains such as sensors, electrode materials, and electromagnetic shielding. In recent years, with the accelerated advancement of nanotechnology, functionalized CNTs, heteroatom-doped CNTs, and CNT composites have emerged as a prominent area of research in materials science, offering a vast frontier for the development of future advanced materials.

2.3 2D nanomaterials

In recent years, the strategic combination of MOFs with 2D Materials has emerged as an essential focus of research within Materials science. The layered structure of MOFs endows 2D Materials with a high specific surface area and relatively thin thickness, which gives rise to properties such as dramatically increased electron mobility, excellent electrical and thermal conductivity, and very strong mechanical UL 94 strength. At the same time, two-dimensional materials display outstanding optical characteristics, including adjustable band gaps and high light absorption, enabling a multitude of possible uses in areas like optoelectronics and photocatalysis.

2.3.1 LDH

Figure 3a indicates that LDHs represent a noteworthy subset of inorganic materials, garnering substantial attention for their distinctive stratified architecture and impressive physicochemical attributes. Commonly formed by metallic cations and hydroxide ions, these layered compounds allow adjustments to both composition and framework, promoting a wide range of tunable properties. This structural design not only enhances performance but also improves durability, making it suitable for harsh operating conditions. LDH exhibits good ionic conductivity and a high specific surface area, both of which contribute to its significant potential in energy storage applications such as batteries and supercapacitors [64]. In addition, LDH has excellent catalytic properties, especially in photocatalytic and electrocatalytic reactions, which can effectively promote the reaction process. LDH is synthesized by various methods, including hydrothermal, sol–gel, and microwave synthesis [65–67], which can effectively control the morphology and properties of LDH. It is particularly

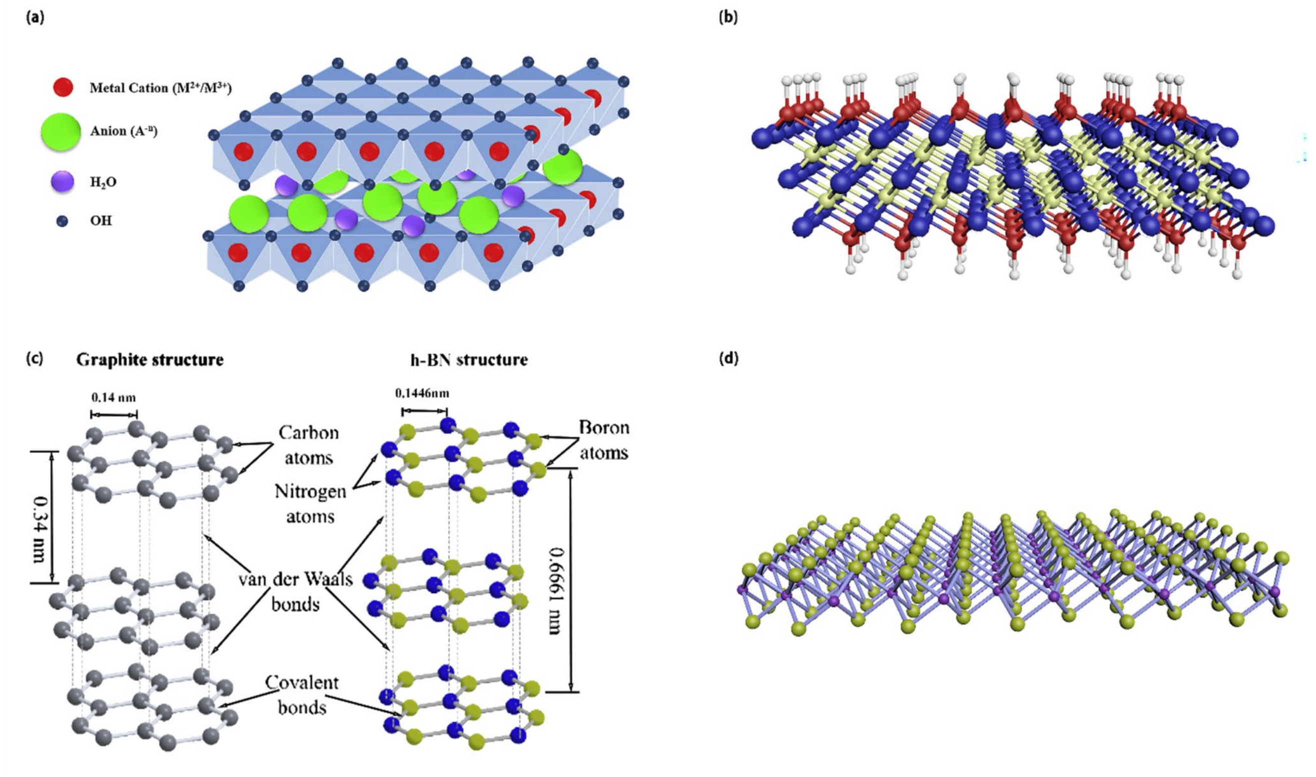

Fig. 3 **a** Schematic illustration of a typical LDH structure. Reproduced with permission from ref. [82]. **b** Schematic illustration of a typical MXene structure. **c** Comparison of graphene and boron carbide structures; reproduced with permission from ref. [83]. **d** Schematic illustration of the structure of MoS_2

noteworthy that the spatial arrangement of MOFs and nanomaterials within the composite plays a critical role in determining the final properties of the material. For example, creating a core–shell structure where MOFs are encapsulated by LDHs can protect the MOFs from environmental degradation while maximizing the conductive pathways [68]. Notably, LDH can be used not only as a stand-alone material, but also with other materials to form LDH films, LDH nanocomposites, and LDH/polymer composites to further enhance its properties. These properties make LDH an important research direction in the development of new functional materials. This multilayer arrangement imparts notable advantages in catalysis, energy storage, and environmental remediation, making LDHs valuable in numerous scientific and technological pursuits [69, 70].

2.3.2 Mxene

As shown in Fig. 3b, MXene is a class of inorganic nanomaterials with a distinctive two-dimensional layered structure. It comprises multiple layers of transition metal carbides or nitrides, with the surface typically modified by terminal groups such as oxygen (–O), hydrogen (–H), and fluorine (–F) [71]. The unique layered framework imparts MXene with superior electrical traits, enhanced conductivity, and distinctive surface chemistry, thereby enabling its diverse applications in energy storage systems, electronic devices, catalysis, and sensing technologies.

The composition and structure of MXene are highly tunable. Their physicochemical properties can be precisely tuned by changing the transition metal species, carbon/nitrogen atom ratio, and surface terminal groups. For example, $Ti_3C_2T_x$ is the most common type of MXene with excellent electrical conductivity and ion transport capability. In energy storage, MXene excels in supercapacitors and battery electrode materials due to its unique interlayer structure and high specific surface area. In catalysis, MXene can be used as efficient electrocatalysts and photocatalysts, showing excellent catalytic performance in reactions such as hydrogen precipitation and oxygen reduction.

In recent years, with the rapid development of nanotechnology, significant progress has been made in the preparation and application of MXene. MXene materials with diverse structures and properties can be obtained through selective etching, chemical functionalization, and interlayer embedding. These materials demonstrate considerable potential for utilization in the domains of electronics, energy, the environment, and biomedicine, offering novel avenues for scientific and technological advancement and industrial growth. Researchers are endeavoring to address the challenges associated with MXene, including stability and scale-up production, with the aim of further expanding its application scope.

2.3.3 Graphene

Graphene is a revolutionary class of two-dimensional carbon nanomaterials. Since its first successful preparation and characterization by the team of Geim and Novoselov at the University of Manchester in 2004 [72], it has attracted much attention from the global scientific community for its unique physicochemical properties and wide range of application potential. The material consists of a hexagonal honeycomb lattice of monolayers of carbon atoms with an ultrathin single-atom layer structure and an extremely unique two-dimensional morphology.

Outstanding electrical properties and mechanical strength are among the distinguishing features of graphene. This is due to its special conjugated π-electron structure and the strong covalent bonding of the carbon atoms [73]. This structure not only provides a fast transport channel for electrons and greatly improves electron mobility, but also gives graphene great potential for applications in electronic devices and conductive materials. In addition, graphene has a wide range of tunable optical properties, as well as excellent thermal conductivity and surface plasmonic effects. Its exceptional characteristics offer substantial promise across multiple domains, encompassing electronics, energy storage, sensor development, composite engineering, and biomedical research.

Moreover, rather than existing purely as an independent material, graphene can also be effectively incorporated into polymer-based nanocomposites, tailored hydrogels, and various graphene-derived structures [74], thereby taking full advantage of its versatile capabilities. Similarly, their functionalization strategies, chemical modifications, and nanoengineered structures provide graphene with an excellent platform for the development of advanced nanomaterials that drive cutting-edge innovations in materials science.

2.3.4 Other 2D materials

The applications of 2D nanohybrids go far beyond this. MoS_2 is characterized by its layered composition, formed by molybdenum and sulfur atoms held together through relatively weak van der Waals interactions (Fig. 3d). This stratified arrangement enables MoS_2 to display distinctive electrical, optical, and mechanical characteristics [75, 76]. As a two-dimensional transition metal sulfide, MoS_2 has an energy band gap of about 1.8 eV in the monolayer state, which provides excellent semiconductor properties [77]. These properties facilitate its deployment in various high-performance electronic devices, optoelectronic systems, and field-effect transistors [78]. In addition, the layered structure of MoS_2 endows it with excellent catalytic properties, especially in hydrogen evolution reactions [79], making it an effective catalyst. Its unique physical properties and wide range of applications provide abundant possibilities for the research and development of MoS_2.

Boron nitride (BN) is an inorganic compound with a layered structure similar to graphite (Fig. 3c). The layers are bound to each other by weak van der Waals forces, which makes them easy to delaminate and gives them excellent lubricity and mechanical strength [37, 80]. In addition to its excellent lubricating properties, BN is widely used as a high-temperature lubricant, insulating material and coating. Due to its excellent electrical insulation and thermal conductivity, BN also shows great potential in electronic devices and thermal management [81]. Especially on the nanoscale, the nanostructures of BN have good optical properties, making them promising for applications in optoelectronic devices, catalyst carriers, and environmental treatment.

2.4 Three-dimensional nanomaterials

2.4.1 MOF-on-MOF hybrids

The structural flexibility of a single MOF or nanomaterial is fundamentally constrained. In contrast to individual MOF materials, MOF-on-MOF composites demonstrate exceptional tunability and possess a multi-layered nanostructure. It is constructed from three-dimensional nano-metal–organic frameworks by precise interfacial growth methods, forming a composite system with a hierarchical structure (Fig. 4a). This structure enables precise tuning between different MOFs, giving the material unique functions and properties.

The composition and structure of MOF-on-MOF are highly tunable. By adjusting the crystallographic parameters, growth direction, and interface modification of the underlying MOF, the growth of the upper MOF can be precisely controlled. For example, Zn-MOF-on-Zr-MOF is a typical representative of a unique multi-layered nanostructure achieved by the epitaxial growth method, exhibiting excellent molecular recognition and selective adsorption properties [84]. Various synthesis approaches have been developed, including ordered and random epitaxial growth methods [85]. Factors influencing interfacial growth include inorganic metals, organic ligands, lattice matching, and nucleation kinetics [86]. A van der Waals integration method has been developed to overcome lattice matching limitations, enabling the creation of highly oriented Cu-TCPP-on-Cu-HHTP thin films with cascading functions. These hybrid architectures demonstrate improved performance in applications such as chemiresistive sensing,

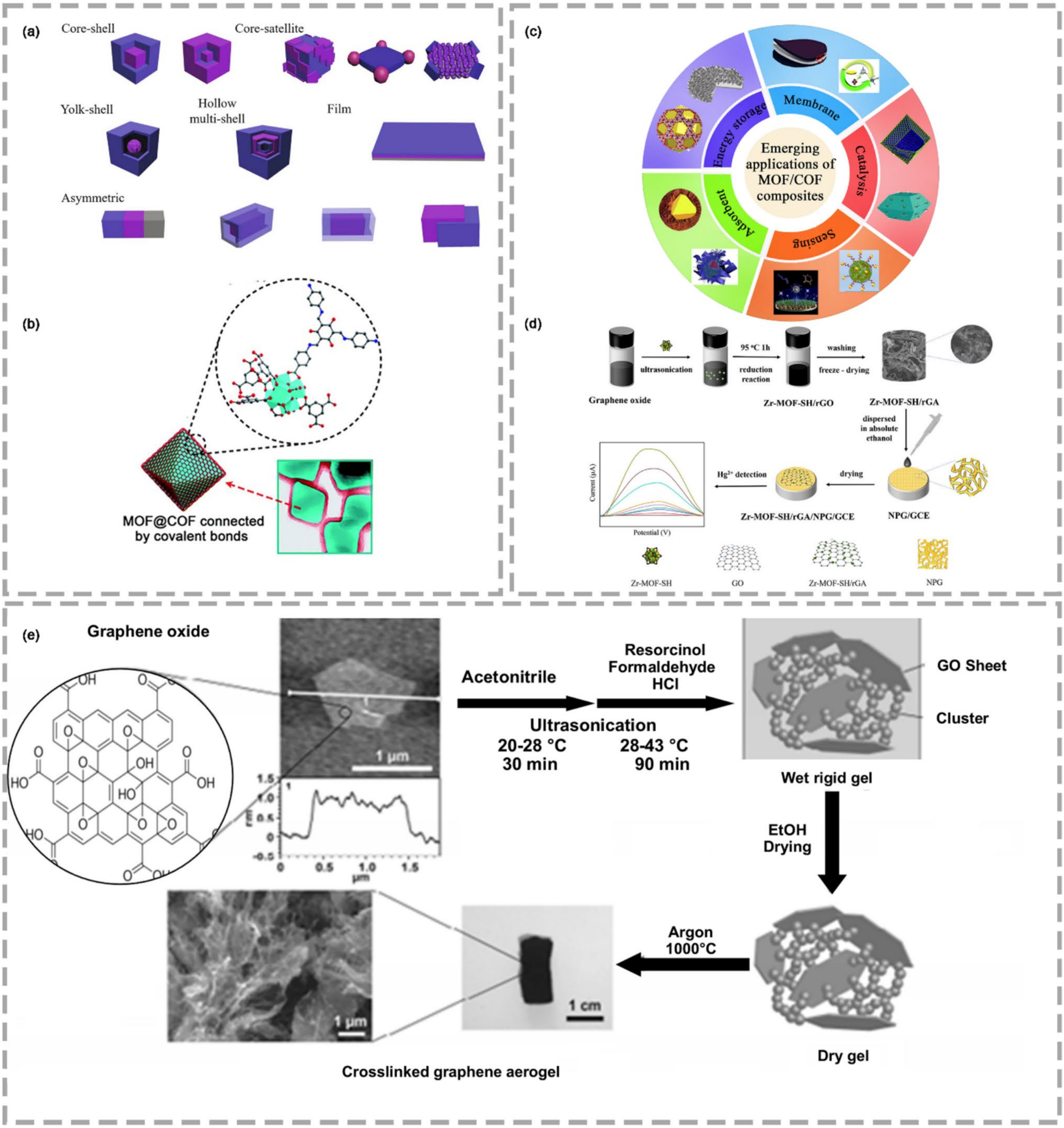

Fig. 4 **a** Schematic illustration of different MOF-on-MOF hybrids. Reproduced with permission from ref. [90]. **b** Schematic illustration of a typical MOF-COF hybrid and **c** its application. Reproduced with permission from ref. [42]. **d** Schematic illustration of the preparation of GA using graphene oxide. Reproduced with permission from ref. [91]. **e** Schematic illustration of crosslinked GA formed by graphene. Reproduced with permission from ref. [89]

showcasing excellent selectivity and responsiveness to specific compounds like benzene [87], and provide a new development path for cutting-edge research in materials science.

2.4.2 MOF-COF hybrids

MOF-COF is a recently developed porous crystalline substance that has garnered significant interest among researchers in Materials science because of its distinctive spatial architecture and adjustable properties. COFs can form a 3D network structure with highly regulated, interconnected pores through precise molecular design, and the precise arrangement of different metal nodes and organic connecting groups endows the material with rich physicochemical properties [41]. The backbone of the 3D COFs is highly symmetric and predictable, and the heteroatoms of nitrogen, oxygen, and sulfur are arranged in the framework in an orderly and alternating manner to form a stable covalent bonding network, which makes the material present an extremely low density, a highly designable internal space, and unique functional groups (Fig. 4b) [88].

MOF-COF hybrid materials showcase exceptional adaptability due to their extraordinarily large specific surface areas, finely tunable pore structures, and distinctive abilities for molecular recognition. These features endow them with significant promise in advanced domains including catalysis, gas storage, separation technologies, sensing applications, and biomedical fields. By adjusting the metal centers and organic linkers, it is possible to fabricate materials tailored for particular functionalities, highlighting their strong potential in crucial sectors like renewable energy, environmental management, and cutting-edge technological innovations. As nanotechnology and supramolecular chemistry continue to advance, research into MOF-COFs is emerging as one of the most vibrant and pioneering areas within materials science (Fig. 4c).

2.5 Graphene oxide aerogel

Graphene oxide aerogel (GA) is an emerging three-dimensional porous material that has received high attention due to its unique physicochemical properties and wide range of application potentials. This material consists of multiple graphene oxide lamellae crosslinked to form a porous network structure (Fig. 4d) with very high specific surface area and good mechanical properties, enabling it to exhibit excellent performance in different fields.

The excellent electrical conductivity and good thermal conductivity of GA is one of its distinctive features, which is attributed to the unique π-π stacking and formation of electron migration channels in its layered structure. This special structure not only provides higher electrical conductivity and thermal conductivity for the movement of ions but also gives GA great potential for applications in electrode materials and thermal management devices [73]. Moreover, GAs exhibit notable porosity and plentiful surface functional moieties, giving rise to remarkable performance in catalysis, gas adsorption, and energy storage applications. Its adjustable pore structure and chemical properties give GA a wide range of applications in clean energy, environmental treatment, and biomedical fields [89]. It is worth mentioning that GA can not only be used as a stand-alone material but can also be successfully combined with other materials, such as metals and polymers, to form composites to further enhance its performance. These properties and applications make GA occupy an important position in modern material science and provide unlimited possibilities for its research in the future.

3 Integration strategy of MOFs with nanomaterials and polymer matrix

3.1 Ectopic growth

Ectopic preparation methods include the integration of individually designed MXene and MOFs using methods such as self-assembly, direct mixing, and electrochemistry. These methods are independent of MOF synthesis conditions and therefore offer a high degree of maneuverability and flexibility.

3.1.1 Self-assembly method

The simplest way to integrate MOFs with nanomaterials is generally to mix them directly and utilize their surface defects or functional groups as MOF growth centers to achieve the preparation of composites. The nanomaterial precursors and raw materials for MOFs are generally mixed first, and then a self-assembly process is performed to provide integration of MOFs with nanomaterials. During the formation of MOF materials, the defects or functional groups on the surface of nanomaterials provide nucleation sites thereby forming MOF crystals. Therefore, during the composite process, there are generally two ways of compositing different kinds of MOF materials and nanomaterials: MOFs embedded in the surface (or inner cavity) and MOFs become inclusions. MOF crystals with relatively large sizes will be formed on the surface of the nanomaterials by embedded nucleation growth, or a certain part of the nanomaterials will be directly half-encapsulated or completely encapsulated during the synthesis process. As shown in Fig. 5a, in the synthesis of ZIF-67@M(OH)(OCH$_3$) utilizing cobalt acetate tetrahydrate and 2-methylimidazole, the incorporation of pretreated M(OH)(OCH$_3$) resulted in the ZIF-67 crystals nucleated and grew on the surface of M(OH)(OCH$_3$), resulting in the formation of a uniform ZIF-67 dodecahedral morphology covered with M(OH)(OCH$_3$) [92]. A unique three-tier structure, UiO66-dopamine (PDA)-Prussian blue analog (PBA), was fabricated by first performing in situ polymerization of PDA onto the UiO-66 surface, which was then followed by a self-assembly process. The growth of a PBA layer was observed, in which the interfacial catalysts of the nickel species exhibited high activity in

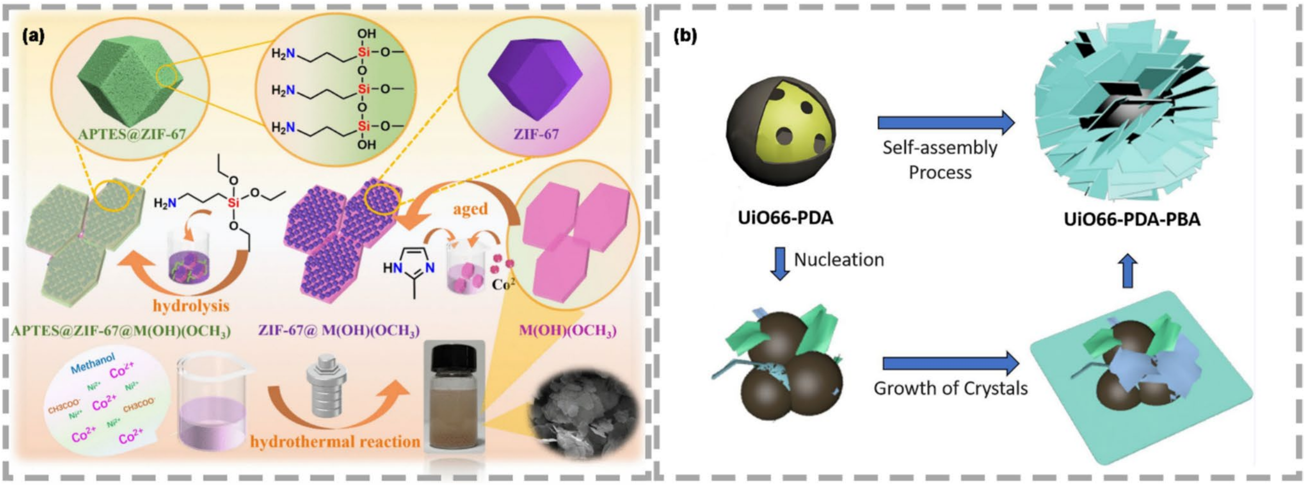

Fig. 5 **a** The schematic illustration of the preparation of the functionally modified M(OH) (OCH_3). Reproduced with permission from ref. [92]. **b** Schematic representation of the synthesis of hierarchical UiO66-PDA-PBA hybrids. Reproduced with permission from ref. [93]

converting the residue into carbon residue with a polycyclic aromatic structure through C–C and C-N coupling reactions [93]. Due to the large crystal size of MOFs and some randomness in the coordination during complexation, the two forms of complexation generally occur simultaneously.

The prepared composites can undergo further carbonization to yield composite functional materials with diverse applications. Conventional high-temperature carbonization under inert gas conditions can yield nanomaterial-loaded MOF-derived materials. Alternatively, MOFs can be utilized as precursors for calcination in air to form uniformly loaded or encapsulated MOFs integrated with nanomaterials. For example, the prepared ZIF-8@CNTs can be calcined in air to obtain composites such as ZnO@MWCNTs with a uniform distribution of ZnO particles [94]. The same methodology can be employed to achieve uniform loading of other metal oxides.

3.1.2 Electrochemical method

The electrochemical preparation process stands out as an efficient approach for integrating MOFs with nanomaterials, offering distinct advantages including mild reaction conditions, simple operation, and precisely controllable parameters [95]. This method can be broadly categorized into three main approaches: direct electrodeposition, sequential multi-step integration, and charge-mediated assembly. Direct electrochemical deposition is the simplest approach, as demonstrated by Chen et al.'s work where Cu-MOF/Au composite films (200–300 nm thickness) were formed on a substrate in just 300 s through current-driven growth [96] (Fig. 6a). The reaction was performed at room temperature with a constant potential of -0.2 V (± 0.01 V) applied for 300 s in 2.0 mM $HAuCl_4$/PBS solution, using GCE electrodes polished to < 5 nm surface roughness with 0.05-µm alumina. Sequential multi-step integration enables more complex architectures, exemplified by the RGO-PDB-MMOF composite synthesis, which involves initial GO reduction on gold electrode to form a conductive film, electropolymerization of promethazine to create spongy polymers (PDB), and final electrodeposition of Ni-Co-BTC bimetallic MOFs (Fig. 6c) [97]. The electropolymerization of PDB was performed under ambient temperature through imipramine redox activation, while the Bi-MMOF electrodeposition occurred at 1.0 mA/cm2 for 30 min on RGO-PDB substrates. The charge-mediated assembly utilizes electrostatic interactions and surface charge modification, including metal cation-functionalized MOFs combining with negatively charged nanomaterials (Fig. 6b) [98], direct binding of compatible MOFs with nanomaterials (e.g., Co2Ni-MOFs with MXene) (Fig. 6d) [99], and surface modification-assisted assembly (e.g., APP-PEI@MXene@ZIF-67 through electrostatic self-assembly) (Fig. 6e) [100]. The electrostatic self-assembly process was conducted under ambient temperature with a monolayer adsorption Duration of 5 min at neutral pH. The versatility of electrochemical methods is further demonstrated in hybrid systems like MXene-based composites, where hydrothermal pre-treatment can be combined with electrochemical deposition to achieve precise control over the final structure, enabling optimization of both the interface quality and the overall composite performance.

3.2 In situ growth techniques

The in situ technique entails incorporating MOF precursors with functionalized nanomaterials that have been dispersed in appropriate solvents. During this process, metal ions begin coordinating with polar groups present on the surface,

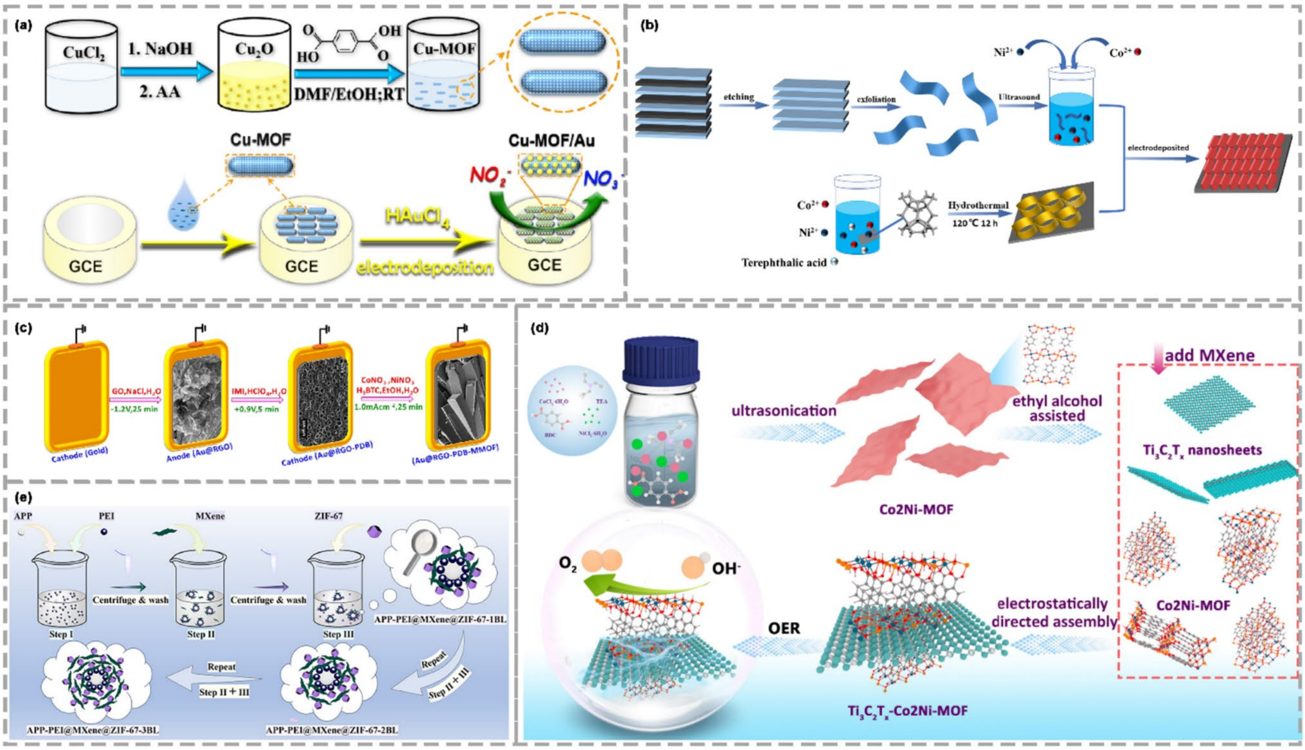

Fig. 6 **a** Schematic of the preparation of Cu-MOF/Au hybrids. Reproduced with permission from ref. [96]. **b** Schematic of the preparation of MXene-Ni-Co@NiCo-MOF/NF. Reproduced with permission from ref. [98]. **c** Schematic of the RGO-PDB-MMOF synthesis process schematic reproduced with permission from ref. [97]. **d** Preparation of Co_2Ni-MOF@MXene complex reproduced with permission from ref. [99]. **e** Preparation of APP-PEI@MXene@ZIF-67 reproduced with permission from ref. [100]

subsequently interacting with organic linkers to facilitate MOF crystal growth. This synthetic approach closely mirrors traditional MOF preparation protocols, with the key distinction being the introduction of nanomaterials into the reaction medium [101]. In situ growth typically involves two key steps: chemically introducing active sites on the surface of the matrix material; then, using these sites to facilitate in situ growth and precise construction of the MOF. To optimize the metal-surface interactions, the procedure typically involves suspending nanomaterials in a metal salt solution for a predetermined period before introducing the organic ligand, thereby promoting efficient metal ion diffusion to the nanotube surface. The successful formation of these nanocomposites can be verified through spectroscopic analysis, where the emergence of distinctive peaks in the hybrid spectra indicates successful MOF integration. By employing the in situ synthesis approach, MOFs are integrated directly into the nanomaterials, creating composites that are both denser and more durable (Fig. 7d). This approach can significantly improve the interfacial interactions, thereby enhancing the overall performance of the composites. For example, Ma et al. [102] employed the interaction between the surface functional groups of attapulgite (ATP) and ZIF-67 organic ligands to modulate the surface properties of ATP and enhance its surface activity. The hybrid materials, designated as ATP@ZIF-67 (Fig. 7a), were prepared by introducing cobalt ions to enable in situ growth of ZIF-67 on the ATP surface. The interfacial bonding between ZIF-67 and ATP was found to be optimal, which effectively prevented the agglomeration of ZIF-67 nanoparticles and markedly enhanced the dispersion and interfacial interactions of the materials. Similarly, Guo et al. [103] developed CoAl-LDH@ZIF-67 hybrids by growing ZIF-67 microcrystals on CoAl-LDH nanoplates (Fig. 7b), which provided abundant nucleation sites. These hybrids were later incorporated into epoxy resins to enhance their thermal stability in high-temperature environments. Graphite oxide nanosheets (GONRs) were also used to create nucleation sites for HKUST-1 growth (Fig. 7c). Through electrodeposition, HKUST-1 nanocrystals were grown on GONRs, forming HKUST-1/GONRs/GCE hybrids. This addressed the inherent electrical conductivity limitations of the HKUST-1 framework [104].

In situ growth avoids MOF particle agglomeration and enhances material stability and dispersion. By synthesizing MOFs directly within the nanospace of matrix materials, precise atomic and molecular bonding is achieved. Additionally, this technique allows for precise control of composite structures by regulating parameters such as precursor

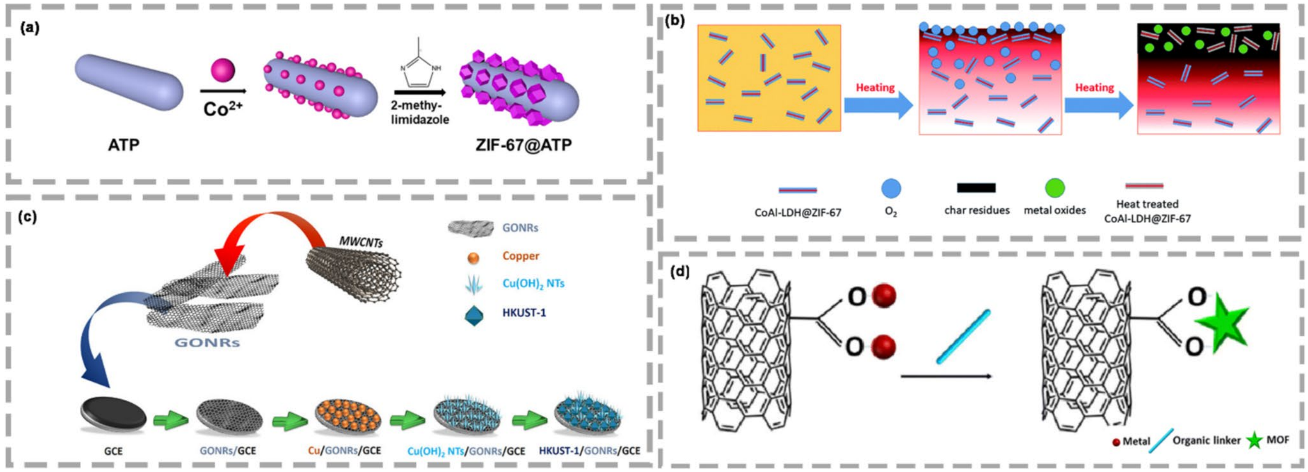

Fig. 7 **a** Schematic of the preparation of ZIF-67@ATP. Reproduced with permission from ref. [102]. **b** CoAl-LDH@ZIF-67 hybrid materials designed to improve the flame-retardant performance of epoxy resins. Reproduced with permission from ref. [103]. **c** Schematic illustration of the fabrication of HKUST-1/GONRs/GCE. Reproduced with permission from ref. [104]. **d** Schematic illustration of the in situ growth method. Reproduced with permission from ref. [101]

concentration, reaction temperature, and potential of hydrogen (pH). This makes in situ growth a powerful tool for preparing high-performance MOF-based composites.

4 The integration of MOFs and nanomaterials in properties and applications of polymer matrix

Bibliometrics is employed in this study as a robust quantitative approach to assess and interpret the landscape of published research concerning the integration of MOFs with nanomaterials in polymeric materials. By systematically counting and analyzing relevant literature, bibliometrics provides valuable insights into production metrics, geographical distribution, and thematic trends within the field [32]. The research harnesses visual analysis software to delve into a comprehensive dataset comprising 992 validated articles sourced from 347 reputable journals. This methodological approach ensures that the analysis is both thorough and representative, eliminating duplicates and applying stringent filtering criteria to maintain the integrity of the data.

Key indicators such as the number of publications and citations per year are critical in gauging the vibrancy and trajectory of research activity. The study's findings, illustrated in Fig. 8a, demonstrate a consistent upward trend in publications related to polymers and MOFs integrated with nanomaterials from January 2019 to December 2024. This trend is further corroborated by the increasing number of citations, which reached 57,852, with the vast majority being external citations, underscoring the field's growing influence and recognition within the scientific community. Geographical analysis reveals that the People's Republic of China is at the forefront of this research area, contributing 45% of all international publications (Fig. 8b). This dominance is followed by India and the USA, accounting for approximately 14% and 10% of publications, respectively. China's leadership is not only reflected in its volume of publications but also in its collaborative efforts with countries like India, the USA, Iran, and Spain. Such international collaborations are pivotal in fostering innovation, knowledge exchange, and the advancement of complex interdisciplinary research.

The study utilizes keyword co-occurrence network mapping to visualize and interpret core themes and emerging trends within the field (Fig. 9a). In this visualization, keywords are displayed as circular nodes, with their size reflecting frequency of occurrence and connections indicating co-occurrence relationships. This analysis reveals that nanoparticles, nanotubes, and thin films are central to current research, underscoring their significance in advancing polymeric materials. The frontier knowledge map (Fig. 9b) highlights that these materials, alongside sensitive detection, drug delivery, and biomedical applications, are among the most prominent research areas. Moreover, coordination polymer mixed matrix membranes are emerging as a focal point of investigation. Core materials such as nanoparticles, nanotubes, and thin films are crucial for developing advanced polymeric materials. Their integration with MOFs offers promising possibilities, particularly in sensitive detection, drug delivery, and biomedical applications. Recent research is emphasizing coordinated polymer hybrid matrix films, showcasing the importance of MOFs and nanomaterials in composites. Additionally, innovative synthesis methods, including room-temperature and ultrasonic synthesis, are gaining attention as researchers seek more efficient and environmentally friendly techniques. The integration of

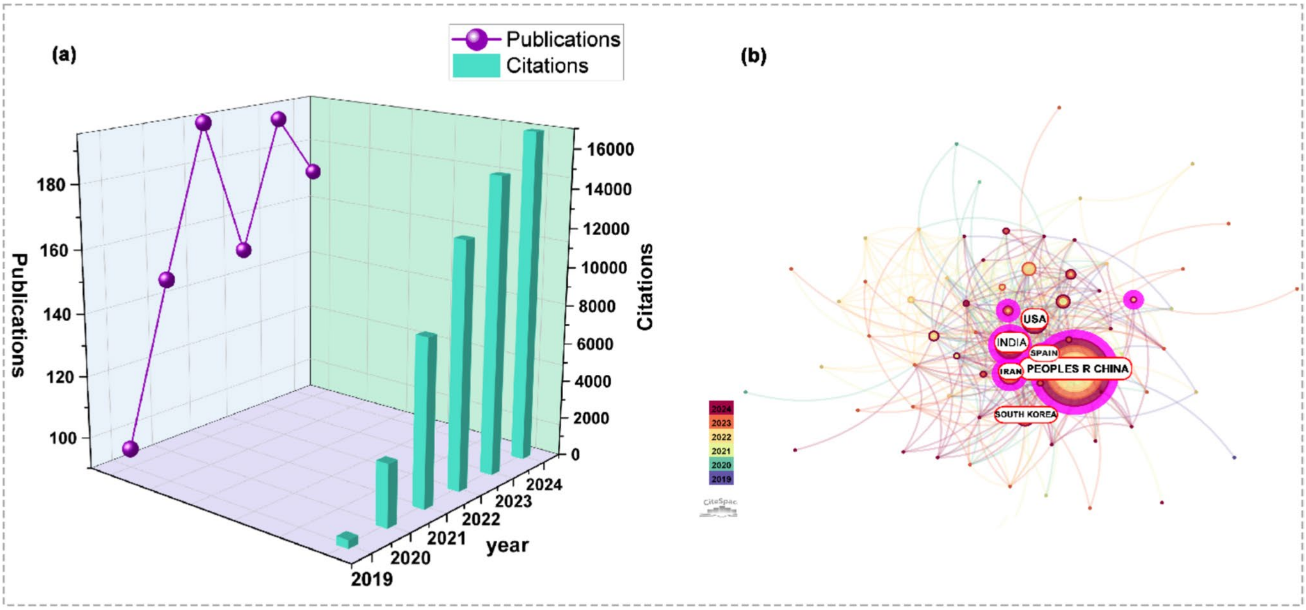

Fig. 8 **a** The dynamics of literature production and citations. **b** Network visualization of co-authorship country

nanomaterials across various dimensions (0D, 1D, 2D, and 3D) is also emerging as a new research direction, broadening applications, especially in biomedicine and water treatment. In summary, this field is experiencing rapid advancement, both in research hotspots and in application prospects.

4.1 Flame retardancy

Flame retardancy of polymer-based nanocomposites is an important area of research, and MOF-based nanocomposites have been incorporated into a variety of polymer matrices including polypropylene (PP) [105–109], polystyrene (PS) [110–113], polyethylene (PE) [114–116], epoxy resins (EP) [103, 117–119], polyurethane (PU) [120–123], and TPU [124]. These materials play a fire-safety and fire-prevention application. These materials play a vital role in fire safety and fire prevention applications. Since conventional polymers are flammable at high temperatures, enhancing their flame retardancy by adding various flame retardants has become a common treatment [51, 125]. The design and preparation of nanocomposites, especially the application of MOF and other nanomaterials, have significantly improved the flame retardancy of polymers by reducing the flame propagation rate and heat release.

Figure 10 presents a comparative analysis of the flame-retardant efficacy of ZIF@Arg-Co-PA, Co_3O_4@OZC, DE@ZIF@ILS, APP@SiO_2@UiO-66-NH_2(Zr), IRMOF-3-P, and ZIF-oV in polymer matrix. Researchers establish the optimal formulation through experimental trials that focus on assessing the flame-retardant characteristics of MOF-based nanocomposites in polymer matrix. By systematically adjusting the proportions and evaluating data from LOI and cone calorimetry tests—such as heat release rate (HRR), total heat release (THR), total smoke production (TSP), and smoke production rate (SPR)—researchers can identify the blend that achieves the most effective balance between flame retardancy and mechanical strength.

Among the tested materials, APP@SiO_2@UiO-66-NH_2(Zr) demonstrated favorable outcomes in reducing THR and TSP, although its enhancement of LOI was relatively modest. In contrast, IRMOF-3-P exhibited the most pronounced improvement in LOI, reaching 32%, indicating its superior effectiveness in enhancing the oxygen index. ZIF@Arg-Co-PA, Co_3O_4@OZC, and DE@ZIF@ILS displayed consistent performance across all metrics. This evaluation of flame-retardant performance highlights the distinct advantages of different MOF-based nanocomposites, with some excelling in reducing heat and smoke release, while others focus on improving the oxygen index. This underscores the importance of selecting appropriate MOFs and nanomaterials based on the specific requirements of the polymer matrix and application context. Table 2, Table 3, and Table 4 provide additional detailed information regarding the integration of MOFs and nanomaterials to enhance the flame retardancy of three polymers: EP, TPU, and PUA.

Significant progress has been made in multiple studies exploring the influence of MOF-based nanocomposites on the properties of polymer matrices. For instance, Xue et al. synthesized ZIF-oV nanorods based on Bio-based vanillin, significantly enhancing the flame retardancy and mechanical properties of epoxy resins. The introduction of ZIF-oV increased the LOI of EP from 22.3 to 30.8%, achieving a

Fig. 9 **a** Network visualization of keyword co-occurrence. **b** Frontier knowledge Map from January 2019 to December 2024

vertical combustion test (UL-94) V0 rating [127]. Another study synthesized a P-ZCD hybrid flame retardant based on β-cyclodextrin and ZIF-67, which demonstrated excellent flame retardant effectiveness in epoxy resin, with the LOI value increasing from 22.1 to 25.1% [128]. Additionally, research has prepared the APHZ flame retardant by grafting phosphorus, nitrogen, and silicon onto ZIF-8, which significantly improves the flame retardant performance in epoxy resin, with the LOI value increasing from 23.5 to 30.7% [129]. At the same time, research on the absorption of phosphonate (DMMP) by ZIF-8 has also demonstrated its potential in enhancing the flame-retardant properties of epoxy resin, with the LOI value increasing by 19.8% [3]. Moreover, PANI@Co-P, as a new type of flame retardant, exhibits excellent performance in PUA, significantly enhancing both flame retardancy and impact strength. By judiciously designing and selecting MOF materials, the flame retardancy and mechanical properties of polymer matrices can be significantly improved, providing new insights for developing high-performance polymers.

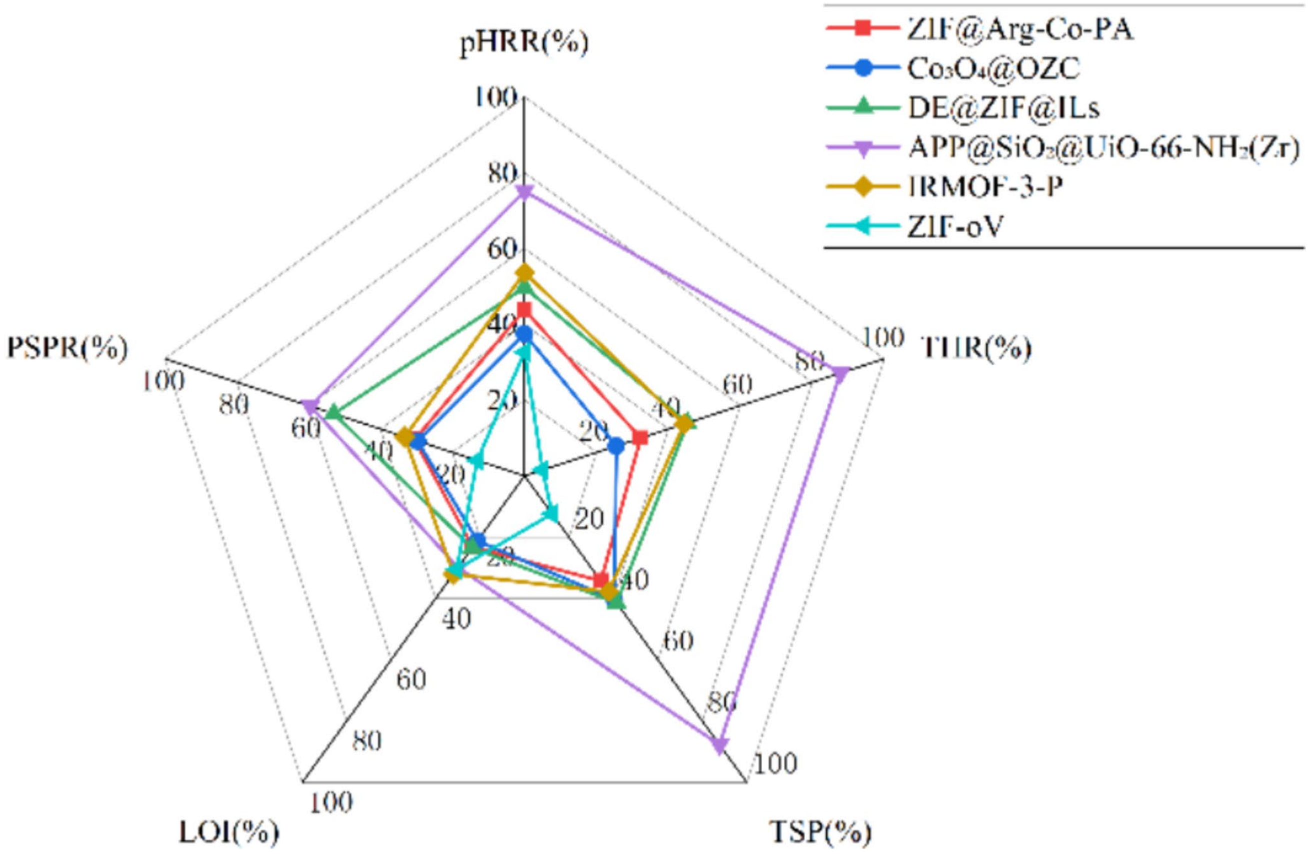

Fig. 10 ZIF@Arg-Co-PA, Co_3O_4@OZC, DE@ZIF@ILS, APP@SiO_2@UiO-66-NH_2(Zr), IRMOF-3-P, and ZIF-oV hybrids were compared with their initial materials in terms of percentage decrease in pHRR, THR, TSP, and PSPR, and percentage enhancement in LOI, respectively (pHRR, peak heat release rate; THR, total heat release; TSP, total smoking production; LOI, limiting oxygen index; PSPR, peak smoke production rate)

Table 2 Combustion behavior of MOF-based flame retardants in EP composites in recent studies

Sample	Loading (wt%)	Main flame retardant results	References
G@Cu-MOF	6	55%, 14%, 59%, and 55% reduction in pHRR, THR, CO production, and CO_2 production	[36]
IRMOF-3-P	3I-P + 6H	Reductions of 53.6% in pHRR, 44.4% in THR, and 56.68% in CO_2 emissions were achieved; the material obtained a UL-94 V-0 certification and demonstrated an LOI value of 32.0%	[126]
ZIF-oV	7	The pHRR decreased by 32.6%, and the THR was reduced by 7.0%. The material achieved a UL-94 V-0 classification and exhibited an LOI of 29.1%	[127]
ZIF-67@PZS	2	34.0%, 30.0%, and 40.5% reduction in pHRR, THR, and TSP	[51]
P-ZCD	2	The pHRR decreased by 54.8%, while the TSP saw a 46.9% decline	[128]
APHZ	3	23.3%, 14.0%, and 21.1% reduction in av-HRR, TSP, and CO production; char residue climbed by 60.6%; a UL-94 V-0 classification was successfully achieved, and the LOI reached 30.7%	[129]
ZIF-8@DMMP	20	46.0%, 19.15%, and 23.0% reduction in pHRR, THR, and TSP; 19.8% of LOI; passed UL-94 V-1 rating	[3]
APP@UiO	10	61.34% and 37.5% reduction in pHRR and the peak smoke production rate (PSPR); 31.2% of LOI	[130]
APTES@ZIF-67@M(OH)(OCH_3)	3	20.0% reduction in pHRR; passed UL-94 V-1 rating; 27.6% of LOI	[92]
MPOFs-P	2	46.6% and 25.2% reduction in pHRR and in TSP; passed UL-94 V-0 rating; 27.0% of LOI	[131]

Table 3 Combustion behavior of MOF-based flame retardants in TPU composites in recent studies

Sample	Loading (wt%)	Main flame retardant results	References
APP-PEI@MXene@ZIF-67-2BL	20	72.75%, 87.25%, 59.58%, and 85.97% reduction in pHRR, THR, PSPR, and TSP	[100]
APP@MOFs	20	75.76%, 86.19%, and 69.74% reduction in pHRR, THR, and SPR; 32.3% increase in char residue	[132]
ZIF-67 H	2	45.4% and 50.2% reduction in pHRR and TSP	[133]
ZIF-8@PA@NH_2 -HBPS	2	A reduction of 35.2%, 25.2%, and 65.5% was observed in pHRR, THR, and TSP, respectively	[134]
APP@SiO_2@UiO-66-NH_2(Zr)	20	THR and TSP experienced decreases of 87.8% and 87.7%, respectively, while LOI was reduced by 29.9%	[135]

Table 4 Combustion behavior of MOF-based flame retardants in PUA composites in recent studies

Sample	Loading (wt%)	Main flame retardant results	References
ZIF@Arg – Co – PA	5	A reduction of 43.8%, 32.3%, and 34.3% was observed in pHRR, THR, and TSP, respectively, while the LOI reached 23.2%	[136]
Co_3O_4@OZC	2	A decrease of 37.5%, 25.5%, and 40.4% was observed in pHRR, THR, and TSP, respectively, along with an LOI value of 21.2%	[137]
d-LDH@ZIF	3	A reduction of 28.8%, 8.3%, and 8.9% was observed in pHRR, THR, and TSP, respectively, achieving a UL-94 V-0 rating	[138]
FePP@MoS_2@Ni-MOF	3	39.76%, 29.33%, 17.86%, and 21.30% reduction in pHRR, THR, PSPR, and TSP	[139]
DE@ZIF@ILs	5	A reduction of 49.7%, 45.3%, 53.0%, and 41.4% was observed in pHRR, THR, PSPR, and TSP, respectively, alongside a 30.7% enhancement in char residue	[140]
2D RP@ZIF	5	A decrease of 48.7%, 10.0%, 20.4%, and 22.2% was observed in pHRR, THR, PSPR, and TSP, respectively, alongside a 31.0% rise in char residue	[141]
PANI@Co-P	2	54.9% and 59.9% reduction in pHRR and PSPR; 70.3% increase in char residue	[142]

The flame-retardant properties of MOF-based nanocomposites vary significantly depending on the specific MOFs used and their integration with nanomaterials. For instance, ZIF-67, when integrated with POSS and phosphorus-containing compounds, forms a highly effective flame retardant system in epoxy resins, enhancing both LOI and peak heat release rate (pHRR) [131]. In epoxy composites containing 2 wt% MPOFs-P, the LOI increases to 27.0% (UL-94 V-0 rating), and pHRR decreases by 46.6%, attributed to co-catalyzed char formation and P/Si/Co multi-elemental effects. In contrast, Ni-MOF, when combined with FePP and MoS2, shows improved thermal stability and flame retardancy in PUA composites [139]. These conclusions are supported by comprehensive performance data demonstrating measurable improvements in key metrics like LOI, THR, and TSP.

The success of these materials can be traced to their fundamental working mechanisms. MOF-based nanocomposites create an integrated defense system within the polymer matrix, addressing multiple aspects of fire protection: they form protective barriers that slow flame spread [128, 143], reduce heat release during combustion [144–146], and minimize smoke production [147, 148]. This multi-modal protection strategy explains why different MOF-based nanocomposites, such as IRMOF-3-P and APP@SiO_2@UiO-66-NH_2(Zr), can excel in different performance aspects while contributing to overall fire safety. The versatility of MOF-based nanocomposite solutions is particularly noteworthy, as evidenced by their successful integration into diverse polymer systems ranging from common thermoplastics like PP and PS to more specialized materials like EP and polyurethanes. This broad applicability stems from MOFs' adaptable chemistry and their ability to form stable, well-dispersed nanocomposites within different polymer matrix. The development of these materials represents a strategic response to the inherent flammability challenges of conventional polymers, offering a sophisticated solution that addresses both immediate fire safety needs and long-term material performance requirements. This approach has effectively bridged the gap between material functionality and safety requirements in modern polymer applications.

4.2 Mechanical properties

The integration of MOFs with nanomaterials as a novel additive can markedly enhance the mechanical attributes of polymers through meticulous design and surface modification. Diverse MOF-based nanocomposites exhibit distinctive nanoscale, high porosity, and optimal nano-material interfaces, interacting with nanomaterials through diverse interfacial engineering mechanisms. This not only markedly elevates the comprehensive performance of polymers but also paves the way for the design of high-performance composites.

To significantly enhance the mechanical properties of glass fiber-polyamide 6 (PA6), Unnikrishnan et al. [149] incorporated Al-MOF, graphene, and glass fiber (GF) composite into the PA6 Matrix. The incorporation of conventional flame retardants into polymers often leads to a reduction in mechanical properties. In this study, the incorporation of a 10% blend of fillers (comprising 5% graphene nanoplatelets and 5% aluminum-based MOF) and 20% glass fiber led to a significant enhancement in the tensile strength and Young's modulus of the composites, exhibiting an increase of 94% and 39%, respectively (Fig. 11a, b). Similarly, the flexural strength and modulus increased 92.3% and 175.7%, respectively. This notable enhancement in performance can be attributed to the formation of hydrogen bonds between the carboxyl functional groups of Al-MOF and the molecular chains of PA6, which facilitates improved interfacial interactions. Additionally, Al-MOF is a "bridge" between the GNPs and PA6, enhancing the compatibility between the filler and the matrix, thereby creating a synergistic enhancement effect.

Conventional additives typically lead to a deterioration in mechanical properties due to weakened interfacial adhesion and a reduction in molecular weight. In the study of EP/ZHS@NCH composites [150], the flexural strength of pure EP was found to be 87.5 ± 4.3 MPa. This value decreased to 70.0 ± 2.7 and 73.2 ± 4.1 MPa with the addition of one-component ZHS and NCH additives, respectively. However, the addition of the ZHS@NCH composite additive resulted in only a slight reduction in flexural strength to 81.3 ± 3.8 MPa. Similarly, the additives affected the tensile strength of the materials. However, as shown in Fig. 11d, ZHS@NCH demonstrated superior performance relative to the other additives, exhibiting a tensile strength of 48.6 ± 2.2 MPa. This can be attributed to its distinctive multicore shell

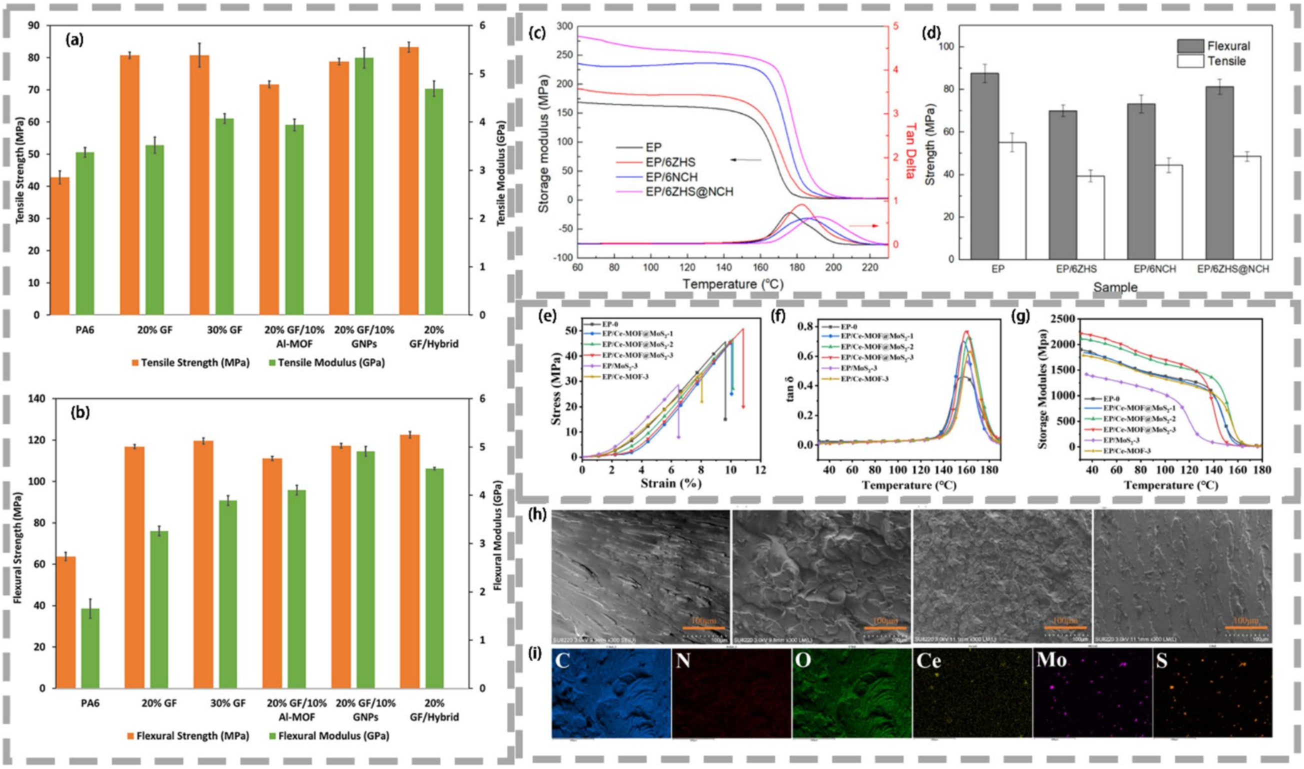

Fig. 11 Tensile (**a**); and flexural (**b**) properties of reinforced composites. Reproduced with permission from ref. [149]. **c** Storage modulus and tan δ curves and **d** flexural and tensile strength of EP and its nanocomposites. Reproduced with permission from ref. [150]. **e** Stress–strain curves of EP and its nanocomposites. **f** Tan δ and **g** storage modulus curves of DMA test from EP/Ce-MOF@MoS_2 nanocomposites. **h** Cross-sectional SEM picture of EP-0, EP/Ce-MOF@MoS_2−3, EP/MoS_2−3, and EP/Ce-MOF-3. Elemental mapping images for **i** EP/Ce-MOF@MoS_2−3. Reproduced with permission from ref. [151]

layer nanostructure and robust interaction with the polymers. Dynamic mechanical analysis (DMA) demonstrated that the energy storage modulus of pure EP was 168 MPa at the initial temperature, which was increased to 281 MPa with the addition of ZHS@NCH. Furthermore, the glass transition temperatures (T_g) of the composites exhibited an increase with the addition of the flame retardants, with EP/6ZHS@NCH exhibiting the highest T_g values. This change can be attributed to the barrier effect of the nanofillers, which impede the movement of molecular chains within the matrix. The width of the tan δ peak is indicative of the relaxation phenomenon exhibited by molecular chains (Fig. 11c). Due to the robust interfacial interactions between ZHS@NCH and the polymers, which restrict the mobility of neighboring epoxy chains, the molecular chains display disparate relaxation behaviors, resulting in the broadening of the tan δ peaks.

Yu et al. [151] prepared a layered Ce-MOF@MoS_2 hybrid structure with the objective of enhancing the thermal management capability of epoxy resin (EP). The hybrid structure has been demonstrated to significantly enhance the mechanical properties of the EP. At low contents of Ce-MOF@MoS_2 (1% and 2%), the composite Materials demonstrate exceptional Ductility, with most tests indicating an elongation rate exceeding 1500%. As the content of Ce-MOF@MoS_2 increases to 3%, although there is a slight decrease in elongation, it still retains good performance. The typical fracture elongation rate of the 3% Ce-MOF@MoS_2/EP composites is 146%, with a toughness of 16.7 J/cm3, effectively able to absorb energy per unit volume (Fig. 11e). The yield strength of the 3% MOF composite ranged from 6.8 to 9.5 MPa, indicating that the EP composite can withstand significant stress without deformation (Fig. 11e, g).

The mechanism of MOF-based nanocomposites to improve the mechanical properties of polymers is mainly reflected in two aspects: interfacial engineering and microstructure modulation. Firstly, the interaction between MOF-based nanocomposites and polymer can be enhanced through surface functionalization to improve the interfacial bonding strength; secondly, the unique morphology and size of MOF-based nanocomposites can effectively hinder dislocation motion and crack extension, thus improving the strength and toughness of the materials. Different types of MOF-based nanocomposites can achieve precise regulation of the mechanical properties of polymers by adjusting the surface modification and addition amount.

4.3 Electrical performance

The synergistic interaction of polymer matrix MOFs with nanomaterials offers an innovative way to improve electrical performance. Conventional MOFs typically exhibit very low electrical conductivity due to their crystalline structure, in which the metal nodes and organic linkers lack continuous conduction pathways. However, when MOFs are integrated with conductive materials, such as CNTs, their electrical conductivity can be significantly enhanced. For example, in Mn-MOFs/CNT composite materials [50], the CNTs provide an additional conductive network, promoting charge transport and effectively resolving the issue of low electrical conductivity in conventional MOFs. As shown in Fig. 12a–l, the composite structure of Mn-MOFs with

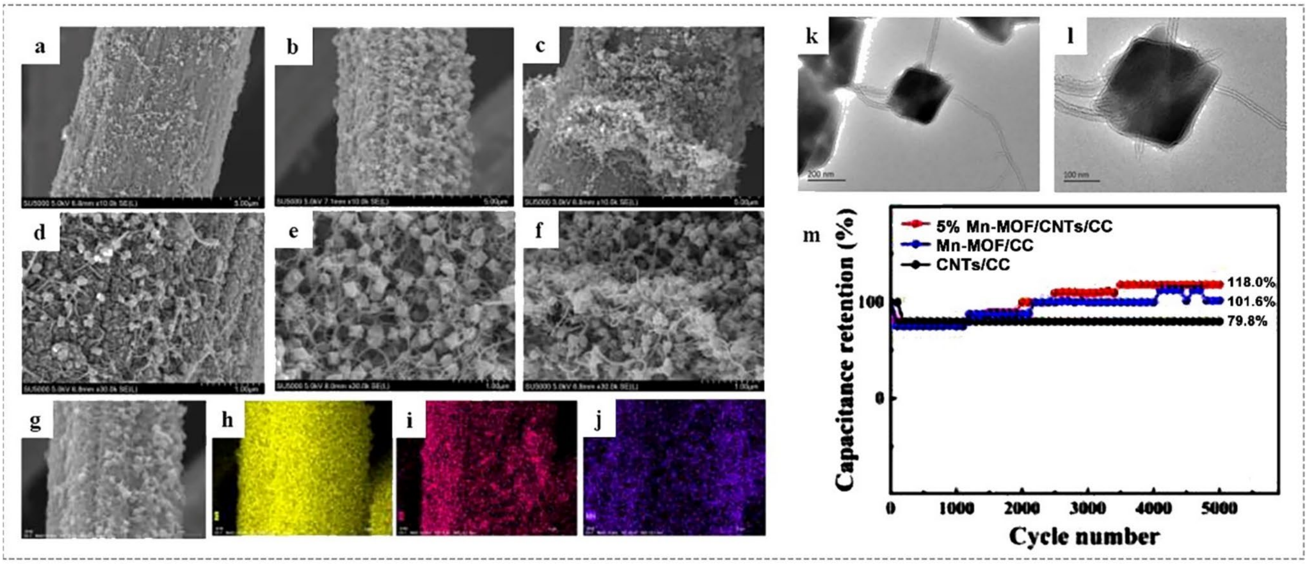

Fig. 12 **a**–**j** MOF/CNT morphology with different CNT doping ratios; **k**, **l** TEM images of CNT-penetrated and bonded MOFs; **m** long-term cycling stability curves. Reproduced with permission from ref. [104]

CNTs was grown directly on carbon cloth (CC) by a one-step hydrothermal method. The carboxyl groups of CNTs provide uniform nucleation sites to support the growth of Mn-MOFs. By growing CNTs on the surface of MOFs, a three-dimensional conductive network is formed. This structure not only improves the electrical conductivity of MOFs but also enhances the overall performance of the composite material. Finally, the Mn-MOFs/CNTs/CC electrode exhibited a specific capacitance of 385.5 mF·cm¯2 and excellent cycling stability in electrochemical tests (Fig. 12m). This composite shows good electrical performance in supercapacitor applications and is particularly suitable for energy storage devices that require high electrical conductivity and good electrochemical performance.

Composite electrode materials based on NiCo-BTC MOFs/N-GONRs/GCE were prepared by Jalal et al. and showed excellent improvement in electrochemical performance [104]. The peak current of the prepared Material was increased by 1.0 mg mL^{-1} N-GONRs, or about 11.5-fold, to 46.6 μA compared to that of the bare GCE (4.0 μA). The unsaturated active sites of the N-GONRs can be attached to the electrode surface through synergistic interactions with the NiCo-BTC MOFs, resulting in the formation of highly conductive three-dimensional network structures, which enhance the electrochemical activity of the electrodes, reduce the charge transport resistance, and improve the electrocatalytic performance. This hypothesis was supported by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). EIS testing indicates that the double-layer capacitance of HKUST-1/GONRs/GCE is 1.4 times and 1.3 times that of GONRs/GCE and HKUST-1/GCE, respectively. Through cyclic voltammetry test, it was shown that the multisite bonding network could effectively trap the charge and improve the electrochemical performance of the electrode. The limit of detection (LOD) of the prepared composites was 0.006 μmol L^{-1}, which was significantly lower than that of the conventional electrodes, and the Linear range of detection covered 0.04–80.0 μmol·L^{-1}, with a detection sensitivity of 45.33 μA·L·μmol^{-1}. Compared with the monometallic MOFs, the NiCo-BTC MOFs/N-GONRs/GCE exhibited better electrochemical performance with electrode stability of up to 95%.

Researchers are generally focused on the designability of MOFs' microstructures, aiming to achieve effective control over electron or ion transport pathways. Additionally, the integration of highly dispersed nanomaterials with MOFs helps overcome the inherent insulating nature of MOFs, transforming them into functional materials applicable in sensing, energy storage, and electrocatalysis. However, existing studies also present aspects that warrant critical reflection. Firstly, the combination of MOFs with conductive nanomaterials still faces challenges in practical processing and large-scale production, as achieving high dispersion often requires complex chemical modifications or precise fabrication techniques, raising concerns about cost and stability. Secondly, the enhancement of electrical performance can sometimes conflict with other properties, such as mechanical strength or flame retardancy, necessitating a holistic optimization approach in material design. Furthermore, the mechanisms underlying the improvement in electrical performance are currently limited to simple descriptions of charge transport pathways, lacking in-depth investigations into the evolution of conductive networks within the microstructure. Expanding theoretical models or employing multi-scale characterization techniques, such as in situ analysis, could further elucidate and enhance the application potential of MOF-based nnanocomposites in the realm of electrical performance.

4.4 Others

In addition to the properties, the integration of nanomaterials and MOFs through hybridization can impart further properties to polymers. The versatility of such MOF-based nanocomposites has led to their widespread use in polymer matrices for a variety of applications. Polymers are susceptible to environmental influences, such as ultraviolet radiation and temperature. There is an inherent trade-off between their flame retardancy and anti-weathering performance, which has prompted a focus on enhancing the anti-weathering performance of polymers in academic research [152, 153]. Majidi et al. [154] successfully prepared PU coatings by synthesizing GO-modified ZIF-7 nanoparticles to improve their weathering and mechanical properties (Fig. 13a). The introduction of GO-ZIF-7 nanohybrids significantly improved the photostability of the PU coatings, and after 600 h of accelerated aging tests, the gloss loss of the PU/GO-ZIF-7 coatings was only 0.76 GU, and they maintained a high degree of transparency. Compared with the control PU, the elongation at break and toughness of PU/GO-ZIF-7 were increased by more than 70% and 85%, respectively. The RMS roughness value of the ZIF-7 coating before weathering was 9.44 nm, which decreased to 8.04 nm after 600 h of weathering, representing a change of about 14%. After 600 h of UV-A exposure (340 nm) at 25 °C with 50% Humidity, the change in contact angle was minimal, decreasing from 81.87° to 77.11°, a change of approximately 5.8%, indicating excellent retention of surface hydrophobicity and moisture resistance. The GO-ZIF-7 nanohybrid can enhance the light stability of the PU coating through a mixed mechanism of UV absorption and free radical scavenging, thereby improving weathering resistance. Similarly, Li et al. [155] successfully designed ZIF-8@g-C_3N_4 (ZCN) smart nanoparticles, which were loaded onto g-C_3N_4 nanosheets by an in situ loading method to significantly enhance the performance of epoxy coatings (Fig. 13b–d). Using the Tafel extrapolation

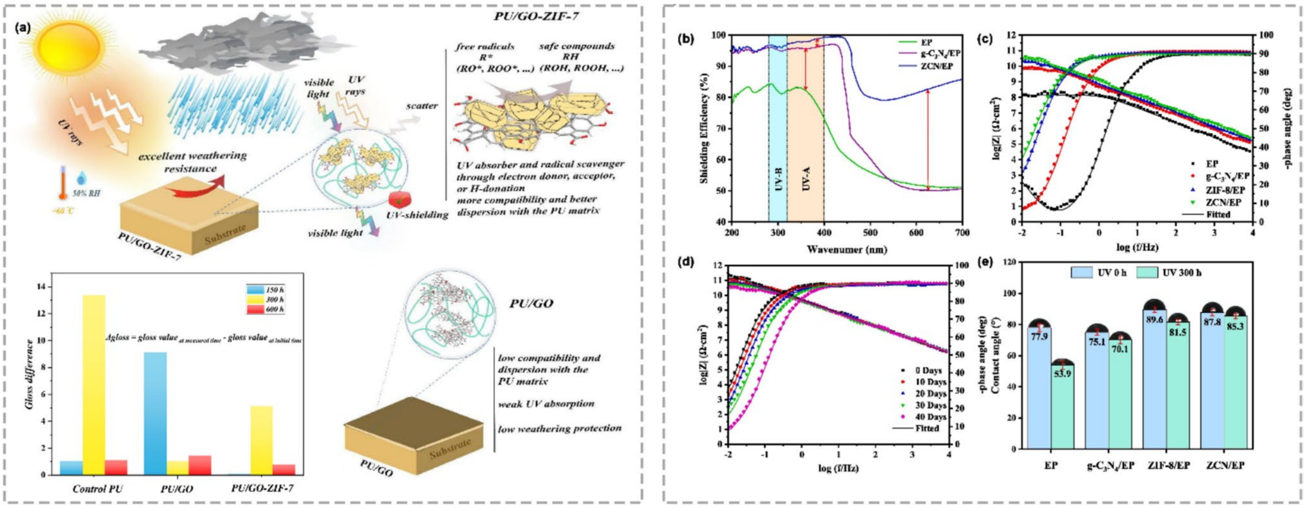

Fig. 13 **a** Schematic diagram of the mechanism of GO-ZIF-7 to improve the UV protection of PU coatings through the dual mechanism of UV absorption and radical scavenging, and the change in gloss of PU-GO-ZIF-7 coatings at different time points. Reproduced with permission from ref. [154]. **b** Evaluation of the effect of ZCN nanoparticles on the UV shielding properties of epoxy resin coatings using UV–vis spectroscopy. **c** EIS was performed to obtain the Bode plot. **d** ZCN/EP coatings after immersion in 3.5 wt% NaCl solution for 0, 10, 20, 30, and 40 days. **e** Water contact angle of EP, $g\text{-}C_3N_4$/EP, and ZCN/EP coatings. Reproduced with permission from ref. [155]

method to analyze the electrochemical corrosion parameters of the coating, ZCN-MS exhibited the lowest corrosion current density (6.25 ± 0.04 μA•cm2) and the highest polarization resistance (4123 ± 5 Ω•cm2), indicating its excellent corrosion resistance performance. Meanwhile, dynamic mechanical thermal analysis (DMTA) tests showed that the crosslinking density of the ZCN/EP coating increased to $2.61 \times 10^{-}3$ mol/m3 after 300 h of ultraviolet exposure, demonstrating its good thermomechanical properties. Furthermore, UV–Vis spectroscopy revealed that g-C3N4 displayed significant UV absorption capability, while ZIF-8 reflected and scattered ultraviolet light within a shorter wavelength range. When combined, the absorption edge of ZCN experienced a noticeable red Shift, further enhancing its UV protective effect, with ZCN significantly improving optical Shielding capability across the entire range from 280 to 700 nm. The nanohybrid material not only possesses acidic pH-responsiveness but also provides UV-reflective and scattering functions, achieving multiple improvements in the barrier, activity inhibition and UV resistance of the coatings.

Another potential application of integrating MOFs with nanomaterials in polymers is the removal of water pollutants. An illustrative example is the report by Bagherzadeh et al. on the synthesis of innovative desalination materials based on thin-film nanocomposite membranes modified with WS_2–Cys–UiO-66-$(CO_2H)_2$ nanocomposites [156]. The authors initially synthesized WS_2-Cys-MOF nanosheets and incorporated them into a polyamide selective layer, thereby enhancing the water flux and contamination resistance of the membrane. The resulting nanocomposite membranes exhibited excellent stability and demonstrated a significant enhancement in water flux, reaching 38.91 LMH during desalination. It was demonstrated that the nanocomposite membranes also demonstrated enhanced anti-pollution characteristics, exhibiting diminished flux decline rates. Furthermore, the authors discovered that the performance of the membranes could be enhanced by optimizing the addition of WS_2-Cys-MOF. This study presents a novel approach to the design and development of thin-film desalination membranes based on WS_2-Cys-MOF nanocomposites, showcasing their potential for water treatment and ion separation applications. In a separate study, Mahmoud et al. [157] constructed a composite comprising titanium-based metal–organic frameworks (Ti-MOF) decorated with TiO_2 nanoparticles, embedded with watermelon peels biochar (WMPB) and functionalized with chitosan hydrogel (CTH). The composites exhibited excellent multifunctionality and efficient decontamination performance, with the removal rates of hexavalent chromium (Cr(VI)) and doxorubicin (DOX) reaching 95.28% and 97.96%, respectively. The composites exhibited remarkable surface porosity, a high specific surface area (366.04 m2/g), and good water stability, and demonstrated excellent recycling performance. This novel bio-nanocomposite represents an efficient, environmentally friendly and sustainable solution for the treatment of water pollution, offering an innovative approach to the remediation of hazardous pollutants in aqueous environments.

Among diverse MOFs, ZIFs (e.g., ZIF-8, ZIF-67) emerge as the most versatile for multifunctional polymer composites.

Their unique sodality topology and tunable organic ligands enable exceptional flame retardancy (e.g., LOI↑ to 29.1% in epoxy; Table 2) and mechanical reinforcement (e.g., 94%↑ tensile strength in PA6; Fig. 11a–b). For energy storage, Mn-MOFs/CNT hybrids (Fig. 12) achieve superior specific capacitance (385.5 mF·cm⁻2), while MIL-101 derivatives dominate water treatment due to ultrahigh adsorption capacity (Sect. 2.3.1). UiO-66's robustness suits high-temperature processing but requires nanomaterial integration for conductivity. Future work should prioritize ZIF-nanomaterial hybrids for all-in-one performance and expand Mn-MOF/MIL studies into flame-retardant designs.

Although nanomaterials possess multifunctionality and tunability, enabling applications in areas such as sound insulation, antibacterial treatments, and sensing, current research primarily focuses on flame retardancy and mechanical reinforcement. There remains ample opportunity to explore the synergistic effects of developing novel composite materials in other domains. Additionally, large-scale production and cost control are pressing demands. Most studies are still at the laboratory stage; achieving industrial-scale production requires consideration of synthesis efficiency and environmental friendliness, including the treatment of reaction byproducts, solvent recovery, and energy consumption. Balancing performance, economic viability, and sustainability continues to be the greatest challenge between materials design and engineering.

5 Industrial applications and manufacturing challenges of MOF-based nanocomposites in polymer matrix

MOF-based nanocomposites demonstrate excellent application potential in several engineering fields. Their versatility and outstanding properties provide innovative solutions for the advancement of materials science. In the field of architectural fire coatings, our research group has provided valuable insights into the integration of MOFs with nanomaterials for flame retardants in polymer matrix. For the first time, we report a novel hybrid flame retardant (MPOFs-P) that combines POSS, phosphorus-containing compounds, and transition metals [131]. Impressively, with only 2 wt% of MPOFs-P, the LOI of the composite could be enhanced to 27.0% and successfully passed the UL-94 V-0 rating. Subsequently, we have also proposed a stepwise etching strategy to prepare hollow nanocages (ZNs-B/CP) carrying ZIFs nanodots, which showed good inhibition of heat and smoke release from epoxy composites [143]. To the best of our knowledge, this is the first report on the application of MOF nanodots in the field of flame retardancy. The synthesis process produced nanodots of ZIF-67 smaller than 10 nm, which are crucial for better performance Due to their high surface area and reactivity. A 43.1% reduction in the pHRR to 648 kW/m2 was observed, compared to pure epoxy. In the field of energy storage, MOF-based nanocomposites are widely used in lithium-ion batteries, supercapacitors, and fuel cells [158–160]. It was shown that by directly growing cobalt phosphide (CoP) nanosheet arrays in Lithium-ion batteries, their electrodes were able to achieve a high discharge capacity of 919.6 mAh/g after 200 cycles and exhibited excellent flexibility and safety, even under mechanical damage. This approach effectively solves the problems of traditional cobalt-based electrodes, which are prone to aggregation and low conductivity [161]. In addition, MOF-based nanocomposites have proven their effectiveness in the efficient adsorption and catalytic degradation of organic pollutants and heavy metals. Jia et al. assembled MOF-derived hollow $CoSe_2$@N-doped carbon materials via one-dimensional CNTs to innovatively optimize electromagnetic wave absorption properties. The unique three-dimensional conductive network structure of the materials, through the uniformly distributed CNTs and hollow $CoSe_2$@N-doped carbon materials, resulted in the lowest reflection loss of − 41.68 dB at a thickness of 3.0 mm, which significantly enhanced the electron transport paths, the interfacial polarization, and the multiple reflection losses, and effectively optimized the impedance matching properties [162]. These findings highlight the critical role of MOF-based nanocomposites in and emphasize their role in various industries.

5.1 Critical challenges

Despite the extensive application prospects of MOF-based composites, there are also several challenges remain in practical applications (Fig. 14), including long-term stability, cost-effectiveness, and environmental concerns:

(1) One of the foremost challenges is the thermal stability of MOFs when incorporated into polymer matrix [92]. Many MOFs exhibit reduced thermal stability, which can significantly impact the thermal properties of the resulting composite materials. The degradation of MOFs under processing conditions or during end-use applications can limit their functionality and lifespan, necessitating the development of strategies to enhance their thermal resilience.

(2) Highly loaded MOFs may result in poor dispersion, disrupting the mechanical integrity of polymers and leading to reduced tensile strength, flexibility, and overall structural stability [145]. Understanding the interplay between MOF loading and polymer matrix characteristics is essential to optimizing the mechanical performance of these composites.

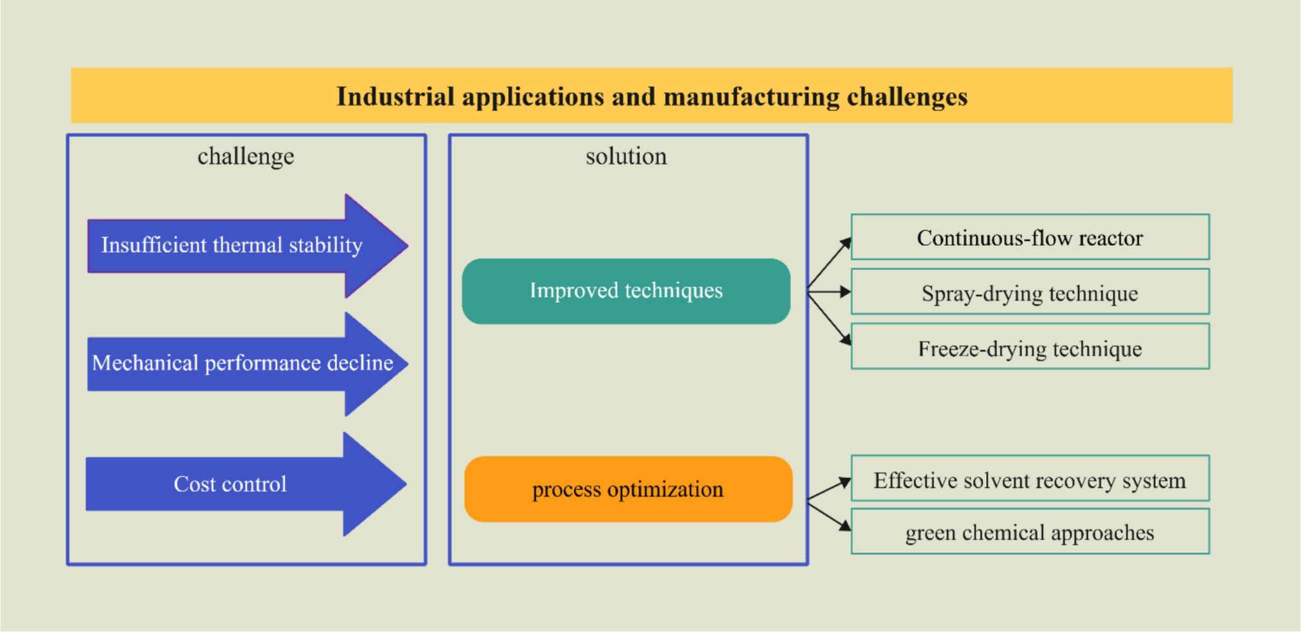

Fig. 14 Application and manufacturing challenges of industrial scalability of MOF-based nanocomposites

Surface functionalization is a powerful approach to improve the compatibility and dispersion of MOFs in polymer matrix. By modifying the surface of MOFs with organic ligands, polymers, or other functional groups, we can significantly enhance their interfacial interactions with polymers. For example, compared with UiO-66 (Zr), NH_2-UiO-66 (Zr) shows more significant improvement [163]. Similarly, surface modification of UiO-66-NH_2 with additional polymers (such as phenylacetyl chloride) can enhance compatibility with Matrimid (a polyimide), thereby making it more suitable for applications in polymer fiber composites [164].

(3) MOF-based composites face significant challenges in terms of long-term stability. In practical applications, these materials may encounter various environmental factors such as water, oxygen, and temperature fluctuations, which can lead to degradation over time. For instance, hydrolysis and oxidation are common issues that can compromise the structural integrity of MOFs in polymer matrix. This degradation can result in a decline in mechanical properties, electrical performance, and flame retardancy. Ensuring the long-term stability of MOF-based nanocomposites requires the development of protective coatings, hybrid matrices, and stabilization techniques that can mitigate environmental degradation.

(4) The cost-effectiveness of MOF-based nanocomposites is a critical factor limiting their widespread industrial adoption [38]. The synthesis of MOFs often requires specific conditions such as controlled temperature, pressure, and reaction time, which can be resource-intensive. Additionally, the use of expensive raw materials and the complexity of fabrication processes contribute to higher production costs. For example, the synthesis of some MOFs involves rare metal ions or complex organic linkers, which significantly increase the overall cost. To address this challenge, researchers are exploring alternative synthesis methods, such as microwave-assisted synthesis and solvent-free approaches, which can reduce energy consumption and material waste. Furthermore, optimizing the loading of MOFs in composites to achieve a balance between performance and cost is essential for commercial viability.

(5) The environmental impact of MOF production and application is another important consideration [165]. The synthesis of MOFs may involve the use of toxic solvents and hazardous chemicals, which can pose risks to both the environment and human health if not properly managed. Additionally, some MOFs contain toxic metal ions and organic linkers that could leach into the environment during their lifecycle. To mitigate these concerns, green chemistry principles are being applied to develop more environmentally friendly synthesis routes. For example, using water-based solvents,

renewable resources, and biodegradable materials can reduce the ecological footprint of MOF production [136]. Additionally, implementing efficient solvent recovery systems and waste management practices can help minimize environmental pollution [166].

5.2 The scalability of large-scale industrial use

To meet industrial demands, the synthesis and application of MOF-based nanocomposites need to be scaled up. Despite challenges in large-scale synthesis of MOF-based nanocomposites, recent advances have facilitated their industrial production. Continuous flow reactors are a common strategy, allowing for efficient synthesis by continuously feeding reactants and enabling controlled mixing and reactions. This method offers advantages such as precise adjustment of reaction parameters, rapid mixing, effective heat transfer, and continuous output [8, 167]. Another effective approach involves spray and freeze-drying techniques [168]. Spray drying atomizes liquid MOF precursors into droplets and dries them with hot air, efficiently producing solid particles suitable for large-scale production. Freeze drying removes solvent from frozen MOF precursors under vacuum, preserving crystal integrity but requiring more time. Both methods produce MOFs with high surface areas, porosity, and thermal stability, making them suitable for various applications and easy to manage and store.

Overall, future research should prioritize improving the scalability of MOFs\-based nanocomposites through process optimization and technological innovation. This includes developing more efficient synthesis methods to reduce production costs while maintaining high quality and performance standards. In addition, exploring green chemistry methods to minimize environmental impacts during the production process is also an important direction for future research. Designing modular production equipment that can flexibly respond to changes in market demand and facilitate the integration of sustainable practices throughout the manufacturing process is another key area for future research.

6 Conclusions and prospects

This review explores the combination of MOF-based nanocomposites with polymers and their applications in the fields of flame retardancy, mechanical reinforcement, energy storage, and water treatment, etc. MOFs have become an important ingredient for enhancing the properties of polymers due to their unique structural properties and functionalities. Through different synthesis methods and modification strategies, the thermal stability, flame retardant efficiency, and mechanical and electrical properties of composites can be effectively improved.

By employing bibliometric analysis and reviewing the existing body of research, it becomes evident that integrating MOF-based nanocomposites with polymers not only boosts the materials' flame resistance but also enhances their mechanical integrity and adaptability to environmental conditions. However, the stability of the fusion of MOF-based nanocomposites and the compatibility with polymers are still the main challenges limiting their wide application. Future research should focus on the following aspects:

1. Developing novel synthesis techniques to improve the dispersion and compatibility of MOF-based nanocomposites in polymer matrix and to ensure the stability of composites under different environmental conditions.
2. Enhancing the interactions between MOF-based nanocomposites and polymer matrix through surface functionalization and interfacial engineering to endow the composites with more functional properties, such as self-repairing, UV, and antibacterial properties.
3. Explore potential applications of the integration of MOFs and nanomaterials in other fields, such as environmental governance and biomedicine, and promote their use in clean energy and sustainable development.
4. To study the scale-up synthesis and application of MOFs-based nanocomposites to meet industrial demands and promote their transformation in practical applications.

In conclusion, the MOF-based nanocomposites in polymer matrix opens a new direction for the design and application of functional polymer materials. With in-depth research and technological advances, it is expected that more innovative composites will emerge in the future to meet the demand for high-performance polymer materials in various industries.

Author Contribution Rongjun Ma: Conceptualization, Formal analysis, Data curation, Investigation, Methodology, Visualization, Writing-original draft, Writing-review & editing. Yanan Hou and Wenchao Zhang: Conceptualization, Supervision. Ye-Tang Pan: Supervision, Validation, Funding acquisition, Resources, Writing-review & editing. Siqi Huo and Congling Shi: Supervision, Validation.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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