

Electrospinning Polyaniline for Sensors

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Abstract. Polyaniline is a conductive polymer (organic metal) with multiple uses as a sensor for mineral acids, ammonia, VOCs etc. The yield of the electrochemical reactions being proportional to the surface area, it is expected that polyaniline nanofibers to provide great opportunities for applications in electronic nanodevices. This article reviews electrospinning configurations (classic, coaxial, with 2 collectors, with rotary collector, with liquid collector etc.) used to obtain 3D structures of electrospun polyaniline, alone or mixed with other polymers, which are used in sensors.

1. Introduction

Polyaniline is an extremely versatile, highly conductive polymer with many uses. Depending on these, the electrospinning systems that can be used vary significantly, especially with respect to the nature of the collector.

2. Electrospinning alternatives for producing PANI nanofibers

There is a relatively large number of configurations used for the electrospinning of polyaniline (PANI), alone or mixed with other polymers. Thus, in order to electrospinn a PANI / polyvinylpyrrolidone (PVP) solution to obtain NO₂ sensors, Bishop uses a configuration comprising a DC voltage source, a programmable syringe pump and an aluminum collector plate. The voltage applied by the power supply is big enough to overcome the superficial tension of solution drops formed at the end of the syringe, causing the formation of a polymer blend jet. The electrostatic forces between the collector plate and the tip of the needle help driving the fibers to the collector. Nanofibers of PVP-PANI and PVP-PANI-Urate are formed at the application of 15 kV and 20 kV voltages, with flow rates ranging



from 5 $\mu\text{L} / \text{min}$ - 50 $\mu\text{L} / \text{min}$ and a distance between the needle and collector of 5- 6 cm [1]. Nanofibers used for ammonia detection were obtained by placing about 0.5 mL of PANI / poly(ethylene oxide) (PEO) solution in a hypodermic syringe and connecting the needle to 0.8 kV with respect to the grounded counter-electrode located at approximately 2 mm from the needle tip (figure 1).

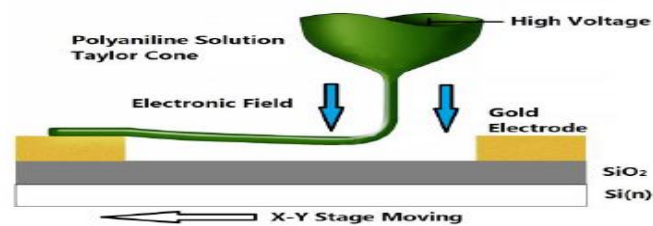


Figure 1. PANI/PEO near field electrospinning and device schematic [2].

The substrate is displaced in a computer controlled trajectory at a speed of 30 mm/s. By applying different trajectories and velocities, the amount and position of the fibers can be controlled [2]. In order to overcome the difficulty of PANI processing into fibers, the production of PANI doped with +camphor-10-sulfonic acid [HCSA] was achieved by coaxial electrospinning followed by the removal of the shell polymer, (figure 2) [3].

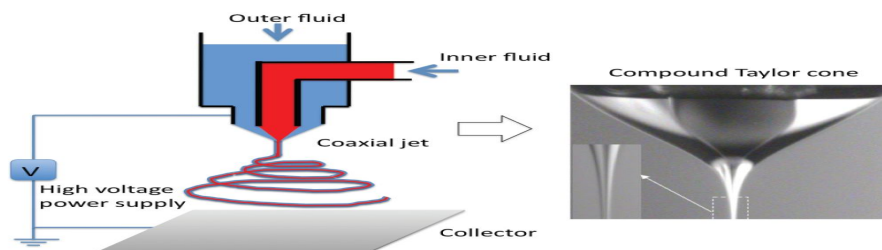


Figure 2. Basic setup for coaxial electrospinning of core-shell nanofibers [3].

The core was 2% by weight PANI, mixed with various amounts of HCSA, dissolved in a 5: 1 mixture of chloroform and dimethylformamide (DMF), and the shell was 15% by weight poly(methyl methacrylate) (PMMA) in DMF. The system behaves as a sensor for ammonia and nitrogen dioxide, both showing high sensitivity and rapid response time [4]. Co-polymer PANI / poly (vinyl chloride - acrylonitrile) nanofibers were obtained using an aluminum foil wrapped on a rotating drum with a 12 cm distance between the spinning nozzle and the collector, a flow rate of 1.0 mL/h, 15 kV voltage and 55% -65% humidity [5].

3. Electrospinning of 3D structures

A general problem that arises in nanofiber electrospinning is the predominantly two-dimensional character of the obtained structures, although a porous 3D-type structure would be more favorable in many areas of use, including sensors. Several

methods have been explored to increase the porosity of the electrospun fibrous matrices.

A common strategy involves electrospinning of mixtures of polymer solution and readily removable materials (such as water-soluble salts or polymers) which are then removed after the process: this method involves risks related to the stability of the nanofibers after eliminating the add-on substances [6-8].

Using a chemical expansion agent (azodicarbonamide) in the electrospinning solution increases the pore size (in the case of poly-caprolactone up to 50-70 nm), creating 3D structures [9]. An alternative approach is the use of ultrasonication, which can increase the pore size of the electrospun structures [10], without producing a true 3D structure, especially in terms of thickness.

It has been attempted to obtain 3D structures by replacing the traditional collector with a spherical collector with a series of needles [11], when reproducible results are difficult to obtain due to the lack of precise control over parameters such as the spherical collector dimensions, needle length, distance etc. Another variant tested for this purpose involves the use of liquid collector systems, which produce high porous 3D fibrous skeletons [12].

4. Electrospinning with nanofibers orientation

As a result of the bending instability, the path of an electrospun polymer jet is extremely chaotic, so that nanofibers are typically collected randomly overlaid in network / nonwoven forms [13] that can be used for certain applications, such as filtration / separation. However, the unilateral alignment of electrospun nanofibers can be crucial for other applications, such as microelectronic devices manufacturing [14,15].

An experimental static system with an alternating electrostatic field between two collectors can be used to improve the control of the orientation and positioning of electrospun fibers of PANI / PEO and PANI / PMMA, allowing the alignment of nanofibers on the substrate between collectors (figure 3) [16].

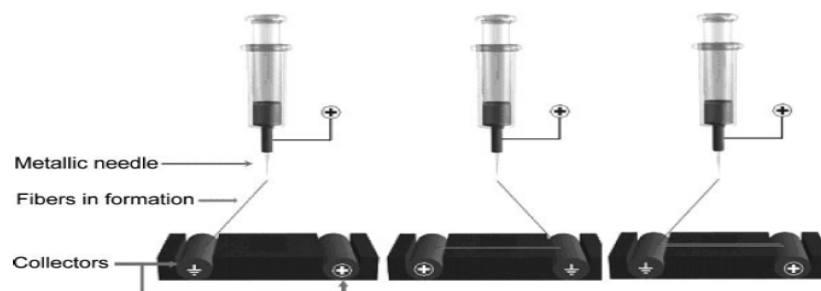


Figure 1. Electrospun fibers alignment set up.

Whereas one collector is grounded, the other is kept at 6 kV and this electric state is alternated between the two collectors using high voltage reed relays, forcing the electrostatically charged polymer to bounce from one collector to the other producing aligned fibers.

Inspired by parallel plates collector and rotary collectors, a rotating drum from copper wire was used to collect aligned fibers [17].

Another electrospinning technique that allows the regular orientation of the obtained nanofibers used a grounded collector consisting of a glass Petri dish, a metal plate being placed inside the bath and covered with distilled water up to a depth of 5 mm. A thin copper wire was passed over the edge of the bath to connect the metal plate to the ground and a motorized pickup roller with a rotation speed equivalent to 0.05 m / sec takes the disordered nanofiber mixture formed on the water surface and deposits it in an orderly manner, as can be seen in figure 4 [18]. Moreover, a dynamic substrate liquid system has been developed to support and assemble the electrospun nanofibers [19].

In a similar approach, a dynamic fluid system in the form of a vortex surface with a rotating drum is used to prepare well-aligned continuous yarns from nanofibers [20]. Another technique of manufacturing uniaxially aligned electrospun fibers uses two needles with opposite voltages that spray simultaneously and the spun fibers with opposite charges attract each other combining into a yarn, which is wound by a cylinder collector rotating at high speed (figure 5) [21].

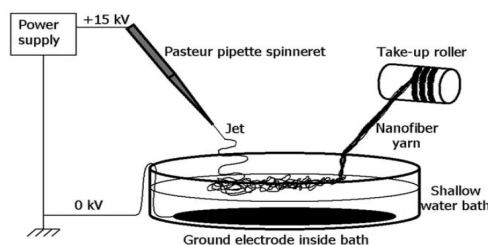


Figure 2. Water bath grounded collector electrode electrospinning.

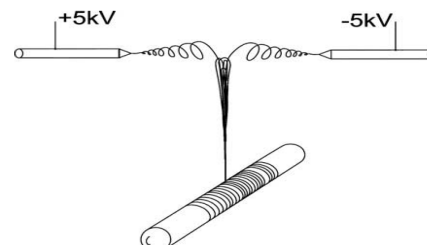


Figure 3. Schematic two needles electrospinning setup.

Rotary drum collectors, unlike stationary or rotatable collectors, provide increased evaporation time and, implicitly, increased ordering, even if the thickness of the nanofibrous deposition is limited and the nanofibers can't be aligned at any time. Other difficulties are related to the fact that not all materials can be electrospun with rotary collectors. Rigid materials, with limited fluidity, lead to fibers that break at lower rotational speed. The rotating collector method is time-consuming and energy-intensive and the degree of fiber alignment decreases with increasing spinning time and fiber layer thickness [17].

The degree of alignment of electrospun nanofibers can be controlled by a magnetic field if the polymer solution contains a small amount of magnetic material, as the magnetized nanofibers are stretched and paralleled (figure 6) [23, 24]. Highly ordered nanofibers can be obtained by using an auxiliary electric field to control nanofiber deposition, stabilizing the unsteady jets by controlling the shape and intensity of the macroscopic electric field between the anode and the cathode (Figure 7) [25-28].

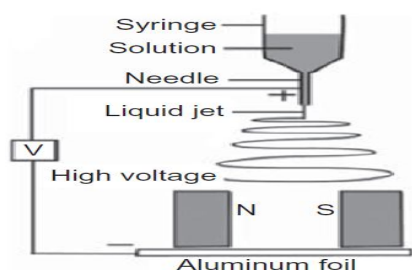


Figure 4. Magnetic electrospinning.

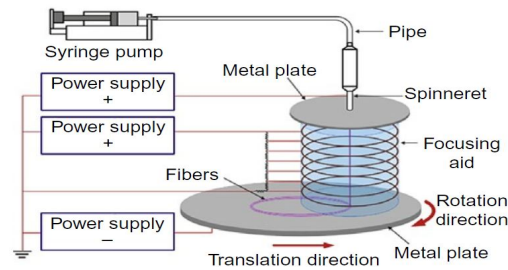


Figure 5. Schematic diagram of the focusing electric-field-assisted electrospinning setup.

Well aligned nanofibers can be obtained by using a modified electrospinning equipment with a rotating nozzle (centrifugal electrospinning), when the forces contributing to stretching the solution droplet into fibers are a combination of centrifugal force and electrostatic force [29-35]. Another method uses a collector obtained by coupling a T-shaped electrode and a rectangular electrode, with the use of a gas stream to force the nanofibers to point to the positive side of the rectangular electrode [36-43]. The Near Field Electrospinning (NFES) method uses a reduced distance between the spinning tip and the collector electrodes (500 μ m to 3 millimeters) to manipulate the electrospun jet into aligned filament structures, (figure 8) [40, 44-54].

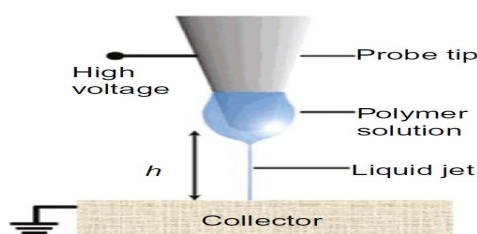


Figure 8. Schematic representation of near field electrospinning.

5. Conclusions

Many electrospinning set-ups (classic, coaxial, with 2 collectors, with rotary collector, with liquid collector etc.) are used to obtain aligned nanofibers or 3D structures of electrospun polyaniline, alone or mixed with other polymers, which are used in sensors. The paper reviews the most significant achievements in these directions.

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