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Chapter 8

Semiconducting Electrospun Nanofibers for Energy Conversion

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Additional information is available at the end of the chapter

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Abstract

Nowadays, semiconducting thin films, thanks to their unique and excellent properties, play a crucial role for the design of devices for energy conversion and storage, such as solar cells, perovskite solar cells, lithium-ion batteries (LIBs), and fuel cells. Since the nanostructured arrangements can improve the behavior of the materials in several application fields, in this chapter we propose the electrospinning process as electro-hydrodynamic deposition to obtain semiconducting materials, in the form of nanofiber mats. The nanostructured mats are able to provide high surface-area-to-volume ratio and a microporous structure, which are crucial aspects for energetic application. In this chapter, we deeply describe the electrospinning process and how nanofibers obtained can be used in energy devices, satisfying all the requirements to improve overall final performances.

Keywords: semiconducting materials, nanofiber mats, electrospinning, energy conversion devices, energy storage devices

1. Introduction

Nowadays, different deposition techniques, based on the application of an external electric potential, are carried out in order to prepare thin film and coatings. A thin film is defined as a layer of material with a thickness in the range from few nanometers (namely monolayer) to several micrometers. All electrodeposition processes, which can be divided in chemical methods and physical methods as proposed in **Figure 1**, ensure the deposition of different classes of materials as metals, semiconductors, ceramics, and organo-ceramics in the form of thin films, onto several substrate materials. Semiconducting thin films show a variety of unique and excellent properties that make them particularly attractive in several application areas. Among them, these materials play a preeminent role for the design of devices for energy conversion, such as solar cells and perovskite solar cells [1]. The behavior of semiconducting materials can be improved toward energy-related applications, when their shape and dimension are controlled

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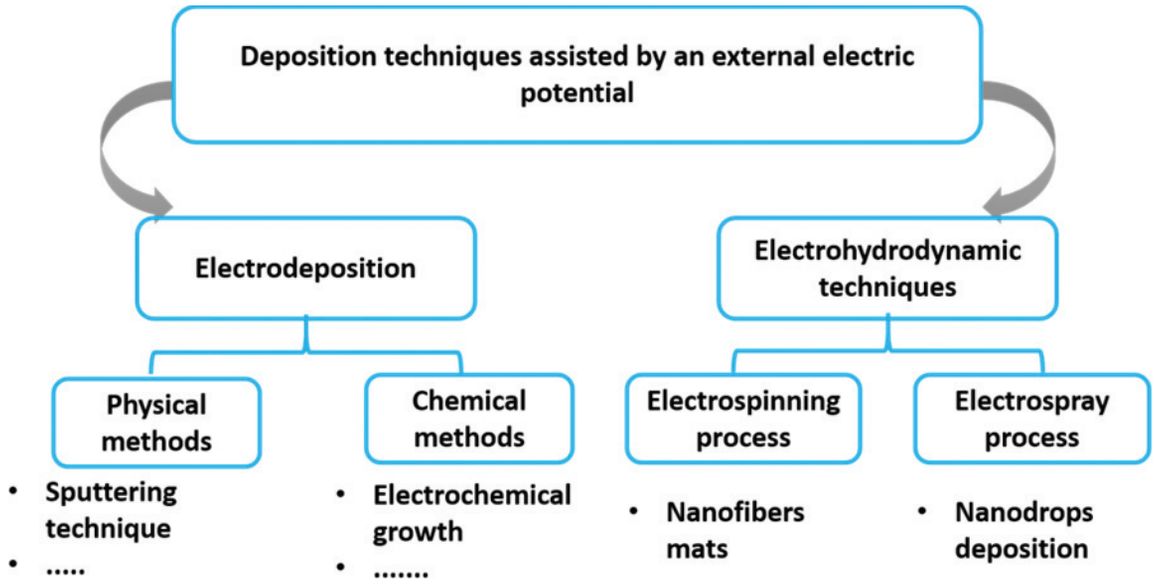


Figure 1. Different deposition techniques obtained by applying an external electric field and/or potential difference. These techniques can be divided in electrodeposition methods and electro-hydrodynamic techniques, as explained in the diagram.

up to the nanometer scale, in the so-called nanostructured arrangements. In this chapter, electro-hydrodynamic depositions are proposed in order to obtain semiconducting materials in the form of nanofiber mats, able to combine high surface-area-to-volume ratio together with a microporous structure well suited for energetic application. The electro-hydrodynamic techniques involve an external electric field applied to a polymeric solution to provide the final deposition of nanomaterial. As proposed in **Figure 1**, two different processes, i.e., electrospinning and electrospray, can be classified as electro-hydrodynamic techniques. Indeed, electrospinning ensures the direct assembly of nanofiber mats with different morphologies and properties, as described in this chapter.

Electrospinning process is based on the principle that strong repulsive forces, induced by external applied electric field, can overcome the surface tension in a charged polymeric jet [2, 3]. Therefore, through this technique, the polymer can be arranged in a mat with a high surface-area-ratio-to-volume, showing a micro−/macroporous structure. Moreover, final nanofibers are based not only on polymers but also on metals, ceramics, and metal oxides, obtained by implementing further different chemical and thermal treatments. However, electrospray technique is an electro-hydrodynamic technique, which occurs at low viscosity values of initial polymeric solution. Indeed, in this case, the surface tension overcomes the viscoelastic forces, and consequently, the instauration of charged droplets with different diameters and concentrations occurs during the process.

During the last decade, different works have been presented in the literature, focusing their attention on nanostructured semiconducting metal oxides (as TiO_2, ZnO, CuO, and SnO_2) in order to design well-performing and green energy systems (such as in dye-sensitized solar cells, lithium-ion batteries (LIBs), fuel cells). In this scenario, nanofibers progressively increased their importance as one of the most important nanostructures to be selected to improve the final performance of the devices.

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2. Electrospinning technique and its principles

The electrospinning is an electro-hydrodynamic process that provides polymer-based fibers with diameter distribution in the range from few nanometers to several micrometers by involving electrostatic forces [4–7]. The process is based on the concept that electrostatic forces induce columbic interactions between charged elements of the polymeric fluid, leading then to overcome the surface tension in a charged polymeric jet and ensuring the nanofiber formation. An electrospinning system is constituted by three major components, as sketched in **Figure 2(a)**: (i) high-voltage supply; (ii) a spinneret, which represents one of the two electrodes, containing the metallic needle of the syringe, where the polymeric solution is loaded; and (iii) the counter electrode, also named grounded electrode, which is the second electrode, where the nanofibers are collected. It involves a high-voltage supply in order to inject charges with a certain polarity in the polymeric solution and then generates a polymeric charged jet, accelerated toward a counter electrode with opposite polarity. In a typical process, the voltage (0–30 kV) is applied between the first electrode (tip of needle) and the second electrode (counter electrode). This implies the indirectly definition of electric field intensity as the ratio between the voltage value and working distance. The working distance is the distance between the first electrode and the counter electrode. The spinneret is linked with a syringe, in which the polymeric (or melt) solution is loaded and a syringe pump allows to control the solution flows with a constant rate, defined as flow rate. When the voltage is applied, the drop at the tip of the needle becomes highly electrified, and the charges are uniformly distributed on its surface. Therefore, the repulsive forces, acted between all charged elements of polymeric solution, induce an elongation of the spherical drop to form a conical shape, known as Taylor's cone. When the repulsive forces

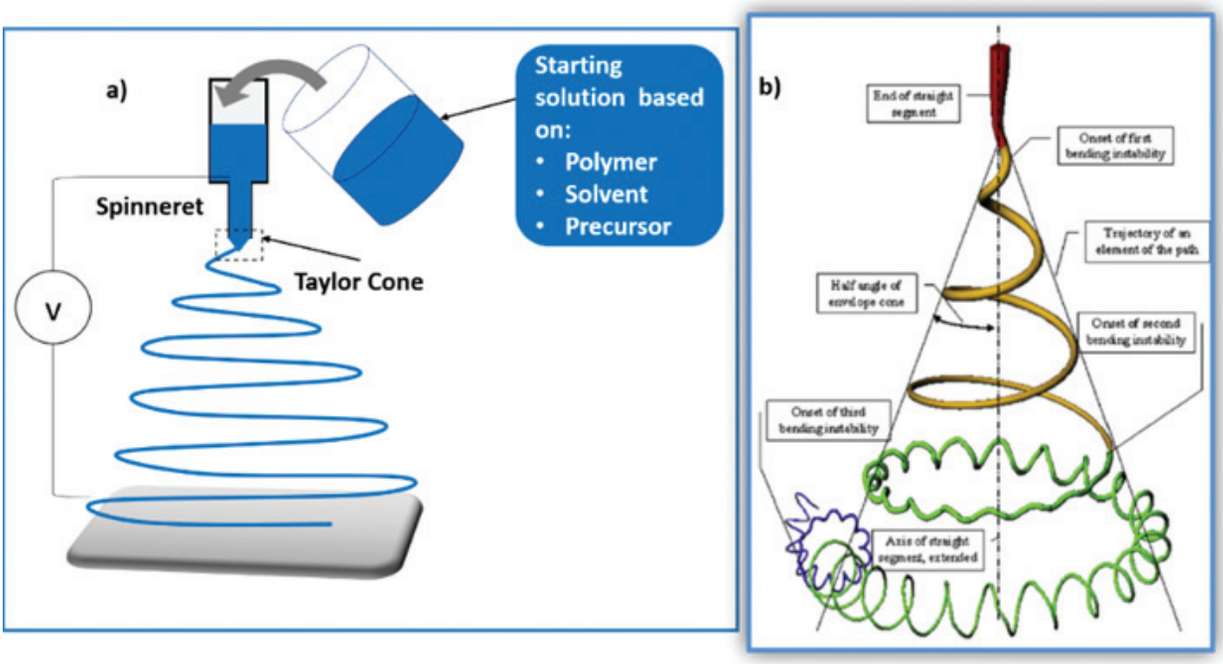


Figure 2. A sketch of electrospinning setup is proposed in (a). In (b) a representation of bending instabilities characterizing the charged polymeric jet during the electrospinning process is proposed. (reprinted with the permission from (polymer, 2008, 49, 2387–2425) copyright (2008) Elsevier).

overcame the surface tension of the droplet, the charged polymeric jet is ejected from the tip of Taylor's cone. During the flight, the solvent evaporation together with the instauration of several instabilities (defined whipping or bending instabilities) [8–10] occurred, leading then to the deposition of nanofiber mat, characterized by a small-size diameter distribution and by a high surface-area-to-volume ratio. In particular, the electrified jet proceeded with a straight path directly toward the counter electrode until the formation of successive instabilities, as sketched in **Figure 2(b)**.

The theoretical principle that explains the correlation between the formation of bending instabilities with the columbic interactions, the external electric field, and the surface tension is not widely investigated in the literature. However, during the process, the free end of the jet shows different envelope loops, which repeats itself in a smaller and smaller scale as the jet diameter is reduced [10]. During the bending instability, the charged jet is divided in sub jets, achieving a progressive diameter reduction, determined by Eq. (1) as explained in the literature [2]:

$$r_0{}^3 = \frac{4\varepsilon \dot{m}_0}{k\pi\sigma\rho} \tag{1}$$

where ε is the fluidic permittivity (C V^{-1} cm^{-1}), $\dot{m}_0$ is the mass flow rate (g s^{-1}) when r_0 (cm) is defined, k is a dimensionless parameter depending on the electric currents, σ is electric conductivity (A V^{-1} cm^{-1}), and ρ is the density (g cm^{-3}) of obtained nanofibers mats. Electrospinning process is applied on the polymer-based materials, including both synthetic and natural polymers. However, metallic carbon nanofibers and ceramic nanofibers can be obtained by electrospinning process, starting from polymeric solutions, and by occurring successive treatments, such as pyrolysis, calcination, and so on. One of the main advantages of this process is represented by the different nanostructures that can be obtained, such as hollow, porous, and dense nanofibers. Therefore, all wide nanostructures are achieved by varying and defining the process parameters, such as electric potential, flow rate, polymer concentration, working distance, and ambient condition.

3. Definition of electrospinning parameters and their correlation with the nanofiber properties

Since the modulation of morphological properties of the nanofiber mats is directly dependent on the process parameters, it is mandatory to define all these process parameters, which can be divided in three main categories [3, 11, 12]:

i. Parameters of the polymeric solution (or polymer melt), i.e., viscosity, concentration, and polymer molecular weight

ii. Parameters of electrospinning process, i.e., voltage, flow rate, and working distance between two electrodes

iii. External parameters, i.e., humidity and temperature

The first two categories are analyzed in the following paragraphs.

3.1. Polymer solution parameters

Several solution parameters, such as viscosity solution, conductivity, dielectric constant, and surface tension, influence the formation of polymeric charged jet and consequently morphological properties of nanofiber mats. The solution viscosity represents the resistance offered by a fluid to its progressive deformation, induced by shear stress or tensile stress. In particular, the viscosity is due to the collisions between all particles that move in a fluid at different velocities. Therefore, solution viscosity can be defined as the measure of force/stress needed to keep the fluid moving in a certain space. The concentration of polymer, dissolved in the solution, directly influences its viscosity the higher the polymeric concentration, the higher the solution viscosity. As determined by several works in the literature, in order to guarantee the instauration of charged polymeric jet during the process, leading to the collection of nanofibers, the viscosity must be in the following range (Eq. (2)) [13–15]:

$$(0.02 \leq \eta \leq 300)\ Pa{*}s \tag{2}$$

The formation of nanofibers with or without defects depends on both viscosity and surface tension of the solution. The surface tension is a polymeric solution property due to all cohesive forces between fluidic molecules, ensuring then/leading then to the distribution of a fluid into the minimum surface area condition. Indeed, in one liquid all inner molecules interact with each neighboring molecule, inducing a resulting force equal to zero and a lower state of energy. On the contrary, since the same number of neighboring does not surround the molecules on the surface, an internal pressure is occurred, which induces the liquid surface to occupy the minimal area, reducing its energy state. According to Laplace's law, the spherical shape can satisfy conditions of minimal area for a liquid [3], minimizing the "wall tension" of the drop surface, as sketched in **Figure 3**. Related to the electrospinning process, the surface tension of polymeric solution ensures the generation of a spherical droplet, suspended at the tip of the needle.

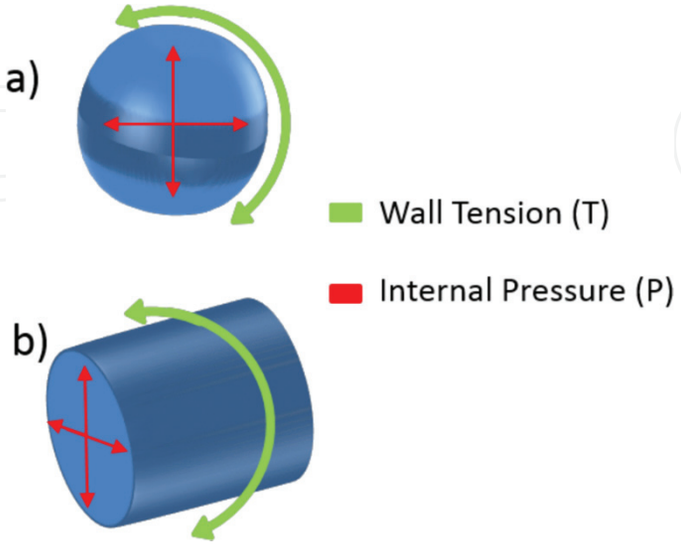


Figure 3. Representation of theoretical concept of Laplace's law (a) represents the cylindrical vessel (T = PR, where R is the radius of tube) and (b) represents the spherical vessel (T = PR/2, where R is the radius of tube).

In order to explain the correlation between the solution concentration, solution viscosity, and surface tension, it is important to distinguish two different electro-hydrodynamic processes, obtained by using polymeric solutions with different viscosity values. Indeed, if viscosity is lower than 0.1 Pa*s ($\eta \leq 0.1$ Pa*s), the surface tension overcomes the viscoelastic forces, a noncontinuous charged polymeric jet is generated, and consequently, droplets with different diameters and with different concentrations are collected. This process is defined as electrospray [13–15]. When viscosity value is higher than 2 Pa*s ($\eta \geq 2$ Pa*s), the electrospinning process is ensured, thus providing the formation of nanofibers. Therefore, the charged polymeric jet travels as a continuous jet toward counter electrode, in which dried nanofiber mats were collected on.

Different works in the literature, moreover, demonstrate that the increment of solution viscosity guarantees the formation of a uniform mat of nanofibers, without the presence of beads, known as one of the most common defects into the nanofibers mats [13]. It is widely explained how the molecular weight of polymer (Mw) and the polymeric concentration can control the presence of defects and diameter distributions inside the nanofiber mats. As the molecular weight increases, the number of beads and droplet is reduced. Since the increasing of the molecular weight can increase the instabilities distribution, the final nanofiber mats show a nonuniform distribution of diameters. Moreover, a low polymer concentration induces thinner fiber diameters, due to the evaporation of the solvent [14]. The direct correlation between polymeric concentration and viscosity modifies the jet deformations induced by viscoelastic forces during electrospinning. Therefore, when the polymeric concentration is too low, the electrospray process results to be the main electrified process deposition. On the contrary, when the solution viscosity is too high, during the electrospinning, the leak of charged jet from the tip of the needle could be compromised.

3.2. Electrospinning process parameters

All the parameters, related to the electrospinning process, such as voltage, flow rate, and working distance, tune the diameter distribution in the nanofiber mats, thus controlling the porosity distributions and the surface area of nanofibers.

Different works in the literature [3] demonstrated that the correlation between the voltage applied and the nanofiber morphology is not well defined. Nevertheless, this process parameter is quite important in order to establish, for each solution, the threshold value, above which the charged polymeric jet is originated, thus ensuring the nanofiber deposition on the counter electrode. Another fundamental parameter is the working distance, whose value can influence the completely evaporation of the solvent. Indeed, it is needed to define the minimum value of distance, able to provide the fiber's sufficient time to dry before depositing on the collector [15–18].

The flow rate is known as the rate at which the polymer solution is injected to the tip of the needle, defining then the flowing mass of solution and consequently the position of Taylor's cone related to the syringe needle. Moreover, a direct correlation between flow rate and the length of liner path, which precedes the bending instabilities, can be observed during the process [3]. At low values of flow rate, Taylor's cone is formed inside the tip of the needle, thus leading to an intermittent polymeric jet; however, at too high values of flow rates, the

charged jet results to be continuous, leading to the formation of nanofiber mats, characterized by a large number of beads together with a nonuniform diameter distribution. Indeed, as the flow rate increases, the diameters of nanofibers mat increase [3].

This overview on all those parameters, which influence the morphology properties of nanofibers nets, provides important instruments in order to tune/control, during the electrospinning, the formation of some defects, i.e., nano-netting, able to optimize nanofiber mats, involved in several applications, like catalysis, sensors, optics, tissue engineering, and energy storage.

The nano-nets appear as spider-weblike structure, characterized by secondary ultrathin nanofibers interconnected with the main nanofibers [19]. There are some works in the literature [20–22] that study spider-weblike nanofibrous mat obtained by using an electrospun colloidal solution, containing the polymer and metal oxide nanoparticles. Kim et al. [20] obtained the nano-netting structure starting from a polymeric solution containing solid powder of ZnO mixed with a solution of nylon-6 and acetic acid. The ZnO nanoparticles induce a solution charge density increase, providing the separation of the thinner fibers from the main nanofiber web.

Moreover, Amna et al. [21] proposed the formation of secondary thinner web when ZnO nanoparticles were dissolved in a sol–gel solution of polyurethane in dimethylformamide (DMF).

4. Hollow nanostructures and coaxial electrospinning

One of the main important aspects of the electrospinning process is represented by the possibility to provide different types of nanofiber morphology, obtained by modifying the electrospinning technique. As an example, coaxial electrospinning is applied to the preparation of polymer core-shell nanofibers and hollow nanofibers composed not only of polymers but also of ceramics. Coaxial electrospinning is obtained by using two syringe supports disposed in a concentric configuration, and each syringe contains different spinning solutions, as sketched in **Figure 4(A)**. All parameters, described above, which influence the formation of polymeric jet during the electrospinning process, are the same. Coaxial electrospinning provides further advantages, when the molecular weight of polymer is too low to ensure the fiber formations, avoiding the droplets and consequently the electrospray process. Incorporating these kinds of polymer as the core into a core-shell nanofibers, it is possible to ensure the formation of a continuous jet and consequently the collection of nanofibers on the counter electrode. Moreover, core-shell fibers can offer a solution when it is needed to keep the functional components (proteins, enzymes, bacteria, viruses) maintaining their functionality. Core-shell nanofibers are characterized by a shell, based on solid materials, such as natural or synthetic polymers, and by a core, which is commonly a solvent (like water) with bio-systems. However, the hollow nanofibers are carried out when a wall is based on inorganic polymeric composites or ceramic materials, and the core results to be empty (as sketched in **Figure 4(B–D)**). There are two different approaches implemented to obtain hollow nanofibers. The first one is based on the concept of sacrificial polymer templates that is then removed. Choi et al. [23] fabricated hollow ZnO nanofibers by using polyvinyl alcohol (PVA) as polymeric template.

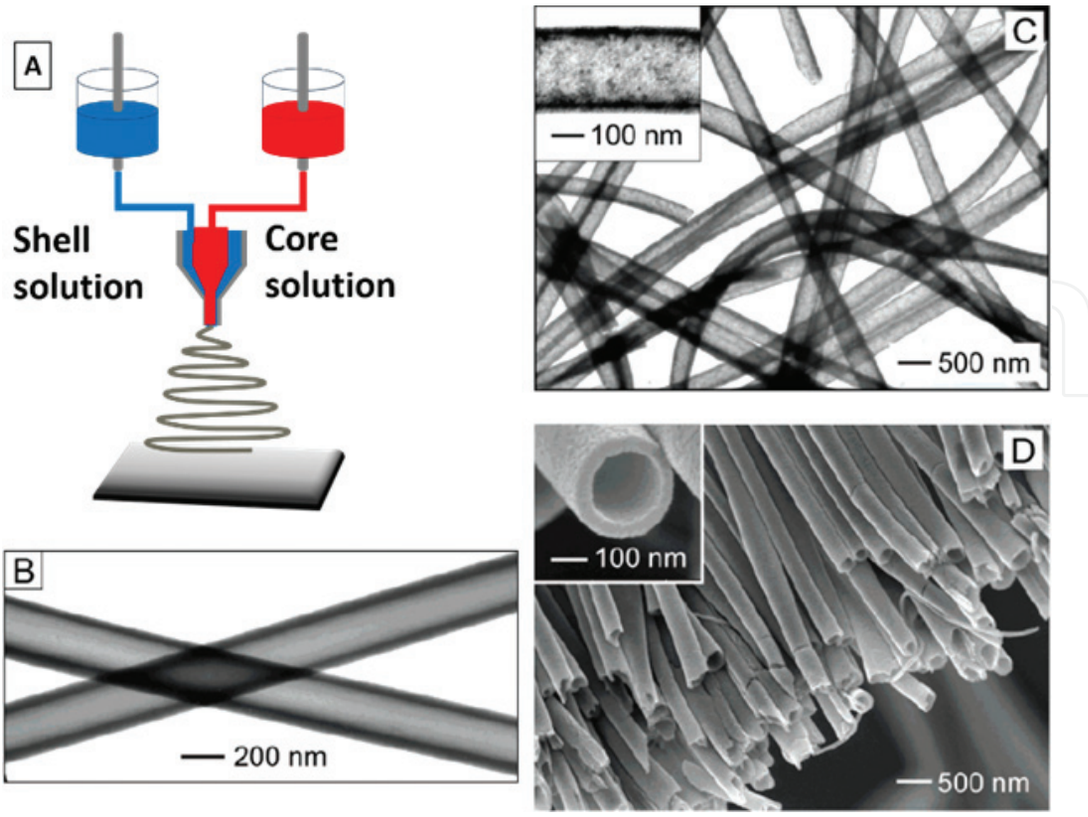


Figure 4. Core-shell nanofibers obtained by coaxial electrospinning (A) and hollow nanofibers (B-C-D) are proposed. The figure is adapted and reprinted with the permission from (Li and Xia [25]. Copyright (2004) American Chemical Society).

Another approach is based on coaxial electrospinning, starting from two immiscible liquids through the coaxial spinneret, followed by a selective removal of the core. Li et al. [24] studied hollow nanofibers, obtained by coaxial electrospinning, and used a polymeric solution of polyvinylpyrrolidone (PVP) and titania precursor (Ti ($O\mathit{i}Pr$)$_4$) as shell and mineral oil as core. An example of the resulting hollow nanofiber is reported in **Figure 4(D)**.

Du et al. [22] used coaxial electrospinning in order to design TiO_2/ZnO core-shell nanofibers as photo-anodes in dye-sensitized solar cells (DSSCs). The resulting DSSC efficiency was close to 5%. This improvement can be related to the enhanced light-harvesting efficiency and electron collection efficiency.

5. Nanofiber deposition controlled by counter electrode and by patterning

The final step of electrospinning process is represented by the deposition of dried nanofiber mats on the counter electrode (collector). The collector is a conductive electrode, connected to the ground potential in order to provide a stable potential difference between the first electrode (tip of needle) and the second one (counter electrode). In electrospinning process, the deposition texture depends on the electrode configurations. Different works in the literature demonstrated the correlation between the morphological and physical properties of nanofibers with different types of counter electrodes. Indeed, different collectors can be divided into

(i) flat-plate collector, (ii) rotating drum collector, (iii) rotating wheel with edge, and (iv) parallel strips [4].

5.1. Flat-plate collector

In the majority of electrospinning setup, a flat-plate collector is used, thus leading to collect a non-woven nanofibers mats, namely as a random distribution of nanofibers on the counter electrode and on all substrate positioned on the top of it. The formation of a non-woven mat of nanofibers is induced by a layer-by-layer deposition on the planar surface. However, some applications required a certain alignment among the nanofibers. In order to induce certain fiber orientations, specific geometries of counter electrode, combined with its motion, are required (as proposed in **Figure 5**).

5.2. Rotating drum collector

Rotating cylindrical collectors combined with high rotating speed (up to 1000 rpm), as represented in **Figure 5(a)**, enhance a distribution of parallel nanofibers on it. In this configuration, the two components of velocity (rotating velocity and linear tangential velocity) play a key role in the alignment of nanofibers. The linear tangential velocity of each point on the collector surface is directly proportional to angular velocity and radius of cylinder. Therefore, when the tangential velocity assumes a threshold value able to guarantee the solvent evaporation of the jet, the nanofibers assumed a circular shape on the collector. However, if the tangential velocity results to be too low, random distribution of nanofibers occurred. Finally, if the tangential velocity is too high, the fiber jet will be broken, and the continuous nanofibers will no collect. Different works in the literature used drum collector in order to obtain aligned metal oxide nanofibers, based on TiO_2 [25, 26] and ZnO [23]. Aligned ZnO nanofibers are

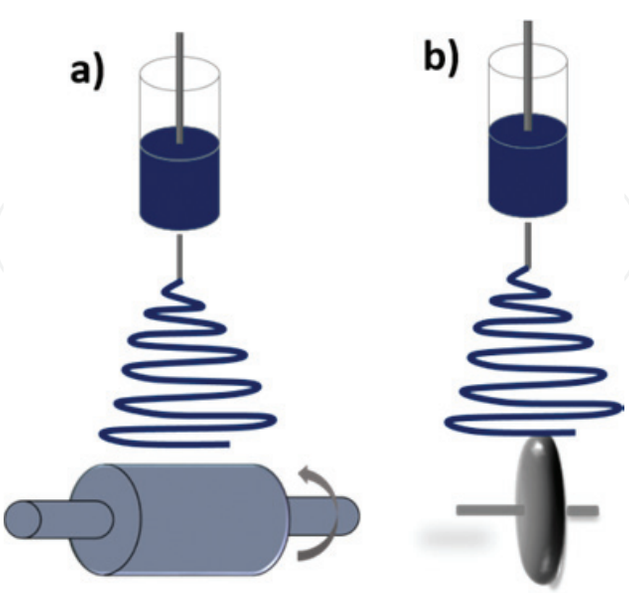


Figure 5. A schematic representation of different electrospinning collectors. In (a) and (b), the rotating drum and disk collectors are shown, allowing the aligned nanofiber mats.

electrospun starting from a gel containing the precursor of metal oxides and zinc acetate. The electrospun ordered nanofibers were then calcined at 450–500°C in oxygen atmosphere to induce the nucleation and growth of ZnO [23]. The aligned ceramic nanofibers show a higher surface-area-to-volume ratio, leading to enhance charge collection and their transport.

5.3. Rotating disk collector

The rotating disk can be defined as a thinner drum collector, on which the nanofibers are deposited on its edge. For this approach, collected nanofibers appear more aligned than the ones obtained with drum collector, described above [12, 27, 28]. **Figure 5(b)** represents a schematic view of rotating disk, and the nanofibers intercept the edge of counter electrode. With this kind of architecture of counter electrode, the rotation of the disk generates a tangential force, which acts on the polymeric jet, carrying out the nanofiber deposition only on the edge of the disk. This force reduces their diameter, stretching the nanofibers. In this configuration, the alignment of nanofibers results to be better than the one obtained by using rotating drum collector. However, the main limitation of this collector is that only a small quantity of aligned fibers can be obtained. In order to overcome the limitations induced by these kinds of counter electrode to obtain aligned nanofibers and to guarantee the formation of oriented nanofibers, several methods can be implemented. In particular, they mainly involve the modulation of external field provided by a specific geometry of counter electrode.

5.4. Patterning designed on counter electrode

Since some applications in energy field requires highly ordered structure, different works in the literature designed different patternings on a planar counter electrode, able to overcome all limitations introduced by different types of counter electrode (drum or rotating disk counter electrode) and enhance the aligned of nanofibers [29]. An example is shown in **Figure 6(A)**. Two gold bars are placed on the planar counter electrode, and their disposition breaks the asymmetry of the deposition, ensuring the deposition of parallel fibers. In a similar way, a quadripolar arrangement of isolated strips of electrodes, as represented in **Figure 6(B)**, induces a cross grating type of fiber deposition. Wu et al. [12] used two silver plate placed on the planar counter electrode, inducing a final aligned nanofiber mat with a highly ordered structure. The initial polymeric solution was made of CuO precursor mixed with PVA, dissolved in deionized water. The aligned CuO nanofibers, obtained after the calcination treatment conducted in air at a temperature of 500°C, enhanced their electrical transfer properties.

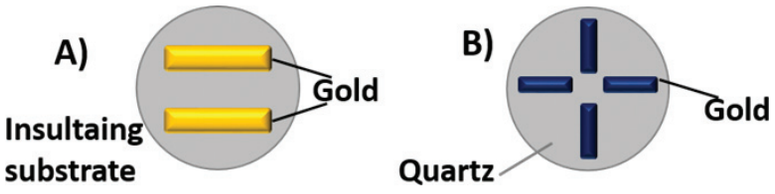


Figure 6. (A) Parallel arrangement of nanofibers induced by two gold strips, placed on planar counter electrode and (B) quadripolar arrangement of isolated strips of electrodes.

6. Application of semiconducting nanofibers

For the last decades, tremendous efforts have been devoted to the exploitation of renewable, efficient, and low environmental impact of energy sources, able to contribute to the rise of new models for a sustainable human development [30]. Nanostructured materials have demonstrated a huge potential in energy devices, significantly contributing to improve the final performance of the systems [31, 32]. Nanofibers by electrospinning belong to this intriguing class of materials. As described in the previous paragraphs, nanofibers offer a wide range of strategies to fine tune their morphology in order to meet the requirements of the final application. This versatility of the process provides the nanofibers with a huge potential for energy-related applications [33, 34].

Good examples exist, showing the integration of nanofibers in energy systems for both energy production and storage. In the following paragraphs, some examples are provided, especially focusing on photovoltaic systems and lithium-ion batteries.

6.1. Energy production

In photovoltaic devices, photons from solar light are directly converted into electrons thanks to the presence of proper materials. In traditional solar cells, adsorption/conversion is granted by a semiconducting material in a thin-film form, as GaAs, InP, and Si. In the most recently proposed systems, conversion is performed by organic molecules, as in dye-sensitized solar cells (DSSCs) [35, 36] or metalorganic lead halide perovskites in the so-called perovskite solar cells (PSCs) [37]. In both cases, a semiconductor is then needed to capture the generated electrons resulting in an electric current generation.

The leading wide bandgap, mesoporous semiconductor in these devices is TiO_2. Since the photo-generated charges have to be efficiently injected in the conduction band of the nanostructured semiconductor, the higher the injection efficiency, the lower the losses associated to the process. For this reason, the design of the semiconductor at the nanoscale plays a key role to obtain high-performing photo-electrodes. Nanofibers are quite promising candidates for obtaining well-performing devices since they offer several strategies to control and tune their morphology as needed by the final application.

As an example, the porosity of nanofiber mats can be considered: in DSSC, the possibility to control the dye uptake and the penetration of viscous, solid, or semisolid is a quite important feature. It is possible to change and control the nanofiber mat porosity, tuning the electrospinning process parameters, in order to optimize nanofiber mats for the design of photo-anodes in DSSC [38]. Nanofibers by electrospinning offer several strategies for low-temperature processing of photo-anodes: this is quite important for an easy integration of nanostructured semiconductors in plastic substrates for flexible devices [39, 40].

Several metal oxide semiconductors have been successfully fabricated by electrospinning, as TiO_2, ZnO, and SnO_2 [39, 40], for the design of well-performing photo-anodes.

Core-shell nanofibers [41]; TiO_2-graphene composite nanofibers [42]; electrospun ZnO photo-electrodes made of ZnO nanofibers with a dense, twisted structure [43]; and SnO_2/TiO_2 core-shell nanofiber-based photo-anodes have been successfully integrated in DSSC devices. Similarly, TiO_2- and Au-decorated TiO_2 nanofibers [44–46] have been proposed in PCSs.

Another important class of devices for energy conversion is represented by fuel cells. They are electrochemical devices, able to convert the chemical energy stored in several classes of molecules, acting as fuels (e.g., H_2, methanol, ethanol) into electricity in the presence of a catalyst. Different types of fuel cells exist according to the fuel that is converted (i.e., direct methanol fuel cells (DMFC)), the electrolyte that they use (i.e., solid oxide fuel cells (SOFCs)), or the catalyst that controls the oxidation process (i.e., microbial fuel cells (MFCs)).

In this area of energy, semiconducting nanofibers are especially proposed to design new cathode, when the oxygen reduction reaction (ORR) occurs at the cathode. As an example, manganese oxide nanofibers are successfully proposed to catalyze the ORR as an alternative to platinum [47]. One of the main disadvantages of metal oxides as catalysts to drive the ORR is related to their low electrical conductivity. To overcome this issue, different strategies have been proposed. A successful method is based on the use of composite nanofibers made of doped semiconductors, as proposed by Alvar et al. that optimized a process to embed carbon nanoparticles into mesoporous Nb-doped TiO_2 nanofibers [48].

6.2. Energy storage

In the area of energy storage, lithium-ion batteries (LIBs) play a crucial role as a promising technology toward sustainability. In a LIB, a negative electrode and a positive electrode are present, both able of reversibly intercalate Li+ions, and separated by a nonaqueous lithium-ion conducting electrolyte. During discharge, Li+ions carry the current from the negative to the positive electrode, through the nonaqueous electrolyte. During charge, an external high voltage is applied that forces lithium ions to migrate from the positive to the negative electrode, where the process known as intercalation occurs, during which they are embedded in the porous electrode material [31].

In this field, semiconducting nanofibers by electrospinning have been especially proposed for the fabrication of high-efficiency anodes. Good examples are represented by TiO_2 nanofibers. Han et al. fabricated TiO_2 hollow nanofibers sheathed with TiOxNy/TiN layers with the aim to optimize capability diffusion of lithium ions and electronic conductivity. The fabrication process was based on electrospinning to fabricate hollow nanofibers, followed by a thermal treatment in NH_3 atmosphere [49]. Another possibility is represented by the synthesis of composite TiO_2-based nanofibers. Zhang et al. proposed the fabrication by electrospinning, followed by a calcination step of TiO_2-graphene composite nanofibers able to behave as highly durable anodes [50].

Another interesting possibility offered by electrospinning is the decoration of carbon-based nanofibers with metal oxide catalysts, by adding the oxide precursor into the solution already containing the carbon precursor. The nucleation of the semiconducting oxide in the form of nanoparticles can then be achieved by the thermal process, which also permits the carbonization of the nanofibers. An interesting example of this process is offered by the work of Ji et al. [51]. They synthetized carbon nanofibers decorated with α-Fe_2O_3 nanoparticles, demonstrating homogenous dispersion of the nanoparticles along the carbon-based nanofibers. The composite mats were tested as anodes in Li-ion batteries; the resulting electrodes showed good reversibility and capacity.

High-capacity anodes for Li-ion batteries can be also designed using SnO_x, but strategies are needed for this semiconductor to improve its stability over cycles. Indeed, the variation of the volume induced by the intercalation process is detrimental for its mechanical stability, resulting in reduced lifetime of SnO_x-based anodes. In order to significantly improve the cycling durability of the resulting anodes, the electrospinning method is used to synthetize carbon-based nanofibers decorated with small-size SnO_x nanoparticles [52].

The possibility to use carbon-based nanofibers in the area of energy storage offers new interesting possibility to design flexible devices. Indeed, carbon-based mats can be processed to be freestanding and usually exhibit very high bendability, offering several possibilities of integration as electrodes in devices for smart electronics. In this area, several processes are developed to decorate the starting carbon mats with metal oxides to design new, well-performing anodes. Samuel et al. [53] decorated carbon-based nanofibers with MnO nanoparticles, demonstrating the possibility to couple the high performances achievable by this semiconducting oxide (923 mAh g^{-1} at a current rate of 123 mA g^{-1} after 90 cycles) with optimal flexibility of the carbon mats.

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