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生物炭基材料及其在电化学传感领域的应用

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摘要：电化学传感技术以其成本低、灵敏度高、选择性好、反应速度快等优点成为分析化学领域的研究热点。将电极敏感材料修饰在传感电极表面，实现电化学信号放大是提高电化学传感器分析检测性能的关键。生物炭材料因其有丰富的孔道结构、较大的比表面积、优异的吸附能力，并且表面含有较多的含氧活性官能团，成为优质的电极修饰材料。然而，因生物炭材料的合成方法多样且生物炭的组成复杂性，导致基于生物炭的电化学传感器检测限还有较大的提高空间，且基于生物炭的电化学传感器的传感机理目前仍不明晰。本文以生物炭基材料在电化学传感检测领域的应用为例，简述了生物炭基材料的合成方法以及不同方法所合成炭材料的结构特性，在此基础上，总结了基于生物炭材料的电化学传感器在环境污染物、药物及生物分子分析领域的研究进展。目前，环境污染物的分析主要集中在酚及醌类化合物领域，正逐渐向新污染物如微塑料等领域拓展。药物检测的目标物质主要为抗生素类化学药品和黄酮类中药，其他物质的检测研究相对较少。而生物分子检测中，葡萄糖、多巴胺、尿酸、抗坏血酸等检测分析应用较多，检测机理也比较明晰。整体来说，构建传感器的检出限、灵敏度还有较大提高空间，并且基于大型电化学工作站的传感器也逐渐向集中化、微小化和便携式传感平台过渡。在此基础上，本文提出基于生物炭材料的电传感分析技术的发展方向：①优化炭材料结构，调控炭材料组成，制备更适配电化学传感器的高性能炭基材料，降低检出限，提高灵敏度；②构建基于生物炭的便携式传感器，实现快速智能化分析检测；③传感机理及检测限降低原因的剖析是生物炭基电化学传感器发展过程中需要深入探讨的问题。

关键词：电化学传感器；生物炭；环境污染物；药物；生物分子

要点：

(1) 电化学传感器作为一种新的检测分析装置，其检出限、灵敏度及线性范围等参数受电极修饰敏感材料的影响。

(2) 归纳总结了三种不同的生物炭制备方法的优缺点及所合成材料的性能参数及技术指标。

(3) 评述了基于生物炭的电化学传感器在环境污染物、药物及生物分子分析中的最新应用进展。

(4) 拓宽检测目标物范围、提高检测性能、实现现场检测及剖析检测机理，是生物炭基电化学传感器发展的趋势。

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电化学传感器是一种通过测定目标物质的电化学信号进行定性或定量检测分析的装置[1]，较传统的仪器分析方法，如高效液相色谱、电感耦合等离子体质谱、紫外光谱法，电化学传感技术以其便宜、灵敏度高、选择性好、反应速度快等优点成为分析化学领域的研究热点[2-5]。其基本原理是利用待测物质与电极表面发生物理、化学作用，引起电化学信号发生变化，经过电化学工作站转为可视化的电化学谱图，通过对谱图的分析实现对目标分子的定性或定量检测[6]。常用的电化学谱图采集方法主要包括循环伏安法 (CV)、差分脉冲伏安法 (DPV)、线性扫描伏安法 (LSV)、方波伏安法 (SWV)、电化学交流阻抗法 (EIS)、差分脉冲吸附溶出伏安法 (DPASV) 及计时安培法 (i-t) 等。分析检测过程中，电极系统中的工作电极表面实现对目标分子的特异性捕获与识别，是影响电化学传感器性能的关键部件[7-9]。而未经修饰的工作电极检测线性范围窄，检出限不足，灵敏度差。因此，有效地将电极敏感材料修饰在电极表面实现电化学信号放大，是提高电化学传感器分析检测性能的关键。

生物炭基材料因其结构独特、广泛可用、高度可持续、经济兼容和可再生等特性，引起了学者们广泛的研究兴趣[10]，其应用主要包括催化[11]、CO_2 捕获[12]、吸附分离[13]、储氢[14]、太阳能电池[15]、水处理[16]、储能[17]和电化学传感[18]等领域。经过合理设计和调控所制备的炭材料具有规则的表面形态、高导电性、高孔隙率、化学稳定性和表面功能化等特点，使其具有重要的研究意义和实际应用价值。将生物炭基材料用于电化学传感领域，不仅可以构建快速、灵敏和稳定的传感器，还可以实现废物再利用。近年来，学者们致力于提高生物炭材料的电化学传感性能，主要方法包括：活化、杂原子掺杂，以及金属/金属合金/金属化合物纳米颗粒的负载[19-20]，通过此类方法增加反应活性位点和表面缺陷、增大材料电活性面积、提高材料物质传输和电子传输能力、改善材料导电性，进而优化检测性能。

本文主要总结了生物质衍生炭基材料在电化学传感领域的应用研究现状。概述了生物炭材料的主要合成策略，对生物炭基材料在环境污染物、药物及生物分子分析中的应用进行概括总结，并对其应用性能进行详细评价和比较，讨论了相关的技术难点。在此基础上，分析了该领域存在的困难，提出未来的发展方向。

1　生物炭合成方法

生物炭的合成方法根据生物质类型及其应用领域而不同，主要包括热解炭化、水热炭化及熔盐炭化等方法。合成方法和相关参数，如温度、压力、炭化时间、pH、气体气氛、溶剂和底物浓度，在决定所得材料的结构和活性方面起着关键作用，合理调控这些合成参数对于调整炭材料的性能以满足特定的要求至关重要。

1.1　热解炭化法

大多数生物炭材料是通过在 N_2、Ar 等惰性气氛下高温热解炭化的方法制备。材料在处理过程中经历不同的化学路径：首先在 100 ~ 300℃ 挥发水分，紧接着在 400 ~ 600℃ 炭化，生成 CO_2、CH_4、CO 等气体；最后在 600℃ 以上进一步转变为石墨化炭骨架。不同的生物质原料，其热解温度和具体合成步骤会稍有差异。

采用热解炭化法制备炭材料时，可以将生物质进行简单的处理，不引入其他试剂直接炭化。直接炭化所制备的炭材料其石墨化程度一般较低，炭化温度高于 900℃ 时，石墨化程度逐渐提高。所制备材料的形貌及孔道结构也主要受其在炭化过程中所产生的气体的影响。例如，Yin 等[21]收集螃蟹腮进行粉碎、干燥等前处理后，在高纯度 N_2 气氛下，首先在 400℃ 下预炭化 1h，随后在 700℃、800℃、900℃ 各炭化 1h，获得不同结构的活性炭材料 CGC-700、CGC-800 和 CGC-900。实验结果表明，CGC-900 具有最高的石墨化程度，而 CGC-800 具有最大的比表面积 (1144.8m^2/g)。通过在生物质中引入其他的催化剂及活化剂，可以有效地提高所制备炭材料的石墨化度和孔道结构等。除了在制备过程中原位引入催化剂或活化试剂达到对炭材料进行改性或功能化的目的，也可以通过物理或化学方法后活化处理，以提高性能。一般采用如 KOH、$ZnCl_2$ 及 K_2CO_3 等物质活化，进一步改善材料的孔隙结构和比表面积，以得到多孔炭。例如，Chang 等[22]以蚕丝为原料，进行脱胶处理并原位引入 $FeCl_3$ 和 $ZnCl_2$ 为催化剂和活化试剂，将得到的丝素蛋白在 Ar 气环境下加热至 220℃ 保持 45min，随后加热至 900℃ 炭化 2h，自然冷却后获得蚕丝衍生炭，所制备材料经 X 射线衍射分析证明具有较高的石墨化。其中 $FeCl_3$ 催化无定形炭向石墨化炭转变，而 $ZnCl_2$ 首先被还原成金属 Zn，随着温度继续升高，Zn 挥发后在炭基体上产生孔结构，提高材料的比表面积。Jin 等[23]收集杜鹃

花经过洗涤、干燥后研磨成粉末, 将杜鹃花粉末在 KOH 溶液中浸泡 3h, 过滤、干燥处理后在 N_2 气氛下 800℃ 碳化 3h 得到多孔炭材料, 其比表面积 788.9m^2/g, 而在制备过程中未加入 KOH 所得炭材料的比表面积为 417.4m^2/g。可见, KOH 的引入是提高炭材料的比表面积的有效方法。热解炭化过程中涉及的步骤非常复杂, 但其机理因反应条件的复杂性, 至今尚不完全清楚。根据文献研究结果分析, 在较低温度下 (400 ~ 500℃) 热解所制备的生物炭, 其表面具有备丰富的官能团, 更适用于污染物吸附领域。例如, Sun 等[24] 通过将稻草在 450℃ 热解 2h, 粉碎处理得到炭材料。经表征, 所得炭材料具有丰富的羧基、内脂基和酚羟基, 在减缓黏性土壤中水的渗透方面展现出良好的应用前景。Huang 等[25] 分别采用小麦秸秆、玉米秸秆和水稻秸秆为原料, 通过在 550℃ 热解 2h, 得到不同的碳材料, 系统地研究了其对酸性土壤保水性的影响。在大于 700℃ 炭化所制备的生物炭, 其具有一定的石墨化程度, 且具有较大的比表面积, 更有利于其电化学应用。热解方法的主要缺点是反应比较缓慢, 制备过程较长, 以及所释放气体对环境有污染, 必须采用适当的气体吸收装置对气体进行处理。

1.2　水热炭化法

1913 年, Titirici 等[26] 首次采用水热炭化法 (HTC) 将纤维素转变为类炭材料, 使用的生物质材料主要包括植物原料、动物废弃物、农业废料或林业副产品。炭化机理主要涉及反应物和溶剂的物理反应及化学反应, 化学相互作用包括水解、脱水、脱羧、聚合和芳构化。HTC 可以分为四类, 即高温 HTC、低温 HTC、微波辅助 HTC 和添加剂辅助 HTC。高温 HTC 有助于生产各种具有高孔隙率和高表面积的炭质材料或者碳量子点 (CQDs); 低温 HTC 所制备的材料大多为单分散的炭质胶球/颗粒。

Yang 等[27] 以香蕉皮为原料, 乙二胺水溶液为溶剂, 在 220℃ 反应 24h, 制备氨基修饰 CQDs-NH_2。结果表明, 姜黄素的加入对 CQDs-NH_2 的蓝色荧光有猝灭作用。在 1 ~ 15μmol/L 的浓度范围内对姜黄素的响应呈良好的线性关系, 检出限为 18.56nmol/L。Xu 等[28] 采用橘子皮为原材料, 通过将橘子皮浸入在乙醇溶液中浸提, 收集浸提液至水热釜中, 在 200℃ 反应 10h, 最终获得尺寸在 2 ~ 4nm 的 CQDs 溶液。Chen 等[29] 将玉米芯干燥、粉碎, 在去离子水中浸泡 30min 后, 于水热反应釜中 200℃ 反应 6h, 将得到的黑褐色悬浮液离心、过滤、干燥处理之后得到 CQDs 粉末, 采用同样的方法以瓜子壳和葡萄籽为原料也得到 CQDs。作者系统研究了三种 CQDs 的光谱学特征, 并以玉米芯 CQDs 为研究对象, 利用其过氧化物酶活性和荧光特性研制了荧光传感平台, 定量检测生物分子多巴胺。采用水热方法制备生物炭时, 所采用的溶剂可以是纯水也可以是其他溶剂, 同时可以在反应体系中引入其他活化试剂或者催化剂。例如, Silva 等[30] 以甘蔗渣为原料, 加入磷酸溶液为辅助试剂, 在相对较低的温度下 (150℃) 反应 14h 制备水热炭, 所制备炭材料呈块状且表面具有丰富的羟基。Sun 等[31] 将松木用 $FeCl_3$ 和 $CoCl_2$ 溶液混合浸泡, 在水热反应釜中 200℃ 下加热 6h, 再使用 800W 微波作为辅助手段将样品加热活化, 制备复合炭基材料将其应用于催化领域。

水热方法的优势在于, 所用试剂毒性小, 炭材料的形态通过改变温度即可调节及所用仪器简单。主要缺点之一是水热反应是在密闭高压水热釜中进行的, 若操作不当容易引起安全事故。其次, 水热炭化法的最终产物为量子点或者大尺寸的炭颗粒, 并不是传感电极材料最佳备选, 在发光及催化领域应用较多。

1.3　熔盐炭化法

熔盐炭化法是将生物质在熔盐介质中转化为炭材料的方法, 所制备产物具有较好的热稳定性和良好传热特性。大多数无机盐在室温下是离子晶体, 但在高于其熔点的温度下会转化为相应的离子液体, 即熔盐。常用的熔盐主要包括碱和碱土金属阳离子的卤化物、硝酸盐、硅酸盐、碳酸盐、氢氧化物和磷酸盐。熔盐具有工作温度范围广、热稳定性好、蒸气压低、热容量大、黏度低、对许多杂质溶解性好等优点, 使其成为生物质炭化和活化的良好反应介质, 既可以作为制备过程中的造孔剂, 又可以实现生物炭掺杂。

熔盐炭化法与热解炭化法过程类似, 生物质的炭化和活化在熔盐中同时进行, 从而大大节省了能源消耗。两者的主要区别在于, 以熔盐为导热介质处理生物质, 能使炭化、活化、除杂同时完成, 生物质在熔盐炭化过程中释放的热量能被熔盐快速吸收、转移和储存, 故熔盐炭化生物质在一定程度上是一个自热过程, 熔盐起到加速生物质到生物炭转化的作用。Liu 等[32] 以葡萄糖为原料, 在熔融盐 (LiCl) 辅助下合成了强疏水性、大比表面积的多孔炭。Li 等[33] 通过在 600 ~ 800℃ 热解大米壳与 LiCl 的混合物制备炭材料, 利用不同的表征技术研究了该生

物炭的物理和化学性质。在 25℃ 和 100kPa 条件下，测试了热解温度和盐/生物质比例对生物炭结构和 CO_2 吸附性能的影响。结果表明：生物炭的 CO_2 吸收量随热解温度的升高先上升后下降，随熔盐和生物质比例的升高而增加。除了使用单一熔盐辅助合成外，也可以同时采用多种熔盐辅助合成生物炭。Jia 等[34]将不同的盐 (即 NaCl、KCl 和 LiCl) 和 KOH 按 1∶1 的摩尔比混合后，分别加入酪蛋白溶液中，并将其置于封闭的石英管中进行热化学处理，在氩气 (99.99%) 保护下，依次加热到 300℃ 和 820℃，并保持 45min 得到黑色固体，用盐酸浸泡去除氯化物、碳酸盐和未消耗的 KOH，获得最终的产物。根据 SEM 图像和 N_2 吸附等温线，发现单独的 KOH 与 KOH 和熔盐的组合之间存在不同的造孔机理，最终获得的材料比表面积差异较大。Cheng 等[35]分别用 $KHCO_3$-KCl 和 K_2CO_3-KCl 两种熔盐体系制备玉米秸秆基多孔碳，并采用系列表征方法探讨熔盐体系对材料理化性质的影响。结果表明，两种熔盐体系均能显著提高炭材料的含氧官能团的含量。不同的是，$KHCO_3$-KCl 体系可以显著提高超微孔比例 (48.6% ~ 66.2%) 和比表面积 (1551 ~ 2512m^2/g)，而 K_2CO_3-KCl 体系则不能。机理研究表明，$KHCO_3$-KCl 体系可以显著影响木质纤维素三组分热解反应之间的相互作用，从而调节材料的理化性质，实现协同活化。

采用熔盐炭化法制备生物炭时，通过选用不同的熔盐，或者不同熔盐的组合，或者熔盐与碱的组合，可以制备具有大比表面积的多孔炭基材料，此类炭材料一般具有优异的吸附性能，所以其应用领域也主要集中的吸附污染物及电容器领域，熔盐炭化法目前存在的主要问题是如何处理合成过程中所使用的盐，反应结束后所得物质为炭材料与熔盐的混合物，产物处理时，一般采用过滤水洗的方式去除熔盐，滤液为大量的熔盐废液，回收再利用较困难。此外，反应容器的腐蚀问题也较难解决[36-38]。

不同生物炭制备方法比较见表 1。

2　生物炭基电化学传感器的应用

通过设计具有不同结构和尺寸的炭基材料，将其修饰在电极表面，可以制备出具有独特性能的新型电化学传感器[39-40]。下面主要总结生物炭基电化学传感器在环境污染物、药物及生物分子分析中的应用及研究进展。

2.1　在环境污染物分析中的应用

人类生活方式的转变、工业化扩张及过度城市化，使得环境污染已成为一个世界性的问题。因此，生物质衍生炭材料在电化学检测环境污染物方面的应用研究日益广泛，常被用来检测有机化合物及重金属等环境污染物。

2.1.1　在有机污染物分析中的应用

有机污染物具有高毒、持久、生物积累性和远距离迁移性，这些特性使得它们在环境中难以降解，并通过食物链累积，最终对位于生物链顶端的人类造成极大的危害。检测有机污染物的常见方法包括分光光度法、气相色谱法等，具体方法取决于污染物的性质和检测需求。近年来，电化学传感技术在有机污染物分析方面也取得了较大进步，文献报道的基于生物炭的传感器，其检测分析的目标物主要包括 N_2H_4、有机农药及酚类化合物。

Sha 等[41]开发了一种新型的油菜籽衍生 CQDs 传感器用于检测 N_2H_4。传感器对肼的灵敏度为 151.5mA/(mmol•cm^2) (R^2=0.997)，检出限低至 39.7 μmol/L。使用加标回收法测定了实际样品包括饮用水和模拟废水中肼的浓度，回收率为 97% ~ 102%，证明其具有较好的实际应用前景。Adiraju 提出了一种通过在缓冲溶液中电化学循环活化来提高杏仁壳生物炭 (AS-BioC) 的电化学性能的方法[42]。这种电化学活化方法增强了 AS-BioC 表面官能团和孔隙度，提高了电极电导率和电化学活性表面积。经活化的 AS-BioC 修饰的丝网印刷电极表现出更强的电化学性能，检测对硫磷灵敏度为 17.3μA/nmol，检出限为 1.35nmol/L，线性范围较宽 (25 ~ 2500nmol/L)。Madhu 等[43]以芒果叶为碳源制备氮掺杂活性炭，

表 1　不同生物炭制备方法比较

Table 1　Comparison of different biochar preparation methods.

制备方法	反应温度	制备材料主要特性	主要应用范围	参考文献
热解炭化法	400 ~ 600℃	表面官能团丰富、石墨化度低	吸附	[21, 24-25]
热解炭化法	700 ~ 1200℃	石墨化程高、导电性良好	电容器、电催化、电化学传感、CO_2 捕获	[22-23]
水热炭化法	100 ~ 300℃	表面官能团丰富、石墨化度低、形貌多为炭量子点或炭颗粒	荧光传感、电催化	[27-31]
熔盐炭化法	900 ~ 1200℃	石墨化程度高、比表面积大	电容器、吸附、电化学传感、CO_2 捕获	[32-35]

所制备的电极被用于 4-硝基苯酚的传感检测。由于杂原子 N 的存在增加了活性位点的数量, 所构建传感器表现出良好的电化学活性, 检测范围为 1 ~ 500μmol/L, 检出限为 0.16μmol/L, 灵敏度 5.810μA/(μmol•cm^2)。Xu 等[44]以竹荪为碳源, 开发了一种环境友好型的多孔氮掺杂碳用于双酚 A 的电化学传感检测, 掺杂的氮原子提供了丰富的反应位点和足够的缺陷, 因此所构建传感器具有良好性能。

通过对生物炭的结构和组成的合理优化, 可以实现同时检测水体中的不同酚类化合物。例如, Zhao 等[45]利用棉花衍生炭作为电极敏感材料构建电化学传感器, 同时测定对苯二酚 (HQ) 和邻苯二酚 (CC)。该传感器对 HQ (0.5 ~ 3000μmol/L) 和 CC (1 ~ 3000μmol/L) 具有较宽的线性范围, 检出限分别为 0.47μmol/L 和 0.4μmol/L。此外, 所制备的传感器还具有特定选择性、长寿命和良好的适用性。对中国湖泊水样的实际检测结果表明, 该传感器具有良好的应用前景。Mahfoz 等[46]课题组采用热解和球磨工艺的直接结合, 从椰枣叶废料中合成生物炭, 并开发了一种修饰玻碳电极 (GCE), 用于高灵敏度和同时检测酚类污染物, 特别是 1-萘酚 (1-NP) 和 2-萘酚 (2-NP)。该项研究开发了两种创新的电化学传感器, 第一种方法采用 1-NP 和 2-NP 的直接氧化电流信号定量, 而第二种方法利用了目标物质与二羟基萘形成醌相关的氧化还原峰电流信号定量。电化学结果表明, 直接电氧化法 1-NP 的检出限为 14μmol/L, 而醌生成法的检出限为 0.64μmol/L。同样, 直接电氧化法 2-NP 的检出限为 11μmol/L, 通过醌生成法降至 0.61μmol/L, 这些结果超越了传统的检测方法。

2.1.2　在重金属分析中的应用

微量金属元素如锰、铁、铜、锌、硒对生物体的新陈代谢非常重要, 而其他重金属如铅、镉、汞、砷和锑等会对环境造成严重威胁, 进而通过食物链影响人体中枢神经系统、皮肤、肾脏、骨骼和牙齿[47]。目前, 电化学传感技术在 Hg^{2+}、Pb^{2+}、Cd^{2+}及 Cu^{2+}的分析中应用较多, 其检测机理主要是电极敏感材料和被测目标物质之间发生氧化还原反应, 导致电极的电流信号发生变化, 进而达到定量的目的。基于不同电极材料所构建的传感器, 因为材料本身物理化学性质的不同, 传感器的检出限、灵敏度及稳定性各有差异。

Silva 等[30]将甘蔗渣炭修饰在碳纸电极上制备了 Pb^{2+}传感器, 采用差分脉冲吸附阳极溶出伏安法 (DPAdSV) 测定 Pb^{2+}。通过优化检测 Pb^{2+}离子的重要参数和伏安技术参数, 得到 0.50 ~ 7.06μmol/L 的线性响应范围, 检出限和定量限分别为 55.0nmol/L 和 181.5nmol/L。采用所建立的伏安法测定自来水和河水样品中 Pb^{2+}, 回收率为 91.19% ~ 109.22%。Xu 等[48]以冬瓜为原料, 同时引入氮源合成了具有丰富边缘缺陷位点的蠕虫状氮掺杂碳框架 (WNCF)。采用 Nafion-WNCF 设计了一种高灵敏度电化学传感器, 用于 DPAdSV 痕量测定重金属 Pb^{2+}, 线性范围为 0.5 ~ 100μg/L, 检出限为 0.2μg/L。Valenga 等[49]将甘蔗渣炭化并采用硝酸活化处理后, 建立了一种测定 Cu^{2+}的 DPAdSV 方法。线性动力学范围为 1.0 ~ 15.0μmol/L, 检出限为 1.09μmol/L, 并具有良好的抗干扰性。Bressi 等[50]以啤酒渣为原料, 经过简单处理之后, 利用水热方法于 240℃ 反应 9h 制备炭材料 CNDs, 以 CNDs 为电极敏感材料所构建的传感器可以同时检测 Hg^{2+}、Pb^{2+}、Cd^{2+}和 Ni^{2+}, 检出限分别为 124、551、453 和 608ng/L, 对应的灵敏度依次为 34.1μA/(nmol•cm^2)、21.3μA/(nmol•cm^2)、32.2μA/(nmol•cm^2) 和 11.4μA/(nmol•cm^2)。检测实际海水和废水样品的加标回收率为 99.8% ~ 102.6%。Sharma 等[51]利用水热结合高温炭化方法制备银胶菊废弃物衍生炭 CGC-600, 进一步利用该材料构建 Hg^{2+}传感器, 采用 DPV 对 Hg^{2+}进行定量检测, 检出限为 6.17μmol/L, 定量限和灵敏度分别为 18.7μmol/L 和 0.4723μmol/(μA•cm^{-2})。Ganaie 等[52]将 SnS_2 修饰在雄花衍生炭上制备复合材料 SnS_2@BC, 以此材料修饰在 GCE 表面构建传感器, DPV 检测结果显示, 对 Pb^{2+}和 Hg^{2+}的检出限分别为 0.28μmol/L 和 0.55μmol/L。

2.1.3　在环境微塑料分析中的应用

塑料制品的广泛使用及其缓慢的自然降解过程导致废弃塑料的大量积累, 塑料进入水体环境并在其中停留数百或数千年, 被光化学过程分解产生微塑料颗粒。近年来, 微塑料已经对水生和陆地生态系统产生较大干扰, 摄入这些颗粒会对野生动物、水生生物及人类健康产生严重后果。微塑料的常用检测方法包括傅里叶变换红外光谱法 (FTIR)、拉曼光谱法 (Raman)、热重-光谱联用分析方法及热裂解-质谱联用分析方法。其中, Raman 和 FTIR 能够检测到微米级别的样品, Micro-Raman 能够检测到 1μm 的样品。而联用技术检测程序复杂, 单个样品检测时间长, 对操作人员要求高, 缺乏专用的微塑料热裂解器, 质谱图解析困难, 这些因素都制约着联用方法的普及应用。

最近,电化学传感器在环境微塑料的检测方面取得突破性进展,能在较短时间内对微纳级的微塑料颗粒进行定性和定量分析。Nguyen 等[53]合成疏水性氧化铈纳米颗粒 (CeO_2 NPs),并将其作为电极修饰材料构建传感器,首次采用电化学传感方法检测两种不同类型微塑料 [聚乙烯 (PE) 和聚丙烯 (PP)]。CV 和 LSV 电化学分析结果表明,传感器对 PE (直径 27 ~ 32μm) 的检测限为 0.226mg/mL,对 PP (直径 ~ 600μm)的检出限为 0.338mg/mL,两者的检测范围均为 0.2 ~ 1.0mg/mL。此外,研究人员通过将天然存在的海星和芦荟炭化,制备了海星炭和芦荟炭两种类型的生物炭,将其作为传感电极材料,用于 ~ 100nm 聚苯乙烯微塑料 (PS) 的电化学检测[54]。电化学结果表明,海星炭电极的灵敏度为 0.2562μA/(μmol•cm^2),检出限为 0.44nmol/L,而芦荟炭的灵敏度为 3.263μA/(μmol •cm^2),检出限为 0.52nmol/L。其检测机理为:所合成的炭材料中的 K、Mg、Ca 和 Cl 等掺杂元素 (M) 与 PS 的活性位点相连接,炭表面的 M−O 或 M−S 或 M−C 键使 PS 微塑料氧化,从而产生电子变化,导致电流信号增强。虽然通过材料调控实现了对 ~ 100nm 的 PS 的定性及定量检测,但是所检测的 PS 只仅仅是微塑料的理论模型,实际水体中的微塑料无论是成分还是颗粒尺寸都要复杂得多,这也是目前基于电化学传感技术检测微塑料遇到的普遍性问题,要采用电化学传感器实现对实际水体样品中的微塑料进行检测,还需要开展更深入的研究。

在污染物检测领域,生物炭基传感器目前涵盖了有机污染物、重金属及微塑料等多种类物质的检测。表 2 列举了不同生物炭基电化学传感器方法对环境污染物监测的参数,不同修饰电极及检测方法对检测目标物的线性范围不同。整体而言,传感器对环境污染物检测的检出限已达到 μmol/L 甚至 nmol/L 级,检出范围大多介于几 μmol/L 到几百 μmol/L 之间。虽然在现实环境中检测的一些问题已经解决,但是对于特殊样品的处理,如何实现现场快速检测等问题仍然需要进一步探讨。期待未来相关研究机构可以制定一套用于开发、数据处理和实施检测的污染物传感器的指南,以快速准确地检测、分析、跟踪和管理污染[55]。

2.2　在药物分析中的应用

药物检测分析中,基于生物炭的电化学传感器在化学药品及中药分析中的研究都取得一定进展。整体来看,化学药品分析中比较常见的检测目标物为对乙酰氨基酚及抗生素类物质,主要是因为所合成炭材料的表面官能团包括—OH、—COOH 等比较容易与此类物质发生物理、化学相互作用,使得电化学信号发生明显变化而被识别,检测机理也比较明晰。

表 2　不同生物炭基电化学传感器方法对环境污染物的检测参数

Table 2　Detection parameters of environmental pollutants by different biochar based electrochemical sensor methods.

修饰电极名称	检测方法	检测目标物	方法线性范围	方法检出限	参考文献
CQD /GCE	计时安培	肼	/	39.7μmol/L	[41]
AS-BioC/SPCE	SWV	对硫磷	0.025 ~ 2.5μmol/L	1.63×10^{-3}μmol/L	[42]
AC900/GCE	LSV	4-硝基苯酚	1 ~ 500μmol/L	0.16μmol/L	[43]
NDC/GCE	DPV	双酚 A	1.0 ~ 50.0μmol/L	1.068μmol/L	[44]
CLC/GCE	CV	HQ CC	0.5 ~ 3000μmol/L 1.0 ~ 3000μmol/L	0.47μmol/L 0.40μmol/L	[45]
DLSNC/GCE	CV	1-NP 2-NP	1.0 ~ 25μmol/L 1.0 ~ 25μmol/L	0.64μmol/L 0.61μmol/L	[46]
HC/CPE	DPAdSV	Pb^{2+}	0.50 ~ 7.06μmol/L	0.055μmol/L	[30]
WNCF/BFGCE	DPAdSV	Pb^{2+}	0.5 ~ 100μg/L	0.2μg/L	[48]
Biochar+CPE	DPAdSV	Cu^{2+}	1.0 ~ 15.0μmol/L	0.36μmol/L	[49]
CNDS/SPCE	SWASV	Hg^{2+} Pb^{2+} Cd^{2+} Ni^{2+}	/	124ng/L 551ng/L 453ng/L 608ng/L	[50]
CGC-600/GCE	DPV	Hg^{2+}	10 ~ 100μmol/L	6.17μmol/L	[51]
SnS_2@BC/GCE	DPV	Pb^{2+} Hg^{2+}	/	0.28μmol/L 0.55μmol/L	[52]
AL-1/GCE	I-V	PS (100nm)	/	520μmol/L	[53]
SF-1/GCE	I-V	PS (100nm)	/	440μmol/L	[53]

Kim 等[56]课题组制备了 $ZnCl_2$-KOH 活化的海藻衍生炭, 采用此材料修饰 GCE, 并进一步对对乙酰氨基酚进行检测, 检出限较低且灵敏度较高。Yalikun 等[57]通过浸渍法在沙枣胶衍生的多孔炭中引入氮、硫和磷三种杂原子, 制备异质元素掺杂型炭材料 NSP-PC。将 NSP-PC 修饰在 GCE 表面, 得到工作电极 NSP-PC/GCE, 用于检测甲硝唑 (MNZ), 检出限低至 0.013μmol/L。同时, 氯霉素、多巴胺、硝基苯酚、尿酸、葡萄糖、抗坏血酸、维生素 E 和氟苯尼考对 MNZ 的检测无干扰作用。Veerakumar 等[58]以决明子壳为生物质碳源, 炭化后负载金属制备了 Pt-Re NPs/PAC 复合物, 并用于电化学测定呋喃唑酮, 检测范围为 1 ~ 299μmol/L, 检出限低至 0.075μmol/L, 灵敏度为 5.52μA/(mmol•cm^2)。Malode 等[59]使用稻壳衍生的石墨烯修饰碳糊电极用于检测非甾体抗炎药甲芬那酸。所构建的修饰电极对十六烷基三甲基溴化铵介质中甲芬那酸的检测具有较高的灵敏度和选择性, 检出限为 2.13nmol/L, 线性动态范围为 0.001 ~ 6000μmol/L, 对共存分子的干扰可以忽略不计, 适用于检测人尿、血清、母乳样品和药物片剂中的甲芬那酸, 回收率较高。Liu 等[60]将蟹壳废弃物在高温下转化为多孔生物炭, 用于建立呋喃西林的定量检测的电化学传感器。采用 SEM、XRD、FTIR 和 N_2 吸附-脱附等分析手段对不同温度下蟹壳碳的形貌和结构特性进行了表征。电化学结果表明, 在 700℃ 炭化条件下制备的蟹壳碳具有更强的快速检测呋喃西林的传感能力, 线性范围为 0.40 ~ 80μmol/L, 灵敏度为 0.55μA/μmol, 检出限为 0.11μmol/L (*S*/*N*=3), 该传感器可用于实际药物 (复方鱼肝油软膏) 中硝基呋喃酮的定量, 回收率满意。Chang[22]课题组利用所制备的蚕丝炭复合材料作为电极材料制备了修饰电极, 利用 DPV 技术检测氯霉素, DPV 峰电流随浓度的增加呈线性关系, 检测范围为 1 ~ 200μmol/L, 低检出限为 0.57μmol/L (*S*/*N*=3)。在此基础上, 评价了该传感器用于氯霉素检测的实用性, 以鱼、虾和鸡肉为分析对象, 采用加标回收法检测, 回收率为 85.96% ~ 106.72%, RSD较低。

除了在化学药品检测中应用广泛外, 生物炭修饰电极也可以用于中药分子的检测分析。Cheng 等[61]通过将平菇热解炭化后水热负载 Au 和 Pt 纳米粒子, 制备 Au-Pt@BPC 复合体, 将其修饰于 CILE 表面作为检测黄芩素的工作电极。在最佳条件下, 该传感器的线性范围为 0.48 ~ 2.0μmol/L 和 4.0 ~ 140.0μmol/L, 检出限低至 0.01μmol/L。该修饰电极成功应用于药物和人体尿液样品中黄芩素含量的检测。Ai 等[62]采用高温热解方法合成香蕉皮衍生多孔炭, 进一步采用自组装方法将其与多壁碳纳米管复合, 并修饰在 GCE 表面, 构建一种用于黄芩素灵敏测定的电化学传感器。采用 CV 研究了黄芩素的电化学响应, 结果表明所构建的传感器具有较高的灵敏度和较低的检出限。

此外, 该类物质的检测机理目前一直认为是黄芩素中的羟基被电极材料氧化成羰基, 产生明显的氧化还原峰信号。文献报道的基于生物炭或者其他材料的电化学传感器用于中药分析时, 黄酮类物质报道相对较多, 其他中药物质的分析相对较少, 可能与中药被测物质的成分复杂等因素相关, 目前的研究重点也比较倾向于降低此类传感器的检出限, 扩大检测范围。表 3 对上述生物炭基传感器检测不同药物的检测参数进行了总结。化学药物检测时, 实际样品的处理相对简单, 检测便捷且结果可靠。中药实际样品检测时, 样品处理阶段稍微复杂, 且同一中药中结构类似的化合物较多, 对传感器的选择性要求高, 或者要求传感器可以同时检测多种物质。

2.3　在生物分子分析中的应用

生物分子是存在于细胞和活体器官中的具有不同功能的物质, 主要包括碳水化合物、脂类、蛋白质、氨基酸、维生素和核酸等物质。目前, 生物炭基传感器在生物分子的检测方面, 主要集中在葡萄糖、多巴胺、尿酸及抗坏血酸等几种物质分析中, 其他物质的检测应用相对较少。

Li 等[63]以柳絮为生物质前驱体, 制备竹叶状 CuO 纳米棒和空心碳纤维复合材料 (CuO NRs@PC), 用于构建非酶葡萄糖传感器, 检测范围较宽 (5 ~ 8000μmol/L), 检出限低至 0.1μmol/L, 灵敏度为 609μA/(mmol•cm^2)。检测性能的提高可能是因为炭基质三维多孔结构明显改善了传质速率, 且材料良好的电导率有利于生物分子与电极表面之间电子的传递。此外, 材料本身的缺陷和微孔提供了有效的葡萄糖分析吸附的活性位点。Qu 等[64]采用玫瑰为碳源, 通过炭化后负载 CoS 纳米花, 制备 CoS@C 复合材料, 修饰在 GCE 表面得到 Nafion/CoS@C/GCE 工作电极, 用于葡萄糖检测, 检测范围为 10 ~ 960μmol/L, 检出限为 2μmol/L。上述非酶法的主要缺点是选择性低及灵敏度较差。为了获得更好的选择性和优异的灵敏度, Shan 等[65]通过将葡萄糖氧化酶 (GOD) 固定在葡萄藤衍生 3D 多孔炭 (3D-CVS) 上, 制备了一种新型的葡萄糖生物传感器, 线

表 3　不同生物炭基电化学传感器方法对药物的检测参数

Table 3　Detection parameters of drugs by electrochemical sensor methods based on different biochar materials.

修饰电极名称	检测方法	检测目标物	方法线性范围 (μmol/L)	方法检出限 (μmol/L)	参考文献
PNC/PGE	DPV	氯霉素	1 ~ 200	0.57	[22]
ZKAKC/GCE	DPV	对乙酰氨基酚	0.01~20	0.004	[60]
NSP-PC/GCE	LSV	甲硝唑	0.1 ~ 45 50 ~ 350	0.013	[57]
Pt−Re NP/PAC/GCE	LSV	呋喃唑酮	1 ~ 299	0.075	[58]
RHG/CPE	SWV	甲芬那酸	0.001 ~ 6000	2.13×10^{-3}	[59]
C-CS-700/GCE	DPV	呋喃西林	0.4 ~ 80	0.11	[60]
Au-Pt@BPC/CILE	DPV	黄芪素	0.48 ~ 2.0 4.0 ~ 140.0	0.01	[61]
BPBC-MWCNT/GCE	DPV	黄芪素	0.004 ~ 100	1.33×10^{-3}	[62]

性响应范围为 0.58 ~ 16mmol/L, 并且具有较高的灵敏度和较低的检出限。

Padmapriya 等[66]提出了一种以香蕉花苞叶提取物为原料水热合成磷氮双掺杂碳量子点 (N,P-CQDs) 的简便方法, 以 N,P-CQDs 为修饰材料构建传感器用于检测多巴胺。因为杂原子的掺杂提高了 CQDs 的电导率, 材料表面的—COOH、—NH_2 和—PO_4^{3-}等基团选择性地吸引阳离子, 由于静电斥力而在溶液中留下阴离子。因此, 所构建传感器对多巴胺具有较高的选择性和灵敏度、较低的检出限 (~ 500pmol/L) 和较宽的线性范围 (6.0 ~ 0.1mmol/L)。此外, 在多巴胺注射实时样品中成功检测多巴胺, 检出限低至 630pmol/L, 线性范围为 2.5mol/L 至 0.16mmol/L。

生物分子分析中, 所构建的传感器大多不是基于纯生物炭材料, 而是非金属 N、P 掺杂生物炭, 或者负载了如上述 CuO 和 CoS 等金属化合物的复合体, 这可能是生物分子的特殊结构决定的, 其较难与纯的生物炭骨架发生作用, 必须通过引入其他非金属或者金属促进反应发生。此外, 可以通过在电极上引入其他物质间接地实现生物分子检测。例如, Jin 等[23]以杜鹃花为碳源, 经高温煅烧和 KOH 活化制备分级多孔碳材料 (KACM), 将 KACM 和硫堇 (Thi) 同时组装在 GCE 表面上, 构建了用于检测抗坏血酸和尿酸的 Thi/KACM 电化学传感器。电化学测试结果表明, 该传感器对抗坏血酸和尿酸氧化具有较强的催化活性, 两个氧化峰具有较好的分离性。在优化条件下, 线性范围宽 (0.05 ~ 9mmol/L), 检出限低 (抗坏血酸 6.4μmol/L, 尿酸 10μmol/L)。此外, 该生物传感器具有良好的选择性、稳定性和重复性。采用 Thi/KACM/GCE 同时检测人体尿液中尿酸的回收率为 99.4% ~ 101.0%。Valenga 提出了一种基于铜离子 (Cu^{2+}) 固定在生物炭上的电化学传感器, 用于间接地测定目标物质[67]。首先, 将 Cu^{2+}富集在甘蔗渣生物炭修饰的碳糊电极表面, 然后继续将肌酐富集在表面上, 因为肌酐-铜络合物的形成导致 Cu^{2+}的伏安信号抑制, 以此响应作为电化学分析指标, 线性检测范围为 300 ~ 700μmol/L, 检出限和定量限分别为 91.0μmol/L 和 300μmol/L。采用标准加入法对模拟尿液样品中肌酐进行测定, 定量限浓度为 300μmol/L, 加标回收率为 101%±7%。

整体而言, 除了上述葡萄糖、多巴胺、抗坏血酸和尿酸等物质的分析, 未来应该探索更多的可以检测的生物分子, 在提高传感器灵敏度等特异性指标的基础上, 扩大其检测目标物质范围, 进一步拓宽传感器的应用领域。

3　展望

基于生物炭的电化学传感器的检测性能, 主要受炭材料的组成、结构、表面官能团及形貌等因素影响。此外, 传感器的检出限、检测范围及灵敏度与具体的传感器构建参数, 如电解液类型、修饰在电极表面的炭材料体积、电解液 pH、离子强度等因素有关。目前, 在环境污染物、药物及生物分子分析中所构建的传感器主要以传统大型电化学工作站为检测系统, 而便携式传感器的发展相对欠缺。此外, 所构建传感器的性能增强机制及传感机理需要进一步深入探索。对于生物炭基电化学传感器的发展, 未来需要关注以下三方面。

(1) 电化学传感器检测性能的提高依赖于修饰电极的合理设计, 主要与电极敏感材料的本征电化学活性和表面修饰技术相关。未来在炭材料合成方

面, 应实现生物炭的组成明确、形貌结构可调的特性, 既有利于提高检测性能, 也有利于探究传感机理。另外, 利用新兴的分子印迹技术修饰电极, 可以提高电极的亲和力和选择性, 对于炭材料与分子印迹技术的结合应用还有待深入研究。

(2) 电化学传感器件在检测各种有毒环境样品领域具有良好的发展趋势, 生物炭基电化学传感器也逐步向便携式传感器发展。新的 3D 打印技术及微型化电化学工作站结合, 可以开发低成本、高灵敏度的便携式电化学传感器件。未来可以将该技术进一步扩展到构建生物炭基智能便携传感器, 实现现场、快速、智能化分析检测。

(3) 对于传感机理及性能增强机制的剖析, 也是生物炭基电化学传感器发展过程中必须深入探讨的问题。未来需要将实验结果和理论计算相结合, 明晰传感器的检测机理及性能增强机制, 进一步优化传感器的性能, 促进生物炭基电化学传感器的发展。

Research Progress of Biochar Based Materials and Their Applications Using Electrochemical Sensors

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HIGHLIGHTS

(1) As a new detection and analysis device, the detection limit, sensitivity and linear range of the electrochemical sensor are affected by the electrode modification materials.

(2) The advantages and disadvantages of three different biochar preparation methods and the performance parameters and technical indexes of the synthesized materials were summarized.

(3) The latest application progress of biochar based electrochemical sensors in the analysis of environmental pollutants, drugs and biomolecules was reviewed.

(4) The development direction of biochar based electrochemical sensors is to broaden the detection range, improve the detection performance, determine the field detection and explore the detection mechanism.

ABSTRACT: Electrochemical sensors have become a research hotspot in the field of analytical chemistry due to their high sensitivity, good selectivity, and fast reaction rate. Using biochar materials to construct electrochemical sensors is a low cost, accessible and effective route to achieve excellent detection performance. This review summarizes the research progress of biochar based electrochemical sensors in the detection of environmental pollutants, drugs and biomolecules on the basis of briefly describing the synthesis methods and the structural properties of biochar-based materials. The synthesized biochar and the corresponding constructed sensors indicate that electrochemical sensors hold significant advantages in high-precision and high-stability chemical-signal testing. Further research will focus on optimizing the structure of carbon materials, regulating the composition of them, and preparing high-performance biochar-based materials that are more suitable for electrochemical sensors, so as to reduce the detection limit and improve the sensitivity. Besides, it is urgent to fabricate portable sensors based on biochar to determine rapid and intelligent analysis and detection, and the sensing mechanism and testing performance improvement mechanism are problems that must be deeply explored. The BRIEF REPORT is available for this paper at http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202403170058.

KEY WORDS: electrochemical sensor; biochar; environmental pollutants; drugs; biomolecules

BRIEF REPORT

An electrochemical sensor is a device used for qualitative or quantitative detection and analysis by measuring the electrochemical signal of the target substance[1]. Compared to traditional instrument analysis methods, such as high-performance liquid chromatography, inductively coupled plasma-mass spectrometry, and ultraviolet spectroscopy, electrochemical sensing technology has become a research hotspot due to its convenience, high sensitivity, good selectivity, and fast reaction rate[2-6]. During the analysis and detection process, the working electrode determines the specific capture and recognition of the substance to be measured, which is the crucial factor that affects the performance of the electrochemical sensor[7-9]. Effectively modifying electrode sensitive materials on the electrode surface to achieve electrochemical signal amplification is the key to enhancing the detection performance of electrochemical sensors.

Biochar based materials have attracted extensive research interest from scholars due to their unique structure, wide availability, high sustainability, economic compatibility, and renewable characteristics[10]. Their applications mainly include catalysis[11], carbon dioxide capture[12], adsorption and separation[13], hydrogen storage[14], solar cells[15], water treatment[16], energy storage[17], and electrochemical sensors[18]. In recent years, scholars have been committed to improve the performance of electrochemical sensors based on biochar materials. The main methods include activation, heteroatoms doping, and loading of metal/metal alloy/metal oxide nanoparticles[19-20].

The applications and research status of biochar-based electrochemical sensors were summarized in this review. The main synthesis strategies of biochar and the applications of biochar-based electrochemical sensors in the analysis of environmental pollutants, drugs and biomolecules were summarized. Besides, the detection parameters were evaluated and compared, and the related technical difficulties were discussed in detail. On this basis, the existing difficulties in this field were analyzed, and the future development direction was proposed.

1. The synthesis methods of biochar materials

(1) Pyrolysis carbonization method. When the pyrolysis carbonization method is used to prepare carbon materials, the biomass can be treated simply, and no other reagents are introduced to direct carbonization. For example, Yin et al.[21] collected crab gills for simple pre-treatment, such as crushing and drying and then carbonized to a prepared biochar. By introducing other catalysts and activators into the biomass, the graphitization degree and pore structure of the prepared carbon materials can be effectively improved[22-23]. The steps involved in pyrolysis carbonization are very complicated, the mechanism is still not completely clear because of the complexity of reaction conditions. According to the analysis of the current research results, the biochar prepared by pyrolysis at a lower temperature (400−500℃) has rich functional groups on its surface, which is more suitable for the field of pollutant adsorption[24-25].

(2) Hydrothermal carbonization method. In 1913, Bergius et al.[26] used the hydrothermal carbonization method to transform cellulose into carbon-like materials for the first time. The biochar prepared by the hydrothermal method is mostly carbon quantum dots[27-29]. As the hydrothermal method was employed to prepare biochar, the solvent used can be pure water or other solvents, and other activation reagents or catalysts can be introduced into the reaction system[30-31]. The advantages of the hydrothermal method are that the reagents used are less toxic, the shape of the carbon material can be adjusted by changing the reaction temperature, and the instruments used are facile. One of the main disadvantages is that the hydrothermal reaction is carried out in a closed high-pressure hydrothermal kettle, which can easily cause accidents if it is improperly operated.

(3) Molten salt carbonization method. The process of molten salt carbonization is similar to that of pyrolysis carbonization, in which the carbonization and activation of biomass are carried out simultaneously in a molten salt medium, thus greatly reducing energy consumption. The main difference between the two methods is that molten salt can act as a catalyst to accelerate the conversion of biomass to biochar. Single NaCl, KCl, LiCl and $ZnCl_2$, or a

combination of them are commonly used as the molten salt medium[32-35]. At present, the main problem of the molten salt carbonization method is how to deal with the salt used in the synthesis process. After the reaction, the obtained material is usually a mixture of carbon materials and molten salt. When the product is treated, the molten salt is generally removed by filtering and washing, and the filtrate is a large amount of molten salt waste liquid, which is difficult to recycle. In addition, the corrosion problem of the reaction vessel is also difficult to solve[36-38].

2. Applications of biochar materials in electrochemical sensors

(1) Application in the analysis of environmental pollutants. Biochar materials have been widely used in electrochemical detection of environmental pollutants, and are often used to detect organic compounds and heavy metals. For example, N_2H_4 and phenolic compounds can be detected by biochar based electrochemical sensors with a low detection limit and good sensitivity. Bedsides, electrochemical sensors based on biochar are widely used in the detection of phenolic compounds[43-46]. By optimizing the structure and composition of biochar, different phenolic compounds in water can be detected simultaneously. The detection mechanism is relatively clear. As for heavy metals, electrochemical sensor technology is widely used in the analysis of Hg^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+}, and its detection mechanism is mainly that the redox reaction between the electrode sensitive material and the measured substance causes the current signal of the electrode to change, so as to achieve the purpose of quantification[30,48-52]. Recently, electrochemical sensors have made a breakthrough in the detection of environmental microplastics[53-54]. Although the qualitative and quantitative detection of ~100nm polystyrene microplastics is realized through material regulation, the detected polystyrene microplastics is only a theoretical model of microplastics, and the actual microplastics in water are much more complex in terms of composition and particle size, which is also a common problem encountered in the detection of microplastics. Further research is needed in the use of electrochemical sensors to detect microplastics in actual water samples.

(2) Application in drug analysis. In drug analysis, biochar based electrochemical sensors have made some progress in chemical drugs[22,56-60] and traditional Chinese medicine[61-62]; the more common detection targets in chemical drugs are acetaminophen and antibiotic substances. This is mainly because the surface functional groups of the synthesized carbon materials, including —OH and —COOH, interact relatively easily both physically and chemically with such substances, resulting in significant changes in electrochemical signals, and the detection mechanism is relatively clear. In the analysis of traditional Chinese medicine, more flavonoids were reported, while relatively few other traditional Chinese medicine substances were analyzed, which may be related to factors such as the complex composition of the measured substances in traditional Chinese medicine. The current research focus is also inclined to reduce the detection limit of such sensors and expand the detection range. In addition, the detection mechanism of flavonoids has always been thought to indicate that the hydroxyl group is oxidized to the carbonyl group by the electrode material, which produces an obvious redox peak signal.

(3) Application in biomolecule analysis. Biochar based sensors in the detection of biomolecules mainly concentrated in the analysis of several substances such as glucose, dopamine, uric acid and ascorbic acid, whereas other biomolecules detection is relatively rare[63-66]. Most of the sensors constructed are not based on pure biochar materials, but non-metallic N and P doped biochar, or loaded with metal compounds such as CuO and CoS. It may be determined by the special structure of biomolecules, which is difficult to interact with a pure biochar skeleton. The reaction must be facilitated by the introduction of other non-metals or metals. In addition, biomolecule detection can be achieved indirectly by introducing other substances on the electrode.

3. Future perspectives

The detection performance of electrochemical sensors based on biochar is mainly affected by factors such as the composition, structure, surface functional groups, and morphology of the biochar materials. In addition, the detection limit, detection range, and sensitivity of the sensor are related to detecting conditions, such as electrolyte

type, volume of carbon material modified on the electrode surface, electrolyte pH, and ion strength. At present, sensors constructed for the analysis of environmental pollutants, drugs, and biomolecules mainly adopt traditional large-scale electrochemical workstations as detection systems, and the development of portable sensors is relatively lacking. In addition, the performance enhancement mechanism and detection mechanism of the constructed sensors need to be further explored in depth. For the development of biochar-based electrochemical sensors, the following three aspects need to be focused on:

(1) The improvement of the detection performance of electrochemical sensors depends on the rational design of modified electrodes, mainly related to the intrinsic electrochemical activity of electrode sensitive materials, surface modification techniques, and sensor detection parameters. In the future, in the synthesis of carbon materials, clear composition and adjustable morphology and structure of biochar should be achieved, which is conducive to improving detection performance and exploring sensing mechanisms.

(2) Electrochemical sensor devices have a promising development trend in detecting various environmental samples, and biochar based electrochemical sensors are gradually moving towards portable sensors. The combination of new 3D printing technology and miniaturized electrochemical workstations can develop low-cost, high-sensitivity portable electrochemical sensor devices. In the future, this technology can be further expanded to build biochar based intelligent portable sensors, achieving on-site, rapid, and intelligent analysis and detection.

(3) The exploration of sensing and performance enhancement mechanisms is also a problem that must be deeply studied in the development of biochar based electrochemical sensors. In the future, it will be necessary to combine experimental results with theoretical calculation to clarify results, further optimizing the performance of sensors and promoting the development of biochar based electrochemical sensors.

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