Conducting Nano-Wires Prepared from Nylon Electrospun Fibres Modified with Polyaniline

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Abstract: Electrospun fibres have a high surface area and mechanical strength compared to conventional extruded or cast films. This has led to application in ultra-thin fabric materials and filtration matrices amongst other applications. The following describes the fabrication of conducting nanofibers prepared from nylon and polyaniline that can find potential utility in sensor and novel filtration materials. The base fibres were prepared using a polymer melt consisting of 22% w/w nylon-6 dissolved in 88% formic acid. The polymer melt was pasted through a spinnert that was polarized at 18 KV with the resultant fibre being captured on an aluminium collector plate. Polyaniline was deposited on the surface of electrospun fibres by diffusion from 0.3 mol/L to 0.6mol/L aniline solution containing 0.35 mol/L HCl and polymeriztion in corresponding molar ratio ammonium persulphate with 0.35 mol/L HCl. Confirmation that the polyaniline had been deposited on the fibre surface was performed using Fourier transform infrared spectroscopy and Scanning Electron Microscopy. The conducting fibres had a diameter of approximately 151.80±57.69 nm with an even coverage of the polyaniline layer. The modified fibres were further characterized using electrochemical impedance spectroscopy that confirm the fibres were conductive although did have a relatively high resistance (94 kohm). The conducting polymer nanofibers have potential to use as the basis for a reagentless immunoassay for biohazard detection.

Keywords: Electrospin, Nylon6, Polyaniline

以电纺尼龙 6 纳米纤维为载体的聚苯胺复合膜的制备与结构表征

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摘　要： 电纺 22%的尼龙 6 甲酸溶液制备出平均直径为 151.80±57.69nm 的纳米纤维，在不同苯胺浓度和反应时间下将聚苯胺和尼龙纤维聚合，傅立叶红外光谱（FTIR）表明，聚苯胺均能与尼龙 6 纤维结合形成高聚物；电化学阻抗谱（EIS）表明 0.4M 苯胺反应 90min 得到的聚苯胺/尼龙 6 高聚物的电阻最小；电镜（SEM）图像显示导电性良好的聚苯胺/尼龙 6 聚合物，聚苯胺覆盖于尼龙 6 纤维表面，尼龙 6 的纤维结构不明显。

关键词： 电纺，尼龙 6，聚苯胺

1 引言

聚苯胺(PANI)单体便宜、易于氧化聚合，产率高，在温和条件下稳定性良好，被认为是很有希望在生物传感器中得到实际应用的生物材料[1−6]。但聚苯胺成型性较差，这限制了它的应用。对于聚苯胺成型性材料的研究目前主要集中在两个方面，一是研究其自支撑膜，就当前情况来看这种材料导电性较好但力学性能不理想，距实际应用尚有差距；另一方面就是近些年发展起来的聚苯胺复合材料。这类材料导电性虽比前

稍差，但其基体材料选择范围广，能满足各种不同需要，因此极具发展前景[7] 尼龙6是一种热塑性聚合物，机械性能良好而且其酰胺键和苯胺或聚苯胺的氨基和亚氨基易于形成氢键而提高其相互作用性[8]。关于以尼龙 6 作为基体材料制备导电聚苯胺的研究，目前已有尼龙 6 薄膜为载体的聚苯胺及掺杂聚合物的研究报道[9-15]，这种材料虽然电导率较高、机械强度往往受到限制；对以聚苯胺改性的电纺尼龙纤维的研究报道则非常有限[16、17]。电纺（electrospinning）是制备人造高分子纳米纤维的一种方法，通过电纺制备的纤维直径比一般纤维纺丝制备的纤维直径小[18、19]、比表面积大、机械强度高，目前已越来越广泛的应用于充电电池、电池干扰防护层、传感器及电致变色显示器等材质[20-23]。本论文以电纺尼龙 6 纳米纤维为基体材料制备导电聚苯胺复合材料、并对其结构进行表征，拟为其在生物传感器中的应用奠定基础。

2. 实验

2.1 化学试剂

试剂级苯胺（Aniline，An），蒸馏至无色，5°C 避光保存；尼龙 6 薄膜，甲酸（88%），过硫酸铵 $[(NH_4)_2S_2O_8]$，盐酸均为试剂级，购自 sigma-aldrich（美国）公司。

2.2 尼龙 6 纳米纤维的制备

电纺溶液的制备：将 22%的尼龙 6 薄膜溶于甲酸（w/w），搅拌 24 小时，用于电纺。

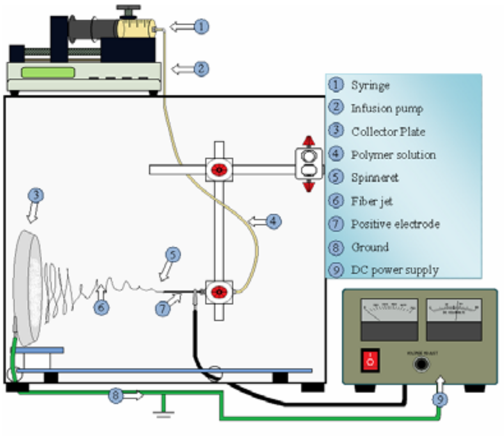

Figure 1. Diagram of the electrospinning system

图 1. 电纺装置图

电纺装置见图 1。规格为 20G × 1½"的不锈钢喷丝头连接直流电源装置（Model ES30P-30W, Gamma High Voltage Research, Ormond Beach, Fla., U.S.A.），电源电压为 18kV，喷丝头通过特氟纶管连接到吸取尼龙甲酸溶液的 30 mL 玻璃注射器，溶液通过输液泵输入喷丝头，输液泵的流速为 0. 1 mL/h，喷丝头到收集铝碟的距离为 15cm。

2.3 导电聚苯胺/尼龙 6 的制备

将尼龙6纳米纤维与一定量的苯胺盐酸溶液（0.35MHCl）40℃反应一段时间，弃去反应液，以苯胺与过硫酸铵为1：1的量加入过硫酸铵盐酸溶液（0.35M HCl）0℃聚合1小时，弃去聚合液，漂洗纤维至无色，室温干燥[13、14]。

2.4 聚苯胺/尼龙 6 的红外光谱分析(FTIR)

红外光谱分析采用IRPrestige-21 FTIR分光计(Shimadzu Corp., Kyoto, Japan)测定，衰减全反射附件(Pike Technologies, Madison, Wis., U.S.A.)。

2.4 聚苯胺/尼龙 6 的电化学阻抗（EIS）测定

采用阻抗分析仪(SI1260, Solartron, France)测定交流电（AC）阻抗谱，电位振幅为 10 mV，频率范围从 100kHz ~100mHz，四探针法测定聚合物电阻，测定时用 1M NaCl 盐溶液润湿样品。

2.5 聚苯胺/尼龙 6 的电镜结构

样品真空溅射喷金，放置于扫描电镜(Hitachi S-570, Tokyo, Japan)样品台上观察，拍照，加速电压为 10 kV，放大倍数为 30k。电纺纤维直径用 Image-ProPlus 6.1 software (Media Cybernetics, Bethesda, Md., U.S.A.)测定，每个电镜图像上取 100 个检测点。

3. 结果与讨论

3.1 聚苯胺/尼龙 6 的电镜结构

图2是电纺尼龙6的电镜结构图，用Image-ProPlus 6.1软件取20个点测量其直径，计算出其平均直径为151.80±57.69nm，说明电纺尼龙6属于纳米级纤维。

图3是不同反应条件下聚苯胺/尼龙6的电镜结构图。其中1-1、2-1、3-1、4-1分别为浓度为0.3M、0.4M、0.5M、0.6M的苯胺反应30min的聚合物图片，图片显示0.3M苯胺浓度形成的聚苯胺在尼龙纤维上的分布

项目来源：加拿大安省农业事务部(OMAFRA)（项目编号：FS080704 TF049376）

Figure 2. SEM images of 22%(w/w) nylon-6 in formic acid fibers electrospun at 18 kV

图 2. 电纺尼龙 6 的电镜结构图

较稀、但表面光滑；0.4M、0.5M 苯胺浓度形成的聚苯胺在尼龙纤维上附着的浓度依次增加；0.6M 苯胺浓度形成的聚苯胺在纤维上的分布也较稀、但纤维表面不光滑，聚苯胺颗粒不明显。1-2、2-2、3-2、4-2 分别为浓度为 0.3M、0.4M、0.5M、0.6M 的苯胺反应 60min 的聚合物图，图片显示 0.3M、0.4M、0.5M 苯胺浓度形成的聚苯胺均能较好的聚合在尼龙纤维表面、聚苯胺颗粒分布明显；0.6M 苯胺浓度形成的聚苯胺在纤维上的颗粒分布不明显，纤维表面不光滑、有碎片。1-3、2-3、3-3、4-3 分别为浓度为 0.3M、0.4M、0.5M、0.6M 的苯胺反应 90mi 的聚合物图，图片显示 0.3M 苯胺浓度形成的聚苯胺较好的聚合在尼龙纤维表面、颗粒分布明显；0.4M 苯胺浓度形成的聚苯胺均匀分布在尼龙纤维表面、纤维结构消失；0.5M 苯胺浓度形成的聚苯胺亦均匀分布在尼龙纤维表面、但尚有明显的纤维结构存在；0.6M 苯胺浓度形成的聚苯胺颗粒在纤维上有明显分布，但颗粒大小不均匀，分布也不均匀。Kyung Hwa Hong 认为，聚合体的纤维表面通常不仅有聚苯胺，还有未聚合的苯胺单体、单聚体及由被破坏的尼龙纤维产生的烷基构成[17]。因此 0.6M 苯胺浓度形成的聚苯胺/尼龙 6 聚合体的结构形成可能是由于苯胺单体浓度过高，较多未聚合的苯胺单体、单聚体及由被破坏的尼龙纤维产生的烷基均存在于纤维表面，导致聚苯胺含量较低。

3.2 聚苯胺/尼龙 6 的红外光谱分析

研究表明，聚苯胺一般在 832、1165、1308、1497 和 1587 cm^{-1} 左右出现较强的吸收峰[17, 24-26]，其中 1587 和 1497cm^{-1} 是聚苯胺中的 NBN（醌型）和 N-A-N（苯型）结构的伸缩振动吸收峰，1308、1165cm^{-1} 的吸收峰分别是苯环中 C-N 伸缩振动、C=N 伸缩振动的吸收峰，831cm^{-1} 处的吸收峰是由苯环中对位取代的 C-H 的弯曲振动峰。图 4 是聚苯胺/尼龙 6 的红外光谱图，图中样品均出现 5 个吸收峰，表明苯胺已经成功氧化成聚苯胺。其中 1-1、1-2、4-3 的吸收峰相对不明显，说明 1-1、1-2 的 0.3M 苯胺浓度、反应 30min、60min 及 4-3 的 0.6M 苯胺浓度、反应 90min 聚合效果不理想；前两者苯胺浓度偏低、后者苯胺浓度较高。2-3 的吸收峰不明显、3-3 的吸收峰朝低频区迁移则可能是和聚苯胺在尼龙纤维表面的分布特点及聚合过程中苯醌/氢醌的形成比例有关并可能影响其电化学行为

3.3 聚苯胺/尼龙 6 的阻抗分析

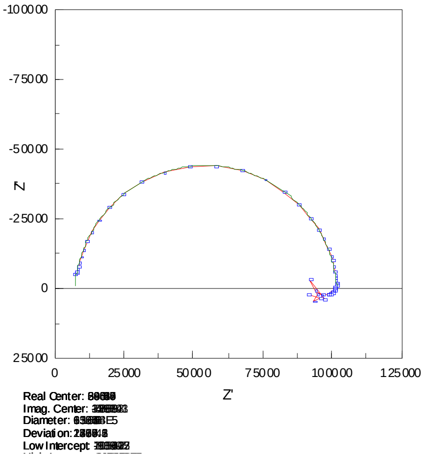

Figure 5. Nyquist diagrams of PANI/nylon-6 fabric

图5. PANI/NYLON6膜的Nyquist图

图5是样品2-3的聚苯胺/尼龙6膜在1M NaCl溶液中的阻抗图，阻抗曲线显示为一半圆弧，半圆直径代表膜层的阻抗，是由电子通过膜发生欧姆极化引起的，半圆的直径越小，说明膜的传荷电阻越小，即导电性能越好[27-28]。

图6是聚苯胺/尼龙6膜的阻抗随苯胺浓度与反应时间变化图。图6的结果表明0.3M、0.4M、0.5M苯胺的反应组阻抗随着反应时间的延长而降低，其中0.4M苯胺反应90min得到的聚苯胺/尼龙6膜阻抗值最小、为94829ohms，导电性相对最强；0.5M苯胺反应90min

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得到的聚苯胺/尼龙6膜阻抗值次之；0.6M苯胺反应组的阻抗随着反应时间变化不大，可能是由于0.6M的苯胺单体浓度过高，较多未聚合的苯胺单体、单聚体及由被破坏的尼龙纤维产生的烷基均存在于纤维表面，造成聚合体电阻升高、导电率下降。

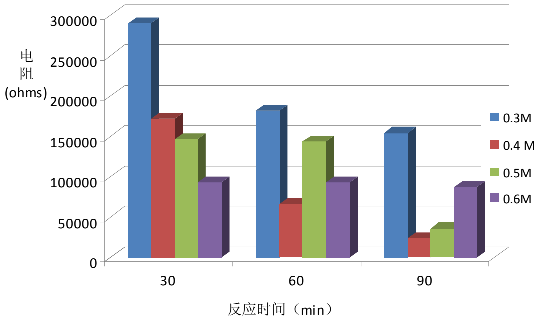


Figure 6. Effect of the diffusion time on the resistance of PANI/ nylon-6 composite electrospun fabrics with different aniline and $(NH_4)_2S_2O_8$ concentrations (diffusion temperature = 40 ℃, polymerization temperature = 0℃, polymerization time = 1 h, aniline/oxidant molar ratio = 1:1).

图6。反应时间对PANI/NYLON6复合电纺膜电阻的影响（反应温度= 40℃，聚合温度 = 0℃，聚合时间= 1 h，苯胺与氧化剂的摩尔质量比= 1:1）

4 小结

0.3M-0.6M苯胺均能与电纺尼龙6纳米纤维形成聚苯胺/尼龙6聚合体，其中0.4M苯胺反应90min得到的聚苯胺/尼龙6的聚合膜导电性最强，有应用于生物传感器的潜能。导电性强的纳米纤维膜聚苯胺均匀覆盖于膜的表面，纤维结构不明显或消失，红外结果显示该导电膜的聚苯胺的特征吸收峰强度减弱。

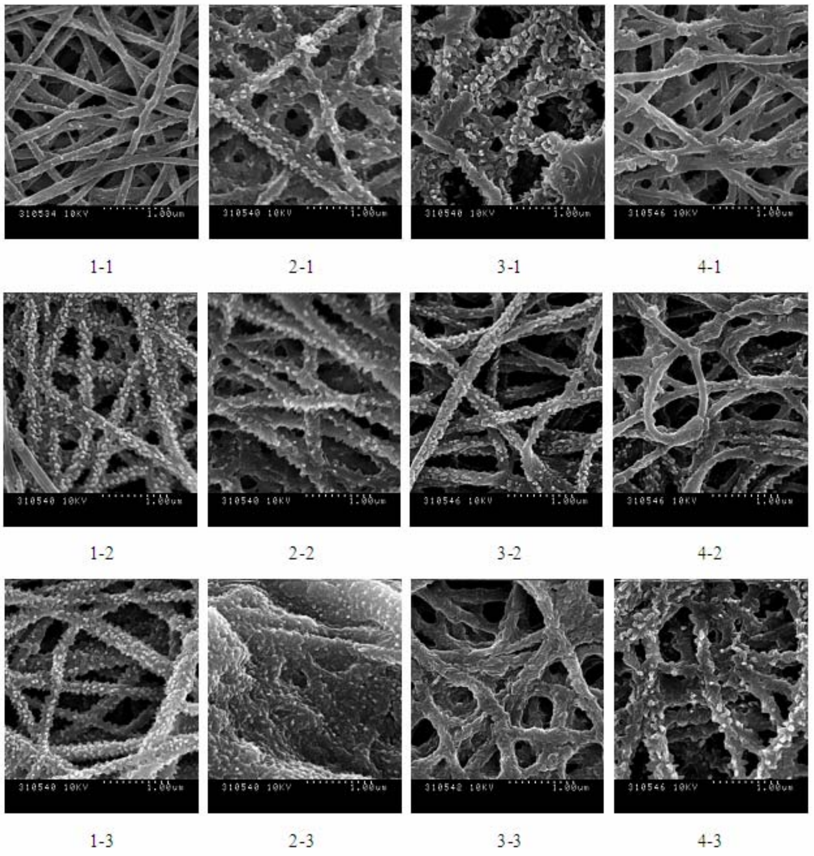
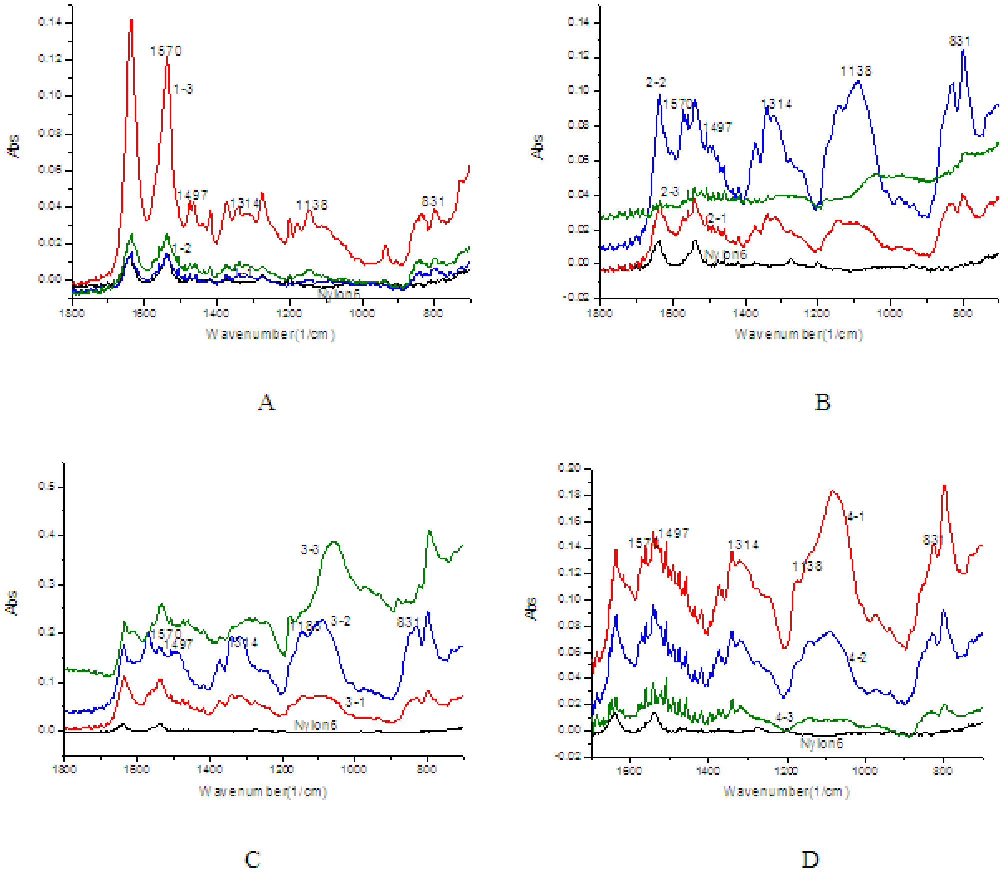

1-1 2-1 3-1 4-1
1-2 2-2 3-2 4-2
1-3 2-3 3-3 4-3

Figure 3. SEM images of PANI/nylon-6 composite fibrics. 1-1: 0.3M An, 30min; 1-2: 0.3M An, 60min; 1-3: 0.3M An, 90min; 2-1: 0.4M An, 30min; 2-2: 0.4M An, 60min; 2-3: 0.4M An, 90min; 3-1: 0.5M An, 30min; 3-2: 0.5M An, 60min; 3-3: 0.5M An, 90min; 4-1: 0.6M An, 30min; 4-2: 0.6M An, 60min; 4-3: 0.6M An, 90min.

图 3. 聚苯胺/尼龙 6 的电镜结构图. 其中：1-1：0.3M An，30min；1-2：0.3M An，60min；1-3：0.3M An，90min；2-1：0.4M An，30min；2-2：0.4M An，60min；2-3：0.4M An，90min；3-1：0.5M An，30min；3-2：0.5M An，60min；3-3：0.5M An，90min；4-1：0.6M An，30min；4-2：0.6M An，60min；4-3：0.6M An，90min。

[27]。



A

B

C

D

Figure 4. The FTIR spectra of pure nylon 6 and PANI/nylon 6. 1-1: 0.3M An, 30min; 1-2: 0.3M An, 60min; 1-3: 0.3M An, 90min; 2-1: 0.4M An, 30min; 2-2: 0.4M An, 60min; 2-3: 0.4M An, 90min; 3-1: 0.5M An, 30min; 3-2: 0.5M An, 60min; 3-3: 0.5M An, 90min; 4-1: 0.6M An, 30min; 4-2: 0.6M An, 60min; 4-3: 0.6M An, 90min.

图4 聚苯胺/尼龙6的红外光谱图（图中标注同图3）

5 致谢

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