Polymer Nanofibers via Electrospinning for Flexible Devices

Subhash B. Kondawar, Chaitali N. Pangul, and Mahelaqua A. Haque

Abstract Flexible devices promise numerous applications in modernization of human life. Accompanying flexibility into planar devices has greatly improved the applicability of the devices. Electrospun polymer nanofibers have shown the major breakthrough due to their high flexibility overcoming the rigidness of the conventional planar devices. Due to innovative methods and manufacturing processes of novel materials, the flexible devices enabled the design of new architectures that are not possible with conventional planar devices. Novel synthesis techniques for flexible nanofibers have bright future prospects toward academic studies and research in one-dimensional nanomaterials. Electrospun polymer nanofibers have emerged as exciting one-dimensional nanomaterials and empowered as a building material into flexible devices. Tremendous efforts have been focused on exploring the electrospun nanofibers for potential functional applications. Electrospun polymer nanofibers with embedded nanoparticles can be easily fabricated to be used for flexible devices by electrospinning technique. The purpose of this chapter is to explore the capability of electrospinning to fabricate various polymer nanofibers for flexible devices. In this chapter, the fabrication of electrospun polymer nanofibers and their potential applications in flexible devices including light-emitting diodes (LEDs), sensors, UV photodetectors, transparent electrodes and nanogenerators are systematically reviewed along with challenges in synthesizing and designing nanofibers for flexible devices.

Keywords Flexible devices · Polymers · Nanofibers · Electrospinning

1 Introduction

The word "nano" has become familiar with almost each and everyone in today's world due to large-scale miniaturation of our daily life utilities. This has not only helped in incorporation of multifaceted components but also increased their functionability, durability, and efficiency. The nanostructure materials are better than

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their bulk counterparts in terms of their physical, chemical, physiochemical, electrical, magnetic, thermal, optical, biological, catalytic, or mechanical properties. The past decades have witnessed tremendous research being carried out in the field of nanoscience and technology. This has offered nanomaterials an extensive application in medicine, biology, textiles, and electronics [1, 2]. Nanomaterials can be broadly classified on account of quantum confinement as 0D (quantum dots), 1D (quantum wires), and 2D (quantum wells). Among these broad spectrum of nanomaterials, one-dimensional (1D) materials became attractive candidates for many advanced applications. One-dimensional (1D) nanostructures especially nanofibers are continuous with sufficient length, high aspect ratio (length to diameter) and extreme flexibility as compared to that of other 1D materials including nanotubes, nanowires, nanorods, etc. Apart from these advantageous, the multiple extra functions incorporated into nanofibers can enhance their structural and mechanical properties beneficial for wide variety of applications [3, 4]. Owing to this specialty, nanofibers have gained popularity as smart materials in designing flexible electronics including cells, displays, telecom, sensors, medical, and memories (Fig. 1) [5]. This quest has led researchers in search of flexible devices that are based on polymer nanofibers. Flexible electronics currently became the topic of interest to modify devices as per requirement

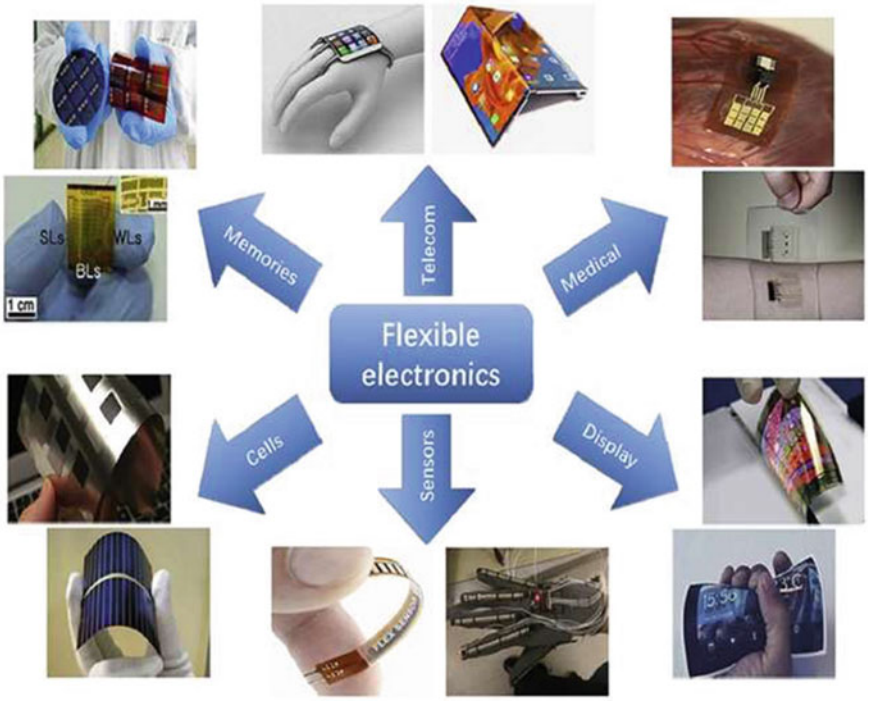

Fig. 1 Applications of flexible electronics (Reproduced with permission from Ref. [5], Copyright (2020) Elsevier)

owing to the stretchability and foldability of the nanofibers. Polymer nanofibers have facilitated the union of metals, organics, inorganics, ceramics, composites, and metal oxides in polymer matrices. This has led to new generation of technological advancement.

Due to extreme flexibility of nanofibers, they are capable of forming networks with high surface area and highly porous structure beneficial for the designing of advanced flexible devices. The significant impact of nanofiber technology has emerged from the variety of fundamental materials such as natural polymers, synthetic polymers, carbon-based materials, semiconducting materials, and composite materials that can be used for the synthesis of nanofibers. The emergence of fabrication of nanofibers techniques has been rapidly reported with the currently available preparation strategies. The fabrication of nanofibers has attracted a lot of researchers due to unique properties such as surface morphology, porosity, and geometry can be tailored or functionalized for flexible devices. Polymer nanofibers can be prepared by a variety of techniques out of which electrospinning is a quite suitable technique with controllable diameter of the nanofibers useful to enhance the properties along with extreme flexibility due to which, electrospun nanofibers are considered an excellent candidate for a variety of flexible purposes. Additionally, electrospinning can be used for fabricating polymer composite fibers by blending additives to get the desired properties. Considering these benefits, electrospinning has gained a remarkable popularity for sharp rise in scientific publications in recent years. Despite the advantages of electrospinning technique for fabrication of polymer nanofibers such as inexpensive setup, ability to control fiber diameter, orientation, and composition, etc., the applications of electrospun nanofibers especially for flexible devices also face some challenges which include the use of organic solvents, the limited control of pore structures and low mechanical strength. More advanced nanofiber configurations, such as core–shell, multilayer, and multicomponent nanofibers, may be prepared through methods like co-axial electrospinning to overcome those problems. Therefore, the variations of this method have been developed as co-axial electrospinning to synthesize core–shell and multilayer composite nanofibrous structures. Looking to inherent applicability especially the flexibility characteristics of electrospun nanofibers, this chapter particularly focuses on the fabrication of a variety of electrospun polymer nanofibers and their application for flexible devices including light-emitting displays, sensors, UV photodetectors, transparent electrodes, and nanogenerators.

2 Electrospun Polymer Nanofibers

Nanofibers are favored in recent times as one of the best 1D nanomaterials on account of their ease of production and miniaturized applications. The versatility of nanofibers, being lightweight and strong structures, has proved its worth as the most successful nanomaterial. High-value sectors are making the best use of nanofibers in their technological innovations. Nanofibers have discovered altogether new properties of the materials already known for decades. The decrease in the

fiber diameter results into a much larger surface area. High aspect ratio makes the nanofibers equipped with particular functions like enhanced solubility, compatibility and recognition that portray these nanofibers as the best candidates in the current technological uprising. Electrospinning provides many controllable parameters that can produce nanofibers of desired diameter with utmost uniformity. The obtained electropsun polymer nanofibers can then be subjected to other treatments to obtain the required end product. Electrospinning has eased the fabrication of various functional materials having different functions and technical aspects. Polymer nanofibers being stretchable and bendable due to flexibility are finding emerging applications. Polymer nanofibers are produced by electrospinning, the simplest method of obtaining nanofibers as a result of uniaxial stretching of a viscoelastic solution by electrical interaction [6–8]. Nanofibers have been synthesized via electrospinning by incorporation of the precursor in polymer solution or by the conventional sol–gel process. The so obtained nanofibers have homogeneous dispersion of the metal salts and appropriate thermal treatment yields the nanofibers of the desired metals or metal oxides (Fig. 2). Another class of electrospun nanofibers exhibiting photonic and magnetic functions include luminescent nanofibers, conjugated polymer-based fibers, and nanofibers with specific magnetic properties. The basic approach in preparation of these polymers is the incorporation of components of polymer blends into conjugated polymers and doping organic and inorganic materials with rare earth complexes which control the emissive property. The resultant nanofibers obtained thereafter are flexible, light-weight, hard, thermally stable, chemical resistant, and optically active [9].

Electrospun nanofibers are found to be the best materials for sensors including polymer composite sensors and inorganic composite sensors. Sensing mechanism requires a large surface for quick sensing and detection activity. Nanofibers fit in the

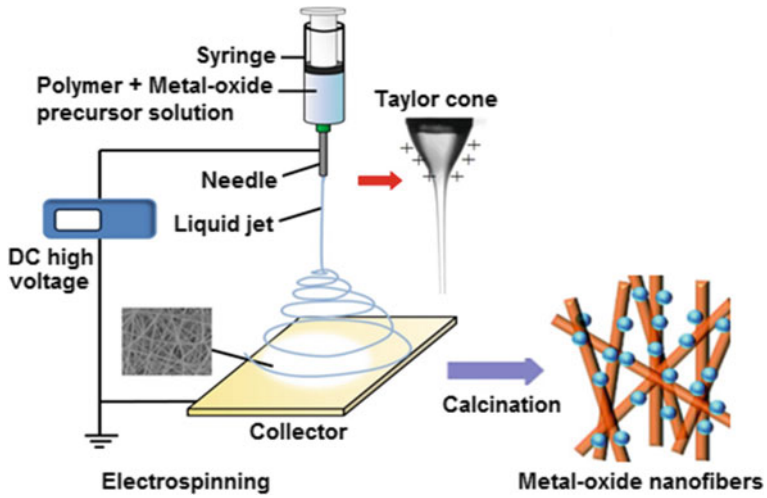

Fig. 2 Preparation of metal oxide nanofiber using electrospinning and calcination

best way and enhance the sensors compared to thin films. Besides these, nanofibers are also used in photocatalytic applications. Thus electrospinning has proved a very significant technique in the preparation of noble polymer nanofibers [10]. Although electrospinning has shown the advancement for preparation of nanofibers, the dimension, quality, design, control and pattern of electrospun nanofibers is equally dependent on the choice of polymer used for electrospinning and hence the name "polymer nanofibers". Polymers form the backbone of nanofibers which gives these nanofibers their characteristic uni-dimensionality. Polymers are basically composed of large number of macromolecules, known as monomers. These macromolecules have chain-like molecular geometry having random orientation and strong Van der Waals forces held them together and cross-linking gives them mechanical strength. It may happen that the monomers may be either all alike or mixed, called as copolymers. However, the electrospinning process requires a solution form of the precursor and the polymer to be fed into the syringe for drawing fibers and hence comes to light the concept of polymer solutions [11]. A solution is obtained by the molecular-level interactions between different chemical species, resulting into a homogeneous phase. Polymer solution basically consists of a polymer material and an appropriate solvent. Anymore addition of other molecular species, polymer, dopants or other materials to this mixture results in the formation of polymer "blends". Dispersion, suspension, emulsion, aerosols, and colloids are some of the other ways of preparing the preliminary polymer solution depending upon the physio-chemical property of the targeted application, but most of the polymer nanofibers are synthesized via solution method [12]. When the polymer is mixed with a suitable solvent, the monomer units interact with the solvent molecules and dissolve in it to produce a homogeneous solution. The dissolution of polymer in the solvent is based on certain factors such as the selection of appropriate solvent, temperature, and the average molecular weight and polydispersity of polymer.

The polymers that are commonly used in electrospinning are mainly of three types- natural polymers, synthetic polymers, and polymer blends. Natural polymers such as silk, chitosan, collagen, gelatine, cellulose find extensive applications in healthcare, biomedical, and pharmaceutical research. Polymers such as polyamides- Nylon-6,12 [13], Polyamide-6 [14], Polyacrylamide [15]; polyacids-Poly(acrylic acid) (PAA) [16], Poly(2-acrylamido- 2-methyl-1-propane sulfonic acid) (PAMPS) [17]; Polyacrylonitrile (PAN) [18], Polyaniline (PANI) [19]; Polycaprolactone (PCL) [20]; Polyoxides-Polyethylene oxide (PEO) [21]; Polyesters-Poly(ethyleneterephthalate) (PET) [22], Poly(butylenes succinate) (PBS) [23]; polyacids; Acrylic polymers Poly(methyl methacrylate) (PMMA) [24]; Styrenics-Polystyrene (PS) [25]; Polyurethane [26]; Polyalcohols-Poly(vinyl alcohol) [27]; Vinyl polymer-Poly(vinyl chloride) (PVC) [28], Poly(vinylidene Fluoride) (PVDF) [29, 30]; Polyamine-Poly(vinyl pyrrolidone (PVP) [31]; and other polymers such as Polysulfone (PSU) [32], Poly(etherimide) (PEI) [33], Poly(ferrocenyl dimethylsilane) [34], Poly(meta-phenylene isophthalamide) [35], Poly(vinylphenol) [36], Polypyrrole [37], Polybenzimidazol (PBI) [38], Aramid (Kevlar49) [39], etc., are widely used in electrospinning. Conducting polymers are extensively used in smart

clothing as supercapacitor, battery and sensors owing to their extraordinary electrical conductivity. Redox polymers, ionic conducting polymers and conjugated double-bond structured polymers are used for this purpose [40]. The choice of solvent is extremely important so as to yield a homogeneous polymer solution and its spinnability. Large numbers of solvents are utilized for this purpose in accordance with the polymer possessing characteristics like surface tension, vapor pressure, boiling point, dielectric constant and good rate of evaporation (volatility). Some of the commonly used solvents are water [41–43], chloroform [37], dimethylformamide (DMF) [44], dimethyl sulfoxide (DMSO) [45], acetone [46], trifluoro acetic acid (TFA) [47], N,N'-dimethyl acetamide (DMAc) [48], tetrahydrofuran (THF) [49, 50], formic acid [51], etc. Along with the electrospinning processing parameters, the morphology of electrospun nanofibers is largely affected by some other parameters of polymer solution such as molecular weight of polymer, polymer concentration (viscosity), solution conductivity and solvent volatility as shown in the Fig. 3.

Researchers have studied the effect of these parameters on the electrospun nanofibers morphology and depending upon the desired application the appropriate parameters need to be fixed. It has been observed that an increase in electrical conductivity results in reduction of fiber diameter, while increase in concentration, that is viscosity of the polymer solution leads to an increase in fiber diameter.

History of fibers can be dated far back in time but significant developments have been witnessed in the past 100 years. Cotton was known as most useful fiber and led to the silver fiber revolution in the eighteenth and nineteenth centuries. With the emergence of three synthetic fibers-polyamide fibers (Nylon 66, Nylon 6), poly(ethylene terephthalate) (PET) fibers and acrylic fibers, along with spandex fiber materializing in the first half of the twentieth century has now become the basis of our everyday clothing. The manipulation of design and control at the nano-level is an important feature of any useful fiber. Nanofiber has the essence of possessing its diameter in the range of nanometer in addition to a large surface area. Robust characteristics can be

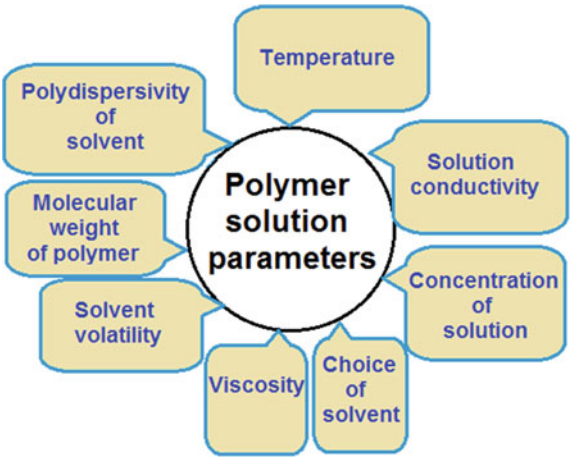

Fig. 3 Parameters of polymer solution for electrospinning

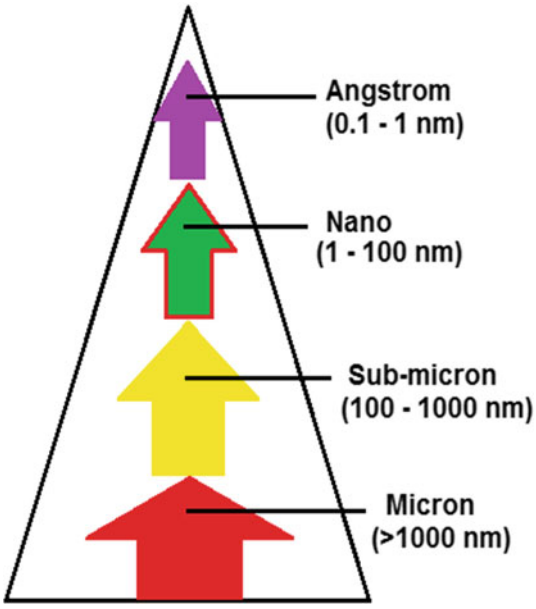

Fig. 4 Relation between fiber diameter sizes in terms of nanometer

identified by controlling the surface area and diameter of these fibers which will add on to multifunctionality of the materials. Nanofibers can be defined as a nano-sized fiber having nanometer order in its dimension. A fiber may have diameter of various sizes ranging from angstrom, nano, sun-micron, and micron.

Figure 4 shows the relation between these sizes in terms of nanometer. Fibers having diameter size in angstrom are basically molecular chains. Fibers having diameters in nano and sub-micron range are classified as "nanofibers", while those in micron range are micron fibers. Conventional fibers have diameter more than few micrometers [52]. Nanosized materials enhance the properties of the materials as a result of size effects caused due to increase in the surface area per volume, along with the reactivity and selectivity ascribed due to decrease in volume. The arrangement of supermolecules is regular, coherent, and self-organized. Nanofibers provide hierarchal structure effect and recognition to cells and biomaterials, and facilitate them to interact and combine. Easy processing, controllability, and design of these nanofibers render enormous potential applications in flexible devices. The scope of nanofibers has increased recently in recent technological advancements. Many physical, chemical, and biological techniques have been reported in literature such as grinding, milling, cryo-crushing, and high-pressure homogenization, laser ablation, physical vapor deposition (PVD), and spinning techniques-flash spinning, centrifugal spinning, electrospinning, electrochemical deposition, interfacial polymerization, polyol, phase separation, microemulsion, hydrothermal, chemical vapour deposition (CVD), sol–gel, hydrothermal, template-assisted synthesis, sonochemical, microwave synthesis, bacterial cellulose synthesis, enzymatic hydrolysis of wood pulp. This has led to increase in the fabrication of nanofibers. The appropriate

fabrication technique can be chosen on the basis of the characteristics of precursor involved and the morphology of desired nanofibers.

Spinning is an age-old technology that uses thin filaments or fibers to form yarns by twisting together. Spinning is basically a physical method but it can be combined with chemical methods to synthesize nanofibers. Various types of spinning techniques have been reported till date. However, they have been broadly classified as electrospinning and non-electrospinning techniques on the basis of forces involved in drawing of fibers. Electrostatic forces are responsible for fiber formation in electrospinning, while non-electrospinning techniques make use of forces (centrifugal, gravitational, air, etc.) other than electrostatic force. Electrospinning set-up comprises of a pipette or plastic syringe provided with a metallic needle, high voltage power supply (20–50 kV), and a metallic collector. The electrostatic force and surface tension of the polymer solution play a vital role in spinning of nanofibers. A drop of viscoelastic polymer solution ejecting from the tip of the needle is uniaxially stretched under the electrostatic force exerted by the high tension power supply. When the electrostatic force exceeds the surface tension of the polymer drop, the drop is stretched to form a charged Taylor cone thereby forming a polymer jet. This jet gets attracted toward the grounded metallic collector forming continuous, non-woven nanofiber mat. Although, electrospinning mechanism is simple and easy, the quality of nanofibers is ruled by a number of parameters concerned with the polymer solution, experimental set-up, and environmental conditions [12, 53]. Figure 5 represents a schematic diagram of electrospinning set-up and the physical (distance, voltage, flow rate, and collector), chemical (concentration, conductivity, molecular weight, viscosity, solvent volatility, and molecular structure), and environmental (humidity and temperature) parameters on which the diameter of the fibers depends.

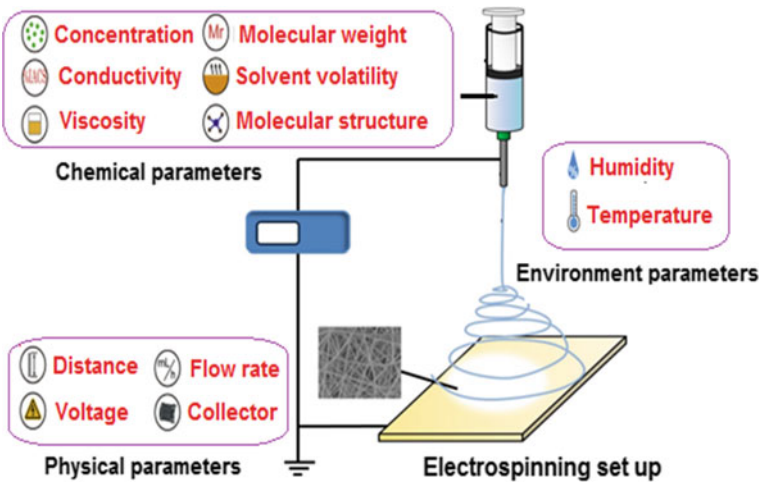

Fig. 5 Schematic diagram of a conventional electrospinning setup with chemical, physical, and environment parameters

3 Application of Electrospun Polymer Nanofibers for Flexible Devices

The concept of wearable and portable electronics has brought about a new aspect to the current material research by investigation of additional functionality of stretchability, foldability, and flexibility of these materials. The devices available today are heavy, rigid, and bulky. When these devices are incorporated in textiles, they alter the fundamental property of these textiles, that is, flexibility. A flexible device is an electronic device that remains stable and retains its electrical behavior, even when it undergoes mechanical deformation in the presence of any kind of stress and strain such as twisting, bending, compressing, folding, and stretching. This gives rise to the concept of electronic devices mounted on flexible substrates to be combined with textiles. However, a major drawback faced with such devices is that laundering and wear and tear of the textile may affect their functionality and affect is reusability. This led to the idea of incorporating the devices within the textile. Since the fibers that are known to us and spun into fabric are mainly insulators; researchers considered it worthwhile to integrate electronic materials into the fiber itself. Fibers are excellent flexible materials and the addition of electrical behavior into these fibers started the notion of fiber-assisted flexible devices which are extremely lightweight and can be easily woven into the fabric to produce flexible textile. This has made the textiles "smart" by providing them with additional functionalities. The amalgamation of textile and electronic technology has brought together the positive qualities of each of these technologies as one. Although fibers act as a substrate for these electronic materials, but it does not pose any danger to the functionality of these fibers and goes hand-in-hand with each other. Nanotechnology has assisted in bringing the concept of flexible textiles on a global technological platform by the introduction of one-dimensional nanomaterials. Nano-engineered functional textiles have gathered perpetual applause due to their ease of application in devices. Large numbers of materials have been investigated for manufacturing fibers. Among these materials, polymers possess the intrinsic property of being mechanically flexible, and are most commonly used to yield different types of fibers. Electrospinning technique has helped in producing flexible and multifunctional nanofibers with the help of polymers and hence called polymeric electrospun nanofibers.

Flexible devices based on polymeric electrospun nanofibers are biocompatible, durable, soft, flexible, stretchable, hydrophobic, antibacterial, conductive, antiwrinkle, and antistatic. The applications of these flexible devices are innumerable [54–56]. In this chapter, application of electrospun polymer nanofibers for flexible devices (Fig. 6) such as light-emitting diodes (LEDs), sensors, UV photodetectors, transparent electrodes, and nanogenerators are explored.

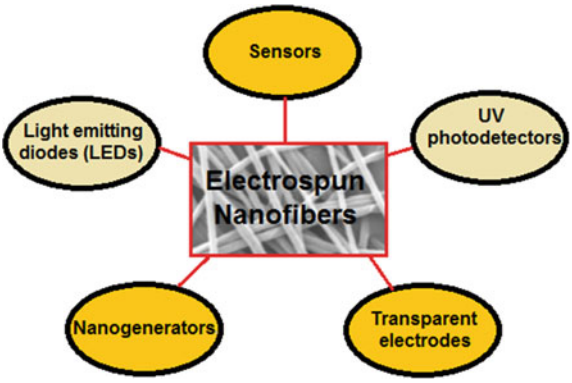

Fig. 6 Application of electrospun nanofibers for various flexible devices

3.1 Light-Emitting Diodes (LEDs)

The light-emitting properties can be obtained in polymer nanofibers by electrospinning and accordingly such electrospun nanofibers can be used as light-emitting diodes (LEDs) [57]. Phosphors emit light due to occurrence of radiative transitions. Non-radiative transitions also occur at the same time which leads to a loss in efficiency of luminescence. Activators and sensitizers act as wheels to keep the process of luminescence on track. Activators are responsible for emission and are doped into the host material. A sensitizer or co-activator is co-doped in the similar fashion, which gathers energy from the source of excitation and passes on to the activator. Innumerable phosphors have been reported with rare earth (RE) elements acting as activators [58]. Inorganic materials have gained enormous popularity in lighting applications. Of these inorganic materials, oxides have attracted remarkable interest. RE activated oxide phosphors have been recorded in many research articles. Several RE-doped metal oxides have been detailed in extensive literature such as phosphates, tungstates, molybdates, aluminates, borates, niobates, titanate, vanadate, titania, fluorides, etc., for innumerable color display applications [59–65].

Electrospun luminescent nanofibers have spurred application for flexible light-emitting display devices by incorporation of optically active molecules, metallic nanoparticles, conjugated polymer nanoparticles, colloidal nanoparticles, fluorescent dyes, bio-chromophores, quantum dots, hybrid (organic–inorganic), composite, conducting, and semiconducting polymers. Carbon quantum dots (CDQs) are excellent luminescent materials emitting red, blue, and green color at appropriate excitation energies. Alam et al. [66] examined transparency and photoluminescent properties of composite electrospun nanofibers of CDQs in polyacrylonitrile (PAN) blend with polyacrylic acid (PAA). The process of co-electrospinning for the fabrication of PAN/PAA/CQDs composite nanofibers and its optical behavior are shown in Fig. 7. They have observed that CDQs/PAN/PAA composite nanofibers exhibited luminescence in agreement with the CDQs, while PAN/PAA fibers showed no luminescence in absence of CDQs. PAN/PAA nanofibers absorb UV light and transmit in the visible

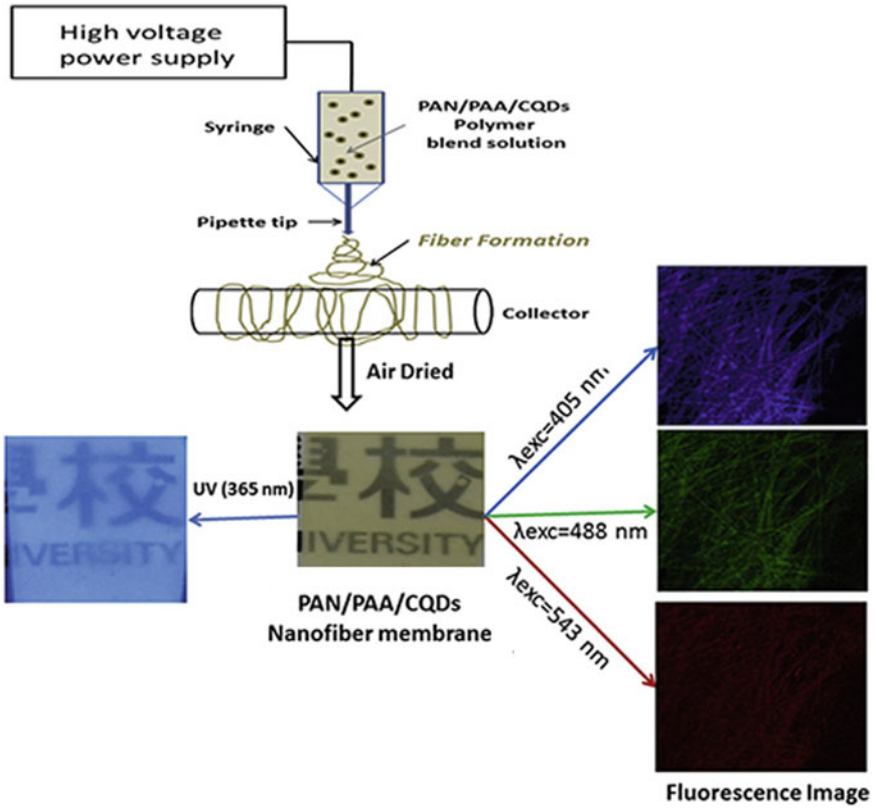

Fig. 7 The process of co-electrospinning for the fabrication of PAN/PAA/CQDs composite nanofibers and its optical behavior (Reproduced with permission from Ref. [66], Copyright (2015) Elsevier)

range with transparency of 65%. However, the addition of CDQs in the polymer array reduced the transparency to 60% for PAN/PAA/CQD composite nanofibers. Electrospun PAN/PAA/CQD composite nanofibers can be the potential candidate for flexible light-emitting display devices.

The fabrication of Keratin/polyvinylalcohol (PVA) blended nanofibers by electrospinning for flexible ZnO@graphene quantum dots (ZGQDs) LEDs demonstrated by Lee et al. [67]. Keratin/PVA fibers have random, bead-free orientation with an average diameter of 180 nm before dipping in water. As the keratin/PVA nanofibers coated with glyoxal were dipped in water, the average diameter increased from 180 to 210 nm along with smoothening of the fiber. This increase in average diameter contributed to increased transparency. Spin coating method was used for the fabrication of ZGQDs LEDs. The main emission peak of ZGQDs is observed at 393 nm (3.15 eV). Figures 8 and 9 depict the fabrication of transparent textile using electrospinning process and fabrication process of ZGQDs LEDs embedded in textile.

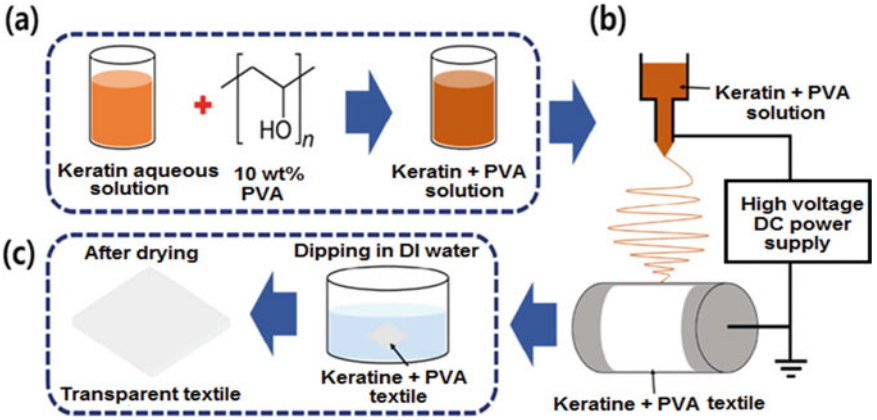

Fig. 8 Schematic illustration of **a** Keratin + PVA solution preparation, **b** loading solution into syringe for electrospinning, and **c** transparent textile formation (Reproduced with permission from Ref. [67], Copyright (2017) Elsevier)

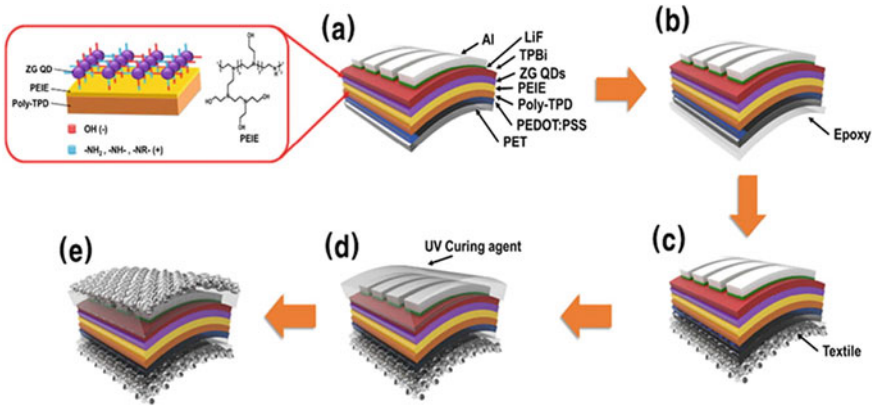

Fig. 9 Fabrication process of ZGQDs LEDs embedded in textile (Reproduced with permission from Ref. [67], Copyright (2017) Elsevier)

For the development of photoluminescence properties in electrospun nanofibers, rare earth ions RE-doped semiconductor are the best suitable as promising hosts for incorporation in nanofibers to improve upon textile industries for designing flexible display devices. Fang et al. [68] reported the preparation of Eu^{3+} doped cerium oxide (CeO_2) nanofibers using electrospinning and studied photoluminescence under excitation wavelength 290 nm. The emission bands ranging from 310–530 nm were reported. The highest peak observed at 367 nm accounted for the band-gap of CeO_2 (3.4 eV). The emission intensities of the Eu^{3+}:CeO_2 nanofibers were found to be increased with increase in Eu^{3+}content as well as heating temperature. The effect of annealing showed improved results.

Ge et al. [69] demonstrated the fabrication of electrospun $Yb_2Ti_2O_7$:Er nanofibers and its red upconversion luminescence properties. The fabrication of electrospun $Yb_2Ti_2O_7$:Er nanofibers by electrospinning is shown in Fig. 10a. For the preparation of electrospun $Yb_2Ti_2O_7$:Er nanofibers, the solution of titanium butoxide (TBOT), N, N-dimethylformamide (DMF), acetic acid (HAC), polyvinylpyrrolidone (PVP), ytterbium trinitrate pentahydrate ($Yb(NO)_3.5H_2O$) and erbium trinitrate pentahydrate ($Er(NO)_3.5H_2O$) prepared and transferred to syringe for electrospinning. As seen from the emission spectrum of $Yb_2Ti_2O_7$:Er nanofibers (Fig. 10b, UCL spectrograph exhibits two peaks corresponding to red and green color 658 nm and 546 nm respectively. Remarkable improvement in red emission occurred due to an increment in the content of Yb host. This dominated the energy transfer from $^2F_{5/2}$ of Yb^{3+} ions to $^4I_{11/2}$ of Er^{3+} followed by relaxation by the transition from $^4F_{7/2}$ to $^4F_{9/2}$, thereby suppressing the transitions of green-emitting level as shown in Fig. 10c.

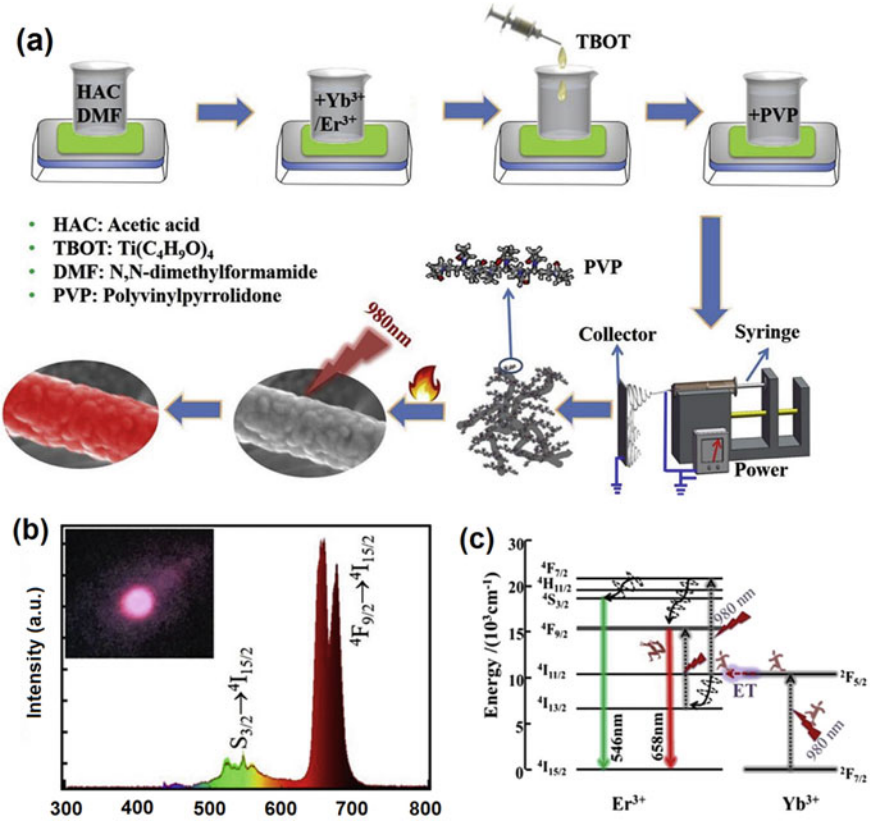

Fig. 10 **a** Preparation of electrospun $Yb_2Ti_2O_7$:Er nanofibers, **b** Emission spectrum of $Yb_2Ti_2O_7$:Er nanofibers, and **c** Schematic energy level diagram for Er^{3+} and Yb^{3+} (Reproduced with permission from Ref. [69], Copyright (2019) Elsevier)

Wei et al. [70] demonstrated the UCL characteristics of electrospun rare earth oxyfluoride GdOF:Er^{3+} nanofibers fabricated by simple electrospinning combined with fluoro-oxidation technique for obtaining nanofibers with variable molar ratios of Er^{3+} as represented in Fig. 11a. GdF_3:Er^{3+} and GdOF:Er^{3+} nanofibers exhibit orthorhombic and rhombohedral phases, respectively, and this corresponding change is attributed to oxidation of GdF_3:Er^{3+} nanofibers.

UC emission spectra of GdOF:9%Er^{3+} nanofibers was characterized with various pumping powers from 330 to 1393 mW as shown in Fig. 11b, the stronger emission intensity of UC luminescence was found at higher pump power. UC emission spectra with 980 nm excitation were observed intense peaks at 523 and 543 nm corresponding to $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} for respectively. The effect of dopant on UCL is clearly visible from the spectra. The UC intensity increased with a relative increase in dopant concentration. The maximum intensity is observed at a concentration of 9% and further increase caused a substantial decrease in intensity. CIE chromaticity analysis suggests potential application

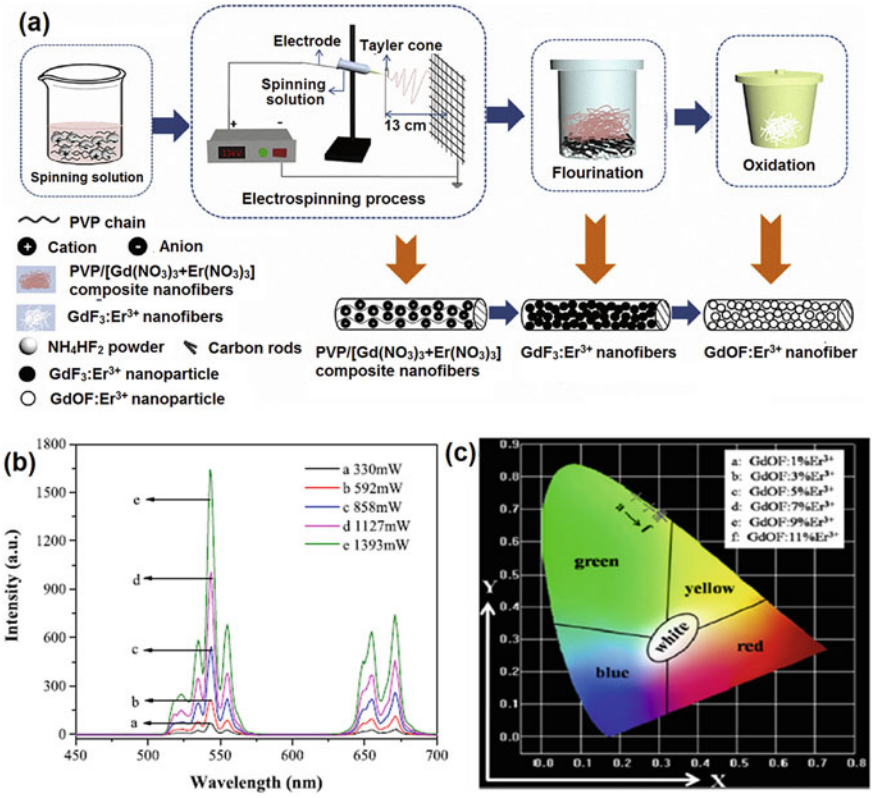

Fig. 11 **a** Schematic of electrospun GdOF:Er^{3+} nanofibers preparation, **b** UC emission spectra of GdOF:Er^{3+} nanofibers, and **c** CIE chromaticity coordinates of GdOF:Er^{3+} nanofibers (Reproduced with permission from Ref. [70], Copyright (2019) Elsevier)

of electrospun GdOF:Er^{3+}nanofibers in light-emitting display devices. Figure 11c represents GdOF:Er^{3+} nanofibers with varied concentration of Er^{3+} marking CIE coordinates (x,y) at (0.242, 0.738) (1%), (0.275, 0.706) (3%), (0.295, 0.688) (5%), (0.301, 0.682) (7%), (0.305, 0.679) (9%), and (0.307,0.676) (11%). Electrospun GdOF:Er^{3+} nanofibers are the potential luminescent materials useful for flexible light-emitting display devices.

With the help of electrospinning, Pangul et al. [71] prepared electrospun Dy^{3+}-doped ZnO nanofibers and studied their photoluminescence characteristics. The intensity of emissions peaks of dopant Dy^{3+} was found to be increased when the concentration of Dy^{3+} increased due to a reduction in fiber diameter. They have also reported the fabrication of electrospun Sm^{3+}-doped ZnO nanofibers and showed orange-red luminescence when excited at 394 nm [72]. They had concluded that the color tunability in electrospun nanofibers can be done by the type of dopant. Different dopant with a specific concentration in electrospun doped ZnO nanofibers can be the potential candidate for designing visible light-emitting diodes as flexible devices.

One approach for the preparation of electrospun polymeric materials for light-emitting displays is to electrospin the polymer blends such as polyfluorene (PF), polyphenylene vinylene (PPV), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinylidene fluoride) (PVDF) using a single solution spinneret for the purpose of reducing aggregation-induced quenching to enhance luminescence efficiency. In another approach, polymeric materials have been synthetically modified with aggregation-induced emission active pendants and subsequently electrospun into flexible light-emitting displays. Itankar et al. [73] demonstrated the fabrication of electrospun Eu^{3+}-doped polystyrene (PS) and polyvinylidene fluoride (PVDF) nanofibers and showed more polarized chemical environment of these polymers for the Eu^{3+} ions due to which bright red emission was observed in photoluminescence spectra. Such electrospun polymer nanofibers can be the potential candidates for flexible visible light-emitting diodes.

Dandekar et al. [74] demonstrated the fabrication of electrospun polymer blend nanofibers using electrospinning technique for photoluminescent fabric designing. They used europium complex $Eu(TTA)_3$phen (TTA = 2-thenoyltrifluoroacetone, phen = 1,10-phenanthroline) and blending of various polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) and prepared Eu(TTA)3phen/PVDF-PS, Eu(TTA)3phen/PVDF-PMMA and Eu(TTA)3phen/PS-PMMA nanofibers. They showed high-intensity peaks in emission spectra obtained due to polymer blends with PVDF and concluded that the increased in fluorescent intensity was due to smaller fiber diameter for PVDF-PMMA, and PVDF-PS blends in composites nanofibers (Fig. 12). CIE chromaticity coordinates for Eu(TTA)3phen/polymer blends nanofibers showed the emission of red color which can be tuned with the various polymer blend combination with PVDF.

Qin et al. demonstrated the fabrication of electrospun Janus nanofibers as flexible white-light-emitting nanofibers prepared by electrospinning. White-light-emitting Janus nanofiber film was consisting of PAN on one side and PVP on other side of electrospun nanofibers [75]. Two different polymer matrix solutions containing certain mass of fluorescent dyes anthracene and rhodamine-B mixed with PAN

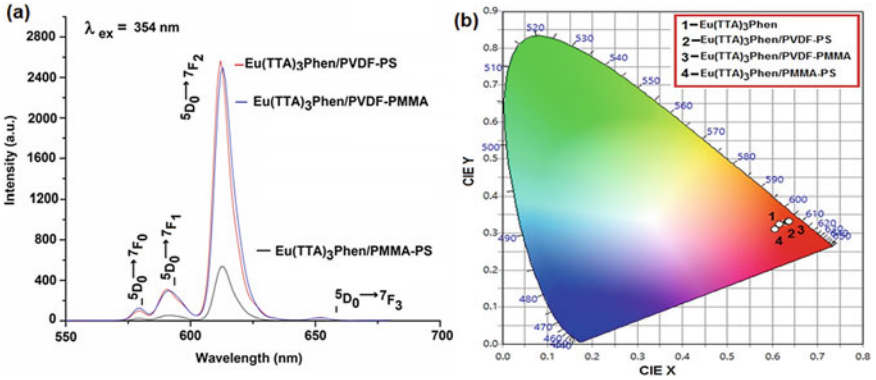

Fig. 12 **a** Emission spectra and **b** Chromaticity of Eu(TTA)3phen with polymer blends nanofibers (Reproduced with permission from Ref. [74], Copyright (2018) Elsevier)

and coumarin-6 mixed with PVP were prepared for the fabrication of fluorescent nanofibers. Such electrospun nanofibers are the potential candidates for flexible light-emitting devices.

3.2 Sensors

The improvement in the sensors with respect to their sensitivity, selectivity, response and recovery rate, and detection limit has been obtained with the advent of nanotechnology particularly one-dimensional nanomaterials such as nanofibers. High flexibility of electrospun nanofibers made them right candidates for the development of flexible sensors. The performance of electrospun nanofibers-based sensors was found to be highly sensitive than that of film-based sensors [55]. Electrospun nanofibers-based sensors have been widely used in flexible devices. Flexible sensors designed by electrospun nanofibers have shown great improvement in their sensor performance due to high absorptive power of nanofibers for analyte molecules to detect [76]. The functional nanofibers for sensors have been well prepared by electrospinning as compared to methods currently available for the preparation of nanofibers [77].

In recent years, different strategies have been applied for doping of noble metals to form heterojunction structures beneficial for tuning low detection limit and various sensing parameters obtained from electrospun composite/hybrid nanofibers [78]. There had been considerable interest in the fabrication of excellent gas sensing materials with the help of metal oxide semiconductors (ZnO, In_2O_3, SnO_2, TiO_2, and Fe_2O_3). Many approaches have been proposed to overcome the disadvantages of metal oxide semiconductors such as its poor selectivity, need of high operating temperature, and low response at low gas concentration. With this background, the construction of core@shell nanofibers became the smart electrospun nanostructure materials due to their individual components for the development of flexible sensors.

Huang et al. [79] demonstrated the preparation of core–shell nanofibers made of two metal oxide semiconductors ZnO@In_2O_3 core–shell nanofibers by coaxial electrospinning for the study of ethanol gas sensing and found that such nanofibers are highly sensitive for ethanol as compared to pure ZnO or pure In_2O_3 nanofibers. Schematic diagram of formation of ZnO@In_2O_3 core–shell nanofibers is shown in Fig. 13a. Two syringes with different nozzle diameters were used for polymer solutions made of precursors of Zn and In. The collected fibers were annealed at 600 °C to obtain ZnO@In_2O_3 core–shell nanofibers.

Schematic diagram and response of ZnO@In_2O_3 core shell nanofibers when exposed to air and ethanol are, respectively, shown in Fig. 13b, c. The sensor demonstrated excellent response and recovery characteristics for ethanol sensing. The high-performance ZnO@In_2O_3 core–shell nanofibers gas sensor for ethanol was due to shell depletion of In_2O_3 layer for increased in electron conduction channel leads to decrease in sensor resistance.

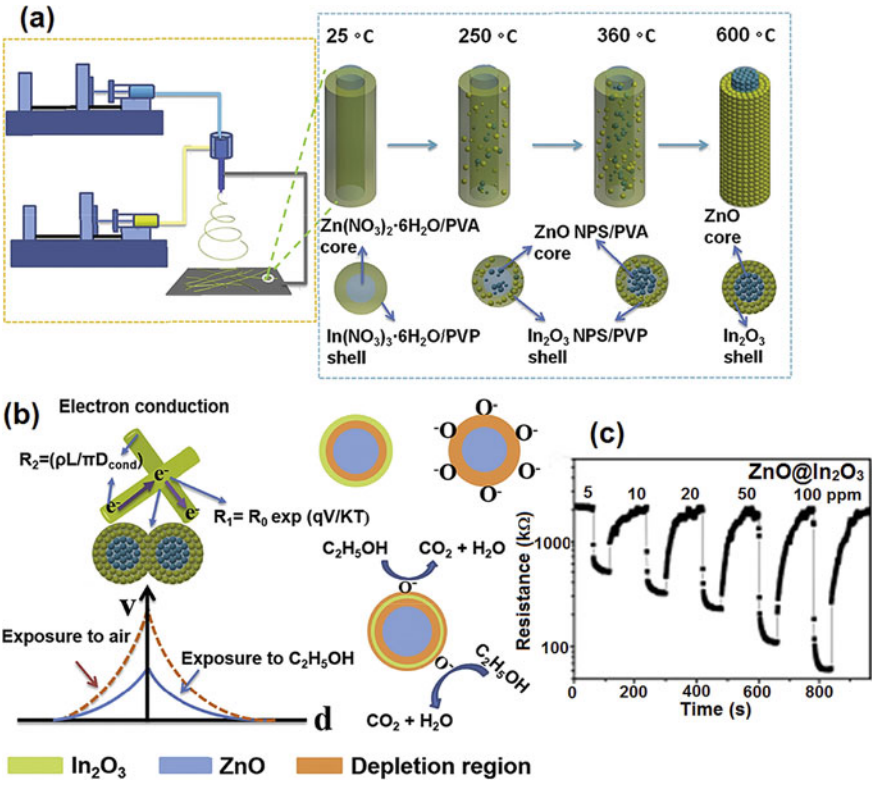

Fig. 13 **a** Formation of core–shell ZnO@In_2O_3 nanofibers, **b** exposure of ZnO@In_2O_3 nanofibers to air and ethanol and **c** sensing performance of ZnO@In_2O_3 nanofibers (Reproduced with permission from Ref. [79], Copyright (2018) Elsevier)

Kim et al. prepared SnO_2–NiO composite nanowebs by electrospinning and studied their gas sensing properties for the detection of hazardous gases [80]. For the electrospinning, they had prepared PVA solution mixed with precursor materials with different concentrations. Fabrication of SnO_2–NiO composite nanowebs with various compositions is shown in Fig. 14a. To investigate the composition dependency of the responses, all compositions were exposed to NO_2, and C_6H_6 gases and their dynamic normalized response was tested with different ppm concentration are shown in Fig. 14b, c, respectively. This shows that such electrospun composites nanowebs-based flexible sensor forms the p-n heterojunction to easily detect oxidizing or reducing gases.

Pang et al. [81] reported the preparation of electrospun cellulose/TiO_2/polyaniline (PANI) nanofibers by electrospinning and polymerization as shown in Fig. 15A. They have studied the dynamic response of the cellulose/TiO_2/PANI composite nanofibers for ammonia sensing (Fig. 15B). The sensitivity of the cellulose/TiO_2/PANI composite nanofibers was found to be significantly improved by TiO_2 nanoparticles as compared to that with out TiO_2. Wang et al. [82] reported the preparation of Pd-SnO_2 composite nanofibers-based nanosensor using electrospinning. They

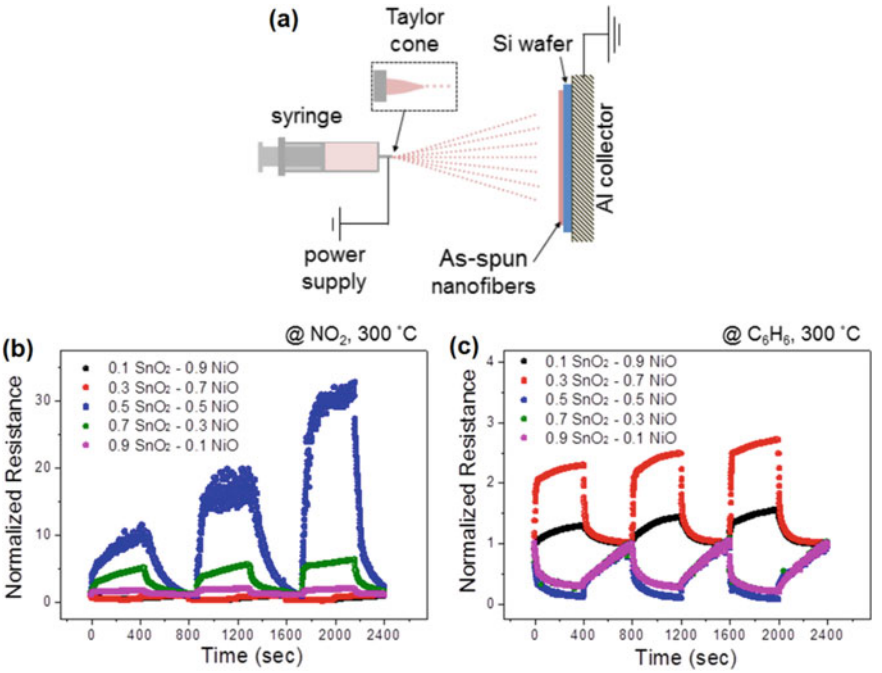

Fig. 14 **a** Electrospinning set-up for preparation of SnO_2-NiO nanofibers, **b** and **c** Dynamic normalized response of SnO_2–NiO composite nanoweb sensors with various composition for NO_2 gas and C_6H_6 (Reproduced with permission from Ref. [80], Copyright (2018) Elsevier)

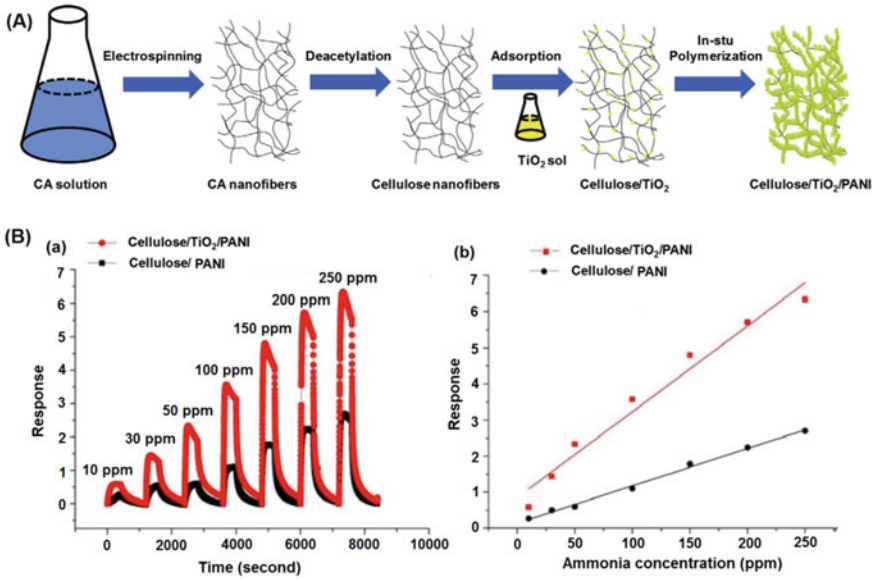

Fig. 15 **A** Fabrication of cellulose/TiO_2/PANI composite nanofibers, **B** Dynamic response for ammonia sensing Reproduced with permission from Ref. [81], Copyright (2016) Elsevier Ltd)

have shown the change in resistance when the material is exposed to hydrogen gas achieving faster response and shorter recovery.

Xu et al. demonstrated the fabrication of NiO/ZnO core–shell composite nanofibers by co-axial electrospinning [83] and studied this nanofibers-based sensor for the detection of H_2S gas. They have shown excellent response and recovery of sensor based on NiO/ZnO core–shell composite nanofibers as compared to individual ZnO nanofibers-based sensor. Yang et al. [84] developed a sensor device based on 9-chloromethylanthracene (9-CMA) fluorophore doped cellulose acetate (CA) electrospun nanofibers. From its sensing performance toward methyl violet, a novel fluorescent sensor based on electrospun nanofibers could be designed.

Al-doped SnO_2 composite nanofibers fabricated by electrospinning showed improved hydrogen sensing as compared to pure SnO_2 nanofibers. It was concluded that the doping of Al into SnO_2 could strongly affect the sensing performances [85]. Sharma et al. [86] reported the fabrication of SnO_2/PANI composite nanofibers by electrospinning technique for hydrogen gas sensing at low temperature. More et al. [87] prepared Ag-SnO_2/PANI nanofibers by electrospinning and found improved sensing performance toward hydrogen gas at low temperature. In all these electrospun nanofibers, the polymer polyvinyl pyrrolidone (PVP) was used during electrospinning process.

Recently, Beniwal and Sunny [88] investigated the analyte sensing properties of Fe_2O_3 and polypyrrole (PPy) infused in electrospun thermoplastic polyurethane

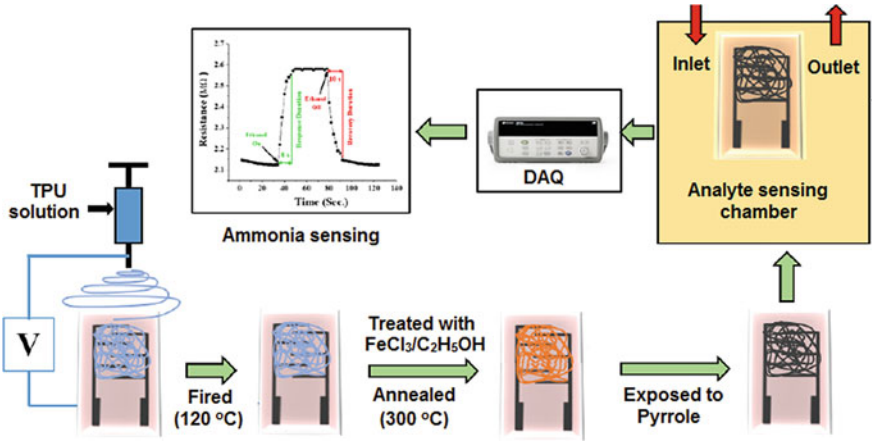

Fig. 16 Fabrication of TPU/Fe_2O_3/PPy nanofibers-based sensor (Reproduced with permission from Ref. [88], Copyright (2020) Elsevier)

nanofibers (TPU) for preparation of TPU/Fe_2O_3 and TPU/Fe_2O_3/PPy nanocomposites. Figure 16 shows the schematic of fabrication of TPU/Fe_2O_3/PPy sensor for ammonia sensing. Using electrospinning, they have systematically collected TPU nanofibers on interdigitated gold electrodes and then treated with FeCle/C_2H_5OH solution so as to form nanofibers of TPU/Fe_2O_3 and exposed to pyrrole for the formation of TPU/Fe_2O_3/PPy sensor. Utility of highly stable ferric oxide and conducting polypyrrole with the thermoplastic polyurethane electrospun nanofibers had been tested for the enhancement of the analyte sensors at room temperature. Inclusion of fillers ferric oxide and polypyrrole had turned out to be advantageous for improving the sensing performance of the thermoplastic polyurethane at room temperature. Busacca et al. [89] investigated the performance of CO gas sensor based on electrospun Co_3O_4 nanofibers. They have reported different morphology of electrospun Co_3O_4 obtained by using ethanol and dimethylformamide (DMF) as solvent mixed with polyvinylpyrrolidone (PVP) during electrospinning for obtaining Co_3O_4 nanofiber by ethanol and Co_3O_4 nanosheets by DMF. While comparing the sensing properties of these Co_3O_4 nanostructures for CO gas sensing, Co_3O_4 nanofibers showed fast response and recovery compared to that of Co_3O_4 nanosheets.

3.3 UV Photodetectors

An emerging need of highly responsive ultraviolet photodetector at high temperature and harsh conditions has been consistently there in the fields of military, optical communication, and space research [90]. Hence, fabrication of UV photodetectors with such operating features enduring visible region of wavelength is an unceasing

course. Superfast imaging, monitoring ultrasonic vibrations, remote optical communication network, homodyne detection of polarized state of weakest signal field are some commercially available photodetection system [91]. The ultraviolet photodetectors are classically identified as vacuum UV photodetectors and solid-state UV photodetectors. Vacuum UV photodetectors based on photomultiplier tubes are heavyweight, low efficient engaging high-power consumption but are relatively mature and high gain devices. Whereas, solid-state UV photodetectors primarily semiconductor UV photodetector devices are classified as photoconductive and photovoltaic UV photodetectors [92, 93]. Researchers have been successively able to achieve these properties in conventional UV photodetectors but with the progression of age and technology the prerequisite for the wearable UV photodetectors are at surge and so is the research progressing in that phase [94]. Polat et al. [95] were positively able to fabricate a variety of flexible prototype devices which were efficaciously integrated with the user-friendly devices and are able to monitor real-time health-related readings even at low power consumption for long range of periods. Another successful attempt was attained by Núñez et al., wherein semiconductor-based flexible UV photodetector devices were fruitfully fabricated and confirmed under various conditions [96]. Utilization of low-cost and simple manufacturing processes for different innovative wide band-gap semiconductor nanomaterials having 1–100 nm dimensions have been discussed and studied for fabricating UV photodetectors. High surface area to volume ratio, a major asset held by electrospun nanomaterials holds the likelihood and valor to show higher responsivity and photoconductivity gain [97].

Reddy et al. [98] prepared electrospun NiO–p/Si–n heterojunction nanofibers and studied its characteristics as UV photodetector (Fig. 17A). Their study had proved the utilization of electrospinning method to fabricate p-NiO nanowire-based photodetector device to be an adequate choice exhibiting optimum properties. In a typical procedure, polyvinyl alcohol and $Ni(NO_3)_2$ composite nanofiber were allowed to deposit over heavily doped n-type Si substrates previously cleaned with hydrofluoric acid and acetone and water. The as-deposited electrospun composite nanofibers were allowed to undergo calcination at 450 °C for 1 h. The calcination process removes the organic residual of polyvinyl alcohol and remains the high crystalline p-NiO nanowires. A shadow mask utilizing electron beam technique was used to deposit aluminum top contacts on p-NiO nanowire—n-Si heterojunction device. The resultant device was annealed for another 1 h which improved the electrical performance. Electrical performance of the p-NiO nanowire—n-Si heterojunction device was studied and then compared with the assortment of the heterojunction devices. Upon calculating the critical parameter to estimate the act of the photodetectors, i.e., responsivity and external quantum efficiency, the highest value of responsivity was achieved for weaker ultraviolet light intensity at a wavelength of 350 nm. The detectivity of the device was also found to pursue the higher value. Both the values are comparable to that of other similar heterojunction photodetectors. The fast photodetection of this heterojunction photodetector device at zero bias has been devoted due to the p-NiO nanowires carrier diffusion length as studied from Fig. 17B. Overall, the electrospun one-dimensional p-NiO nanowire—n-Si heterojunction for self-powered

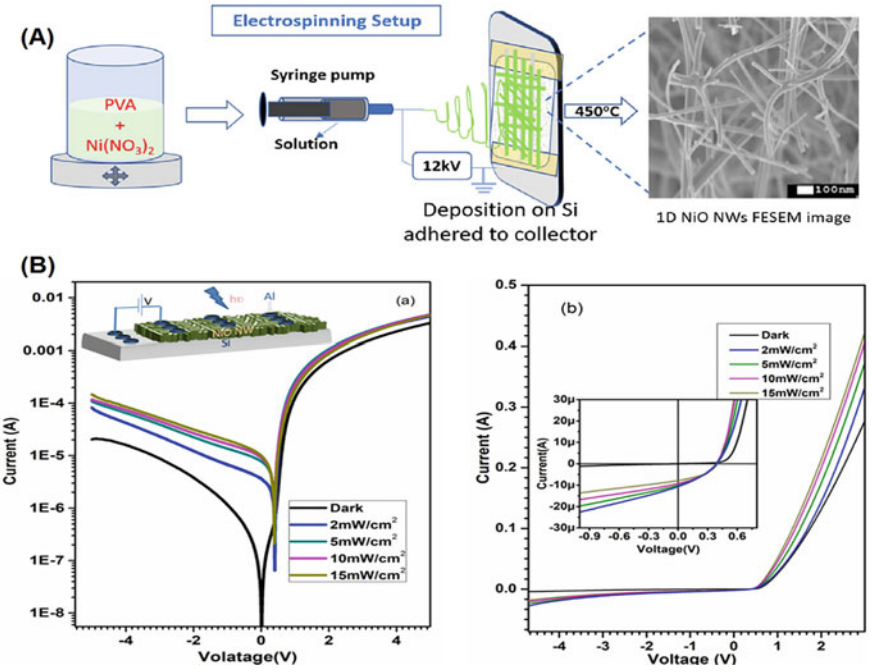

Fig. 17 **A** Fabrication of electrospun NiO nanowires and its SEM image, **B** I–V characteristics of NiO/Si under dark and different illumination of light (Reproduced with permission from Ref. [98], Copyright (2020) Elsevier)

UV photodetector has proved itself as the demanding device owing to their astounding properties.

Kim et al. [99] had innovatively utilized the *Kirigami* pattern for flexible and transparent electrospun nanofiber network-based UV photodetectors. Conceptualizing *Kirigami* into metalized nanofiber network has actually enhanced the mechanical performance of the as-fabricated UV photodetectors. A very precise method was adapted to fabricate the stretchable photodetectors where a zinc oxide seed layer was deposited over the electrospun PVP nanofibrous mat by RF sputtering method. Over these zinc oxide layered PVP nanofibers gold coating was deposited which further carefully transferred onto the Kirigami polydimethylsiloxane proprietary mold. Figure 18 displays the detailed process of the fabrication of *Kirigami* UV photodetector along with the SEM images of the hybrid zinc oxide layered nanofibers. This device was further examined for UV detection against strain parameter and it is noteworthy to mention that photoresponsivity for the device was dynamic even under the 80% of the strained conditions. Integration of flexibility into the UV photodetectors has encompassed countless ways for the utilization in real-time monitoring and assortment of applications.

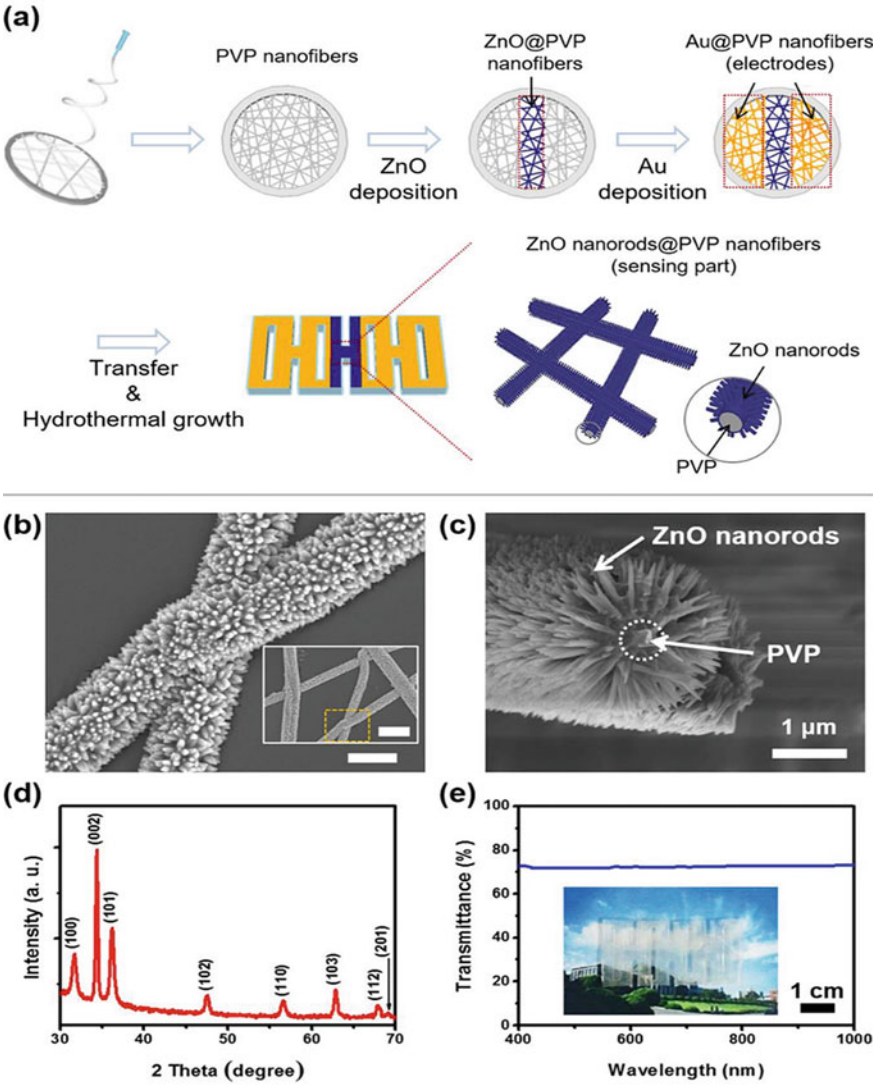

Fig. 18 **a** Fabrication of ZnO@PVP nanofibers for the kirigami photodetector, **b** SEM image of a junction of two ZnO nanorods@PVP nanofibers, **c** Cross-sectional SEM image for the ZnO nanorods@PVP nanofibers, **d** XRD image for ZnO nanorods grown on PVP nanofiber surfaces, and **e** Optical transmittance spectrum of the photodetector (Reproduced with permission from Ref. [99], Copyright (2020) Elsevier)

3.4 Transparent Electrodes

Serving as cathode or anode for the optoelectronic devices and to allow the passage of light with minimal losses is the basic utility of the transparent electrodes. Transparent electrode needs to be compatible with the harsh environments. Electrodes that are electrically conductive and optically transparent had manifest its place in the grounds of the light-emitting diodes, photodetectors, integrated modulators, electrochromic devices, solar cells, etc. [100]. Indium-tin-oxide (ITO) thin films have been commercially used in electronic devices as transparent electrode owing to the virtuous performance and chemical stability. However, the rigidness and brittleness had hindered their utilization in the application point of view with the mounting technology. Continuous efforts have been carried out to overcome this problem. Lee et al. [101] investigated the formation of multilayered transparent electrodes composed of ZnO:Ga (GZO)/Ag/GZO layers as shown in Fig. 19.

Jeong et al. have successfully fabricated the hybrid transparent electrode with metal mesh which is confirmed to have good transmittance and lower sheet resistance [102]. Essaidi et al. have studied indium-free transparent electrode made of WO_3/Ag/WO_3 multilayer structures which when used as transparent anode in organic photovoltaic cells performs as good as ITO transparent electrode [103]. Scopes of transparent electrodes have been further explored in a variety of fields. A novel biosensor based on nanostructured ITO transparent electrode has been fabricated and tested for monitoring cardiovascular diseases by Pruna and the team [104]. Thus, the introduction of nanostructure into transparent electrodes provides more surface area to react and thus improving the outcome of the device. Ultra-thin layers of alternative materials such as conducting polymers, carbon nanotubes, graphene, and metal nanowire grids show unique electronic transport and optical properties. Furthermore, the intrinsic conductivity of metals categorized high conductivity and

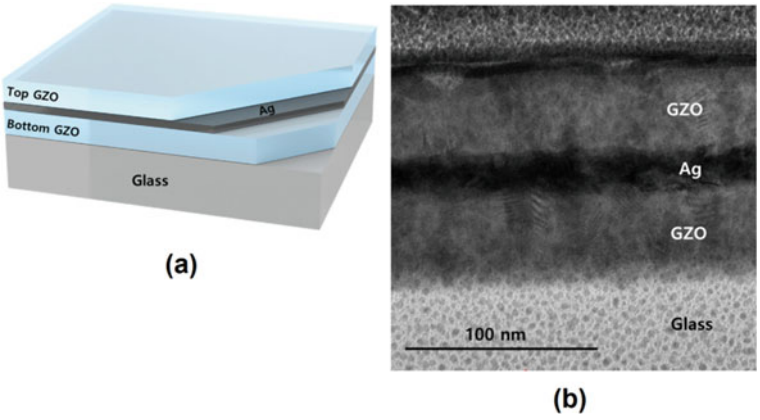

Fig. 19 **a** Schematic and **b** TEM image of a fabricated GZO/Ag/GZO transparent electrode (Reproduced with permission from Ref. [101], Copyright (2018) Elsevier)

ultra-fine diameter of each electrospun nanofiber leads to high transparency which allows metallic nanofibrous used for transparent electrodes. Fuh et al. [105] reported the fabrication of a new combination of additive manufacturing and electrospinning called near-field electrospinning (NFES) for random metal nano/microwire networks used as flexible transparent electrodes. This has proved to be a powerful technique which recently developed to print out uniaxially aligned fibers with precise control of fiber size in fabrication of polymeric flexible transparent electrodes.

Yousefi et al. [106] premeditated electrospun flexible electrodes which are found to exhibited notable transparency over the entire visible light range and relatively trivial sheet resistance. A combination of additive manufacturing method along with electrospinning termed as near-field electrospinning has been utilized by the team to obtain uniaxially aligned fibers with controlled size of fiber diameter and its placements. In a multi-process of manufacturing, polymeric fibers of polystyrene were allowed to deposit over the gold-coated polyethylene terephthalate in dimension-specific pattern. To enhance the connectivity within the gold and the specific pattern of the polystyrene layer, the as-obtained electrospun fibrous sheet was annealed and thereafter the etching of the gold-coated polyethylene terephthalate layer was carried out while the polystyrene acts as the mask for the gold particles to remain beneath the specific pattern. Figure 20 represents the (a) schematic of NFES, (b) Wet chemical etching, (c) removal of PS fibers, (d) prepared 2 × 1.5 cm electrodes, and (e) representation of optical clarity of electro-printed sample. The so obtained gold-coated polyethylene terephthalate electrodes having a specific pattern were then examined via conductivity measurements, transparency measurements, and bending tests. The transparency tests of the substrates with the lateral distance of 500 μm exhibits constant transmittance over the visible wavelength range. With the increase in the number of the printed fibers, the lateral distance is condensed and this roots the final electrode to parties lower resolution which ultimately hampers the transparency of the electrodes. However, when the impact of bending tests was studied as a function of the sheet resistance on the substrate with lateral distance of 500 μm, it was observed that the looked-for flexibility and the sheet resistance remains steady up to 600 cycles. The learning of the electrode size varying from 5 to 25 mm was supported on the conductivity of the sample and the sheet resistance was found to increase, respectively. Thus, a transparent and conductive electrospun fibrous network was fabricated by the team and concluded it to be the finest aspirant as a transparent electrode which could be used as an alternate for conventional rigid electrodes.

Jiang et al. [107] introduced a novel transparent electrode based on copper silver core–shell metal electrospun nanofibers prepared by combination of redox heating process and electrospinning. A very simple procedure was utilized to fabricate the copper-silver core–shell electrospun nanofibers. Firstly, the copper nanofibers were electrospun which after oxidation and reduction were allowed to coat by silver ink. The copper=silver nanofibers were thoroughly studied and characterized and core–shell nanofibers are found to have good transmittance and low resistance. Transparent copper silver nanofiber electrodes were simply transferred over polydimethylsiloxane substrates. This transparent electrode was used as anode, polydimethylsiloxane substrates as hole transport layer while eutectic indium–gallium material

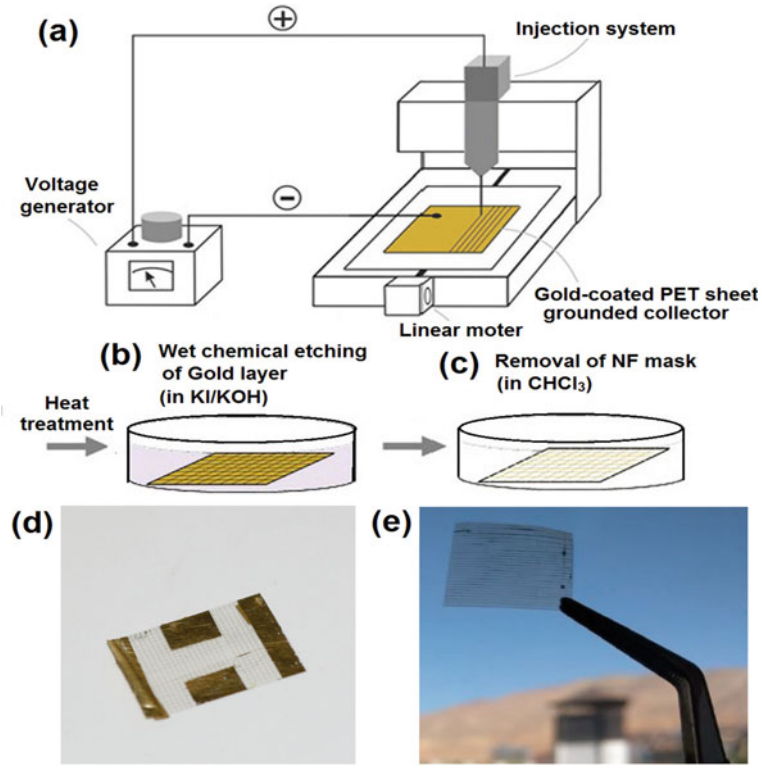

Fig. 20 **a** The schematic view of NFES printing of microfibers, **b** wet chemical etching for removal of Au coating, **c** removal of PS fibers, **d** prepared 2 × 1.5 cm electrodes and **e** representation of optical clarity of electro-printed sample (Reproduced with permission from Ref. [106], Copyright (2019) Elsevier)

was used as cathode. Such a formation was used to produce flexible optoelectronic device which shows improved luminous efficacy and high degree of transparency and flexible bending while electrospinning improves the transparency and conductivity of the transparent electrodes.

Wu et al. [108] fabricated and investigated continuous nanotrough networks from a wide variety of functional materials, including silicon, indium-tin-oxide, and metals such as gold, silver, copper, platinum, aluminum, chromium, nickel, and their alloys. Polymeric ultra-long and continuous nanofibers were drawn through electrospinning which was then coated with thin layer of the active materials. This nanofibrous network was then carefully transferred onto the substrates. The polymer templates were then submerged into organic solvents thereby remaining the continuous nanotrough networks of the active materials. The metal nanotrough networks show good transmittance owing highest to the copper nanotrough networks. The metal nanotrough networks demonstrate flat transmittance spectra from 300 to 2000 nm which is a desirable quality in transparent electrodes. The bending and

stretching ability of the metal nanotrough were also studied. A real-time application device has also been setup using gold nanotrough network on 178 mm thick polyethylene terephthalate substrate as a replacement of ITO/PET transparent film in four-wire analogue-resistive touch-screen display device which ensures the real-time application of the metal nanotrough network.

3.5 Nanogenerators

Sustainable and stable energy source has been in request to cope with the evolving technology of portable electronics. Owing to the limitations like limited battery lifetime, probable health, and environmental hazards, batteries are becoming hostile as power source. Nanogenerators are broadly classified according to the source of energy harvested into three types namely triboelectric nanogenerators, piezoelectric nanogenerators, and pyroelectric nanogenerators. Triboelectric nanogenerators are devices that harvest friction into static electricity using electrostatic induction. These kinds of nanogenerators are usually robust and environmentally friendly [109, 110]. External energy of piezoelectric materials is harvested by piezoelectric nanogenerators [111, 112]. Piezoelectric nanomaterials are generally used in nanogenerators because such materials can harvest small mechanical vibrations from ambient environment and easily convert the vibrational energy into electric energy. Piezoelectric-based nanogenerators generally use thin films, nanowires, and nanofibers. Piezoelectric polymer PVDF nanofiber prepared by electrospinning has been extensively studied due to its flexibility, ultralong length, and long-term stability compared with normal inorganic piezoelectric materials for further improvement in nanogenerators. The zinc oxide piezoelectric nanogenerator on solid and flexible substrate formation as shown in Fig. 21, is demonstrated by Heever et al. [113].

As the name suggests, nanostructures have always been the part of nanogenerators but the variation in the nanomaterials, variety of nanostructures have been a part of constant research. Ding et al. [114] studied piezoelectric nanogenerator based on formamidinium lead halide perovskite nanoparticles combined with poly (vinylidene fluoride) polymer. These piezoelectric nanogenerators show the uppermost

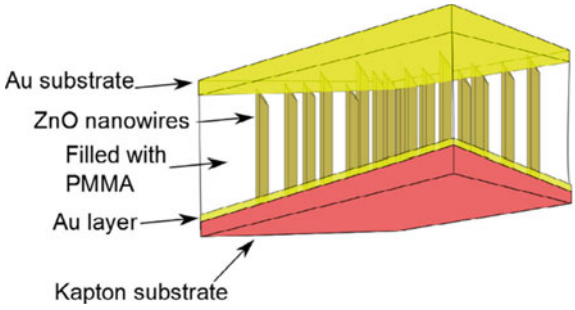

Fig. 21 ZnO piezoelectric nanogenerator formation on Kapton film (Reproduced with permission from Ref. [113], Copyright (2012) Elsevier)

outstanding outputs with voltage and good current density. Bakar et al. [115] studied the probability of indium-tin-oxide free, barium titanate, and graphene quantum dots doped polyvinylidene fluoride polymer nanocomposite-based flexible nanogenerator. The presence of graphene dots is supposed to enhance the output of the device. The output voltage, current, and power density of nanogenerators could be enhanced by directing the surface charge density. Usage of high-performance dielectric materials like polarized nanoparticles, polymers or polymer nanocomposites has been effectively proven to improve charge density [116].

Shi et al. [117] reported the fabrication of electrospun polyvinylidene fluoride nanofiber mat composed of graphene and barium titanate nanoparticles for high-performance flexible piezoelectric nanogenerators. Barium titanate and graphene embedded polyvinylidene fluoride nanocomposite nanofibers were fabricated through electrospinning whereas, barium titanate/polyvinylidene fluoride nanofiber, and graphene/polyvinylidene fluoride nanofiber were also fabricated in order to study the effect of nanoparticles on the device performance. Interfacial interactions within the barium titanate and graphene with the polyvinylidene fluoride tend to the crystallization of polyvinylidene fluoride chains. The fabricated nanogenerator was also tested to examine the stain and frequency parameter and showed that output remains constant for almost over 1800 cycles. The device is further investigated for real-time application for harvesting biomechanical from the ambient environment of daily life. Figure 22 displays the real-time use of the nanogenerator.

Veeramuthu et al. [118] fabricated smart garment energy generator using electrospun nanofibers. A very facile method was utilized for the study of the energy-generating smart garment. Inter weaving of two kinds of fibers was optimized to form a smart garment where one kind is three-dimensional elastic nanoconductive fibers (NCF) and the latter is three-dimensional elastic coated nanoconductive fibers (CNCF). Polystyrene butadiene styrene elastic fibers were electrospun to form nanoconductive fibers and pristine polytetrafluroethylene, pristine polyurethane and different blends of polytetrafluroethylene and polyurethane were dip-coated with as prepared nano conductive fibers. Also, silver nanoparticles were dip coated over the nano conductive fibers A suitable combination of blends of polytetrafluroethylene and polyurethane was examined and the compatible composition was used for the fabrication of coated nano conductive fibers. Moreover, this smart garment fabricated by interweaving of the nanoconductive fibers and coated nano conductive fibers was again then coated with strontium-aluminate, a phosphorescent material that results in the formation of an incorporated smart garment. The incorporation of phosphorescent material had empowered the intensification in the luminescence of the light which is the outcome of the energy harvested via smart garment. The manufacturing process of the smart garment is shown in Fig. 23. In a very comprehensive manufacturing process, five various classes of the smart garment were fabricated reliant to the polytetrafluroethylene and polyurethane blends ratio. After the detailed morphological, mechanical, and electrical studies of the smart garment, SG2 (polytetrafluroethylene: polyurethane = 8:2) had turned out to be optimum and most reliable for the practical application. A practical test was conducted with SG2 where the mechanical deformation of the garment was used to see the energy harvesting in the form

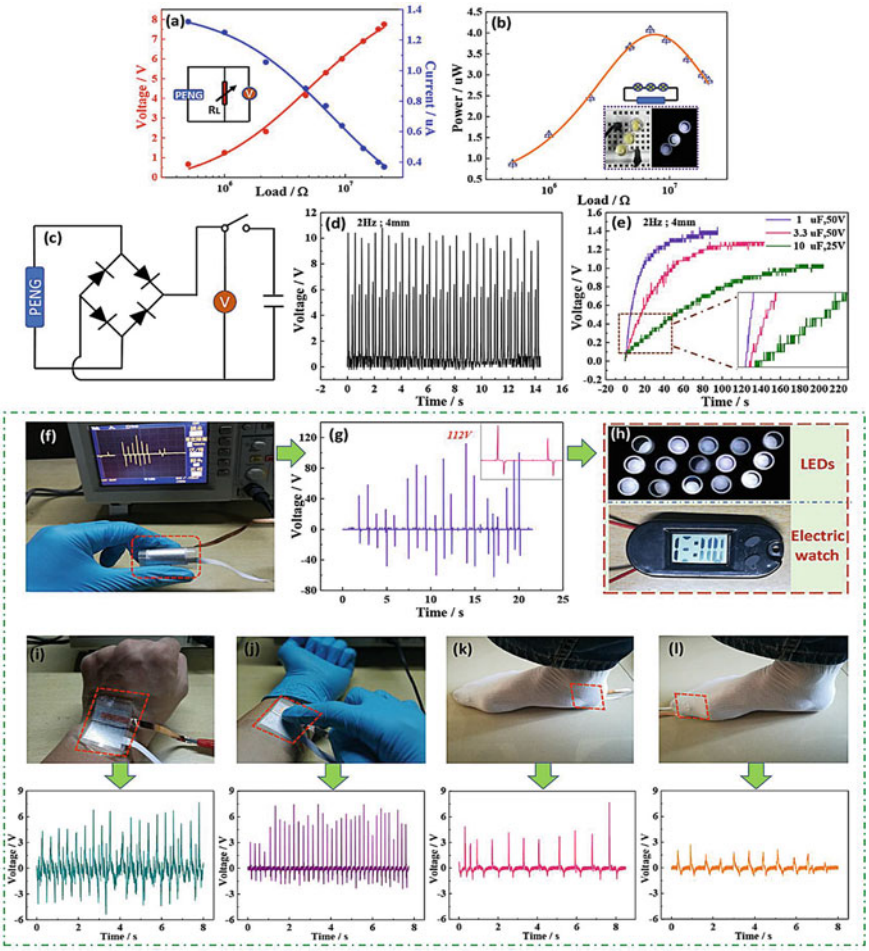

Fig. 22 Real-time use of nanogenerator based on electrospun barium titanate and graphene embedded polyvinylidene fluoride nanocomposite nanofibers (Reproduced with permission from Ref. [117], Copyright (2018) Elsevier)

of glowing red LED. This SG2 further was coated with phosphorescent material to achieve incorporated smart garment which is again allowed to undergo another experiment.

They have also demonstrated the application of strontium-aluminate-incorporated smart garment (SG) in the footwear and showed the exceptional use of the electrospun nanofibers in the field of energy harvesting which had proven its real-time application along with the durability [118]. They have prepared strontium-aluminate-incorporated smart garment (Fig. 24) by depositing strontium-aluminate on the surface of nonconductive fibers as-fabricated by electrospinning. It was observed that the light was emitted from strontium-aluminate-incorporated smart

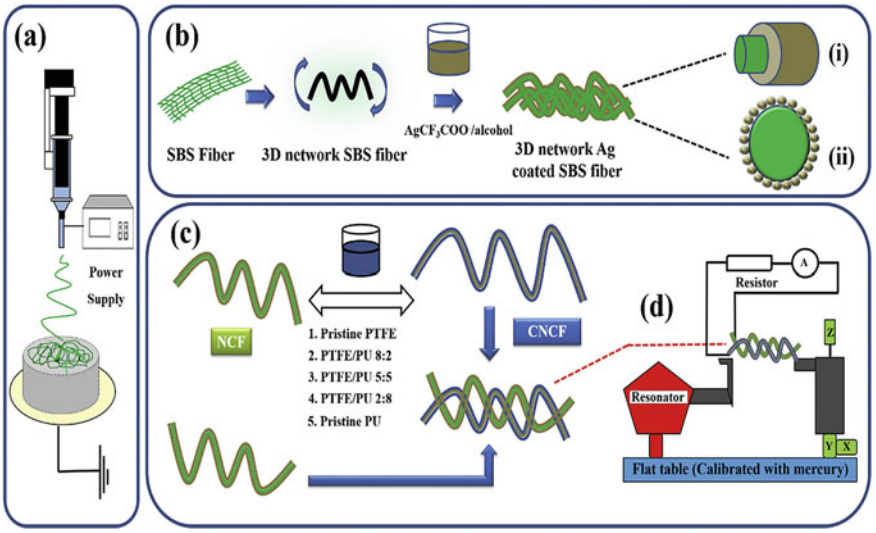

Fig. 23 Smart garment energy generator based on electrospun nonconductive and coated nonconductive nanofibers (Reproduced with permission from Ref. [118], Copyright (2019) Elsevier)

garment when exposed to sunlight and hence they have concluded that the strontium-aluminate-incorporated smart garment can be well useful in footwear designing.

4 Conclusions

Functional polymeric nanofibers have been easily fabricated by using electrospinning technique which can be further modified for the fabrication of polymer composites or core–shell nanofibers. Electrospun polymer nanofibers owing to their amazing properties like high mechanical strength with porous fibrous structure are the potential candidates for wide range applications. The exceptional performance and multifunctionality of electrospun nanofibers with high flexibility and stretchability useful for designing flexible devices which have brought about a cutting edge in wearable and portable electronics. Due to innovative methods and manufacturing processes of smart materials, the flexible devices enabled design of new architectures that are not possible with conventional planar devices. Accompanying flexibility into planar devices has greatly improved the applicability of the devices. The current chapter has projected the capability of electrospinning to fabricate varied polymeric nanofibers by modifications in design, instrumentation, precursor form, polymer matrix, environmental conditions, etc. Various controllable parameters stated have given researchers the power to examine every possible aspect of nanofibers. Polymer nanofibers and

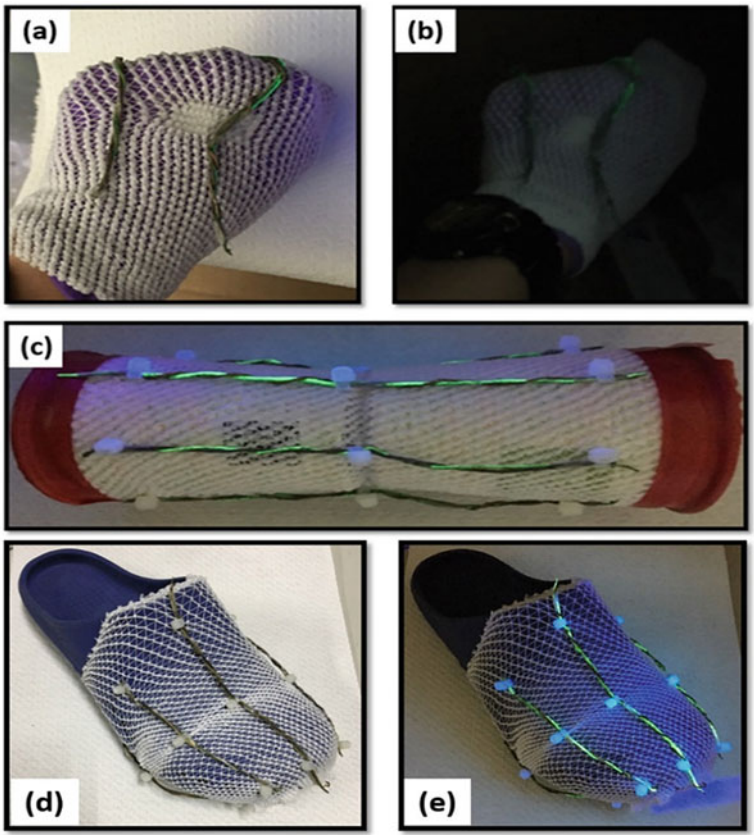

Fig. 24 Strontium-aluminate-based smart garment (Reproduced with permission from Ref. [118], Copyright (2019) Elsevier)

polymer hybrid composite structures are still fabricating by well cost-effective electrospinning. Despite the advantages of electrospinning technique for fabrication of polymer nanofibers such as inexpensive setup, ability to control fiber diameter, orientation, and composition, etc., the applications of electrospun nanofibers especially for flexible devices also face some challenges which include the use of organic solvents, the limited control of pore structures and low mechanical strength. More advanced nanofiber configurations, such as core–shell, multilayer, and multicomponent nanofibers, may be prepared through methods like co-axial electrospinning, electro-hydrodynamic direct writing or mechano-electrospinning, to overcome those problems. Mechano-electrospinning technique uses electrical and mechanical forces to drive the polymer solution in a viscous form for direct writing of polymer ink link on the substrate. As-fabricated nanofibers can be directly or indirectly modified with the help of coating, decorating or embedding nanoparticles over/into the fibers, which can be enormously useful in flexible devices due to their extreme flexibility

with high mechanical strength apart from very large surface area. The potential applications of electrospun polymer nanofibers prepared by electrospinning or co-axial electrospinning methods in light-emitting diodes (LEDs), sensors, UV photodetectors, transparent electrodes, and nanogenerators are enormous and systematically explored in this chapter.

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