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移动扫码阅读

## 生物质衍生炭质材料应用于研制 摩擦纳米发电机的进展

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**摘要:** 摩擦纳米发电机(Triboelectric Nanogenerators, TENGs)能够将机械能转换为电能, 在可穿戴设备、环境监测和能源收集等领域已经得到应用。生物质衍生炭质材料(Biomass-Derived Carbon Materials, BDCMs)因其来源广泛、绿色环保以及良好的导电性, 在近些年已被诸多研究者应用于高性能TENGs的研制中。首先简要介绍了TENGs和BDCMs相关概念, 随后总结了制备BDCMs的几种炭化方法, 包括热解炭化法、水热炭化法以及激光诱导炭化法; 并对BDCMs结构的调控方法进行了论述, 包括模板法和活化法。选择适宜的炭化和调控方法有助于调节BDCMs的比表面积和孔隙结构, 以提升基于BDCMs的TENGs的开路电压、短路电流等输出性能及其稳定性。进一步综述了基于BDCMs的TENGs作为供能型器件和传感型器件2种自供电器件的研究与应用进展, 发现大蒜壳、咖啡渣和蛋壳膜等各类生物质均已被用于TENGs的制造, 并成功应用于能量收集、电能供应、健康监测和手势识别等领域。最后, 对BDCMs在TENGs中应用存在的问题进行了探讨, 以期为BDCMs的创新应用提供借鉴参考。

**关键词:** 摩擦纳米发电机; 热解; 生物质衍生炭质材料; 结构调控; 自供电

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### Advances in the applications of biomass-derived carbon materials in triboelectric nanogenerators

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**Abstract:** Triboelectric nanogenerators (TENGs), which convert mechanical energy into electrical energy, have been applied in the fields of wearable devices, environmental monitoring, and energy harvesting. In recent years, many researchers have utilized biomass-derived carbon materials (BDCMs) for the development of high-performance TENGs due to their wide range of sources, green environmental protection, and good electrical conductivity. This paper provides a brief introduction to the concepts of TENGs and BDCMs, followed by a summary of several carbonization methods used in the preparation of BDCMs, including pyrolytic carbonization, hydrothermal carbonization, and laser-induced carbonization. The regulation methods for the structure of BDCMs are also discussed,

including the use of template and activation methods. The selection of suitable carbonization and regulation methods helps to adjust the specific surface area and pore structure of BDCMs, thereby further improving the output performance, including open circuit voltage and short circuit current, and stability of BDCMs-based TENGs. The paper presents a comprehensive review of the research and application progress of BDCMs-based TENGs in energy-supplying devices and sensing devices. Various biomass materials such as garlic shells, coffee grounds, and eggshell membranes have been successfully used in the manufacture of TENGs and have found applications in energy harvesting, electricity supply, health monitoring, and gesture recognition. Finally, the paper discusses the problems existing in the application of BDCMs in TENGs, providing reference for the innovative use of BDCMs.

**Keywords:** Triboelectric nanogenerator; Pyrolysis; Biomass-derived carbon materials; Structural regulation; Self-powered

## 0 引言

随着物联网的发展,小型设备如便携式及可穿戴电子设备在日常生活中逐渐广泛应用,然而,此类设备大多依靠电池供电。传统电池因续航时间短、回收困难、寿命短等问题<sup>[1]</sup>难以满足当前需求,因此开发新型供电技术使小型设备实现自供电至关重要。2012年,FAN等<sup>[2]</sup>发明了摩擦纳米发电机(Triboelectric Nanogenerators, TENGs),该发明基于摩擦起电和静电感应效应,可以将周围环境中耗散的机械能,包括风能<sup>[3]</sup>、水能<sup>[4]</sup>以及

人体运动产生的能量<sup>[5]</sup>转化为所需的电能,该发明在实现小型设备自供电方面具有良好的应用前景<sup>[6]</sup>。TENGs通常由摩擦层和导电层构成(图1),其工作模式主要分为4种:垂直接触-分离模式、水平滑动模式、单电极模式以及独立层模式<sup>[7]</sup>。根据不同环境和工作需求,选择不同模式和结构的TENGs<sup>[8]</sup>。制备TENGs常用的导电材料包括金属(如铝、铜)以及常用的摩擦材料包括聚合物(如聚四氟乙烯、聚对苯二甲酸乙二醇酯),然而其中大多数材料都不可降解<sup>[9]</sup>,在当前低碳背景下,开发绿色环保的TENGs材料显得尤为重要。

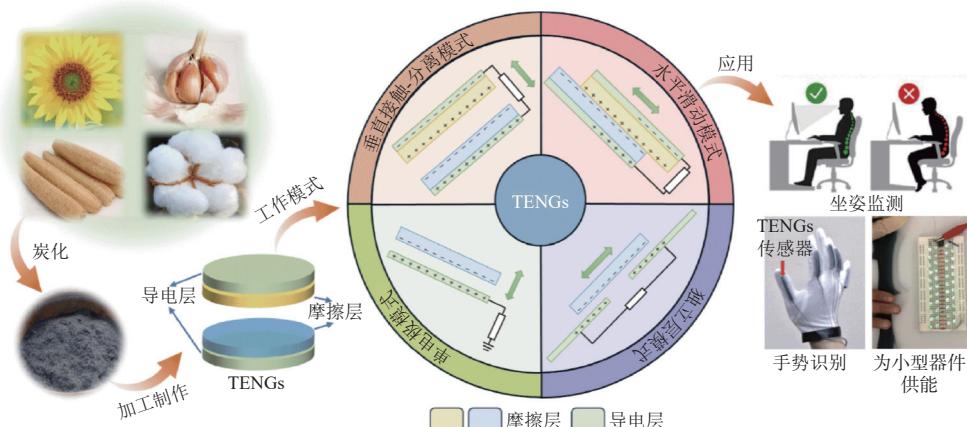


图1 以生物质为原料制成TENGs的示意图<sup>[6,10]</sup>

Fig. 1 Schematic fabrication process of the TENGs made from biomass<sup>[6,10]</sup>

生物质作为一种可再生资源,具有丰富的种类和广泛的来源<sup>[11]</sup>。生物质资源包括木材及其废料、农作物及其废料副产品、食品加工废弃物和水生植物废弃物等<sup>[12]</sup>,经炭化后得到生物质衍生炭质材料(Biomass-Derived Carbon Materials, BDCMs)。与传统制备TENGs材料相比,BDCMs具有来源广泛、绿色环保、成本低廉、应用潜力大、导电性

能好等优点<sup>[13]</sup>,其中以生活中的废弃物为生物质,其炭化后有利于环境保护和资源再利用。BDCMs经过炭化、调控后,通常具有高比表面积、良好的化学稳定性以及适当的孔隙结构等特点<sup>[14]</sup>,其在TENGs应用中有助于提高能量转换效率并保持长时间稳定工作。BDCMs通常作为导电层应用于TENGs中,还可以作为摩擦层或同时用作导电层

和摩擦层。以最常见的垂直接触-分离模式为例, TENGs 工作原理通常是当 2 种不同材料的表面发生物理接触时, 2 个接触的表面上会产生摩擦电荷, 一旦分离就会形成电位差, 电子会从一个导电层转移到另一个导电层, 最终在 2 个表面完全分离时达到平衡<sup>[15]</sup>。基于 BDCMs 的 TENGs 通常具有输出性能好、可塑性强、成本低廉等优点, 部分生物质制成的 TENGs 还具有耐高温与低温、防潮、抗菌、防辐射等优点<sup>[8]</sup>, 已成功运用于健康监测<sup>[6]</sup>、手势识别<sup>[10]</sup> 及各种自供电系统<sup>[16]</sup>, 如图 1 所示。

尽管目前已有很多种材料应用于 TENGs 的综述类文章, 但炭质材料的应用报道较少, 主要集中于石墨烯和碳纳米管, 且原料为非生物质来源。同时, 有关 BDCMs 的综述也大多围绕超级电容器和传感器展开, 缺乏 BDCMs 在 TENGs 中作为自供电器件应用于各种场景的系统报道。本文首先对 BDCMs 进行系统介绍, 包括其炭化方法与结构调控方法, 接着对 BDCMs 在 TENGs 的最新应用进行详细介绍, 最后对基于 BDCMs 的 TENGs 的研究进行展望。

## 1 生物质衍生炭质材料简介

### 1.1 生物质衍生炭质材料的制备方法

生物质在炭化过程中会经历许多反应, 形成具有不同结构和性质的 BDCMs。不同的炭化方法直接决定了产物的物理与化学性质, 如比表面积、孔隙率和石墨化程度等<sup>[17]</sup>, 进而影响 TENGs 的性能。以下将讨论几种典型的炭化方法, 包括热解炭化、水热炭化以及激光诱导炭化。

#### 1.1.1 热解炭化

生物质的热解通常在 350 ℃ 以上、惰性气氛下进行<sup>[18]</sup>。生物质在完全缺氧或供氧有限的条件下大多转化为气体、液态生物油和固体生物炭<sup>[19]</sup>。由于热解的高效性, 热解炭化被认为是制备生物质衍生材料最常用的方法。根据升温速率, 可将其分为快速热解和慢速热解, 其中慢速热解可以产生更多炭质残留物<sup>[20]</sup>, 更适用于制备生物质基炭质材料<sup>[21]</sup>。YUE 等<sup>[22]</sup> 将玉米秸秆作为原料, 经 KOH 活化和尿素掺杂后进行热解炭化, 在氮气环境下加热至 800 ℃ 并保持 2 h, 所制备的 BDCMs 呈现出以介孔和微孔为主的多孔结构, 比表面积达到 2 152 m<sup>2</sup>/g, 有利于电解质离子的快速传输, 展现出在 TENGs 的应用潜力。

#### 1.1.2 水热炭化

水热炭化法是一种经济环保的炭化方式, 于 1913 年由 BERGIUS 首次提出<sup>[23]</sup>。水热炭化法较热解炭化更适用于含水量高的生物质原料<sup>[24]</sup>, 该方法通常在较高温度(180~260 ℃)和较高压力(2~6 MPa)下进行<sup>[18]</sup>, 进而合成富碳固体产物<sup>[25]</sup>。由于该过程是在有溶剂(通常为水)的情况下进行, 故可省略湿生物质预干燥的需求<sup>[26]</sup>, 使炭化过程更为简便。LI 等<sup>[27]</sup> 以山药废弃物为原料, 采用低成本、简便的水热炭化法和化学活化工艺(活化剂为 KOH)制备了 BDCMs。对比之下, 炭化温度为 200 ℃、炭化时长为 16 h 的 BDCMs 电化学性能最佳, 比表面积达到 1 952 m<sup>2</sup>/g, 有望在 TENGs 中应用。

#### 1.1.3 激光诱导炭化

2014 年 LIN 等<sup>[28]</sup> 首次提出使用激光辐照从聚合物中制备三维多孔石墨烯薄膜, 该石墨烯薄膜表现出高导电率。激光可以在短时间内产生极高的温度(通常大于 2 500 ℃<sup>[29]</sup>), 因此可以用于诱导生物质的炭化, 该方法是一种成本低且对环境友好的炭化方法。与传统的长时间炉内热解相比, 激光炭化的时长仅为毫秒级别, 大幅缩短了制备时长<sup>[30]</sup>。通过激光炭化的导电炭质材料可用于多个领域, 如传感器、电化学储能、电催化等。YANG 等<sup>[31]</sup> 将不同产地的柚子皮干燥后进行激光诱导炭化, 生成的激光诱导石墨烯产率约为 30%(质量分数), 不仅展现出多孔结构, 还具有较高的电导率。该石墨烯制成的光学传感器处于黑暗环境中时, 传感器电流仅为 1.25 nA, 当光照强度为 1、10、20 mW/cm<sup>2</sup> 时, 电流分别增加到 4.36、21.10、33.80 μA, 具有较高的灵敏度, 有利于 TENGs 作为可穿戴电子设备在环境监测等方面的发展。

如上所述, 本文主要介绍了热解炭化、水热炭化以及激光诱导炭化 3 种炭化方式, 表 1 按照炭化方式分成 3 类, 并分别总结了 3 类炭化方式的生物质来源、炭化温度、退火时长以及比表面积和活化剂。目前研究对象主要集中在植物类, 如农业和林业废弃物, 表中使用激光诱导炭化的研究相对较少, 经过热解炭化和水热炭化的部分 BDCMs 可达到 3 000 m<sup>2</sup>/g 以上的比表面积。

### 1.2 生物质衍生炭质材料的结构调控方法

除选择合适的生物质原料以及炭化方法以外, 选择合适的炭化和调控方式, 能有效提高比表

表 1 不同生物质炭化实例  
Table 1 Examples of different biomass carbonization

| 炭化方式   | 生物质来源 | 炭化温度/℃ | 退火时长    | 比表面积/(m <sup>2</sup> ·g <sup>-1</sup> ) | 活化剂                                    | 参考文献 |
|--------|-------|--------|---------|---|--|------|
| 热解炭化   | 芒草    | 1 200  | 1.00 h  | 545.3                                   | —                                      | [32] |
|        | 胡萝卜   | 1 000  | 2.00 h  | 682.0                                   | —                                      | [33] |
|        | 茄子    | 900    | 2.00 h  | 3 128.0                                 | Zn(OH) <sub>2</sub> 、ZnCl <sub>2</sub> | [34] |
|        | 竹子    | 850    | 1.00 h  | 345.0                                   | —                                      | [35] |
|        | 猕猴桃   | 800    | 2.00 h  | 1 226.2                                 | ZnCl <sub>2</sub>                      | [36] |
|        | 玉米秸秆  | 800    | 2.00 h  | 1 724.6                                 | KOH                                    | [37] |
|        | 板栗    | 800    | 3.00 h  | 2 645.7                                 | KOH                                    | [38] |
|        | 柳絮    | 800    | 2.00 h  | 157.5                                   | —                                      | [39] |
|        | 枸杞    | 700    | 2.00 h  | 3 344.0                                 | 三聚氰胺、KOH                               | [40] |
| 水热炭化   | 棉籽    | 550    | 0.25 h  | 1 221.0                                 | NaOH、K <sub>2</sub> CO <sub>3</sub>    | [41] |
|        | 马尾藻   | 210    | 4.00 h  | 52.0                                    | —                                      | [42] |
|        | 石莼    | 210    | 4.00 h  | 44.8                                    | —                                      | [42] |
|        | 果皮    | 200    | 24.00 h | 3 909.3                                 | H <sub>3</sub> PO <sub>4</sub>         | [43] |
|        | 荞麦壳   | 200    | —       | 470.5                                   | H <sub>3</sub> PO <sub>4</sub>         | [44] |
|        | 竹笋    | 200    | 24.00 h | 3 250.0                                 | KOH                                    | [45] |
|        | 椰壳    | 180    | 4.00 h  | 873.5                                   | KOH                                    | [46] |
|        | 山茶壳   | 180    | 24.00 h | 377.6                                   | —                                      | [47] |
|        | 竹秆    | 180    | 6.00 h  | 3 132.0                                 | KOH                                    | [48] |
|        | 红毛丹   | 170    | 1.50 h  | 1 487.1                                 | KOH                                    | [49] |
| 激光诱导炭化 | 柚子皮   | ≥2 500 | —       | —                                       | —                                      | [31] |
|        | 软木    | ≥2 500 | —       | 4.6                                     | —                                      | [50] |
|        | 椴木    | ≥2 500 | —       | —                                       | —                                      | [51] |
|        | 蟹壳    | ≥2 500 | 32 s    | —                                       | —                                      | [52] |
|        | 木材和树叶 | ≥2 500 | —       | —                                       | —                                      | [53] |

面积、改善形貌特征和孔隙结构<sup>[54]</sup>。几种常用提高BDCMs的多样性及稳定性的调控方法如下所述,主要包括模板法和活化法。

### 1.2.1 模板法

模板法应用广泛,具有良好的结构可控性,制备的炭质材料通常拥有较高的比表面积、孔隙丰富、孔径分布有序等优点<sup>[55]</sup>。模板法又可分为软模板法和硬模板法<sup>[56]</sup>。硬模板法通过共价键维持特定结构,软模板法通过分子或分子之间的相互作用维持特定结构<sup>[57]</sup>。硬模板通常是指固体和刚性材料,一般为共价化合物<sup>[58]</sup>,常见的硬模板材料如胶体晶体模板、生物模板和聚合物模板等<sup>[59]</sup>。WELDEMHRET等<sup>[6]</sup>以有序介孔二氧化硅材料KIT-6为硬模板,甘蔗和米糠为生物质原料制作BDCMs,应用于TENGs时可作为自供电传感器检测背部运动。软模板主要是有机分子或嵌段共聚

物<sup>[58]</sup>,如表面活性剂和离子胶束<sup>[29]</sup>。HOU等<sup>[60]</sup>以稻壳为生物质原料、二氧化硅为硬模板,所制备的BDCMs表现出优异的微观形貌,从而促进了良好的电化学性能,在0.2倍率的电流密度下,循环100次后的充电比容量仍可达到679.9 mAh/g。TU等<sup>[61]</sup>以木质素基胶束为软模板,经热解炭化后制备出木质素基纳米管。在900 ℃的炭化条件下该纳米管直径为10~80 nm,长度为1~3 μm,具有良好的石墨化程度和稳定性。结果表明,将胶束作为软模板对纳米管的形貌和结构的调控具有重要作用,为木质素的高值化利用提供了新思路,也为BDCMs在TENGs的应用提供了思路。

### 1.2.2 活化法

生物质衍生炭质材料的活化方法通常可分为物理活化和化学活化。

物理活化通常在高温、合适气体氛围下进行,

其中  $\text{CO}_2$  和水蒸气活化是最常见的物理活化方式<sup>[29]</sup>。GUNASEKARAN 等<sup>[62]</sup>以大麻纤维为生物质来源,在热解炭化过程中加入  $\text{CO}_2$  进行物理活化,活化后比表面积可达  $1\ 060\ \text{m}^2/\text{g}$ 。ZHOU 等<sup>[63]</sup>以竹子为生物质来源,以水蒸气为活化剂,制备了具有高比表面积和高吸附性能的绿色环保型活性炭吸附材料。当活化温度为  $850\ ^\circ\text{C}$  时,比表面积可达  $1\ 315\ \text{m}^2/\text{g}$ 。

通过物理活化制得的多孔炭的堆叠密度较高,且无法调节其表面化学性质,具有一定的局限性<sup>[64]</sup>。相比于物理活化,化学活化因活化时间短,制得的炭质材料孔隙均匀,使用更广泛。目前常见的活化剂有  $\text{KOH}$ 、 $\text{ZnCl}_2$ 、 $\text{H}_3\text{PO}_4$  和  $\text{KHCO}_3$  等<sup>[64]</sup>。其中,  $\text{KOH}$  是使用最为广泛的化学试剂。ARUMUGHAM 等<sup>[65]</sup>以棕榈壳为生物质来源,通过对超声浸渍进行  $\text{KOH}$  化学活化,发现在活化温度为  $750\ ^\circ\text{C}$ 、超声浸渍时间为 40 min 的条件下,BDCMs 最大比表面积和最高碘吸附率分别为  $138.21\ \text{m}^2/\text{g}$  和 45.36%。FERREIRA 等<sup>[66]</sup>将蓖麻籽热解炭化制备 BDCMs,并以  $\text{H}_3\text{PO}_4$  为活化剂,活化后 BDCMs 拥有更高的孔隙率和比表面积(比表面积可达  $310.94\ \text{m}^2/\text{g}$ ),远高于未经活化的 BDCMs(比表面积仅为  $16.53\ \text{m}^2/\text{g}$ )。诸多研究表明,经化学活化的 BDCMs 往往拥有更高的比表面积和丰富的孔隙结构<sup>[67-69]</sup>,在 TENGs 的制作方面表现出良好的应用潜力。

## 2 生物质衍生炭质材料在摩擦纳米发电机的应用

TENGs 在实际应用中大致可以分为 2 类: 供能器件和传感器件。供能型器件更侧重于作为电源为电子设备供电,最常见的小型电子器件如发光二极管和电子手表等,需要具备长时间稳定运行和可持续供能的特点<sup>[70-72]</sup>。传感型器件一般兼具供能和传感的功能,在应用方面更偏向于感知各种被测物体的信息并转化为电信号,例如进行人体运动监测,需要具备高灵敏度和稳定的输出特性,为适应各种场景有时也需具备小型化、柔性化等特点<sup>[73-75]</sup>。下文将分别介绍这 2 类基于 BDCMs 的 TENGs 的实际应用。

### 2.1 供能器件

TENGs 作为供能器件可以将机械能转换为电能,为电子器件的正常运行提供电能。XING 等<sup>[16]</sup>以大蒜壳为原材料制备了纤维素纳米纤维

(Cellulose Nanofiber, CNF),将其与 MXene 充分混合后使用真空辅助过滤法得到了 MXene/CNF 复合膜,并将其应用到 TENGs 中,发现该装置可在  $3.5\ \text{Hz}$  的频率下产生约  $1\ 120\ \text{V}$  的开路电压、 $25\ \mu\text{A}$  的短路电流以及  $100\ \mu\text{C}/\text{m}^2$  的电荷密度,成功为电容充电并为商用电子手表供电,如图 2(a)所示。TANG 等<sup>[76]</sup>以丝瓜络为生物质来源,将其炭化后与芳香族无规共聚酯(Ecoflex)制成单电极模式的 TENGs。该 TENGs 工作时能产生  $19.3\ \text{V}$  的开路电压、 $0.22\ \mu\text{A}$  的短路电流以及  $0.75\ \text{nC}$  的转移电荷,如图 2(b)所示。制得的 TENGs 可以点亮大约 50 个发光二极管,并且成功为电子手表供电。在经历 10 000 次循环测试后依旧保持长期稳定性,作为可穿戴的供能器件,具有良好的应用前景。CHOMJUN 等<sup>[77]</sup>以天然橡胶和人类头发作为原料,首次将人类的生物质废弃物和天然生物质制备高性能的可生物降解 TENGs,可产生  $232\ \text{V}$  的开路电压、 $16\ \mu\text{A}$  的短路电流以及  $242\ \text{mW}/\text{m}^2$  的最大功率密度,其中功率密度几乎是未加人类头发材料的 3 倍。该装置也可为小型电子设备供电,产生的电能能瞬间点亮 44 个发光二极管,同时还可为商用电容充电或将电能存储在电容中为其他小型设备供电,如图 2(c)所示。YUE 等<sup>[78]</sup>以丝瓜络为生物质来源,制成了一种柔性导电水凝胶并应用于 TENGs 上,工作时开路电压、短路电流和转移电荷分别达到  $60.5\ \text{V}$ 、 $348\ \text{nA}$  和  $1.52\ \text{nC}$ ,该 TENGs 产生的电能成功点亮约 40 个发光二极管。YUE 等还设计了一套自供电传感系统,将 TENGs 作为电源,为其他传感器供电,在智能自供电传感微系统中具有巨大潜力。

此外,除了将 BDCMs 作为原材料制成 TENGs 为其他器件供电,还有不少学者将其他材料制成的 TENGs 作为电源、BDCMs 作为催化剂构成一种自供电降解系统,拓展了 BDCMs 在 TENGs 的应用。例如,ZHU 等<sup>[79]</sup>以艾叶合成的 BDCMs 作为电芬顿系统的阴极催化剂,并制作了一种结构稳定、高输出特性的印刷柔性波浪状结构的 TENGs,其最大开路电压和短路电流可分别达到  $610\ \text{V}$  和  $1.93\ \text{mA}$ 。这款 TENGs 将电芬顿技术、3D 数字打印技术与电催化降解有机污染物技术巧妙结合,如图 3(a)所示,为 TENGs 自供电技术在电芬顿降解系统的大规模应用提供了新思路。GAO 等<sup>[80]</sup>以长豆为原料,  $\text{KHCO}_3$  为活化剂,在  $800\ ^\circ\text{C}$  下热解 2 h,洗涤干燥后制成阴极催化剂。

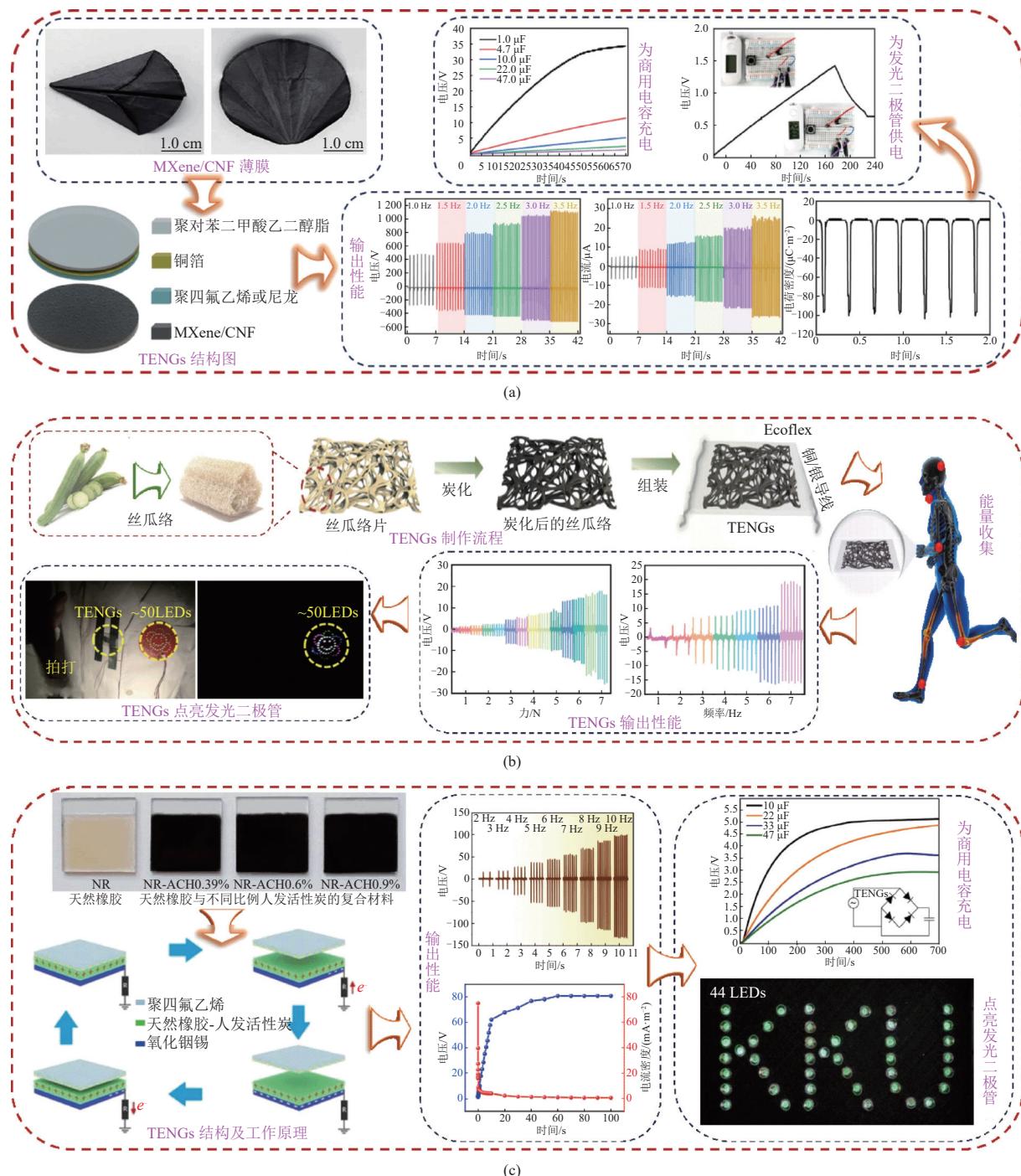


图 2 (a) 基于 BDCMs 的 TENGs 为商用电子表供电<sup>[16]</sup>, (b) 基于 BDCMs 的 TENGs 为发光二极管供电(生物质来源为丝瓜络)<sup>[76]</sup>, (c) 基于 BDCMs 的 TENGs 用于为发光二极管供电(生物质来源为人发和天然橡胶)<sup>[77]</sup>

Fig. 2 (a) BDCMs-based TENGs powers commercial electronic watch<sup>[16]</sup>. (b) BDCMs TENGs supplies power to the LEDs (the biomass source is loofah)<sup>[76]</sup>. (c) BDCMs-based TENGs powered the LEDs (the biomass source is human hair and natural rubber)<sup>[77]</sup>

同时制备了一种柔性的多层 TENGs, 如图 3(b)所示, 该 TENGs 共有 6 个摩擦层, 其瞬时开路电压、短路电流分别达到 750 V 和 650  $\mu$ A, 可以同时点亮 100 个发光二极管, 并成功实现了 4-二甲氨基偶氮苯的自供电降解。此外, 利用玉兰花<sup>[81]</sup>和梧

桐树皮<sup>[82]</sup>等 BDCMs 作为催化剂与 TENGs 结合的自供电降解系统同样可以达到出色的效果。

## 2.2 传感器件

TENGs 作为传感器件可以通过感知外界的物理量, 如压力、摩擦力及形变等, 进而应用于健康

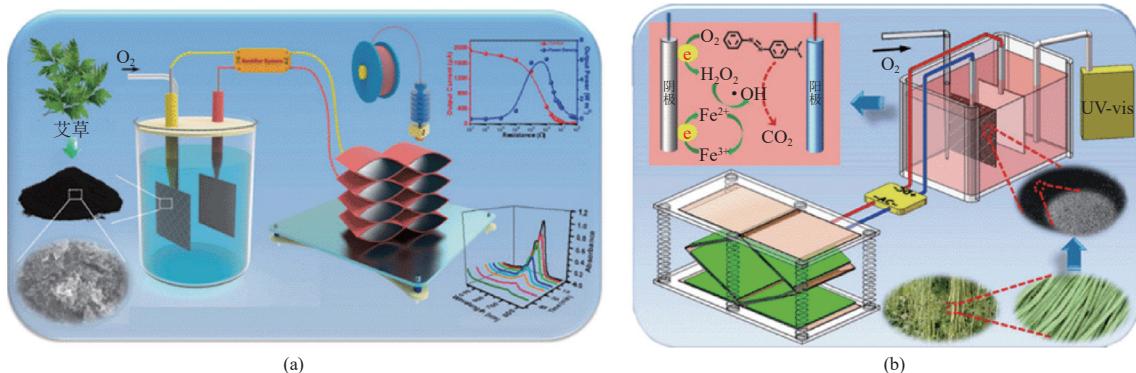


图 3 (a) 基于 BDCMs 的 TENGs 与 3D 打印技术结合用于为电芬顿降解系统供电<sup>[79]</sup>, (b) 基于 BDCMs 的 TENGs 用于 4-二甲氨基偶氮苯的自供电降解<sup>[80]</sup>

Fig. 3 (a) BDCMs-based TENGs combined with 3D printing technology for powering electro-Fenton degradation systems<sup>[79]</sup>  
(b) BDCMs-based TENGs for self-powered degradation of 4-dimethylaminoazobenzene<sup>[80]</sup>

监测、动作识别、手势模拟等领域。TENGs 在工作中可以实现自供电,大大节约了电力资源。WELDEMHRET 等<sup>[6]</sup>从甘蔗和米糠中提取蔗糖和植酸,使用硬模板法合成了磷掺杂介孔碳,将其作为聚氨酯泡沫的涂层,制备了一种具有阻燃功能的 TENGs,开路电压可达 158 V。如图 4(a)所示,将其安装在椅子上,根据人背部运动产生电输出,从而点亮发光二极管提醒人们纠正坐姿。LI 等<sup>[10]</sup>利用咖啡渣为生物质原料,热解炭化后与Ecoflex 制作出一种无金属的环保型 TENGs,工作时能产生 150 V 的开路电压、2.1  $\mu$ A 的短路电流,并可以实现准确的实时姿势评估、运动监测和手势模拟。如图 4(b)所示, TENGs 安装在手套上,可分别感应 5 根手指的动作,将复杂的手指姿势转换为可识别的电输出,展现出精确的手势识别能力,将其佩戴在手肘处还可以检测手臂弯曲程度,为可穿戴设备提供了良好的范例。YAN 等<sup>[83]</sup>以蛋壳膜(ESM)与膨体聚四氟乙烯(ePTFE)为原料制作 TENGs,在对比未经加工的蛋壳膜(RESM)、加热后的蛋壳膜(HESM)以及炭化后的蛋壳膜(CESM)3 种原材料制成的 TENGs 后,发现 CESM 性能最好,开路电压、短路电流分别可达到 156.12 V、15.95  $\mu$ A,将其绑在膝盖或脚上,通过走路或跑步产生输出电压产生电力。如图 4(c)所示,它还可用于监测各种人体运动,并显示出高灵敏度,例如当不同数量的手指接触 TENGs,输出波形也会显示出不同的峰值,当其作为人体运动监测器件时在生物医学应用中存在巨大的潜力。陈宏涛等<sup>[84]</sup>采用水生植物大藻及槐叶萍作为生物质前驱体,炭化后分别制成 2 种植物

基 TENGs,由大藻、槐叶萍制成的 TENGs 开路电压分别达到 7.81 V、20.30 V,短路电流分别达到 1.22  $\mu$ A、3.68  $\mu$ A。二者都可监测人体运动,在人体进行各种运动时输出灵敏的电信号响应,不同的动作产生的电信号也截然不同,其在智能穿戴设备领域展现出良好的发展前景。

表 2 总结了不同生物质来源、不同工作模式和炭化方式制得 TENGs 的输出性能。可以看出,林业、农业、固体废弃物等各类生物质均可用于 TENGs 材料的制备,其中使用较多的是纤维素和木质素类生物质。在工作模式方面,目前研究者多集中于单电极模式和垂直接触-分离模式,在传感领域对单电极模式应用更多。炭化方式也主要以热解炭化法为主。在输出性能上,不同模式、材料的性能输出也各有不同,其中以大蒜壳为原料制备得到的 TENGs,在垂直接触-分离模式下,其开路电压最高输出达到千伏级别。

### 3 结论与展望

本文对 BDCMs 的制备方法、调控方法与 BDCMs 在 TENGs 中的应用进行了综述。TENGs 结构多样、用途广泛,已应用于可穿戴设备、环境监测、蓝色能源的收集、传感器等领域。生物质作为原料来源广泛、制备过程相对简单且成本较低,相对于传统 TENGs,基于 BDCMs 的 TENGs 对环境更友好、柔韧性和拉伸性好、更具可控性。

虽然 BDCMs 应用于 TENGs 具有很多优点,但是仍存在一些问题需要进一步研究。

(1) 在原料选取方面:虽然已经有不少生物质作为原料应用至 TENGs 中,但较传统 TENGs 材

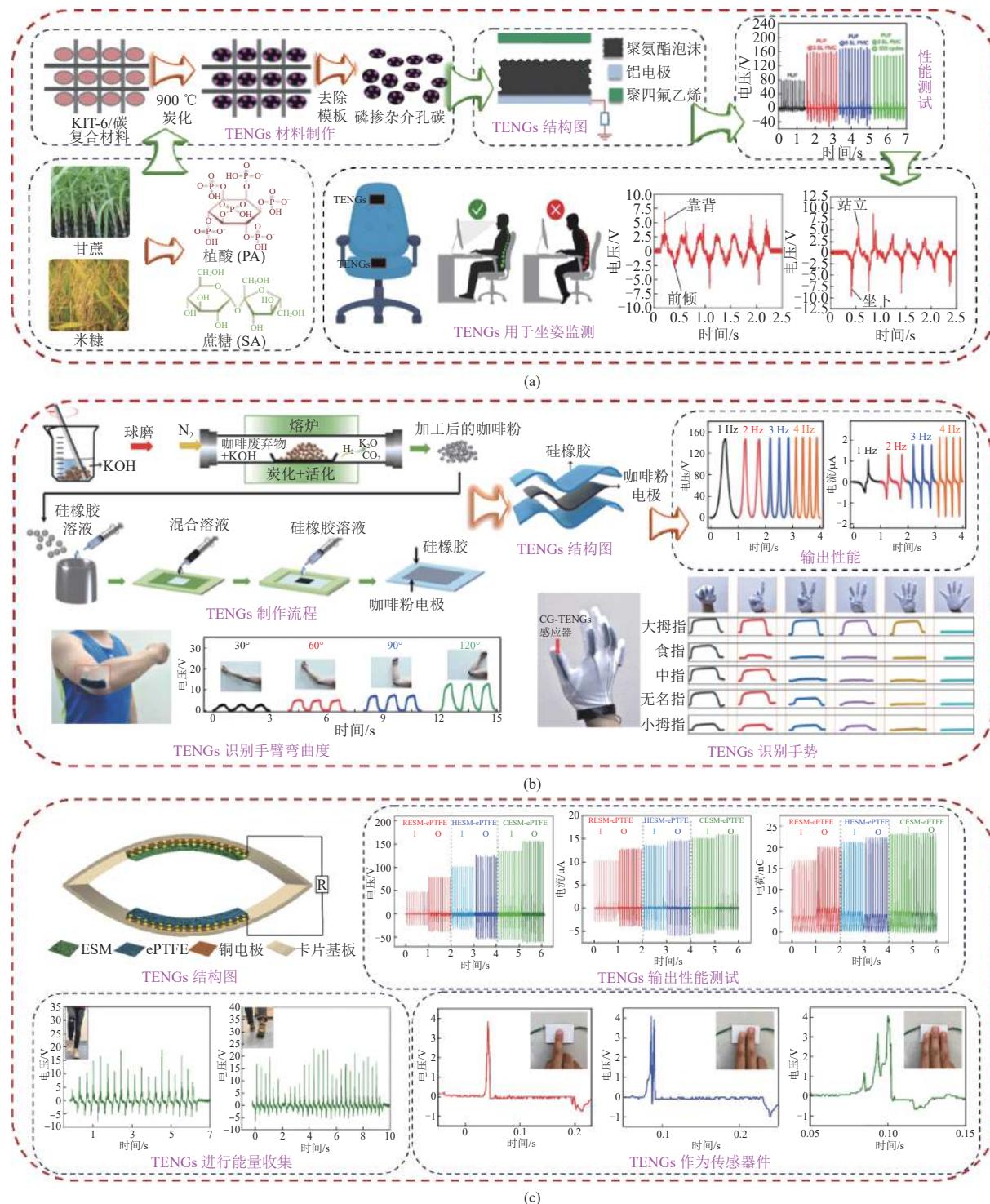


图 4 (a) 基于 BDCMs 的 TENGs 在生物力学的应用<sup>[6]</sup>, (b) 基于 BDCMs 的 TENGs 在手势识别的应用<sup>[10]</sup>, (c) 基于 BDCMs 的 TENGs 在检测手指数量的应用<sup>[83]</sup>

Fig. 4 (a) BDCMs-based TENGs applied in biomechanical system<sup>[6]</sup>. (b) BDCMs-based TENGs applied in gesture recognition<sup>[10]</sup>. (c) BDCMs-based TENGs applied in detecting the number of fingers<sup>[83]</sup>

料,其电输出性能还有待进一步提升。可以从生物质原料的组成、可获取性等因素入手,选择合适的生物质原料,不断发掘更具优势的生物质资源。

(2)在制备工艺方面:炭化工艺对 BDCMs 的

性能有重要影响,不断探索更合适的炭化温度、炭化时间和反应气氛等条件来改变炭质材料的结构和性能。此外,添加适当的活化剂或添加剂以及功能负载也可以改善炭质材料的孔隙结构、表面

**表 2 基于 BDCMs 的 TENGs 的应用**  
**Table 2 Applications of BDCMs-based TENGs**

| 应用   | 生物质来源   | 工作模式      | 炭化方式   | 输出性能   | 参考文献 |
|------|---------|-----------|--------|--|------|
| 供能器件 | 大蒜壳     | 垂直接触-分离模式 | 水热炭化   | 产生1120 V的开路电压、100 $\mu$ C/m <sup>2</sup> 的电荷密度           | [16] |
|      | 丝瓜络     | 单电极模式     | 热解炭化   | 产生19.3 V的开路电压、0.22 $\mu$ A的短路电流、0.75 nC的转移电荷             | [76] |
|      | 天然橡胶和人发 | 单电极模式     | 热解炭化   | 产生232 V的开路电压、16 $\mu$ A的短路电流、242 mW/m <sup>2</sup> 的功率密度 | [77] |
|      | 丝瓜络     | 单电极模式     | 热解炭化   | 产生60.5 V的开路电压、348 nA的短路电流、1.52 nC的转移电荷                   | [78] |
|      | 软木      | 垂直接触-分离模式 | 激光诱导炭化 | 产生35 V的开路电压  | [85] |
| 传感器件 | 甘蔗和米糠   | 单电极模式     | 热解炭化   | 产生158 V的开路电压、2.26 $\mu$ A/cm <sup>2</sup> 的短路电流密度        | [6]  |
|      | 咖啡渣     | 单电极模式     | 热解炭化   | 产生150 V的开路电压、2.1 $\mu$ A的短路电流、52 nC的转移电荷                 | [10] |
|      | 蛋壳膜     | 垂直接触-分离模式 | 水热炭化   | 产生156.12 V的开路电压、15.95 $\mu$ A的短路电流、23.55 nC的转移电荷         | [83] |
|      | 大藻      | 单电极模式     | 热解炭化   | 产生7.81 V的开路电压、1.22 $\mu$ A的短路电流                          | [84] |
|      | 槐叶萍     | 单电极模式     | 热解炭化   | 产生20.3 V的开路电压、3.68 $\mu$ A的短路电流                          | [84] |
|      | 棉花      | 单电极模式     | 热解炭化   | 产生83 nA的短路电流、6.2 nC的转移电荷                                 | [86] |
|      | 灯心草     | 单电极模式     | 热解炭化   | 产生19 V的开路电压、480 nA的短路电流、43 $\mu$ C/m <sup>2</sup> 的电荷密度  | [87] |
|      | 木材      | 垂直接触-分离模式 | 热解炭化   | 产生232 V的开路电压、12 $\mu$ A的短路电流、1.6 W/m <sup>2</sup> 的功率密度  | [88] |

特性和导电性能。在制备工艺中不断优化工艺参数,筛选出一套系统完整的制作流程,以提高BDCMs在TENGs中应用的潜能。

(3) 在工作模式方面: 目前基于BDCMs的TENGs大多为单电极模式和垂直接触-分离模式,随着需求的不断提升,研究者可以根据使用需求对这2种模式进行结构创新(如改变常用接触方式等)或选择其他模式进行研究。同时也需不断探索开发新的模式,拓展BDCMs在TENGs上的应用领域。

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