

藻类生物质衍生功能性碳材料的制备与应用研究进展

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摘要: 面对日益严峻的环境污染与能源危机, 开发以绿色可再生生物质为碳源的功能性碳材料, 是实现“双碳”目标与可持续发展理念的关键路径。藻类生物质作为第三代生物质资源, 兼具不占用耕地、生长周期短、单位产量高、可修复水体富营养化及天然富含杂原子的优势, 无需额外添加掺杂剂即可实现碳材料杂原子原位掺杂, 为功能性碳材料制备提供了理想前驱体。系统综述藻类生物质衍生功能性碳材料的研究进展。首先, 分析了藻类生物质原料特性, 梳理不同藻类的工业分析、元素分析及成分组成数据, 明确其作为碳源的潜力。随后, 阐述了制备工艺, 涵盖热解碳化、水热碳化、微波碳化 3 种基础碳化方法, 并对比各工艺参数对产物性能的影响。同时, 详解了物理活化、化学活化、金属盐/氧化物修饰 3 类活化改性技术, 阐述其在优化碳材料孔隙结构与表面官能团方面的作用。进而, 综述了藻类生物炭在吸附、储能、催化 3 大领域的应用研究。最后, 总结了当前研究面临的挑战, 包括藻类收集成本高、成分稳定性差, 碳材料结构调控难度大、部分性能不及商用碳材料及规模化工艺不成熟等问题, 为后续理论与产业化应用提供参考。

关键词: 藻类; 碳材料; 吸附; 催化; 储能

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Advances in Preparation and Applications of Algal-Derived Functional Carbon Materials

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Abstract: Amidst growing concerns over global environmental pollution and fossil fuel depletion, developing functional carbon materials from green and renewable biomass is a promising strategy that aligns with "dual carbon" goals and sustainable development principles. Among various biomass resources, algal biomass, regarded as a highly promising third-generation feedstock, offers unique advantages. It does not occupy arable land or compete with food crops, and its short growth cycle enables rapid proliferation, resulting in a per-unit-area yield significantly higher than that of traditional biomass. Additionally, algae can effectively absorb nutrients such as nitrogen and phosphorus from water during growth, thus contributing to the remediation of water eutrophication. Moreover, algae are naturally rich in heteroatoms such as nitrogen and oxygen, allowing for in-situ heteroatom doping

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during carbon material synthesis without the need for additional dopants. These characteristics make algae an excellent precursor for preparing functional carbon materials. This review systematically summarizes the research progress on functional carbon materials derived from algal biomass. First, it provides an in-depth analysis of the raw material characteristics of various algal types, including proximate analysis, elemental composition, and specific component data, thereby highlighting their potential as high-quality carbon sources. Subsequently, the review elaborates on relevant preparation methods, covering three fundamental carbonization techniques: pyrolytic carbonization, hydrothermal carbonization, and microwave carbonization. It also compares the effects of key processing parameters on the performance of the resulting carbon materials. Furthermore, it thoroughly discusses three commonly used activation and modification strategies—namely, physical activation, chemical activation, and metal salt/oxide modification—and their roles in optimizing pore structures and tailoring surface functional groups. The review also highlights the applications of algal biochar in three key areas: adsorption, energy storage, and catalysis, demonstrating its diverse application potential. Finally, it summarizes the major challenges in current research, including high algae collection costs, batch-to-batch compositional inconsistency, difficulty in fine-tuning the microstructures, performance gaps with commercial alternatives, and the absence of mature large-scale production technologies. This review provides valuable insights and a reference for future theoretical studies and industrial applications.

Keywords: Algae; Carbon materials; Adsorption; Catalysis; Energy storage

0 引言

面对日益严重的环境污染和全球能源危机,迫切需要开发可持续的清洁能源。高性能的功能性碳材料因具有高比表面积、优异的导电性、良好的化学稳定性及可调的微观结构,在吸附、储能、催化等关键领域展现出不可替代的应用价值,已成为材料、能源、环境等领域的研究热点。然而,传统碳材料多采用煤炭、石油等化石原料作为前驱体,不仅加剧资源消耗,还伴随着较高的碳排放,与“双碳”目标及可持续发展理念相悖。因此,以绿色、可再生的生物质作为碳源替代化石原料,成为碳材料领域发展的核心方向之一。

以来源为依据,生物质资源可以分为3代。第一代生物质资源主要来源于粮食作物,具体包括甘蔗、甜菜等糖料作物,土豆、玉米等淀粉类作物,以及大豆、棕榈等可提炼植物油的作物^[1]。然而,这类生物燃料的应用存在显著争议,其生产需占用大量农业用地,且对水资源、肥料的需求量较高,不仅加剧了土地资源枯竭与环境污染问题,还直接与粮食供应形成竞争关系,因此其发展空间逐渐受限^[2]。在第一代生物质资源的争议背景下,提出了第二代生物质资源,其原料主要为城市垃圾与木质纤维素类物质^[3]。相较于第一代,第二代

生物质资源具备明显优势:既不直接与人类食物链争夺资源,还能减少净碳排放、提升能源利用效率^[4]。与此同时,第二代生物质资源也面临两大核心瓶颈:一是原料种植或收集仍可能与粮食生产用地、土地利用规划产生冲突;二是木质纤维素原料中的木质素去除成本高昂,且将纤维素类生物质转化为可发酵产品需依赖特殊酶预处理等昂贵技术,暂无法实现大规模经济化生产,其产业化进程受到制约^[5]。藻类生物质作为第三代生物质资源,不仅无需占用耕地、水源、肥料等有限资源,而且具有生长周期短、单位产量高等优势;同时,藻类生物质可以吸收水体中的氮磷有机物,避免水体的富营养化,对环境有一定的修复作用,并且具有良好的固碳作用,是碳循环中的重要一环^[6]。尤其是在制备功能性碳材方面,藻类成分富含碳、氮、硫、磷等元素,无需额外添加掺杂剂即可实现碳材料的杂原子原位掺杂,为功能定制提供天然优势^[7]。

近年来,藻类生物质衍生功能性碳材料(以下简称“藻类生物炭”)的研究取得显著进展:从早期简单碳化制备多孔碳,逐步发展为通过活化、模板、水热等技术实现孔结构、形貌与表面化学性质的精准调控,进而拓展至吸附、储能、催化等多元应用领域^[6,8]。然而,当前研究仍面临诸多挑

战,如大规模收集藻类成本较高(尤其是微藻采收需离心或絮凝工艺)、批次间成分稳定性差;制备过程中精准调控碳材料孔结构与杂原子掺杂位点的技术难度大;部分性能(如超级电容器的倍率性能、催化材料的长期耐久性)与商用碳材料(如活性炭、碳纳米管)仍存在差距,且规模化制备工艺尚未成熟。

基于此,本文系统综述了藻类生物炭的研究进展,其核心框架与涵盖维度如图1所示,具体包括藻类生物质的原料特性、碳材料的主要制备方法,以及衍生功能性碳材料在吸附、储能、催化三大领域的应用。最后总结当前研究面临的挑战,并展望未来发展方向,旨在为藻类生物炭的理论研究与产业化应用提供参考。

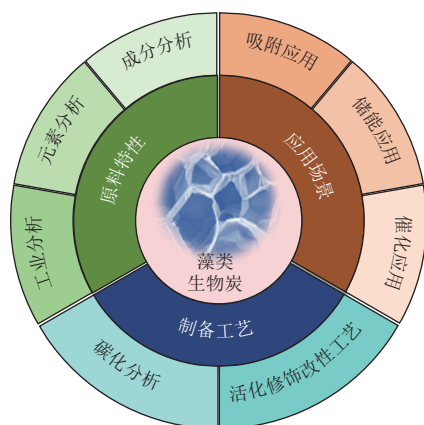


图1 藻类生物炭的制备与应用

Fig. 1 Preparation and applications of algal-based biochar

1 藻类生物质的原料特性

藻类生物质是一类具有突出生态价值与应用潜力的新型生物质资源。从生物学属性来看,藻类大多为可以释放氧气、进行光合作用的自养型无胚真核生物,自身是重要的含碳能源来源^[9]。需特别说明的是,蓝细菌(蓝藻)虽为单细胞细菌,但因具备产氧光合特性,在学术语境中被纳入“微藻”范畴^[10]。同时,藻类参与的光合作用活动约占地球总量的一半,是全球碳循环的关键环节。在生长效率方面,藻类生长速度显著优于其他生物材料。据统计,其生长速度约为其他生物材料的500~1 500倍,能快速形成规模化原料储备,为后续开发提供稳定供应。

通过形态特征的不同,藻类按细胞大小可分为微藻与大型藻2类。微藻尺寸多介于几微米至

几百微米之间,以单细胞或细胞链形式存在,且无根茎叶等器官分化;大型藻长度上限可达80米,常见种类包括海带、裙带藻等^[11]。从分类学角度,虽受基因序列系统发育学发展影响,微藻类分类存在争议,但总体可归纳为绿藻(如绿藻门)、红藻(红藻门)、褐藻(如异鞭藻门褐藻纲)、硅藻(如异鞭藻门硅藻纲)及金藻(如金藻纲)等核心类别^[12]。在成分组成上,藻类生物质主要包括脂质、蛋白质及碳水化合物等基础成分,同时富含色素(如藻蓝素、虾青素)、维生素及酚类抗氧化剂等高价值成分,该组成特征与第一、第二代生物质存在显著差异。其中,以粮食作物为代表的第一代生物质,成分以碳水化合物(淀粉、蔗糖)为主,蛋白质与活性成分含量极低;以水稻秸秆、木屑为代表的第二代生物质,则以纤维素、半纤维素和木质素为主要成分,其蛋白质与脂质含量远低于藻类。此外,藻类的脂质含量(部分微藻可达20%~50%)通常高于第二代生物质,且蛋白质氨基酸组成更均衡,这些成分特性使其在能源转化与高值化产品开发中,较第一、第二代生物质更具独特优势。表1展示了部分藻类生物质的原料特性,不同藻类的工业分析、元素组成及成分含量存在显著差异。工业分析层面,微藻普遍具有较高挥发分含量(70.40%~81.13%),灰分含量却较低,仅为6.10%~7.80%;而浒苔、羊栖菜、马尾藻等大型藻灰分含量显著更高,其中马尾藻灰分含量最高可达31.30%,可见大型藻的矿物质含量更为丰富。元素分析结果显示,微藻碳含量普遍高于浒苔,这反映微藻的有机质更丰富。通过对比成分分析发现,螺旋藻、小球藻等微藻相对大型藻,具有更高的蛋白质与脂质含量,大型藻则具有更高的多糖含量。这些差异为后续碳材料功能定制提供了依据,例如高蛋白质微藻适合制备氮掺杂碳材料,高脂质微藻有利于能源转化,高灰分大型藻则需针对性优化预处理工艺,以提升碳材料性能。

藻类生物炭的特性与其原料藻类生物质的特征紧密关联,既继承了藻类生物质的优势属性,也受其固有局限影响,且可通过改性进一步优化。从优势特性来看,藻类生物质因木质素含量低,无需复杂预处理即可用于制备生物炭;同时,其生长不依赖土壤、可利用水生领域的特点,间接保障了藻类生物炭制备过程中的资源便利性与可持续性。与木质纤维素生物炭相比,通常藻类生物炭氮、氧含量更高,碳含量更低,呈现高O/C比与低

表 1 藻类生物质原料特性
Table 1 Characteristics of algal biomass raw materials

类型	工业分析					元素分析					成分分析			参考文献
	水分	挥发分	固定碳	灰分	w(C)	w(H)	w(O)	w(N)	w(S)	多糖	脂质	蛋白质		
微藻	螺旋藻	8.00	70.70	15.20	6.10	51.90	7.10	30.50	9.60	0.90	26.1	5.40	55.60	[15]
	钝顶螺旋藻	7.62	81.13	5.08	6.17	47.58	6.33	28.15	11.26	0.51	10.71	10.30	65.20	[16]
	小球藻	6.70	73.50	13.20	6.60	49.80	6.60	31.90	11.00	0.70	23.40	2.90	57.80	[15]
	小球藻	5.60	70.40	16.20	7.80	47.32	6.96	27.78	8.79	0.35	22.18	24.57	45.45	[17]
	微拟球藻	4.23	79.21	10.26	6.30	50.61	7.31	28.46	6.68	0.64	18.67	30.00	40.80	[16]
大型海藻	浒苔	7.02	58.16	4.05	30.77	26.99	4.47	32.85	2.17	2.75	49.31	1.10	11.80	[16]
	浒苔	4.86	55.90	10.69	28.56	29.42	3.96	21.76	6.73	2.45	20.21	4.31	42.06	[18]
	浒苔	8.65	64.09	6.25	26.56	26.04	4.41	38.97	1.06	2.96	—	—	—	[19]
	羊栖菜	—	30.70	51.40	17.90	40.60	8.70	27.70	5.10	—	34.00	8.00	17.10	[20]
	马尾藻	12.40	48.90	7.30	31.30	33.60	2.70	60.30	2.00	1.40	—	—	—	[21]

C/N 比的特性^[13];且依托藻类生物质的组成特点,藻类生物炭还常具备更高的阳离子交换能力、氮含量与 pH,这使其在吸附、储能、催化等领域表现出应用潜力^[14]。从局限特性而言,藻类生物质缺乏木质纤维素,所制备的藻类生物炭孔隙率(比表面积和孔体积)较低,进而导致其吸附能力显著弱于木质纤维素原料制备的生物炭,在一定程度上限制了应用场景^[6]。不过,该局限可通过活化改性,改善优化藻类生物炭的孔隙体积、孔径、比表面积及理化性质,使其应用可能性得以进一步拓展。

2 藻类生物质衍生功能性碳材料的制备工艺

2.1 碳化工艺

藻类生物质转化为碳材料的过程与其他生物质类似,基于藻类生物质的不溶性,其主要碳化方法包括热解碳化、水热碳化以及微波碳化(图 2)。

2.1.1 热解碳化

热解碳化是制备藻类生物炭的基础工艺,其过程具有明确的温度依赖性:热解温度低于 200 ℃ 时,大型藻类中的水分率先蒸发;200~500 ℃ 范围内多糖与蛋白质发生分解;350~550 ℃ 时脂质开始分解;纤维素则在 315~400 ℃ 下挥发或裂解为左旋葡聚糖,左旋葡聚糖进一步脱水生成羟甲基糠醛,再经芳构化、缩合、聚合最终形成固体生物炭^[22]。

热解碳化制备的藻类生物炭性能受热解温度、升温速率、热解时间等条件显著影响,且热解

全程需通过无氧或通入惰性气体保障工艺稳定。具体来看,热解温度越高、升温速率越快,藻类生物炭产率越低。低温热解产物孔径与比表面积更小、亲水性更佳、含氧官能团更丰富,更适合用于土壤改良^[23]。较高温度则会促使藻类生物质中的脂肪族烷基与酯基断裂,挥发性物质及元素蒸发,进而增大生物炭的表面积与孔隙度,同时降低其 O/C 比和 H/C 比,提升碳含量、pH 与芳香性,使其具备疏水性与热稳定性。且高温下化学键重排会引入羧基、内酯、酚、吡啶等新表面官能团^[24],这些官能团作为优良电子供体/受体可改善生物炭电化学性能,因此高温热解产物更适合作为吸附剂、催化剂,且温度越高,生物炭的电化学性能与电极电容越好^[25-26]。KHAN 等通过人工神经网络与元启发式算法的集成框架预测可知,热解温度(权重 56%)、停留时间(权重 23%)和升温速率(权重 8%)是影响生物炭产量的主要参数^[27];而在碳材料制备中,慢速热解技术应用更广泛,因其较低的加热速率配合较长热解时间,能在缺氧或厌氧条件下更有效促进生物质发生二次化学反应,从而生成质量更优、性能更佳生物炭^[28]。

热解碳化虽能实现藻类生物质向高附加值碳材料的转化,但技术应用中仍面临多重挑战与不足。原料预处理环节存在显著制约,该技术对生物质干燥度要求严苛,而藻类尤其是微藻采收后含水率高,脱水过程需消耗大量能源,显著增加预处理成本。此外,在高温碳化的过程中,过高的温度会导致制备的生物炭孔道坍塌,限制了孔隙结

构的发展。同时,从原料的角度来说,大型藻高灰分特性会干扰热解反应的稳定性,而微藻中蛋白质、多糖等组分的热解转化效率差异较大,导致产物可控性降低,进一步限制了热解碳化的应用。

2.1.2 水热碳化

水热碳化(HTC)作为一种特定压力下低温转化生物质的技术,因无需干燥高水分原料、工艺温和且产物价值高,成为藻类生物质资源化利用的重要方法,近年来相关研究取得显著进展。HTC以水为介质,在低温(通常 175~260 ℃)、低压(2~6 MPa)下将藻类生物质转化为富碳固体产物水热炭,同时生成含有机物与矿物质的液体及以 CO₂ 为主的气体^[29]。该技术优势显著,不仅节省干燥预处理,降低能耗与成本,还能降解原料中有害化合物及残留污染物,且水热炭相比热解生物炭,具有产率高、灰分低、表面基团丰富的特点,在能源与环保领域应用潜力大^[30]。

工艺参数对 HTC 过程及产物具有较大的影响,其中温度是核心因素,不同组分降解所需温度不同,如微藻中半纤维素水解温度为 180~200 ℃,纤维素降解需 200~260 ℃,且适当提高温度有助于提升水热炭中碳含量以及引入更多的酸性基团,但一定程度上会降低固体的产率^[31-32]。停留时间方面,短停留时间更适合藻类加工,既能保证转化效率,又可减少能耗,过长停留时间对产物的提升并不显著^[33]。此外,液固比、压力及原料粒度也有影响,比如减小藻类颗粒尺寸可增加传质表面积,促进反应进行^[34]。在产物应用与实例方面,HTC 产物多元化。水热炭应用广泛,可作为高能量密度燃料,如 ARUN 等利用微藻水热炭磷吸附量达 2 505 mg/g^[35]。部分水热藻类生物炭经活化后性能更优,如富氮微藻水热生物炭经 KOH 活化后制备的氮掺杂微孔碳,比表面积高达 1 800~2 200 m²/g^[36]。

总的来说,水热碳化凭借无需干燥原料的优势在藻类转化中备受关注,但技术瓶颈限制其产物性能与产率,仍亟待突破。通常,单一水热碳化工艺制备的生物炭无法直接用于功能性碳材料,需要进一步高温活化以获得理想的孔隙结构。此外,在环保方面,水热碳化工艺的液相产物中有机物回收技术不成熟,可能引发二次污染风险。

2.1.3 微波碳化

微波碳化作为一种新型热化学技术,凭借独特加热特性,在藻类生物炭制备领域展现出显著

优势,为解决传统工艺痛点提供了有效路径。其核心原理是利用 0.3~300.0 GHz 频率的电磁波,使藻类内部偶极子分子(如水分)高频往复运动产热,实现由内而外的均匀快速加热,区别于传统由外而内的加热方式,大幅提升了加热效率与产物均一性^[8]。

在工艺特性方面,微波碳化参数可精准调控产物分布:较低温度与较短气体停留时间利于生成液体产物,较高温度则促进合成气产出^[37]。相较于传统热解与水热炭化,微波碳化优势突出:一是适用于大粒径藻类生物质,无需粉碎,简化预处理;二是能耗低、成本低,无需搅拌与流化,产物更清洁,还可利用生成的高发热值合成气原位发电;三是藻类自身水分可提升加热速率,且热解前水分去除能增加生物炭孔隙度,添加微波吸收剂(如 SiC)与催化剂还可进一步提高热解效率与目标组分浓度^[38-39]。在产物性能上,微波碳化制备的藻类生物炭微孔结构更有序、尺寸更均匀,而传统热解产物表面形貌更复杂、炭化更充分且表面裂纹更多。不过,微波碳化存在内部温度与升温速率难精确控制的问题,导致生物炭表面官能团因挥发分释放有所减少,对储能等高精度应用有一定限制,但适合大型藻类生物炭的规模化生产,可用于土壤肥料等领域。目前,微波碳化在木质纤维素生物质热解领域研究较多,针对藻类的研究虽有限,但已展现出良好应用前景。未来通过优化工艺参数、完善温度控制技术,其在藻类生物炭规模化制备中的潜力将进一步释放,为藻类生物质高值化利用提供重要支撑。

总体而言,热解、水热、微波这 3 种直接碳化方式虽各有特点,但用于制备藻类生物炭时仍存在明显不足,难以满足功能性要求,需进一步活化改性优化性能。其中,热解碳化法作为经典碳化手段,虽操作流程简便且易调整,但其直接制备的藻类生物炭电极电化学性能存在局限;水热碳化法能在较温和条件下处理高含水量藻类原料,且所得生物炭可保留丰富含氧官能团,却在孔隙率上表现欠佳;微波碳化法虽具备加热均匀、效率高的优势,但其直接制备的藻类生物炭在结构规整度与性能稳定性上仍有提升空间。可见,仅依靠这 3 种方式直接碳化,难以获得满足特定应用(如超级电容器对高能量密度、高功率密度及长循环寿命等)需求的高性能藻类生物炭,因此必须结合活化、改性或其他辅助处理技术,优化其孔隙结

构、表面化学特性等关键参数,才能使其功能性达到实际应用标准。

2.2 活化修饰改性工艺

多数藻类生物质经单一碳化处理后,所得碳材料普遍存在孔隙结构欠发达、比表面积偏低的问题。这类材料的结构特性难以满足吸附、储能、催化等领域对碳材料“高比表面积、精准孔道

分布、丰富活性位点”的核心需求,极大限制了其在多领域的规模化应用。因此,需通过针对性改性处理优化材料结构与功能,在碳化过程中引入活化修饰改性策略成为提升藻类衍生碳材料综合性能的关键路径。目前,主流的活化改性策略包括物理活化、化学活化以及金属盐/氧化物修饰(图2)。

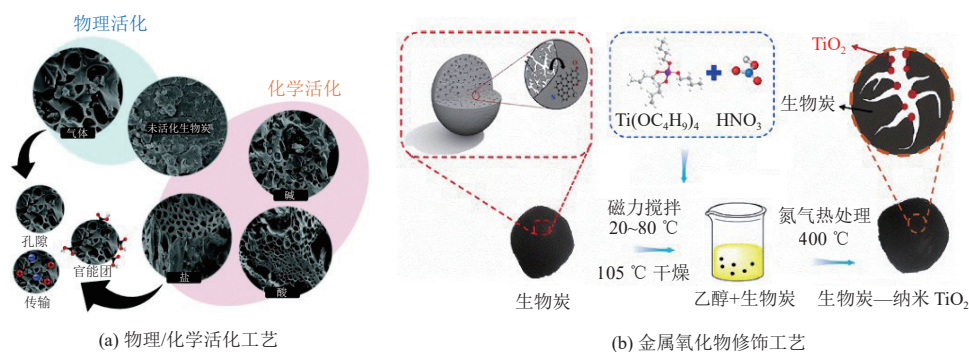


图2 藻类生物炭活化修饰改性工艺^[40-41]

Fig. 2 Activation and modification processes of algae-based biochar^[40-41]

2.2.1 物理活化改性

物理活化作为藻类生物炭结构优化与性能提升的重要路径之一,其核心原理是通过气体氧化或机械作用,实现藻类生物炭的孔隙疏通、扩孔与新孔构建,同时调控表面化学性质,最终满足吸附、催化、储能等领域的应用需求。目前主要包括气体活化与机械活化两类^[42]。

气体活化是藻类生物炭物理活化的主流方式,以 CO_2 、水蒸气、臭氧、 NH_3 等为活化剂,通过高温下的选择性氧化与气化反应优化材料结构^[43]。 CO_2 活化依赖吸热的Boudouard反应($\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$),在 $700 \sim 900\text{ }^\circ\text{C}$ 下选择性刻蚀非晶态碳与孔边活性位点,既能去除碳化残留的焦油以疏通闭塞孔隙,又能构建微孔-介孔分级结构,且可通过调控 CO_2 流速、活化温度与反应时间避免碳骨架坍塌^[44]。CHO等通过 CO_2 辅助红藻热解碳化可提升生物炭孔隙率,使其在50 min内对亚甲基蓝实现近完全去除^[45]。YU等在铜绿微囊藻与 Fe_2O_3 共热解体系中发现, CO_2 不仅能够活化孔隙结构,还具有pH缓冲作用,抑制焦油生成并改变裂解路径,使生物炭对微囊藻的吸附量提升2.8倍^[46]。水蒸气活化则在 $200 \sim 800\text{ }^\circ\text{C}$ 下,通过甲烷化、水气变换等反应构建多孔结构,其反应动力学优于 CO_2 ,能更高效地扩大既有孔隙并生成新孔,同时在藻类生物炭表面引入羟基、羧基等含氧官能团,

提升亲水性与离子交换能力^[47-48]。臭氧活化因强氧化性,可在常压下实现微孔的构建,且反应后剩余臭氧自发转化为 O_2 ,无二次污染,还能诱导藻炭表面生成醚类、酮类等酸性官能团,显著提升阳离子交换容量,适用于重金属吸附场景^[49-50]。此外, NH_3 活化不仅可通过氧化刻蚀优化孔结构,还能实现氮元素原位掺杂^[51],同步提升藻类生物炭的导电性与催化活性,为储能与催化领域提供功能定制化材料。

机械活化以球磨法为代表,通过研磨过程中的机械力减小藻类生物炭粒径、破坏团聚结构,从而暴露更多活性位点并提升比表面积。SEO等通过球磨处理使黄褐盒管藻衍生生物炭比表面积从 $46\text{ m}^2/\text{g}$ 增至 $216\text{ m}^2/\text{g}$,粒径降至亚微米级($<1.0\text{ }\mu\text{m}$),有效地暴露了活性位点,实现双氯芬酸的高效降解(去除率 $>99\%$),且反应后溶液pH接近中性,生态安全性显著^[52]。然而,球磨法存在活性衰减较快等问题(5次循环后下降40%),需通过后续固载或复合改性进一步优化稳定性。

2.2.2 化学活化改性

化学活化作为调控藻类生物炭结构与功能的主流技术,通过将化学试剂与藻类生物质或半焦混合并经高温热处理($400 \sim 900\text{ }^\circ\text{C}$),实现孔隙构建、表面官能团定制及性能优化,相较于物理活化具有活化温度低、比表面积提升显著、功能可调

性强等优势,已发展出酸活化、碱活化、盐类活化及自活化等多元化技术路径。

酸活化剂主要包括 HNO_3 、 H_2SO_4 、 H_3PO_4 、 HCl 等,通过质子化与氧化刻蚀双重作用优化藻类生物炭性能。一方面,酸性活化剂可抑制大型藻类热解过程中有机大分子副产物(如焦油)的合成,同时促进纤维素脱水并降低官能团断键温度,减少碳骨架坍塌。另一方面,能在生物炭表面引入特异性活性基团,如 H_2SO_4 可引入磺酸基团,为催化吸附提供充足酸性位点^[53]; H_3PO_4 通过溶胀分离纤维素并引入含磷基团,并同步提升孔隙度^[54]; HNO_3 则在预活化阶段溶解无机氧化物并生成内酯基团,进一步扩大孔容^[55]; HCl 修饰则能使藻炭表面氨基($-\text{NH}_2$)质子化形成带正电的 $-\text{NH}_3^+$,增强对负电污染物的静电吸引力^[56]。已有研究表明,经 HCl 修饰的藻类生物炭比表面积、孔体积及平均孔径分别提升至 $38.3 \text{ m}^2/\text{g}$ 、 $0.073 \text{ cm}^3/\text{g}$ 与 7.42 nm ,且酸改性后生物炭的比表面积、孔隙度及复合结构稳定性均因表面官能团(羟基、羧基、酮基)增加而显著增强^[57]。

碱活化主要以 KOH 、 NaOH 为活化剂,凭借强蚀刻作用成为藻类生物炭高比表面积构建的主流方式。碱性活化剂与藻类生物质接触时,会提供碱性环境并引发脱水、裂解、聚合等浸渍活化反应,碱性活化剂中金属离子与生物炭反应可在热解过程中产生大量微孔,同时去除孔隙内无机杂质,进一步提升孔隙率^[58]。此外,碱活化还能使生物炭表面产生正电荷位点,增强对带负电物质的作用能力。 KOH 与 NaOH 的活化机制存在差异: K^+ 可有序插入碳晶体层间使晶格膨胀,后续与碳反应生成的 CO 、 CO_2 等气体进一步扩孔;而 Na^+ 无法有序嵌入,易导致碳层缺陷增多,虽比表面积提升效果略逊于 KOH ,但经济性更优^[59]。研究认为, KOH 是碱性活化的优选试剂,当温度处于 $675\sim 1\,000\text{ }^\circ\text{C}$ 时,生物炭的孔隙大小与总表面积随温度升高而增加,超过该范围则因燃烧效应与微孔坍塌导致性能下降。WEI 等利用 NaOH 处理的浒苔生物炭比表面积达 $1\,238 \text{ m}^2/\text{g}$ ^[60];而 WU 等通过 KOH 修饰的浒苔生物炭,与未活化时相比展现出更优异的吸附性能,吸附量达到 744 mg/g ^[61]。碱改性生物炭通常具有更大的表面积、更高的 H/C 比与 N/C 比及更低的 O/C 比,体现出更高的表面芳香性与更低的亲水性^[62]。

盐类活化以 ZnCl_2 、 NH_4Cl 活化剂为代表,其

中 ZnCl_2 因高脱水能力与独特的物理特性成为常用试剂。 ZnCl_2 能在低活化温度下渗透藻类生物炭内部,且高温下保持液态,可高效催化纤维素降解并构建极多孔结构,显著提升生物炭的微介孔率、比表面积、孔体积及官能团丰富度,为后续功能应用奠定结构基础^[63]。WANG 团队以紫菜为基材,采用 ZnCl_2 作为活化剂,成功制备了具有优越微介孔分级结构的分级多孔碳。这种材料不仅电化学性能出色,还实现了超过 30% 的碳收率^[64]。然而,需要注意的是,当活化温度大于 $800\text{ }^\circ\text{C}$ 时, ZnCl_2 的显著挥发可能削弱其模板效应,进而引发孔隙结构的塌陷问题^[65]。

此外,还存在自活化这一绿色创新路径,利用藻类自身含有的盐类(如 NaCl 、 K_2CO_3)作为内源性活化剂,无需额外添加化学试剂,如原始海藻(海带、裙带藻、浒苔)在 $800\text{ }^\circ\text{C}$ 热解 60 min ,即可制备比表面积达 $621\sim 1\,140 \text{ m}^2/\text{g}$ 的多孔藻类生物炭,有效避免外源性试剂残留问题^[66]。

2.2.3 金属盐/金属氧化物修饰改性

金属盐/金属氧化物修饰作为藻类生物炭功能增强的关键技术,改性工艺主要包括原位负载与后浸渍。原位负载是将金属盐/氧化物与藻类原料混合后热解,后浸渍则是先制备生物炭再经金属溶液浸泡处理,通常可与活化工艺协同调控材料结构与功能,显著拓展其在吸附、储能、催化领域的应用潜力^[67]。

在修饰方法与机制上,常用金属盐/氧化物涵盖 Fe 、 Mg 、 Al 、 Mn 、 Zn 系等^[68-69]。藻类生物炭表面丰富的官能团(羟基、羧基)可与金属离子(Fe^{3+} 、 Al^{3+} 、 Zr^{4+} 、 La^{3+})形成配位键,实现金属氧化物原位负载。磁性物质修饰通过铁浸渍-热解等工艺,使生物炭具有磁性,便于外磁场回收。在储能方面, SALIMI 等将刚毛藻与 FeCl_3 混合振荡后 $500\text{ }^\circ\text{C}$ 热解,制备的磁性生物炭比表面积达 $296.4 \text{ m}^2/\text{g}$,在锂离子电池中的容量达到 $740 \text{ mA}\cdot\text{h/g}$,循环 500 次容量保持率 91%^[70]。POURHOSSEINI 等利用 Fe 复合藻类生物炭制备电极材料组装的非对称超级电容器展现出优异能量与功率密度^[71]。在吸附领域中,金属修饰通过静电作用、络合反应或沉淀作用增强选择性与容量, ZnCl_2 修饰可通过形成 ZnOHCl 活性位点^[72]。 MgCl_2 修饰不仅能促进含磷废水中 MgP 沉淀生成,同时强化孔隙度和表面活性位点^[73]。LIU 等利用 $\text{La}(\text{NO}_3)_3/\text{KOH}$ 共改性,借助 La-O-P 络合作用,改性藻炭对磷酸盐去除率

储能领域极具潜力的绿色电极材料。

在超级电容器应用中,藻类生物炭的性能优化核心在于构建分级多孔结构、提升杂原子掺杂量及增强界面离子传输效率。LI 等通过绿色三元 (NaCl/KCl/ZnCl_2) 混合盐辅助碳化法,以螺旋藻渣为原料,通过调控盐料比与碳化温度,使最佳样品在 1 mol/L H_2SO_4 和 6 mol/L KOH 电解质中分别实现 215 F/g 和 207 F/g 的比电容,组装对称电容器在循环 10 000 次后电容保持率 $\geq 90\%$ ^[85]。此外,碱蚀刻技术为提升金属硅酸盐基藻类生物炭性能提供新路径,ZHANG 等将绿藻基生物炭经 3 mol/L NaOH 蚀刻 12 h 后,所构建的固态混合超级电容器面比电容、能量密度显著提升,且在 1 000 次弯曲与 180°折叠后仍保持 97% 的电容^[86]。GUO 等基于海藻酸钠合成了具备“蛋壳”结构气凝胶,在 1 A/g 下比电容高达 873.3 F/g,8 A/g 下循环 5 000 次保持率 87.1%,其柔性复合膜可举起 1 kg 重物,为可穿戴电子设备提供支撑^[87]。BAGHERI 等基于热解碳化以及 CO_2 活化制备了马尾藻衍生的自掺杂多孔碳(图 4(a)),在有机电解质中能量密度达 36.1 W·h/kg,组装柔性固态器件弯曲 1 000 次后仍保持 97% 的比电容^[88]。为了优化藻类生物炭

的电化学性能,研究人员提出通过藻类与木质纤维素生物质的相互作用进一步优化藻类生物炭的结构性能。LI 等基于熔融 $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ 共热解钝顶螺旋藻与竹屑,所制备分层多孔碳比表面积达到 1 326.58 m^2/g ;同时,碳材料氮含量提升 108.7%,且吡啶-N/吡咯-N 活性位点占比高达 81%,在 0.25 A/g 下比电容达 306.2 F/g,5 000 次充放电循环后稳定性保持 91.3%^[89]。YUAN 等通过芦苇和小球藻的协同耦合,以 K_2CO_3 为绿色活化剂,采用一步法制备了三维氮掺杂互联多孔碳(图 4(b)),在电流密度为 1 A/g 时表现出 340.4 F/g 的优异比电容,即使在 20 A/g 时,电容也可以达到 265.5 F/g,显示出卓越的速率能力^[90]。ZHANG 等在木棉与小球藻共热解的基础上结合微波辅助热解碳化,使多孔碳比表面积达 2 909.78 m^2/g ,比电容提升至 380 F/g,组装对称器件能量密度达 8.09 W·h/kg,循环 10 000 次后保持率为 98.49%^[91]。

在二次电池方面,藻类生物炭的结构设计更倾向于缓解活性物质体积膨胀、提升电子传导效率。SANG 等采用海藻凝胶碳包裹 Si@NiO/Ni 纳米花的复合材料(图 4(c)),利用碳层减轻硅纳米颗粒体积效应,扩展了离子输运路径,在 1 A/g 下循环

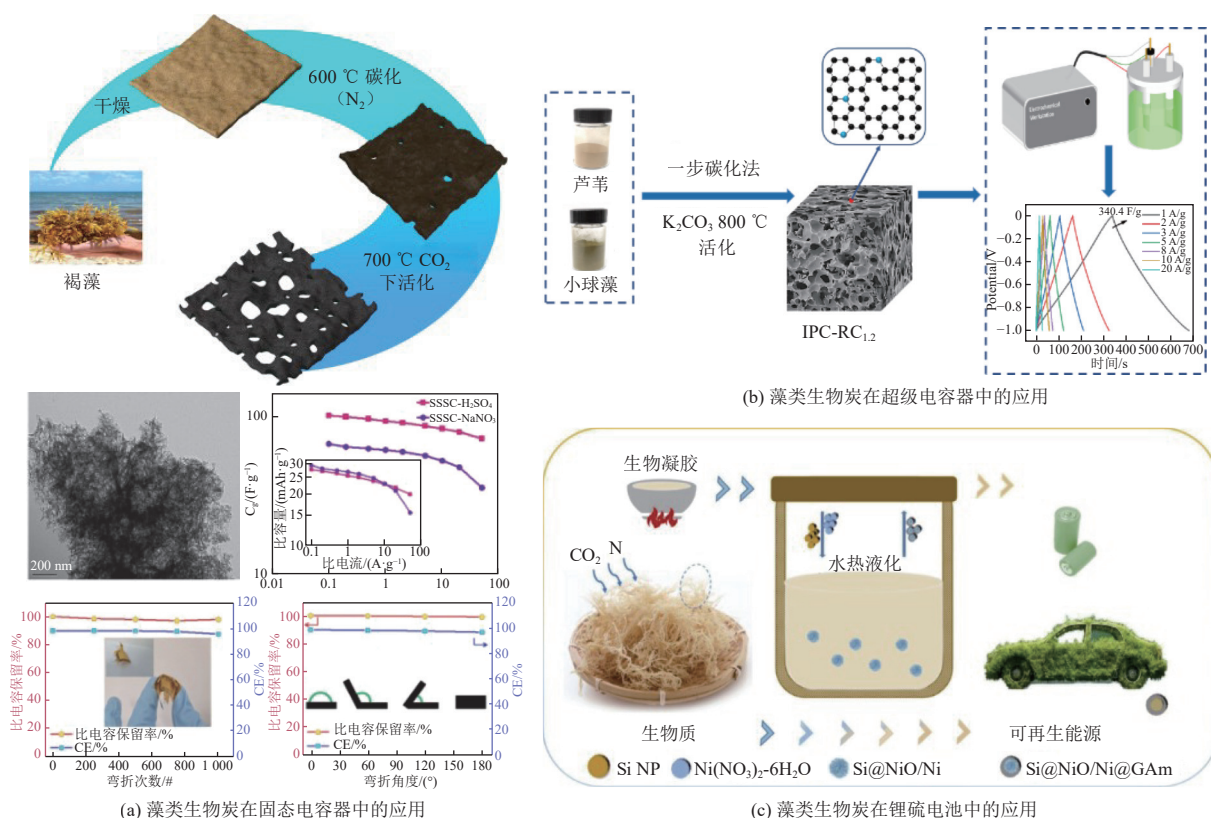


图 4 藻类生物炭在储能领域的应用^[88, 90, 92]

Fig. 4 Applications of algae-based biochar in energy storage^[88, 90, 92]

1 000 次后可逆容量仍达 1 245.12 mA·h/g^[92]。LI 等通过红藻衍生的铁离子复合水凝胶经碳化活化制备硫掺杂碳气凝胶,具有 4 037.0 m²/g 的超高比表面积与分级孔结构,可实现 80% 的硫负载量,锂硫电池循环 400 次后仍保持优异稳定性^[84]。此外,藻类生物炭在新型储能器件中也崭露头角,如以马尾藻为原料制备的摩擦电纳米发电机,输出电流、电压与功率分别达 47 μA、775 V 和 2 880 μW^[92]。

3.3 催化应用

藻类生物炭除了在污染物吸附与储能领域被广泛应用,大量研究也尝试将其用于催化实验中,包括热催化、光催化等。

藻类生物炭凭借天然杂原子(如氮)掺杂特性、可调多孔结构及丰富表面官能团,经活化改性后可作为高效热催化剂,在生物质催化热解制备高附加值产物中展现出显著优势。SHEN 等以褐藻为前驱体,采用 KOH 作为活化剂,通过两步活化法制备活性生物炭。在对木屑的催化热解中,活性生物炭通过促进脱水、脱碳与脱羧反应,结合

介孔结构与吡啶-N 官能团作用,使生物油中单酚类产率达 48.99%^[94]。CAO 等以条浒苔为原料,在不同碱性活化剂(KOH/NaOH)和碳化气氛(N₂/CO₂)下制备了具有不同孔隙结构以及表面官能团的藻类生物炭,用于木屑的催化热解(图 5(a))。结果表明,CO₂ 作为弱氧化气氛,NaOH 作为活化剂时,所制备生物炭使生物油中单酚类化合物相对含量提高至 59.46%^[95]。进一步利用响应面法与人工神经网络等建模工具对藻类生物炭催化剂进行调控与优化,使生物质热解生物油中单酚类相对含量提升至 60%,苯酚、甲酚与乙酚总浓度达 35.54 mg/g_{bio-oil},有效实现了木屑的定向热解^[96]。除了将藻类生物炭应用于对木质纤维素类生物质的催化热解,YUAN 等将羊栖菜衍生生物炭用于废气植物油的催化热解,表现出良好的脱羧效果;同时通过 Cu 对生物炭进行修饰(图 5(b)),有效强化了催化效果,促进了生物油中长链烃与芳烃的生成^[97]。

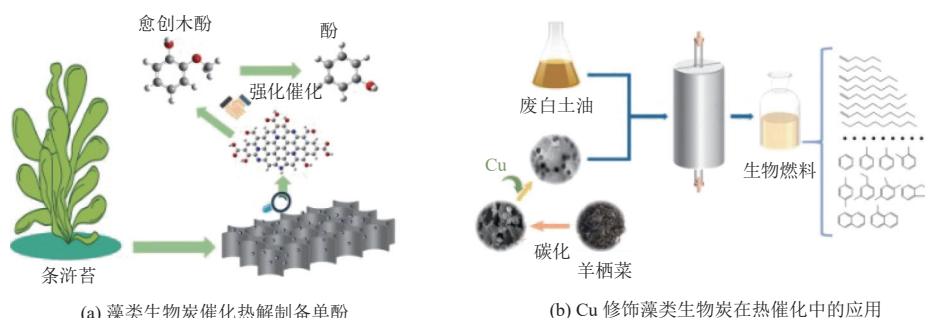


图 5 藻类生物炭在催化领域的应用^[97-98]

Fig. 5 Applications of algae-based biochar in catalysis^[97-98]

除了作为热催化剂,藻类生物炭因具有适当电导率,可作为电子陷阱和传输通道,也可以用于光催化剂的载体。藻类生物炭作为催化剂载体能够促进光诱导电荷载流子对的分离和迁移,强化氧化还原反应,从而提高光催化活性^[99]。CHEN 等将钼酸铋与胶网藻生物炭复合制备出新型光催化材料,在可见光照射实现了磺胺甲基嘧啶的有效降解^[100]。RABIE 等以马尾藻为载体,成功合成纳米 ZnO 及 Co-ZnO 复合材料,在 pH=7 条件下,分别投加 ZnO/藻类复合材料与 Co-ZnO/藻类复合材料,仅需 10 min 即可实现 5 mg/L 孔雀石绿的完全降解,对 10 mg/L、15 mg/L 的高浓度孔雀石绿溶液也能保持高效降解性能^[101]。

4 结论与展望

本文系统综述了藻类生物质衍生功能性碳材料(藻类生物炭)的研究进展,主要结论如下。

藻类作为第三代生物质,具有不占耕地、生长快、能修复水体且天然含 C、N、S、P 杂原子的优势,工业、元素及成分分析均证实其为优质碳源。

在制备方面,目前已形成“基础碳化+活化修饰”体系,热解、水热、微波 3 种碳化法各有特点,物理、化学、金属盐/氧化物修饰 3 类活化工艺可优化碳材料性能。

在应用研究方面,藻类生物炭在污染物吸附、储能、催化领域取得成效显著。

当前在藻类生物质制备生物炭的研究仍存挑战,如藻类收集成本高、成分不稳定,碳材料结构调控难,部分性能不及商用材料且规模化工艺不成熟,需后续研究突破。考虑以下几种潜在的解决方案和未来的前景。

原料供应与预处理优化: 开发新型低成本微藻采收技术, 建立预处理标准化流程以提升原料稳定性, 同时拓展赤潮藻、养殖废弃藻等来源, 实现“以废治废”, 降低成本并提升资源利用率。

制备工艺精准化与绿色化: 借助分子模拟、AI 构建碳材料结构-性能模型, 精准调控孔结构与杂原子掺杂; 推广自活化绿色工艺, 减少化学试剂使用, 研发微波连续碳化炉等设备, 推动规模化生产。

性能提升与功能拓展: 针对性优化超级电容器倍率性能、催化材料耐久性; 推动与石墨烯、MOFs 复合, 开展工况模拟, 评估材料长期服役稳定性与寿命。

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