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Abstract

The advent of flexible, wearable electronics has placed new demands on energy storage systems. The demands for high energy density achieved through the use of highly conducting materials with high surface area that enable facile electrochemical processes must now be coupled with the need for robustness and flexibility in each of the components: electrodes and electrolytes. This perspective provides an overview of materials and fabrication protocols used to produce flexible electrodes and electrolytes. We also discuss the key challenges in the development of high performance flexible energy storage devices. Only selected references are used to illustrate the myriad of developments in the field.

Keywords

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Flexible Electrodes and Electrolytes for Energy Storage

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Abstract

The advent of flexible, wearable electronics has placed new demands on energy storage systems. The demands for high energy density achieved through the use of highly conducting materials with high surface area that enable facile electrochemical processes must now be coupled with the need for robustness and flexibility in each of the components: electrodes and electrolytes. This perspective provides an overview of materials and fabrication protocols used to produce flexible electrodes and electrolytes. We also discuss the key challenges in the development of high performance flexible energy storage devices. Only selected references are used to illustrate the myriad of developments in the field.

Key Words: Flexible electrode, Flexible electrolyte; Wearable energy storage; Batteries; Supercapacitors.

1. Introduction

It is now hard to imagine a world without portable electronic devices, and wherein wearable componentary is on the increase. Devices, such as smart phones coupled to wearable sensors to monitor vital physiological signs are part of a growing trend towards the seamless integration of electronic devices and humankind. More sophisticated implantable electronic systems already allow the deaf to hear, parkinsons disease

symptoms to be controlled and epileptic seizure to be monitored. The performance of these wearable implantable devices is critically dependent on the realization of appropriately configured energy supply systems. At present, such systems are predominantly energy storage devices: batteries or supercapacitors. All-solid-state power sources are preferred, not just for safety in that liquid electrolyte leakage can be avoided, but also due to the flexibility available in shaping and forming. An ever-increasing demand for portable electrical devices will remain a driving force for the continuing development of new inexpensive, flexible/wearable, light-weight and environmentally benign energy storage devices [1] and a number of excellent reviews have appeared [2-8].

Flexible batteries/supercapacitors consist of three main components: electrode, electrolyte and separator (**Figure 1**) [9]. These components can be assembled as flat or fiber. In the flat film configuration, solid electrolyte is sandwiched between the flexible cathode and anode. They typically show a five-layer structure, for the cathode and anode with an integrated current collector. They are commonly assembled into a prismatic cell for use. They may be packaged into a flexible polymer-based case (pouch cell). Fiber batteries contain the same essential elements. With fibers the omni-directional flexibility facilitates integration into different forms and structures including knitting or weaving into textiles [10, 11]. Flexible electrodes need to meet the requirements of high capacity/capacitance, high rate capability, low self-discharge, excellent cycling stability, and robust flexibility. Solid electrolytes should possess high ionic conductivity, negligible electronic conductivity, and a wide electrochemical window, coupled with thermal and mechanical stability.

2. Flexible Electrodes

2.1 Planar Thin Film.

Flat flexible batteries originated from all solid-state thin film batteries. They may be constructed by sequential vapor deposition of cathodes ($LixMn_2O_4$ or V_2O_5), solid electrolyte ($Li_{2.9}PO_{3.3}N_{0.46}$) and anodes (Li), and subsequently encapsulated with a protective coating [12]. The use of thin metal foils as the deposition substrate facilitated development of flexible batteries [13]. The use of elastomeric materials as the substrates

results in a battery that is not just flexible but bendable [14] or even stretchable [15,16]. Most recently, the use of low cost cellulose-based or textile-based materials as substrate has accelerated the application of flexible electrodes and devices [5, 7, 17, 18].

Flexible, mechanically strong, free-standing papers or films, such as bucky paper [19], graphene paper [20] and conducting polymer papers [21] offer an alternative approach. They can be used directly as battery or supercapacitor electrodes without the use of low capacity conducting additives and insulating binder (Figure 2). Also they can be easily engineered into the desired shapes or structures by conventional mechanical techniques.

2.1.1 Free Standing Planar Films

Free-standing flexible thin film electrodes based on organic conductors (carbon nanotubes or graphene) can be produced from dispersions using evaporative casting or filtration to remove the solvent media [22-25]. The stable dispersion containing those individual tubes or sheets (colloid) is formed by breaking up large bundles of CNTs or graphene oxide / graphene particles with an ultrasonic energy with or without the assistantance of amphiphilic molecules (dispersants). During the filtration process, CNTs or graphene oxide/graphene were held together *via* strong π-π stacking and van der Waals forces, along with the interdigitation of CNTs tubes or interlocked/tiled graphene sheets due to their large aspect ratio.

CNTs based thin film electrodes consist of randomly entangled and cross-linked carbon nanotubes. The open space between the entangled fibrils creates a porous structure, offering high accessible surface area. These structures provide a highly conductive network. These papers possess the advantage of high power and cycling stability as an energy storage electrode [19, 26]. They can also be used as high surface area substrate for the deposition of conducting polymer/metal oxides, forming composites [27]. In these composites, CNTs function as a three-dimensional robust conductive network, facilitating effective charge transport and efficient ion diffusion. The CNT network also provides mechanical robustness, thus improving the cycling stability, energy and power density [28, 29].

Graphene papers possess a unique layered structure, in which graphene sheets are interlocked/tiled together in a near-parallel fashion. However, the aggregation or restacking of the graphene nanosheets (GNs) due to the strong π-π stacking and van der

Waals forces limits the available surface area and limits charge storage capacity. The unique properties available from the individual sheets, such as high surface area and extraordinary electronic transport, cannot be delivered. The strategies to inhibit the restacking of graphene sheets mainly include incorporation of spacers separating the graphene sheets, and creation of three-dimensional porous networks [30]. Hydrothermal and freeze drying are two common techniques used to construct a three-dimensional porous graphene assembly [31,32]. It is generally believed that the addition of spacers (such as CNTs, ICPs or metal oxides) in-between the graphene sheets can effectively inhibit restacking to maximize the available surface area, and thus improve the charge storage capacity. The incorporation of these active components induces much higher charge storage capability too. Highly conductive GNs also act as a conducting matrix in such hybrid structures, which has a direct impact on improving the coulombic efficiency, rate capability and cycle life. A synergistic effect can be driven from both components in the graphene-based composite materials [33-37].

Flexible free standing films of inherently conducting polymers (ICPs) with controlled thickness and morphology can be produced using electropolymerisation [38]. A free-standing film can be peeled from the conductive substrate where it is electrodeposited. These films can be shaped into the desired structures and used directly as battery or supercapacitor electrodes [39-41]. However, ICPs suffer from poor electrochemical stability associated with the swelling and shrinkage of the polymers due to ion ingress / egress during the oxidation and reduction. This has limited commercial application [42, 43]. A common strategy to overcome this drawback is to synthesize CPs composites with carbon-based materials [44, 45]. Carbon-based materials play the role of a perfect backbone for a homogenous distribution of CPs in the composite. It preserves the CPs active material from mechanical changes (shrinkage and breaking) during long cycling. The presence of highly conductive carbon based backbones also improves charge transfer capabilities enabling a high charge/discharge rate.

2.1.2 Planar Films with Support.

A variety of substrates can be used to produce flexible electrodes, based on metal foils, membranes or textiles (Figure 3) [5,7,46]. The fabrication techniques mainly include vapour deposition, electropolymerization, coating or printing.

Vapor deposition. Physical vapor deposition (PVD) including RF and DC magnetron sputtering or thermal evaporation has been used to produce metal, metal oxide or other metal compound thin film electrodes [47]. Magnetron sputtering can be used to produce a wide range of cathode, anode and solid electrolyte films for lithium ion batteries. Materials, such as $LiMnO_4$, LiCoO2, $Li_8V_2O_5$, $Li_1Mn_{1.5}Ni_{0.5}O_4$ cathodes, Si, V_2O_5 anodes, and LiPON electrolyte have been deposited [48-52]. Lithium thin film electrodes for use as anodes are normally produced by evaporation of lithium metal under a low pressure.

Chemical Vapor Deposition (CVD) can be used to deposit materials with structural control at the atomic to nanometer scale [53]. The thin film produced demonstrates superior cycling stability compared with that of powder-based electrodes due to their microstructural stability, and short ion diffusion pathways in thin films [54]. This technique can produce metal oxides, such as vanadium oxide [55], silicon crystalline-amorphous core-shell nanowires or amorphous silicon [56, 57]. CVD is being widely used in the production of CNTs, GNs or CNTs/GNs hybrid films/sheets electrodes for flexible high energy and power densities batteries or supercapacitors. When those carbon-based films/membranes are produced on a soft or flexible substrate such as carbon cloth, they can be directly as electrodes [58-62]. For those produced on hard substrates, normally a wet process is applied to transfer them onto the desired flexible substrate [63, 64].

Electropolymerization. This is a simple and inexpensive alternative route for direct polymerization of active materials on conductive flexible substrate. It is widely used in the deposition of conducting polymers, metal oxides, and composites for energy storage application [65-68]. The morphology and properties of the produced materials can be easily tuned via control of the deposition parameters, electrolyte concentration or pH, and temperature. This *in situ* deposition approach can be used to coat complex shapes. Deposition on to flexible substrates mainly include carbon cloth/fabric [69,70], CNTs mats [71,72], graphene papers [73,74], textiles [75-77] and polymer membranes [78].

Coating or printing. A thin film can be directly obtained by coating the electroactive materials dispersions or slurry on a flexible substrate surface. This technique is easy to control and cost-effective. It is commonly used in the fabrication of commercial battery or supercapacitor electrodes via a roll-to roll process. With those low concentration

dispersions, drop-casting [79, 80], spray coating [81-83], or brush-coating [84] processes can be applied manually. Automatic inkjet printing method not only provides a non-contact deposition method for obtaining thin films, but also allows a precise control of the pattern geometry, pattern location, film thickness and uniformity of the films. This technique plays a critical role in the fabrication of micro-electrodes and devices. It enables the new designs for fabrication flexible micro energy devices [85-87]. Moreover, the printable energy devices can be fully integrated with the fabrication process in current printed electronics and easily scaled up. These printing/coating techniques normally produce a very thin film, which displays a high energy density in the metric unit of mass, but not in volume or areal size.

2.2 Fibre Electrodes.

Compared with flat flexible planar film electrodes, fiber electrodes possess much higher flexibility. Their omni-directional flexibility enables them to be twisted, weaved, sewn or braided, forming a textile structure. It is easy to connect fiber-type batteries / supercapacitors in parallel or series to provide the required power or energy density in a textile.

Structures that consist of a coating on a fiber substrate can be fabricated using the same techniques described above for planar films [88- 93]. Free-standing fiber electrodes can be produced by wet-spinning and drawing/spinning from 2D membranes (Figure 4). Although electrospinning is a simple processing technique to fabricate high aspect ratio nanofibers with high electron and thermal diffusivity, and tailorable pore distribution at a commercial scale [94], this technique will not be discussed herein because the resultant fibers are too tiny to be used individually.

Wet Spinnining. This is a process used to inject a spinning dope into a coagulation bath wherein the material solidifies in the form of a fiber. It is a facile and promising fabrication technique to produce long length materials with a large aspect ratio and high alignment [95, 96]. It has been used in the fabrication of conducting polymers [97-99] and carbon-based nanomaterails: CNTs, grahene and their composites [97, 100- 104]. These fibers are mechanically strong and highly conductive. They provide high charge storage and high cycling stability when used as battery or supercapacitor electrodes. In addition, their properties can be tuned by tunning parameters during a wet-spinning

process. Solution viscosity, coagulation bath composition used and the degree of stretch applied during spinning are critical parameters [105-107].

Drawing/spinning from 2D membrane. Currently there is an emerging interest to produce 1D fiber-like material from 2D thin membranes/films. The commonly used 2D membrane to produce fiber via a drawing/spinning process is CNTs forest with superaligned arrays, in which the CNTs are aligned parallel to one another and are held together by van der Waals interaction to form bundles [108]. Multi-ply, torque-stabilized, mechanically strong yarns can be produced by introducing twist during spinning [109], which moves further towards practical application. The incorporation of functional materials into these yarns greatly expanded their application in energy storage. These functional materials can be powders of particle, nanofibers/nanosheets, or conducting polymers. In this composite fiber, CNTs act as the matrix to contain these functional materials, and also provide a highly conductive network facilitating effective electron transfer. The incorporation of functional materials produces porous structures, providing high surface area for easy accessibility of electrolyte and ion transport. All lead to improved electrochemical properties. These functional materials can be deposited on CNTs membrane via filtration [110, 111], in situ polymerization [112], and even electrospinning [113].

2. 3 Stretchable Electrodes

Stretchable electrodes are those flexible electrodes that can maintain the function under an extreme condition – large deformation. They can be wrapped conformally around complex and unconventional shapes including body shape. Their use in wearable electronics can minimize discomfort. Stretchable electrodes can be achieved via two ways: use of new structural layouts in conventional materials and new materials in conventional layouts [114]. The former strategy is commonly used. The structural layouts to accommodate the applied strain mainly include wavy structure [115,116], net-shaped structure [117], and helical shape [118], thus avoiding substantial strain on the material itself.

At present, stretchable electrodes for batteries/supercapacitors are fabricated by integrating an active material onto/into an elastic substrate that is either a polymer or a

textile. Elastic polymer substrates include polydimethylsiloxane (PDMS) [15, 119-121], latex [122], and poly (styrene-*block*-isobutylene-*block*-styrene) (SIBS) [123, 124]. The elastic or stretchable fabric is the ideal substrate for those electrodes that can be made into breathable textile formats with stretchability. In addition, the textile's instrinsic porous structure is beneficial to electrolyte and ion access leading to better electrochemical properties [16, 17, 125, 126]. Similar techniques as those for planar and fiber substrates can be applied to integrate the active materials with the elastomeric substrates, and will not be discussed herein.

3. Polymer Electrolyte

Polymer electrolytes are inherently flexible and provide processing options that should enable realization of practical devices. These electrolytes enable the fabrication of flexible, compact solid-state structures free from leaks. The ideal polymer electrolyte should be of high ionic conductivity ($\sim 10^{-1}$–10^{-4} S cm^{-1}), negligibly small electronic conductivity ($\sim 10^{-8}$ S cm^{-1}), very low activation energy (lower than 0.1 eV), ionic transference number $t_{ion} \sim 1$ and a wide electrochemical window [127]. Polymer electrolytes consist of an ionic conductor and a high-molecular-weight polymer matrix.

Lithium ion polymer electrolyte. Polymer hosts used to entrap lithium ion conductors include poly(ethylene oxide), poly(acrylonitrile), poly(methyl methacrylates), poly(vinyl chloride) and poly(vinylidence fluoride). They are commonly formed by dissolving the lithium salt into a polymer matrix, with subsequent casting onto a substrate to form a thin membrane. Some excellent reviews on the fabrication and application of these polymer electrolytes have been published [128-131].

Proton or alkaline polymer electrolyte. Phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) are two common types of proton conductors [81,92,132-135], and polyvinyl alcohol (PVA) is a commonly used host. Same formulations have been shown to be stretchable achieving a fracture strain as high as 410% elongation [124]. PVA can also be used to fabricate gel electrolytes with alkali, such as potassium hydroxide (KOH). This type of electrolyte is for use in supercapacitors and alkaline batteries (i.e. NiMH, Zn-air) [136-139]. This type of electrolyte is highly conductive (10^{-3} to 10^{-2} S cm^{-1}), but can only offer a narrow electrochemical widow (not higher than 1 V) limiting the energy density.

Biopolymer electrolyte. Biopolymer electrolyte is a type of polymer electrolyte using biocompatible or biodegradable polymer acts as the host for the ionic conductors. Natural polymers may include cellulose, starch, chitosan, agar, pectin and gelatin [140- 145]. The conductors used mainly include lithium salts, sodium iodide, ammonium bromide or ionic liquid. A fully biocompatible polymer electrolyte can only be achieved with a biopolymer host along with a biocompatible conductor, such as biocompatible ionic liquid [146,147].

Ionogel. Ionic liquids offer a variety of advantages, such as low volatility, low flammability, high thermal stability and wide electrochemical window for electrochemical devices [148-150]. Researchers have demonstrated their application in lithium-ion [151], lithium-sulfur [152], lithium-air batteries [153] and supercapacitors [154,155]. Ionic liquid can be immobilized within a polymer or silica-like network, forming an ionogel [156-158], that allows its use as a flexible electrolyte. Ionogel can be stretchable within a stretchable polymer matrix, such as poly(methyl methacrylate) (PMMA) [159].

4. Challenges and Prospective.

There is no doubt that significant improvements have been achieved in the fabrication of inexpensive, flexible, light-weight and environmentally benign energy storage devices. However, there is still room for improvement to provide more robust structures with higher energy and power density. Future work may include the following aspects to improve and develop flexible energy storage devices.

i) New materials. At present, work on flexible electrode materials mainly focuses on organic conductors due to their intrinsic flexibility. This includes carbon based materials and conducting polymers or composites containing them. There is a need for continued development of fabrication strategies to allow such materials to be created in different forms either through printing or spinning to produce long length of fibers. Solid electrolytes suffer from low conductivity, and gel electrolytes are commonly used instead. New electrolyte systems with improved robustness (tough gels) and resistant to leakage under mechanical duress are needed.

ii) Device fabrication. Despite a series of impressive high performance flexible devices based on thin film electrodes being reported, they are still some way from

practical application in terms of volumetric energy and power density. As film thickness increases, energy density is reduced and mechanical properties are compromised. To ensure that the inventory of inherently flexible electrode and electrolyte materials can be integrated into battery structures, we must think outside the box in seeking appropriate fabrication protocols. 3D printing offers an interesting approach. In addition, spinning long lengths of fiber electrodes and their assembly using knitting weaving or braiding apparatus offers an interesting alternative 3D assembly approach.

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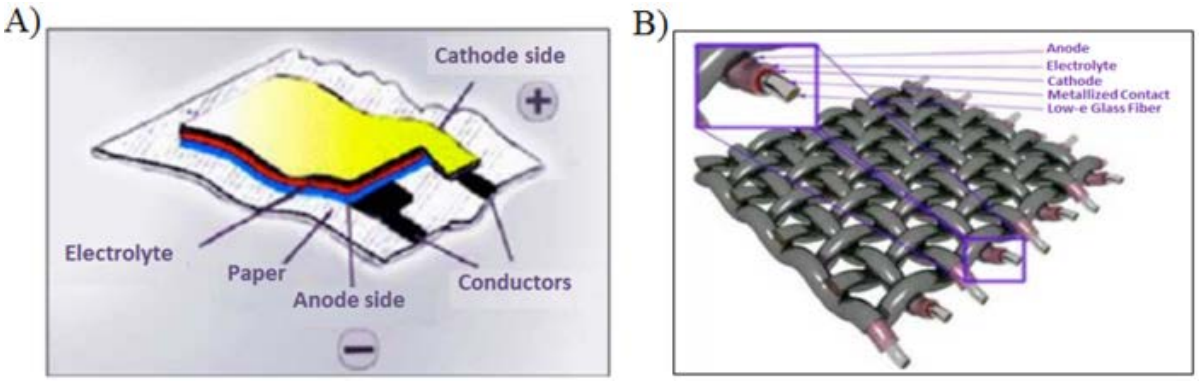

Figure 1 Scheme of a flat flexible battery (A), a fiber battery and a demonstration of fiber batteries weaved into textile (B) (Adapted from reference 9 with permission).

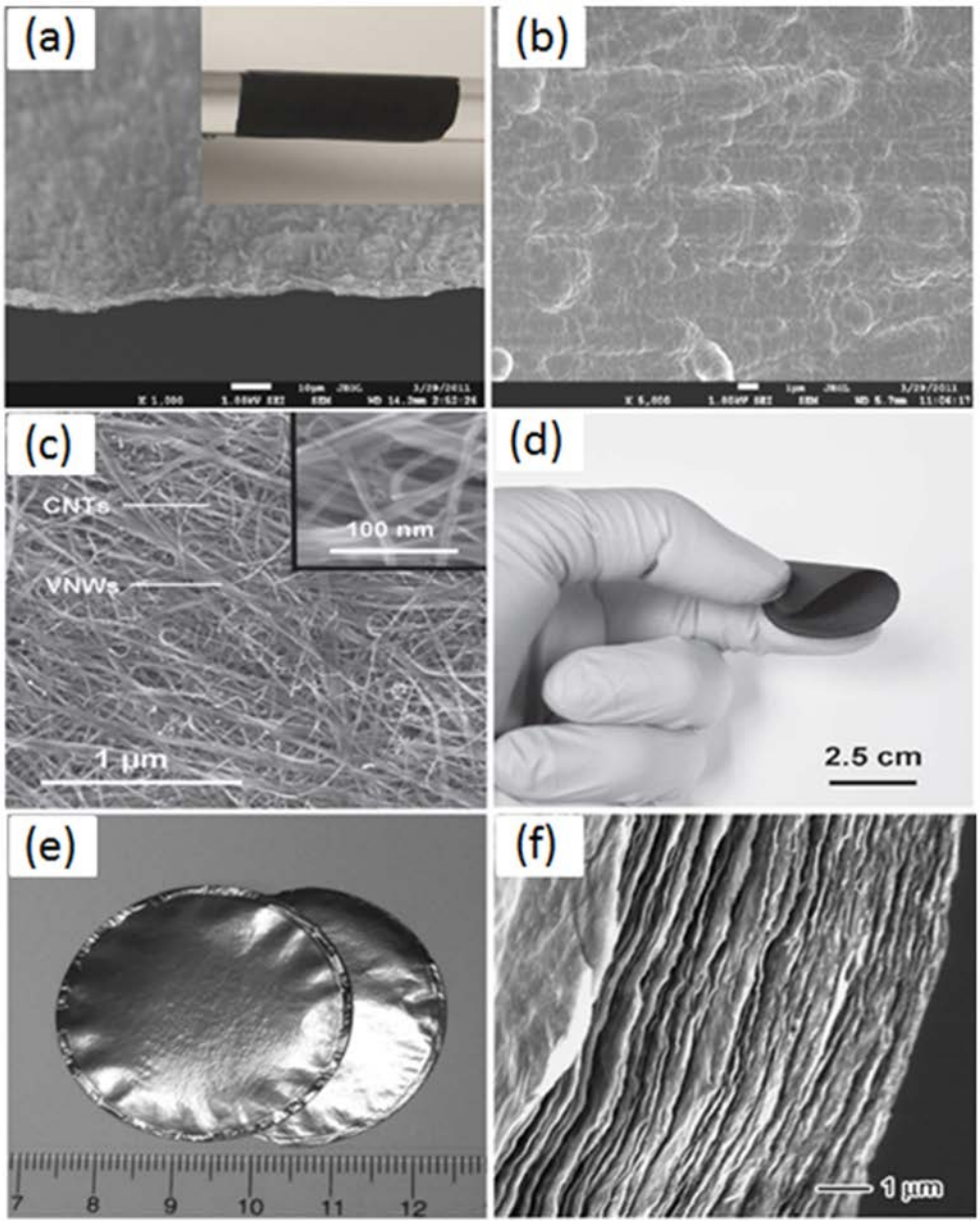

Figure 2 Digital and SEM images of free-standing paper–like materials that can be used directly as battery or supercapacitor electrodes, including conducting polymers (polpyrrole) (a, b), carbon natube-V_2O_5 nanowire (c, d) and graphene paper (e,f). (Adapted from references 26, 29 and 39 with permission)

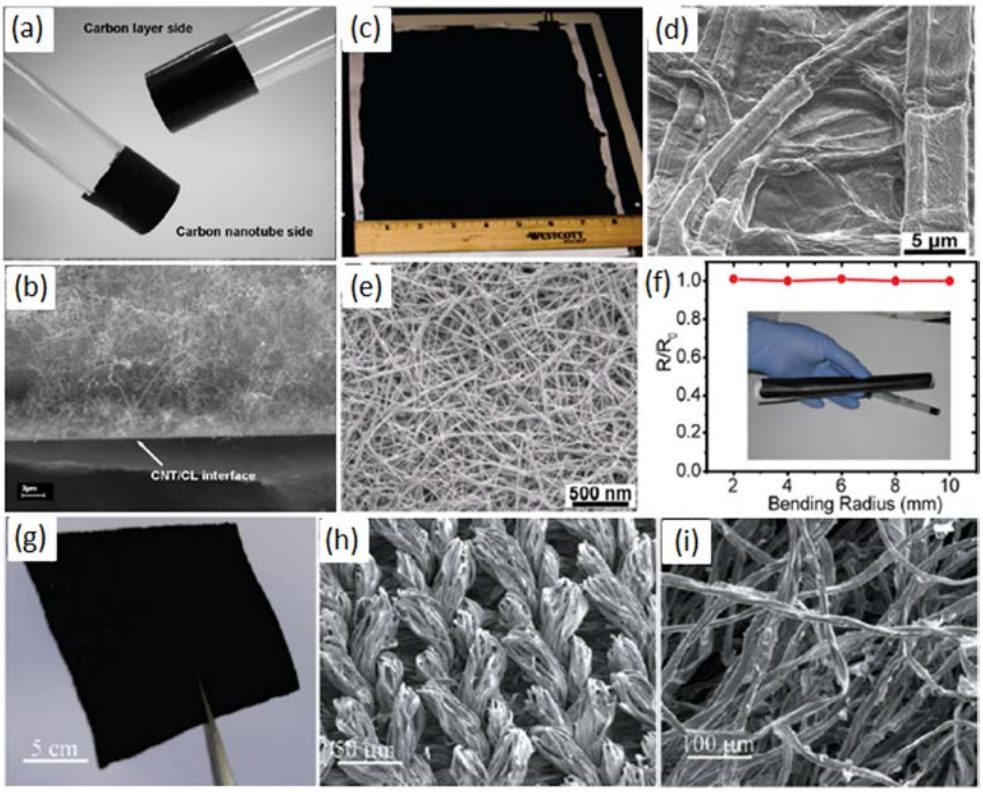

Figure 3 Digital or SEM images of carbon nanotubes electrodes with a mechanical support of carbon layer (a, b), daily-used print paper (c-f) and and textiles (g-i). (Adapted from references 17, 58 and 82 with permission)

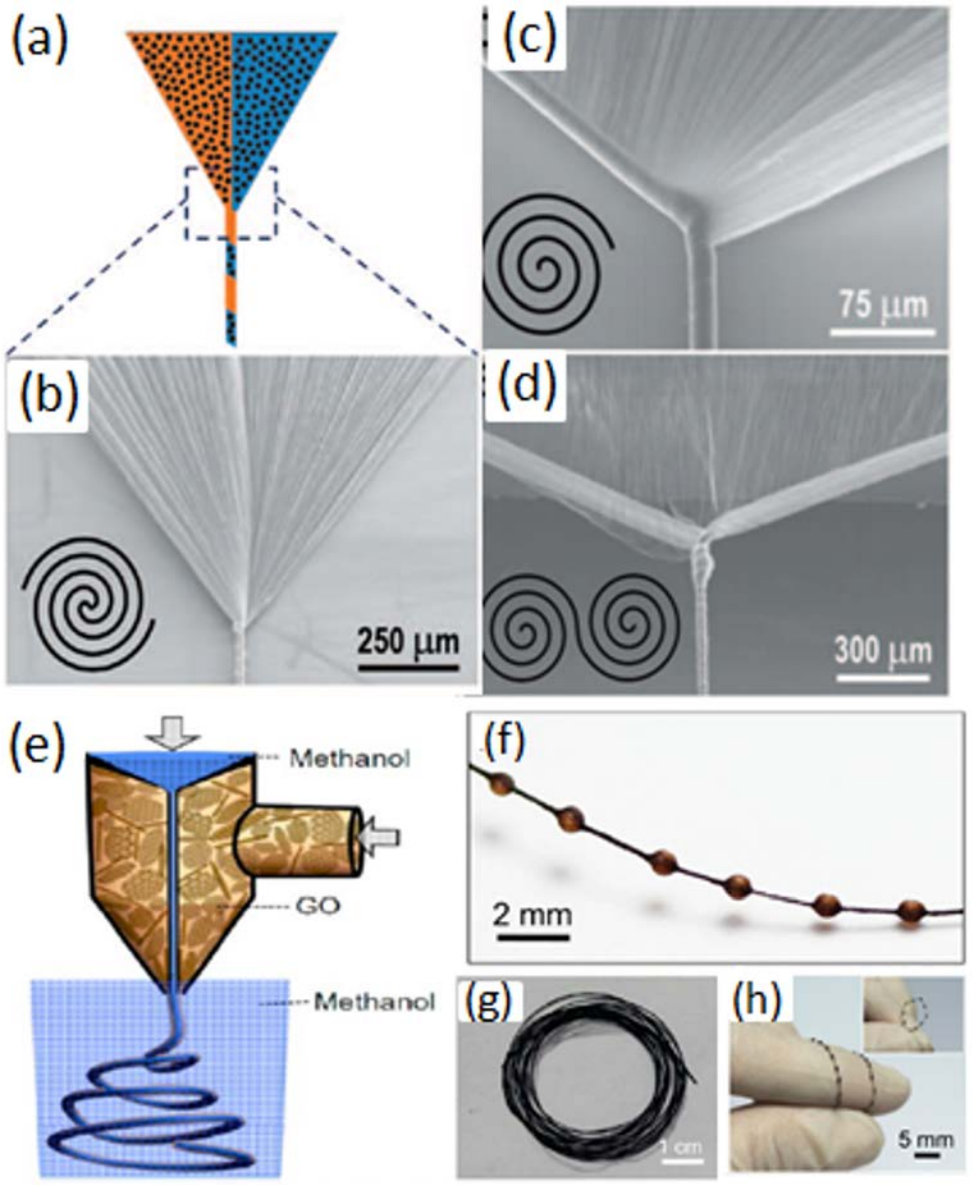

Figure 4 Schematic procedures of two typical methods to produce fiber electrodes without mechanical support and their images. a-d); biscrolling nanotube yarns by twist insertion and SEM images. e-h); a dual-capillary spinneret to directly spin graphene oxide hollow fibers (e, g) or produce novel necklace-like structure (f, h) by controlling the air flow rate. (Adapted from references 107 and 110 with permission)

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