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导电材料强化微生物直接种间电子传递产甲烷的研究进展

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摘要：厌氧条件下，微生物可以通过厌氧代谢产生甲烷(CH_4)，由此衍生的厌氧消化技术可实现能源的回收利用。产 CH_4 的关键步骤是刺激发酵细菌和产甲烷古菌之间的有效电子转移，电活性微生物可以取代传统的氢/甲酸盐实现直接种间电子传递，其电子传递效率更高。添加导电材料可以促进直接种间电子传递并提高 CH_4 产率，是一种更有效的强化电子传递方式。本文在梳理直接种间电子传递发展和机理的基础上，综述了常见的促进直接种间电子传递的碳基和铁基导电材料，对其结构特征、电子传递机理、强化产 CH_4 和中间产物消耗等方面进行了系统总结。旨在为导电材料促进直接种间电子传递的研究提供参考，并探讨了未来可能的研究方向。

关键词：厌氧消化，甲烷，直接种间电子传递，导电材料

厌氧产甲烷(CH_4)是地质微生物参与的重要地球化学过程，也是自然界碳循环的重要环节[1]。以产 CH_4 为核心的厌氧消化(anaerobic digestion，AD)可以生产清洁的可再生能源，逐渐成为能源领域研究和应用的热点[2]。AD 包括 3 个阶段：水解、产酸和产 CH_4[3]。在水解酸化阶段，在水解酶的作用下，有机物大分子转化为短链脂肪酸和醇等中间体。产酸阶段产生大量 H_2 使分压增加($\Delta H > 0$)，产 CH_4 反应在热力学上不能自发进行，只有当同营养微生物(两种微生物均需要对方为自身的生长提供必要的代谢支持[4])将 H_2 去除时才可行。由于产甲烷古菌代谢缓慢，对环境敏感，挥发性脂肪酸(volatile fatty acids，VFAs)的积累和 H_2 分压升高会抑制产 CH_4 过程，造成 AD 效率低和稳定性差[5]。以 H_2/甲酸盐作为电子载体，细菌和产甲烷古菌之间可以发生营养代谢，进行间接种间电子传递(mediated interspecies electron transfer，MIET)[6]，从而消除产 CH_4 过程中的障碍。最近研究表明，除了种间 H_2/甲酸盐转移，一些电化学活性细菌和产甲烷古菌之间还可以发生直接电子传递[7–8]。这些细菌通过鞭毛上分布的导电菌毛和 c 型细胞色素(c-type cytochrome，

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c-Cyts)发挥作用，将电子转移到产甲烷古菌[9–11]，这种电子转移机制被称作直接种间电子传递(direct interspecies electron transfer，DIET)。这种电子传递方式不需要添加额外的能量产生 H_2 作为电子穿梭体就可以促进 CH_4 的高效产生[12–14]。

DIET 过程的强化，可以进一步提升 CH_4 的产生效率，逐渐成为 AD 领域研究的热点。近年来研究表明，导电材料(conductive material，CM)可以加强 DIET 作用，其中碳基与铁基 CM 研究最为广泛，例如石墨毡[15]、活性炭[16]、生物炭[17]、水热炭[18]、碳布[19]、碳纳米管[20]、磁铁矿[21]、纳米零价铁[22]的添加可以刺激 DIET 的发生，改变微生物群落，促进功能微生物富集，加快 VFAs 的消耗，从而提高 CH_4 产生率[23–24]。

本文在归纳 DIET 发展与机理的基础上，梳理可强化 DIET 的碳基和铁基 CM 及其对 AD 过程的影响，从而归纳出 DIET 的未来前景与发展方向。

1 DIET 发展与机理

首次发现 DIET 是在 *Geobacter metallireducens* (金属还原地杆菌)和 *Geobacter sulfreducens* (硫还原地杆菌)的共培养体系中，以富马酸为电子受体，乙醇为电子供体，发现微生物形成导电聚集物，且聚集物形成一种突变，该突变能够增强 c-Cyts 的生成。长而灵活的导电菌毛为微生物间的电接触提供通道，并且具有足够的导电性以满足微生物的电子传递需求[25]。敲除两细菌的基因 *omcS* (一种多血红素 c-Cyts 基因)或 *pilR*(结构性菌毛蛋白基因)均无法进行电子互营，表明 c-Cyts 和菌毛在 DIET 中都发挥重要作用[26]。由此揭开了 DIET 研究的序幕。

微生物中有各种各样的氧化还原蛋白，c-Cyts 参与氧化还原介导的与呼吸有关的电子传递反应，且不同的电子传递模式下发挥作用的 c-Cyts 种类各不相同(图 1)。参与 DIET 最常见的 *Geobacter* (地杆菌)中包括 OmcB、OmcC、OmcS 和 OmcE 多种蛋白质[27]。*Geobacter sulfreducens* 电子转移过程的关键途径是由各种 c-Cyts (OmcB 和 OmcC)介导。*Geobacter sulfreducens* 还原细胞外金属氧化物时，多血型 c-Cyts 起关键作用，敲掉 *omcS* 和 *omcE* 任一基因都会降低 Mn(IV)和 Fe(III)氧化物的还原能力[28]。细胞色素中有专门的功能蛋白可以通过电子穿梭将电子送到更远的电子受体。如在硫还原地杆菌中，膜结合蛋白 NADH-脱氢酶通过细胞色素链穿过膜[29]；在 *Shewanella oneidensis* (奥奈达希瓦氏菌)中的电子转移是由甲酸脱氢酶起作用[30–31]。参与较薄生物膜的胞外电子传递的主要蛋白质为 OmcS 和 OmcE，较厚生物膜的胞外电子传递的主要为菌毛蛋白(PilA)[32]。

菌毛通常被称为微生物纳米线，是一种具有类似金属导电性的蛋白质细丝，在适当条件下可以促进远距离的电子传递，还可以进行微生物之间的 DIET[34]。这些纳米线参与了土壤和沉积物中碳和矿物的循环、生物修复、有机物向 CH_4 或电能的转化等一系列氧化还原过程[35]。富含 PilA 的 *Pseudomonas* (假单胞菌属)和 *Desulfurella* (硫还原菌属)能够直接利用复杂有机物作为电子供体，进行 DIET 介导的同营养代谢[36]。在 *Geobacter* 和 *Methanosaeta* (甲烷鬃毛菌)或 *Methanosarcina* (甲烷八叠球菌)的同营养菌共培养中，发现了导电菌毛介导的 DIET 产 CH_4 作用[37]。然而，最近研究表明，导电菌毛并不是由 PilA 构成，而是由

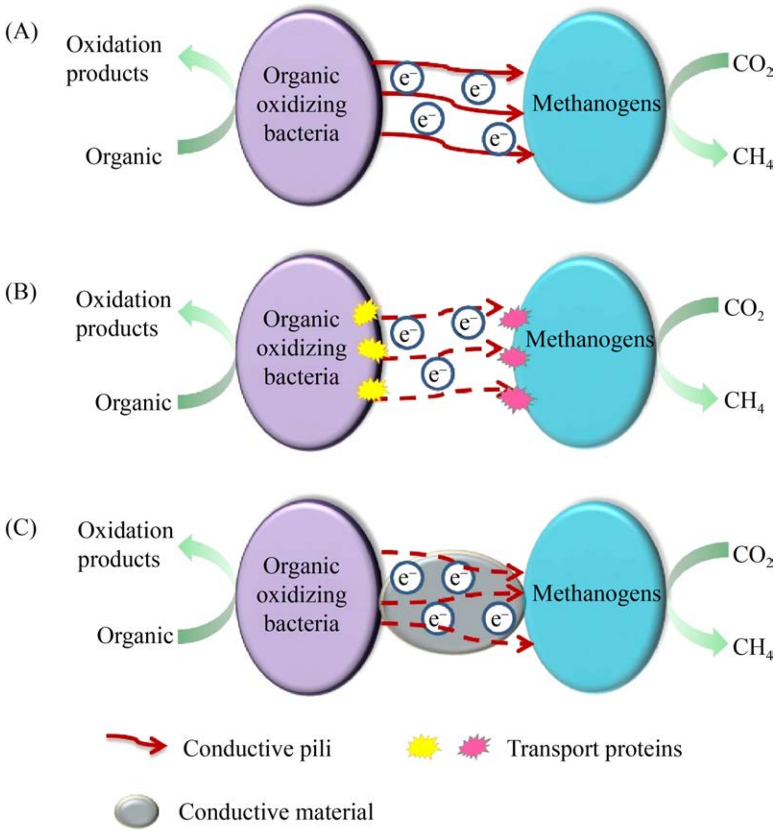

图 1. DIET 发生的三种途径(该图修改自文献[33])

Figure 1. Three pathways of DIET[33]. A: conductive pili; B: transport proteins; C: conductive material.

OmcS 聚合链组成。PilA 的作用是调节 OmcS 纳米线以及其他多血红素细胞色素的分泌。PilA 的过度表达伴随着 OmcS 细丝的过度产生，并将 OmcS 分泌到细胞外环境中[38]。因此，关于不同细菌纳米线的组成及功能，还需要进一步研究。

AD 是一种经济有效的处理有机废物的方法，可以提高消化质量和 CH_4产量。但是传统的 AD 面临着一些瓶颈：启动时间长；有机物水解率低，有毒物质和 VFAs 的积累会抑制 CH_4的生成；H_2 的积累抑制产乙酸细菌的氧化辅酶[39]。DIET 是微生物同营养氧化代谢中一种有效的途径，可以提高 AD 的速率和效率。外生电细菌可以通过 c-Cyts 或导电菌毛将电子转移到电子受体细菌[40]。AD 与 DIET 的结合可克服上述存在的问题，改善酸的积累并提高 CH_4产率。CM 的添加可以替代 c-Cyts 和导电菌毛成为电子连接装置，为细胞节省能量，还可以实现远距离电子传输，加速 DIET 现象[15]。CM 会促进氧化还原蛋白如 c-Cyts 和黄素蛋白的表达[41–42]。添加 CM 的 DIET 可以显著提高底物的降解和 CH_4产率，抑制 VFAs 的积累，并且可缩短系统启动时间和提高 AD 系统的稳定性[43]。因此，CM 强化 DIET 过程促进产 CH_4作用引起越来越多的关注与研究。

2 CM 介导 DIET 促进产 CH_4 原理及应用

DIET 过程可以通过 CM 刺激并发生强化，CM 在微生物之间形成导电管道实现电子传递。CM 可以起到与 c-Cyts 和菌毛相似的作用，这方面研究主要集中在碳基与铁基 CM。碳基 CM 为微生物提供更大的反应表面积，有利于微生物的附着。还可以利用自身的大孔径吸附有毒化合物，以避免干扰产 CH_4 过程[44]。碳基 CM 的导电性比菌毛更高，在 *Geobacter metallireducens* 与 *Methanosarcina barkeri* (巴氏甲烷八叠球菌)的共培养中，可以代替菌毛进行电子传递[45]，比菌毛具有更好的产 CH_4 性能。铁基 CM 在缺乏菌毛蛋白的 *Geobacter* 中具有双重作用，既可以刺激关键酶的分泌，又可以促进 DIET 相关蛋白的表达[46]。结晶的纳米级矿物可以使微生物的菌毛延伸并且使微生物集合体具有导电性，从而与细胞外电子受体建立联系[47]。在导电磁铁矿纳米颗粒和半导电赤铁矿纳米颗粒的存在下，一些 c-Cyts 基因例如 *omcJ*、*pgcA* 和 *omcK* 的表达会上调[48]。由于生物膜中很容易嵌入纳米级矿物，所以它们构成的紧密界面系统可以提供更多的活性位点，有利于微生物的接触。因此，碳基和铁基 CM 在 DIET 促进产 CH_4 的研究中日益兴起。

2.1 碳基 CM

碳基 CM 具有高比表面积和优异的导电性，这些特性对于促进 DIET 提高甲烷产率至关重要[49–50]。碳基 CM 的多孔结构和高比表面积可为微生物提供更大的附着空间和合适的生长环境，促进微生物的生长代谢，有利于电子供体微生物、充当电子转移站的 CM 和电子受体微生物之间更好地接触，从而发生 DIET 以促进 CH_4 产生[51–52]。CM 的导电性和表面氧化还原官能团也与 DIET 的效率密切相关，表面氧化还原官能团可显著提高 CH_4 产生速率[53]。醌和对苯二酚与 CM 的氧化还原官能团有关，它们能够提供和接受电子使 CM 具有氧化还原活性。具有氧化还原活性的 CM 可以作为电子穿梭体促进电子供体微生物和电子受体微生物之间的 DIET[17]。碳基 CM 存在一定缺陷，比如：生物炭在低热解温度(<350 °C)下制备具有较丰富的官能团，但导电性较差；在较高热解温度(>700 °C)下电导率有所提升，但表面官能团有所减少。因此，最近很多研究采用对生物炭改性的方法来提高其各种性能，例如负载硫改性纳米零价铁[54]、铁锰改性生物炭复合材料[55]、负载 Fe_3O_4[56]和芬顿污泥衍生的含磁铁矿生物炭[57]。金属材料与碳基 CM 的结合不仅有利于碳基 CM 的分离和回收，还改善了不同微生物之间的协作关系[53]。然而，碳基 CM 的制备过程，大多需要高温高压的条件，操作较为复杂，还有毒性有机试剂的应用，未来需探索更为简便有效、节能环保的制备方法。

碳基 CM 的添加可显著促进产 CH_4 过程。图 2 比较了文献报道的不同碳基 CM 在混菌中温(35–38 °C)厌氧反应器中不同剂量下的 CH_4 产率。碳基 CM 使 CH_4 产率提高了 0.26%–890.76%[16,20,24,58–75]。颗粒活性炭和生物炭研究较多[76–91]。CH_4 产率整体上随 CM 用量的增加而增加，其中石墨烯在此方面的规律性最为明显。其他碳基 CM 并未观察到明显的规律，可能是由于材料制备工艺的差别。向厌氧消化池中添加石墨烯可显著提高 CH_4 产量，并增加 *Geobacter* 和 *Methanosarcina* 等电活性微生物的数量[24]。

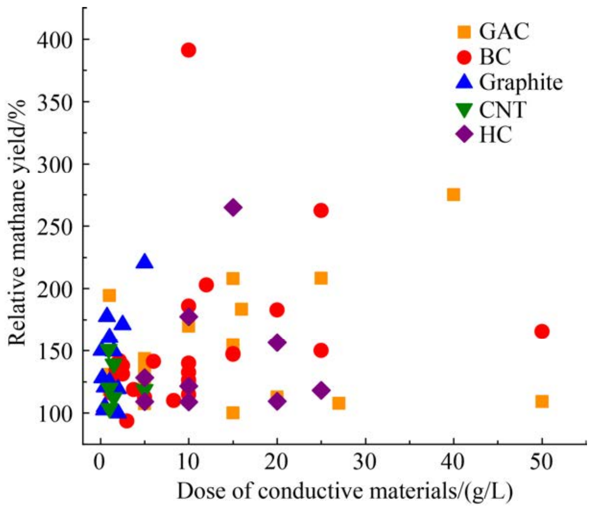

图 2. 不同碳基 CM 的产 CH_4 反应器性能的比较[16,20,24,58–91]

Figure 2. Performance comparison of CH_4 reactors with different carbon based CM[16,20,24,58–91].

Igarashi 等通过同位素标记实验检测了共培养的碳通量，证明了 DIET 依赖的 CO_2 还原是石墨烯促进 CH_4 化的原因，亲水性胺官能化的石墨烯实现最高的 CH_4 生成率，证明表面亲水性与 DIET 促进效率呈正相关[92]。添加生物炭可缩短产 CH_4 的滞后时间和增加最大 CH_4 产率，生物炭表面存在的醌和氢醌官能团可以促进电活性微生物之间的电子传递[74]。向 AD 系统添加适量 $MnFe_2O_4$ 改性生物炭能够建立起 DIET，提高系统的缓冲能力，促进污泥中可溶性蛋白质和碳水化合物的降解，从而提高 CH_4 产量[55]。在 400 °C 下热解芬顿污泥可获得含磁铁矿的生物炭，具有高的电容量和电导率，磁铁矿充当电子管道，促进营养细菌和产甲烷古菌之间的 DIET，从而提高 CH_4 产率[57]。污泥衍生的水热炭在 10 g/L 剂量下对 CH_4 产生速率的促进效果最佳，且不控制 pH 条件下最大 CH_4 产率更高，说明污泥衍生的水热炭在抑制条件下(如低 pH)更能够促进 CH_4 的生成[58]。有碳布存在的 AD 系统中，种间电子交换的主要工作模式是 DIET，因此形成稳定的产 CH_4 作用。互营微生物都倾向于附着在碳布上进行种间电子交换，可以节省细胞能量和产生更少的细胞外生物电连接[12]。单壁碳纳米管形成电子传输纳米线通过 DIET 连接乙酸盐氧化和产甲烷古菌之间的电子传递，类似导电菌毛的纳米线，可以使污泥获得更高的电导率，从而对电子传输产生积极影响[93]。未来，除继续探究碳基 CM 对产 CH_4 的促进作用外，还需关注其使用后的回收与再利用。

碳基 CM 可提高 VFAs 的消耗速率，减少中间代谢产物的积累。石墨毡可以替代导电菌毛充当 VFAs 氧化菌与产甲烷古菌在同营养代谢过程中的导电物质，在高 H_2 分压下利用 DIET 作用机制确保丙酸和丁酸的转化[15]。颗粒活性炭修饰的厌氧消化池中乙酸的最大浓度仅为对照组的一半，并且浓度会逐渐下降直到完全消失[92]。适量的柑橘皮生物炭可以缓解高有机负荷导致的系统酸化，其结构中的碱性官能团能有效地中和部分 VFAs，促进 VFAs 向 CH_4 的转化并加速 pH 恢复。柑橘皮生物炭刺激微生物形成 DIET 加速 H_2 的消耗，使丙酸的降解反应热力学平衡右移[74]。柑橘皮生物炭的加入不仅降低总 VFAs 中丙酸的含量，减轻丙酸对产 CH_4 的抑制作用，还可降低本应该升高的丙酸的降解产物乙酸的含量[60]。高浓度的氨氮会对 AD 系统产生毒性，$MnFe_2O_4$ 改性生物炭的较强吸附力能有效缓解氨抑制，减少滞后时间并提高系统的稳定性，低浓度的 $MnFe_2O_4$ 改性生物炭可以有效地促进 VFAs 的转化效率和提高系统的缓冲能力，微量元素 Mn、Fe 的补充还可以增强底物的水解酸化过程[55]。由此可见，碳基 CM 可改善产甲烷古菌的生存环境，避免对其生长造成抑制。

2.2 铁基 CM

铁基 CM 在 AD 过程中应用十分广泛，用于 AD 系统中促进 DIET 的铁基材料有零价铁[94–95]、磁性纳米颗粒[95]、硫改性纳米零价铁[96]、磁铁矿[97–98]等，分别用于氨氮胁迫条件下废活性污泥、有机污染物的厌氧还原、污泥与餐厨垃圾厌氧共消化和上流厌氧污泥床反应器中。零价铁已应用于地下水净化、污水处理和土壤修复，是一种低成本且寿命长的导电材料[99]。零价铁可以降低系统的氧化还原电位，为厌氧微生物提供更适合生长的环境[43,100–101]。不过在运行中，零价铁表面可能会产生铁(氢)氧化物而抑制活性[102]。在表面涂覆硫化物形成硫改性纳米零价铁可以提高其活性[103]，同时，硫改性纳米零价铁比纳米零价铁的比表面积更大、反应活性更高、生物毒性更低[104]。铁氧化物 Fe_3O_4 具有理想电势，可以作为电子通道刺激 DIET 促进 CH_4 的产生[105]。磁铁矿是土壤和沉积物中一种导电矿物，很多研究用其建立 DIET 以促进产 CH_4 作用[106]。铁基 CM 可通过绿色环保的生物方法制备，部分铁基 CM 也来自自然界，因此可以实现规模化应用。

铁基 CM 对 AD 产 CH_4 有明显的促进作用。图 3 比较了文献中的不同铁基 CM 在混菌中温(35–38 °C)厌氧反应器中不同剂量下的 CH_4 产率。添加铁基 CM 使 CH_4 产率提高了 1.13%–254.74%[46,57,95-96,105,107–110]，铁基 CM 的种类和剂量影响 CH_4 产率[111–129]。CH_4 产率随着磁铁矿、硫改性纳米零价铁、零价铁和赤泥投加量的增加而逐渐增大，但当赤铁矿用量超过 16 g/L 时，对 CH_4 产率不再有促进作用。对比零价铁、磁性纳米颗粒和颗粒活性炭在氨胁迫条件下的表现，发现添加零价铁的系统产 CH_4 性能最好，其次是磁性纳米颗粒[60]。零价铁通过抑制氨促进

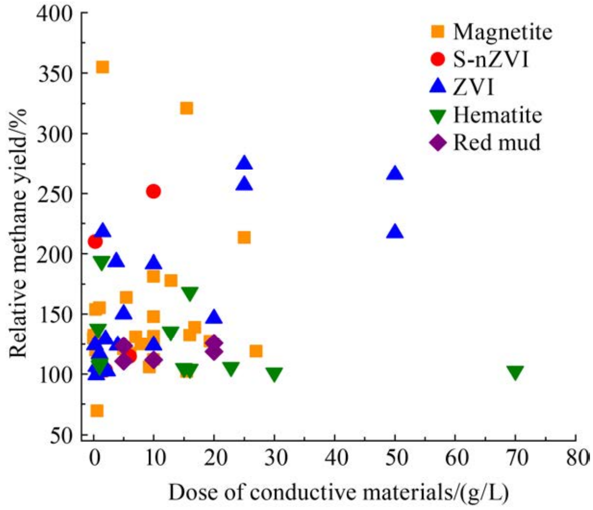

图 3. 不同铁基 CM 的产 CH_4 反应器性能的比较[46,57,95–96,105,107–129]

Figure 3. Performance comparison of CH_4 production reactors with different iron-based CM[46,57,95–96,105,107–129].

了微生物的抗毒活性，使 CH_4 生成率降低最少，滞后时间最短，污泥减量率最高。零价铁可能取代促进 DIET 的醌氧化还原酶(EtfAB 酶)的作用[95]，可以通过刺激酶活性、产生额外的 H_2 和减少酸的积累，从而提高 CH_4 产率[102]。与零价铁增强 AD 的机制不同，硫改性纳米零价铁可以提高底物的利用率，并且通过更有效的电子传递促进 H_2 向 CH_4 的转化[96]。Fe_3O_4 会与产甲烷古菌竞争电子，从而轻微抑制产 CH_4 作用。但 Fe_3O_4 会强化水解-酸化过程，生成更多的 CO_2/H_2 转化成 CH_4。增强作用高于抑制作用，所以最终表现为促进 CH_4 生成[97]。在富含硫酸盐废水的上流式厌氧污泥反应器中，添加磁铁矿的 CH_4 产率在第 40 天达到 157 mL/d，不添加磁铁矿的反应器中 CH_4 产率稳定在 48 mL/d 左右，只有前者的 1/3。进水硫酸盐浓度增加后，添加磁铁矿比未添加磁铁矿的平均 CH_4 生产率高 3–10 倍，差距进一步增大[98]。然而，有研究表明 Fe(III)会抑制 AD 中 CH_4 的生成[130]，因此铁基 CM 的长期效应，值得进一步评估。

铁基 CM 可以促进中间产物的快速消耗。在污泥的厌氧发酵池中添加 20 g/L 零价铁,可以促进短链脂肪酸向中链脂肪酸和长链醇的转化。零价铁剂量与促进作用呈正相关，最高剂量(20 g/L)零价铁仍然具有促进作用。零价铁的存在还可以促进废活性污泥的增溶过程，以及多糖、蛋白质和溶解性化学需氧量的释放和氨基酸的酸化[95]。在氨胁迫条件下，零价铁对 VFAs 的降解作用最好[94]。而没有氨胁迫条件下，Fe_3O_4 对 VFAs 的降解效果优于零价铁[131]。VFAs 快速被消耗后，环境条件得以改善，可有效提高产甲烷古菌的活性。

3 CM 影响微生物群落结构

CM 的添加会使微生物群落结构发生变化[132]，根据 16S rRNA 基因高通量测序的门级鉴定分析显示，不添加 CM 的样本中以 *Firmicutes* (厚壁菌门)、*Euryarchaeota* (广古菌门)、*Bacteroidetes* (拟杆菌门)、*Chloroflexi* (绿弯菌门)、*Aminicenantes* (氨酸菌门)、*Proteobacteria* (变形菌门)和 *Synergistetes* (互养菌门)为主[53]。CM 的添加使 *Firmicutes* 的相对丰度显著增加，该菌属含有能够降解 VFAs 的同营养细菌，可加速乙酸盐的产生。*Firmicutes* 中最丰富的 *Clostridium* (梭状芽孢杆菌)可提高 VFAs 的水解率[133]。属于 *Firmicutes* 的 *Trichococcus* (毛球菌属)的相对丰度也有所增加，其可将葡萄糖降解为乳酸、乙酸和乙醇，但无直接证据表明 DIET 的发生[53]。

在 CM 刺激下富集的电子供体微生物如 *Trichococcus*[94]、*Clostridium*[133]、*Candidatus* (念珠菌)[133]、*Syntrophomonas*[95]和 *Desulfovibrio* (脱硫弧菌)[15]等，其作用都是通过降解 VFAs 或与产甲烷古菌形成同营养代谢以促进 CH_4 产生，但无直接证据表明其参与了 DIET。因此这些细菌仅仅是 DIET 的潜在功能微生物，并不能完全证明 DIET 的发生。*Geobacter* 是至今所发现的唯一可以在不同微生物之间发生 DIET 的细菌[26]。*Geobacter* 是在 DIET 中最丰富和活跃的同营养细菌，在微生物群落中担任主要角色，成为 DIET 发生的“标志”。但表 1 和表 2 显示，在 CM 刺激 DIET 的反应体系中有接近半数研究并未检测到 *Geobacter* 或者丰度很低(5%以下)，原因可能是 DIET 并没有真正发生，CH_4 增加是由于 CM 发挥其他作用所导致，如增加微生物附着、刺激有机物降解；也可能是因为存在尚未被证实的电活性细菌，难以证实已发生的 DIET[134]。由此可见，能进行 DIET 的微生物不仅限于 *Geobacter*，DIET 功能微生物资源值得深入挖掘，尤其在添加 CM 的体系中，DIET 过程进行得更剧烈，可能会富集更多的 DIET 功能微生物，但如何证明潜在功能物种的 DIET 能力是未来研究的方向。

Methanosaeta 和 *Methanosarcina* 是最常见的两种利用乙酸盐产 CH_4 的物种，也是具备细胞外电子交换能力的微生物。CM 可以刺激这两类电活性产甲烷菌的富集以进行 DIET。*Methanosaeta* 利用乙酸盐产 CH_4，*Methanosarcina* 既可以利用 CO_2 产 CH_4，又可以将乙酸分解生成 CH_4，是一种多功能产甲烷古菌[135]。CM 存在时，*Methanosaeta* 和 *Methanosarcina* 都可以成为 *Geobacter* 的共营养体。*Geobacter* 氧化有机物产生的电子传递到 CM，再转移到 *Methanosaeta* 中用于消耗 CO_2 产 CH_4，其中 CM 充当电子储存器的作用，这就是以 DIET 为基础的高效同营养产 CH_4 反应体系[74]。在添加 CM 的嗜热(55 °C)环境中 *Methanosaeta* 和 *Methanosarcina* 总比率是对照组的 2 倍[95]。

Methanosaeta 是对氨抑制最为敏感的厌氧菌，因此在氨抑制条件下维持 *Methanosaeta* 的生长优势是影响产 CH_4 性能的关键，CM 的添加就可起到上述作用，从而证明 CM 对 DIET 的促进作用[53]。除以上产甲烷古菌外，*Methanolinea* (甲烷绳菌属)、*Methanobacterium* (甲烷杆菌属)、*Methanothrix* (甲烷丝菌属)、*Methanomassiliicoccus* (甲烷马赛球菌)、*Methanomethylovorans* (甲烷嗜甲基菌属)的相对丰度在添加 CM 的厌氧体系中也有所增加(表 1、表 2)。其中 *Methanobacterium* 属于氢营养

表 1. 产 CH_4 体系中碳基 CM 的作用识别及富集微生物种类

Table 1. Functions of carbon-based CM in CH_4 production system with enriched functional microbes

Type	Dosage	Inoculum	Substrate	Identification techniques	Functions	Enriched microbes	References
HC	10.0 g/L	UASB reactor	Glucose	qPCR 16S rRNA	Improve CH_4 yield Reduce lag time Alleviate ammonia inhibition	*Firmicutes* *Methanolinea*	[53]
BC	15.0 g/L	AD system	Phenol	FT-IR EC MER/MEO	Improve microbial activity Improve CH_4 yield	*Geobacter* *Syntrophorhabdus* *Methanobacterium*	[74]
BC	10.0 g/L	AD system	Food waste/Waste activated sludge	16S rRNA	Enhance pollutant degradation	*Geobacter* *Sphaerochaeta* *Sporanaerobacter*	[137]
BC	1.0 g	AD system	Nitrate/Activated sludge	CV EIS CA Nyquist	Enhance microbial denitrification Promote nitrate reduction	*Proteobacteria* *Bacteroidetes* *Firmicutes* *Pseudomona*	[138]
CPBC	2.0 g	AD system	Sludge/Food waste	Boehm titration 16S rRNA	Buffer acid Reduce lag time	*Geobacter* *Syntroprobacter* *Methanosaeta*	[59]
GAC	0.2 g	AD system	Kitchen waste lipid-rapeseed oil	16S rRNA	Improve CH_4 yield Reduce acidification	*Syntrophomonas* *Geobacter* *Methanosarcina*	[139]
GAC	5.0 g/L	AD system	Anaerobic sludge	16S rRNA	Accelerate start-up Resist to organic load	*Desulfuromonas* *Thermotogaceae* *Methanosarcina*	[62]
GAC	40.0 g/L	AD system	Anaerobic sludge	16S rRNA	Improve CH_4 yield Enhance COD removal	*Synergistaceae* *Cloacibacillus*	[140]
GAC	75.0 g/L	UASB reactor	Incineration leachate	Metagenomic analysis	Resist to high organic load	*Methanothrix* *Methanosarcina* *Geobacter*	[141]
Graphite felt		SBR reactor	Anaerobic sludge	16S rRNA	Accelerate VFAs degradation Promote microbial growth and CH_4 production	*Geobacter* *Methanosarcina*	[15]
Graphite powder	7.0 wt%	An-IFFAS reactor	Anaerobic sludge	Four-probe measurement 16S rRNA	Promotes CH_4 production	*Geobacter* *Syntrophobacter* *Smithella* *Methanothrix*	[9]
Acetylene Black	1.0 g/L	AD system	Vinegar residue	16S rRNA	Improve CH_4 yield Promote acetate conversion	*Syntrophomonadaceae* *Methanosarcinaceae*	[18]

HC: hydrochar; BC: biochar; CPBC: citrus peel biochar; GAC: granular activated carbon.

表 2. 产 CH_4 体系中铁基 CM 的作用识别及富集微生物种类作用

Table 2. Roles of iron-based CM in CH_4 production system with enriched functional microbes

Type	Dosage	Inoculum	Substrate	Identification technique	Functions	Enriched microbes	References
S-nZVI	0.3 g/L	AD system	Nitrobenzene	Tian et al. 16S rRNA CV	Enhance performance delivery Promote VFAs transformation Provide key enzyme activity	*Caldisericum* *Methanosphaerula* *Methanomassiliicoccus*	[107]
ZVI	10.0 mmol/L	AD system	Anaerobic sludge	The phenol-sulfuric method Lowry-Folin method 16S rRNA	Improve CH_4 yield Antitoxicity Be the role of substituted proteins	*Syntrophomonas* *Tepidimicrobium* *Anaerosphaera*	[96]
AC/ Magnetite	5.0 g/L	UASB reactor	Coal gasification wastewater	Lowry-Folin method 16S rRNA	Accelerate syntrophic metabolism Improve CH_4 production	*Geobacter* *Methanothrix*	[142]
Fe-Mn/BC	1.5 g	AD system	Anaerobic sludge	16S rRNA	Promote methanogens activity Alleviate ammonia inhibition	*Methanosaeta* *Methanosarcina* *Methanobacterium*	[55]
BC/S-nZVI	1.0 g/L	UASB reactor	Nitrobenzene	1,10-phenanthroline 16S rRNA	Accelerate organic biodegradation Improve system stability	*Bacteroides* *Longilinea* *Methanosarcina*	[143]
Fe_2O_3/CC		AD system	Propionic acid	CER LSCV The chronoamperometry 16S rRNA	Improve CH_4 yield Promote electron transfer	*Levilinea* *Methanothrix* *Methanobacterium*	[23]
ZVI	20.0 g/L	AD system	Anaerobic sludge	LDH The diphenylamine colorimetry	Promote electron transfer	*Firmicutes* *Proteobacteria* *Bacteroidetes* *Oscillibacter* *Methanobacterium*	[94]
S-nZVI	10.0 g/L	AD system	Sludge/Food waste	ETS Lowry-Folin 16S rRNA	Improve CH_4 yield Promote electron transfer	*Euryarchaeota* *Chloroflexi* *Methanomicrobia*	[96]
Fe/BC	1.0 g/L	AD system	Nitrobenzene	EPR CV DPV	Promote nitrobenzene transformation Improve electrochemical activity	*Geobacter sulfreducens*	[144]
Magnetite/ BC	30.0 mmol/L	AD system	Anaerobic sludge	CV 16S rRNA	Improve AD performance	*Clostridiaceae* *Methanobacteriaceae* *Methanomicrobiaceae*	[57]
Fe_3O_4/Coke	1.0–3.0 mg/L	AD system	Coal pyrolysis wastewater	Metagenomic analysis	Enhance pollutant removal	*Syntrophorhabdus* *Geobacter* *Alicycliphilus*	[145]

S-nZVI: sulfidemodified nanoscale zero valent iron; ZVI: zero valent iron; AC: activated carbon; BC: biochar; CC: carbon cloth.

性产甲烷菌，可将 CO_2 和 H_2 转化为 CH_4，有研究表明 *Methanobacterium* 可以通过 DIET 直接接受电子产 CH_4[136]。*Methanothrix* 可通过 DIET 与还原铁细菌建立电子连接产 CH_4[23]。DIET 过程中接受电子的产甲烷古菌在 CM 强化体系内的种类及分布特征，还需深入研究。

4 结论和展望

DIET 所涉及的微生物包括给电子细菌和产甲烷古菌，CM 材料的作用是将给电子细菌氧化有机物释放的电子传递给产甲烷古菌，进而利用 CO_2 产生 CH_4[44]。CM 使参与 DIET 的物种间形成导电通路，并加速产甲烷菌的生长。生长速度较快的细菌可以更快地适应新环境，表现出较短的滞后时间，因此获得更高的甲烷产量和甲烷产率[146]。纳米级 CM 可穿透 *Methanosarcina barkeri* 的细胞膜和细胞质来加速细胞内电子传递，从而提高 CH_4 产量[147]。CM 强化产 CH_4 过程有以下几个途径：(1) 为微生物提供适宜的生存环境和附着空间；(2) 吸附有毒物质减轻对微生物的抑制作用；(3) 促进中间产物 VFAs 的降解，避免微生物被毒害和系统酸化；(4) 加速产甲烷古菌的生长，促进给电子细菌和产甲烷古菌之间的电子传递；(5) 富集 DIET 功能微生物。但是，DIET 作用在 CM 强化产 CH_4 过程中的贡献率还有待进一步确认。

添加 CM 增强 DIET 促进产 CH_4 作用是提升 AD 效率的有效途径。本文系统总结了最为常见的碳基与铁基 CM 对 DIET 性能的影响，CM 的添加不仅可以提高产 CH_4 速率，还可以缩短滞后时间，促进 VFAs 的降解，提高微生物活性，抵抗氨抑制作用和高有机负荷。同时，对参与 DIET 的微生物进行了系统梳理。目前对于 DIET 的研究还处于初期阶段，有一系列问题尚待解决，未来需重点突破以下几个方面：在机理层面，需探究 DIET 发生的直接证据。尽管 CM 可以通过 DIET 增强产 CH_4，但已报道的均为间接证据，至今尚未有佐证 DIET 发生的直接证据。在 CM 方面，需设计开发性能更优、更利于回收的导电材料，除碳基、铁基 CM 外，还可以关注其他类型的材料。在微生物层面，需进一步挖掘 DIET 功能微生物资源，开发并利用更多的 DIET 功能菌。在实际应用层面，除了产 CH_4，还可以利用其去除地质环境中的其他污染如硝酸盐、高价重金属等。

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Research progress on enhancement of methane production through direct interspecific electron transfer by conductive materials

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Abstract: Under anaerobic conditions, microorganisms produce methane (CH_4) through anaerobic metabolism. The derived anaerobic digestion technology realizes energy recovery. The key step of CH_4 production is to stimulate the effective electron transfer between fermentation bacteria and methanogens. Electroactive microorganisms can replace the traditional hydrogen/formate to achieve direct interspecific electron transfer, with higher electron transfer efficiency. The addition of conductive materials promotes direct interspecific electron transfer and increase the yield of CH_4, which is a more effective way to enhance the electron transfer. Based on the development and mechanism of direct interspecific electron transfer, carbon-based and iron-based conductive materials that promote direct interspecific electron transfer are comprehensively reviewed. The structural characteristics, electron transfer mechanism, enhanced CH_4 production and intermediate consumption by these materials are systematically summarized. This review aims to provides reference for the research of conductive materials promoting direct interspecific electron transfer, and to explore the possible research direction in future.

Keywords: anaerobic digestion, methane, direct interspecific electron transfer, conductive material

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