水蒸发驱动柔性自支撑复合发电碳膜

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2018-07-06 收稿, 2018-08-10 修回, 2018-08-13 接受, 2018-09-04 网络版发表

国家自然科学基金(51672097, 51606082, 51322210, 61434001)和中国博士后科学基金(2015M570639, 2017M610471)资助

摘要 利用自然界中无处不在的蒸发作用, 收集利用环境中总量巨大的低品位热能是一种新型可持续能源技术. 本文制备了一种可直接通过蒸发驱动流动的方式将环境热能转化为电能的柔性自支撑复合碳膜. 该复合碳膜由碳颗粒和玻璃纤维组成, 具有类似钢筋混凝土结构, 因而有良好的柔性和抗拉伸性能. 一片尺寸为1 cm×4.5 cm×0.13 mm的复合碳膜最高可获得~1 V的开路电压和~0.86 μ A的短路电流. 通过放大面积, 最高可得到单个器件~1 V的开路电压和~28 μ A的输出电流. 复合碳膜的这些性质显示了其作为一种新型的可收集环境能源材料, 在绿色可持续能源利用方面的应用前景.

关键词 蒸发, 毛细流动, 能量收集, 柔性, 复合碳膜

收集环境中存在的各种微能源(包括机械能、热能、化学能), 并将其转化为电能是一种极具潜力的绿色可持续发展能源技术^[1]. 近年来, 先进微纳制造技术的发展为新型环境能源转化提供了新的机遇, 产生了多种环境能源收集技术, 如压电发电机^[2-5]、摩擦发电机^[6-8]、驻极体发电机^[9,10]、浓差电池^[11]、渗透能量转换^[12-15]和湿气发电^[16-18]等. 环境中的热能无处不在, 且总量巨大, 但由于其品位较低, 收集利用十分困难. 如何直接利用环境中的低品位热能进行发电的工作鲜有报道.

自然界中广泛存在的蒸发现象是一种利用环境热能将水从液态变成气态的基本现象^[19]. 最近, 我们证明蒸发过程在一片纳米多孔碳膜上可以作为稳定的驱动力源驱动水流动发电, 从而将无处不在的环境热能转化成一种可用的新型能源^[20,21]. 基于多孔碳膜的水蒸发流动发电器件在自然环境条件下, 可产生1 V的稳定开路电压, 并且经过100 h电压几乎

没有衰减^[20,21]. 蒸发发电广泛存在于多种碳材料系统(包括碳纳米管、乙炔碳黑、甲苯碳黑、戊醇碳黑), 是一种普适现象^[20]. 在我们的前期工作中, 火焰法和印刷法制备的碳膜都需要刚性基底(玻璃载玻片或氧化铝陶瓷片)支撑, 该结构限制了碳膜的应用场合, 以及碳膜自身尺寸(比如厚度)的调控能力.

本文设计了一种由碳纳米颗粒和玻璃纤维(carbon nanoparticles/glass fiber, CNGF)组成的自支撑复合碳膜, 并将其用于蒸发诱导水流发电. CNGF复合碳膜与此前报道的发电碳膜相比, 具有如下优点: (1) 完全自支撑, 不需要基底, 更便于实际应用; (2) 具有良好的机械稳定性. 类钢筋混凝土结构使得CNGF复合碳膜具有良好的柔性和抗拉伸性能; (3) 更高的单位面积输出功率. CNGF复合碳膜稳定的机械结构, 使得我们可以将碳膜的厚度设计得更厚, 从而获得更大的水蒸发面积和更大的横截面水流量; 而且水可以从碳膜的两面同时蒸发, 进一步增大蒸

引用格式: 丁天朋, 刘抗, 李嘉, 等. 水蒸发驱动柔性自支撑复合发电碳膜. 科学通报, 2018, 63: 2846–2852

Ding T P, Liu K, Li J, et al. Evaporation induced electricity generation in freestanding and flexible carbon-based hybrid film (in Chinese). Chin Sci Bull, 2018, 63: 2846–2852, doi: 10.1360/N972018-00675

发面积和流量. 最终, 水蒸发驱动柔性复合碳膜在环境条件下可稳定输出开路电压 ~ 0.93 V, 单个器件输出电流达到 $28\text{ }\mu\text{A}$.

1 材料制备

CNGF复合碳膜的具体制备过程如下: (1) 将松节油透醇、乙基纤维素、火焰法制备的甲苯碳黑^[22]和玻璃纤维按照一定的比例在无水乙醇中加热搅拌, 获得均匀的浆料; (2) 采用印刷的方法将配好的浆料按照一定的尺寸涂覆在氧化铝陶瓷基底上面; (3) 将涂有浆料的陶瓷基底放入马弗炉中, 在 370°C 的空气氛围下退火 150 min , 自然冷却至室温; (4) 将退火后的碳膜从陶瓷基底上揭下来(图1(a)), 获得了如图

1(b)所示的柔性自支撑复合碳膜. 扫描电子显微镜(SEM)表征结果(图1(c)~(e)和S1)表明, CNGF复合碳膜由玻璃纤维和粒径约 80 nm 的碳纳米颗粒组成, 膜厚约 $130\text{ }\mu\text{m}$ (图S2). 微米级的玻璃纤维交错穿插于碳纳米颗粒之间, 形成类似于钢筋混凝土结构, 这种结构极大地提高了碳膜的机械性能, 包括弯曲性能和拉伸性能. 复合碳膜的机械性能和导电性, 都与碳黑和玻璃纤维比例有关. 如图1(f)所示, 随着玻璃纤维(glass microfiber, GMF)和碳纳米颗粒(carbon nanoparticles, CNP)的质量比从 0.15 提高到 0.6 , 尺寸为 $1\text{ cm}\times 4.5\text{ cm}\times 0.13\text{ mm}$ 的复合碳膜能承受的最大拉应力从 0.4 MPa 提高至 4.9 MPa . 但是, 当GMF/CNP比例达到 1.2 时, 最大拉应力反而降至 1.6 MPa . 由此可见,

图1 (网络版彩色)CNGF复合碳膜的基本结构性质. (a) 结构示意图. (b) 光学图片. SEM俯视图(c), 高分辨图(d)和截面图(e). (f) 复合碳膜能承受的最大拉应力、电阻与GMF/CNP比例的关系. (g) 弯曲测试

Figure 1 (Color online) Structure and characterization of the CNGF film. (a) Schematic of the free-standing CNGF carbon film. (b) Optical photograph of the carbon film. (c) SEM image of the carbon film in top view. (d) Magnified SEM image. (e) SEM image of the cross-sectional view. (f) Dependence of tensile property and area resistances on the mass ratio of GMF to CNP. (g) Bending test of the free-standing film

复合碳膜在机械性能上存在一个最优GMF/CNP比例, 大约在质量比0.6附近. 复合碳膜的电阻随着玻璃纤维含量的增加而增加, 且不随膜的弯曲而改变. 如图1(g)所示, CNGF复合膜(GMF/CNP=0.6)在经过10000次90°弯曲后, 其电阻基本没有变化.

2 水蒸发驱动流动发电性能

根据机械性能和电阻测试结果, 我们选择机械性能和电阻合适、纤维碳黑质量比为0.6的CNGF复合膜(GMF/CNP=0.6)进行后续的发电性能测试. CNGF复合碳膜的上下两端分别用涂覆碳纳米管墨水的方式负载一层5 mm宽的碳纳米管层作为电极, 碳纳米管电极与漆包线连接, 连接处用环氧树脂密封. 将制备好的器件一端置于去离子水中时(图2(a)), 纳米多孔碳膜内部毛细力会驱动水沿着碳颗粒之间的微通道从下往上传输. 碳膜上水分的不断蒸发, 形成碳膜内部源源不断的水流动. 由于微通道的尺寸较小, 通道壁面处形成的双电层互相重叠. 碳颗粒

Zeta电位约-33.2 mV, 因而通道壁带负电, 整个通道排斥带同种电荷的阴离子(OH^-), 而优先通过带异种电荷的阳离子(H^+). 碳膜内部由蒸发导致的水流动便会造成带正电荷的离子从底部向上端的定向运动, 形成了动电电流和电压^[23-26], 实现环境能量的收集和转换. 图2(a)显示了尺寸为1 cm×4.5 cm×0.13 mm的复合碳膜在环境条件下的电压输出曲线. 在环境相对湿度RH~50%, 温度25℃条件下(图S3), 器件开路电压达到~0.93 V, 并且可持续保持长达10 h基本没有变化. 短路电流达到~0.86 μA (图2(b)和S4), 该电流大小是火焰法制备的纯碳膜器件的5倍以上^[20]. 造成电流增加的原因主要有2个: (1) CNGF复合膜的厚度远超过纯碳黑膜, 因而在单片碳膜上可以实现更大的水流量; (2) CNGF碳膜的正反两面都可以进行水分蒸发, 因此CNGF碳膜中水的流速以及流量都得到了提高.

图2(c)为测试装置被密封时器件的输出电压. 从图中可以看到, 实验装置被完全密封后, 碳复合膜上

图2 (网络版彩色)CNGF复合碳膜的发电性能. (a) 开路电压测试曲线及实验装置示意图; (b) 器件干燥时和工作时被水部分浸润状态下的 I - V 曲线; (c) 测试装置被周期性密封时器件的输出电压; (d) 周期性的吹风对开路电压的影响, 风速 0.15 m/s

Figure 2 (Color online) Electricity generation performance of the CNGF film. (a) Long lasting open-circuit voltage of a chosen device with carbon film. The inset is the experiment setup. (b) The current-voltage curves of the device at original dry state and working state. (c) Measured open-circuit voltage when the device is periodically sealed and unsealed by a beaker. (d) Open-circuit voltage variation when the devices under periodic blowing with the wind velocity of 0.15 m/s

的水分蒸发逐渐减弱,直至完全不蒸发,器件的开路电压也从 ~ 0.93 V逐渐降低,并最终接近0 V.而当实验装置解密封后,输出电压会随着蒸发的恢复逐渐恢复至原来的大小.由此可见,蒸发是整个发电过程的驱动力源,增强蒸发过程可以进一步提高器件输出.如图2(d)所示,当器件被置于 0.15 m/s的风吹下,碳膜表面水分的蒸发速率便会加快,器件的开路电压也从 ~ 0.89 V上升到 ~ 1.1 V;而当风吹停止时,器件的开路电压便会从 ~ 1.1 V回复到初始无风时的 ~ 0.89 V.对于密封测试和吹风测试,器件的开路电压均表现出很好的稳定性和可重复性.

复合碳膜采用印刷的方式制备,因此可以比较容易地制备大面积器件,从而提高电能输出.如图3(a)所示,随着碳膜宽度的增加,器件的开路电压保持 ~ 0.93 V基本不变,短路电流随着宽度的增加呈线性增加,因此我们可以通过增大碳膜的宽度来获得高的电流输出,从而提高整体功率输出.实验中,我们制备了最大宽度为 40 cm的复合碳膜,整个器件的短路电流达到 ~ 28 μ A;而且由于复合碳膜自身具有优异的柔性,一片 4.5 cm $\times$ 40 cm的复合碳膜可以卷成半径为 2.5 cm的圆柱体.增加器件的输出电流及输出功率的同时,还可以保证小的整体占用体积.如图3(b)所示,复合碳膜卷起来后(保持层间适当间隙),器件在环境条件下的短路电流仍为 ~ 28 μ A,开路电压为 ~ 1 V,这样的输出功率已经足以驱动一些小型电子设备.

为了进一步展示CNGF发电复合碳膜在应用方面的潜力,我们用发电复合膜在环境条件下产生的电实现了亚甲基蓝溶液(methylene blue, MB)的电降

解.具体实验装置如图4(a)插图所示:首先将2个卷叠发电复合膜器件(尺寸为 4.5 cm $\times$ 40 cm,直径 2.5 cm)串联在一起,获得了 ~ 1.6 V的开路电压和 ~ 23 μ A的短路电流(图S5).两片铂片分别与串联器件的正负极相连后作为电降解的阳极和阴极,插在 7.5 mL的亚甲基蓝溶液中(浓度为 4.5 mg/L).如图4(a)所示,在进行电降解时,阴极和阳极两端的工作电压为 ~ 1.3 V,通过2个电极的电流为 ~ 6 μ A.为了测试亚甲基蓝的降解速率,每隔 6 h对亚甲基蓝溶液进行一次紫外吸收光谱测试(图4(b)),选取 664.5 nm处的吸收峰作为电降解程度的指示峰.随着时间的推移,特征峰的吸收强度出现明显的降低,在 30 h内达到 96% .电解前后的光学照片也显示,经过电解之后,亚甲基蓝溶液明显变得透明.由此可见,CNGF发电复合碳膜在环境条件下,可以自发收集环境热能发电,产生的电可以有效地实现亚甲基蓝溶液的降解,显示了其应用潜力.

3 结论

本文利用碳颗粒和玻璃纤维,制备了一种可用于蒸发驱动流动发电的柔性自支撑复合碳膜.该复合碳膜具有类似钢筋混凝土结构,因而具有良好的柔性和抗拉伸性能.同时与此前报道的发电碳膜相比,CNGF发电复合碳膜具有更高的电能输出,一片尺寸为 1 cm $\times$ 4.5 cm $\times$ 0.13 mm的器件最高可获得 ~ 1 V的开路电压和 ~ 0.86 μ A的短路电流.CNGF复合碳膜易于制备大面积器件,通过扩大面积获得了单个器件 ~ 1 V的开路电压和 ~ 28 μ A的输出电流.该器件

图3 (网络版彩色)大尺寸CNGF复合碳膜的发电性能. (a) 碳膜输出的开路电压和短路电流与碳膜宽度的关系. 实验中碳膜的高度固定为 4.5 cm,厚度固定为 130 μ m; (b) 宽度为 40 cm的复合碳膜卷起来时的短路电流输出. 插图为器件的光学照片

Figure 3 (Color online) Scaling up of the device. (a) Dependence of open-circuit voltage and short-circuit current on the widths of the device with a fixed height of 4.5 cm and thickness of 130 μ m. (b) Short-circuit current variation of a rolled-up device after being fully infiltrated. Inset shows the photo of the device

图 4 (网络版彩色)卷叠器件用于亚甲基蓝电降解. (a) 降解过程中阴极和阳极之间的电压以及通过 2 个电极的电流, 插图为实验装置图; (b) 不同降解时间后亚甲基蓝溶液的紫外吸收光谱(取样时间间隔 6 h), 左上插图为亚甲基蓝的降解率随时间的变化关系, 右插图为降解前后亚甲基蓝溶液的光学照片

Figure 4 (Color online) Demonstration of MB electrodegradation with two rolled-up devices as power source. (a) Load voltage and current across the cathode and anode. Inset shows the schematic of the experimental setup. (b) Absorption spectra of the MB solution at different processing time (with time intervals of 6 h). The left inset shows the degradation percentage versus the electrodegradation time. The right insets are the optical images of MB solution before and after 30 h electrodegradation

产生的电可直接电解浓度为 4.5 mg/L 的亚甲基蓝溶液. CNGF 复合碳膜优异的机械性能和蒸发发电性能

显示了其作为一种新型的环境能源收集技术的应用前景.

致谢 感谢武汉大学沈爱国教授对 Zeta 电位测试的帮助, 华中科技大学分析测试中心提供的测试支持.

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Summary for “水蒸发驱动柔性自支撑复合发电碳膜”

Evaporation induced electricity generation in freestanding and flexible carbon-based hybrid film

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Energy harvesting from ambient environment attracts widespread interest for its great potential in green and sustainable development. Very recently, evaporation, a ubiquitous process existing in nature was demonstrated as a reliable process, which can convert low-grade thermal energy in environment into electricity. Evaporation-driven water flow within a piece of carbon black sheet or printed porous carbon film could generate sustainable direct-current electricity with open-circuit voltage (V_{oc}) up to 1 V, and with lifetime over hundreds of hours. However, both the flame-deposited carbon black sheets and all-printed porous carbon films need to be deposited or printed on rigid substrates (e.g., silica glass and Al_2O_3 plate) in the previous work, which has decreased the effective evaporation area and occupied excessive space, thus limiting the application of this new energy harvesting strategy as a practical power source.

In this work, we present the fabrication of a flexible and freestanding carbon nanoparticles/glass fiber hybrid film (CNGF) for electricity generation via evaporation-driven water flow within it. The CNGF hybrid film has a structure of reinforced concrete, thus exhibits good flexibility and mechanical properties. The carbon film with the size of 1 cm×4.5 cm×0.13 mm and glassfiber/carbon nanoparticle mass ratio of 0.6, has a max tensile stress of 4.9 MPa. The electrical resistance of the carbon film keeps nearly unchanged after 10000 bends at a max bending angle of 90°, indicating its excellent flexibility.

Without the limit of rigid substrates, the double-side evaporation enables higher water flow rate through the film. The freestanding carbon film thus has higher electrical power output than the carbon films reported before. A device with the size of 1 cm×4.5 cm×0.13 mm generates an open-circuit voltage of ~1 V and current of ~0.86 μ A under ambient condition. The hybrid carbon film can also be easily scaled-up. We demonstrated a carbon film with the maximum width of 40 cm, which has an output current of ~28 μ A. Furthermore, the excellent flexibility allows the film to be rolled up to save space, even with a high power output.

To demonstrate the application of carbon film, we successfully degraded methylene blue (MB) by using our device as power source. Given the simple fabrication, robust mechanical property, high electricity output, such a freestanding and flexible carbon-based hybrid film shows great potential in environmental energies harvesting for green and sustainable development.

evaporation, capillary flow, energy harvesting, flexible, hybrid-carbon film

doi: 10.1360/N972018-00675