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生物质碳与MOF功能复合材料的应用研究新进展

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摘 要:生物质碳具有独特的多孔结构,含有氧、氮和其他元素,具有较多的活性位点且价廉易得。而金属-有机骨架材料(MOF)也是一类多孔材料,具有丰富多样的形貌、高比表面积、化学可调控性和结构稳定性。通过原位生长工艺和煅烧处理,结合水热反应,可制备生物质碳与MOF功能复合材料。生物质碳与MOF功能复合材料比单独的生物质碳或MOF具有更大的比表面积和更多的活性位点,表现出许多优异的特性。本文重点介绍生物质碳与MOF复合材料在吸附剂、催化剂、电化学传感器、超级电容器、吸波材料和太阳能蒸发器等领域的最新应用研究进展,同时对该类复合材料未来的发展前景进行了展望。

关键词:生物质碳;MOF;复合材料;应用

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Recent Advances of Biomass Carbon and MOF Functional Composites and the Applications

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Abstract: Biomass carbon has a unique porous structure, containing oxygen, nitrogen and other elements, with more active sites and low cost. Metal-organic frameworks (MOF) is a class of porous materials with diverse morphology, large surface area, chemical tunability and structural stability. Biomass carbon and MOF composites can be prepared by in-situ growth process and calcination treatment combined with hydrothermal reaction. The biomass carbon and MOF composites have larger specific surface area and abundant active sites than biomass carbon or MOF, which have many excellent characteristics. This paper focuses on the novel application of biomass carbon and MOF composites in the fields of adsorbents, catalysts, electrochemical sensors, supercapacitors, solar evaporators and electromagnetic wave absorbing materials. At the same time, the development prospects of this kind of composites are expected.

Keywords:biomass carbon; metal-organic frameworks; composite; application

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随着绿色发展理念的提出,科学家们将目光转移到生物质的合理利用上。生物质是一类以动植物废弃物为原料获得的可再生有机物,可在相对简单、温和、无氧(或缺氧)条件下于一定的温度直接碳化形成固体粉末生物质碳材料。生物质碳由于其前驱体成本低、制备工艺简单、环保、具有较大的活性表面积、较高的孔隙率和优异的化学稳定性等特点已成为研究热门领域之一[1-5],已在环境、能源、传感等领域获得了广泛的应用[6-13]。生物质碳通常在KOH、$ZnCl_2$或H_3PO_4等化学试剂存在下通过热解生物质来进行制备。例如,Peng等通过高温碳化和KOH活化由5种废弃茶叶制备了生物质碳材料[14]。Chang等采用回收的废滤纸作为碳前体,通过$ZnCl_2$活化制备分级活性生物质碳材料[15]。Dai等利用H_3PO_4预处理、水热碳化,再用KOH活化制备了用于高性能超级电容器的艾蒿基生物质碳电极材料[16]。通过改变活化剂和生物质碳前体的质量比、活化温度以及活化时间,可控制活化过程中微孔的产生和纳米片的形成。

金属-有机骨架材料(Metal-Organic Frameworks,MOF)又称多孔配位聚合物,是一类具有超低密度、高比表面积和高孔隙率的新型纳米多孔材料,由金属阳离子(或簇)与有机配体组装而成的具有无限网络的多孔晶体材料[17-20]。通过设计和功能化次级结构单元、配体以及孔隙环境,可微调MOF材料的物理和化学性质,使其在气体存储、分离、催化、传感、药物输送等领域获得广泛应用[21-26]。

通过生物质直接碳化制备生物质衍生碳基材料可获得含有多种元素的多孔结构,结合MOF材料的特性,通过简单的原位生长工艺和煅烧处理,协同水热反应,可制备生物质碳与MOF复合材料,MOF可负载到生物质碳内壁和表面[27-28],故由生物质碳与MOF结合所制备的复合材料比单独的生物质碳或MOF具有更大的比表面积和更丰富的活性位点,能有效促进电子转移和传质[29],在吸附、催化和电化学传感等领域具有广阔的应用前景[30-32]。

1 生物质碳与MOF复合材料的应用

生物质碳与MOF复合材料充分体现这2种前体材料的优越特性,从而提高了复合材料的活性以及应用范围[33]。本文总结了生物质碳与MOF复合材料的应用,见表1[34-52]。

表1 生物质碳与MOF功能复合材料的应用

Table 1 Applications of biomass carbon and MOF functional composites

复合材料类型	前体	主要元素	应用类型	样品	参考文献
ZIF-67/CS@C	Corn stalk, ZIF-67	C, N, Co	adsorbent	imidacloprid and thiamethoxam	[34]
ABAC/Cu-BTC	Ashitaba, Cu-BTC	C, Cu	adsorbent	methylene blue	[35]
Biomass-C@MIL-53-C	Kapok fibers, MIL-53	C, Fe	adsorbent	various kinds of oils and organic solvents	[36]
MIL-53(Al)@AC-x	Rice husk, MIL-53(Al)	C, Al	adsorbent	p-nitrophenol	[37]
ZIF-8/AG	Agarose, ZIF-8	C, N, Zn	adsorbent	organic pollutants	[38]
HKUST-1-P@corncob-400	Corncob, HKUST-1	C, Cu	catalyst	4-nitrophenol	[39]
Co@N-PC	Poplar sawdust, ZIF-67	C, Co	catalys	methylene blue	[40]
CC@CNCo	Cotton, ZIF-67	C, Co	catalyst	bisphenol A	[41]
Zn-MOF@AC	Gingko barks, Zn-MOF	C, Zn	catalyst	anionic and cationic dyes	[42]
Au/PN-MPC900	Pine needles, ZIF-9, ZIF-12		catalyst	p-nitrophenol	[43]
AC/UiO-66-NH_2	Pine cones, UiO-66-NH_2	C, Zr	electrochemical sensor	Pb^{2+} and Hg^{2+}	[44]
BC/Cr_2O_3/Ag	Walnut shells, Cr-MIL-101	C, Cr, Ag	electrochemical sensor	nitrofurazone	[45]
BC/Co_3O_4/$FeCo_2O_4$	Pine cones, ZIF-67	C, Fe, Co	electrochemical sensor	dopamine, acetaminophen, and xanthine	[46]
CoBC	Hemp stems, ZIF-67	C, Co	electrochemical sensor	NO_2	[47]
Co/MnO/$CoMn_2O_4$@RHs	Rice husk, Co/Mn-MOF	C, Co, Mn	supercapacitor	—	[48]
hetero-fNCs	Cosmetic cotton, ZIF-8/ZIF-67	C, Co, Zn	supercapacitor	—	[49]
WS@Ni-MOF/SPANI	Walnut shell, Ni-MOF	C, Ni	supercapacitor	—	[50]
Fe@NPC@CF	Cotton, Fe-MOFs	C, Fe	electromagnetic wave absorber	—	[51]
MOF-801@CL	Carbonized loofah, MOF-801	C, Zr	solar evaporator	—	[52]

1.1 新型吸附剂

由于生物质碳与MOF复合制备的复合材料可获得更大的比表面积和更多的孔隙,同时形成高度分散的微结构,能提高其吸附性能。Yang等设计了由ZIF-67和农业废弃玉米秸秆(CS)衍生的低成本磁性多孔碳基材料ZIF-67/CS@C,应用于吸附去除水中的吡虫啉和噻虫嗪,该吸附剂对吡虫啉和噻虫嗪的吸附能力分别高达189和133 mg/g,经过6次连续循环使用后,吸附效率仍保持在95%以上,具有出色的可重复使用性[34]。Xue等以明日叶为原料制备生物质活性碳与Cu-BTC复合材料,将其应用于水溶液中亚甲基蓝的吸附,该吸附剂对染料具有较高的吸附能力[35]。Zhao等通过高度空心生物质木棉纤维与MIL-53直接碳化制备了具有分级结构的碳气凝胶(生物质-C@MIL-53-C),该吸附剂对各种油类和有机溶剂的吸附能力是自身重量的35.0~119.5倍[36]。Qi等将MIL-53(Al)与稻壳活性碳(AC)结合,构建了一系列复合材料MIL-53(Al)@AC-x,用于处理高毒性酚类废水,结果显示MIL-53(Al)@AC-10对对硝基苯酚的吸附率比MIL-53(Al)高36%,最大吸附能力达250 mg/g[37]。Wang等利用廉价易得的琼脂糖(AG)生物质作为碳前体,将具有高孔隙率的ZIF-8引入AG气凝胶以增加比表面积并实现杂原子掺杂,在惰性气氛下热解后,ZIF-8/AG衍生的氮掺杂碳气凝胶获得高度互连的多孔迷宫状结构复合材料ZIF-8/AG-CA,该吸附剂对不同的有机溶剂和普通油类具有出色的吸附能力[38]。

1.2 催化剂

开发环保、高效、经济的催化剂具有重要意义,生物质碳与MOF复合材料催化效率高,很容易从溶液中分离出来,具有良好的可回收性。Wang等在不同温度下焙烧玉米芯与Cu-MOF复合材料,获得了一系列P掺杂的$Cu/Cu_2O/C$异质结构,HKUST-1-P@玉米芯-400可在90 s内对4-氨基苯酚进行有效催化还原,利用该催化剂进一步对氧氟沙星进行催化还原研究,10 min内转化率可达95.7%[39]。由于Co^{2+}与木材中丰富的含氧官能团配位,ZIF-67可以在具有管胞骨架的杨木屑表面原位均匀生长,Wang等通过碳化制备了具有微纳米多孔结构的磁性催化剂Co@N-PC,通过活化过氧单硫酸钾去除亚甲基蓝来研究其催化能力,结果表明该催化剂对亚甲基蓝的降解效率在30 min内达100%,表现出优异的催化性能,该催化剂可通过外部磁铁从溶液中分离和重复使用,且具有良好的稳定性[40]。Zhang等采用廉价易得的棉花作为ZIF-67的理想载体,Co^{2+}与棉花中羟基和2-甲基咪唑中的氮配位制备催化剂前驱体Cot@ ZIF-67,高温衍生后获得催化剂CC@CNCo,该催化剂能在5 min内将双酚A完全去除[41]。Govindaraju等在银杏树皮表面修饰Zn-MOF异质结构制备复合材料Zn-MOF@AC,该光催化材料有助于在紫外线照射的环境中在90 min内以86.4%和77.5%的速率降解阳离子和阴离子染料[42]。Liu等将沸石咪唑骨架材料ZIF-9和ZIF-12负载到松针纤维素气凝胶上作为金属催化剂有效激活过氧单硫酸盐降解罗丹明B、盐酸四环素和对硝基苯酚,气凝胶/过氧单硫酸盐系统可在1 h内去除约90%的对硝基苯酚[43]。

1.3 电化学传感器

纯MOF的导电性不足限制了其应用,为了克服这个缺点,通常在惰性气体气氛中热解或将MOF与生物质碳材料等结合以获得更高的电导率。Zou等制备了一种基于松果活性碳AC/UiO-66-NH_2的新型电化学传感器,用于同时测定水样中Pb^{2+}和Hg^{2+},检测限低至1.0 ng/L仍然可以检测到这两种重金属离子[44]。呋喃西林(NFZ)具有良好的抗菌作用,但具有潜在的致畸和致癌性,Cheng等利用银纳米粒子在Cr-MIL-101表面生长得到Cr-MIL-101/Ag,再与核桃壳生物质碳一起煅烧得到复合材料BC/Cr_2O_3/Ag,在复合材料表面添加分子印迹聚合物(MIP)提高修饰电极对NFZ的特异性识别能力,修饰电极BC/Cr_2O_3/Ag/MIP/GCE对NFZ的检测具有高灵敏度、高选择性、良好的重现性和良好的稳定性[45]。Lu等利用松果生物质碳与ZIF-67衍生材料Co_3O_4/$FeCo_2O_4$构建了一种新型传感系统BC/Co_3O_4/$FeCo_2O_4$/GCE同时检测多巴胺、对乙酰氨基酚和黄嘌呤,获得较宽的检测范围和较低的检测限,具有令人满意的选择性、稳定性和可重复性[46]。Chen等利用具有良好导电性和分级结构的麻茎生物质碳为载体,以ZIF-67为模板,通过真空辅助和煅烧法原位生长合成CoBC复合材料,该复合材料对NO_2具有良好的响应,在室温环境中具有很好的重复性和稳定性[47]。

1.4 超级电容器

超级电容器(SC)通过电双层存储电荷,因其具有高能量密度、快速充放电、低维护成本和长循环寿命引

起了科学家们的极大兴趣。Kim等设计了在稻壳多孔碳网络通道中生长Co/Mn-MOF，置于氮气气氛中热解，在纳米碳中产生了Co、MnO和$CoMn_2O_4$混合物，当在稻壳多孔碳通道内生长更小的微晶双金属Co/Mn时，可获得更高的比电容[48]。Zhao等在化妆棉废弃生物质上原位生长核壳结构ZIF-8@ZIF-67，碳化后制备具有高柔性的氮掺杂碳异质结构hetero-fNCs，利用该材料制备的SC电极具有较高能量密度和良好的电容保持率[49]。Zhang等以核桃壳(WS)生物质碳和Ni-MOF制备了新型混合纳米材料用于SC电极，该复合材料在1 A/g电流密度下的比电容为WS生物质碳的4倍，进一步加入硫化聚苯胺(SPANI)明显加速了电解质离子的转移，防止了Ni-MOF团聚，WS@Ni-MOF/SPANI的比电容是WS生物质碳的14倍，且具有较高的循环稳定性[50]。

1.5 吸波材料

电磁波吸收材料已广泛应用于电子设备和无线通信等领域中，以解决日益严重的电磁污染和辐射问题。多孔碳材料被认为是一种新型的电磁波吸收材料，而MOF材料由纳米孔和开放通道组成，通过热分解MOF前驱体，可合成磁性纳米粒子粘附在多孔碳基体上的电磁波吸收材料。Li等通过原位合成和热分解过程成功制备了Fe-MOF/棉花衍生的Fe@纳米多孔碳@碳纤维复合材料(Fe@NPC@CF)，通过Fe纳米颗粒、NPC和CF之间的协同作用大大提高了电磁波吸收性能[51]。

1.6 太阳能蒸发器

具有良好亲水性和丰富孔隙结构的MOF材料不仅可以提高碳材料的亲水性，还可以提供额外的水输送通道。受植物维管束输送水分的启发，Guo等选用网状结构碳化丝瓜(CL)生物质碳和MOF-801构建太阳能蒸发器，MOF-801为光吸收层内的快速水输送提供了丰富的通道，CL优异的光热转换性能提高了水的蒸发效率，结果表明MOF-801@CL复合材料的水分蒸发效率约为CL的1.2倍，太阳能驱动的水蒸发效率达到88.9%，在水净化方面具有巨大的应用潜力[52]。

2 结论与展望

生物质碳与MOF复合材料具有较大的比表面积和丰富的活性位点等诸多优异特性，已在吸附剂、催化剂、电化学传感器、超级电容器、吸波材料和太阳能蒸发器等领域获得了广泛的应用。尽管生物质碳与MOF复合材料的研究已取得巨大的应用研究进展，但仍然存在着许多挑战：(1)在制备复合材料的过程中如何有效地控制所需的形貌和孔结构以获得最佳的活性是该领域的主要挑战之一；(2)复合材料通常比单一材料具有更好的性能，产生"协同效应"，但当前发表的文献并没有详细阐述其作用机理，如何利用相关技术(如原位分析技术)分析中间过程的物相和形态变化并对其机理做出系统、全面的解释是另一重要挑战之一。

将生物质碳与MOF复合材料同其他功能材料(如碳纳米管、石墨烯和MXene等)复合，制备三元复合材料，使之具有光学、电学及磁性等方面的优异特性，从而进一步拓展其应用范围，是该领域未来研究的一个重要方向。随着绿色清洁能源与材料逐步进入人们的视野，如何采用更加绿色经济的方法来制备生物质碳与MOF复合材料并使之用于工业化是当前研究者们需要关注的问题。此外，可将生物质碳与MOF复合材料同便携式荧光检测仪、便携式传感器和智能手机等结合，开发出低廉、便捷和准确的化学测量方法，是该领域未来研究的另一个重要方向。

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