

· 综述 ·

金属有机框架基高分子抗菌材料的合成及应用研究进展

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摘 要 金属有机框架材料(MOF)具有高度有序的多孔结构和超大比表面积,在材料领域备受关注.然而,其在抗菌应用中仍面临结构稳定性不足、生物相容性有限及释放行为难以精准调控等挑战.将MOF与高分子材料有效结合,不仅可以增强MOF的抗菌性能,而且可改善其加工性能、降低生物毒性.因而,制备MOF基高分子可有效扩大MOF应用领域.本文综述了近五年来MOF基高分子抗菌材料在合成、抗菌机制及抗菌应用方面的研究进展,为高性能MOF基抗菌材料的设计与开发提供参考.

关键词 MOF基高分子; 抗菌材料; 合成策略; 抗菌机理; 应用进展

引用: 李亭瑶, 孙小娟, 李天宇, 王镡, 张亚苹, 宋鹏飞. 金属有机框架基高分子抗菌材料的合成及应用研究进展. 高分子学报, doi: 10.11777/j.issn1000-3304.2026.26051.

Citation: Li, T. Y.; Sun, X. J.; Li, T. Y.; Wang, K.; Zhang, Y. P.; Song, P. F. Research progress on the synthesis and application of metal-organic framework-based polymeric antibacterial materials. *Acta Polymerica Sinica* (in Chinese), doi: 10.11777/j.issn1000-3304.2026.26051.

1995年Yaghi等在《Nature》上首次报道了基于 Co^{2+} 与均苯三甲酸(BTC)的二维配位聚合物,正式提出了“金属-有机框架(metal-organic framework, MOF)”的概念^[1].随后在1999年,该团队成功合成了MOF-5,其具有去除客体后不坍塌的稳定孔道结构,标志着MOF从二维拓展到三维空间^[2],迈出了历史性的一步.MOF材料以金属离子或金属簇为连接点与有机配体通过配位键自组装形成,具有高度有序的晶体结构、超高的比表面积和可调节的孔道结构以及丰富的化学组成^[3],随着MOF的官能化改性^[4]、合成后修饰(post-synthetic modification, PSM)^[5]等技术持续发展,已构建出十万余种结构功能多样的MOF^[6-9].MOF独特的结构使其在吸附与分离、能源储存、催化和生物医药等领域展现出广泛的应用前景^[10-13].然而,在实际应用中,MOF多以

粉末状态存在,面临机械强度低、加工适应性差和化学稳定性不足等挑战^[14],亟需通过材料设计、复合与改性修饰等策略进行优化.

为实现MOF性能调控,选择金属纳米颗粒、金属氧化物、多孔材料(如沸石、多晶型二氧化硅),以及碳基硬材料和软材料(如氧化石墨烯、碳纳米管)作为复合组分,制备得到功能性MOF复合材料^[15-18].虽然扩展了MOF基材料在水处理^[19]、储能^[20]、传感^[21]等方面的应用,但并未彻底解决MOF机械性能差等问题.高分子结构和功能的可设计性能够改善MOF材料的功能特性^[22],越来越多的研究将高分子材料引入MOF,从而突破传统MOF材料在应用方面的局限性^[23,24].目前,将高分子与MOF结合主要有共混法、原位生长法和表面修饰法等几种方式(图1),另外,从化学键角度可将二者的结合分为共价键

2026-02-21收稿, 2026-03-23录用, 网络出版.

基金项目: 国家自然科学基金(基金号 22161040, 22561045), 甘肃省自然科学基金重点项目(项目号 24JRRA125), 甘肃省高校教师创新基金项目(项目号 2025A-006).

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doi: 10.11777/j.issn1000-3304.2026.26051; CSTR: 32057.14.GFZXB.2026.7580

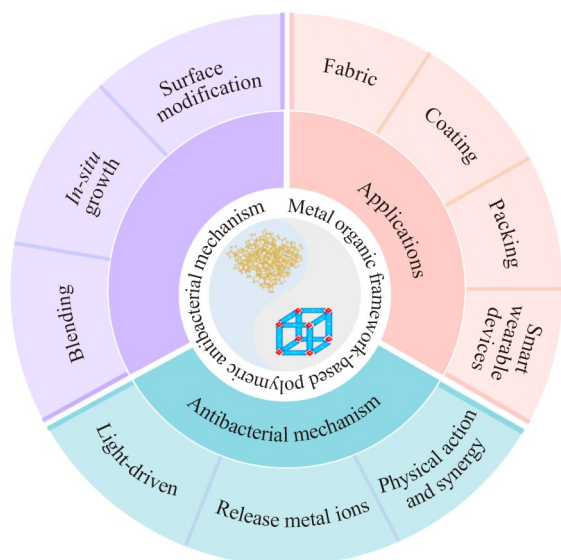


Fig. 1 Summary of the synthetic methods, antibacterial mechanisms, and applications of MOF-based polymeric antimicrobial materials.

结合^[25]与非共价键结合^[26].

MOF与高分子结合的关键在于二者经共价键或非共价键相互作用形成了复合材料,可显著增强材料的综合性能^[27,28],促进其在传感^[29-31]、环境修复^[32,33]、生物相容性提高^[34]、储存^[35]以及抗菌^[36]等领域的应用.高分子材料的引入可改善MOF在复杂环境中稳定性不足^[37]、生物相容性差^[38]的问题,进而推动其在多领域的应用.其中,MOF与高分子结合后,在抗菌织物、抗菌涂层、抗菌包装膜、智能可穿戴抗菌材料等领域的应用研究广泛.

致病性细菌感染一直是全球范围内对人类健康最严重的威胁之一,且由于各种抗菌、抗炎等药物的大量甚至过度使用引起的耐药菌问题,限制了传统抗菌治疗手段的作用,产生高发病率和高死亡率^[39-42],这也使得病菌感染问题始终是全球公共卫生领域面临的重大挑战之一^[43,44],开发新型高效、生物相容、耐药性低的抗菌材料成为研究热点.MOF因其高度有序的孔道结构、良好的药物负载能力与可控释放特性,已被应用于抗菌领域^[45,46].此外,MOF也具有半导体材料的特性,能够在特定波长光照下产生活性氧(ROS),进而通过物理/化学协同策略实现杀菌^[47],这为抗生素替代品的生产提供了新思路.然而,将MOF作为载体递送药物杀菌的方法,其效果会随着小分子的消耗而减弱.同时,依赖光照产生

的ROS对机体本身会产生一定的损伤^[48].并且在上述2种抗菌机理下,容易产生局部抗菌剂浓度过高,造成耐药等问题^[49].由于高分子链结构的有序性和功能组成的可设计性,研究者通过将MOF与高分子材料结合,以期调控其抗菌活性.例如,通过环境响应(pH、温度、湿度等^[50])调控药物释放速率、改善材料稳定性与力学性能^[51],进而降低因抗菌剂暴露过度带来的耐药风险^[52].高分子的引入有助于MOF实现长效抗菌与良好的生物相容性,为解决“超级细菌^[53]”带来的难题提供了有力支撑.

本文梳理了近五年MOF基高分子用于抗菌研究的工作,重点综述其合成、抗菌机理及抗菌应用,旨在总结高分子的引入对MOF结构、抗菌活性和抗菌机理的影响,进而为高性能、低毒性、环境友好的MOF基高分子抗菌材料的设计提供理论依据与实践支持.

1 MOF基高分子抗菌材料的合成策略

1.1 共混法

MOF基高分子抗菌材料的共混合成是指将MOF分散在高分子基体中^[54],进一步纺丝^[55]或涂覆成膜^[56].这种方法操作简便,无需复杂的化学反应和设备,可以直接将MOF粉末与高分子聚合物在共混状态下均匀混合.Ananthi等^[57]将铁基卟啉金属有机框架@氮掺杂碳点(Fe-PM@N-CDs)配置成悬浮液,再通过简单的共混法掺入明胶基底液中,形成明胶/Fe-PM@CD复合膜,显著增强了对革兰氏阳性菌和革兰氏阴性菌的抗菌活性(图2(a)).然而,此策略下MOF颗粒在高分子基体中团聚或分布不均,可能会导致材料内部应力集中,从而降低材料的力学性能和功能性^[51,58],这是共混合成目前所面临的主要挑战.

1.2 原位生长法

原位生长法是一种能使MOF在高分子基底表面原位生成的合成策略^[59],可有效解决共混法存在的均一性问题.例如,在化学交联的纤维素气凝胶(Cu/CA)上一锅负载Cu,然后通过其与有机配体之间的反应原位生长Cu-MOF,得到铜-苯二羧酸盐/纤维素气凝胶复合材料(CuBDC/CA),对多种菌株具有很高的杀灭效率^[60].此外,还可在聚合过程中引入金属离子和有机配体的原

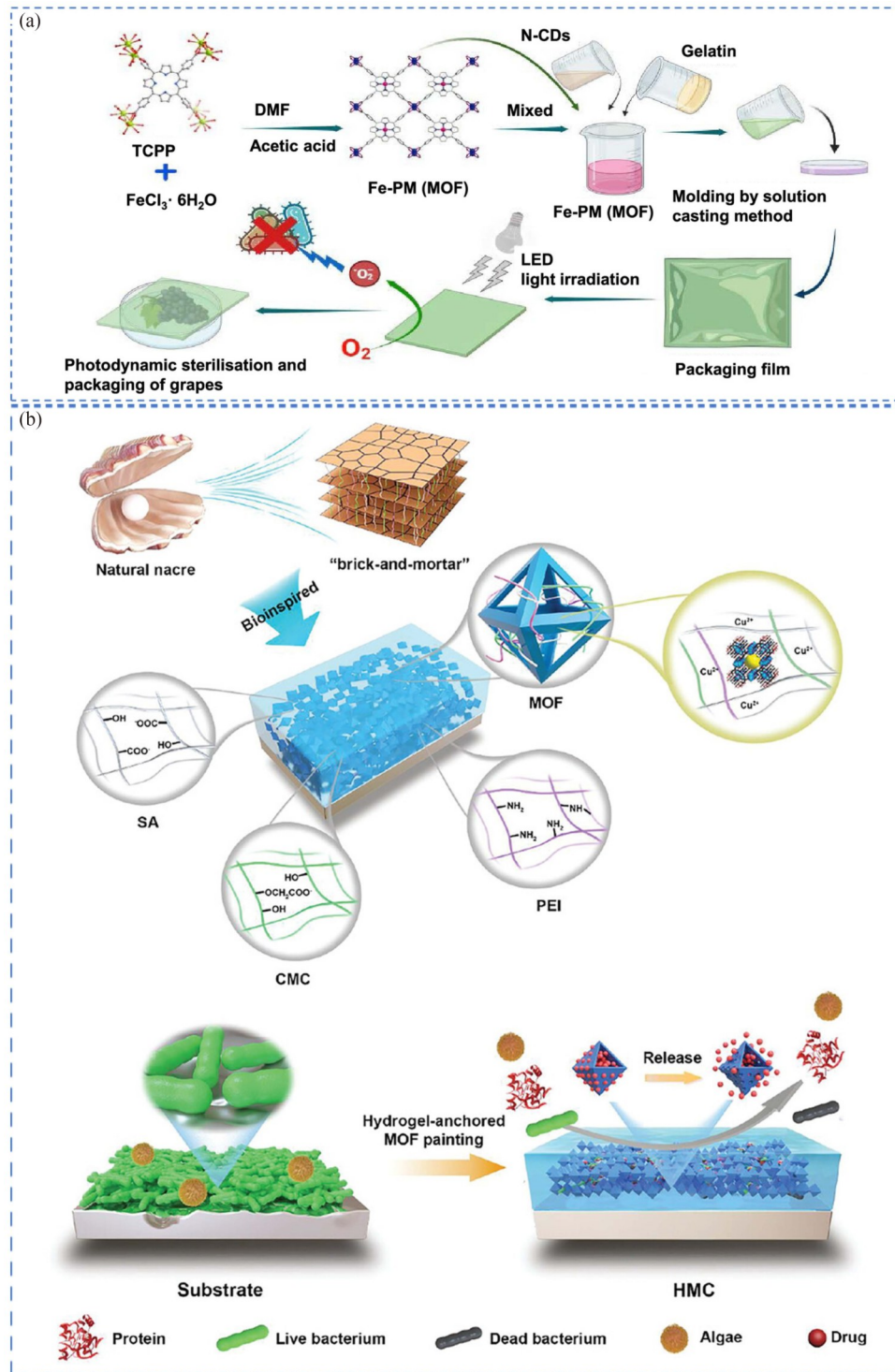


Fig. 2 Several typical synthesis methods of MOF-based polymeric materials: (a) preparation of gelatin/Fe-PM@CD composite membranes *via* the blending method (Reprinted with permission from Ref. [57]; Copyright (2025) American Chemical Society); (b) preparation of pearl-like hydrogel MOF coatings *via in situ* growth (Reprinted with permission from Ref. [62]; Copyright (2023) Wiley-VCH GmbH).

位制备技术, 可使MOF与高分子之间形成更紧密的结合, 提高材料的稳定性和功能性^[61]. Wang等受珍珠层启发, 在基材上构建可模拟天然珍珠层的水凝胶, 靶向海藻酸盐中的金属离子, 在沉

积有机连接剂后原位生成了纳米级MOF, 成功得到了高度有序的珍珠水凝胶MOF涂层(图2(b))^[62].

相较于共混法, 原位生长能够提供分布较为均匀的活性位点以供MOF的成核以及结晶生长.

但目前为止大多数MOF生长条件苛刻,使得这一方法在实际应用中受到一定限制.

1.3 表面修饰法

表面修饰法是对MOF或高分子的表面进行化学修饰,以便通过化学键将两者连接起来^[63],主要包括:(1)利用高分子配体来合成,即合成前修饰;(2)利用MOF表面基团来合成,即合成后修饰.

合成前修饰,即先制备聚合物有机配体,再将其与金属离子结合制备MOF.如Johnson等^[64]利用嵌段聚合物配体制备了polyMOF-5纳米颗粒;Cohen等^[65]将金属离子与柔性聚合物配体结合制备了block co-polyMOFs.基于合成前修饰策略能够制备结构更稳定的MOF材料,主要因为聚合物有机配体的稳定性要明显优于小分子有机配体.然而,此策略下的抗菌性能研究有待开发,且聚合物有机配体的设计较为困难.

合成后修饰的应用更为普遍,通过对MOF表面进行修饰,使其带有与高分子反应的官能团,然后再与聚合物连接.其中UiO-66-NH₂就是一类典型的可修饰材料,其表面裸露的氨基可与多种聚合物链进行反应^[66].例如,Zhang等^[67]使用UiO-66-NH₂、超支化聚酰胺胺、二乙烯三胺和对苯二醛构建出一系列超交联超支化聚合物@金属有机膜(HHMOP),该材料展现出可调的机械性能、优良的自愈合性能和生物活性.Li等^[68]通过静电纺丝技术在纤维基底成功修饰了一层致密的MOF层,如图3所示,其表面的MOF防护层不仅优化了Cu²⁺的释放,还赋予了静电纺丝纤维优异的抗菌性和良好的生物相容性.

与共混法和原位生长法对比,表面修饰法通过在MOF与聚合物之间构建紧密联系,使其形成更为牢固的界面连接.后续应关注合成前修饰策略,设计功能聚合物有机配体,以提升材料的稳定性和抗菌活性.

2 MOF基高分子抗菌材料的抗菌机理

在MOF基高分子抗菌材料中,引入高分子不仅作为简单的“桥梁”连接MOF及多种功能组分,更通过多种机制,主动且协同增强材料的综合抗菌性能.其中高分子材料的作用主要有以下3点:(1)形成致密的高分子膜或水凝胶网

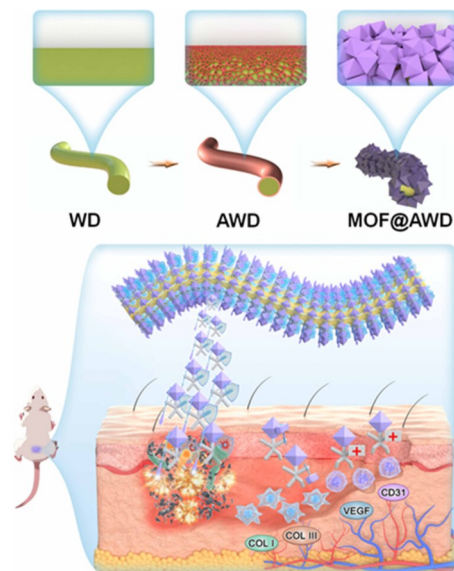


Fig. 3 The Cu-MOF armor (Reprinted with permission from Ref. [68]; Copyright (2025) American Chemical Society).

络,物理性阻隔细菌的附着和侵入;(2)高分子基质包裹MOF颗粒,控制金属离子或功能分子的释放速率^[69],实现长效抗菌,并避免MOF在复杂环境中过快分解.(3)许多高分子本身具有抗菌性,当其与MOF复合后,能够提供接触式抗菌表面.

如图4所示,MOF基高分子材料的抗菌作用可分为以下3类:一是光驱动抗菌,在纤维等高分子中引入MOF,利用MOF在光照下可作为高效光敏剂,产生ROS,对细菌进行光动力或热效应杀菌,造成细菌结构的不可逆氧化损伤(图4(a)),提升MOF柔性的同时拓宽纤维等的应用领域;二是在MOF表面引入高分子,调控金属离子(如Zn²⁺、Cu²⁺等)的释放速率(图4(b)),破坏细菌细胞膜完整性并干扰其内酶的正常活性;三是协同抗菌,上述2种机制与活性高分子之间的协同作用,形成“1+1>2”的协同杀菌效果.其中,协同抗菌主要是物理作用和其他机制的共同作用.典型的物理杀菌有:MOF尖锐的表面或聚合物经过调控后的特异形状能够通过物理作用破坏细菌细胞壁/膜从而杀灭细菌(图4(c)).另外,高分子所赋予材料的亲疏水性能、表面正电荷(图4(d))等也能发挥较好的抗菌效果.

2.1 光驱动抗菌

MOF基高分子材料的光驱动抗菌作用主要基于2种机制:光动力疗法(PDT)与光热效应(PTT)^[70-72].而MOF的引入可以促进材料对可见

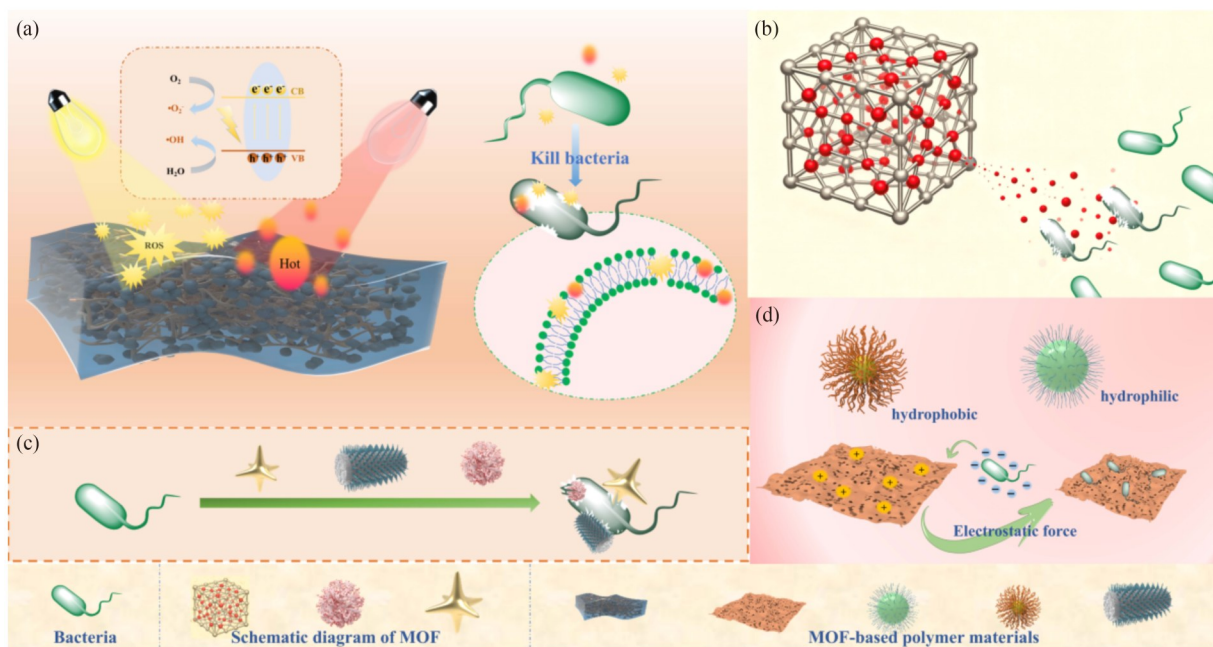


Fig. 4 Schematic diagram of antibacterial mechanisms of MOF-based polymer materials. (a) Photothermal synergistic antibacterial; (b) Antibacterial *via* metal ion release; (c) Antibacterial *via* sharp morphology; (d) Antibacterial *via* hydrophilic-hydrophobic property and electrostatic interaction.

光的响应, 进而增强抗菌活性. PDT是一种基于光敏剂、光源和氧分子三者协同作用的非侵入性治疗技术, 通过光化学反应产生ROS^[73]选择性杀伤病变细胞(如肿瘤细胞、细菌或真菌). MOF材料中的光敏剂(如卟啉配体^[74]、TiO₂^[75])在自然光或特定波长光照下被激发, 通过能量转移或电子跃迁产生ROS. 而引入的聚合物还可以通过封装或者负载的形式引入光敏性单体从而在光照下产生ROS(如, ·O₂⁻、·OH), 进而产生氧化应激作用. 其中, ·O₂⁻还可通过还原或歧化反应生成H₂O₂^[76], 能以类似的氧化机制杀灭细菌. PTT是指利用热能杀菌, MOF基高分子材料中的光热组分(如碳骨架、金属纳米颗粒)吸收光能并转化为热能, 通过局部高温破坏细菌膜结构^[77]. 如将封装了碘的复合材料(AuNR@SiO₂@UiO-66)整合到聚偏二氟乙烯(PVDF)薄膜中, 形成碘基抗菌薄膜(图5(a))^[78], 拓宽了PVDF薄膜的应用. 目前, MOF基高分子材料的光驱动抗菌策略主要依赖于紫外或可见光激发, 这些光源的组织穿透能力有限. 并且这种借助光驱动的抗菌机制, 需要引入光敏剂或者调节材料的带隙能, 以满足对可见光的响应. 因此, 以光驱动抗菌为主要机制的材料亟需在能带结构、稳定性及环境适应性等方面实现进一步突破.

2.2 金属离子释放抗菌

MOF基高分子材料中金属离子主要有3种存在形式: (1) MOF自身结构中的金属离子^[79]. 高分子材料与MOF结合后, 调控MOF中金属离子(Ag⁺、Cu²⁺、Zn²⁺)的释放速率, 进而有效抑制细菌的生长繁殖^[80]. 例如, 银基MOF释放Ag⁺, 可与细菌细胞膜上的蛋白质巯基结合, 干扰细胞的正常代谢, 对革兰氏阴性菌和阳性菌都有较强的抑制作用^[81]; 铜基MOF所释放的Cu²⁺, 能通过氧化应激反应产生ROS从而达到广谱抗菌性的效果^[82]; 钼基MOF(如UiO-66)能够通过阻止细菌粘附和繁殖来实现抗菌(图5(b))^[83,84]. (2) MOF利用自身的多孔结构富集金属离子. 此时, 引入的高分子与(1)中的效果一致. MOF的微/介孔结构(UiO-66, 0.8 nm; Ag-MOF, 1.2 nm)可富集金属离子, 形成局部高浓度区域, 显著提升与细菌的接触概率, 放大抗菌效应^[85,86]. (3) MOF中的金属离子可与聚合物中的部分结构形成配位键, 不仅可解决MOF的团聚, 还能有效改善因金属离子过渡释放造成的毒性问题^[87].

2.3 协同抗菌

MOF基高分子材料的协同抗菌效果主要体现在“1 + 1 > 2”的作用. 典型的协同机制源自于以下2种结合: (1) “物理作用”, 主要指通过

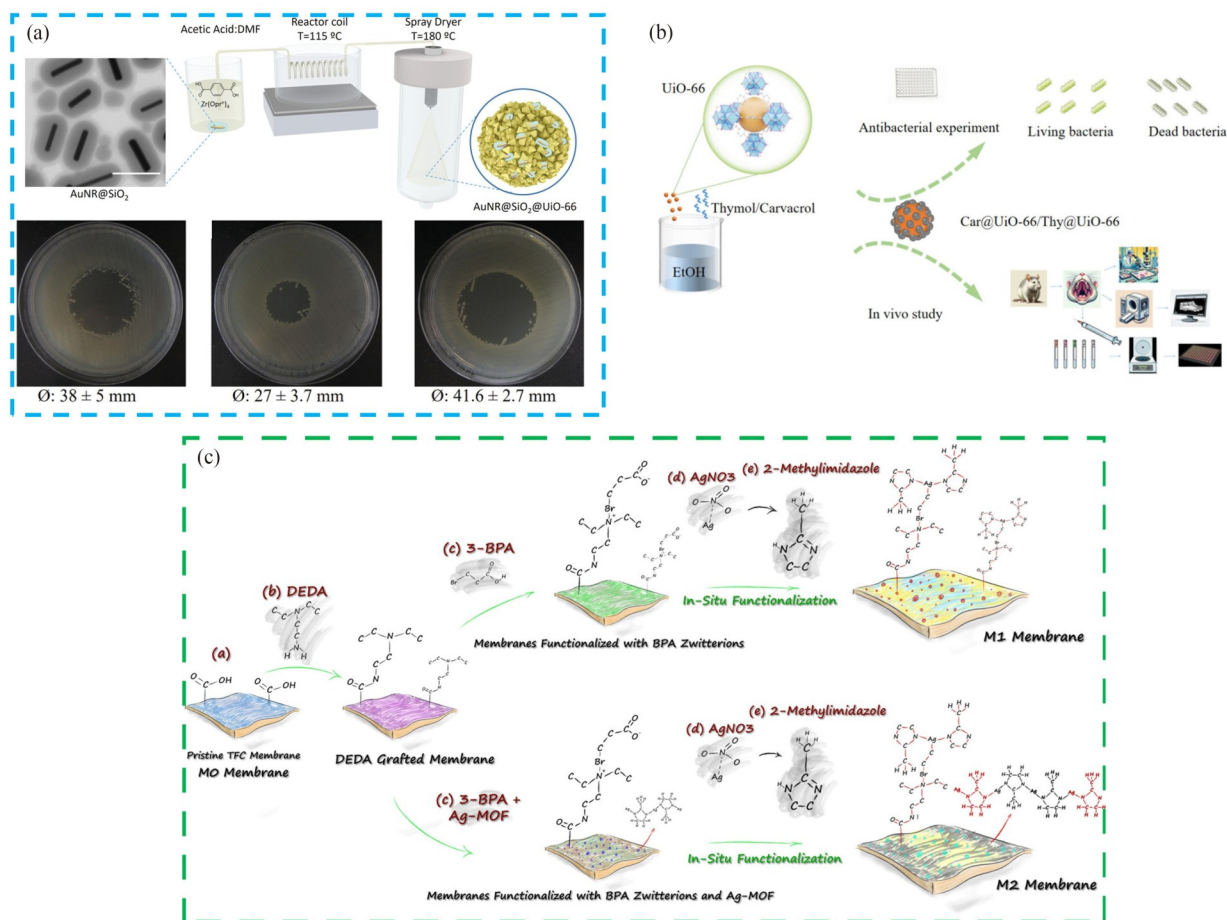


Fig. 5 (a) Schematic illustration of the spray-drying synthesis of AuNR@SiO₂@UiO-66 microbeads and the inhibitory effect of the product on *Escherichia coli* in different environments (Reprinted with permission from Ref. [78]; Copyright (2022) Open Access); (b) Car@UiO-66 and Thy@UiO-66 promising candidates for the treatment of oral infectious diseases and repairing bone defects (Reprinted with permission from Ref. [84]; Copyright (2024) American Chemical Society); (c) Illustrative scheme of the steps involved in the preparation of ZW-Ag-2MI nanocomposites starting (Reprinted with permission from Ref. [90]; Copyright (2020) American Chemical Society).

材料表面亲疏水性、水合层、电荷状态、形貌/屏障效应等非化学共价作用减少细菌吸附/定殖；(2) “高分子抗菌剂”的作用，主要包括两性离子聚合物、亲水聚合物(如聚多巴胺、PEG)、天然高分子(如甲壳素)、杂环聚合物、阳离子聚合物等发挥的抗菌活性。通过结合上述2种作用，可实现高分子抗菌+MOF内源性抗菌机制的有效协同，既能减少细菌的粘附，又能有效杀灭已附着的细菌，进而显著提升抗菌持久性和生物安全性^[88,89]。

基于高分子的亲水结构与MOF中金属离子的释放协同杀菌。一方面，两性离子或亲水高分子通过电荷、羟基、氨基等基团结合水分子，在材料表面形成致密水合层，以物理性阻隔细菌及有机污垢的接近与附着；另一方面，由高分子锚

定的MOF可持续释放金属离子，对少数突破水合层屏障的细菌进行高效清除，从而实现“防附-杀菌”的协同增强效果，如Ag-MOF与两性离子液体结合的协同抗菌(图5(c))^[90]。这种策略不仅可以保障金属离子的缓慢释放，减缓毒性作用，还可以发挥二者的协同杀菌作用，实现高效杀菌效果。

含有丰富孔道结构的MOF可作为主体结构，与引入的客体抗菌小分子的缓释之间的协同杀菌。Chen等^[91]对含端基结构的MOF进行双键化改性，将其与pH响应性单体聚合，通过调控pH控制内包抗菌小分子的释放，进而发挥与MOF协同抗菌的作用。此外，还可将MOF作为抗菌聚合物的主体结构，引入具有抗菌活性的高分子，进而发挥二者的协同抗菌作用。Wang等^[92]将阳

离子聚合物引入MOF中,发挥金属离子释放和阳离子协同抗菌的作用.并且,他们将海藻酸用于形貌诱导剂,通过丙烯酸酯噻唑的原位聚合成

功得到了具有自驱动效应的双金属有机框架微马达材料,以此实现协同捕获和杀菌(图6(a))^[93].

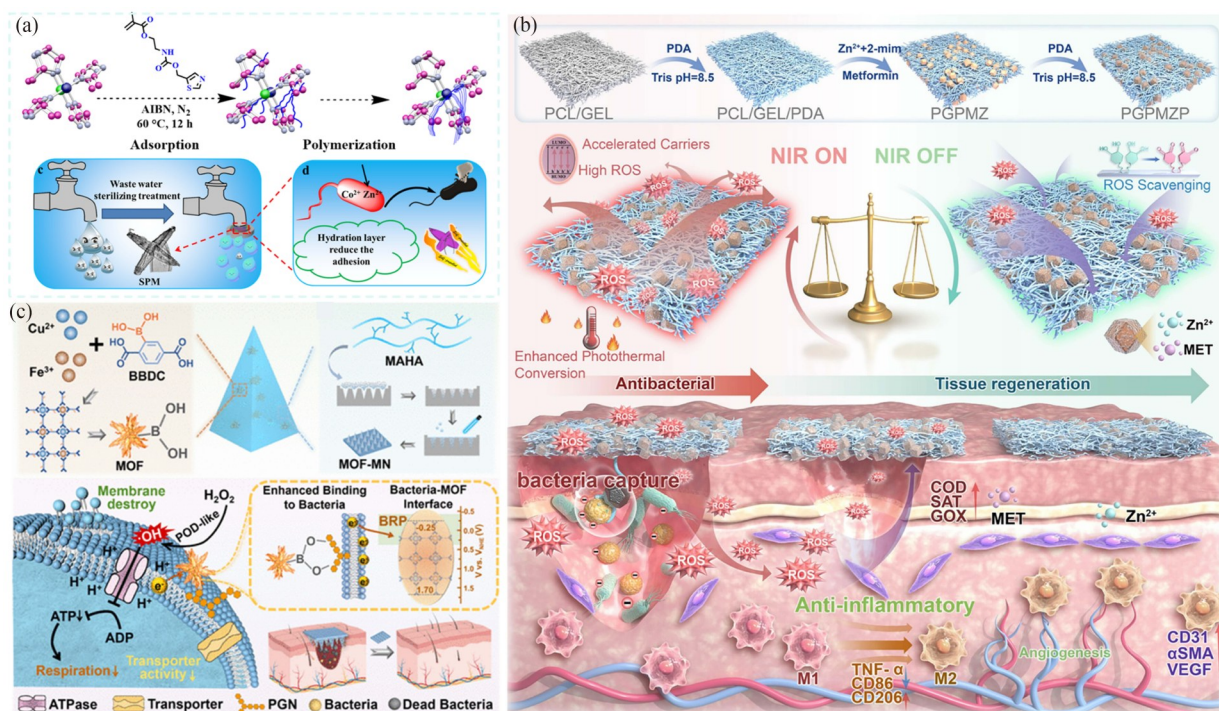


Fig. 6 (a) Self-propelled bimetallic MOF with synergistic capture-and-kill capabilities (Reproduced with permission from Ref. [93]; Copyright (2023) The Royal Society of Chemistry); (b) Synthesis, functional attributes, and biological effects of the PGMZP material (Reprinted with permission from Ref. [95]; Copyright (2025) American Chemical Society); (c) Schematic illustration of the preparation of Fe/Cu-BBDC nanozyme-integrated microneedle patches and its application in combating bacterial infection and promoting wound healing (Reprinted with permission from Ref. [99]; Copyright (2025) American Chemical Society).

以天然高分子(如甲壳素、纤维素)为载体构建协同抗菌体系.天然高分子在提供亲水、生物相容且稳定的纤维/多孔结构,以物理作用抑制细菌定殖的同时,也提升了材料的可加工性,在食品保鲜和医用领域发挥抗菌功效^[94].

ROS与MOF的协同抗菌.近红外光响应体系(如聚多巴胺(PDA)、阳离子染料修饰高分子)可对光照产生智能响应,进而可控产生抗菌因子,实现“光控防黏附-杀菌-促愈合”的协同增强(图6(b))^[95].

除此之外,具备纳米尺寸和特殊结构的MOF可促进其与细菌间的相互作用(图6(c))^[96,97],高分子诱导产生的尖锐形貌发挥尺寸效应和物理作用的协同杀菌效果^[98,99].

单一抗菌机制抗菌活性不强,抗菌耐久性较差,协同抗菌不仅能提升抗菌性能,还可引入催化降解、养分缓释等其他功能活性,为设计和构

建高效、安全的抗菌材料提供了理论基础与设计方向.

3 MOF基高分子抗菌材料的应用

高分子材料的引入拓展了MOF材料的应用领域,主要包括传感、储能、环境修复和抗菌等领域.本综述以其在抗菌织物、抗菌涂层、抗菌包装薄膜、智能可穿戴抗菌材料领域的应用为例,展开详细的介绍.

3.1 MOF基抗菌织物

MOF基抗菌织物的应用主要涉及以下2种:(1)通过原位生长技术,将MOF纳米颗粒均匀地生长在织物表面,发挥其抗菌作用.这种方法既能解决MOF纳米颗粒的团聚问题,又能提升纤维材料的抗菌应用效果.如Diao等^[100]通过简单的配位工艺合成了一种由Cu-MOF和L-半胱氨酸(L-Cys)形成的新型L-Cys@Cu-MOF,并将其嵌

入棉纤维表面得到了具有抗菌活性的纤维材料. 该织物对大肠杆菌(*E. coli*)和金黄色葡萄球菌(*S. aureus*)的抑制率近100%, 10 min内可完全灭活phi-X174噬菌体, 对H1N1-PR8流感病毒(类SARS-CoV-2)也能高效灭活, 无血凝反应和病毒感染活性. 此外通过共价键将MOF纳米纤维固定在织物表面这一举措, 大幅提升了其使用寿命, 使织物经200次摩擦或50次洗涤循环后, 抗菌抗病毒性能几乎无衰减, 细菌减少率仍保持100%, 抗病毒能力依旧显著, 解决了传统防护织物(如口罩熔喷布)仅能物理过滤病原体, 易引发交叉感染^[101]的问题.

(2) 基于化学修饰改性的原位合成策略, 能

够有效避免MOF纳米颗粒在织物表面的脱落问题. 例如, Wei等^[102]开发了一种基于重氮化学的通用策略, 即ZIF-67在羧基化棉织物表面原位生长, 形成共价结合的MOF涂层(ZIF-67-CT), 再通过浸泡负载香芹酚(carvacrol)等精油, 获得ZIF-67-CT/Carvacrol复合材料(图7). 该材料对*E. coli*和*S. aureus*抗菌效率达99.99%; 与ZIF-67-CT依赖钴离子杀菌相比, 负载香芹酚后形成“钴离子+精油”协同抗菌作用. 除抗菌外, ZIF-67-CT/Carvacrol还具备超疏水、自清洁、防污、油水分离、抗紫外、抗结冰、降解有机污染物等多重实用功能, 突破了传统织物“功能单一或功能冲突”的局限.

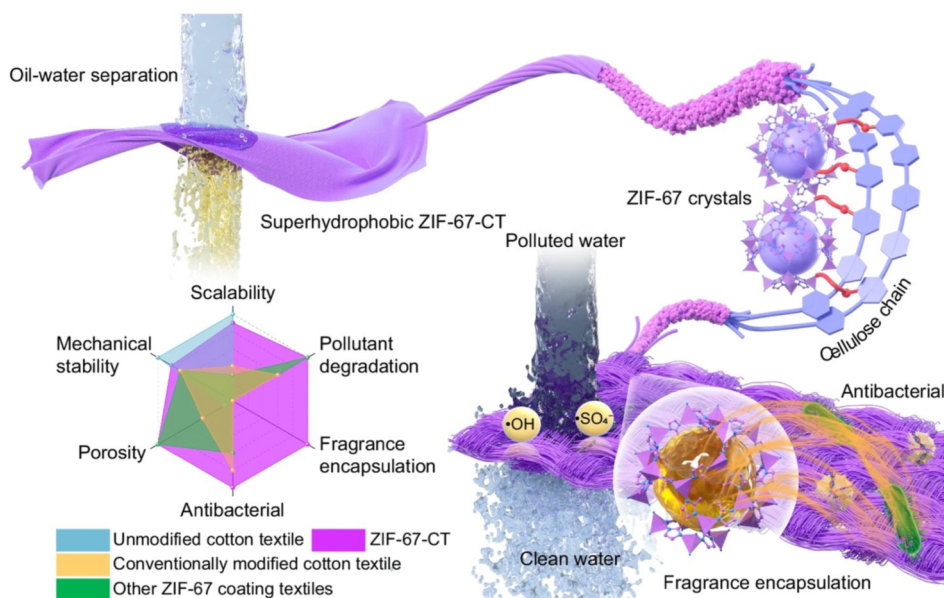


Fig. 7 The preparation of scalable manufacture washable MOFs-textiles and their application (Reprinted with permission from Ref. [102]; Copyright (2024) Open Access).

3.2 MOF基抗菌涂层

基于MOF材料的抗菌涂层主要分为3类: 基于金属离子释放、基于光动力和基于光热效应^[103]. Xu等^[98]受天然生物被膜的自调节解体过程的启发, 首次开发出一种基于 Cu^{2+} 与D型氨基酸功能单元的手性MOF涂层(DMOF). 该研究首先构筑了简便通用的无定形金属多酚网络(MPN), 用于稳定锚定 Cu^{2+} 成核位点, 在手性氨基酸介导作用下, 构建了手性MOF基复合涂层(MPN-DMOF). MPN-DMOF中的D-氨基酸配体使得涂层具有广泛的生物膜扩散信号, 促进了铜催化的化学动力学反应和本身的机械杀菌活性, 这种协同机制产生了优异的抗生物污染功效, 增

强了广谱抗菌活性.

Mo等通过简单的喷涂法, 成功制备了一种含聚苯硫化物(PPS)和巴西棕榈蜡(CW)抗菌多功能涂层 UiO66@Ag/CW/PPS , 该涂层具有耐腐蚀性、自清洁性的无氟超疏水抗菌多功能涂层 UiO66@Ag/CW/PPS ^[104]. 所制备的涂层除了优异的防水性能外, 还具备物理防护和化学灭菌相结合的双重抗菌附着机制, 对*E. coli*和*S. aureus*均有强灭杀效果. MOF基高分子抗菌涂层通过其可定制的结构和多重协同机制, 实现了从“被动防护”到“智能主动防御”的跨越, 并且在长效性、安全性以及功能集成方面展现出显著优势, 是下一代高性能抗菌涂层的重要发展方向.

3.3 MOF基抗菌包装膜

食品行业对保鲜的需求明显,促进了食品行业对性能优异的包装材料的需求,以有效防止或减缓食物的腐败和变质速度.因此,MOF凭借其自身优势结合高分子材料在食品包装领域展现出关键潜力.Xiyanu等^[105]采用ZIF-67、单宁酸(TA)和几丁质纳米纤维(CNF)合成了多功能MOF纳米复合材料(ZIF-67@TA/CNF).在酸性条件下,纳米复合材料降解,进而释放具有强抗菌性能的 Co^{2+} 和TA,通过破坏生物膜、损伤细菌细胞膜等干扰细菌细胞的正常代谢,在草莓保鲜方面应用效果良好.Zhao等^[106]以超声法合成的Cu-MOF(对苯二甲酸为配体)作为功能填料,通过溶液流延技术将其均匀分散于壳聚糖/明胶(CS/Gel)基质中,形成了CS/Gel@Cu-MOF复合膜.经过纸片扩散法和菌落计数法验证,该薄膜对*E.coli*杀菌率达94.2%,对*S.aureus*杀菌率达99.6%.其抗菌机制源于Cu-MOF缓慢释放的 Cu^{2+} .此外,Cu-MOF的加入显著提高了薄膜的机械强度(拉伸强度较纯CS/Gel膜提升68.49%)、氧和水蒸气阻隔性,还赋予其优异的紫外线屏蔽能力.2023年Kathuria等^[107]综述了MOF在食品接触应用中的研究进展,详细介绍了适用于食品领域的MOF种类,阐述了其在食品包装中的应用、生物相容性和细胞毒性.2025年,Xie等^[108]总结了MOF可作为天然抗菌剂/抗氧化剂载体,在高分子封装作用下不仅能实现控释,还可吸附乙烯与有害气体、实时监测果蔬新鲜度及农药残留,并调节包装膜的阻隔与力学性能.在食品保鲜领域,未来应进一步研究其长期毒性和作用机制,开发绿色、稳定、生物相容性好的MOF基高分子抗菌材料,助力其在食品保鲜领域的实际应用.

3.4 MOF基智能可穿戴抗菌材料

Wang等^[109]基于具有良好生物相容性和降解—重建特性的2种生物分子金属—有机框架(Bio-MOFs),构建了一种自供电多功能柔性可穿戴设备.将具有高压电响应的Zn-Car_MOF(有机配体为肌肽(Car))与图案化聚二甲硅氧烷(PDMS)膜结合,制备出具有协同输出的摩擦—压电混合纳米发电机(TPHG),可用于环境能量收集和生物医学传感器.另外,合成的六棱柱形Cu-HHTP_MOF(有机配体为2,3,6,7,10,11-六羟基三苯(HHTP))能够在电催化条件下产生 H_2O_2 和

ROS($^1\text{O}_2$ 和 $\cdot\text{OH}$)用于高效杀菌.此外,将百里酚(Thy)负载于Cu-HHTP_MOF的腔体内,与自供电柔性Zn-Car_TPHG器件相结合,实现了高效的ROS氧化损伤和药物释放协同广谱杀菌治疗.此类柔性的可穿戴材料的制备可通过步态监测和识别提供全面的用户信息,使得其在结合人工智能的医疗诊断和基于互联网的远程监控方面展示了良好的应用前景.

4 总结与展望

细菌感染已成为全球公共卫生领域的重大威胁,抗生素滥用导致的耐药问题更是日益凸显,传统抗菌药物疗效持续衰减,开发新型、高效且不易引发耐药性的抗菌材料已成为当前研究热点.MOF基高分子材料结合了MOF独特的多孔结构、可控的金属中心活性位点,以及高分子材料的功能性和可加工性,展现出作为高性能抗菌材料的潜力.本文围绕MOF基高分子抗菌材料的合成策略、抗菌机理及其在织物、涂层、包装等方面的应用展开综述.与其他抗菌材料相比,MOF基高分子抗菌材料优势明显,但在结构稳定的材料合成、生物相容性和抗菌持久性、抗菌机制以及应用拓展等方面还需要深入开展相关研究,具体如下:

(1)在合成方面,基于非共价键策略合成的MOF基高分子抗菌材料存在活性位点易流失、抗菌持久性不足等问题.虽然共价键策略已经被用于调控MOF的抗菌耐久性,但基于内包抗菌剂释放的杀菌机制,材料会随着抗菌小分子的耗散而失去抗菌活性.为此,应重点研究MOF与高分子之间的界面相容性问题,设计合成结构稳定、长效抗菌的MOF基高分子抗菌材料.

(2)在抗菌机制方面,MOF基高分子材料在细胞与分子水平的抗菌机制尚不完全明确.未来研究应以明晰抗菌机理为目标,结合表征分析和理论计算模拟动态杀菌过程,进而指导新型MOF基高分子抗菌材料的设计与制备.

(3)MOF基高分子抗菌材料潜在应用广泛,能够涵盖MOF和高分子的典型应用领域.因此,后续研究应以实际应用为导向,结合环境适应性、持久抗菌性、生物相容性等需求开展抗菌材料的设计和应用研究,进一步拓展MOF基高分子抗菌材料的应用范围.



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Review

Research Progress on the Synthesis and Application of Metal-Organic Framework-based Polymeric Antibacterial Materials

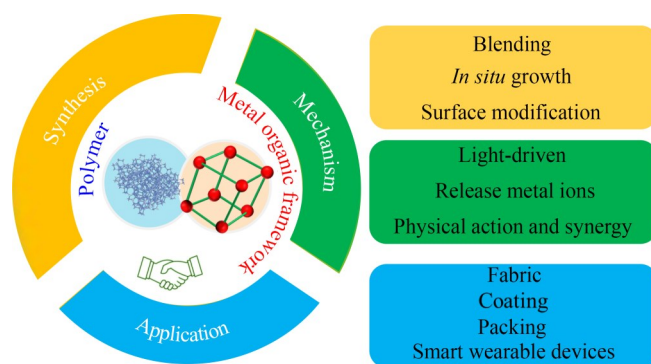
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Abstract Metal-organic frameworks (MOFs) have highly ordered porous structures and ultra-large specific surface areas, attracting extensive attention in materials science. However, challenges remain in their antibacterial applications, such as insufficient structural stability, limited biocompatibility, and difficulty in precisely controlling the release behavior. Integrating MOFs with polymeric materials can enhance their antibacterial performance, improve processability, and reduce biological toxicity. Therefore, the preparation of MOF-based polymers can effectively expand the scope of MOF applications. This paper reviews the research progress on MOF-based polymeric antibacterial materials over the past five years in terms of synthesis strategies, antibacterial mechanisms, and applications, providing a reference for designing and developing high-performance MOF-based antibacterial materials.

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Keywords MOF-based polymer; Antibacterial materials; Synthesis strategy; Antibacterial mechanism; Application progress