Large-Scale Direct-Writing of Aligned Nanofibers for Flexible Electronics

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Nanofibers/nanowires usually exhibit exceptionally low flexural rigidities and remarkable tolerance against mechanical bending, showing superior advantages in flexible electronics applications. Electrospinning is regarded as a powerful process for this 1D nanostructure; however, it can only be able to produce chaotic fibers that are incompatible with the well-patterned microstructures in flexible electronics. Electro-hydrodynamic (EHD) direct-writing technology enables large-scale deposition of highly aligned nanofibers in an additive, noncontact, real-time adjustment, and individual control manner on rigid or flexible, planar or curved substrates, making it rather attractive in the fabrication of flexible electronics. In this Review, the ground-breaking research progress in the field of EHD direct-writing technology is summarized, including a brief chronology of EHD direct-writing techniques, basic principles and alignment strategies, and applications in flexible electronics. Finally, future prospects are suggested to advance flexible electronics based on orderly arranged EHD direct-written fibers. This technology overcomes the limitations of the resolution of fabrication and viscosity of ink of conventional inkjet printing, and represents major advances in manufacturing of flexible electronics.

1. Introduction

Flexible electronics represent a burgeoning technology that offers the electrical functions of conventional, rigid wafer-based microelectronics but with the ability to be stretched, compressed, twisted, bent, and conform onto arbitrary shapes.[1–7] It draws forth wide percussive applications such as flexible display,[8] flexible solar cell,[9] touch screen,[10] sensory skins and actuators,[11,12] implantable medical devices,[13] and soft robots,[14] etc., due to its unique characteristics of the large area,[15] lightweight,[16] deformability,[17] and roll-to-roll manufacturing.[10] Fabrication of these flexible electronics is usually based on lithographic patterning and undercut etching, which provides the most well-established routes for high performance electronics/optoelectronics. However, the choice of plastic substrates, which are the most attractive type of flexible substrates for plenty of applications, requires rather many extra concerns of the chemical or thermal degradation of the plastics. The complicated lithography and etching methods more or less involve of wet chemical etching by the use of hazardous etchants or heat tempering process that may damage the supporting substrates.[18–20] Additionally, the above methods are difficult to fabricate curved flexible electronics that can conform arbitrarily curved surfaces (e.g., biological organs[21,22]), without worrying about mechanical fatigue or any significant change in operating characteristics. Thus an electronics technology that extends fabrication from planar process to conformal process is as always highly desirable so as to overcome the fundamental mismatch in mechanics and form of the rigid and planar integrated circuits technologies that exist today.

Printing methods, which implement the depositing and patterning of functional materials in a digital, drop-on-demand manner, have attracted great attention in the fabrication of flexible electronics, for the solution-processable electronic materials provide enormous opportunities for the printing techniques. Inkjet printing has become a robust, effective, and powerful technique for electronic manufacturing due to its purely additive operation, compatibility with large-area substrates, low-temperature process, capability of conformal manufacturing, and cost effectiveness.[23,24] In the past decade, tremendous interests have been drawn toward inkjet printing of flexible electronics. Unfortunately, such technique encounters an obstacle that it is difficult to break through the resolution limitation of 20 μm and ink-viscosity range of 5–100 cps.[25] It is rather tough to fabricate high-resolution structures and devices (e.g., organic thin film transistor and the pixel of the flexible display), and is totally incompatible with highly viscous ink such as polymeric solution and silver paste. EHD printing, which adopts electrical force to pull the jet from the spinneret,
is considered as a next-generation inkjet printing technique, owing to its unique advantages of ultrahigh resolution for patterning and excellent compatibility with highly viscous inks. Such technique originates from people’s interest on the behavior of thin liquid jet in electric fields which contributes to the establishment of several famous theories, including Rayleigh Limit Theory[26] that a column of liquid will break up into droplets when its length exceeds its circumference and Taylor Cone Theory[27] that describes the deformation of small-volume liquid under the high electric field. EHD printing consists of three types of printing mode, i.e., EHD jet (E-jet) printing for small dots, EHD direct-writing for fine fibers, and electrospray for thin films, and it offers an attractive solution to resolve the limitation of the conventional inkjet printing systems. Sub-100 nm jet or droplet can be easily formed, even smaller than one thousandth of the nozzle orifice, making such technique the focal point of current research in printed electronics.[28–35]

EHD direct-writing enables directly depositing of nanofibers onto large-area substrates in an additive, non-contact, and reproducible manner. It is rooted in the traditional electrospinning that is rather versatile for preparing chaotic fibers with diameter from microscale to nanoscale.[36–39] A reasonable explanation for such chaotic nature is fully achieved by Reneker’s mathematical model,[40] and this method also brings in a new manner to study and control the EHD printing process. Recently, considerable improvements have been made in the precise deposition of high-aspect-ratio electrospun nanofibers with a controllable orientation and location. Large-scale microstructures based on micro/nanofibers can be easily direct-written. This ability to control individual or arranged micro/nanofibers has drawn great interest in the fabrication of flexible electronics. This work summarizes the ground-breaking research progress in EHD direct-writing technology, including the accurately control the position and morphology of micro/nanofibers, and the applications in fabrication of flexible electronics. Meanwhile, some limitations and the future development tendency will be discussed in the paper as well.

2. Evolution of EHD Direct-Writing

2.1. Basic Knowledge of EHD Printing

Contrary to the conventional inkjet printing, where the ink droplets are pushed out of the nozzle as required through thermal buckling or acoustic (Figure 1a),[41] the EHD printing is a “pull” processing as an extra electric field is employed, the resolution of which is improved significantly.[42–44] When a proper electrical potential is employed to the extraction electrode at the outlet of a nozzle, a liquid droplet with a stable shape would be formed as the balance of the gravity force $F_g$, the surface tension force $F_s$, and the electric field force $F_e$ (Figure 1b). If the potential is not too high, the droplet surface experiences a considerably electrostatic pull. The surface deformation is further triggered and the electric field results in charge concentration that will start to form a hemispherical liquid cone at the tip of the capillary. When the critical potential reached, the repulsive electrical forces overcome the surface tension forces, and the liquid cone will be distorted into a Taylor cone and form a liquid jet.[44] By carefully adjusting the ink flux (back pressure), the offset height, and the applied voltage or potential difference, three types of EHD printing (E-jet printing, EHD
direct-writing, and electrospray) can be realized via the same setup. The E-jet printing is based on a drop-on-demand operation of ink droplets, which can be driven by DC voltage, DC pulsed voltage, or AC-pulsed voltage (Figure 1c,f). It can produce droplets at least an order of magnitude smaller than the nozzle size, and complex patterns with high-resolution as small as sub-micrometer can be printed. EHD direct-writing is a straightforward, cost-effective and high-efficient method to print fibers with diameters ranging from several micrometers to tens of nanometers (Figure 1d,g), which overlaps contemporary textile fiber technology. Electrospray utilizes electrical field to disrupt the liquid cone for liquid atomization (Figure 1e,h), and large area thin films in nanoscale thickness could be easily fabricated.

As a novel additive direct writing technology, EHD direct-writing utilizes an external electrostatic force to draw fibers from a liquid polymer solution or melt. Generally, the applied voltage elongates the solution into a Taylor cone at the tip of a
spinneret and generates a cone-jet from the apex of the Taylor cone. The charged jet involves the rapid stretching and accelerates toward collector, then experiences a short stable straight segment near the tip of the nozzle, next suffers a catastrophic bending instability, which would forms a chaotic mat under a proper nozzle-to-collector distance.\cite{56,57} In the EHD direct-writing process, both of the stable straight and first whipping segments of the jet can be adopted to directly write orderly micro/nanostructures because of their relatively slow acceleration.\cite{57} This brings about the near-field electrospinning (NFES)\cite{58} when the distance from the spinneret to the collector is restricted within the straight segment, and the mechano-electrospinning (MES)\cite{28} or the helix EHD printing technique (HE-Printing)\cite{51} by extending to that of the first whipping segment. As the charged jet is ejected from the tip of the Taylor cone, the diameter of the jet is not limited by the inner diameter of the spinneret and can reach sub-micrometer or even nanometer scale, which shows much more advantages than other printed methods as shown in Figure 1i. Besides the cone-jet mode, several other jet modes would be formed by tuning the applied electric potential. Lee et al.\cite{59} had carried out a systematic investigation to finally find out the processing windows of the EHD printing, where 6D parameters were organized for the ethanol/terpineol mixtures, as shown in Figure 2. On account of the scientific and technical workers’ endeavors, the control of the orientation and position of deposited fibers has been significantly improved over the past decade. The EHD direct-writing technology provides a direct and efficient way to print micro/nanostructures with high-resolution patterns, which could highly fulfill the requirement in the development of all-printed electronics.

2.2. A Brief Chronology of EHD Direct-Writing

Since it is rooted in the traditional electrospinning, the evolution of EHD direct-writing technology approximately experiences three stages: the traditional electrosprinning for fabrication of nonwoven mat, the field-induced electrosprinning for assembly of aligned fibers, and the digital direct-writing that consists of NFES, MES, and HE-Printing for orderly arranged microstructures. A timeline outlining the major milestones toward the development of EHD direct-writing is depicted in Figure 3.

As the jet path of conventional electrosprinning is very chaotic,\cite{36} it is unable to fabricate microstructures in electronic devices where highly aligned architectures are required. To broaden its application in the field of electronic devices, many efforts have been devoted to improving the orderliness of electrospun fibers, and many methods have been developed through clever manipulation of the setup and solution composition since the early 2000s. Systems employing a dynamic collector such as a rotating wheels,\cite{60,61} rotating mandrel,\cite{62,63} or rotating drums,\cite{64,65} the large area of aligned fibers can be fabricated through dragging polymer jet out of the spinner. Theron et al.\cite{60} described the earliest alignment approach by introducing a grounded wheel-like bobbin, and nanofibers in parallel arrays with controllable average separation can be effectively assembled. Nevertheless, it is unable to retain high alignment at the same rotating speed when the electrospun fibers are thicker. By use of an electrostatic lens element and collection target of opposite polarity, the bending instability could be dampened and it enabled controllable deposition of sub-micrometer polymer fibers on a substrate.\cite{66} As the jet path is quite sensitive to the assistant electrical field, orderly straight\cite{67–71} or wave\cite{2,71} fibers can also be assembled via auxiliary electrodes. Li et al.\cite{71} used a collector consisting of a pair of parallel conducting electrodes to successfully fabricate uniaxial aligned nanofibers made of organic polymers, ceramics, and polymer/ceramic composites across the gap in between the electrodes. Such suspended nanofibers could be conveniently transferred onto other substrates for subsequent treatments and various applications. By replacing the parallel electrodes with parallel-positioned permanent magnets,
Yang et al. developed a facile and effective approach to fabricate well-aligned nanofibers arrays and multilayer grids through involving a magnetized polymeric solution with small amounts of magnetic nanoparticles. Even without adding magnetic particles, aligned straight and wavy electrospun fibers of different materials could have been prepared as well. These methods can fabricate an anisotropic alignment of active components, bringing in a group of new features and applications in electronics; however, depositing large-scale isolated electrospun fibers with controlled orientation, position, or quantity is still impossible to directly assemble electronic devices.

With a burning desire to further explore the possibilities of using electrospun nanofibers in fabricating micro/nanodevices such as FETs, researchers have proposed several direct-writing techniques since then. To improve the deposition accuracy of electrospun fibers, numerous analytical and experimental investigations have been conducted to study the fundamental physics and chemistry of electrospinning, such as applied voltage, electrode-to-collector distance, and substrate speed. A real sense of EHD direct-writing technique has appeared until Sun et al. developed NFES in 2006. Generally, the electrode-to-collector distance of NFES is kept in the range of 500 μm to 3 mm, and it allows sub-100 nm nanofibers deposition in a direct, continuous, and controllable manner with a relatively low potential. Since the polymer solution on the needle-tip (tungsten spinmeret, atomic force microscope tip) is consumed as the process proceeds, it is just able to create limited-area nanofiber patterns. Fortunately, this problem was well overcome by attaching a solution reservoir to the needle, and it is capable to create a large scale grid from electrospun fibers with a precision of about 250 μm. In 2010, Zheng et al. had built up a computation based on Maxwell viscoelastic theory to analyze the deposition behavior of single nanofiber via NFES. Borrowed the ideas from “Chinese kite” by involving mechanical drawing force and electric field force, Huang et al. developed an alternative method in 2012, named MES that improves the jet deposition accuracy by using a high-speed motion collector. The MES was able to fabricate straight fiber array with controlled diameter and position, orderly bead-on-string microstructures in a continuously tunable manner, and other sacrificial structures or polymer templates for micro/nanofabrication. Based on previous experimental researched on the fabrication of serpentine microstructures via electrospinning, Huang et al. presented a mathematical illustration of this type of printing mode named HE-Printing in 2017. It could individually manipulate the fiber flying in a helical manner and directly fabricate various serpentine nano/microfibers through a linear motion collector. The HE-Printing exhibits great potential in the fabrication of flexible and stretchable electronics. Now, the EHD direct-writing is able to fabricate not only 2D micro/nanopatterns but also 3D frameworks, through either solution or melt-based electrospinning. When multi-nozzle is adopted, much more efficient system can be achieved compared to the inkjet printing system. These achievements will no doubt advance the development of EHD direct-writing in flexible electronics manufacturing.

3. Applications via EHD Direct-Writing

As it holds the capability to controllable precision deposition of a single fiber that can be adopted as sacrificial/masking structures or fiber templates for micro/nanofabrication, and individual electronic component, the EHD direct-writing technique exhibits great potential in the fabrication of fiber-based micro/nanodevices. This effect greatly expands the application fields of traditional electrospinning, particularly the newly emerging flexible electronics, such as flexible displays, wearable devices, and so on.

3.1. Conducting Electrodes

Patterning of conducting electrodes on a sub-micrometer scale is quite essential to achieve high devices integration. Owing to its high-resolution, large-scale, fast preparation, and efficient material consumption characteristics, the additive EHD direct-writing technique has attracted growing interests in the fabrication of transparent, flexible/stretchable conducting electrodes recently. Pyrolysis of binding polymer and metal fiber-like precursors along with concurrent nucleation and growth of metal nanoparticles is the common strategy to prepared orderly aligned metal nanowire arrays or grids. After devoting tremendous efforts to examining many kinds of viscous binding polymers and Cu precursors, Lee et al. succeeded in transforming electrospun poly(vinylpyrrolidone) (PVP) and Cu(II) trifluoroacetate (Cu(CO2CF3)2, CTA) composite nanofibers into polycrystalline copper nanowire (CuNWs) based on EHD nanowire printing (ENP, another name of MES), shown in Figure 4a,b. The polymer and precursor components are decomposed in the air during the first step (500 °C, 1 h), leading to the formation of CuO nanowires as indicated by the energy dispersive X-ray spectroscopy (EDXS) spectra in Figure 4c. Then these CuO nanowires were transformed into CuNWs at 300 °C for 1 h under the hydrogen atmosphere. The diameter of single CuNW was around 710 nm and it had a resistivity of 14.1 μΩ cm, which is slightly higher than that of bulk Cu (1.68 μΩ cm). By replacing the composite of PVP/CTA with that of PVP/silver trifluoroacetate/CTA, silver nanowires (AgNWs) with an average diameter of about 695 nm and low resistivity of 5.7 μΩ cm had also formed after one calcination step under ambient (350 °C, 20 min). It should be noted that the addition of a small amount of CTA is quite essential to maintain the continuous structure of AgNW, because the formed CuO in the composite nanowires that has a high melting temperature (Tm ≈ 1326 °C) hinders the Ag agglomerated in the high temperature. Large-area highly aligned AgNW array with grid pitch size of 100 μm showed high transparency (94.7%), low sheet resistance (26.9 Ω sq−1), low optical haze (<1%) (at 550 nm, Figure 4d), and high thermal stability in the air (up to 350 °C). The cyclic bending test demonstrates that the electrodes that are transferred onto flexible substrate have superior mechanical flexibility (Figure 4f). By carefully tuning printing process parameters, metal nanowire array with stripe, grid, or wavy-curve patterns can be easily prepared. The aligned array had also been
applied to organic light-emitting diodes, transparent heaters, and touchscreen panels (Figure 4e).

As common sense, the thinner of grid filaments and narrower of pitch sizes, the better performance of metal grid based transparent electrode. So far, only very few approaches can achieve high-throughput preparation of high-quality, orderly aligned metal nanowires, meanwhile the pitch gaps are commonly above 100 µm as the limited motion accuracy of the motorized translation stage. Fortunately, Bai et al. [112] proposed a continuous draw spinning method to fabricate extra-long (in kilometers range) silver sub-micrometer fibers with the minimum diameter of around 200 nm from AgNO₃/PVP composite precursors, combined with a subsequent heat treatment (250 °C, 2 h) as shown in Figure 5a. This approach enabled the high-throughput (≈8 m s⁻¹) production of consecutive silver nanofibers, and the formation of uniform arrays with a pitch of down to 5 µm as shown in Figure 5d. It also enabled the generation of not only supported Ag nanofibers arrays film but also free-standing, suspended ultrathin fibers and patterns (Figure 5b,c). Systematic studies show that a higher solution viscosity would result in a larger fiber diameter, while its diameter decreased when the rotational speed of substrate increased for the enlarged shear stress (Figure 5e,f). Transparent electrodes based patterned silver fiber meshes exhibited high performance (7 Ω sq⁻¹ at 96%), remarkable flexibility and stretchability (a strain tolerance of 130%).

Highly aligned and patterned silver nanowires can also be produced by EHD printing of silver nanowires or nanoparticles suspension with polymer host matrix composite. [113–115] By means of MES, Lee et al. [113] had successfully aligned the AgNWs inside the electrospun AgNWs/Poly(ethylene oxide) (PEO) composite ribbon (Figure 6a–d), they found that the shear effect caused by the velocity distribution of the charged jet near the nozzle tip is one of the main factors for orderly aligning. Yang et al. [114] adopted NFES to synthesize anisotropic AgNWs from an AgNWs/PVP composite. When the applied electric field was over 1.4 × 10⁷ V m⁻¹, AgNWs were broken down into nanoparticles. The diameter of synthesized AgNWs/PVP fibers ranged from 500 nm to 10 µm, and the films could be used as transparent conductive electrodes for its superior conductivity (0.125 Ω sq⁻¹) and medium transmissivity (51–67%). A similar work had been carried out by Pan et al. [115] by using silver nanoparticles (AgNPs) and AgNWs sol-gel precursors. Straight electrospun AgNPs fibers were obtained via the NFES process with 10 kV applied voltage as shown in Figure 6e. The corresponding films with a thickness of 1.6 µm exhibited outstanding conductivity (0.032 Ω sq⁻¹), which was superior to the commercial indium tin oxide (ITO).

Orderly aligned electrospun fibers can serve as patterned substrates for the deposition of conducting materials as well. [116–118] Incorporated mesoscale metal wire (1–5 µm in diameter) into metal nanowire transparent conducting electrodes, Hsu et al. [116] achieved at least one order of magnitude reduction in sheet resistance at a given transmittance (Figure 6f). Luo et al. [117] had constructed polyvinylidene fluoride (PVDF) grid-structured template on paper via NFES as shown in

Figure 4. a) Schematic diagram of preparation of CuNWs array. Reproduced with permission. [109] Copyright 2014, Wiley-VCH. b) Digital image of pentacene FET with CuNWs electrode array on Si/SiO₂ substrate, scale bar:1 mm. c) Scanning electron micrograph (SEM) images and EDXS spectra of pristine PVP/Cu(CO₂CF₃)₂ composite nanofiber, CuO nanowire, and CuNW, respectively. d) Transmittance (at 550 nm) versus sheet resistance of AgNW arrays with other related transparent electrodes. Reproduced with permission. [110] Copyright 2016, Wiley-VCH. e) Demonstration of AgNW array-based TSP. f) Cyclic bending test of AgNW/PI and ITO/PET with bending radius of 7.5 mm.
After dipped coating of carbon nanotubes, the conductivity of the flexible electrodes could achieve $≈ 850 \text{ S m}^{-1}$, which is quite suitable for the current collector of flexible micro-supercapacitor.

### 3.2. Thin Film Transistor

Due to the inherent functions of switch and amplification in electronic circuits, field-effect transistors are one of the most important components in flexible electronics, in particular, the flexible active matrix organic light emitting display and epidermal electronics. Until now, tremendous efforts have been devoted to accelerating the pace of real applications of thin film transistors (TFTs), mainly focusing on the synthesis of high-quality semiconductors and the development of efficient integration techniques. Carriers mobility and current on/off ($I_{\text{on}}/I_{\text{off}}$) ratio are two critical parameters to evaluate the performance of a TFT. As the enhanced $\pi-\pi$ interaction along the wire axis and the subdued grain boundary blocking effect, a 1D semiconductor exhibits much more superior charge transport property compared to that of thin film. This fact makes electrospinning, a facile formation approach of individual nanofibers on a massive scale, rather appealing in the fabrication of high-quality 1D semiconductors for TFTs.

Since Pinto et al. proposed the first nanofiber-based semiconductor through electrospinning of a blend of camphorsulfonic acid doped polyaniline and polyethylene oxide, many interests have been attracted toward this type of TFTs in the past decade, particularly the appearance of orderly deposition electrospun nanofibers seen in Table 1. With a rotating collecting electrode, Liu et al. had fabricated a single aligned electrospun poly(3-hexylthiophene) (P3HT) nanofiber-based TFT as shown in Figure 7a,b. This transistor exhibited much more superior electrical transfer properties than that of randomly distributed nanofiber, with a hole mobility of $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the saturation regime and a $I_{\text{on}}/I_{\text{off}}$ of $10^3$ in the accumulation mode. This study drew great inspiration for the fabricating of 1D organic TFT since then. With a mixture solution of P3HT and poly($\varepsilon$-caprolactone) (PCL) in chloroform, Lee et al. had successfully collected uniaxial aligned P3HT/PCL semiconducting nanofibers between parallel metal wires (separated by $≈ 3$ cm). Based on such P3HT/PCL nanofibers and 1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide ([EMIM][TFSI])/PEO ionic-gel gate dielectric, they had fabricated high-performance flexible ion-gel gated organic TFTs with an average field-effect mobility $≈ 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $I_{\text{on}}/I_{\text{off}}$ of $10^5$, shown in Figure 7c. And the maximum on-current could be controllably adjusted by the number of collected nanofibers as shown in Figure 7d. When associated with the coaxial-electrospinning technique, well-aligned high-quality nanofibers with the uniform diameter and smooth surface could be fabricated, and this would result in a better electronic performance.

The above alignment methods of electrospun nanofibers indeed benefited the superior performance of fiber-based TFTs; however, the poor control of orientation and position, and low
uniformity of device characteristics on large-area arrays limited their wide application. This problem was well solved since the recent development of ENP as shown in Figure 8a.[80,110,131] The technique enabled controllable deposition of electrospun nanofibers with exact numbers of wires, their orientations, and their dimensions on the rigid or flexible device substrate without any transfer printing process. Large-scale complementary inverter circuit array could be directly created by precise deposition of well-aligned P3HT /PEO and poly{[N,N0-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,50-(2,20-bithiophene)}(N2200)/PEO electrospun nanofibers.[80] The devices exhibited the typical switching characteristic with a gain of $\approx 17$ (Figure 8b,f). The electrospun fibers can also be incorporated as patterned electrodes. By replacing the Au film with AgNW S/D electrodes, Lee et al.[110] fabricated an all-nanofiber-based transistor array with P3HT semiconducting nanofibers, AgNW S/D nanoelectrodes, and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFe)) gate insulator. The all-nanofiber FET exhibited a rather high field-effect mobility (average: $\approx 1.63$ cm$^2$ V$^{-1}$ s$^{-1}$, maximum: $\approx 2.08$ cm$^2$ V$^{-1}$ s$^{-1}$, Figure 8c,g).

Meanwhile, nanofibers can be served as sacrificial masks to fabricate TFTs with nanoscale channel length and channel width.[132–135] A single P3HT/PEO nanofiber FET with a ion-gel dielectric of poly(styrene-block-methylmethacrylate-block-styrene) (PS-P MMA-PS) triblock copolymer in an ionic liquid, [EMIM][TFSI], show a maximum carrier mobility of 9.7 cm$^2$ V$^{-1}$ s$^{-1}$ (average of 3.8 cm$^2$ V$^{-1}$ s$^{-1}$) and a high average $I_{on}/I_{off}$ of $1.70 \times 10^6$ (fiber diameter: 309 nm, source/drain gap: $\approx 300$ nm, shown in Figure 8d,e).[80] The dimension of micro/nanochannel is programmable and easily manipulated by tuning the process parameters such as the nozzle-to-substrate distance, applied voltage, and fluid supply, and can be fabricated on both Si wafer and flexible plastic substrates (Figure 8h).[134] The flexible small-channel organic TFT exhibits rather high mobility (0.62 cm$^2$ V$^{-1}$ s$^{-1}$) and $I_{on}/I_{off}$ ratio ($2.47 \times 10^6$), and excellent bending stability (120 cyclic bending tests of the device with a bending radius from 25 to 2.75 mm, shown in Figure 8i,j). With poly(9-vinyl carbazole) (PVK) nanofibers as etching masks, Xu et al.[135] provided a rapid, low-cost, and efficient method to fabricate large-scale-aligned graphene nanoribbons, which show significant gating effects and high on/off current ratio at room temperature. In perspective, the reliable EHD direct-writing technique would make it rather easy to fabricate large-area flexible small-channel organic TFTs which can be integrated into flexible and wearable devices in the near future.

### 3.3. Nanogenerators

Since the rapid development of wearable electronics and the limited battery life, flexible nanogenerators (NG) that harvest...
Semi./nanofibers field-effect transistors.

<table>
<thead>
<tr>
<th>Year</th>
<th>Semiconductor</th>
<th>Aligning technique</th>
<th>Dielectric material</th>
<th>Fiber Dia. [nm]</th>
<th>Channel len. [µm]</th>
<th>Meas. condition</th>
<th>Av. mobility [cm² V⁻¹ s⁻¹]</th>
<th>Av. I(on)/I(off)</th>
<th>Ref.</th>
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<tr>
<td>2003</td>
<td>PANI/PEO</td>
<td>Electrospinning: disorder</td>
<td>200 nm Si/SiO₂</td>
<td>300</td>
<td>12</td>
<td>297 K, Vacuum</td>
<td>1.4 × 10⁻⁴</td>
<td>2</td>
<td>[124]</td>
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<tr>
<td>2005</td>
<td>P₃HT/T (PCL (20 wt.%)</td>
<td>Electrospinning: disorder</td>
<td>200 nm Si/SiO₂</td>
<td>670</td>
<td>=54</td>
<td>300 K, 5 × 10⁻⁴ Torr</td>
<td>4 × 10⁻⁴</td>
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<td>[125]</td>
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<td>2005</td>
<td>P₃HT/T</td>
<td>Electrospinning: aligned by rotating collector</td>
<td>150 nm Si/SiO₂</td>
<td>180</td>
<td>10</td>
<td>297 K, 10⁻⁴ Torr</td>
<td>0.03</td>
<td>10³</td>
<td>[126]</td>
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<td>P₃HT/T/PCL (20 wt.%)</td>
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<td>200 nm Si/SiO₂</td>
<td>500</td>
<td>10</td>
<td>Ion-gel package</td>
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<td>10²</td>
<td>[127]</td>
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<td>2010</td>
<td>P₃HT/T/PCL (20 wt.%)</td>
<td>Electrospinning: aligned by parallel metal wire</td>
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<td>=400</td>
<td>10</td>
<td>Ion-gel package</td>
<td>=2</td>
<td>10³</td>
<td>[128]</td>
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<td>200 nm Si/SiO₂</td>
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<td>25</td>
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<td>0.192</td>
<td>4.45 × 10⁴</td>
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<td>194</td>
<td>19.1</td>
<td>N₂-filled glovebox</td>
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<td>1.3 × 10⁵</td>
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<td>EHD direct-writing</td>
<td>100 nm Si/SiO₂</td>
<td>=780</td>
<td>50</td>
<td>Ion-gel package</td>
<td>0.015</td>
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<td>PMMA</td>
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<td>50</td>
<td>Ion-gel package</td>
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<td>[EMIM][TFSI]/PS-PMMA-PS</td>
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<td>3.8</td>
<td>1.70 × 10⁷</td>
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<td>P₄HT/PEO</td>
<td>EHD direct-writing</td>
<td>500 nm P(VDF-TrFe)</td>
<td>=695</td>
<td>100</td>
<td>Ion-gel package</td>
<td>1.63</td>
<td>–</td>
<td>[110]</td>
</tr>
</tbody>
</table>

IZO film (AgNWs S/D)  
Pentacene film (AgNWs S/D)

energy from mechanical vibration of building, automobiles, appliances, and human movements have drawn tremendous attention recently. Achieving efficient conversion of mechanical energy into electricity is, as always, the endless impetus in searching or designing applicable structural materials toward NG. Up to now, kinds of materials are developed to satisfy the construction of high-performance NGs, including ZnO nanowire arrays, lead zirconate titanate (PZT) nanofibers, BaTiO₃ nanomaterials, and piezoelectric PVDF nanofibers, etc. Combining a transferring process with electrospinning, Chen et al. reported a piezoelectric NGs based on laterally aligned electrospun PZT nanofibers that perfectly attached onto polydimethylsiloxane (PDMS) substrate, shown in Figure 9a. When a pressure was applied to the film, a combined tensile and bending stresses in the PZT nanofibers would be generated. These stresses would induce charge separation in nanofibers, then finally formed a potential difference between two adjacent electrodes. The power output of NG could be enhanced if interdigitated electrodes were chosen, and the piezoelectric nanofibers between each pair of adjacent electrodes were connected in parallel. The PZT NGs could produce an output voltage of 1.63 V and power of 0.03 µW under periodic stress. On the basis of a vertically aligned electrospun PZT nanofibers array, Gu et al. proposed newly type integrated flexible NG with ultrahigh output voltage of 209 V and the current density of 23.5 µA cm⁻², which could instantaneously light up a commercial light-emitting diode (LED) without any other power supply (Figure 9b). To make clear of the effects of nanofibers orientation to the average output signal of NG, Yan et al. had carried out comparison experiments among three types of arranged electrospun BaTiO₃ nanofibers array (randomly aligned: BTNF-R, horizontally aligned: BTNF-H, vertically aligned: BTNF-V, seen in Figure 9c). The average output voltage was around 0.56, 1.48, and 2.67 V for BTNF-R, BTNF-H, and BTNF-V, respectively. The highest output voltage of BTNF-V possibly originated from much more efficient poling and rather a large amount of electric charges accumulation on the electrodes due to their ceramic density and compliant to mechanical stress. The NG with BTNF-V could achieve high piezoelectric performance (P(output): 0.1841 µW, V_max: 2.67 V, I_max: 261.40 nA) under a low mechanical stress of 0.002 Mpa, and the harvested energy was able to directly power a commercial LED. Among the existing piezoelectric materials, PVDF and its derivatives won the most attention in the fabrication of flexible or stretchable NGs. Generally, a higher content of the PVDF would enhance the output performance of NG, and Yan et al. directly deposited a piezoelectric NG based on electrospun PVDF nanofibers on flexible working substrates with in situ mechanical stretching and electrical poling as shown in Figure 9d. As the strong electric fields (∼10⁷ V m⁻¹) and stretching forces led to plenty of nonpolar α phase dipoles (random orientation) in the nanofiber crystal were transformed into polar β phase, inducing a significant enhancement in the polarity of the electrospun PVDF nanofibers. A typical electrical output of more than 50 tested NGs were 5–30 mV and 0.5–3 nA as the substrate was bent by an axial stress. The electrical
outputs of piezoelectric response exhibited positive correlation versus the numbers of aligned nanofibers. Such NGs exhibited various advantages such as high energy conversion efficiency (12.5%), manufacturability, and the capability of integration with other micro/nanofabrication processes, attracting them great attention as a renewable integrated power source for future wearable electronics.[137,139,141,152,159,161]

3.4. Strain and Pressure Sensors

Micro/nanoscale electronic devices with outstanding flexibility or stretchability have attracted increasing interest in recent years for a range of new applications, such as epidermal health monitors or motion detectors.[4,5,164–167] Since they can exploit deformations induced by small forces, through pressure, mechanical vibration, elongation/compression, bending or twisting, conductive and piezoelectric fibrous polymers demonstrate superior performances and occupy a dominant position in this area, and the orderly arranged fibers arrays commonly show a better performance than non-woven mats or isolated strands.[51,95,162,168–170]

By virtue of the basic piezoelectric effects, flexible/stretchable pressure or strain sensors can be constructed with PVDF nanofibers arrays.[171–173] For instance, Persano et al.[162] prepared a pressure/force sensors with ultrahigh sensitivity for pressure measurement using well-aligned electrospun P(VDF-TrFe) nanofibers that collected by a rotating disk (Figure 10a,b). Due to the mesoscopic joints between aligned fibers, the mechanical property and flexibility of the nanofibrous film have been significantly enhanced (Figure 10c). As the preferential longitudinal alignment of the main molecular chains and the enhanced transversal orientation of piezoelectric active dipoles along a P(VDF-TrFe) fiber, flexible piezoelectric sensors based on such nanofibrous arrays reveal a large response to even small applied pressures (down to ≈0.1 Pa, Figure 10d). When the fiber arrays are exposed to dynamic bending experiments, a periodic alternation of positive and negative output peaks would be measured, and there is no significant changes in output voltage or current up to 1000 cycles of bending and relaxing, showing their great potential application in flexural sensors (Figure 10e). Besides, the P(VDF-TrFe) fiber arrays could also be applied to other sensory applications, such as detecting environmental vibrations induced by sound pressure levels of 60–80 dB (Figure 10f) and acting as an orientation sensor on a inclined plane with variable angle (Figure 10g). Similarly, an aligned microfibrous arrays of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)-PVP

Figure 7. Chemical structure, fluorescence and SEM images of a) P3HT nanofiber, and b) the corresponding \( I_D \) versus \( V_D \) curves of the fiber-based FET with effective channel length of 10 \( \mu \)m and diameter of 180 nm. Reproduced with permission.[126] Copyright 2005, AIP Publishing. c) Photograph of an array of transistors on flexible substrate, and the output transfer characteristics (\( I_D \) vs \( V_G \)) of individual FET based on P3HT nanofibers, as well as d) the maximum \( I_D \) versus the number of fibers. Reproduced with permission.[128] Copyright 2010, American Chemical Society.
Such composite fibers demonstrate a high room-temperature conductivity of $1.6 \times 10^{-5}$ S cm$^{-1}$, and a good linear elastic response to strain up to 4%, as well as excellent repeatability and durability. This exhibits potential applications in some fields such as soft robotics and elastic semiconductors.

The development of electronic systems that could offer elastic responses to large strain deformations ($>100\%$) is quite essential to make them bendable, stretchable, or twistable. Up to now, by adopting an island–bridge design and buckled/serpentine/self-similar interconnect is the dominating strategy to achieve such goal. On account of the overall adhesion reliability, encapsulation simplicity, and deformable capacity, in-surface buckled (serpentine/self-similar) structures exhibit much more superior performance and attract rather greater people’s attention. However, producing such structures in a low-cost, high-efficiency, and controllable manner is still very critical. By using MES to direct-write and in-situ polarize straight PVDF nanofibers onto a prestrained PDMS substrate, fibers array with out-of-surface (normal-to-surface/incline-to-surface) and in-surface buckling modes could be easily fabricated when the prestrained substrate is released (Figure 11a,b).[95,161] Both experimental and finite element analysis (FEA) results show that the buckling behavior is mainly
determined by the cross-section of a micro/nanofiber, less dependence on the material properties (Figure 11c). And in-surface buckling mode is always favorable for cross-sections having equal moments of inertia in two directions, e.g., circular and square (Figure 11d). While a changing point may exist by comparing the critical buckling strains in different directions for most other sections that have unequal moments of inertia. Stretchable piezoelectric devices with a highly synchronized serpentine fibers array could be easily formed, the in-surface deformation and stable piezoelectric performance of which can be maintained up to the failure strain of PDMS ($\approx 110\%$). Since their output current increase with the applied strain and remain approximately constant during the cyclic stretch-release, the buckled fibers can be used for strain sensors as well (Figure 11g).

Due to their large deformation capability, self-similar structures are rather favorable for stretchable electronics. However, challenges still exist for low-cost, high-efficiency, and controllable manufacturing. Recently, a HE-printing has been proposed to realize controllable direct-writing of large area, highly aligned serpentine micro/nanofibers by introducing the rope coiling effect into printing process, which shows great capability in the versatile and rapid fabrication of flexible/stretchable electronics.\(^{[52]}\) By adopting such technique in combination with in-surface self-organized buckling, hyper-stretchable self-powered sensors have been successfully fabricated using aligned self-similar PVDF nano/microfibers on PDMS substrate (Figure 11h).\(^{[51,168]}\) During the preparation of self-similar structures, distinct buckling behaviors and modes on compliant substrates have been observed under specific conditions. After systematic experimental and theoretical investigations, it revealed that the buckling mechanics of serpentine microfibers are mainly governed by the magnitude and direction of prestrain, the geometry of a serpentine fiber, and the fiber cross-sectional geometry. Except for the fiber cross-sectional geometry as similar as the straight fiber, a critical angle ($\theta_0$, angle between the fiber segment and the direction of the uniaxial prestrain as shown in Figure 11e) or a proper ratio ($\phi = \varepsilon_{\text{prey}}/\varepsilon_{\text{prey}}$, ratio of the orthogonal parts of a applied biaxial strain as shown in Figure 11f) should be achieved to buckle the deposited wavy-shaped fibers to form self-similar shapes. The self-similar structures can always increase the tensile ability by decreasing the strain level inside compared with the initial serpentine structures. The optimal device exhibited excellent performance with the high stretchability of over 300%, the low detection limit of 0.2 mg, and excellent durability of more than 1400 times at strain 150% (Figure 11i). In summary, the collective results demonstrated that electrospun nanofibers could be constructed into a variety of sensory components, with attractive mechanical properties and potential for implementation over large areas at low cost, as well as application opportunities in wearable electronics such as human gesture recognition and motion monitoring.\(^{[152,179]}\)
Compared to bulk materials or 2D systems such as thin films, electrospun nanofibers revealed much enhanced performances in terms of charge and energy transport as well as thermal dissipation due to the 1D anisotropic structures of rather large length-diameter, making them ideal building blocks for many optoelectronic applications from light generating [180–187] to guiding or detecting [184,188–191].

In the last two decades, great attention has been drawn toward light-emitting nanofibers (LENFs) for their unique properties, especially for nanoscale dimension light emission [181,192–194] and optical anisotropy [195]. By electrospinning of ionic transition metal complexes [ruthenium(II) tris(bipyridine)] embedded in PEO ([Ru(bpy)3]2+(PF6)2/PEO), Moran-Mirabal et al. [196] achieved localized electroluminescence in the visible (λmax ≈ 600 nm) from electrospun nanofibers between two adjacent electrode fingers, shown in Figure 12. As the size of the light source is determined by the inter-electrode spacing, they can realize a point light source as small as 240 × 325 nm² (Figure 12c). These light sources should be easily integrated into micro/nanofluidic devices for on-chip illumination if the precise positioning of electrospun nanofibers could be realized. Similarly, Yang et al. [193] adopted coaxial-electrospinning to realize the direct fabrication of 1D electroluminescent device, a single core–shell organic LEDs (OLEDs) with a galinstan liquid metal core cathode, a [Ru(bpy)3]2+(PF6)2/PEO shell electroluminescent layer, and an ITO anode layer that deposited by evaporation as shown in Figure 12d. Such 1D polymer light sources are flexible, lightweight, and conformable, and they exhibit great potential in applications of bioimaging, high-resolution microscopy, and flexible panel displays if large-scale high-quality well-aligned LENFs are widely available.

Since Camillo et al. [184] introducing near-field electrospinning of LENFs as shown in Figure 12e, the limitation to precise positioning and integration of LENFs was well overcome. Light emission in the visible (λmax = 600 nm) from electrospun nanofibers between two adjacent electrode fingers, shown in Figure 12. As the size of the light source is determined by the inter-electrode spacing, they can realize a point light source as small as 240 × 325 nm² (Figure 12c). These light sources should be easily integrated into micro/nanofluidic devices for on-chip illumination if the precise positioning of electrospun nanofibers could be realized. Similarly, Yang et al. [193] adopted coaxial-electrospinning to realize the direct fabrication of 1D electroluminescent device, a single core–shell organic LEDs (OLEDs) with a galinstan liquid metal core cathode, a [Ru(bpy)3]2+(PF6)2/PEO shell electroluminescent layer, and an ITO anode layer that deposited by evaporation as shown in Figure 12d. Such 1D polymer light sources are flexible, lightweight, and conformable, and they exhibit great potential in applications of bioimaging, high-resolution microscopy, and flexible panel displays if large-scale high-quality well-aligned LENFs are widely available.

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luminance at the same current density, maximum current efficiency (100.1 cd A$^{-1}$, ITO-based: 86.3 cd A$^{-1}$), and maximum external quantum efficiencies (25%, ITO-based: 20.7%).$^{[110]}$ By high-speed large-area fabrication and precise positioning of PVK fiber pixel separator arrays, Cho et al.$^{[198]}$ had realized precise, chemical-free, and low-cost pixel patterning of large-area flexible OLED displays with high resolution and throughput.

### 3.6. Photodetectors

Since their high specific surface areas, a wide range of spectral responses, plentiful categories, etc., great interests have been paid to electrospun nanofibers for high-performance photodetectors.$^{[199–207]}$ Compared with nonwoven mat nanofibers films, photodetectors based on highly aligned nanofibers array exhibit higher photoconductivity and faster response speed.$^{[208,209]}$ By means of NFES, Liu et al.$^{[204]}$ demonstrated an all-printable ZnO granular nanofibers (GNFs) array ultraviolet (UV) photodetector on polyimide substrate after calcination of electrospun zinc acetate/PVP nanofibers array (Figure 13a–d). A device with five GNFs array demonstrated four orders of magnitude selectivity for 365 over 600 nm wavelength as shown in Figure 13e. Systematic investigations showed that their ZnO nanofiber photodetector revealed superior excellent performance including high internal gain ($2.6 \times 10^7$) and responsively ($7.5 \times 10^6$ A W$^{-1}$) at low bias (+1 V), and ultrahigh detectivity ($3.3 \times 10^{17}$) (Figure 13f). They found that the unique band-edge modulation along the GNF axial direction resulted in such excellent performance. In order to broaden the spectral response range of ZnO from UV to visible light, Zheng et al.$^{[205]}$ carried out a further research by fusing CdO into ZnO nanofiber. The obtained
polycrystalline ZnO-CdO hybrid nanofibers exhibited a mixture absorption property of pure ZnO and CdO nanofibers, the array of which could be assembled into fully transparent (95%), wide spectral response range (400–800 nm), fast response speed (3 s), and high stable flexible UV-vis photodetector (Figure 13g,h). Figure 13i shows that the photodetector can withstand a bending radius of 10 mm while maintaining its original properties even after 200 bending cycles.

As heterostructures enable spatial separation of the photo-generated carriers, incorporating such structures into photodetectors could significantly improve the photoelectric properties.[210–214] Tian et al.[210] had fabricated ZnO-SnO2 heterojunction nanofibers by thoroughly calcination of electrospun Zn(NO3)2/SnCl2/PVP precursor composite nanofibers. The heterojunction nanofibers can be applied to fully transparent high-performance photodetectors for the high UV-sensitivity and photo-dark current ratio, and fast response speed characteristics, showing great potential in the application of the visible-blind UV-light sensor. Huang et al.[211] had designed and constructed a highly transparent (>85%) heterojunction photo-diode by precisely aligning SnO2 nanobelts on top of NiO thin film. The formed heterojunction exhibited a distinct rectifying characteristic and an ultrahigh photosensitivity of up to 105 with accelerated response speed under reverse bias. Nie et al.[212] found that an interfacial electron collection layer of aligned TiO2 nanofibers could significantly enhance the performance of inverted organic photodetectors. The detector exhibited an ultrahigh detectivity of 2.93 × 1013 at zero bias and a quite short rise time of 2.3 µs. That is because the better crystallization of the aligned TiO2 nanofibers array facilitated charge separation at the organic–inorganic interface and electron transport within the interfacial layer. To sum up, these developed EHD direct-writing techniques pave the way for efficient high-performance flexible and portable photodetector fabrication in the future.

3.7. Nonvolatile Memories

As nanoscale in size nature of electrospun fibers, they have attracted great attention in the field of memorizer because of the high-density integration potential.[91,215–219] Xu et al.[91] adopted MES to synthesize 2D arrays of perpendicularly aligned PVP/CTA nanofibers. After two-step calcination, individually conductive CuNWs were produced along with a nanometer-scale CuO layer sandwiched at the junction, which was confirmed by the elemental distribution analysis (Figure 14a–d). As shown in Figure 14e,f, this CuNW-CuO-CuNW array exhibited reproducible resistive switching behavior, high on/off current ratio (Ion/Ioff ≈ 106) and stable data retention time (>2 × 104 s). Flexible memorizer could be realized by the adoption of wave-like polymer nanofibers precursor. He et al.[216] reported a single Ni/NiO core–shell electrospun nanowire based resistive-switching (RS) memory. The memory resistive-switching is triggered by a high Icc, while the threshold RS appears by setting a low Icc. Interesting, the reset process is achieved...
without setting an $I_{CC}$. Cagli et al.\[215\] had also achieved a RS crossbar memory based on Ni/NiO core–shell nanowires. Chang et al.\[217\] presented flexible organic memories on polyethylene naphthalate substrate using 1D electrospun nanofiber of P3HT:Au nanoparticles (AuNPs) hybrid as the channel (Figure 14g,h). The P3HT:Au-CF$_3$ hybrid nanofiber channel as potential wells led to the charge being stored or erased by applying appropriate gate voltage. The flexible transistor memories had low operation voltages (±5 V), large threshold voltage shifts (3.5–10.6 V), long retention ability (up to 10$^4$ s) and good stress endurance (>100 cycles).

Jian et al.\[218\] used a single electrospun poly(4-vinylpyridine) nanofiber as an additional dielectric in organic field-effect transistors to significantly enlarge the on/off current ratio (>10$^6$), demonstrating a high-performance nonvolatile memory. Hwang et al.\[219\] fabricated non-volatile ferroelectric memories with orderly aligned P3HT nanofiber channel and ferroelectric P(VDF-TrFe) insulator.

### 3.8. Chemical Sensors

Compared to randomly distributed nanofibers films, chemical sensors based on controlled orientation or position nanofibers array exhibit not only much higher sensitivity that originates from a high yield of contacts and a much larger specific surface area\[220–222\] but also stronger potential in high-intensity devices integration.\[223,224\] With a sequential process of sputtering deposition of ZnO and calcination removal of polymer core, Choi et al.\[221\] succeeded in preparation of hollow ZnO fibers with the wall thickness in a range from 100 to 40 nm using electrospun polyvinyl-acetate fibers as sacrificial templates. Thanks to their high surface area schematically depicted in Figure 15a, the hollow ZnO fibers film exhibited much higher sensitivity than reference ZnO thin film specimens. Interestingly, the quasi-aligned fibers were more sensitive than their disorder counterparts toward NO$_2$ sensing, presumably due to the high yield of electrical contacts, shown in Figure 15b. A similar work was carried out to align ZnO nanotubes for H$_2$ sensing.\[222\] The sensitivity of such aligned nanotubes sensor toward 100 ppm H$_2$ would increase from 2.3 to 3.6 when the temperature increased from 200 to 400 °C, and it also shows an increase in sensitivity compared with that of the ZnO film.

Precise deposition of electrospun fiber could benefit the integration of sensors arrays as well as their sensing properties. A micropatterned ZnO nanorods array gas sensor had been fabricated from zinc acetate (ZnAc)/PEO composite via MES as shown in Figure 15c.\[223\] Figure 15d shows that the ZnO nanorods array has a good ohmic behavior and high response toward oxidizing gas NO$_2$ at low concentrations (1–100 ppm, at 225 °C), and demonstrates rather fast response and recovery time. By taking account of the preparation parameters such as
Figure 14. a) SEM image of CuNWs cross junction and b) TEM image of cross-sectional view of junction site. c,d) Electron energy loss spectroscopy elemental mapping of the intersection of CuNWs junction (green: Cu, red: C, yellow: O). e) The I–V curves for the resistance switching behavior of cross-shaped CuNW resistive memory. Retention of ON/OFF states of f) the cross-shaped CuNW and h) the hybrid nanofibers based memory device. Reproduced with permission.[91] Copyright 2016, Wiley-VCH. g) Schematic diagram of the P3HT: Au-CF3 hybrid nanofibers based flexible transistor memory devices and the corresponding TEM image of hybrid nanofibers. Reproduced with permission.[217] Copyright 2013, Wiley-VCH.

Figure 15. Schematic illustrations of the NO2 adsorption on the electronic transport properties of a) ZnO planar thin films and aligned hollow fibers, and b) the resistance response R/R0 during cyclic exposure to increasing concentrations of NO2 at 350 °C. Reproduced with permission.[221] Copyright 2009, American Chemical Society. Schematic diagram of c) the growth process of aligned ZnO nanorods array and variation of sensitivities, response and d) recovery times of the ZnO nanorods array sensors at different concentrations of NO2. Reproduced with permission.[223] Copyright 2015, Royal Society of Chemistry.
the growth time, the solution concentration, the nature of the precursor layer, and the deposited pattern, further investigations were carried out to synthesize hierarchical ZnO nanorods array. It demonstrated that an optimal seed concentration of ZnAc is required for fast response, and the distribution of hierarchical nanorods is sensitive to the MES deposition process, finally affecting the NO2 sensing performance. On the basis of the optical response of waveguiding polycrylamide nanofibers when exposed to specimens, a group of high-performance optical humidity/gas sensors have been achieved as well. As the superior performances of array sensor are mainly attributed to the unique structures of electrospun fibers themselves, introducing of novel nozzles, such as multi-nozzle, coaxial nozzle, blow-assisted electrospinning, and parallel nozzle to control fiber morphology is a widely accessible inspiration in the preparation of high-performance sensors. Undoubtedly, combining these specific nozzles with EHD direct-writing technique, it would provide a digital, low-cost, and mask-free manufacturing approach for the preparation of superior low-power sensor arrays (so-called electronic nose) on desired substrates.

3.9. Bioelectronics

Since their plenty of available binding sites for biological recognition element immobilization, fast mass transfer rates, and facile surface functionalization of various groups, electrospun nanofibers have demonstrated rather a high potential in biological applications, including biosensors, drug delivery, water treatment, or tissue engineering. Precise deposition of fiber arrays is essential in determining the functionalities of biomimetics devices and provides great versatility for incorporation into multiplexed, portable, wearable, and even implantable medical devices. Micro/nanofluidic is a key issue technology for biological analysis and basic cell biology, and rapid, high-efficiency and cost-effective fabrication of complex footpaths with a resolution in micrometer/nanoscale are highly demanded. As electrospun fibers can serve as sacrificial templates on a variety of soft, transparent, flexible, and biocompatible polymers as shown in Figure 16a. EHD direct-writing provides a rather facile and low-cost way to fabricate large-scale well-defined channels that can be easily integrated into lab-on-chip devices, replacing the complex and expensive lithographic techniques. By selectively washing away the electrospun fibers, Vempati et al. had successfully fabricated aligned microtubes/microchannels onto a self-standing flexible polymer film, showing great potential for tissue engineering. Bellan et al. used sacrificial water-soluble PEO nanofibers embedded in PDMS to form nanofluidic channels for single molecule observation and manipulation (Figure 16b). Similarly, nanofibers made of a heat-decomposable material were also adopted to construct nanofluidic channels. To serve electrospun nanofibers as shadow mask, chip-to-chip micro/nanofluidic channels with the inner diameter of 50 nm–5 μm could be fabricated to connect two separated chips as well. Single molecule studies could be realized by the use of isolated hollow nanofibers, which were produced either using coaxial electrospinning or evaporation of material around a sacrificial core nanofiber. Moreover, suspended hollow nanofibers could be served as a nanoscale resonator containing fluids, which is extraordinarily useful for performing small mass measurements in solution. Highly aligned electrospun fibers also exert a widespread potential application in biomedical engineering. Fuh et al. succeeded in controlling the human embryonic kidney cells orientation on well-aligned electrospun chitosan nanofibers arrays. By means of direct-writing melt electrospinning. Brown et al. prepared 3D complex porous lattices of PCL fibers with dimensions that allow cell and tissue invasiveness. Recently, by using PEO sheath wrapped around P3HT core nanofibers, Xu et al. designed and fabricated an artificial synapse with gate voltage spikes served as presynaptic spikes (output current corresponding to postsynaptic current) in the biological synapse, shown in Figure 16d. Single short-gate negative spike (−1 V, 50 ms) would trigger an excitatory postsynaptic current with an amplitude of ≈4 nA, which is because the accumulation of anions near core–shell nanofibers that soaked in ion gel induced holes in the channel. An increase in the number of presynaptic spikes (so-called long-term plasticity) resulted in synaptic strength and tended to greatly increase electrical responses of neurons to stimuli (Figure 16e). In particular, the artificial synapse for individual nanofibers exhibited an ultralow energy consumption of ≈1.23 fJ per synaptic event (Figure 16f). This achievement is a significant step toward fabrication of brain-inspired electronic devices and presented important inspiration for the development of high-density and soft brain-inspired computational systems with low-power consumption. By adopting a low-voltage electrospinning patterning, Li et al. had realized the direct printing of living bacteria and protein on a range of substrates, from conducting to insulating in nature, and from hydrogels to solids as well. If other novel nozzles such as multi-nozzle were introduced to control fiber morphology, perhaps much more science-fiction biological electronic devices would be created out to further broaden the nanofiber-based future electronics.

4. Conclusions

In this review, we summarized the ground-breaking research progress in this field EHD direct-writing, including the brief chronology of EHD direct-writing techniques, basic principles and alignment strategies, and applications in flexible electronics (e.g., sacrificial templates, fiber precursors, and individual electronic components). The encouraging achievements highlighted in this article have indeed demonstrated its unique advantages in controllable deposition and feasible integration of individual or arranged micro/nanofibers. EHD direct-writing demonstrates a rather excellent compatibility with highly viscous inks, even silver paste (100 000 cps) can be directly printed into sub-micrometer fiber on flexible substrates (PET, metal foil, glass foil). Interest in EHD direct-writing has also been driven by its potential to directly fabricate more elaborate micro/nanostructures, such as the mask for high-resolution lithography (=100 nm) in thin film transistor fabrication and serpentine fibers for ultrastretchable sensors, with a large area and high throughput on substrates from rigid to flexible, planar to...
curved, which is rather difficult for the conventional manufacturing process. Furthermore, characterized by its non-contact, additive and reproducible processing, and environmentally friendliness, it provides a high-efficiency and cost-effective solution-processable technique to satisfy the increasing demands of large-scale flexible electronics manufacturing.

Despite recent rapid progress, a continuing need exists for further development to turn EHD direct-writing technique into a reliable fiber manufacturing candidate for a variety of functional applications in nanostructures and devices. Future advances are potentially carried out from the following aspects: (1) deep researches on EHD direct-writing mechanism including theoretical simulation and path planning technology to compensate the resulting error; (2) comprehensive combination of EHD direct-writing with novel nozzles to develop devices with innovative concepts and structures; (3) further extending of the EHD direct-writing technique to print 2D/3D microdevices onto non-planar irregular platform; (4) industrial-scale digital manufacture of nanofiber-based electronics would be accompanied by development of materials, process, and equipment.

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The authors declare no conflict of interest.

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