

基于 MOFs 传感器的食品细菌污染检测研究进展

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摘要 食品细菌污染检测方法的研究对降低食源性疾病爆发和食品腐败具有重要意义。金属有机骨架(MOFs)是由金属离子或金属离子簇和多重有机配体通过配位形成的结构高度有序的晶体配位聚合物。基于 MOFs 独特的结构和特性,构建了荧光传感器、比色传感器、电化学传感器等多种传感检测系统,并对食品细菌污染进行检测。本文主要介绍 MOFs 的传感器类型、构成要素以及基于 MOFs 传感器的食品细菌污染检测方法研究进展,指出 MOFs 传感器检测方法的局限性以及未来发展方向。

关键词 金属有机骨架; 传感器; 细菌污染; 检测; 食品

文章编号 1009-7848(2022)06-0423-12 **DOI:** 10.16429/j.1009-7848.2022.06.043

近年来,由食品细菌污染引起的食品安全事件引起各国政府和消费者对食品质量与安全的高度关注^[1]。这些污染细菌不但可使食品腐败变质,还会引发食源性疾病爆发,给社会经济和医疗体系带来严重负担^[2-3]。食品中细菌污染检测方法的建立对降低食源性疾病爆发和食品腐败具有重要意义。目前,病原微生物监测多基于菌落总数和聚合酶链式反应(PCR)技术^[4-5]。一般来说,这些分析方法费时费力,难以完全满足现代食品工业快速在线检测需求。高灵敏度、快速检测、方便和适合现场实时检测的新型传感技术研发成为当前的关注点。

传感器是利用传感元件与目标物特异性结合后通过光电、光物理或机械特性等信号对物质进行监测的装置,通常由感测单元和转换单元组成^[6]。传感器技术是现代新技术革命的重要基础,是自动检测技术不可或缺的重要组成部分。灵敏度、选择性、响应时间、稳定性等是传感器重要的性能指标^[7-8]。传感材料的选择和设计是决定传感器性能的关键。目前,多种具有不同特性的纳米材料被用于食品污染物传感器设计中,如碳基纳米

材料(碳点、碳纳米管、石墨烯及其氧化物),金属/金属氧化物,量子点和上转换纳米粒子^[9-13]等,这些性能优异传感材料的开发极大促进了传感器的研究和应用。

金属有机骨架(Metal-organic frameworks, MOFs)又称多孔配位聚合物(Coordination polymers, CPs),是一类由金属离子或金属离子簇与多重有机连接剂通过配位作用形成的结构均匀杂化多孔材料^[14]。可通过改变金属离子、有机连接剂及次级结构单元种类获得具有不同结构及理化性质的 MOFs^[15]。与其它纳米材料相比,MOFs 孔隙率高、比表面积大、结构可调、催化活性高、易修饰、光电信号稳定,已成为光电型传感器的理想传感元件^[16]。MOFs 被广泛用于气体吸附^[17-18],传感器构建^[19-20],药物释放^[21-22],分离^[23-24]和催化^[25-26]等领域。

目前,多种基于 MOFs 传感器的检测方法用于食源性致病菌检测,为食品中细菌污染的早期监测提供了新的技术手段。本文综述 MOFs 传感器的主要种类及其在食品细菌污染检测方面的最新研究进展,指出 MOFs 传感器检测方法的局限性和未来发展方向。

收稿日期: 2021-06-21

基金项目: “十三五”国家质量重点研发计划重点专项
(2017YFF0211300)

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1 MOFs 传感器种类

1.1 发光传感器

MOFs 发光可由有机配体(含共轭 π 键化合物,如芳香族化合物)、中心金属离子(如镧系元素

或金属离子团簇等)、中心离子与配体间电子转移或封装于 MOFs 中的发光客体(如量子点)实现^[27]。当 MOFs 通过自身孔隙结构或修饰于其表面的分子识别元件与目标物结合时,MOFs 可产生两种信号变化,一种为“信号关闭”,即 MOFs 发光强度降低或衰减,这主要是由于目标物通过电子转移、竞争吸收和(或)荧光共振能量转移使 MOFs 发生荧光淬灭;另一种为暗背景下的“信号开启”,即目标物与 MOFs 结合后发生荧光发射强度增强、发射波长移动或产生新的荧光发生峰^[28-30]。当前,制备的 MOFs 材料多以单发射中心为主,基于这种材料构建的发光传感检测方法易受外界环境的影响。研发构建具有多发射中心的 MOFs 发光传感器,建立比率荧光检测方法是提高分析选择性、灵敏度、抗干扰能力的有效方法^[31]。

1.2 电化学传感器

电化学传感器是基于电化学系统中分析物的氧化还原反应来工作的,其检测限和灵敏度很大程度上取决于信号转换器的电化学性能^[7]。MOFs 具有较大的表面积,可调的孔隙率和空腔结构等独特结构优势,使其在电化学传感应用中显示出巨大潜力。然而,大多数 MOFs 材料是绝缘体或半导体,因此增强其电化学性能是当前需要解决的关键问题^[32]。导电配体和金属节点之间形成长距离离域电子是提高电荷迁移率的可行方法,因此可以将活性金属离子或配体作为结构单元引入 MOFs 以获得氧化还原或催化活性位点^[33]。此外,MOFs 与其它功能材料(如碳基质,金属及金属氧化物纳米颗粒,酶,聚合物和导电性基质)构建复合材料也是提高其导电性、机械稳定性和催化能力等性能的有效方法^[34-39]。

1.3 比色传感器

比色传感器是以颜色变化为响应信号来指示分析物的传感器,具有操作简单、检测快速、不需要任何复杂仪器等特点,且适合现场快速检测。基于 MOFs 纳米酶的比色传感器稳定性好,易制备,结构组成可控、催化活性可调,是一种理想的比色检测工具^[40-41]。研究表明,Cu-MOF/Fe-MOF 纳米粒子具有过氧化物酶活性,在 H_2O_2 存在下能催化 3,3',5,5'-四甲基联苯胺(TMB)产生显色反应,基于该原理已实现对多种物质的比色检测^[42-43]。

1.4 表面增强拉曼光谱

表面增强拉曼光谱(Surface-enhanced Raman scattering, SERS)是一种超灵敏振动光谱分析技术,该方法具有样品消耗量少,响应迅速,无损分析、高特异性等特点。SERS 检测性能很大程度上依赖于活性基底的信号增强能力^[44-46],MOFs 以其独特的理化特性满足了高效 SERS 基底需求。MOFs-SERS 技术不仅可以提供超灵敏的指纹图谱,而且具有分子富集,选择吸附,气体传感和信号增强等能力^[47]。MOFs 基底在 SERS 检测分析中探索应用极大的推动了 SERS 技术应用范围。

2 MOFs 复合材料种类

为改进 MOFs 电导率、电催化性能、机械稳定性及水环境稳定性,多种材料如碳基材料、金属纳米粒子、金属氧化物、量子点等已成功与 MOFs 复合,大大提高了金属有机骨架材料的各种性能,扩大了应用范围^[48-49]。

2.1 碳基材料

碳基材料包括碳纳米管、石墨烯、氧化石墨烯等,是一种低成本、高电导率、理化性质稳定、光学性能优越的新型材料^[39,50-53]。MOFs 与碳基材料结合可以增强其稳定性和导电性能,极大促进了其在电化学分析中的应用。Lu 等^[54]通过原位合成技术制备了 MOFs-石墨烯气凝胶(UiO-66-NH₂-GA)复合材料,该复合材料中 GA(Graphene aerogel)不仅充当主链,而且通过加速基体的电子转移增强了复合材料的电导率,并构建了性能稳定、高灵敏度的 UiO-66-NH₂-GA 电化学传感器。碳基材料还可改进 MOFs 材料的发光特性,Jalili 等^[51]将发射黄光和蓝光的双色碳点封装到 ZIF-8 骨架材料中,制备了双发射波长 MOFs (BYCDs @ ZIF-8)荧光传感器,该传感器通过 MOFs 的尺寸选择性与目标物结合,通过荧光强度变化实现目标物含量的可靠检测。此外,碳基材料还具有模板效应,可影响所合成 MOFs 尺寸和形貌特征^[51]。

2.2 金属/金属氧化物纳米粒子

金属/金属氧化物纳米材料具有电导性好、比表面积高、生物相容性好等优点,成为 MOFs 复合材料研究的热点。此外,部分金属纳米粒子还具有独特的光谱特性和磁性,增加了 MOFs 传感复合

材料的选择空间^[49,56-57]。MOFs 利用自身独特的孔隙结构封装金属/金属氧化物纳米粒子后,有效避免了游离金属/金属氧化物纳米粒子的聚集,并且提高了 MOFs 材料的电化学性质^[58]。Chen 等^[59]构建了一种基于金纳米粒子(AuNP)修饰的Cu-MOF 的电化学传感平台,该平台对亚硝酸盐具有较高的灵敏度,检测限为 82 nmol/L。Ma 等^[60]将双发射碳点和 Fe₃O₄ 磁性纳米颗粒封装到 MOFs 材料中,构建了一种新型磁性比率荧光纳米探针。该纳米探针结合了磁分离和比率传感的双重优势,实现了对 HClO 的灵敏检测。此外,MOFs 材料具有分子富集与尺寸选择能力,与等离子体金属纳米材料(Cu,Ag,Au 等)结合后可进一步增强 SERS 的信号强度^[47]。Cai 等^[61]采用层层组装方式合成了 Au@MIL-101 纳米 MOFs 材料,MOFs 表面的羧基基团与乌洛托品之间的强结合作用拉近了“热点”与目标物的距离,显著增强了乌洛托品的拉曼散射光谱信号强度,大大提高了 SERS 检测方法的灵敏度。

2.3 量子点

量子点是具有独特光电性质的半导体纳米晶,尺寸为 2~10 nm,该材料具有高光稳定性、高量子产率、高摩尔消光系数、低成本等优点^[49,62-63]。量子点所特有的尺寸限域使其具有量子效应,包括表面效应、量子尺寸效应等,这种性能已广泛用于传感、催化和显示成像等领域^[64-67]。量子点与 MOFs 材料的杂化复合不但减少了量子点的表面缺陷,提高了系统荧光量子产率,还赋予了 MOFs 材料新的光电性能^[62]。Chen 等^[68]通过直接浸渍法,将平均尺寸为 3.1 nm 的石墨烯量子点结合到卟啉 Zr-MOFs 中,得到石墨烯量子点@Zr-MOF 复合材料。该复合材料孔隙率变小,电导率却是 Zr@MOF 材料的 100 倍。Chen 等^[69]在 Eu-MOF 中原位合成封装了钙钛矿量子点形成复合材料,在聚甲基丙烯酸甲酯(PMMA)薄膜制备过程中加入该复合材料成功实现了 PMMA 膜的光谱可调(红色到绿色)发射。

2.4 其它材料

除上述材料外,与 MOFs 复合的材料还包括有机染料和有机聚合物^[70-75]。Hassanzadeh 等^[71]将

过氧化氢和有机荧光染料罗丹明 B 封装到 Co-MOFs 的纳米孔中形成复合材料,并将其负载到纸上形成纸基化学发光传感器,实现了食品样品中总酚含量的灵敏检测。有机聚合物质量轻、易于生产、稳定性好,Gupta 等^[72]开发了一种基于 Cu-MOF/聚苯胺复合材料的大肠杆菌电化学生物传感器,该传感器对目标物显示出高特异性和灵敏度(检测限为 2 CFU/mL)。

3 MOFs 传感器中的分子识别元件

MOFs 通常与选择性识别元件(酶、抗体、适配体和印迹聚合物等)结合以获得满意的特异性。MOFs 中固有的孔隙率、大比表面积、表面丰富的官能团及连接剂的共轭结构为分子识别元件的偶联提供了有利条件。

3.1 酶

酶是一种具有高催化活性和选择性的蛋白,是 MOFs 传感器中常用的一种分子识别元件。但游离状态下的酶对周围环境敏感性高、稳定性差、易变性失活,这极大限制了酶的应用范围^[50,76]。将酶固定于 MOFs 材料表面大大提高了酶的稳定性和活性,也提高了 MOFs 对目标物的选择性^[77-78]。

3.2 抗体

基于抗原抗体特异吸附原理的检测方法(酶联免疫吸附检测方法、化学发光免疫检测方法、荧光免疫检测方法等)已广泛用于食品安全检测^[79]。抗体偶联 MOFs 的传感器具有高特异性和选择性,广泛用于电化学及光学免疫传感^[80-83]。此外,将 MOF 包封酶与抗体偶联可有效改善酶联免疫吸附试验的效果^[84]。

3.3 适配体

核酸适配体(Aptamer, APT)是基于指数富集配体系统进化技术在体外寡核苷酸文库中筛选得到的一段寡核苷酸链,可通过 G-四链体(G-quadruplex)、发夹(Hairpin)、环(Loop)、假结(Pseudoknot)等结构与把目标特异性结合,是一种具有广阔应用前景的新型分子识别元件^[48,85-87]。APT 经修饰后可通过表面吸附、共价结合等方式偶联于 MOFs 材料表面,不仅可改善 APT 的生物活性,还提高了 MOFs 在电化学、比色分析、荧光

传感等分析检测过程的特异性和灵敏度^[48,86]。

3.4 印迹聚合物

分子印迹聚合物(Molecularly imprinted polymer, MIP)是一种在模板分子、功能单体、交联剂等试剂存在下通过化学或物理条件引发聚合形成的高分子聚合物,具有制备简单、耐有机溶剂、可重复使用,对目标物具有特异性识别和结合能力,是生物抗体的理想替代材料^[88-89]。目前,MIP作为分子识别元件已成功在MOFs材料表面制备,且对目标物具有更快速的传质速率,这有利于食品安全快速检测方法的建立^[90-91]。

4 食品中细菌污染的检测

4.1 金黄色葡萄球菌

金黄色葡萄球菌(*Staphylococcus aureus*, *S. aureus*)是一种常见的食源性致病微生物,分布广且毒力强,约70%的金黄色葡萄球菌在经巴氏消毒后仍可产生肠毒素引起食物中毒^[92-93]。Bhardwaj等^[94]首次利用戊二醛法将合成的MOFs(NH₂-MIL-53(Fe))材料与噬菌体偶联构建用于金黄色葡萄球菌检测的荧光生物传感器,该传感器与金黄色葡萄球菌特异性结合后可引起荧光猝灭,猝灭程度与细菌浓度有良好的相关性。研究结果显示,最优条件下建立的荧光检测方法对金黄色葡萄球菌具有优越的检测性能,检测限为31 CFU/mL,线性范围为40~4×10⁸ CFU/mL。Wang等^[95]以2-氨基对苯二甲酸为配体、以Cu(NO₃)₂为金属离子,通过混合溶剂热法合成了表面富氨基的Cu-MOFs纳米粒子,研究发现该纳米粒子具有类过氧化物酶活性,在H₂O₂存在下可催化TMB发生显色反应。然后,作者以金黄色葡萄球菌的适配体为细胞识别元件分别偶联于合成的Cu-MOFs纳米粒子和磁性Fe₃O₄纳米粒子表面,当体系中含有金黄色葡萄球菌时,这两种偶联适配体的纳米粒子都结合在目标菌表面,在磁场作用分离得到游离的Cu-MOFs纳米粒子,加入TMB催化显色,颜色深浅与体系中金黄色葡萄球菌浓度呈负相关关系。该方法结合了适配体识别技术和磁分离技术,实现了金黄色葡萄球菌的快速灵敏检测,最优条件下检测方法的检测限为20 CFU/mL,线性范围为50~1×10⁴ CFU/mL。

4.2 大肠杆菌

大肠杆菌(*Escherichia coli*, *E. coli*)是评价食品污染程度的重要指标。大肠杆菌菌株O157:H7在低剂量下也可引起严重的食源性疾病,已在世界范围内多次爆发^[96-99]。Sun等^[100]将合成的MOF(UiO-66)材料联合CRISPR-Cas9的链置换扩增和滚环扩增技术开发了一种用于大肠杆菌O157:H7的荧光检测方法。该方法以荧光染料标记的ssDNA为荧光探针,合成的UiO-66通过静电吸附作用吸附荧光探针并猝灭荧光染料荧光。大肠杆菌O157:H7目的毒力基因被CRISPR-Cas9系统识别和切割,触发链置换扩增和滚环扩增。放大反应后,大量产物与吸附在MOFs上的探针杂交,荧光恢复。该荧光检测方法灵敏度高、特异性强,在最优条件下对大肠杆菌O157:H7的检测限为40 CFU/mL,适用于实际样品检测。Zhong等^[101]通过原位包封法合成了沸石咪唑酯骨架(ZIF-8)与硫化镉量子点(CdS)的复合材料(CdS@ZIF-8),并将其作为信号放大标签用于大肠杆菌O157:H7的电化学免疫检测。首先,电极与CdS@ZIF-8表面分别修饰氨基以结合大肠杆菌抗体,加入大肠杆菌后偶联抗体的电极与CdS@ZIF-8在电极表面形成抗原-抗体夹心结构。然后,将电极浸润于HCl中,固定于电极表面的CdS@ZIF-8金属骨架材料释放出大量Cd²⁺,显著提高了差分脉冲伏安法电化学传感器检测大肠杆菌O157:H7的灵敏度,是以单一CdS量子点为信号标签构建传感器灵敏度的16倍。在最优的条件下,该方法的检测限为3 CFU/mL(S/N=3)。

4.3 铜绿假单胞菌

铜绿假单胞菌(*Pseudomonas aeruginosa*, *P. aeruginosa*)是一种典型的条件致病菌,主要影响免疫功能低下的患者,其分布广,易通过污染环境水和食物而引起感染。此外,铜绿假单胞菌在低温下仍可分解有机物,是冷鲜肉中的特定腐败菌^[102-104]。Zhang等^[105]设计合成了一种Cu-ZrMOF@APT@DNA纳米复合材料识别探针,并将其与负载有高导电性Super P和AuNP的金电极结合,构建了一种用于铜绿假单胞菌检测的新型无酶电化学传感器。该研究首先合成了具有较大表面积的ZrMOF材料,与Cu²⁺进一步偶联后获得H₂O₂催化活性,

然后再与 DNA 和铜绿假单胞菌核酸适配体偶联合成 ZrMOF@APT@DNA 纳米复合材料识别探针;电极修饰方面首先引入 Super P 炭黑以增加电极电子转移能力,再将 Au 纳米粒子固定于电极表面用于偶联铜绿假单胞菌抗体。当体系中存在铜绿假单胞菌时,适配体修饰的纳米复合材料(Zr-MOF@APT@DNA)和抗体偶联的电极与目标菌结合形成抗体-*P. aeruginosa*-APT 夹心结构,加入 H_2O_2 后, Cu^{2+} 催化 H_2O_2 分解增强电信号,显著增加了电化学传感器的检测灵敏度。最优条件下,该方法对铜绿假单胞菌检测的检测限为 2 CFU/mL(S/N=3),为食品中铜绿假单胞菌污染的高灵敏检测奠定了基础。

4.4 沙门氏菌

沙门氏菌(*Salmonella*)是导致食源性疾病的第二大病原菌,污染食品后存活时间长。蒋晓华等^[106]基于 UiO-66-NH₂ 材料构建了检测沙门氏菌的荧光生物传感器。首先,选用荧光素修饰的沙门氏菌适配体作为目标菌特异识别的信号相应部分;其次,均匀分散在溶液中的 UiO-66-NH₂ 金属骨架材料吸附适配体并猝灭其荧光;当体系中存在沙门氏菌时,沙门氏菌与适配体结合并从 MOFs 表面解脱下来,适配体上的荧光素荧光恢复。基于该作用机制建立的荧光检测方法准确可靠、特异性高、灵敏度好,最优条件下对沙门氏菌检测的检出限为 7 CFU/mL,用于虾肉中沙门氏菌检测的加标回收率为 90%~108%。

4.5 芽孢

芽孢是产芽孢菌在营养缺乏等恶劣环境中形成的细菌休眠体,抗逆性强,经高温、紫外线、电离辐射等灭杀条件下仍能存活。2,6-吡啶二羧酸(2,6-pyridinedicarboxylic acid, DPA) 是细菌芽孢的主要成分,占芽孢干重的 5%~15%^[107-109],通过对食品中 DPA 含量的分析能够预测食品受细菌污染的情况。Li 等^[110]在 ZIF-8 中原位引入罗丹明 6G(R6G)和 CdS 量子点(QD),构建了一种用于 DPA 检测的比率荧光探针。其中,R6G 的荧光不受 DPA 的影响,作为内置校正荧光;而 CdSQD 荧光可被体系中的 Eu^{3+} 猝灭,当 DPA 存在时,DPA 捕获 Eu^{3+} 使 QD 荧光恢复。该比率荧光传感器消除了复杂系统中的背景干扰,具有良好的特异性,对

DPA 的检测限为 67 nmol/L。Guo 等^[111]将 Tb^{3+} 与 L-组氨酸(His)官能化的 ZIF-8 金属有机骨架通过配位作用结合得到了一种用于 DPA 检测的复合纳米探针 His@ZIF-8/ Tb^{3+} 。 Tb^{3+} 的高配位数使之在与 His 的氨基或羧基配位后仍可与 DPA 配位。当体系中存在 DPA 时,DPA 与 Tb^{3+} 特异性结合并敏化 Tb^{3+} 发出黄绿色荧光,荧光强度与 DPA 浓度相关。研究结果显示,该检测方法对 DPA 检测的灵敏度高,检测限为 20 nmol/L。Wu 等^[112]以 Eu^{3+} 为金属离子,以 2-氨基-1,3,5-苯三羧酸(NH₂BTC)为配体合成了一种非发光 Eu-MOF(MOF1),MOF1 在 DPA 作用下可发生单晶相变,使 MOF1 转变成单晶 MOF2,并伴随着荧光强度的 10⁵ 倍增强。研究结果显示,MOF1 具有较强的抗干扰能力,对 DPA 具有高选择性和灵敏度,检测限为 3.8 μ mol/L。

4.6 脂多糖

脂多糖(Lipopolysaccharide, LPS)是一种细菌内毒素,可引发免疫系统失衡、败血症、器官衰竭,甚至死亡。作为革兰氏阴性菌外膜的主要成分,LPS 已成为革兰氏阴性菌检测的有效生物标志物^[113-114]。Shen 等^[115]建立了一种以 Au 纳米粒子修饰的铜金属-有机骨架(AuNPs/Cu-MOFs)为催化剂,靶触发二次循环信号放大的比率电化学超灵敏检测 LPS 方法。该方法具体过程如下:1)首先体系中的 LPS 与发卡探针 1(HP1)中的适配体序列结合(包括 3 个域:LPS 适配体序列,引物互补序列和探针单链颈序列)结合形成 G-四联体结构,然后引物与之结合,在聚合物酶作用下互补对从 HP1 的 3 端延伸到 5 端获得新的 DNA,此时导致 LPS 从 HP1 上脱落下来,并参与下一个循环;2)获得的 DNA 与固定于金电极表面二茂铁(Fc)标记的发卡探针 2(HP2)杂交并形成缺口位点,然后在缺口内切酶作用下,使 DNA 从杂交结构中释放出来进入下一个杂交过程,同时使二茂铁固定于电极表面的 HP2 探针上脱落;3)留在电极表面的一段 DNA 单链与 AuNPs/Cu-MOFs 修饰的 HP3 探针杂交。该检测过程中电极表面二茂铁的脱落造成电信号降低,AuNPs/Cu-MOFs 材料的结合又使电信号增强,从而实现比率电化学信号输出。在检测液中加入葡萄糖,AuNPs/Cu-MOFs 可催化葡萄糖氧化,实现信号的再次放大。该研究通过二次循

环信号放大和催化氧化信号放大显著提高了方法对 LPS 检测的灵敏度,最优条件下检出限为 0.33 fg/mL。此外,该课题组基于 Au 纳米粒子修饰的 Ce-MOFs(AuNPs/Ce-MOFs)催化性能和 Zn²⁺依赖型 DNA 酶循环切割信号放大作用设计了另一种 LPS 检测方法,最优条件下该方法对 LPS 的检出限为 3.3 fg/mL,线性范围为 10 fg/mL~100 ng/mL^[16]。

5 结论与展望

MOFs 以其独特结构和特性(可调节的孔隙结构、高比表面积、易修饰等)已构建了荧光传感器、比色传感器、电化学传感器等多种传感检测系统,并对食品细菌污染检测进行了探索。碳基材料、金属/金属氧化物纳米粒子、量子点等功能材料与 MOFs 的复合,以及酶、抗体、核酸适配体等识别元件对 MOFs 的修饰大大提高了基于该材料传感器对细菌检测的灵敏度和特异性。然而,能够应用于食品细菌污染监测的 MOFs 传感器种类依然有限,针对细菌这种单细胞生物体开发更多高效的传感器类型将对推动食品安全微生物检测技术的发展具有重要意义。

为开发新型食品细菌检测 MOFs 传感器类型,提高 MOFs 传感器在食品细菌污染监测中应用,可从以下方面进行研究:1)制备适合 SERS、石英晶体微天平、表面等离子体共振等检测技术的新型 MOFs 材料,探索将其固定于传感器表面的方法;2)合理设计 MOFs 中心金属离子和配体比例和类型,提高该材料在水环境中检测信号的稳定性;3)制备 MIP 细菌细胞识别元件,探索基于 MOFs 材料的 MIP 原位聚合、后合成修饰或封装客体的方法,构建 MIP-MOFs 传感元件;4)构建高通量、集成化、多功能、复合型 MOFs 传感器,提高传感检测方法区分活或死细菌的能力。相信随着 MOFs 合成技术的发展和理论研究的深入,该材料将在食品细菌污染监测领域展现出更广阔的发展前景。

参 考 文 献

[1] NAVARRO -GONZALEZ N, WRIGHT S, AM-INABADI P, et al. Carriage and subtypes of food-

borne pathogens identified in wild birds residing near agricultural lands in California: a repeated cross-sectional study[J]. *Applied and Environmental Microbiology*, 2020, 86(3): e01678-19.

- [2] BHARDWAJ N, BHARDWAJ S K, NAYAK M K, et al. Fluorescent nanobiosensors for the targeted detection of foodborne bacteria[J]. *TrAC Trends in Analytical Chemistry*, 2017, 97: 120-135.
- [3] ZHENG F, WANG P, LIU N, et al. Simultaneous and ultra-sensitive detection of foodborne bacteria by gold nanoparticles -amplified microcantilever array biosensor[J]. *Frontiers in Chemistry*, 2019, 7: 232.
- [4] YENI F, ACAR S, POLAT Ö G, et al. Rapid and standardized methods for detection of foodborne pathogens and mycotoxins on fresh produce[J]. *Food Control*, 2014, 40: 359-367.
- [5] WEI S, DALIRI E B M, CHELLIAH R, et al. Development of a multiplex real - time PCR for simultaneous detection of *Bacillus cereus*, *Listeria monocytogenes*, and *Staphylococcus aureus* in food samples[J]. *Journal of Food Safety*, 2019, 39(1): e12558.
- [6] FANG X, ZONG B, MAO S. Metal-organic framework-based sensors for environmental contaminant sensing[J]. *Nano-Micro Letters*, 2018, 10: 64
- [7] VIKRANT K, TSANG D C W, RAZA N, et al. Potential utility of metal-organic framework-based platform for sensing pesticides[J]. *ACS Applied Materials & Interfaces*, 2018, 10(10): 8797-8817.
- [8] KRENO L E, LEONG K, FARHA O K, et al. Metal-organic framework materials as chemical sensors[J]. *Chemical Reviews*, 2012, 112(2): 1105-1125.
- [9] LIU J M, HU Y, YANG Y K, et al. Emerging functional nanomaterials for the detection of food contaminants[J]. *Trends in Food Science & Technology*, 2018, 71: 94-106.
- [10] LIU J, CHEN Y, WANG L, et al. Modification-free fabricating ratiometric nanoprobe based on dual-emissive carbon dots for nitrite determination in food samples[J]. *Journal of Agricultural and Food Chemistry*, 2019, 67(13): 3826-3836.
- [11] PAN M, XIE X, LIU K, et al. Fluorescent carbon quantum dots-synthesis, functionalization and sensing application in food analysis [J]. *Nanomaterials*, 2020, 10(5): 930.

- [12] SCHROEDER V, SAVAGATRUP S, HE M, et al. Carbon nanotube chemical sensors[J]. *Chemical Reviews*, 2018, 119(1): 599–663.
- [13] ZHANG L, SALMAIN M, LIEDBERG B, et al. Naked eye immunosensing of food biotoxins using gold nanoparticle–antibody bioconjugates[J]. *ACS Applied Nano Materials*, 2019, 2(7): 4150–4158.
- [14] JANIAC C, VIETH J K. MOFs, MILs and more: concepts, properties and applications for porous coordination networks(PCNs)[J]. *New Journal of Chemistry*, 2010, 34(11): 2366–2388.
- [15] LI H, EDDAOUDI M, O'KEEFFE M, et al. Design and synthesis of an exceptionally stable and highly porous metal–organic framework [J]. *Nature*, 1999, 402(6759): 276–279.
- [16] KUMAR P, DEEP A, KIM K H. Metal organic frameworks for sensing applications[J]. *TrAC Trends in Analytical Chemistry*, 2015, 73: 39–53.
- [17] HAN X, YANG S, SCHRÖDER M. Porous metal–organic frameworks as emerging sorbents for clean air[J]. *Nature Reviews Chemistry*, 2019, 3(2): 108–118.
- [18] MENG L, YANG L, CHEN C, et al. Selective acetylene adsorption within an imino functionalized nanocage–based metal–organic framework [J]. *ACS Applied Materials & Interfaces*, 2020, 12(5): 5999–6006.
- [19] TIAN X M, YAO S L, QIU C Q, et al. Turn-on luminescent sensor toward Fe^{3+} , Cr^{3+} , and Al^{3+} based on a co (ii) metal–organic framework with open functional sites [J]. *Inorganic Chemistry*, 2020, 59(5): 2803–2810.
- [20] LI X, ZHOU S, LU S, et al. Lanthanide metal–organic framework nanoprobe for the *in vitro* detection of cardiac disease markers[J]. *ACS Applied Materials & Interfaces*, 2019, 11(47): 43989–43995.
- [21] SURESH K, MATZGER A J. Enhanced drug delivery by dissolution of amorphous drug encapsulated in a water unstable metal–organic framework (MOF) [J]. *Angewandte Chemie*, 2019, 131(47): 16946–16950.
- [22] WANG H L, YEH H, LI B H, et al. Zirconium–based metal–organic framework nanocarrier for the controlled release of ibuprofen[J]. *ACS Applied Nano Materials*, 2019, 2(6): 3329–3334.
- [23] CHEN B, GAO J, QIAN X, et al. Mixed metal–organic framework with multiple binding sites for efficient $\text{C}_2\text{H}_2/\text{CO}_2$ separation [J]. *Angewandte Chemie International Edition*, 2020, 59(11): 4396–4400.
- [24] WANG T, PENG Y L, LIN E, et al. Robust bimetallic ultramicroporous metal–organic framework for separation and purification of noble gases[J]. *Inorganic Chemistry*, 2020, 59(7): 4868–4873.
- [25] LIU Q, DORDICK J S, DINU C Z. Metal–organic framework–based composite for photocatalytic detection of prevalent pollutant[J]. *ACS Applied Materials & Interfaces*, 2019, 11(34): 31049–31059.
- [26] LIANG T Y, SENTHIL RAJA D, CHIN K C, et al. Bimetallic metal–organic framework–derived hybrid nanostructures as high–performance catalysts for methane dry reforming[J]. *ACS Applied Materials & Interfaces*, 2020, 12(13): 15183–15193.
- [27] WANG P L, XIE L H, JOSEPH E A, et al. Metal–organic frameworks for food safety [J]. *Chemical Reviews*, 2019, 119(18): 10638–10690.
- [28] DONG J, ZHAO D, LU Y, et al. Photoluminescent metal–organic frameworks and their application for sensing biomolecules[J]. *Journal of Materials Chemistry A*, 2019, 7(40): 22744–22767.
- [29] LIU Y, XIE X Y, CHENG C, et al. Strategies to fabricate metal–organic framework (MOF)–based luminescent sensing platforms[J]. *Journal of Materials Chemistry C*, 2019, 7(35): 10743–10763.
- [30] ZHANG Y, YUAN S, DAY G, et al. Luminescent sensors based on metal–organic frameworks[J]. *Coordination Chemistry Reviews*, 2018, 354: 28–45.
- [31] WU S, MIN H, SHI W, et al. Multicenter metal–organic framework - based ratiometric fluorescent sensors[J]. *Advanced Materials*, 2020, 32(3): 1805871.
- [32] XU Y, LI Q, XUE H, et al. Metal–organic frameworks for direct electrochemical applications[J]. *Coordination Chemistry Reviews*, 2018, 376: 292–318.
- [33] LIU W, YIN X B. Metal–organic frameworks for electrochemical applications[J]. *TrAC Trends in Analytical Chemistry*, 2016, 75: 86–96.
- [34] KEMPAHANUMAKKAGARI S, VELLINGIRI K, DEEP A, et al. Metal–organic framework composites as electrocatalysts for electrochemical sensing applications [J]. *Coordination Chemistry Reviews*, 2018, 357: 105–129.
- [35] WANG Y, WANG L, HUANG W, et al. A metal–organic framework and conducting polymer based

- electrochemical sensor for high performance cadmium ion detection[J]. *Journal of Materials Chemistry A*, 2017, 5(18): 8385–8393.
- [36] FU J, WANG X, WANG T, et al. Covalent functionalization of graphene oxide with a presynthesized metal–organic framework enables a highly stable electrochemical sensing[J]. *ACS Applied Materials & Interfaces*, 2019, 11(36): 33238–33244.
- [37] SU F, ZHANG S, JI H, et al. Two–dimensional zirconium–based metal–organic framework nanosheet composites embedded with Au nanoclusters: A highly sensitive electrochemical aptasensor toward detecting cocaine[J]. *ACS Sensors*, 2017, 2(7): 998–1005.
- [38] ZHANG C, WANG X, HOU M, et al. Immobilization on metal–organic framework engenders high sensitivity for enzymatic electrochemical detection[J]. *ACS Applied Materials & Interfaces*, 2017, 9(16): 13831–13836.
- [39] LIU C S, LI J, PANG H. Metal–organic framework–based materials as an emerging platform for advanced electrochemical sensing [J]. *Coordination Chemistry Reviews*, 2020, 410: 213222.
- [40] AI L, LI L, ZHANG C, et al. MIL - 53 (Fe): a metal–organic framework with intrinsic peroxidase -like catalytic activity for colorimetric biosensing[J]. *Chemistry –A European Journal*, 2013, 19 (45): 15105–15108.
- [41] LI S, LIU X, CHAI H, et al. Recent advances in the construction and analytical applications of metal–organic frameworks–based nanozymes[J]. *TrAC Trends in Analytical Chemistry*, 2018, 105: 391–403.
- [42] WANG J, HU Y, ZHOU Q, et al. Peroxidase–like activity of metal–organic framework [Cu (PDA) (DMF)] and its application for colorimetric detection of dopamine[J]. *ACS Applied Materials & Interfaces*, 2019, 11(47): 44466–44473.
- [43] ZENG L, CUI H, CHAO J, et al. Colorimetric determination of tetrabromobisphenol A based on enzyme–mimicking activity and molecular recognition of metal–organic framework–based molecularly imprinted polymers [J]. *Microchimica Acta*, 2020, 187 (2): 142.
- [44] NIE S, EMORY S R. Probing single molecules and single nanoparticles by surface –enhanced Raman scattering[J]. *Science*, 1997, 275 (5303): 1102–1106.
- [45] GRUENKE N L, CARDINAL M F, MCANALLY M O, et al. Ultrafast and nonlinear surface –enhanced Raman spectroscopy[J]. *Chemical Society Reviews*, 2016, 45(8): 2263–2290.
- [46] LEE H K, LEE Y H, KOH C S L, et al. Designing surface –enhanced Raman scattering (SERS) platforms beyond hotspot engineering: emerging opportunities in analyte manipulations and hybrid materials [J]. *Chemical Society Reviews*, 2019, 48(3): 731–756.
- [47] LAI H, LI G, XU F, et al. Metal–organic frameworks: opportunities and challenges for surface–enhanced Raman scattering–a review[J]. *Journal of Materials Chemistry C*, 2020, 8(9): 2952–2963.
- [48] LI Z, GE X, LI C, et al. Rational microstructure design on metal–organic framework composites for better electrochemical performances: design principle, synthetic strategy, and promotion mechanism[J]. *Small Methods*, 2020, 4(3): 1900756.
- [49] ZHU Q L, XU Q. Metal–organic framework composites [J]. *Chemical Society Reviews*, 2014, 43 (16): 5468–5512.
- [50] TONG P, LIANG J, JIANG X, et al. Research progress on metal–organic framework composites in chemical sensors[J]. *Critical Reviews in Analytical Chemistry*, 2020, 50(4): 376–392.
- [51] LIU X W, SUN T J, HU J L, et al. Composites of metal–organic frameworks and carbon–based materials: preparations, functionalities and applications[J]. *Journal of Materials Chemistry A*, 2016, 4 (10): 3584–3616.
- [52] ZHU L, MENG L, SHI J, et al. Metal–organic frameworks/carbon–based materials for environmental remediation: A state–of–the–art mini–review[J]. *Journal of Environmental Management*, 2019, 232: 964–977.
- [53] PAN M, YIN Z, LIU K, et al. Carbon –based nanomaterials in sensors for food safety[J]. *Nanomaterials*, 2019, 9(9): 1330.
- [54] LU M, DENG Y, LUO Y, et al. Graphene aerogel–metal –organic framework –based electrochemical method for simultaneous detection of multiple heavy–metal ions[J]. *Analytical Chemistry*, 2018, 91 (1): 888–895.
- [55] JALILI R, KHATAEE A, RASHIDI M R, et al. Dual–colored carbon dot encapsulated metal–organic

- framework for ratiometric detection of glutathione[J]. *Sensors and Actuators B: Chemical*, 2019, 297: 126775.
- [56] FALCARO P, RICCO R, YAZDI A, et al. Application of metal and metal oxide nanoparticles@MOFs [J]. *Coordination Chemistry Reviews*, 2016, 307: 237–254.
- [57] ANIK Ü, TIMUR S, DURSUN Z. Metal organic frameworks in electrochemical and optical sensing platforms: a review[J]. *Microchimica Acta*, 2019, 186(3): 196.
- [58] YANG Q, XU Q, JIANG H L. Metal-organic frameworks meet metal nanoparticles: synergistic effect for enhanced catalysis[J]. *Chemical Society Reviews*, 2017, 46(15): 4774–4808.
- [59] CHEN H, YANG T, LIU F, et al. Electrodeposition of gold nanoparticles on Cu-based metal-organic framework for the electrochemical detection of nitrite[J]. *Sensors and Actuators B: Chemical*, 2019, 286: 401–407.
- [60] MA Y, XU G, WEI F, et al. One-pot synthesis of a magnetic, ratiometric fluorescent nanoprobe by encapsulating Fe₃O₄ magnetic nanoparticles and dual-emissive rhodamine B modified carbon dots in metal-organic framework for enhanced HClO sensing [J]. *ACS Applied Materials & Interfaces*, 2018, 10(24): 20801–20805.
- [61] CAI Y, WU Y, XUAN T, et al. Core-shell Au@metal-organic frameworks for promoting Raman detection sensitivity of methenamine [J]. *ACS Applied Materials & Interfaces*, 2018, 10(18): 15412–15417.
- [62] AGUILERA-SIGALAT J, BRADSHAW D. Synthesis and applications of metal-organic framework-quantum dot (QD@MOF) composites [J]. *Coordination Chemistry Reviews*, 2016, 307: 267–291.
- [63] XUE Y, ZHENG S, XUE H, et al. Metal-organic framework composites and their electrochemical applications [J]. *Journal of Materials Chemistry A*, 2019, 7(13): 7301–7327.
- [64] ALIVISATOS A P. Perspectives on the physical chemistry of semiconductor nanocrystals[J]. *The Journal of Physical Chemistry*, 1996, 100(31): 13226–13239.
- [65] CHUNG S, REVIA R A, ZHANG M. Graphene quantum dots and their applications in bioimaging, biosensing, and therapy [J]. *Advanced Materials*, 2021, 33(22): 1904362.
- [66] CAO W, QIN Y, HUANG H, et al. Extraction of high-quality quantum dot photocatalysts via combination of size selection and electrochemiluminescence [J]. *ACS Sustainable Chemistry & Engineering*, 2019, 7(24): 20043–20050.
- [67] LI Y F, CHOU S Y, HUANG P, et al. Stretchable organometal-halide-perovskite quantum-dot light-emitting diodes[J]. *Advanced Materials*, 2019, 31(22): 1807516.
- [68] CHEN Y C, CHIANG W H, KURNIAWAN D, et al. Impregnation of graphene quantum dots into a metal-organic framework to render increased electrical conductivity and activity for electrochemical sensing[J]. *ACS Applied Materials & Interfaces*, 2019, 11(38): 35319–35326.
- [69] CHEN W, LIU H, FAN R, et al. Formation and encapsulation of lead halide perovskites in lanthanide metal-organic frameworks for tunable emission[J]. *ACS Applied Materials & Interfaces*, 2020, 12(8): 9851–9857.
- [70] WEI Z, CHEN D, GUO Z, et al. Eosin Y-embedded zirconium-based metal-organic framework as a dual-emitting built-in self-calibrating platform for pesticide detection[J]. *Inorganic Chemistry*, 2020, 59(8): 5386–5393.
- [71] HASSANZADEH J, AL LAWATI H A J, Al Lawati I. Metal-organic framework loaded by Rhodamine B as a novel chemiluminescence system for the paper-based analytical devices and its application for total phenolic content determination in food samples [J]. *Analytical Chemistry*, 2019, 91(16): 10631–10639.
- [72] GUPTA A, BHARDWAJ S K, SHARMA A L, et al. Development of an advanced electrochemical biosensing platform for E. coli using hybrid metal-organic framework/polyaniline composite[J]. *Environmental Research*, 2019, 171: 395–402.
- [73] HIBBARD H A J, BURNLEY M J, RUBIN H N, et al. Porphyrin-based metal-organic framework and polyvinylchloride composites for fluorescence sensing of divalent cadmium ions in water [J]. *Inorganic Chemistry Communications*, 2020, 115: 107861.
- [74] LIU G, LI L, GAO Y, et al. A beta-cyclodextrin-functionalized magnetic metal organic framework for efficient extraction and determination of prochloraz and triazole fungicides in vegetables samples[J]. *E-*

- cotoxicology and Environmental Safety, 2019, 183: 109546.
- [75] ZENG Z, FANG X, MIAO W, et al. Electrochemically sensing of trichloroacetic acid with iron (II) phthalocyanine and Zn-based metal organic framework nanocomposites[J]. ACS Sensors, 2019, 4(7): 1934-1941.
- [76] SCHMID A, DORDICK J S, HAUER B, et al. Industrial biocatalysis today and tomorrow[J]. Nature, 2001, 409(6817): 258-268.
- [77] ZHOU Z, HARTMANN M. Progress in enzyme immobilization in ordered mesoporous materials and related applications [J]. Chemical Society Reviews, 2013, 42(9): 3894-3912.
- [78] LIAN X, FANG Y, JOSEPH E, et al. Enzyme-MOF (metal-organic framework) composites [J]. Chemical Society Reviews, 2017, 46(11): 3386-3401.
- [79] XUE Z, ZHANG Y, YU W, et al. Recent advances in aflatoxin B1 detection based on nanotechnology and nanomaterials-A Review [J]. Analytica Chimica Acta, 2019, 1069: 1-27.
- [80] DEEP A, BHARDWAJ S K, PAUL A K, et al. Surface assembly of nano-metal organic framework on amine functionalized indium tin oxide substrate for impedimetric sensing of parathion[J]. Biosensors and Bioelectronics, 2015, 65: 226-231.
- [81] BHARDWAJ N, BHARDWAJ S K, BHATT D, et al. Highly sensitive optical biosensing of *Staphylococcus aureus* with an antibody/metal-organic framework bioconjugate[J]. Analytical Methods, 2019, 11(7): 917-923.
- [82] GUPTA A, GARG M, SINGH S, et al. Highly sensitive optical detection of *Escherichia coli* using terbium-based metal-organic framework[J]. ACS Applied Materials & Interfaces, 2020, 12(42): 48198-48205.
- [83] LIU T Z, HU R, ZHANG X, et al. Metal-organic framework nanomaterials as novel signal probes for electron transfer mediated ultrasensitive electrochemical immunoassay[J]. Analytical Chemistry, 2016, 88(24): 12516-12523.
- [84] WANG C, GAO J, TAN H. Integrated antibody with catalytic metal-organic framework for colorimetric immunoassay[J]. ACS Applied Materials & Interfaces, 2018, 10(30): 25113-25120.
- [85] SONG S, WANG L, LI J, et al. Aptamer-based biosensors[J]. TrAC Trends in Analytical Chemistry, 2008, 27(2): 108-117.
- [86] QIU Q, CHEN H, WANG Y, et al. Recent advances in the rational synthesis and sensing applications of metal-organic framework biocomposites [J]. Coordination Chemistry Reviews, 2019, 387: 60-78.
- [87] SHARMA R, RAGAVAN K V, THAKUR M S, et al. Recent advances in nanoparticle based aptasensors for food contaminants[J]. Biosensors and Bioelectronics, 2015, 74: 612-627.
- [88] HAUPT K, MOSBACH K. Molecularly imprinted polymers and their use in biomimetic sensors [J]. Chemical reviews, 2000, 100(7): 2495-2504.
- [89] HAUPT K. Peer reviewed: molecularly imprinted polymers: the next generation[J]. Analytical Chemistry, 2003, 75(17): 376 A-383 A.
- [90] QIAN K, FANG G, WANG S. A novel core-shell molecularly imprinted polymer based on metal-organic frameworks as a matrix[J]. Chemical Communications, 2011, 47(36): 10118-10120.
- [91] GUO T, DENG Q, FANG G, et al. Upconversion fluorescence metal-organic frameworks thermo-sensitive imprinted polymer for enrichment and sensing protein[J]. Biosensors and Bioelectronics, 2016, 79: 341-346.
- [92] KHATEB H, KLÖS G, MEYER R L, et al. Development of a label-free LSPR-Apta sensor for *Staphylococcus aureus* detection[J]. ACS Applied Bio Materials, 2020, 3(5): 3066-3077.
- [93] RUBAB M, SHAHBAZ H M, OLAIMAT A N, et al. Biosensors for rapid and sensitive detection of *Staphylococcus aureus* in food [J]. Biosensors and Bioelectronics, 2018, 105: 49-57.
- [94] BHARDWAJ N, BHARDWAJ S K, MEHTA J, et al. MOF-bacteriophage biosensor for highly sensitive and specific detection of *staphylococcus aureus* [J]. ACS Applied Materials & Interfaces, 2017, 9(39): 33589-33598.
- [95] WANG S, DENG W, YANG L, et al. Copper-based metal-organic framework nanoparticles with peroxidase-like activity for sensitive colorimetric detection of *Staphylococcus aureus* [J]. ACS Applied Materials & Interfaces, 2017, 9(29): 24440-24445.
- [96] ZHOU C, ZOU H, LI M, et al. Fiber optic surface plasmon resonance sensor for detection of *E. coli*

- O157: H7 based on antimicrobial peptides and Ag-NPs-rGO[J]. *Biosensors and Bioelectronics*, 2018, 117: 347–353.
- [97] IŞIK H, TOPALCENGİZ Z, GÜNER S, et al. Generic and Shiga toxin-producing *Escherichia coli* (O157:H7) contamination of lettuce and radish microgreens grown in peat moss and perlite[J]. *Food Control*, 2020, 111: 107079.
- [98] RANGEL J M, SPARLING P H, CROWE C, et al. Epidemiology of *Escherichia coli* O157: H7 outbreaks, united states, 1982–2002[J]. *Emerging Infectious Diseases*, 2005, 11(4): 603.
- [99] MIKHAIL A F W, JENKINS C, DALLMAN T J, et al. An outbreak of Shiga toxin-producing *Escherichia coli* O157: H7 associated with contaminated salad leaves: epidemiological, genomic and food trace back investigations[J]. *Epidemiology & Infection*, 2018, 146(2): 187–196.
- [100] SUN X, WANG Y, ZHANG L, et al. CRISPR–Cas9 triggered two-step isothermal amplification method for *E. coli* O157: H7 detection based on a metal-organic framework platform[J]. *Analytical Chemistry*, 2020, 92(4): 3032–3041.
- [101] ZHONG M, YANG L, YANG H, et al. An electrochemical immunobiosensor for ultrasensitive detection of *Escherichia coli* O157: H7 using CdS quantum dots-encapsulated metal-organic frameworks as signal-amplifying tags[J]. *Biosensors and Bioelectronics*, 2019, 126: 493–500.
- [102] GAO R, ZHONG Z, GAO X, et al. Graphene oxide quantum dots assisted construction of fluorescent aptasensor for rapid detection of *Pseudomonas aeruginosa* in food samples[J]. *Journal of Agricultural and Food Chemistry*, 2018, 66(41): 10898–10905.
- [103] DAS R, DHIMAN A, KAPIL A, et al. Aptamer-mediated colorimetric and electrochemical detection of *Pseudomonas aeruginosa* utilizing peroxidase-mimic activity of gold NanoZyme[J]. *Analytical and Bioanalytical Chemistry*, 2019, 411(6): 1229–1238.
- [104] JIA F, XU L, YAN W, et al. A magnetic relaxation switch aptasensor for the rapid detection of *Pseudomonas aeruginosa* using superparamagnetic nanoparticles[J]. *Microchimica Acta*, 2017, 184(5): 1539–1545.
- [105] ZHANG X, XIE G, GOU D, et al. A novel enzyme-free electrochemical biosensor for rapid detection of *Pseudomonas aeruginosa* based on high catalytic Cu–ZrMOF and conductive Super P[J]. *Biosensors and Bioelectronics*, 2019, 142: 111486.
- [106] 蒋晓华, 丁文捷, 栾崇林, 等. 金属有机骨架材料-核酸适配体荧光法检测沙门氏菌[J]. *分析测试学报* 2018, 5(37): 556–561.
- JIANG X H, DING W J, LUAN C L, et al. Fluorescence detection of *Salmonellae* based on metal organic frameworks and aptamer[J]. *Journal of Instrumental Analysis*, 2018, 5(37): 556–561.
- [107] RAZA W, KUKKAR D, SAULAT H, et al. Metal-organic frameworks as an emerging tool for sensing various targets in aqueous and biological media[J]. *TrAC Trends in Analytical Chemistry*, 2019, 120: 115654.
- [108] SNYDER A P, THORNTON S N, DWORZANSKI J P, et al. Detection of the picolinic acid biomarker in *Bacillus* spores using a potentially field-portable pyrolysis-gas chromatography-ion mobility spectrometry system[J]. *Field Analytical Chemistry & Technology*, 1996, 1(1): 49–59.
- [109] YANG W W, PONCE A. Validation of a *Clostridium* endospore viability assay and analysis of Greenland ices and Atacama desert soils[J]. *Applied & Environmental Microbiology*, 2011, 77(7): 2352–2358.
- [110] LI X, LUO J, DENG L, et al. In situ incorporation of fluorophores in zeolitic imidazolate framework-8 (ZIF-8) for ratio-dependent detecting a biomarker of anthrax spores[J]. *Analytical Chemistry*, 2020, 92(10): 7114–7122.
- [111] GUO L, LIANG M, WANG X, et al. The role of l-histidine as molecular tongs: a strategy of grasping Th^{3+} using ZIF-8 to design sensors for monitoring an anthrax biomarker on-the-spot[J]. *Chemical Science*, 2020, 11(9): 2407–2413.
- [112] WU D, ZHANG Z, CHEN X, et al. A non-luminescent Eu-MOF-based “turn-on” sensor towards an anthrax biomarker through single-crystal to single-crystal phase transition[J]. *Chemical Communications*, 2019, 55(99): 14918–14921.
- [113] SUN J, ZHU P, WANG X, et al. Cell based-green fluorescent biosensor using cytotoxic pathway for bacterial lipopolysaccharide recognition[J]. *Journal of Agricultural and Food Chemistry*, 2018, 66(26): 6869–6876.
- [114] WU J, ZAWISTOWSKI A, EHRMANN M, et al.

- Peptide functionalized polydiacetylene liposomes act as a fluorescent turn-on sensor for bacterial lipopolysaccharide[J]. *Journal of the American Chemical Society*, 2011, 133(25): 9720-9723.
- [115] SHEN W J, ZHUO Y, CHAI Y Q, et al. Cu-based metal-organic frameworks as a catalyst to construct a ratiometric electrochemical aptasensor for sensitive lipopolysaccharide detection [J]. *Analytical Chemistry*, 2015, 87(22): 11345-11352.
- [116] SHEN W J, ZHUO Y, CHAI Y Q, et al. Ce-based metal-organic frameworks and DNAzyme-assisted recycling as dual signal amplifiers for sensitive electrochemical detection of lipopolysaccharide[J]. *Biosensors and Bioelectronics*, 2016, 83: 287-292.

Research Progress on Detection of Bacterial Contamination in Food Based MOFs Sensor

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Abstract The research on the detection methods of food bacterial contamination is of great significance to reduce the outbreak of food borne diseases and food corruption. Metal organic frameworks (MOFs) are highly ordered crystal coordination polymers formed by metal ions or metal ion clusters and multiple organic ligands via coordination bonds. A variety of sensor detection systems including fluorescent sensor, colorimetric sensor, electrochemical sensor and so on have been constructed based on MOFs due to its unique structure and characteristics. This paper mainly introduces the types and components of MOFs-based sensors, as well as the research progress of detection methods of food bacterial contamination based on MOFs sensors. The limitations and future development direction of detection methods of MOFs sensors are also prospected.

Keywords metal organic frameworks; sensor; bacterial contamination; detection; food