β-环糊精改性聚氨酯基摩擦纳米发电机的湿度阻抗研究

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摘要：目的 通过 β-环糊精（β-CD）在聚氨酯膜表面进行分子自组装来增加聚氨酯表面的羟基数量，进而增强改性聚氨酯分子在高湿度环境下的电输出性能。**方法** 采用分子自主组装的方法获得改性聚氨酯膜。聚氨酯颗粒在 N，N-二甲基甲酰胺中溶解并通过流延法成膜后，先后在 γ-缩水甘油醚氧丙基三甲氧基硅烷/甲醇溶液和氨基环糊精溶液中浸泡、干燥，得到 β-CD 功能面。以改性的聚氨酯为摩擦纳米发电机（TENG）的电正性摩擦层，以聚四氟乙烯（PTFE）为电负性摩擦层，组装得到风驱动摩擦纳米发电机。**结果** β-环糊精的改性增加了聚氨酯膜表面的羟基数量，使聚氨酯膜在高湿度环境中可以与水分子形成氢键，固定水分子一同参与摩擦起电，增加了聚氨酯基摩擦纳米发电机在高湿度环境中的电输出性能。当湿度从 15%增加到 95%后，改性聚氨酯基摩擦纳米发电机的短路电流增加了 432%，且湿度越大，电输出越大。同时，改性聚氨酯基摩擦纳米发电机在喷洒水滴的情况下，也能点亮 248 个 LED 灯。**结论** β-环糊精的改性可以显著提升聚氨酯基摩擦纳米发电机在高湿度环境下的电输出性能，且电输出随湿度的增加而增加，显示了出色的耐湿性，对扩展聚氨酯基摩擦纳米发电机的应用具有重要意义，尤其是在高湿度环境下。

关键词：β-环糊精；分子自组装；摩擦纳米发电机；耐湿性；氢键

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Enhanced Humidity Resistance of Polyurethane-based Triboelectric Nanogenerator by Molecular Self-assembly of β-cyclodextrin

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ABSTRACT: Since the invention of the first triboelectric nanogenerator (TENG), more and more attention has been focused on this energy harvesting device due to its wide range of energy sources, low cost, and high reliability. There are many factors that affect the output performance of triboelectric nanogenerators, including the surface structure and composition of the friction pair

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material, frictional motion conditions, environmental factors, structure of the device and composition of the circuit. Especially for solid-solid triboelectric nanogenerators, ambient humidity has a significant impact on their output performance, which not only affects the energy harvesting efficiency and working reliability of triboelectric nanogenerators, but also greatly reduces their practical application range, especially in high humidity areas. Typically, ambient humidity accelerates the transfer, neutralization or dissipation of triboelectric charges on the friction surface, resulting in lower output of triboelectric nanogenerators. On the one hand, in a high-humidity environment, water molecules in the air are adsorbed on the surface of the friction pair to form a conductive water film, which can increase the conductivity of the friction interface and enable rapid transfer or neutralization of triboelectric charges. On the other hand, water molecules in the air accelerate the dissipation of charges on the friction surface during the migration process. Therefore, in previous reports, the output performance of solid-solid triboelectric nanogenerators generally decreases with increasing humidity, which greatly limits its practical application for energy harvesting in high-humidity environments. To solve this problem, β-cyclodextrin (β-CD) was introduced on the surface of thermoplastic polyurethane (TPU) film by molecular self-assembly to increase the number of hydroxyl groups to enhance the contact electrification (CE) performance of modified polyurethane molecules in a high-humidity environment. β-Cyclodextrin was a hydroxyl-rich bio-based macromolecule, which could spontaneously form hydrogen bonds with water molecules in the environment under high humidity, thereby immobilizing the water molecules on the surface of modified polyurethane. The bound water fixed on the surface of the polyurethane participated in triboelectric charging with the polyurethane as a whole. Since water was very triboelectrically positive, and polyurethane was also a triboelectrically positive material, the triboelectrically positive superposition effect of the two ultimately led to an increase in the electrical output of the modified polyurethane-based TENG. In addition, the surface of the modified polyurethane film was patterned, which not only greatly increased the contact area between polyurethane and PTFE during triboelectric electrification, but also improved the separation speed of the two, which further improved the electrical output performance. When the humidity increased from 15% to 95%, the short-circuit current of the TPU-based TENG increased by 432%. The electrical output of the modified TPU-based TENG was increased by 409% compared with the pure TPU-based TENG in a high-humidity environment. This TENG could light up 248 LEDs in the state of continuous spraying of water droplets, showing excellent moisture resistance. Besides moisture resistance, the improved electrical output of the modified TPU-based TENG also benefited from the introduction of β-cyclodextrin to increase the dielectric properties of the TPU film, which enabled more positive charges and storage in the triboelectric process. Due to the high performance of the modified TPU-based TENG under high humidity, this smart self-powered system can efficiently harvest wind energy in the marine environment and store energy by converting wind energy to power small electronic devices.

KEY WORDS: β-cyclodextrin; molecular self-assembly; triboelectric nanogenerator; humidity resistance; hydrogen bonding

随着非可再生能源的消耗和便携式电子设备数量的急剧增加，开发与能量存储相关的技术至关重要[1]。自 2012 年第一台摩擦纳米发电机（TENG）诞生以来，由于其能量来源广泛[2]、成本低廉[3]、可靠性强[4]，越来越多的注意力集中在这种能量收集装置上。然而，高湿度环境中的水分子严重影响了 TENG 的应用。一般而言，影响 TENG 电输出的因素包括材料的介电性和摩擦电极性[5-7]、表面的结构[8-10]、材料的厚度[11-13]、环境的温度[14-16]、湿度[17-22]和气氛[23-24]等。就环境湿度而言，环境中的水分子附着在摩擦层的表面，导致聚合物之间的摩擦起电量降低[25-26]；同时，水分子的迁移会携带摩擦层表面的电荷进入环境中，导致聚合物表面电荷的耗散加剧。

为了改善摩擦纳米发电机在高湿度环境中的电输出性能，研究者们已经采用了几种方法，包括密封摩擦纳米发电机来隔离水分子、使用疏水或超疏水材料来减少水分子在摩擦表面上的吸附、使用疏松结构来增加材料的渗透性[27-29]。然而，这些将摩擦纳米发电机进行封装或疏水化摩擦电极的方法麻烦且复杂，对某些材料和大规模应用而言不容易实现，并且这些方法不能完全改变湿度对摩擦纳米发电机性能的降低趋势。因此，从材料设计的角度出发，从根本上改善摩擦界面的耐湿性，设计出在高湿度下具有高输出性能的新型摩擦纳米发电机，是迫切的挑战，可以提升摩擦纳米发电机的适应性。

在本文中，制备了一种新型的改性聚氨酯基摩擦纳米发电机。聚氨酯的表面通过 β-环糊精进行改性，增加羟基的数量，使其可以与水分子形成氢键从而固定自由水，使水分子作为电正性更强的材料参与摩擦带电，以获得更高的输出。与未改性的聚氨酯基摩擦纳米发电机不同，改性的聚氨酯基摩擦纳米发电机的电输出随环境湿度的增加而增加。实验结果显示，当

湿度从 15%增加到 95%后，改性聚氨酯基摩擦纳米发电机的短路电流增加了 432%，并且湿度越大，电输出越大。同时，改性聚氨酯基风驱动摩擦纳米发电机在喷洒水滴的情况下，也能点亮 248 个 LED 灯。基于其出色的耐湿性，聚氨酯基摩擦纳米发电机在高湿度环境中具有巨大的应用潜力，例如雨天、雾天、海洋环境等。

1　实验部分

1.1　材料与试剂

热塑性聚氨酯弹性体（TPU，粒径 1 mm，分子量 50 000）购买自东莞市乐睿塑料有限公司，γ-缩水甘油醚氧丙基三甲氧基硅烷（KH-560 硅烷偶联剂）购买自阿拉丁试剂公司，聚四氟乙烯膜（PTFE，0.05 mm）购买自镇江弘科橡塑有限公司，氨基-β-环糊精和 N，N-二甲基甲酰胺购买自国药试剂公司。铜胶带、铜导线和绿色 LED 灯购买自当地的超市。

1.2　实验过程

1.2.1　表面图案化的聚氨酯弹性体薄膜的制备

5 g 聚氨酯弹性体颗粒与 25 gN，N-二甲基甲酰胺混合后搅拌 2 h，使聚氨酯溶解。随后，将混合后的胶液倒入硅基底的模具上（改性模具具有激光刻蚀的反向锥形结构）。然后，将模具置于 40 ℃的烘箱中干燥 4 h，将聚氨酯的膜从硅基底揭下，裁剪成“4 cm×4 cm”的尺寸，备用。

1.2.2　β-环糊精改性的聚氨酯弹性体的制备

聚氨酯薄膜在 KH560/甲醇（1 wt%）溶液中浸泡 3 h。在 80 ℃风箱中干燥 2 h 后，将环氧基团接枝到表面。聚氨酯膜在氨基环糊精的 10 mg/ml 二氯甲烷溶液中 80 ℃浸泡 24 h，用无水乙醇洗涤 3 次，氮气流干燥得到 β-环糊精功能面。

1.2.3　表征

使用 SR570 低噪声电流放大器（Stanford Research System, America）收集摩擦过程中的接地电流信号，滤波频率为 10 Hz。数据通过数据采集卡（DAQ）以及 LabVIEW 软件获得。使用 JEOL JSM-6710F 场发射扫描电子显微镜（FE-SEM）表征聚氨酯膜的表面形态。介电常数利用日本 AET 高频介电常数测试仪进行测试，聚氨酯膜样品的厚度为 0.1 mm，面积为“4 cm×4 cm”的正方形。X 射线光电子能谱（XPS）用 Kratos 轴超仪器记录，该仪器采用单色 Al Kα 源（1 486.69 eV），半球形分析仪采用混合（静电和磁）透镜系统，用丝产生的磁通道低能电子进行电荷中和，延迟线探测器（DLD）。

2　结果与讨论

2.1　聚氨酯基风驱动摩擦纳米发电机的组装

图 1 是聚氨酯基风驱动摩擦纳米发电机（TENG）的制备及结构示意图。该 TENG 将聚四氟乙烯（PTFE）

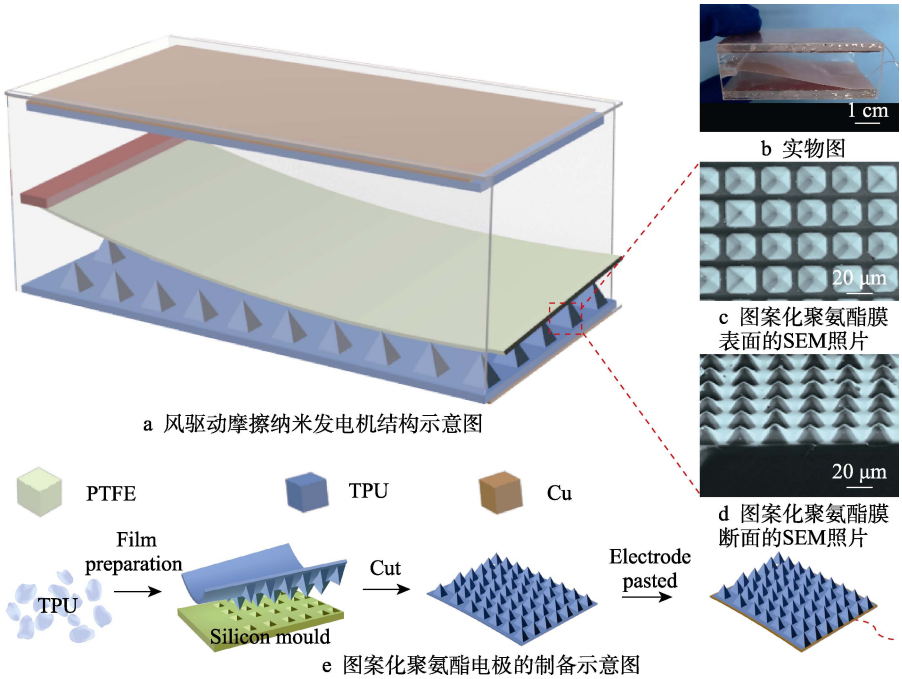


图 1　风驱动聚氨酯摩擦纳米发电机的组装与结构

Fig.1 Assembly and structure of polyurethane wind-driven triboelectric nanogenerator: a) Schematic diagram of wind-driven triboelectric nanogenerator structure; b) physical drawings; c) SEM photo of the patterned polyurethane membrane surface; d) SEM photo of the patterned polyurethane membrane section; e) Schematic diagram of the preparation of patterned polyurethane based electrode

作为电负性摩擦层，将热塑性聚氨酯弹性体（TPU）作为电正性摩擦层。整个风驱动摩擦纳米发电机用亚克力板作为支撑，其结构图和实物图分别见图 1a 和 1b。特别地，为了增加摩擦层之间的接触面积并加快分离速率，聚氨酯的表面进行了图案化处理，如图 1c 和 1d 所示。聚氨酯图案化的过程为：5 g 聚氨酯弹性体颗粒与 25 gN，N-二甲基甲酰胺混合后搅拌 2 h，使聚氨酯溶解。随后，将胶液倒入硅基底的模具上，于 40 ℃的烘箱中干燥 4 h，揭膜并裁剪成“4 cm× 4 cm”的尺寸（图 1e）。

2.2　β-环糊精对图案化的聚氨酯弹性体表面的改性

聚氨酯作为具有高介电常数和良好的摩擦起电性的高分子聚合物，常被用作摩擦纳米发电机的电正性摩擦层。然而，由于其在高湿度环境下的电输出极低，严重影响了聚氨酯基摩擦纳米发电机的应用。为了提高聚氨酯基摩擦纳米发电机在高湿度环境下的电输出，对聚氨酯的表面进行了亲水化处理，如图 2a 所示，聚氨酯薄膜在 KH560/甲醇（1 wt.%）溶液中浸泡 3 h。在 80 ℃风箱中干燥 2 h 后，将环氧基团接枝到表面。聚氨酯膜在氨基环糊精的 10 mg/ml 二氯甲烷溶液中 80 ℃浸泡 24 h，用无水乙醇洗涤 3 次，氮气流干燥得到 β-环糊精功能面。未改性的聚氨酯膜的 XPS 测试结果如图 2b 所示，样品在 532 eV、399 eV 和 285 eV 处分别出现了 O 元素、N 元素和 C 元素的吸收峰。然而，经过 β-环糊精修饰的聚氨酯样品在 102 eV 处出现了 Si 元素的吸收峰，说明 KH560 已经被成功修饰到表面上；同时，经过修饰后的聚氨酯膜的接触角从 63°降低到 32°，说明羟基被成功引入了聚氨酯的表面，即 β-环糊精在第 2 步反应中被成功修饰到了聚氨酯的表面。

2.3　改性聚氨酯基摩擦纳米发电机的电输出性能

图 3 为基于 PTFE 的柔性 TENG 器件的工作示意图。最初，当 PTFE 薄膜向上移动并与顶部的改性聚氨酯薄膜接触时，改性聚氨酯中的电子由于电负性的差异转移到 PTFE 中，导致聚氨酯表面带正电荷，而 PTFE 表面带负电荷。当 PTFE 中间摩擦层随风下移时，PTFE 与顶部铜电极之间的电位差可将负摩擦电荷从 PTFE 驱动到铜电极表面。一旦 PTFE 薄膜向下

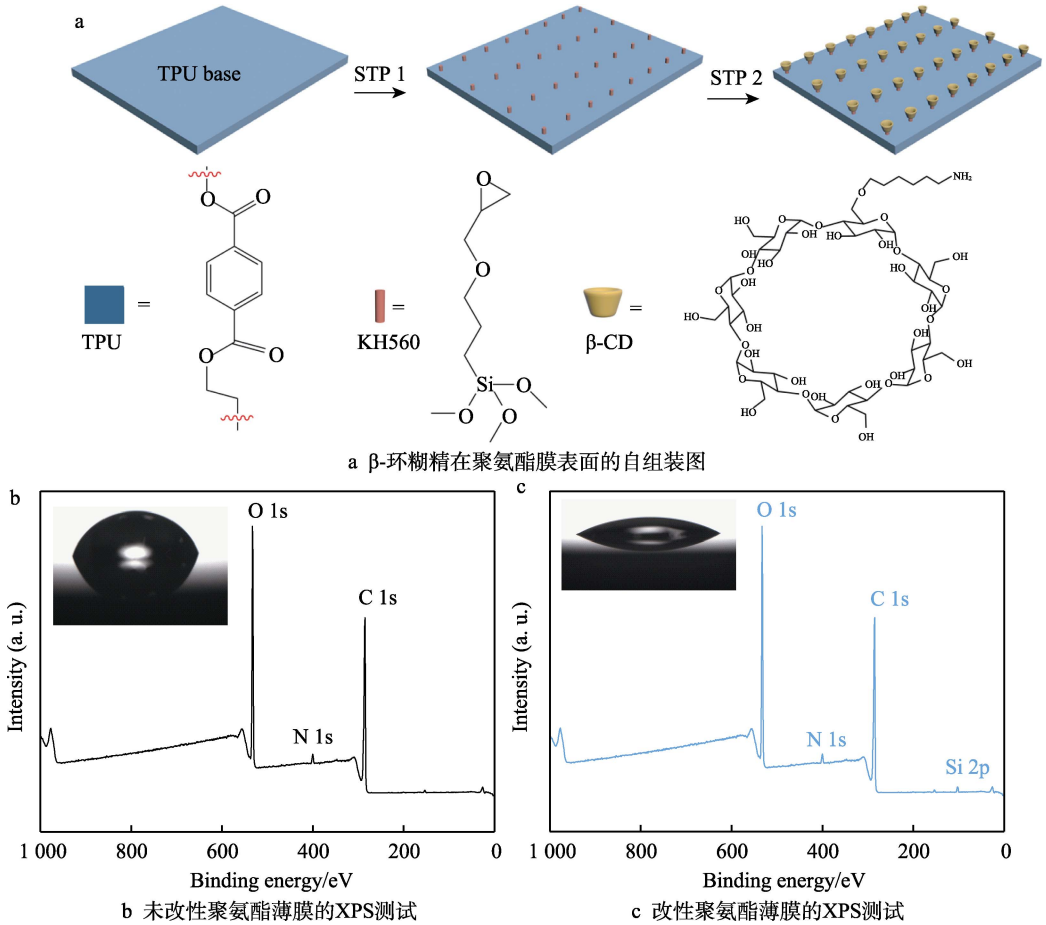


图 2　改性聚氨酯膜的制备与表征

Fig.2 Preparation and characterization of modified polyurethane membrane: a) self-assembly diagram of β-cyclodextrin on the surface of polyurethane membrane; b) XPS test of unmodified polyurethane film; c) XPS test of the modified polyurethane film

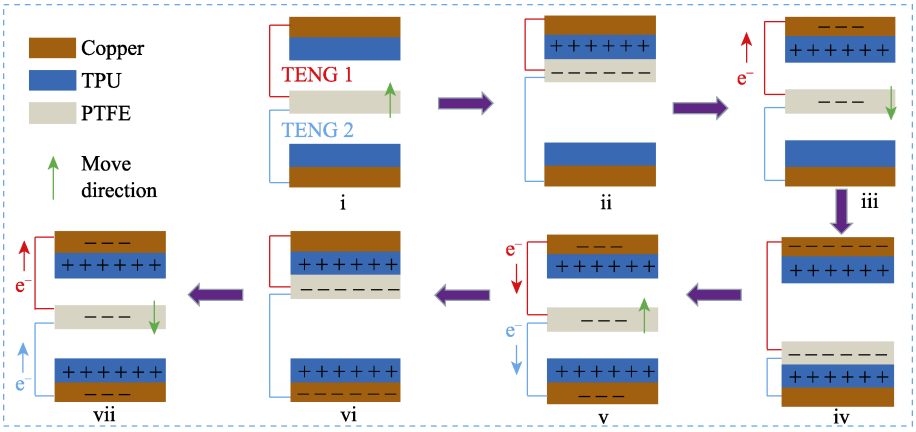


图 3　改性聚氨酯基风驱动 TENG 的工作机理示意图

Fig.3 Schematic diagram of working mechanism of modified polyurethane based wind-driven TENG

移动并与底部的改性聚氨酯薄膜接触，由于静电感应效应，聚四氟乙烯和改性聚氨酯表面产生了等量的正负摩擦电荷。同时，在静电感应作用下，聚氨酯表面和 TENG 顶部的铜表面也分别带着等量的正电荷和负电荷。同样，当 PTFE 中间摩擦层向上移动时，负摩擦电荷从 PTFE 转移到 TENG 底部的铜电极表面，使 PTFE 与顶部铜表面之间产生电位差，将负摩擦电荷从顶部铜表面驱动到 PTFE。同样，当聚四氟乙烯薄膜向上移动与顶部的改性聚氨酯接触时，来自顶部铜电极的负摩擦电荷全部转移。同样，聚四氟乙烯表面和顶部的聚乙烯醇表面会分别产生等量的负电荷和正电荷。同时，聚氨酯和铜电极底部表面也分别产生相等的正电荷和负电荷。当聚四氟乙烯中间摩擦层因风致振荡而向下移动时，聚四氟乙烯与顶部铜电极之间的电位差将负摩擦电荷从聚四氟乙烯转移到铜电极表面。负电荷转移过程可能会在 PTFE 和底部铜电极之间产生电位差，从而将负摩擦电荷从底部铜电极表面驱动到 PTFE。最后，TENG 器件的运动状态和电荷分布恢复到如图 3b 中Ⅳ所示的状态。此时，TENG 装置将按照图 3b 中Ⅳ到Ⅶ的运动方式进行摩擦产电过程，并以此循环往复进行。

将制备好的改性聚氨酯与聚四氟乙烯组装成摩擦纳米发电机，并对其电性能进行测试。由于风驱动摩擦纳米发电机的模型难以在控湿的密闭箱中进行测试，所以将其分解处理，将马达驱动摩擦纳米发电机的 2 个电极进行撞击，并在透明密闭箱中将湿度控制为 15% RH、35% RH、55% RH、75% RH 和 95% RH 以测试其不同湿度下的电性能。结果显示，未改性的聚氨酯基摩擦纳米发电机的短路电流随湿度的增加而降低（图 4a）。当湿度从 15%增加到 95%时，电流从 2.0 μA 降低至 0.2 μA，降低了 90%。同样地，电压输出随湿度的变化也显示出了相同的趋势（图 4b）。然而，对改性聚氨酯基摩擦纳米发电机而言，短路电流随湿度的增加而增加（图 4c）。当湿度从 15%增加到 95%时，电流从 3.7 μA 增加到 16.1 μA，增加了 335%，并且输出电压也出现了相同的变化趋势（图 4d），说明 β-环糊精的引入增加了聚氨酯表面的羟基数量，使改性聚氨酯表面的羟基可以与环境中的水分子之间形成氢键，使水分子与改性聚氨酯一同参与摩擦起电。由于水分子是一种电正性极大的化合物，所以两者的叠加效应整体上增大了聚氨酯基摩擦纳米发电机的电输出。

2.4　改性聚氨酯基摩擦纳米发电机的耐湿机理

一般来说，摩擦副的摩擦起电状态受到许多因素的制约，包括摩擦副的化学成分和结构、摩擦运动条件、摩擦纳米发电机的装置设计、环境温度、湿度等因素。在上述基于改性和未改性的聚氨酯基摩擦纳米发电机的对比实验中，严格控制了这 2 组摩擦纳米发电机的组装时条件、摩擦运动条件、材料表面的光滑度、测试温度及其他因素一致，而只是改变环境湿度。因此，在测试系统中，摩擦起电性能的变化主要是由环境湿度的变化引起的。一般情况下，环境中的水分子参与抑制材料表面的摩擦和带电，从而加速表面电荷向环境的累积耗散。而对基于改性的聚氨酯基摩擦纳米发电机而言，实验结果显示出相反的趋势，其摩擦带电性能随环境湿度的增加而增加，这表明存在其他的机制，例如改性聚氨酯的表面引入新的官能团改变了其表面的极性，导致这一趋势发生。

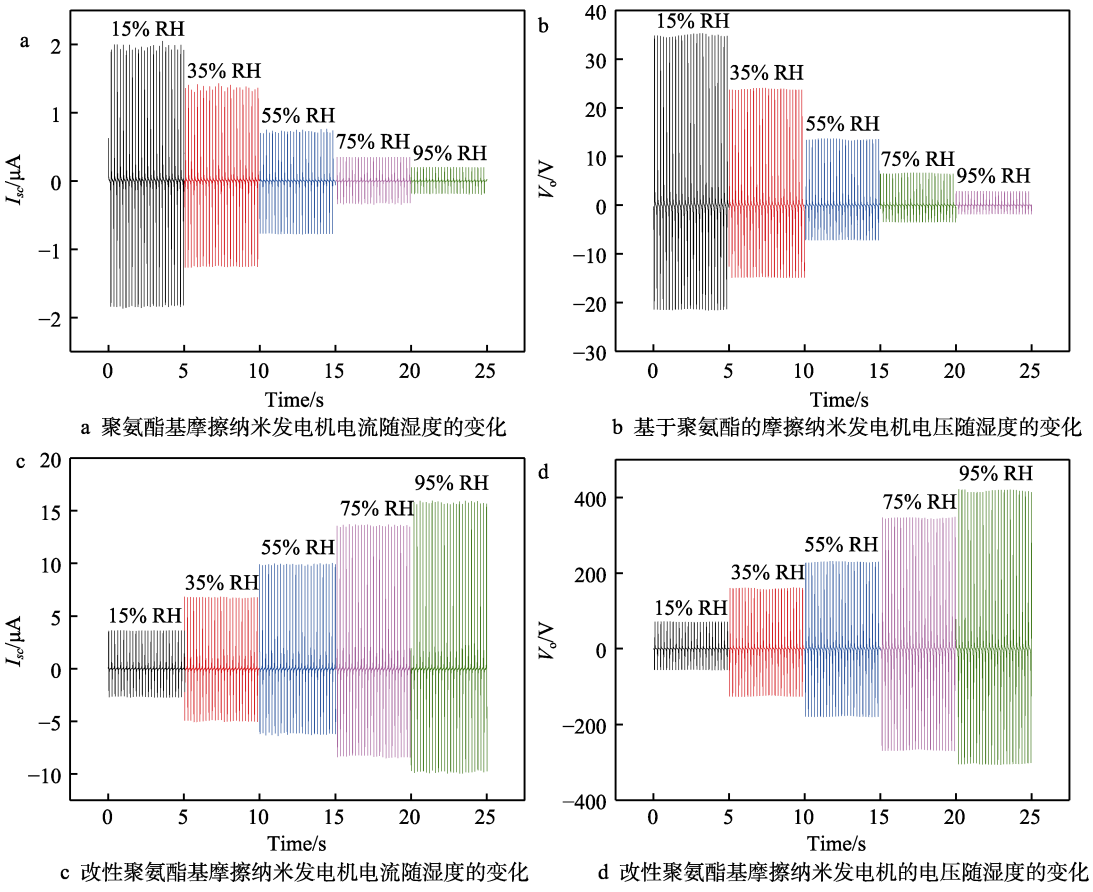
为了确定这一过程的机理，我们对改性聚氨酯进行了红外光谱测试以检测在这一过程中的化学成分的变化，如图 5a 所示。在红外光谱中，从 3 300 cm^{-1} 到 3 500 cm^{-1} 得到了—OH 的伸缩振动吸收峰。随着湿度的增加，—OH 的吸收峰向低波移动（红移）。此外，湿度越高，红移的波数越大，说明形成的氢键越多。此外，为了进一步证明在不同湿度下输出电流的变化是由不同数量的氢键引起的，测试了在 95%湿度下吸湿不同时间的改性聚氨酯膜的红外光谱和对应的摩擦纳米发电机的电输出，如图 5b 和 5c 所示。

与完全干燥的不吸水的聚氨酯膜相比，吸水 1 h 的聚氨酯膜的羟基吸收峰从 3 304.1 cm^{-1} 转移到 3 284.4 cm^{-1}。与之相对应，改性聚氨酯基摩擦纳米发电机的电流从 3.4 μA 快速大幅增加到 8.4 μA。随着吸水时间的持续增加，从 1 h 到 5 h，羟基吸收峰的波数移动到 3 261.4 cm^{-1}，说明聚氨酯膜吸水时间越长，羟基与水分子之间形成的氢键越多。当吸水时间从 1 h 增加到 5 h 时，电流从 8.4 μA 增加到 16.2 μA。因此，改性聚氨酯基摩擦纳米发电机的电输出随湿度的增加而增加的机理与氢键的形成有关，即在高湿度环境下，改性聚氨酯中的羟基（来自 β-环糊精）自发地与空气中的水分子形成氢键，将自由水转变为结合水固定在摩擦层的表面。此外，聚氨酯膜的摩擦电极性位于摩擦电极性序列中相对电正性的位置，即在摩擦起电过程中会带正电荷。而水是一种摩擦电正性极强的材料，固定在摩擦层表面的结合水在摩擦起电过程中会携带大量的正电荷，使富含羟基的摩擦层的电正性进一步增加，并且环境中的水分子越多（湿度越大），被羟基分子固定的水分子越多，摩擦起电过程中产生的正电荷就越多，改性聚氨酯基 TENG 的电输出也就越大。

随后，测试了空白聚氨酯膜和改性聚氨酯膜的介电性，如图 5d 和 5e 所示。在 1 000 HZ 的频率下，改性聚氨酯膜的介电常数从 4.45 增加到 5.42，说明 β-环糊精的修饰明显增加了聚氨酯膜的介电性，使其摩擦产电的能力增加，进一步增加了改性聚氨酯基摩擦纳米发电机的电性能。

2.5　改性聚氨酯基摩擦纳米发电机的应用

由于改性聚氨酯基风驱动摩擦纳米发电机具有出色的耐湿性能，可以作为摩擦电能量收集器在高湿度环境中为小型电子设备供电。图 6a 显示了在喷水的情况下，风驱动摩擦纳米发电机进行能量收集的示意图。实验结果显示，随着水滴的不断洒入，聚氨酯表面固定水分子参与摩擦起电，电流值不断增加。在 470 s 内，电流从 3.8 μA 增加到 7.3 μA（图 6b），显示了风驱动改性聚氨酯基摩擦纳米发电机出色的耐湿性。测试开始和结束时的电流峰形和数值如图 6c

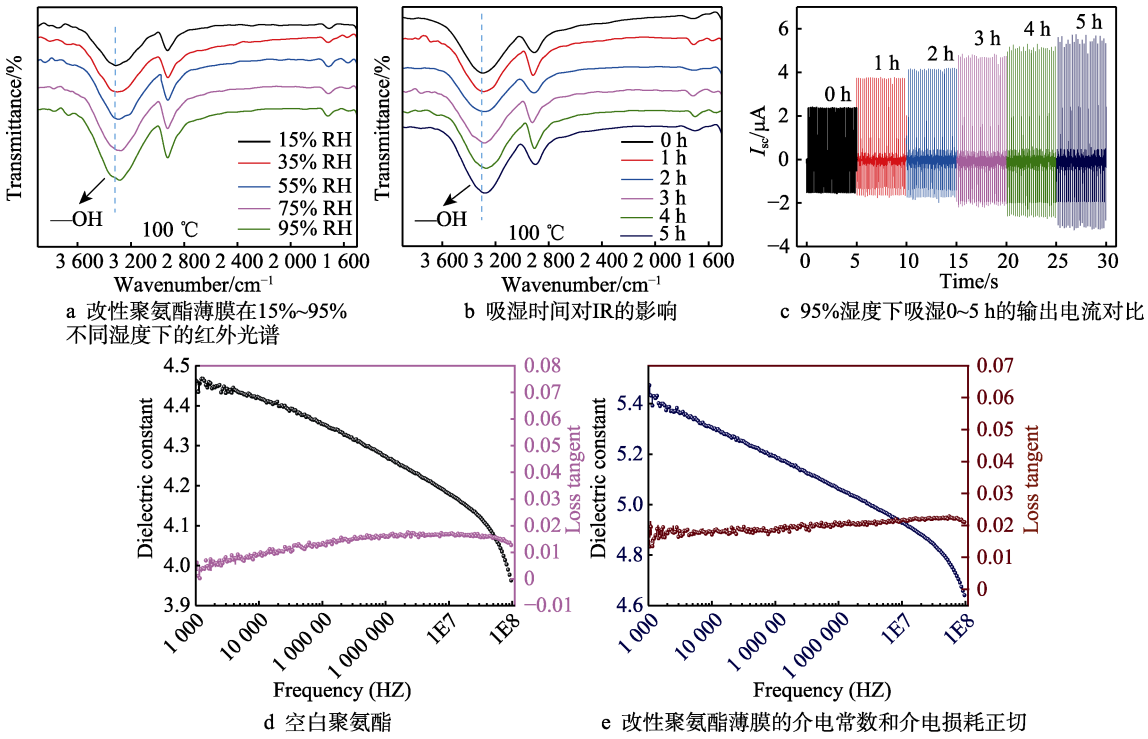


a 聚氨酯基摩擦纳米发电机电流随湿度的变化　　b 基于聚氨酯的摩擦纳米发电机电压随湿度的变化

c 改性聚氨酯基摩擦纳米发电机电流随湿度的变化　　d 改性聚氨酯基摩擦纳米发电机的电压随湿度的变化

图 4　聚氨酯基摩擦纳米发电机和改性聚氨酯基摩擦纳米发电机在不同湿度下的电输出比较

Fig.4 Comparison of the electrical output of polyurethane based triboelectric nanogenerators and modified polyurethane based triboelectric nanogenerators at different humidity: a) variation of current of polyurethane based triboelectric nanogenerator with humidity; b) variation of the voltage of the triboelectric nanogenerator based on polyurethane with humidity; c) variation of the current of the modified polyurethane based triboelectric nanogenerator with humidity; d) variation of voltage of modified polyurethane based triboelectric nanogenerator with humidity

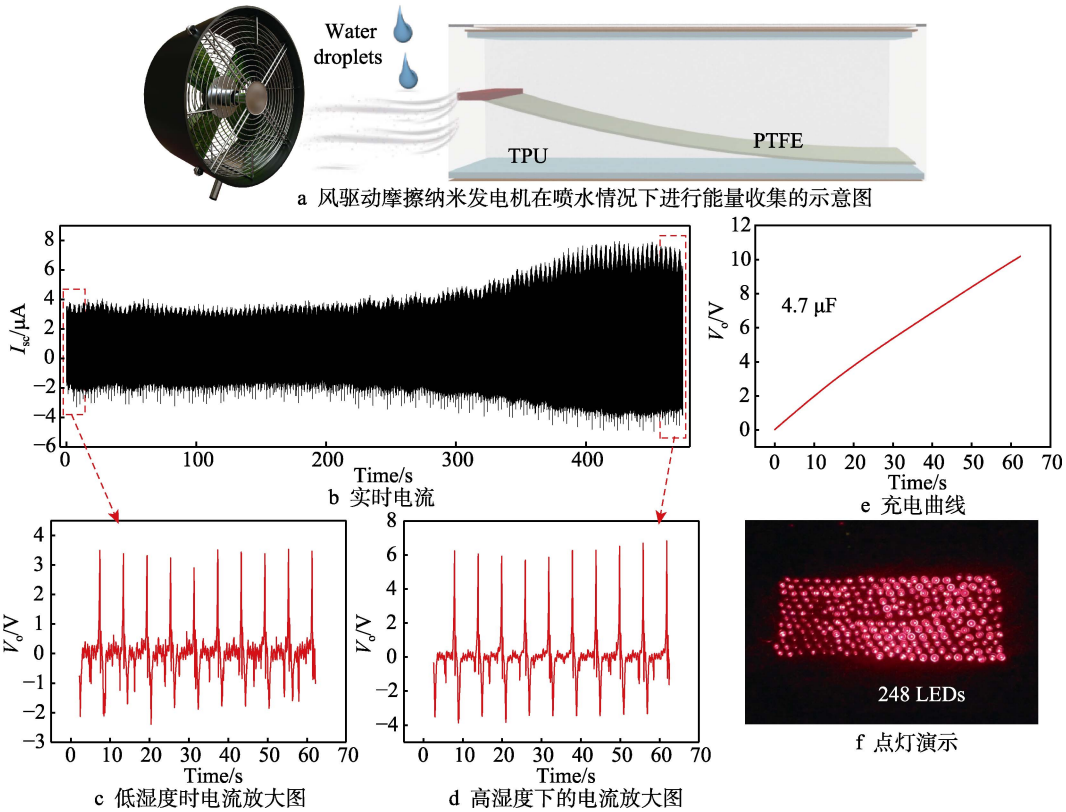


a 改性聚氨酯薄膜在15%~95%不同湿度下的红外光谱　b 吸湿时间对IR的影响　c 95%湿度下吸湿0~5 h的输出电流对比

d 空白聚氨酯　e 改性聚氨酯薄膜的介电常数和介电损耗正切

图 5　改性聚氨酯基摩擦纳米发电机的耐湿机理

Fig.5 Humidity resistance mechanism of modified polyurethane based triboelectric nanogenerator: a) IR spectrums of PVA membranes under varying humidity from 15% to 95%; b) effect of moisture absorption time on IR; c) output current comparison of moisture absorption for 0~5 hours under 95% humidity; d) dielectric constant and dielectric loss tangent of blank polyurethane; e) modified polyurethane membrane



a 风驱动摩擦纳米发电机在喷水情况下进行能量收集的示意图

b 实时电流　e 充电曲线

c 低湿度时电流放大图　d 高湿度下的电流放大图　f 点灯演示

图 6　改性聚氨酯基摩擦纳米发电机的应用

Fig.6 Application of modified polyurethane based triboelectric nanogenerator: a) schematic diagram of wind-driven triboelectric nanogenerator for energy collection in the case of water spraying; b) real-time current; c) enlarged view of current at low humidity; d) enlarged view of current at high humidity; e) charging curve; f) lighting experiments

和 6d 所示，在整个过程中，电流的峰形没有发生反转，说明增强电流值的原因是水分子参与了摩擦起电，而不是聚氨酯本身电性能的变化。在这个过程的第 400 s 时，对 4.7 μF 的电容充电，发现在 60 s 内可以充至 10 V 电压（图 6e），并可以同时点亮 248 个 LED 灯（图 6f）。

3 结论

本文通过在聚氨酯表面进行分子自组装 β-环糊精，得到了具有丰富的表面羟基且亲水的功能面。该改性聚氨酯作为摩擦纳米发电机的电正性摩擦层时，可以与环境中的水分子之间形成氢键，从而使水分子与改性聚氨酯一同参与摩擦起电，增加了摩擦纳米发电机在高湿度环境中的电输出性能。与未改性的聚氨酯基 TENG 相比，β-环糊精改性的聚氨酯基 TENG 在 95%湿度下的电输出增加了 432%。此外，由于 β-环糊精的引入，聚氨酯膜的介电常数增加了 22%，提高了摩擦层捕获电荷的能力，进一步提高了 TENG 在高湿度下的电输出。本文所述的改性策略适用于所有的电正性聚合物，对拓展摩擦纳米发电机的应用范围具有重要意义，尤其是在高湿度环境中。

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