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Combination of covalent organic frameworks (COFs) and polyoxometalates (POMs): the preparation strategy and potential application of COF–POM hybrids

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Both covalent organic frameworks (COFs) and polyoxometalates (POMs) show excellent properties and application potential in many fields, thus receiving widespread attention. In recent years, COF–POM hybrid materials were prepared by combining COFs and POMs through physical or chemical methods. COF–POM hybrids have shown high performance in many fields, such as catalysis, sensing, energy storage, and biomedicine. In this review, we introduced the preparation strategy and application of COF–POM hybrids in detail. We believe that the combination of COFs and POMs will provide more abundant functions and broad application prospects.

Wider impact

Covalent organic frameworks (COFs) have attracted extensive attention all over the world, and show great application potential in many fields. Polyoxometalates (POMs) are a unique class of inorganic compounds that consist of a cluster of metal cations, typically transition metals, bound to a large number of oxide or hydroxide ions in a polyhedral structure. POMs can range in size from small molecules to extremely large complexes consisting of hundreds of metal and oxide ions. They also exhibit a variety of chemical and physical properties that make them interesting for a wide range of applications. POMs can be incorporated into COFs either by post-synthesis modification or by covalent synthesis, depending on the nature of the POMs and COFs. The resulting materials exhibit a range of interesting properties such as high stability, enhanced proton conductivity, and improved electrocatalytic activity. COF–POM hybrid materials are commonly prepared by physical blending, electrostatic interaction, *in situ* synthesis, framework building and covalent modification. In this review, we summarized the current research progress of COF–POM hybrid materials and provide prospects for their development. This review can help people to understand the current status of the application of COF–POM hybrid materials, which is especially important for those who are just starting out.

1. Introduction

Covalent organic frameworks (COFs) and polyoxometalates (POMs) are two famous materials that have attracted significant attention in recent years due to their unique properties and potential applications.

COFs are a type of porous material made up entirely of lightweight, organic building blocks linked by covalent bonds.[1,2] This results in a crystalline structure that is highly ordered and tunable, with the ability to customize properties such as pore size, density, and functionality.[3,4] COFs can be synthesized using a variety of methods, including a solvothermal method, microwave-assisted method, mechanochemical method, interface-assisted method and so on.[5–10] With the development of COFs, metal-based building blocks have also been employed to construct the metal based COFs, which not only enriches the types of COFs, but also offers more properties.[11–13] As reported, COFs possess a wide range of potential applications, including gas storage and separation,[14,15] catalysis,[16,17] sensing,[18,19] advanced electronics,[20,21] and drug delivery.[22,23] They are also extremely lightweight and have a high surface area, making them attractive for use in energy storage systems such as batteries[24,25] and supercapacitors.[26,27] In recent studies, scientists have thoroughly investigated the topological semimetal and higher-order topological insulator properties of COFs through quantum chemical calculations, which are important for a deeper

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understanding of COFs and for the design and development of their properties.[28–30] In order to expand the usage of COFs and improve their performance, they are also mixed with other materials, such as graphene,[31] carbon nanotubes,[32] metal oxides,[33] metal nanoparticles,[34] conductive polymers,[35] MOFs (metal–organic frameworks),[36] MXenes[37] and so on. Recently, POMs were introduced into COFs to construct COF–POM hybrids.

POMs are anionic inorganic compounds composed of clusters of metal atoms that are linked together by oxygen atoms.[38] These metal-oxide clusters have a range of shapes and sizes, and are usually composed of transition metals such as tungsten, molybdenum, and vanadium, coordinated with oxygen atoms.[39] POMs consist of a central metal oxide cluster surrounded by a shell of metal oxide and/or hydroxide ions, which gives the molecule its characteristic cage-like or wheel-like shape.[40] POMs often exhibit good chemical and thermal stability, high oxidizing ability, and unique redox and catalytic properties.[41] POMs have a wide range of possible applications, such as catalysis,[42] electrochemistry,[43] energy storage,[44] and biomedical applications.[45] Due to their large size and complex structures, their properties can be easily tuned by modifying their structure or the metals within the clusters. POMs can also be incorporated into hybrid materials with other materials such as COFs, for new or improved functions.

For now, researchers have begun exploring the combination of COFs and POMs to create hybrid materials with improved properties and potential applications. By combining the advantages of both materials, it is possible to create materials with new and enhanced properties that cannot be achieved with either material alone.

In this review, we summarize the current research progress of COF–POM hybrid materials and provide prospects for their development.

2. Brief introduction of POMs and COFs

COFs are an emerging artificial crystalline organic porous materials based on light elements (C, O, N, S, Si, H, *etc.*) linked by covalent bonds (B–O, C═N, C–C, C–N, –CO–NH–, *etc.*).[46–48] For instance, Jiang and co-workers reported the first luminescent and semiconducting COF (TP-COF), which consists of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and pyrene-2,7-diboronic acid (PDBA) linked by a six-membered boroxol ring.[49] Huang and co-workers prepared a series of three-dimensional (3-D) COFs linked by –C═N– linkages through a Schiff base condensation reaction as photoredox catalysts.[50] Liu and co-workers prepared a stable COF (COF-JLU33) linked by –CO–NH– linkages through transforming Schiff base bonds into amide bonds.[51] Qiu and co-workers prepared a sp^2-COF linked by –C–C– linkages through the condensation of 1,3,6,8-tetrakis(4-formylphenyl)pyrene and 1,4-phenylenediacetonitrile.[52] At present, there are various type of bonds for connecting the building blocks, and a large number of COFs with different structures have been continuously reported.[18]

Since the first COFs were reported, this fascinating material has attracted increasing attention because of their unique physical/chemical properties which allow them to be utilized in gas separation and storage, chemical sensors, photo/electro-catalysis, photoelectric device, energy storage, pollution management, drug delivery, and so on. Xu and co-workers synthesized a thiadiazole-functionalized COF by Schiff base condensation of thiadiazole-functionalized diamine and aldehyde. The prepared TH-COF-1 exhibited high CO_2 uptake capacity with good selectivity.[53] Qiu and co-workers prepared a Kadsura-shaped fluorescent COF by adopting 2,5-dimethoxyterephthaldehyde (DMTP) and 1,3,5-tris(4-aminophenyl)benzene (TAPB) as building blocks *via* an one-step reaction strategy at normal temperature. The prepared COF was explored for simultaneous sensitive detection and effective removal of TNP.[54] Eddaoudi and co-workers synthesized a piperazine linked COF *via* a solvothermal condensation reaction between hexaketocyclohexane octahydrate and 2,3,6,7-tetraaminophenazine hydrochloride. The reported Hex-Aza-COF-3 was applied as a photocatalyst for selective oxidative [3+2] cycloaddition of phenols with olefins.[55] Banerjee and co-workers prepared a β-ketoenamine-linked COF with redoxactive anthraquinone, which showed high performance for supercapacitance.[56] Zargoosh and co-workers synthesized a porous triazine-based COF through the hydrothermal method, which can be applied as a superadsorbent for the removal of Hg^{2+} ions from industrial effluents.[57] Negishi and co-workers constructed a 3-D COF (TUS-84) with scu-c topology by the solvothermal reaction of DPTB-Me and TAPP. TUS-84 showed high efficient drug loading, sustained release property and controlled release behavior.[58] Various building blocks were reported to construct COFs, as shown in Fig. 1. The building blocks with different symmetrical structures are capable of assembling a wide variety of COFs with different spatial structures, including 2-D and 3-D COFs. As displayed in Fig. 2, 2-D COFs can be assembled by selecting the building blocks with C_2, C_3, C_4, C_5 and C_6 geometries. The self-condensation of C_2-symmetric units enables the construction of 2-D COFs with **hcb** topology, such as triazine and boroxine linked COFs.[59,60] The combinations of [C_2+C_3], [C_3+C_3] and [C_2+C_{2v}] yield **hcb** topology,[61–63] while [C_2+C_4] and [C_4+C_4] combinations generate **sql** topology[64–66] and [C_2+C_2], [C_2+C_6] and [C_3+C_6] combinations form the COFs with **rho**, **trigonal** and **kdg** topology respectively.[67–70] The **hcb**, **rho**, **kdg**, **sql** and **trigonal** topologies are the most common forms of 2-D COFs. Besides these shapes, the **kgm** and **cem** topologies can be formed through combinations of [C_2+C_2] and [C_2+C_5] respectively.[71–73] In recent years, 3-D COFs have been increasingly studied due to their unique structural properties and porosity. The spatial structure of 3-D COFs is more complicated than that of 2-D COFs. The COFs with **bor** and **ctn** topologies are constructed using the [T_d+C_3] combination.[74,75] The **dia** topology is formed using the [T_d+T_d] and [C_2+T_d] combination.[76,77] The **pts** topology can be designed using the [T_d+C_2] and [T_d+C_4] combination.[78,79] The combinations of [C_3+C_2] and [C_4+C_6] can generate **ffc** and **she** topology respectively.[80,81] In addition, the topology of 3-D COF also includes **rra**, **srs**, **lon**, **stp**, **acs**, **tbo**, **bcu**, **mhq**, **spn**, **fjh** and so on.[82–85]

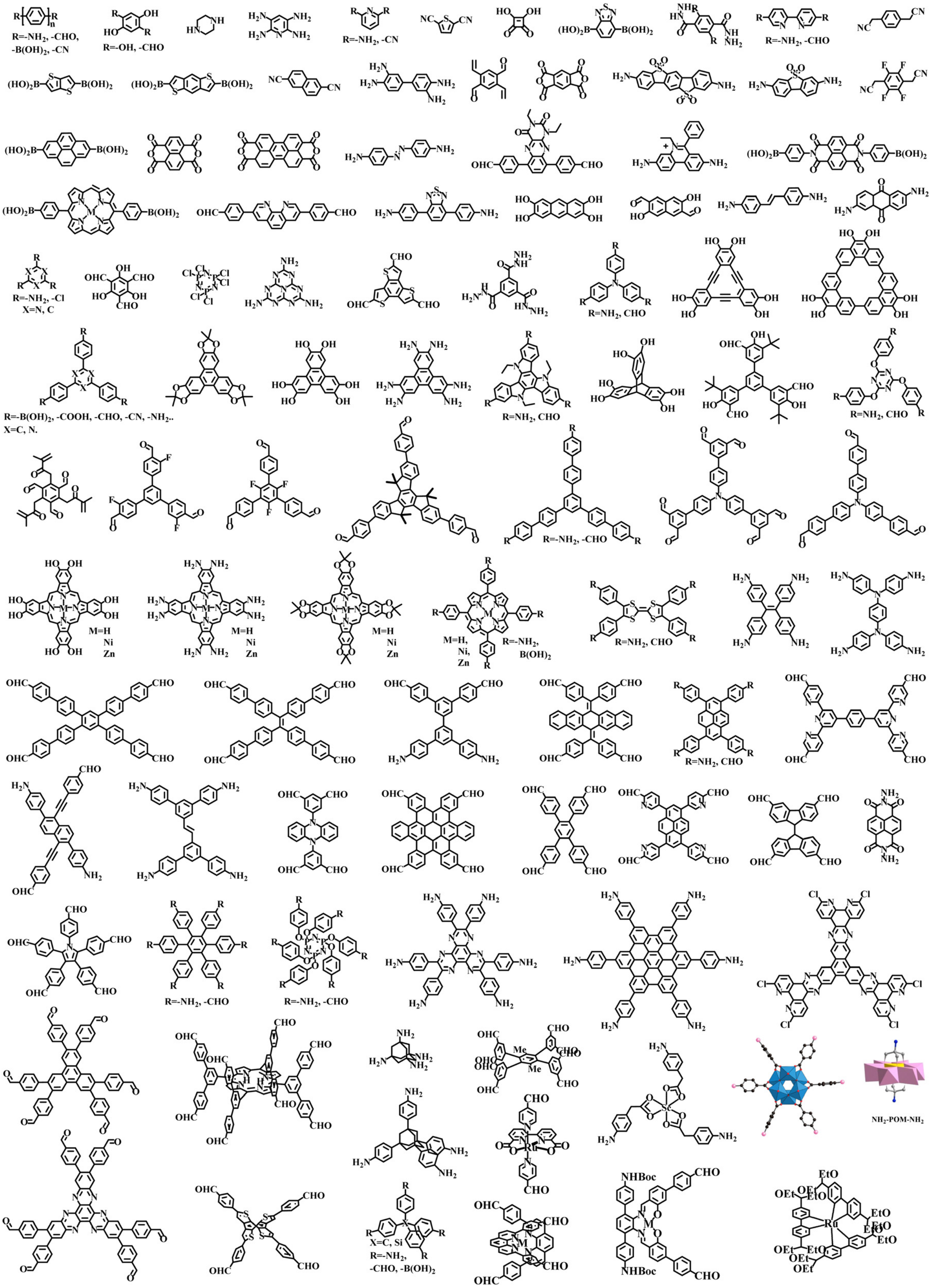

Fig. 1 Building units of COFs.

The building blocks are usually organic groups with a rigid structure, but with the development of research, more and more metal-containing monomers are also utilized to construct COFs. The COFs synthesized from building units containing

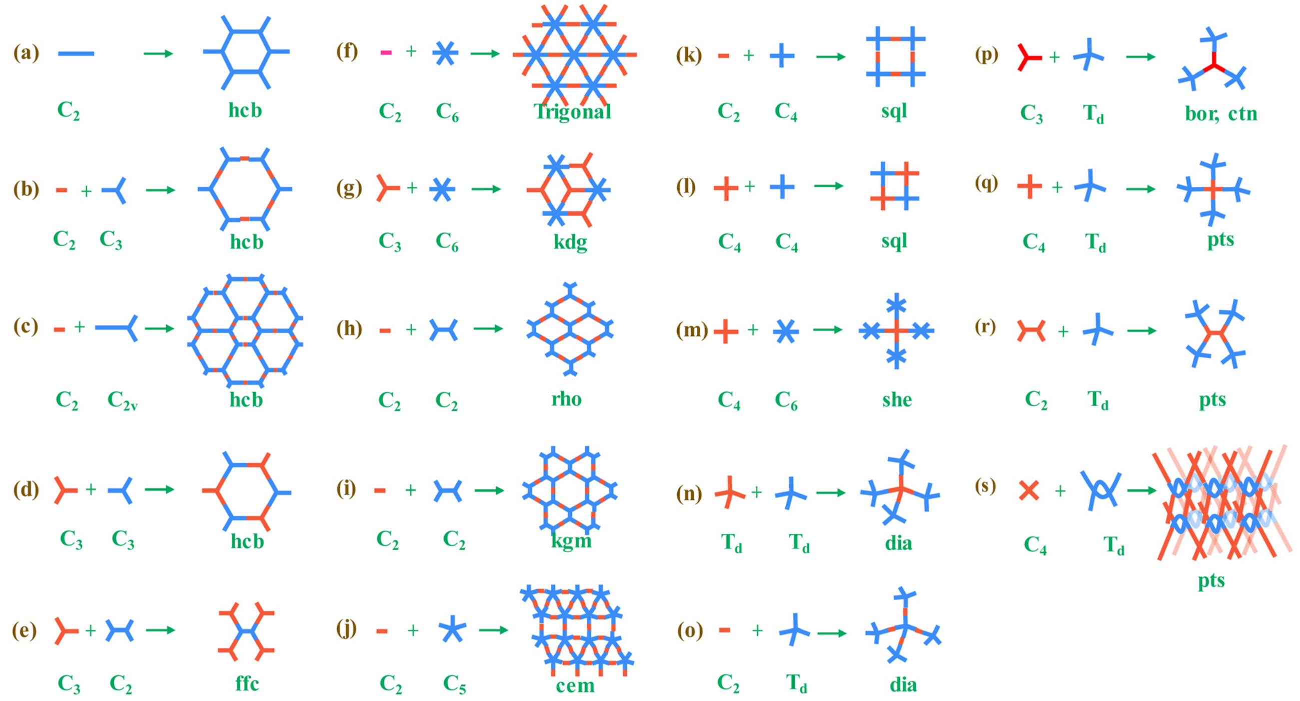

Fig. 2 Topology diagrams for 2-D and 3-D COFs constructed from the building units with different symmetries.

metals have shown great research value in many fields such as catalysis (photocatalysis), chromatography, sensors and energy storage. Gu and co-workers synthesized 3-D metal based COF bearing $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine)-based units in the skeleton, which showed high photocatalytic activity for visible light driven H_2 evolution.[86] Cui and co-workers prepared Zn(salen)-based COFs by Schiff base condensation of ethanediamine and tetrahedral tetra(salicylaldehyde)-silane or -methane derivatives in the presence of Zn^{2+} ions. The prepared COFs were utilized to test the separation effect in liquid chromatography.[87] Zuo and co-workers constructed the metal-COFs based on Ni-bis(dithiolene) units with a high surface area, conductivity and chemical stability. The prepared metal-COFs showed excellent lithiophilicity and high Li-ion conductivity.[88] Li and co-workers synthesized two vinylene-linked silver(I)–organic frameworks *via* Knoevenagel condensation. The prepared material not only can enable selective sensing of Au with a low LOD, but also can extract the trace amount of Au from complex liquids with high selectivity and efficiency.[89]

In addition, COFs can also be used in conjunction with other materials to obtain diverse properties. The combination of these materials with COFs can be achieved through physical or chemical interactions. In recent years, POMs have also been introduced into COFs and have shown remarkable application prospects.

POMs are a unique class of inorganic compounds that consist of a cluster of metal cations, typically transition metals (Mo, W, V, *etc.*), bound to a large number of oxide or hydroxide ions in a polyhedral structure.[90] POMs are characterized by their intricate structures, ranging in size from small molecular species to large clusters, and their diverse chemical and physical properties.[91] These structures, which are typically negatively charged, are stabilized by cations or organic ligands. As an important branch of coordination chemistry, POMs chemistry attracted widespread attention since the first POMs, $(NH_4)_3[PMo_{12}O_{40}]$ (PMo_{12}), reported by Berzelius in 1826.[92] As shown in Fig. 3, there are six major typical structures of POMs including Keggin, Dawson, Lindqvist, Anderson, Waugh and Silvertone type. With the development of POMs, Weakley, Standberg, Finke, and Preyssler structures have been founded, which enriched the structure of POMs.[93]

POMs can range in size from small molecules to extremely large complexes consisting of hundreds of metal and oxide ions. They also exhibit a variety of chemical and physical properties that make them interesting for a wide range of applications.[94] One of the defining properties of POMs is their high charge density, which arises from the presence of multiple metal cations within a single cluster. This charge density contributes to their unique electronic and optical properties, making them useful in photocatalysis, electrochemistry, and photovoltaics. The high charge density of POMs also allows them to interact strongly with other molecules, making them useful in separation and purification processes.[95] In addition, POMs possess excellent redox activity. Many POMs can undergo reversible changes in oxidation state, which makes them useful in energy storage and conversion applications.[96] POMs can also act as catalysts by facilitating chemical reactions through the provision of a unique, active site for reaction intermediates.[97,98]

POMs have several applications in various fields of science and technology due to their unique chemical and physical properties, such as catalysis, energy storage, photocatalysis, biomedical applications, environmental remediation, sensors

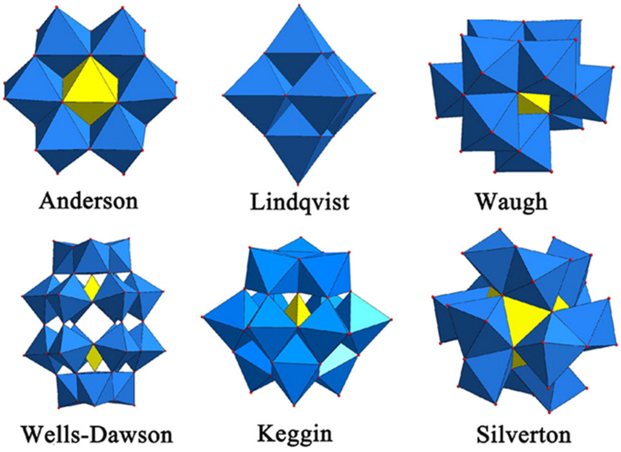

Fig. 3 Six typical structures of POMs: Keggin, Dawson, Lindqvist, Anderson, Waugh and Silvertone.

and so on. POMs are excellent heterogeneous catalysts that can efficiently catalyze several chemical reactions such as oxidation, reduction, hydrolysis, and isomerization with high stability and selectivity. Mirzaei and co-workers synthesized a heterogeneous catalyst $TBA_8[Zr(W_5O_{18})_2]\cdot17H_2O$ ($Zr(W_5)_2$) (TBA^+ = tetrabutylammonium), which is a sandwich-type POM formed by connecting two mono-lacunary Lindqvist $[W_5O_{18}]^{4-}$ anions with a zirconium ion. The prepared $Zr(W_5)_2$ exhibited a good catalytic effect on the synthesis of 1,5-benzodiazepines through the reaction of 1,2-phenylenediamine with ketones, chalcones, 1,3-diketones and aldehydes.[99] The high electrochemical stability makes POMs ideal for use as electrode materials in energy storage devices such as batteries and supercapacitors. They showed fast charging/discharging rates and longer lifetimes compared to conventional materials. Chu and co-workers prepared four Sb-capped Dawson-type molybdate clusters with 3-D supramolecular channel structures. The prepared materials exhibited excellent supercapacitance performance. Their work not only expands the class of Dawson-type $\{P_2Mo_{18}\}$ derivatives but also provide ideas for improving the performance of POMs-based energy storage device.[100] POMs have unique photoactive properties that enable them to convert light energy into chemical energy. They can be used as photocatalysts for various reactions such as water splitting, dye degradation, and organic synthesis. Feng and co-workers synthesized the W/Mo-heteropoly blue-modified defective $W_{18}O_{49}$ heterojunction nanocomposites by electro-reduction and subsequent solvothermal method for the first time. The prepared r-HPW/$W_{18}O_{49}$ and r-HPMo/$W_{18}O_{49}$ showed high performance for N_2 photofixaiton without any sacrificial agents and cocatalysts.[101] POMs have shown promising results in biomedical applications such as drug delivery, cancer treatment, and imaging. They have high biocompatibility, low toxicity, and can be easily functionalized for targeted delivery and imaging. Karimian and co-workers synthesized an antitumor active POM, $(TBA)_4H_3[GeW_9V_3O_{40}]$, which demonstrated outstanding results against U87 cells.[102] Guo and co-workers prepared POMs@MIL-100 (Fe) composites also showed great activity for cancer therapy.[103] POMs can be used as effective adsorbents for the removal of heavy metals, dyes, and other pollutants from water and wastewater. They have high selectivity, stability, and reusability, making them eco-friendly alternatives to traditional adsorbents. Li and co-workers synthesized a polyoxometalate framework $[Ni(bipy)_2]_2(HPW_{12}O_{40})$ through the chemical coprecipitation method. The prepared $[Ni(bipy)_2]_2(HPW_{12}O_{40})$ showed good adsorption ability for removing rhodamine B from aqueous solutions with excellent recycling ability. In addition, this POM also possesses the ability to remove Cr^{4+} ions from aqueous solution.[104] Moreover, POMs can be applied in chemical sensors with high selectivity and sensitivity. Wang and co-workers prepared an electrochemical sensor based on $[(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot33H_2O]$ (NMo_{36}) and MoS_2. The POMs-based sensor showed high performance for detecting hydroquinone (HQ), catechol (CC) and resorcinol (RS) with low detection limits (0.54 μM, 0.60 μM, 0.67 μM) and wide linear ranges (2–245 μM, 1.5–150 μM, 1.5–135 μM).[105]

Both COFs and POMs are functional materials with excellent performance and have been developing rapidly in many fields for a long time. Given their differences and complementarities, scientists have considered combining the two materials to enhance functionality and exploit new properties. Compared with COFs, POMs can provide more surface active sites and possess the ability to reversibly exchange a large number of electrons, but there are some problems in their application, such as difficult excitation, poor stability, easy agglomeration or loss. In recent years, there has been a growing research interest in the immobilization of heterogeneous POMs composites on solid carriers in order to prepare highly active and stable composites. COFs offer the advantages of stability, intrinsic porosity, recyclability, and the designability of function and structure. The combination of these two famous materials can improve the dispersion and recyclability of POMs, enhance stability during application, and expose more active sites, thereby raising the activity of the material. The synergistic effect between COFs and POMs enables COF–POM hybrid materials to exhibit better performance than when used individually. Although other materials (such as CNTs, graphene, *etc.*) can also be utilized as the carrier of POMs, they are single-function, difficult to functionalize, easy to agglomerate, and difficult to form a stable composite with POMs, and there are defects such as easy-to-lost and short service life in the process of application. Therefore, the hybrid materials prepared by combining COFs and POMs can obtain superior performance, which deserves more research and attempts.

In recent years, research on the combination of COFs and POMs has gradually emerged due to their unique structure and outstanding properties.

3. COF–POM hybrid materials

Polyoxometalate–covalent organic framework (POM–COF) materials are a type of hybrid material consisting of POMs incorporated into COFs. POMs can be incorporated into COFs either by post-synthesis modification or by covalent synthesis,

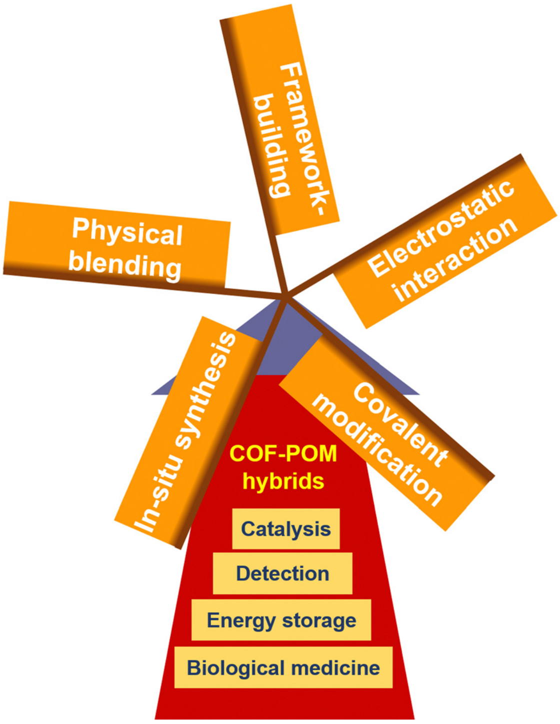

Fig. 4 The synthetic strategies and applications of COF–POM hybrid materials.

depending on the properties of the POMs and COFs. The resulting materials exhibit a range of interesting properties such as high stability, enhanced proton conductivity, and improved electrocatalytic activity. As reported, COF–POM hybrid materials were commonly prepared by physical blending, electrostatic interaction, *in situ* synthesis, framework-building and covalent modification (Fig. 4).

The COF–POM hybrid materials exhibited excellent properties in the fields of catalysis, sensing, energy storage, and biomedicine, with enormous development value and application prospects (Fig. 4).

3.1 Synthetic strategies for COF–POM hybrid materials

In most studies, the ligands that make up COFs are organic, and in recent years, metal containing ligands have also been used to construct COFs. At present, some researchers use POMs as building blocks for constructing COFs after processing, and the synthesis strategies are shown in Fig. 5.

Functionalized POMs, usually amino functionalized POMs, can be prepared through grafting NH_2-tris on the opposite sides of the POMs. The linear linker NH_2–POM–NH_2 with two amino groups could be served as building blocks for constructing 2-D/3-D functional COFs. Yang and co-workers synthesized a series Anderson POMs built-in COFs (M-Anderson-COFs).[106] The linear linker NH_2–{MMo_6}–NH_2 (M = Mn, Co, Fe) was connected with tetrahedral tetrakis(4-formylphenyl)silicon (TFPS) to construct 3-D M-Anderson-COFs with **dia** topology through Schiff base condensation. Zhang and co-workers synthesized a series 2-D POM based COFs with **sql** topology through the amine-aldehydes condensation of linear amino-containing POMs and planar tetra-aldehyde building blocks.[107] Two Anderson type POMs with two active amino groups located on the opposite positions (NH_2–{$CoMo_6$}–NH_2 and NH_2–{$MnMo_6$}–NH_2) were employed as building blocks. The prepared POM-OFs presented high crystallinity and robustness. Fang and co-workers prepared two highly crystalline 3D covalent polyoxometalate-organic frameworks (CPOFs) with **dia** topology through Schiff base reaction.[108] Ciesielski and co-workers synthesized two polyoxometalate–covalent organic frameworks (POCOF) by condensation reaction between H_2N–($CoMo_6$)–NH_2 and two different aldehyde building blocks (benzene-1,3,5-tricarbaldehyde (BTC) and 2,4,6-triformylphloroglucinol (TFP)) respectively through one-pot solvothermal strategy.[109]

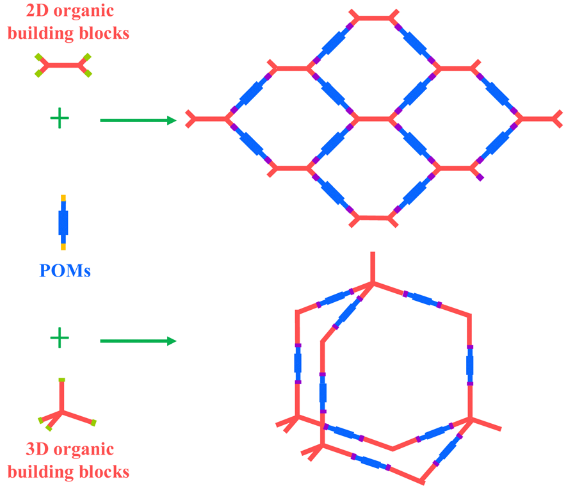

Fig. 5 Construction of POM-linked COFs using POM-based building blocks.

In recent years, in order to prepare heterogeneous POMs-based catalysts with high activity and stability, the research of immobilizing POMs on a solid support has attracted more and more attention.[110,111] Some porous materials, such as porous carbon materials,[112,113] mesoporous molecular sieves,[114,115] silica,[116,117] metal–organic frameworks (MOFs)[118,119] have been widely used as supports. Recently, COFs were employed as support for POMs by simple physical blending, as shown in Fig. 6.

Jia and co-worker successfully synthesized COF-300 through Schiff base reaction between terephthaldehyde and tetra-(4-anilyl)-methane, and then the PMA@COF-300 composites were prepared by blending COF-300 and 12-phosphomolybdic acid (PMA) aqueous solution with stirring for 24 h.[120] Lou and co-worker prepared COF-300, COF-LZU1 (Schiff base reaction between 1,3,5-triformylbenzene and *p*-phenylenediamine)[121] and CIN-1 (Schiff base reaction between melamine and piperazine-1,4-dicarboxaldehyde)[122] first. Then the prepared COFs were dispersed in ultrapure water under ultrasonic for 1 h, the PMA aqueous solution was added to the above solutions with stirring, respectively. At last, the $Fe(NO_3)_3$ solution was added and the mixture was stirred for 24 h to obtain Fe/PMA@COFs, Fe/PMA@COF-LZU1 and Fe/PMA@CIN-1,

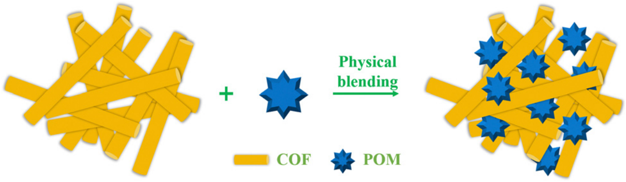

Fig. 6 Preparation of COF–POM composites by physical blending.

respectively.[123] Yang and co-workers prepared Tp-TTA through Schiff base reaction between 1,3,5-triformylphloroglucinol (Tp) and 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA). The nano-COF/POM composites (nTp-TTA/POM) were fabricated by simply mixing the cetyltrimethylammonium bromide (CTAB)/sodium dodecyl sulfate (SDS) micelle stabilized nano Tp-TTA colloid solution with $Na_3PW_{12}O_{40}$.[124] Chen and co-workers synthesized a bipyridine-COF through imine condensation of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde and 2,2′-bipyridine-5,5′-diamine. Then the Pt@COF-TB was obtained through the coordination interaction between N atom in bipyridine groups and the Pt ions. The Pt@COF-TB was impregnated in 11-molybdo-1-vanadophosphoric acid solution and stirred to prepare POM-Pt@COF-TB.[125]

In situ growth preparation is a method of synthesizing materials where the material is grown directly on a substrate or template. This method allows for precise control over the properties of the resulting material, such as crystal orientation, particle size, and surface morphology. This level of control is not possible with other methods of material preparation. COF–POM hybrid material with excellent performance can be obtained by combining POMs with COFs through *in situ* growth strategy, the preparation process was presented in Fig. 7.

Yan and co-workers prepared a COF (EB-TFP) through Schiff base reaction between ethidium bromide (EB) and 1,3,5-triformylphloroglucinol (TFP). Then the EB-TFP was added to the solution of Eu_4W_8 to prepare Eu_4W_8@EB-TFP.[126] Peng and co-workers first mixed 2,5-dimethoxyterephthaldehyde (DMTP) and heteropoly blue (HPB) in acetonitrile, then added 1,3,5-tris(4-aminophenyl)benzene (TAPB), and finally allowed them to react to obtain HPB@COF.[127]

The functionalized POMs were immobilized by covalent bonds and confined in the pores of COFs, so that COF–POM hybrid material with stable structure, uniform dispersion and excellent performance can be achieved, as shown in Fig. 8.

Lan and co-workers synthesized COFs by a [4+3] condensation reaction. The TCOF and ECOF were synthesized by a Schiff base condensation between tetrakis(4-formylphenyl)tetrathiafulvalene (TTF-4CHO), 4-[4-[1,2,2-tris[4-(4-formylphenyl)phenyl] ethenyl]phenyl] benzaldehyde (ETBC) and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT), respectively. Subsequently, the $MnMo_6$–$2NH_2$ was immobilized in the pores of COFs by the reactions between the periodic uncondensed –CHO in pores and $–NH_2$ in POMs.[128] Wang and co-workers synthesized vinyl-containing COF through Schiff base reaction between 1,3,5-tris-(4-aminophenyl) benzene (TPB) and 2,5-divinylterephthalaldehyde (DVA). The PW_9 was functionalized by 3-mercaptopropyl trimethoxysilane. Then the functionalized PW_9 was covalently conjugated onto vinyl-containing COF *via* thiol–ene click reaction to produce COF-MPW_9.[129]

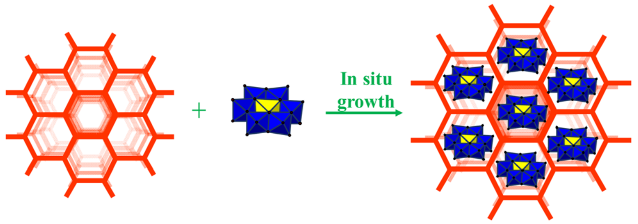

Fig. 7 Preparation of COF–POM composites by an *in situ* growth strategy.

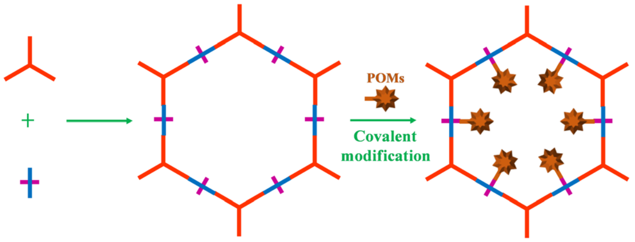

Fig. 8 Preparation of COF–POM composites by covalent modification.

POMs can also be introduced into the pores of COFs through electrostatic interactions, thereby obtaining POMs-modified COFs, as shown in Fig. 9. The organic cations are readily combined with large POM anions through electrostatic interactions. Han and co-workers reported a simple method that combines POMs with imidazolyl ionic liquid (IL)-modified COFs through a simple ion exchange process.[130] Two TD-COFs were synthesized by Schiff base reaction between 1,3,5-tri(4-aminophenyl)benzene (TAPB), 2,5-dihydroxyterephthalaldehyde (DHPA) and 2,5-dimethoxyterephthalaldehyde (DMTA), respectively. Then the COFs were modified by 1-methyl-4-bromobutylimidazole bromide ([BMIm]Br) to prepare ImTD-COFs. At last, the negatively charged PW_{12} and positively charged imidazole salts bound through electrostatic interactions on the skeleton of ImTD-COFs, greatly improving the stability of the hybrid material.

3.2 Applications of COF–POM hybrid materials

At present, the COF–POM hybrid materials are rarely reported, but these advanced materials have a wide range of potential applications. The unique properties of both POMs and COFs make these hybrid materials promising for a variety of applications in various fields, such as catalysis, energy storage, sensing, and biological medicine.

COF–POM hybrid materials exhibit excellent performance in the field of catalysis, including photocatalysis, electrocatalysis, and heterogeneous catalysis of chemical reactions. M-Anderson-COF (M = Mn, Co, and Fe) exhibited high catalytic activity in photodegradation of RhB and MB in water. Moreover, M-Anderson-COFs showed excellent performance for photocatalytic sulfide oxidation with extraordinary selectivity and conversion rate.[106] The TCOF-$MnMo_6$, reported by Lan and co-workers, showed a high CO production rate of

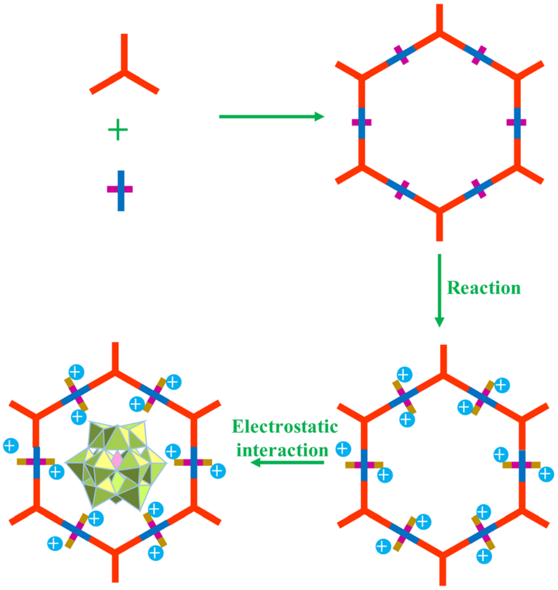

Fig. 9 Preparation of COF–POM composites by electrostatic interaction.

37.25 μmol g^{-1} h^{-1} with 100% selectivity in a gas–solid CO_2 photoreduction reaction.[128] Yang and co-workers reported that the prepared nTp-TTA/POM composites showed high performance for photocatalytic NADH regeneration with a yield of 97% and a turnover frequency of 72.0 mmol g_{COF}^{-1} h^{-1}.[124] As reported by Chen and co-workers, the prepared Co/Fe-based COF composites showed high performance in the electrocatalytic oxygen evolution reaction (OER), and the obtained POM-Pt@COF-TB exhibited excellent performance in the oxidation of methane.[125] Lou and co-workers investigated catalytic properties of the obtained Fe/PMA@COFs. The results showed that Fe/PMA@COF-LZU1, Fe/PMA@CIN-1 and Fe/PMA@COF-300 yielded 69%, 88% and 62% conversion rate of epoxidation of cyclooctene with high selectivity of epoxide (99%).[123] The catalytic performance of PMA@COF-300 for the epoxidation of olefins was investigated by Jia and co-workers. The results showed that PMA@COF-300 can be used as an efficient heterogeneous catalyst for the epoxidation of cyclooctene.[120] Han and co-workers reported that the POM@ImTD-COF showed high efficiency for the CO_2 cycloaddition reaction under mild conditions with good recyclability.[130] The 2-D NKPOM-OFs prepared by Zhang *et al.* showed excellent performance for catalytic oxidation of sulfites as biomimetic catalysts with high crystallinity, stability and good recyclability.[107]

Both COFs and POMs possess their own advantages, some new performance can be generated by combining the advantages of POMs and COF monomers or their synergistic effects. Cationic COFs have broad application prospects in the construction of new materials using anionic complexes, as well as in the fields of catalysis and luminescence.[131,132] The Eu_4W_8@EB-TFP improved the weak luminescence defect of COFs and maintained the structural stability of COFs. In addition, Eu_4W_8@EB-TFP showed highly sensitive detection of Ag^+ and liver cancer biomarkers (CG) through a dual-response strategy. The LODs of Ag^+ and CG were 0.024 mg mL^{-1} and 0.014 mg mL^{-1}, respectively. The Eu_4W_8@EB-TFP can serve as an excellent fluorescence sensor with great potential for the determination of Ag^+ in the environment and CG in biological systems.[126]

As mentioned above, both COFs and POMs have shown excellent performance in energy storage, but their integration for energy storage applications has rarely been studied. COF–POM hybrid materials have unique properties that make them promising candidates for energy storage. POMs are capable of storing multiple charges, which can be used for energy storage. COFs, on the other hand, provide a stable and porous matrix for the POMs, which can enhance the charge storage capacity. Fang and co-workers applied the 3-D porous crystalline covalent polyoxometalate–organic frameworks (CPOFs) as anode materials for lithium-ion batteries (LIBs). The first discharge and charge capacities of prepared JUC-526 were 750.6 mA h g^{-1} and 509.6 mA h g^{-1} respectively, the initial coulombic efficiency (CE) was calculated to be 67.9%. JUC-526 also presented discharge/charge capacities of 550.6/548.6 mA h g^{-1} with the coulombic efficiency of 99.6% at a current density of 100 mA g^{-1} after 500 cycles, which demonstrates higher stability.[108] As reported by Ciesielski and co-workers, the prepared POM-COF, POCOF-1 and POCOF-2 showed a specific capacitance of 125 F g^{-1} and 84 F g^{-1}, an areal capacitance of 248 mF cm^{-2} and 170 mF cm^{-2}, a volumetric capacitance of 41.9 mF cm^{-3} and 28.6 mF cm^{-3} at a current density of 0.5 A g^{-1}, the maximum energy density of 56.2 W h kg^{-1} and 38.2 W h kg^{-1}, and maximum power density of 3.7 kW kg^{-1} and 3.6 kW kg^{-1}, respectively. In addition, POCOF-1 and POCOF-2 presented greater cyclability with a capacitance retention of 90% and 74% 5000 GCD cycles.[109]

COF–POM hybrid materials have recently been investigated for their potential applications in biological medicine due to their unique properties. With the development of medicine, it is of great significance to study therapeutic and diagnostic drugs with good biocompatibility, targeting, and stability. Heteropoly blue (HPB) is an effective photothermal therapeutic agent with good photothermal conversion efficiency. COFs can serve as ideal carriers with good biocompatibility. Peng and co-workers prepared the HPB@COF for pH-responsive photothermal therapy (PTT). The HPB@COF NPs showed high performance for effectively inhibiting tumour growth with desirable biocompatibility and safety.[106] In addition, the COF-MPW$_9$ prepared by Wang's group can be used for the enrichment of glycoproteins and phosphoproteins in complex biological sample matrices with high selectivity. Oxygen enriched PW$_9$ regulates the surface properties of COFs from hydrophobicity to hydrophilicity, ensuring the hydrophilicity interaction with phosphate groups in phosphoprotein and oligosaccharide in glycoprotein. The adsorption capacities for immunoglobulin G (IgG) and β-casein (β-Ca) were 378 mg g^{-1} and 740 mg g^{-1}, respectively.[129]

4. Conclusions and prospects

In conclusion, the combination of COFs and POMs represents a promising area of research for the development of new and improved materials with a wide range of potential applications. COF–POM hybrid materials, in particular, exhibit unique properties and have the potential to be used in various fields, including catalysis, energy storage, and sensing, and biological medicine.

POMs present high and uniform charge density, fast charge transfer, good thermal stability, and strong Lewis acidity, and are non-toxic and non-polluting, and their energy bands, charges and redox properties can be regulated and designed by deficiency doping. But its direct application has certain limitations, for example, HOMO–LUMO has a large energy gap, and the transition of electrons in its outer orbital requires a large amount of energy, small specific surface area and low efficiency when used alone; most POMs are soluble in water or other polar organic solvents, which makes it difficult to recycle them, and so on. Therefore, in practical applications, it is usually necessary to immobilize POMs on suitable carriers to enlarge the surface area, disperse active sites, improve stability, and facilitate recycling. Hence, the design and preparation of new POM composites that are water-resistant, easy to separate, insoluble (new chemical bonds are generated between the POMs and the carrier), and have a large specific surface area and pore structure are of great significance for the efficient utilization of POMs. From this point of view, COFs have become a smart choice for combining with POMs by virtue of their unique nature.

At present, the main strategies for preparing COF–POM hybrids are *in situ* synthesis, physical blending, framework building, covalent modification and electrostatic interaction. Some of these preparation strategies are relatively complex and difficult, but the structures and properties of their products are more controllable and stable, such as framework building and covalent modification methods. Some other methods are relatively easier to operate, but the structures and properties of their products are not as stable as the former and are also more difficult to control, such as *in situ* synthesis, physical blending, and electrostatic interaction. Therefore, appropriate preparation methods should be flexibly selected according to actual needs.

In the current situation, there are not many studies on COF–POM hybrid materials. More COFs and different kinds of POMs can be used to prepare this material. As we know, COFs showed flexible designability, it is easy to construct COFs with various physical/chemical properties by selecting different building blocks and connection methods. COFs with appropriate pore and surface properties can be designed and prepared according to the actual requirements, and then the COF–POM hybrids can be prepared by combining the COFs and suitable POMs *via* the abovementioned strategies. In addition, the prepared COFs can be decorated by post-synthetic modification (PSM) after synthesis,[133–135] or the POMs can be functionalized, and then the COF–POM hybrids can be obtained by combining these two famous materials through physical or chemical processes.

COFs and POMs have shown outstanding application potential in many fields, so when these two materials combine, they will also present more abundant functions and be applied in more complex environments. The application fields of COF–POM hybrids need to be further expanded, such as electrochemical sensors, gas selective adsorption and separation, and environmental pollution treatment, especially in the field of photocatalysis. We believe that there must be some challenges in the development of COF–POM hybrid materials, but it has great development potential and application prospects.

Author contributions

Conceptualization, Wu Yang and Guo-Yu Yang; writing – original draft preparation, Rui Xue and Yin-Sheng Liu; and writing – review and editing, Rui Xue, Yin-Sheng Liu, Ming-Yue Wang and Hao Guo. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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