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## Sustainability Spotlight Statement

Wearable electronic devices necessitate sustainable and safe energy storage devices to power them. Flexibility, bendability, twistability are the required features need to be adapted for the wearable supercapacitors. The increasing demand for sustainable energy storage devices are manifested by UN Sustainable Development Goal: 7: Affordable and Clean Energy. Carbon fibers-based hybrid/nanocomposite electrodes are highly sustainable materials for developing high-performance flexible and wearable supercapacitors.



## Data Availability Statement

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Data sharing not applicable – no new data generated. Data availability is not applicable to this article as no new data were created or analysed in this study.



# Recent Advancements on Carbon Fibers-Based Sustainable Electrodes for Flexible and Wearable Supercapacitors

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## Abstract

Electrochemical energy storage devices such as rechargeable batteries and supercapacitors have replaced conventional batteries and dielectric capacitors due to their excellent charge storage capabilities. Supercapacitors (SCs) are excellent in their high-power density and can deliver high-power on demand in fraction of seconds. SCs utilize water-based electrolytes, hence are safe and reliable energy storage devices for application in portable and wearable electronic devices. A major challenge in fabricating a flexible and wearable SC is the rigidity of electrodes prepared due to the usage of rigid metallic current collectors. This hinders SCs in their successful implementation to power the commercial wearable electronic device. The flexibility to a SC is mainly imparted by its electrodes hence the preparation of electrode is utmost important. In this review, we report the facile fabrication of SCs using carbon fiber (CF) including carbon microfiber and carbon nanofiber. CF is a sustainable environment-friendly material that can be used in electrochemical energy storage devices. CF functions as both an electrode-active material and a current collector during the fabrication of a SC. A major bottleneck in using the CF as an electrode-active material in SCs is their low specific capacitance. The specific capacitance of CF-based SCs can be enhanced by preparing hybrid or nanocomposite electrodes by combining CF with other high-performing electrode-active materials such as electronically conducting polymers, nanocarbons, MXenes, transition metal oxides, etc. We have provided a detailed discussion on the various strategies adopted for the synthesis of CF-based hybrid/nanocomposite flexible electrodes for SC application. The electrochemical performance evaluation of CF-based SC electrodes is reviewed and emphasis is given to their flexible and wearable features. This article helps to get an in-depth insight about the preparation of sustainable CF-based flexible electrodes for the next-generation wearable SCs.

**Keywords:** Supercapacitor, Carbon Fiber, Wearable Electronics, Electrochemical Energy Storage, MXene

## 1. Introduction

Tremendous development in portable and wearable electronics have triggered the research and development of flexible energy storage devices to power them [1, 2]. The increased explorations in the field of energy science and technology helped the consumer electronic industry to emphasize design and manufacture consumer electronic products with features such as flexibility, portability and a miniaturized size. Such products hold various fantastic



1 functionalities like rolling-up display, on-body sensors, wearable cloth fabric with self-  
2 charging utility, etc. to name a few [3-5]. The efforts put forwarded in the field of consumer  
3 electronics necessitated gigantic modifications to the energy storage systems in terms of their  
4 flexibility and safety in implementation rather than merely possessing high energy density,  
5 power density and long cyclic stability. Hence importance has been given to the mechanical  
6 features such as flexibility, bendability, stretchability, etc in fabricating energy storage devices  
7 for wearable electronic devices [6-8]. Among the various available choices, rechargeable  
8 metal-ion batteries and supercapacitors (SCs) are the two contemporary choices that evolved  
9 to save the current energy demand due to energy scarcity [9-11]. Rechargeable metal-ion  
10 batteries such as lithium-ion batteries, sodium-ion batteries, etc are excellent in their energy  
11 densities but they fail to deliver high-power on demand. On the other hand, SCs are best in  
12 their high-power density but exhibit low energy density. A major demerit of using rechargeable  
13 metal-ion batteries is their recyclability where the disposal become a nightmare. In contrary,  
14 SCs utilizing water-based electrolytes are environment-friendly candidates and can be made  
15 sustainable devices if the components used are sustainable materials. Hence, water-based SCs  
16 become a major focus of research now-a-days. The rapid development in the field of portable  
17 electronic devices, it is mandatory to develop flexible energy storage devices such as flexible  
18 SCs where the SC can be bendable, twistable etc during its operation [12]. The stress-strain  
19 relationship of a flexible energy storage device can be linearly elastic, anelastic or plastic [13].  
20 A flexible SC should necessary to hold the features such as bendability, foldability,  
21 stretchability characteristics and safest operation [14, 15]. Recently, researchers are dedicated  
22 their efforts to introduce mechanical flexibility in rechargeable batteries by imparting  
23 flexibility to their individual components in order to demonstrate it for practical industrial  
24 applications but their flammability remains a major challenge [16, 17].

25 With respect to the features of flexible electronic devices, the power sources are needed  
26 to be mechanically flexible in terms of their bendable and twistable features. The bulky and  
27 cumbersome architecture of the energy storage devices are not encouraged as it will be difficult  
28 to integrate with the available portable electronic device [18]. The development of planar  
29 energy storage devices that can easily be integrated with textile fabrics by weaving or other  
30 means become an area of research for both the materials scientists as well as the energy  
31 researchers [19]. There are large number of studies reported in the literature that discuss the  
32 design and mechanism underlying with the flexible energy storage systems when there is a  
33 mechanical deformation [20]. To make flexible energy storage systems for practical purposes,  
34 each component in the system must be sustainable, conformable with shape, hold higher  
35 efficiency, heat resistant, cost-effective, and scalable but majority of the materials doesn't fully  
36 satisfy the criteria [21, 22]. One of the major challenges facing in the development of these  
37 sustainable materials is the availability of the material. The other features such as easiness in  
38 their synthesis, reliability and shape-conformability are also equally important. The current  
39 developments in the field of nanostructured materials for application as electrode-active  
40 materials made a stimulation in the field of electrochemical energy storage devices [23, 24].  
41 The different types of electrode-active materials used are electronically conducting polymers,  
42 transition metal oxides, carbon nanomaterials, biomass nanofibers, etc. Among the various  
43 choices, carbon nanomaterials have achieved great interest due to their efficient chemical,  
44 thermal, mechanical and electronic properties [25]. In the family of carbon materials, carbon  
45 fiber (CF), including carbon nanofiber (CNF) and carbon microfiber (CMF), have achieved  
46 great acceptance in developing flexible electrode fabrication.

47 CF is a unique type of carbon materials contains a carbon content of >90 wt%. This  
48 fibril form of the carbon consists of tubostratic carbon layers with graphite crystallites oriented  
49 in the fiber axis. With respect to its structural and compositional features, these materials are  
50 extraordinary tensile strength, higher value of modulus and stiffness, efficient temperature and



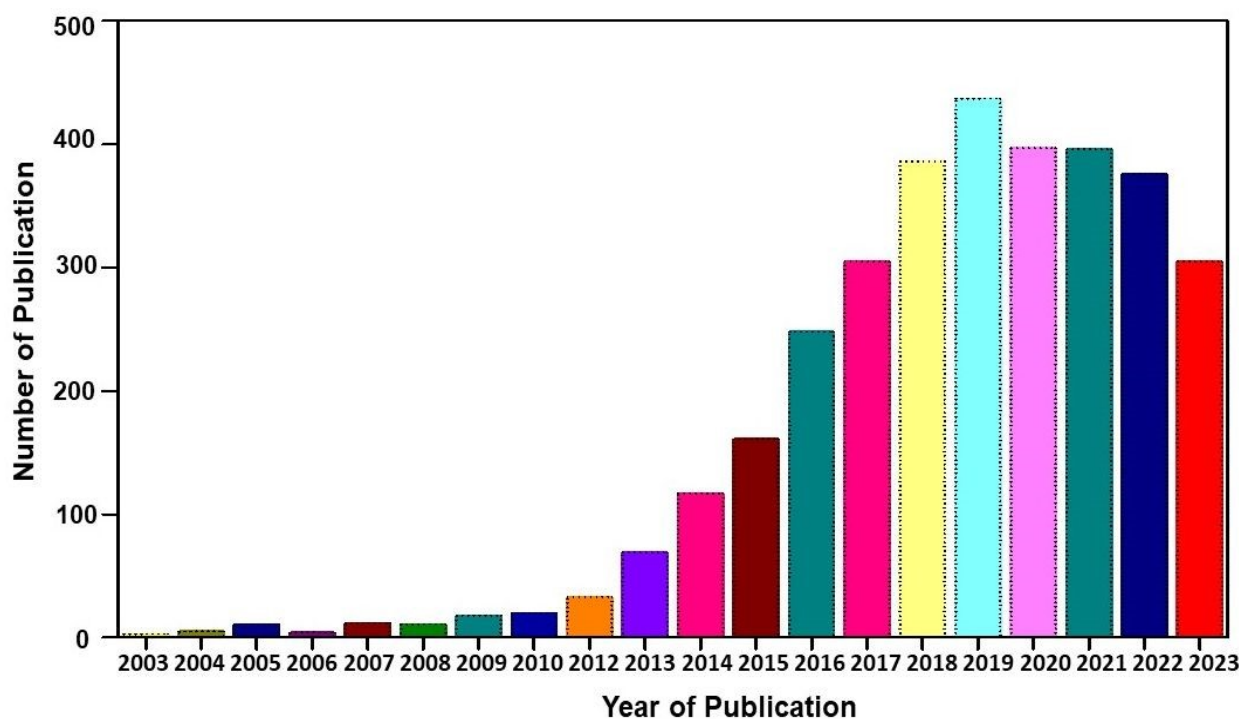
1 fatigue resistance, good electrical conductivity and low specific density [14]. CF-based  
2 materials are developed at an industrial scale from sources such as polyacrylonitrile (PAN) and  
3 pitch precursors and the production has begun from the year 1960. CF and CF-reinforced  
4 composites become a fascinating substrate for high-performing and indispensable structural  
5 combinations. Since CF exhibits excellent mechanical strength and lightweight, it become an  
6 inevitable material of choice in the field of aerospace, automobiles, biomedical, electrical  
7 components, etc. Commercially available CF consists of thousands of monofilaments in a  
8 diameter range of 5-10  $\mu\text{m}$ . In accordance with the synthesis approaches, various forms of CF-  
9 based components such as CF fabric, CF paper, CF textile, CNF fabric, etc are developed in  
10 the recent past [26]. CF prepared in both laboratory and industry is classified in accordance  
11 with the precursors used for its synthesis. PAN, isotropic pitch and mesophase pitch are  
12 synthesized by the spinning of the individual precursors such as PAN, isotropic pitch and  
13 anisotropic mesophase pitch, etc., followed by the reactions such as stabilization and  
14 carbonization at an elevated temperature, such as 1300°C [20]. Mechanical and other  
15 fundamental properties of CF depend upon the characteristic features of precursors used in the  
16 synthesis and also the method adopted. The precursors should be easily spun to a filamentary  
17 architecture, which can able to decompose to a stable form without producing any melting at a  
18 slow rate. The carbon content of the product should be very high after the pyrolysis procedure  
19 and produce a maximum yield [26]. The CF hold good crystallinity in the direction of fiber  
20 axis.

21 Flexible electronic devices are bendable and twistable, sometimes twistable hence the  
22 SCs integrated with such devices also should possess the same features. SCs utilizing water-  
23 based electrolytes and flexible electrodes are highly preferred for wearable electronic device  
24 application due to their safe in application and easiness in integration [8] A term called “smart  
25 electronics” is also evolved in the recent past, which has more functional features to attract the  
26 market such as wifi-charging, facial recognition monitoring, etc [27]. SCs can be coupled with  
27 renewable energy conversion technologies such as solar cells, piezoelectric/triboelectric  
28 nanogenerators, etc. for the effective utilization of waste energy for charging the SC  
29 instantaneously. But a proper design is mandatory and the charging capability of the energy  
30 conversion device should be matched with the electronic device which is going to utilize the  
31 power from the SC. In the case of flexible SCs, these energy conversion devices should be  
32 flexible too for their easy integration with wearable electronic devices. The main components  
33 of a SC are electrodes, current collector, electrolyte separator, electrolyte and sealing material.  
34 The main component that determines the performance of a SC is the electrode-active material.  
35 But the main component in a flexible SC is the supporting substrate at which the electrode-  
36 active material is composed with. During the fabrication of SC electrode, the electrode-active  
37 material is coated over an electronically conducting substrate (such as metal sheet, metal foil,  
38 metal foam, etc). Hence the flexibility to the electrode is actually imparted by the substrate  
39 used in the fabrication process. If metal substrates are used for the fabrication of Sc electrode,  
40 the prepared electrodes become rigid and hence become non-flexible. Hence flexible substrates  
41 are mandatory in developing flexible electrodes for SCs. The choices for flexible electronically  
42 conducting substrates are plastics (such as indium-doped tin oxide coated polyethylene  
43 terephthalate), carbon cloth, CMF sheet/mat, CNF sheet/mat, etc. Among the limited available  
44 choices, CF is the best option to use as substrates for fabricating flexible electrodes due to their  
45 environment-friendliness, low specific gravity, biodegradability, sustainability, low cost, easy  
46 processing, etc. CF-based SC electrodes with planar architecture are highly preferred for  
47 sustainable energy conversion and energy storage devices due to their extraordinary flexibility  
48 [20]. CF can easily be integrated with wearable electronic textiles by simple weaving  
49 procedures, which has boosted their demand in developing wearable SCs [11]. To compete  
50 with the requirements of current wearable devices with varying sizes and shapes, it is necessary



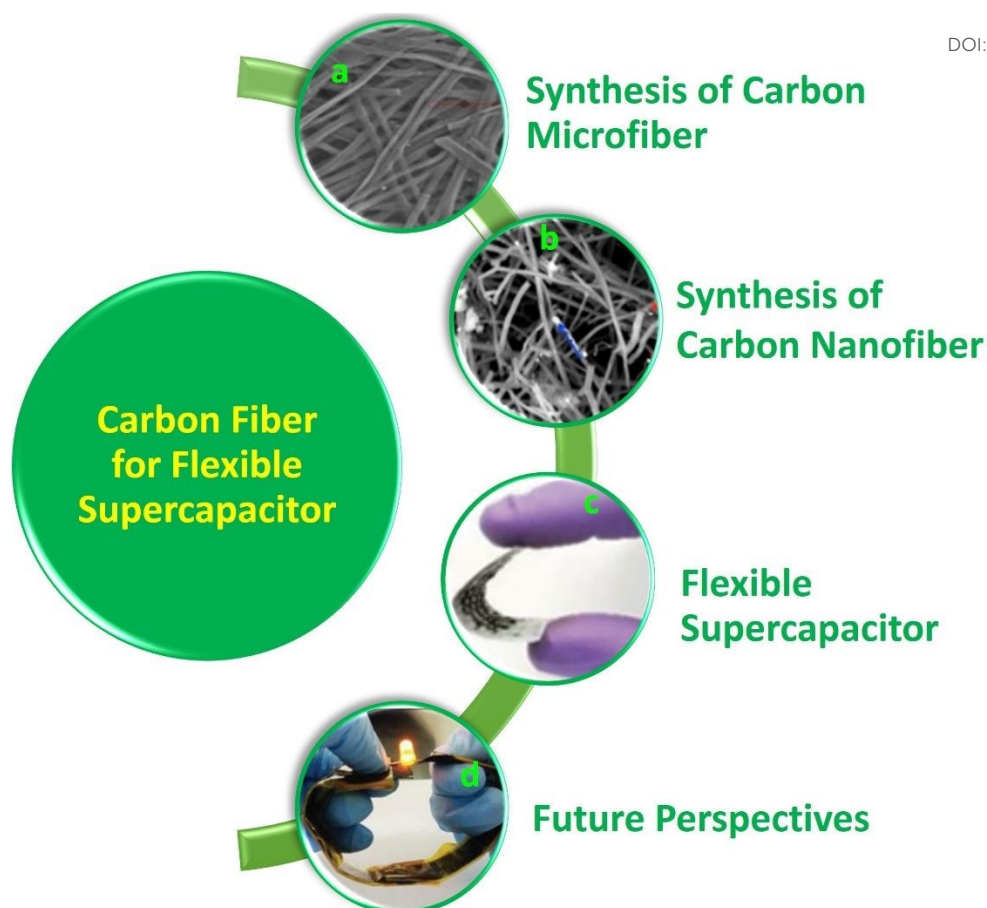


1 to introduce CF-based fibrous electrodes with efficient physical, chemical, mechanical and electrochemical properties [28]. The CF can be used in SC electrodes in three different ways:  
2 (i) substrate for the electrode-active material, (ii) current collector for the electrode-active  
3 material, and (iii) an electrode-active material for the SC. In some cases, CF is used as  
4 electrode-cum-current collector for developing SCs [29]. There are number of studies carried  
5 out using CF-based SCs in the literature. But a comprehensive review in the field of CF-based  
6 SCs is lacking in the literature. This motivated us to write this review article. A graphical  
7 analysis of number of publications based on CF-based SCs from 2004 to 2023 is given in  
8 **Figure 1**. It can be seen that a rise in number of publications happened from the year 2013 and  
9 received an exponential growth towards year 2019 and become stable thereafter. The reason for  
10 this saturation can be considered as the limited electrode designs that can be applied to the SC  
11 electrode as well as to the SC devices using CF as the flexible component in it. In this review  
12 article, we discuss the synthesis of CF such as CMF and CNF, and their successful  
13 implementation in SC electrodes. The recent progresses and challenges of various  
14 nanocomposite electrodes based on CF such as CF/electronically conducting polymer  
15 nanocomposites, CF/layered double-hydroxide nanocomposites, CF/carbon nanostructures  
16 nanocomposites, etc. are emphasized with their preparation methods and characterizations. The  
17 electrochemical performance evaluations of CF-based nanocomposite electrodes for SC  
18 application are discussed in detail using various tools such as electrochemical impedance  
19 spectroscopy, cyclic voltammetry (CV), and galvanostatic charge/discharge (GCD)  
20 measurement, etc. The major contents of the present review are schematically shown in **Figure**  
21 **2**.



24 **Figure 1:** Statistical analysis of number of publications based on CF for SC application from  
25 the year 2004 to 2023 [Source: Web of Science].  
26  
27  
28





**Figure 2:** Contents of the present review; (a) SEM image of carbon microfiber. Reproduced with permission from [30] Copyright(2013) Nature Scientific Reports; (b) SEM image of carbon nanofiber. Reproduced with permission from [31] Copyright (2015) American Chemical Society; (c) digital photograph of carbon fiber based flexible supercapacitor. Reproduced with permission from [32] Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (d) LED indicator lighted by two  $(\text{Ni}_{0.1} \text{Co}_{0.9})_9\text{Se}_8@ \text{CFC} // \text{PVA} / \text{KOH} // \text{rGO} @$  carbon fiber cloth asymmetric supercapacitors connected in series. Reproduced with permission from [33] Copyright (2018) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

## 2. Synthesis of Carbon Microfibers

Lopez et al. [34] introduced the synthesis of CMF from the polymer, PAN using N,N-dimethylformamide as solvent. Here, the PAN microfiber is synthesized by electrospinning by varying the PAN concentration and it possess high porosity when is carbonized at a temperature range of 800 - 900°C with a polymer concentration greater than or equal to 10%. Using mechanical wood fibers, Wang et al. [35] synthesized a liganocellulose nanofibrils (LCNF) and it further kept for wet spinning in order to prepare CMF. Cellulose and lignin present in the LCNF producing a direct route of synthesizing CMF by carbonization procedure thus eliminates the thermal stabilization procedure. The authors of this work found that this LCNF as such doesn't produce a microfiber or filament by wet spinning. Thus, it needs a smaller quantity of lignin-free nanofiber, like anionic cellulose nanofibrils (TOCNF) which improves the spinnability of LCNF. Improving the quantity of TOCNF is truly influencing the spun fiber properties, before and after performing the carbonization steps. It can be observed that the TOCNF contributing to the evolution of pores through carbonization, conserving the

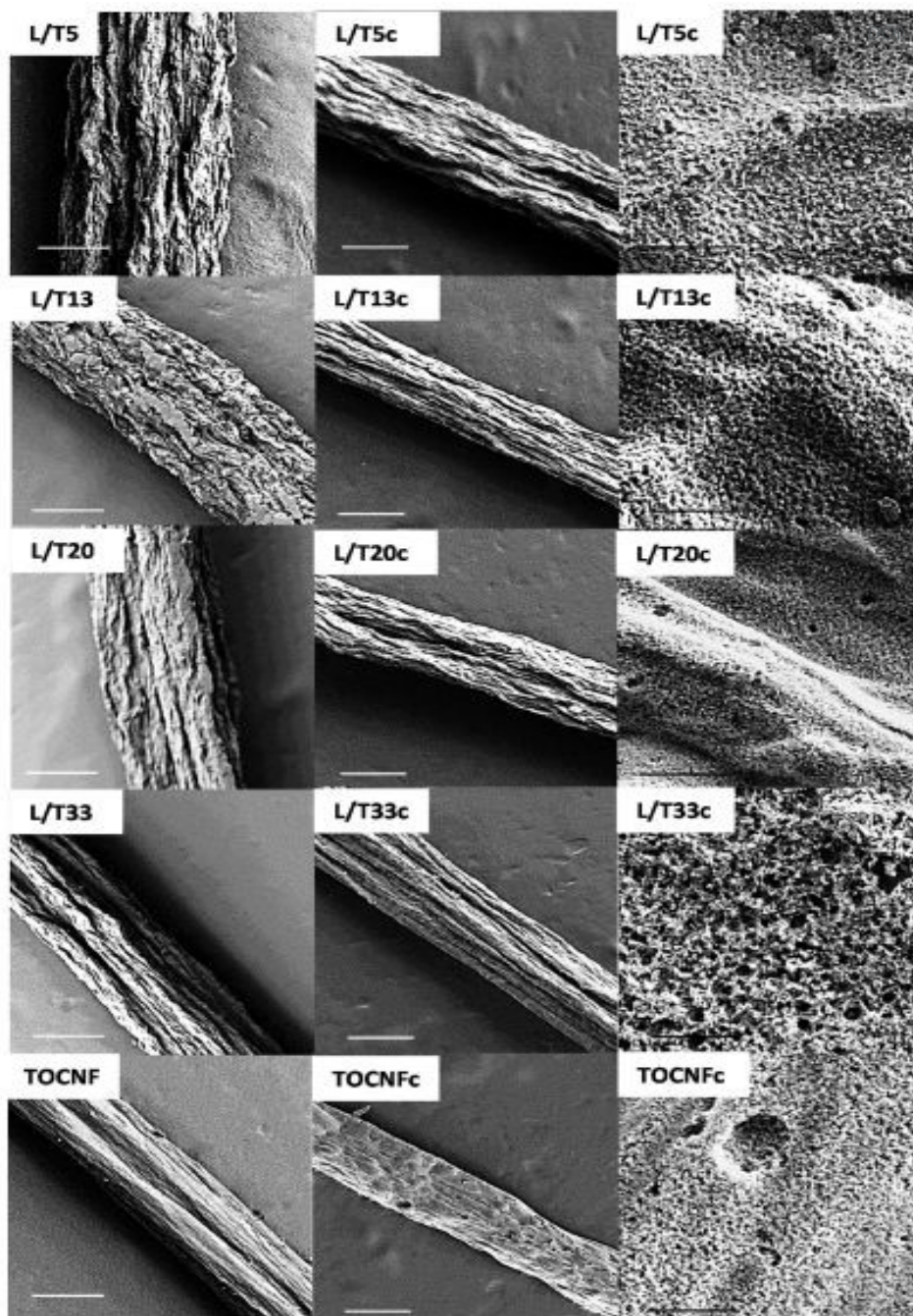




1 procedures such as surface activation, electrochemical treatment and particle deposition. The  
2 surface morphology of the as-synthesized LCNF/TOCNF microfibers before and after  
3 performing carbonization analysed by scanning electron microscope (SEM) imaging is given  
4 in **Figure 3**. With higher TOCNF content, the microfiber holds thinner and it holds a smooth  
5 surface, as shown in the first column. After the carbonization step, the microfibers shrunk in  
6 transverse axis given as second column. High-magnification SEM image of CMF is given as  
7 third column in **Figure 3**. The SEM images clearly shows that the CMF exhibits a porous  
8 morphology. Introduction of pores with improved addition of TOCNF resulting the glycoside  
9 bond cleavage and gasification. Saxena et al. [36] synthesized CMF by chemical vapour  
10 deposition (CVD) using turpentine oil decomposition with the presence of nickel sulfate  
11 catalyst on graphite host. The authors of this work obtained CMF with diameter in the range of  
12 3-5  $\mu\text{m}$  with a length of 5 mm with a twisted morphology. By using natural electrospun fiber  
13 silk cocoon, Liang et al. [30] synthesized a one-dimensional (1D) porous CMF. In this report,  
14 the authors of this work synthesized a biopolymer from silkworm by inartificial electrospinning  
15 approach, where silkworm spin like microfiber producing a cocoon through it. It is observed  
16 that by applying a feasible carbonization treatment, the electrospun natural cocoon microfiber  
17 is directly transfer to a 1D CMF having average diameter of 6  $\mu\text{m}$ , as shown in **Figure 4**.  
18

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**Figure 3:** SEM images show LCNF/TOCNF microfiber surface morphology before (first column) and after (second column) carbonization. High-magnification SEM images of CMF is given in third column. Reproduced with permission from [35] Copyright (2020) American Chemical Society.

From this study, it is found that these 1D CMF hold large number of carbon nanoparticles with a size ranging from 10 to 40 nm and it interconnected with each one to introduce a three-dimensional (3D) porous network architecture. These carbon nanoparticle units possess majorly a microporous structure, with compact and loose aggregation points to a mesoporous to microporous structure. A direct carbonization of this natural biopolymer without holding any harsh environment directs the introduction of micro/nanostructure. Synthesis of CMF from natural polymers envisages the environment-friendliness and hence its acceptance.





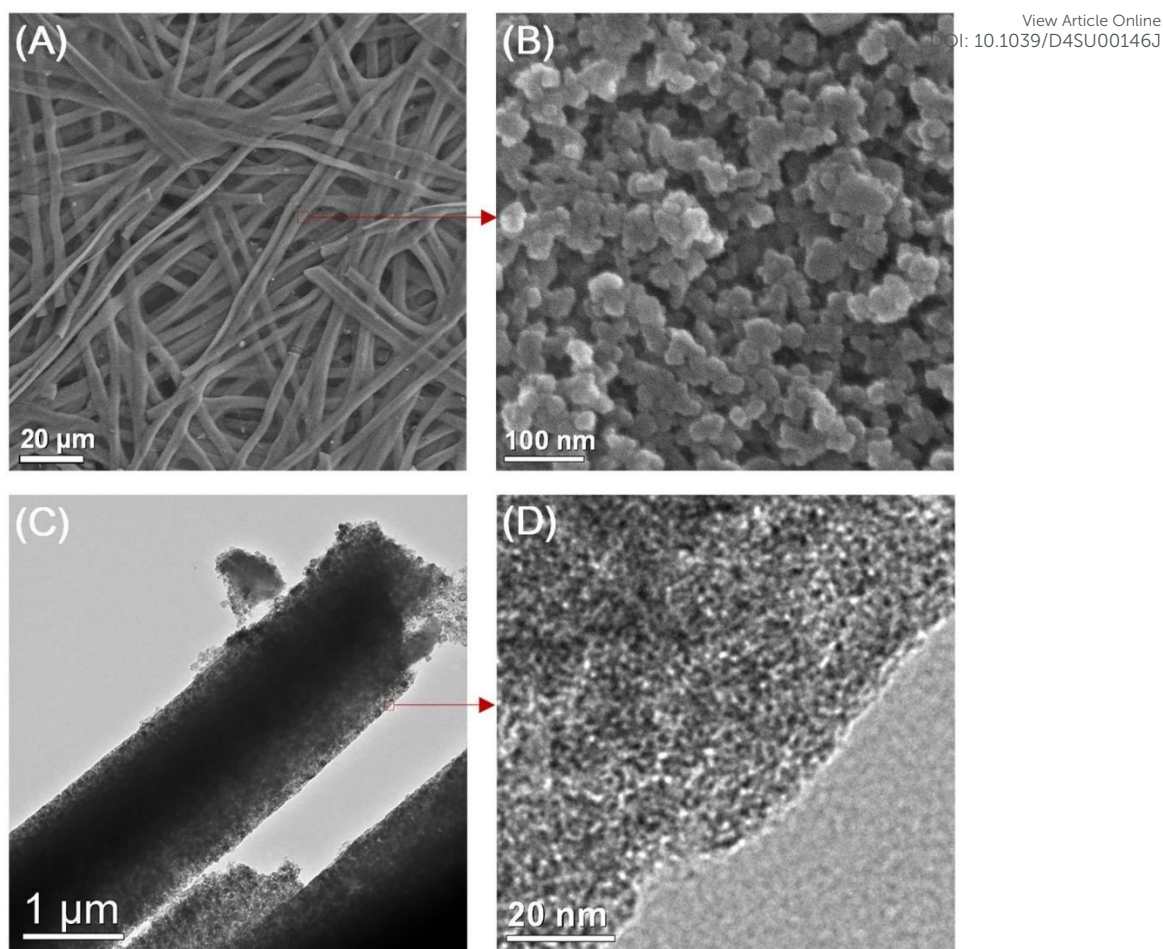
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**Figure 4:** Pictorial representation of preparation of hierarchical porous CMF from silk cocoon. Reproduced with permission from [30] Copyright (2013) Nature Scientific Reports.

The SEM and transmission electron microscope (TEM) images of the as-prepared porous CMF are given in **Figure 5**. After performing the carbonization treatment at a temperature of 900°C, the prepared CMF holds a uniform fibrous morphology, as depicted in **Figure 5a**. A CMF with diameter of 6 μm can be observed from this image, it exhibits a smaller diameter than silk microfibers, represents that this fibrous network producing a shrinkage as part of carbonization due to the burning of non-carbon element and other carbon-containing components. From the high-magnification SEM image (**Figure 5b**), it can be seen that the CMF possesses a fibrous framework which is interconnected with diameter of 10-40 nm formed during high-temperature pyrolysis. A CMF obtained through this procedure hold a prominent network of porous network architecture, which can be clearly visible from the TEM images given in **Figure 5c,d**. Using carbonization and activation approach, Taer et al. [37] synthesized a MCF from spiderweb. In this report, the carbonisation is performed under nitrogen atmosphere by adopting a multi-step heating profile to a temperature of 400°C. The activation procedure is performed using potassium hydroxide as active agent. A CMF with a diameter of 0.5-25 μm is obtained and it found that the CMF possesses an amorphous character with a carbon content of about 84%. There are various reports in the literature that describes the synthesis of CMF-based nanocomposites such as the formation with FeS using molten salt approach [38], ZnO through green template procedure [39], single template approach [40], etc.





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**Figure 5:** a) and b) SEM image; c) and d) TEM image of highly porous CMF. Reproduced with permission from [30] Copyright(2013) Nature Scientific Reports.

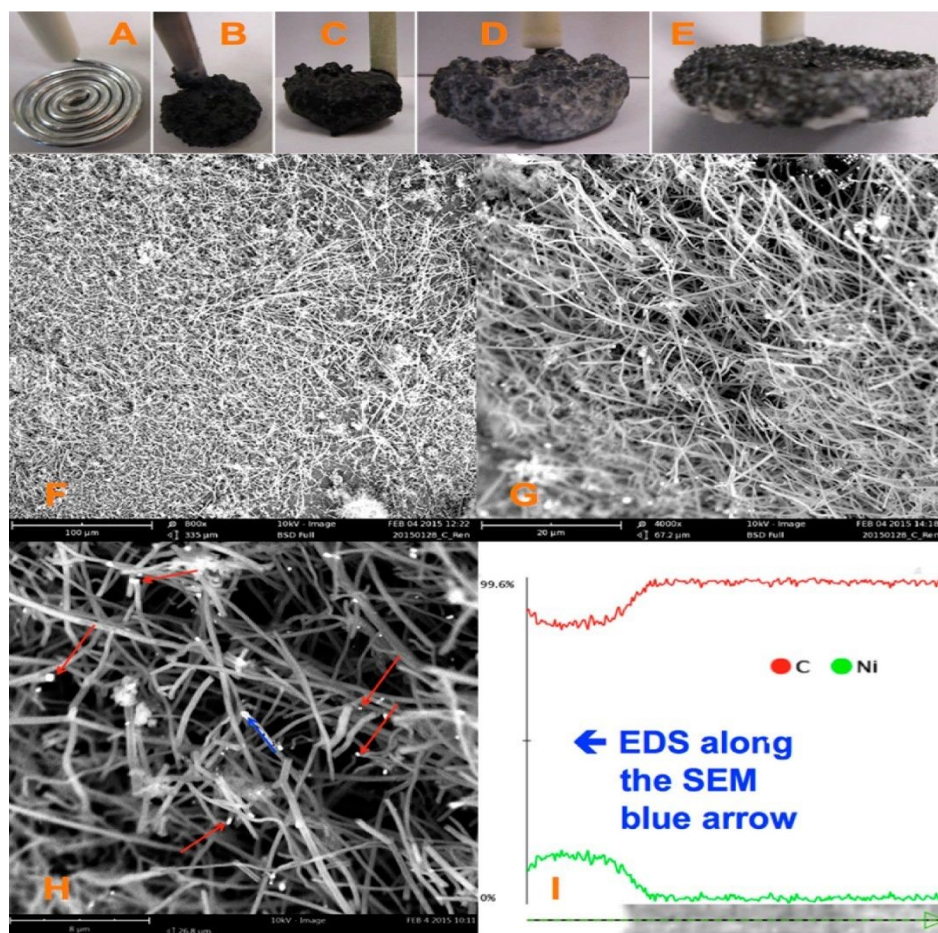
### 3. Synthesis of Carbon Nanofibers

CNF is hydrophobic in nature. The surface chemistry of CNF can be tailored with the help of various functional groups and are used in a variety of fields such as electrochemical energy storage, sensors, water purification, etc. The major synthesis methods of CNF include chemical vapour deposition [41-43], template-assisted approach [44-46], filament assisted-sputtering [47, 48], etc. Ahmed et al. [49] synthesized CNF by the impregnation of nickel ion ( $\text{Ni}^{2+}$ ) in powdered activated carbon. CVD approach with the application of acetylene gas, and hydrogen gas are employed for this synthesis procedure. The as-synthesized CNF possessed an average diameter in the range of 100 - 160 nm and the presence of Ni particles are confirmed by energy dispersive X-ray spectroscopy (EDX) analysis. Ren et al. [31] reported a large-scale synthesis of CNF with higher strength, flexibility and conductivity using facile approach of electrolytic conversion of  $\text{CO}_2$  dissolved in atmosphere molten carbonates. The molten carbonates consisting of almost 20 mol/L of reducible tetravalent carbon but air contains tetravalent carbon only about  $1.7 \times 10^{-5}$  mol/L. This approach eliminates any other procedures to concentrate  $\text{CO}_2$ . With the adsorption of  $\text{CO}_2$  from air, these molten carbonates introduce an increase in the reducible tetravalent concentration to million-fold, which is available for splitting to carbon inside electrolysis chamber. Here, the higher concentration of reducible tetravalent carbon sites logarithmically reduces the electrolysis potential and facilitates the transfer of charges at a lower electrolysis potential. In this procedure,  $\text{CO}_2$  is bubbled into molten carbonates, and during electrolysis, oxygen is going to evolve into anode, but a thick solid carbon is built in



1 cathode (**Figure 6**). It is observed that the molten carbonate is splitted into carbon which  
 2 approaches to 100% Coulombic efficiency, otherwise carbonates are mixing with hydroxides.  
 3 In another case, there exists a co-generation of oxygen and carbon and it sustains the formation  
 4 of carbon with higher current densities and a similar phenomenon at the cathodes of carbon,  
 5 platinum or steel **can also be observed**. Fuel cell electrolysis potential is happened at higher  
 6 temperature and higher amount of oxide concentration with respect to a higher current density.  
 7 It is found that the dissolved carbon dioxide in molten carbonates is going to be an uncontrolled  
 8 mixture of graphite and amorphous carbon. The product introduced by cathode electrolysis, as  
 9 shown in the SEM image (**Figure**) contains controlled carbon fiber with points of metal  
 10 nucleation. The majority of Ni particles are located in the nanofiber tip, but some of the  
 11 particles are stayed aside and not associated with the CNF growth. This fiber is found to be  
 12 homogeneous in the cathode, which hold a diameter of 200 - 300 nm with length in the range  
 13 of 20 - 200  $\mu\text{m}$ . Here, the fibers are synthesized through electrolysis at 10  $\text{cm}^2$  galvanized coil  
 14 steel wire cathode and the generation of oxygen by nickel anode in a molten  $\text{Li}_2\text{CO}_3$  fixed at a  
 15 temperature of 730°C initiated with a low current of 5  $\text{mA}/\text{cm}^2$  in cathode, followed by a  
 16 constant current electrolysis phenomenon at higher current range of 100  $\text{mA}/\text{cm}^2$  for a duration  
 17 **2 to 4 h**. Here, the cooled product consists of fibers mixed by solidified electrolyte. The  
 18 resultant product readily falls in cooled cathode when it became uncoiled. A Coulombic  
 19 efficiency of greater than 80% is achieved and the as-synthesized product after washing the  
 20 electrolyte contains more than 80% of pure CNFs.

21



22

23

24 **Figure 6:** Formation of  $\text{CO}_2$  to CNF introduced in a coiled galvanized steel cathode with anode  
 25 as nickel at 0.05 A, then a constant current electrolysis at 1 A. There is no addition of  $\text{Li}_2\text{O}$  to  
 26 molten  $\text{Li}_2\text{CO}_3$  electrolyte at 730°C; f-h) SEM images holding different magnifications of



1 product removed from cooled and washed cathode; a) SEM image of 10 cm<sup>2</sup> coiled nanowire  
2 with diameter of 0.12 cm cathode which is prior to electrolysis. Anode material is the inner  
3 wall of 20 mL Ni crucible which consists of electrolyte; b)-e) maximum amount of variation  
4 in cathode which is subsequent to the removal of carbonate electrolyte after 4 Ah electrolysis  
5 in molten carbonate. Red arrow contained in h) corresponds to Ni nucleation sites and the blue  
6 coloured arrow corresponds to introduction at one of the Ni sites and which moving in CNF  
7 path; i) EDS mapping in 6 μ blue arrow path which is represented in SEM image h).  
8 Reproduced with permission from [31] Copyright (2015) American Chemical Society.

9  
10 Gaud et al. [50] synthesized CNF from organic waste product such as plant waste in a cost-  
11 effective and eco-friendly way. The morphological analysis of the CNF showed that CNF with  
12 diameter lie in the range of 40 - 60 nm and a few micrometers in length. The as-synthesized  
13 CNF possessed a smooth surface. The EDX analysis reveals that it doesn't contain any  
14 impurities such as halides and oxides. Kotanjac et al. [51] synthesized CNF on woven cloth  
15 using CVD approach with nanoscale metal catalyst with the decomposition of hot hydrocarbon  
16 vapour. This report showed that an effective production of thin single layer fibers with a  
17 dimension of 25 x 30 cm.

#### 18 **4. Carbon Fibers for Flexible Supercapacitors**

19 SCs are new-generation electrochemical energy storage devices exhibiting high power density,  
20 high charge/discharge rates, long cycle life, etc. Based on the charge storage mechanism, SCs  
21 are classified in to three types: electrochemical double layer capacitors, pseudocapacitors (or  
22 redox capacitors) and battery-type hybrid SCs. SCs have received great attention in the field of  
23 energy storage devices. Wearable electronic devices necessitate flexible and wearable SCs to  
24 power them. Wearable SCs must possess features such as flexibility, bendability, twistability  
25 to a higher extend in order to integrate with the wearable electronic devices. But the limited  
26 availability of a flexible substrate, shedding effect, and non-uniform distribution in the  
27 electrode-active materials limit their potential integration. To eradicate these issues, CF-based  
28 SCs have been developed in the recent past. This section describes the CF-based  
29 nanocomposite electrodes for application in high-performance SCs.

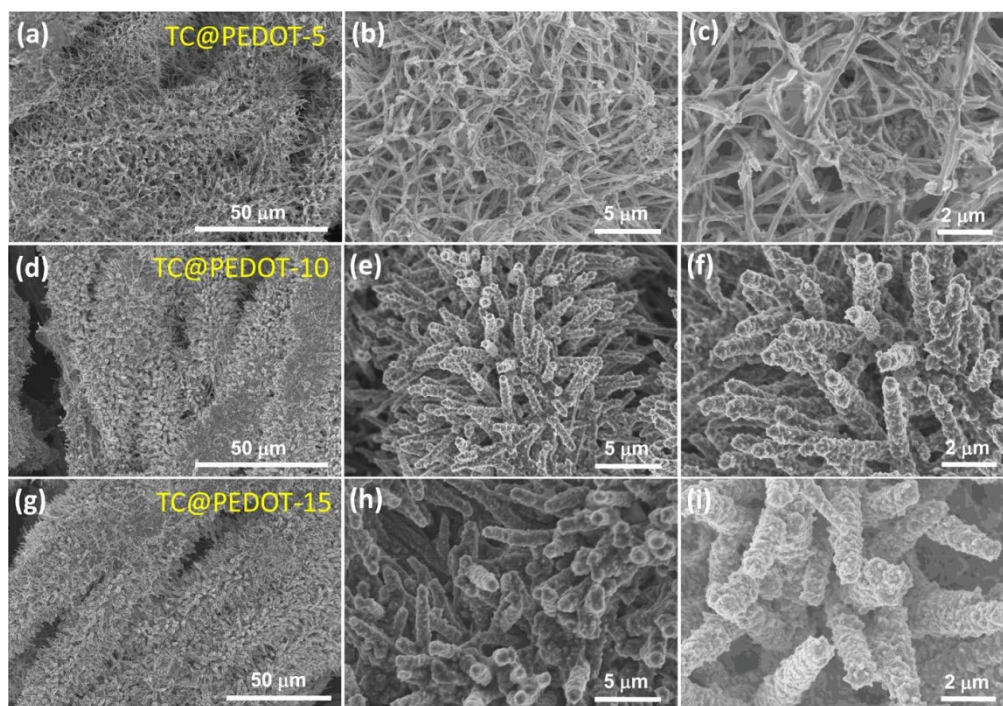
#### 30 **4.1 Carbon Fiber/Electronically Conducting Polymer Nanocomposite Electrodes**

31 Electronically conducting polymers are the best candidates for SC electrode application due to  
32 their intrinsic conductivity, easy in synthesis, good redox activity, etc. Examples of  
33 electronically conducting polymers used in SC electrodes are polyaniline (PANI), polypyrrole  
34 (PPY), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene):  
35 polystyrenesulfonate (PEDOT:PSS), poly(3-hexylthiophene), etc. Ling et al. [52] prepared a  
36 flexible, foldable and light-weight CF paper substrate using wet-lay technique and it possesses  
37 a reduced internal resistance and large porosity. Here, a γ-MnO<sub>2</sub> wrapped over PANI led to a  
38 core-shell architecture, and a step-wise modified in-situ polymerization approach is applied for  
39 the uniform distribution of the polymer. The SC electrode thus prepared exhibited a high  
40 specific capacitance of 642.5 F/g at a current density of 1 A/g. A SC was fabricated using these  
41 nanocomposite electrodes, which delivered an energy density of 114.2 Wh/kg at a  
42 corresponding power density of 798.6 W/kg. This SC exhibited a capacitance retention of  
43 81.3% even after completing 5000 cycles. Introduction of an electronically conductive polymer  
44 to a flexible substrate makes it electrically conducting and it can be further used for fabricating  
45 SC electrode with good mechanical properties. Niu et al. [53] used electrochemical  
46 polymerization technique to prepare SC electrode comprising of coral-like  
47 PEDOT nanotube array over textile CF (TCs). In this study, ZnO nanowire grown over TCs  
48 act as a sacrificial template. PEDOT polymerization follows by the removal of ZnO nanowire  
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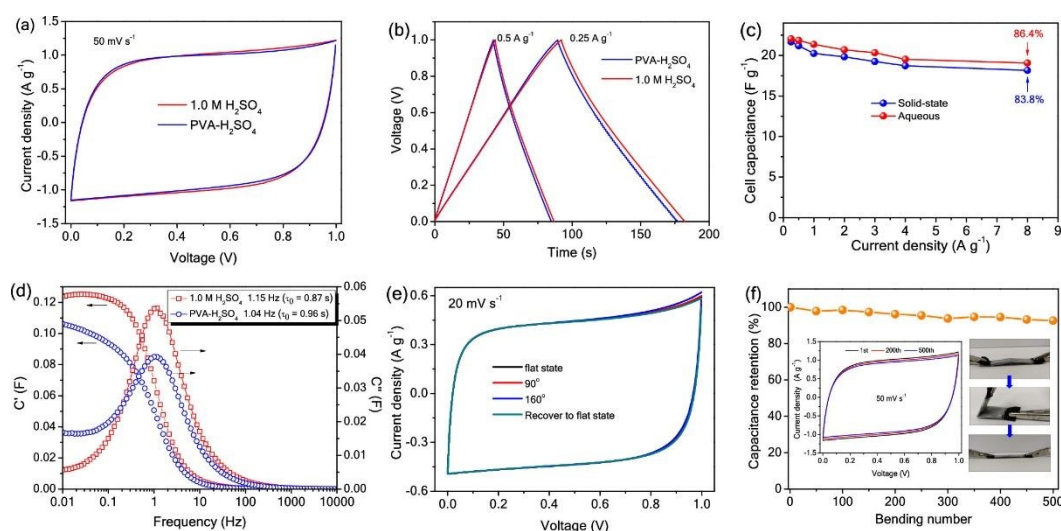
1 template creates a composite of PEDOT nanotube which was vertically grown over TC. Morphology hold by PEDOT is highly depends upon the time for deposition as given in SEM  
 2 image **Figure 7**. During a smaller deposition time of about 5 minute (**Figure 7(a-c)**), PEDOT  
 3 possesses a nanofiber-like structure with a diameter of  $\sim 200$  nm and length of  $\sim 10\mu\text{m}$  (**Figure**  
 4 **7d-f**). Fibers are interconnected each other and generating a highly porous network of CF. But  
 5 a longer duration of deposition ( $\sim 10$  minutes), PEDOT formed a coral-like structure where the  
 6 PEDOT nanorods are forming a growth in vertical direction and it helps in rapid transport of  
 7 electrons. Like ZnO nanowire structure, the PEDOT showed a reduction in its diameter from  
 8 base to tip (**Figure 7f**). Also, the PEDOT nanotubes achieve a length in the range of tens of  
 9 micrometers, where its diameter increases within a range of  $\sim 0.5 - 1\ \mu\text{m}$  (**Figure 7f**). If the  
 10 deposition time increases to 15 minutes (**Figure 7g-i**), PEDOT is increasing its diameter in a  
 11 continuous manner and reaches upto 800 nm (**Figure 7i**). The coral-like PEDOT nanotube  
 12 exhibits efficient conductivity that make the TC@PEDOT-10 as an efficient electrode material.  
 13 To introduce the prepared electrode material for practical applications, the authors of this work  
 14 developed two SCs consisting of TC@PEDOT-10 as an electrode with 1 M aqueous  $\text{H}_2\text{SO}_4$   
 15 and PVA- $\text{H}_2\text{SO}_4$  as electrolytes. From this study, it is found that the two SCs hold an ideal  
 16 behaviour with rectangular shape possessing a similar current response at a constant rate of 50  
 17 mV/s (**Figure 8a**), indicating the similarity in the electrochemical characteristics due to similar  
 18 ionic conductivity introduced by the PVA- $\text{H}_2\text{SO}_4$  gel electrolyte. The charge/discharge  
 19 characteristics of SCs are examined using GCD measurements performed at different current  
 20 densities (**Figure 8b**). The triangular-shaped GCD curves possessing coincident curves that  
 21 represent a complete doping/de-doping reaction in reversible style, that executes in an  
 22 electrochemical method. From the variation in specific capacitance of SCs at different current  
 23 densities (**Figure 8c**) show that the SCs with  $\text{H}_2\text{SO}_4$  aqueous electrolyte exhibited a capacitance  
 24 of 22.1 F/g at 0.25 A/g and it holds a capacity retention of 86.4% at 8 A/g.  
 25



27  
 28  
 29 **Figure 7:** TC@PEDOT SEM images in various magnifications (a-c) TC@PEDOT-5 (d-f)  
 30 TC@PEDOT-10 and (g-i) TC@PEDOT-15 electrode. Reproduced with permission from [53]  
 31 Copyright (2020) American Chemical Society.  
 32



1 The specific capacitance obtained for this SC is found to be higher than the SC fabricated with  
 2 PVA-H<sub>2</sub>SO<sub>4</sub> gel electrolyte holding a specific capacitance of 21.7 F/g with a capacity retention  
 3 of 83.8%. A plot that shows the variation in the capacitance with respect to frequency is given  
 4 in **Figure 8d**. With maximum  $C''$  and corresponding  $f_0$ , relaxation time constant  $\tau_0$  of device  
 5 in both these electrolytes can be introduced, it reveals the shortest time taken for the  
 6 discharging of all energy in an efficiency greater than 50%. The ' $\tau_0$ ' value calculated for the  
 7 SC utilizing H<sub>2</sub>SO<sub>4</sub> and the SC utilizing PVA-H<sub>2</sub>SO<sub>4</sub> gel electrolyte are 0.87 s and 0.96 s,  
 8 respectively. The flexibility of SC utilizing PVA-H<sub>2</sub>SO<sub>4</sub> gel electrolyte was tested by bending  
 9 the SC at different bending angles and recovered its initial state after the bending test. When  
 10 the SC bend at an angle of 160°, the CV profiles correspond to SC utilizing PVA-H<sub>2</sub>SO<sub>4</sub> gel  
 11 electrolyte found to be unaltered (**Figure 8e**), which reveals the integrity of the SC electrode  
 12 and the high flexibility of the SC. The cyclic stability of SC utilizing PVA-H<sub>2</sub>SO<sub>4</sub> gel  
 13 electrolyte was examined by carrying out CV analysis for 500 bending cycles at a constant scan  
 14 rate of 50 mV/s and shown in **Figure 8f**. The CV profile of SC utilizing PVA-H<sub>2</sub>SO<sub>4</sub> gel  
 15 electrolyte shows a retention of ~92%, even it is bending at 120° for 500 cycles.

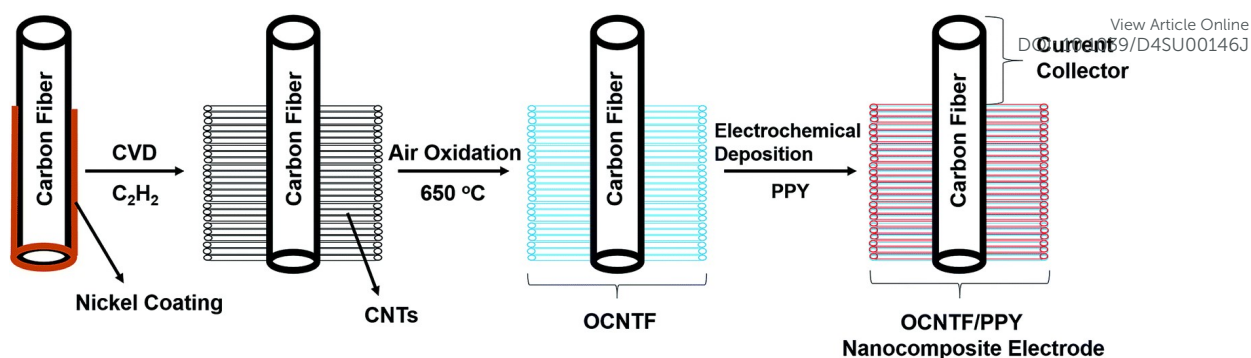


**Figure 8:** (a) CV curve at 50 mV/s; (b) GCD profiles at 0.5 A/g and 0.25 A/g; (c) rate capability diagram in the range 0.25–8 A/g; (d) real ( $C'$ ) and imaginary part of ( $C''$ ) specific capacitance as a function of frequency ( $f_0$ ); (e) CV curve representing solid state SC device with various bending state; (f) retention in capacity after bending device for 500 cycles at 120°. Reproduced with permission from [53] Copyright (2020) American Chemical Society.

25 An ultra-flexible SC using oxidized carbon nanotubes (CNTs) grown over CF (OCNTF)/PPY  
 26 brush-like electrode was reported recently [54]. Initially, the OCNTF was synthesized using  
 27 CVD method followed by air-oxidation. Further, PPY was coated over the OCNTF substrate  
 28 by electrochemical polymerization method with varied deposition time. **Figure 9** represents  
 29 the steps involved in the synthesis of OCNTF/PPY nanocomposite.

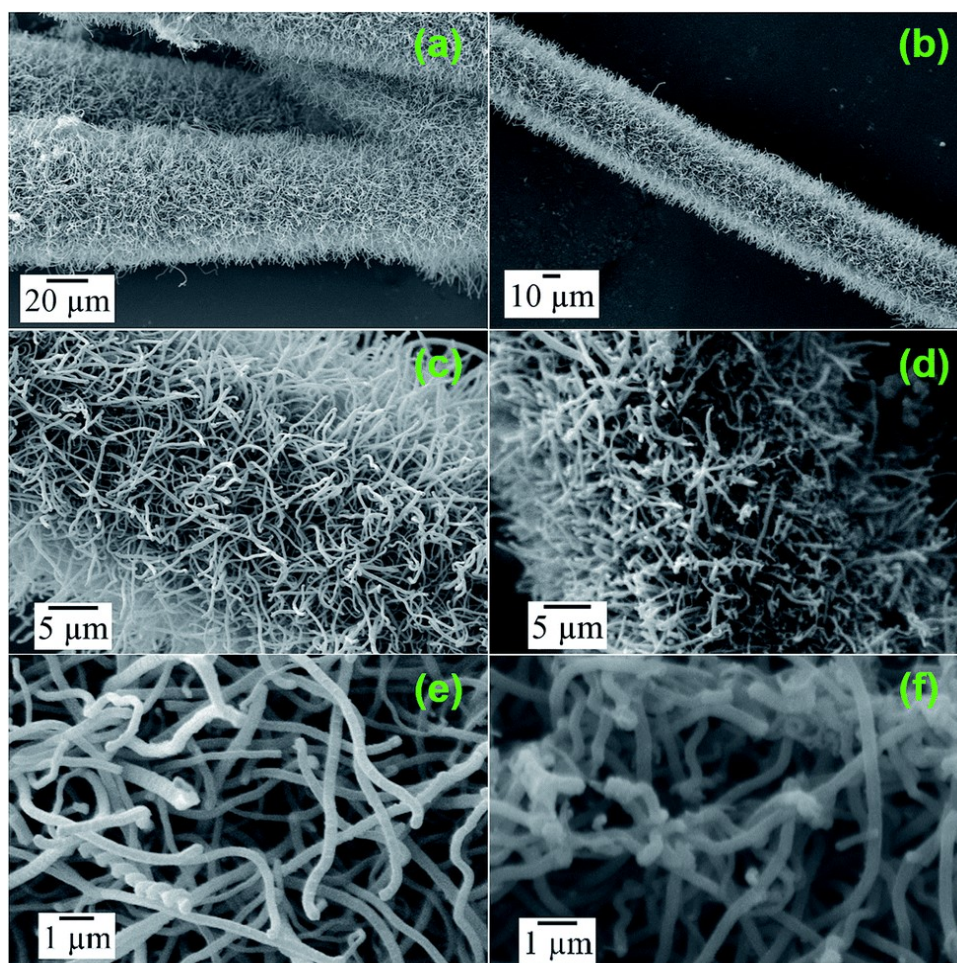






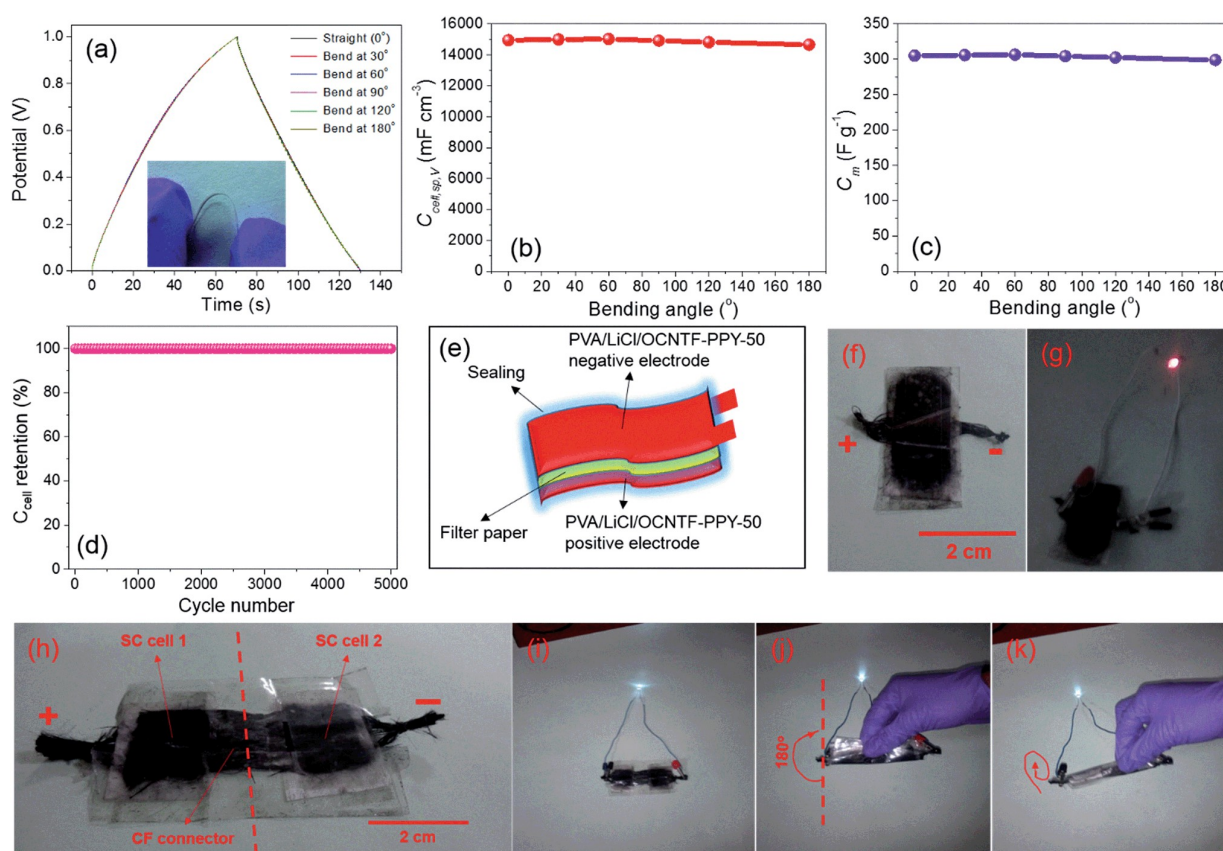
**Figure 9:** Pictorial representation of fabrication of electrode. Reproduced with permission from [54] Copyright (2016) Royal Society of Chemistry.

The SEM images of CNTs synthesized over CF by CVD is given in **Figure 10(a-c)** and **(e)**. From these images it can be observed that there exists a higher density of CNTs grown over the CF substrate vertically. The oxidation of CNTs is introduced by the high-temperature annealing under oxygen environment. The SEM images of OCNTF are shown in **Figure 10d** and **f**.



**Figure 10:** SEM images of CNTF (a-c) and (e) and OCNTF (d and f). Reproduced with permission from [54] Copyright (2016) Royal Society of Chemistry.

1 The OCNTF/PPY nanocomposites are prepared at different deposition intervals. The  
 2 electrochemical deposition performed at a deposition time of 50 minutes show a dendritic  
 3 structured PPY over the OCNTF. This OCNTF/PPY nanocomposite is further used as an  
 4 electrode-active material for the fabrication of a flexible SC. In order to analyse flexibility of  
 5 fabricated electrode, GCD measurements are performed by bending the SC electrode at  
 6 different bending angles of  $0^\circ$  (straight position),  $30^\circ$ ,  $60^\circ$ ,  $90^\circ$ ,  $120^\circ$  and  $180^\circ$  at a constant  
 7 current density of  $2.5 \text{ mA/cm}^2$ . From the GCD curves (**Figure 11a**) it is clear that there is no  
 8 change in the curve while it bends from the straight position towards  $180^\circ$ . Also, there no  
 9 change in its volume specific capacitance (**Figure 11b**) and gravimetric capacitance (**Figure**  
 10 **11c**) was observed during the bending towards  $180^\circ$ . The fabricated electrode exhibited a higher  
 11 cyclic stability after 5000 charge/discharge cycles (**Figure 11d**). A schematic diagram  
 12 representing the solid-state SC fabricated with this electrode material is given in **Figure 11e**  
 13 and its digital image is provided in **Figure 11f**. This working of the as-fabricated solid-state  
 14 SC is studied by lighting-up a red light-emitting diode (LED) and depicted in **Figure 11g**. By  
 15 using these solid-state SCs, a flexible SC module with two similar SCs connected in series is  
 16 fabricated and its digital image is given as **Figure 11h**. This module is charging to a voltage of  
 17 4 V initially, and it efficiently lighting a white LED (**Figure 11i**). The flexibility of this SC  
 18 module is verified at its straight position as well as by bending it at an angle of  $180^\circ$  (**Figure**  
 19 **11i and j**). In order to verify its flexibility in terms of twisting the SC, the fabricated SC module  
 20 is rolled to the shape of a cylinder on discharging it through a white LED (**Figure 11k**) and no  
 21 significant variation in the intensity of lighting the LED is observed. This shows the high  
 22 efficiency of OCNTF/PPY nanocomposite-based SC for practical applications.



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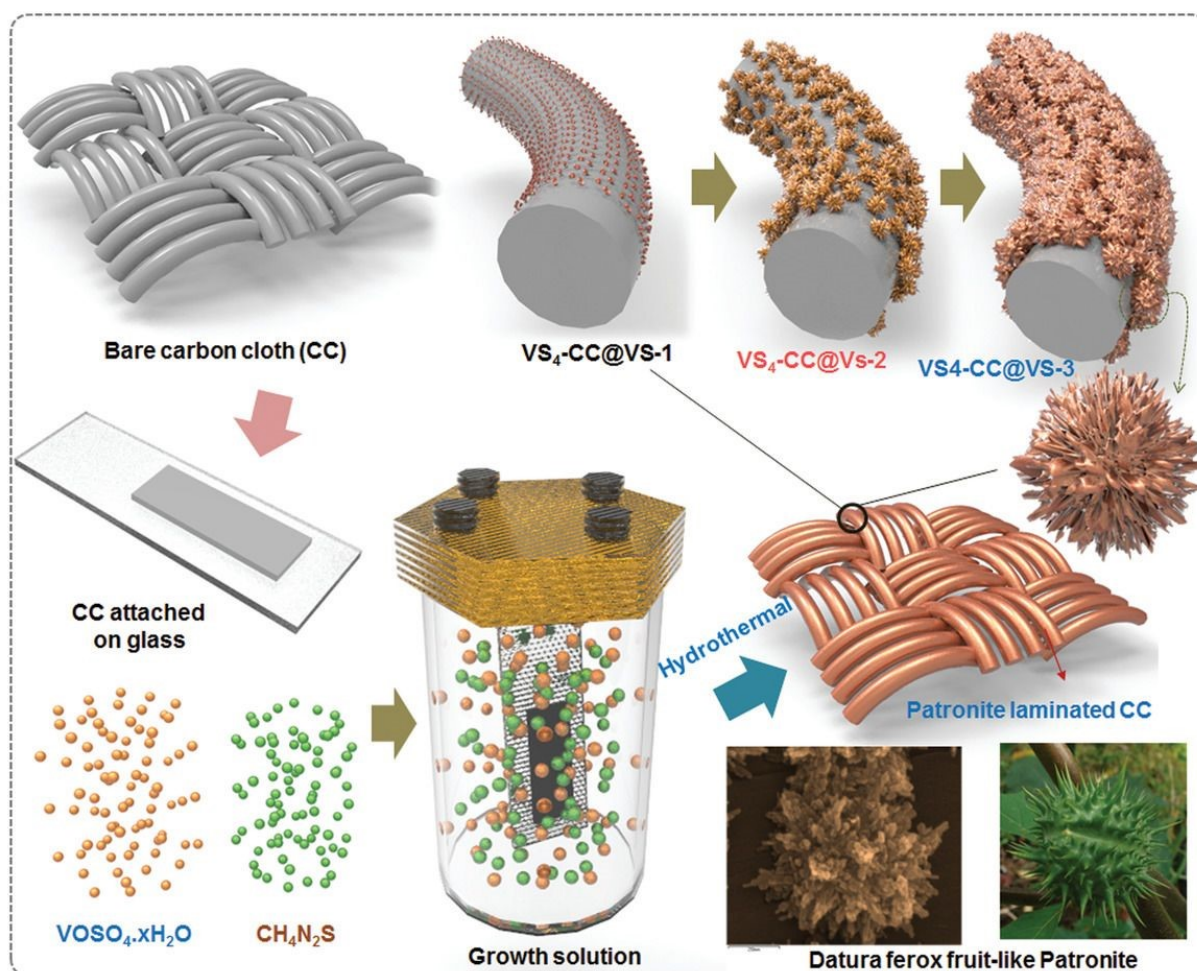
26 **Figure 11:** (a) GCD curve at a current density of  $2.5 \text{ mA/cm}^2$  for the fabricated SC electrode  
 27 bending at different angles; (b) volumetric specific capacitance; (c) gravimetric specific  
 28 capacitance in various angles; (d) capacitance retention with cycle number; (e) diagrammatic





1 and (f) digital image of SC; (g) digital image of lighting a red LED; (h) module lighting up a  
 2 white LED; (i) module lighting the white LED bending at 180°; (j) module rolling in form of  
 3 cylinder and (k) lighting a white LED. Reproduced with permission from [54] Copyright  
 4 (2016) Royal Society of Chemistry.

5  
 6 Using an aerobic pyrolysis method, Zhou et al. [55] extracted CF from a CF-reinforced  
 7 polymer under oxygen atmosphere. During the pyrolysis, the reclaimed fiber surface is etched  
 8 to a surface of groove-shape and it is modified by creating oxygen-containing surface  
 9 functional groups, which produces an enhancement in the negative potential window of the  
 10 reclaimed CF to -1.4 V. By increasing the working potential to 2.4 V, it produces a capacitance  
 11 retention of **93.6%** after completing 10000 cycles in Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Manikandan  
 12 Ramu and team [56] synthesized hierarchical VS<sub>4</sub> nanostructures over CF by hydrothermal  
 13 method and the procedure is schematically shown in **Figure 12**. During the synthesis process,  
 14 the growth solution containing VOSO<sub>4</sub>.xH<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>NS with complexing agent CH<sub>3</sub>COOH  
 15 were prepared. It created a VS<sub>4</sub> nanostructure without any binder on CF cloth substrate with  
 16 good adhesion. The authors of this work synthesized various samples at different growth  
 17 conditions by varying pH and are labelled as VS<sub>4</sub>-CC@VS-1 (pH 2.5), VS<sub>4</sub>-CC@VS-2 (pH  
 18 2.3) and VS<sub>4</sub>-CC@VS-3 (pH 2.1). The microstructure and morphology of these samples are  
 19 studied by using FESEM imaging and it is given in **Figure 13**.  
 20



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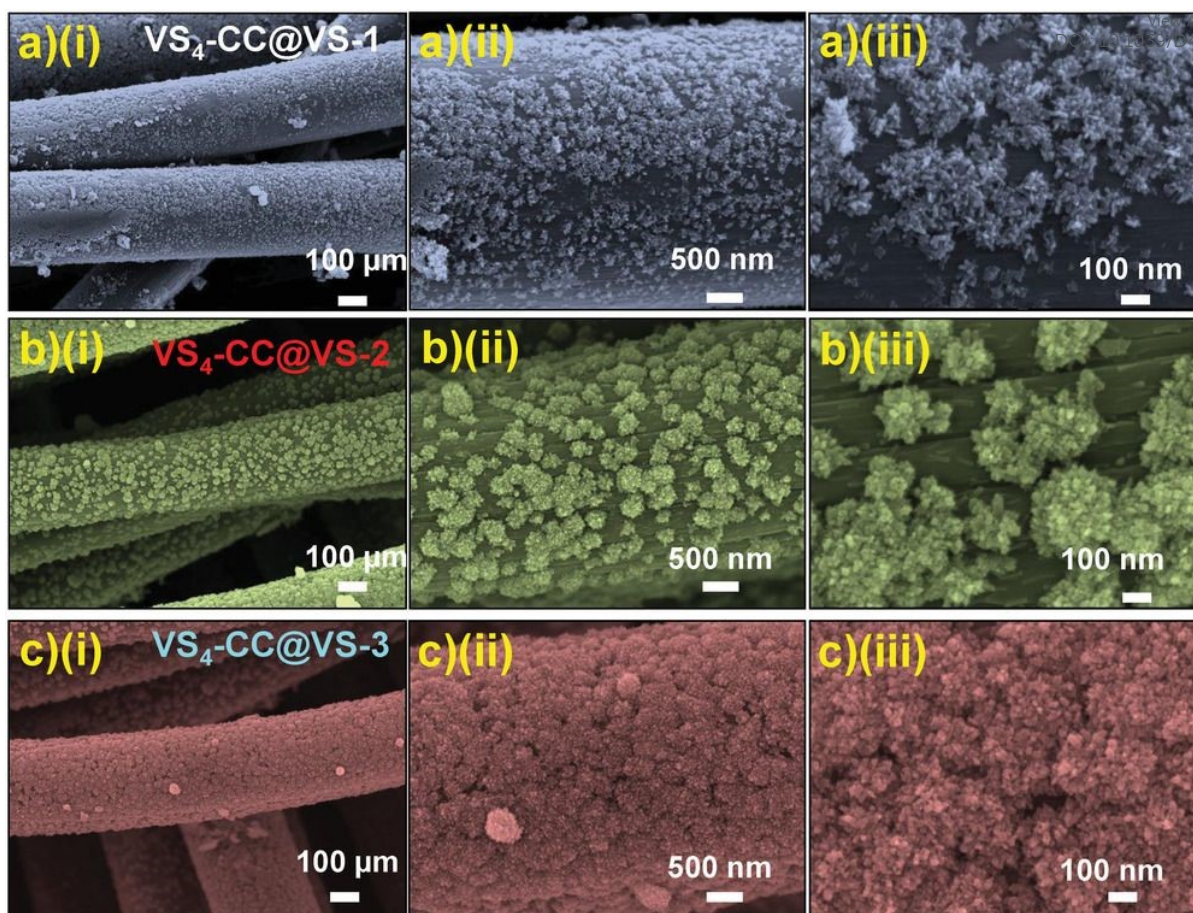
1 **Figure 12:** Pictorial representation of synthesis procedure of ferox-fruit like patronite (VS<sub>4</sub>)  
2 nanostructure over a flexible carbon cloth substrate in a growth medium with controlled pH.  
3 Reproduced with permission from [56] Copyright (2020) WILEY-VCH Verlag GmbH & Co.  
4 KGaA, Weinheim.

5  
6 The SEM images of VS<sub>4</sub>-CC@VS-1 are shown in **Figure 13a(i-iii)**. In this sample, the VS<sub>4</sub>  
7 holds a nanospike-like agglomerated particles, which produces a non-uniform distribution over  
8 the CF cloth substrate. With an increase in concentration to twice, the VS<sub>4</sub>-CC@VS-2, an  
9 increased growth of VS<sub>4</sub> over CF cloth was observed, as depicted in **Figure 13b(i-iii)**. A  
10 discreetness in nanospike bunches visible in the first sample, which exhibits a flower-like  
11 morphology. Due to the non-uniformity in alignment over CF cloth surface, the concentration  
12 was further increased and VS<sub>4</sub>-CC@VS-3 was prepared. **Figure 13c(i-iii)** shows the SEM  
13 images, which portraits a large growth with datura ferox fruit-like morphology with the  
14 availability of large number of electrochemically active sites. Further, SC electrodes were  
15 fabricated using these three different samples and the electrochemical performances were  
16 examined. The electrochemical performance of the SC electrodes is analysed in a three-  
17 electrode cell using 1 M 1-ethyl-3-methylimidazolium trifluoro methane sulfonate in  
18 acetonitrile ([EMIM][Otf]) ionic liquid electrolyte. The pictorial representation of fabrication  
19 of symmetric SC constructed VS<sub>4</sub>-CC@VS-3 electrodes is given in **Figure 14a**. A comparison  
20 of CV curves of the three SC electrodes (VS<sub>4</sub>-CC@VS-1, VS<sub>4</sub>-CC@VS-2 and VS<sub>4</sub>-CC@VS-  
21 3) showed that the electrode-active materials exhibit a pair of redox peaks and possess a quasi-  
22 rectangular shape, which portraits their pseudocapacitive charge storage (**Figure 14b**). A  
23 comparison of GCD measurement of the three SC electrodes (VS<sub>4</sub>-CC@VS-1, VS<sub>4</sub>-CC@VS-  
24 2 and VS<sub>4</sub>-CC@VS-3) showed that the electrode-active materials exhibit a symmetric with  
25 nearly distorted triangular curves showing the reversibility and pseudocapacitive nature of  
26 material, as shown in **Figure 14c**. The CV curves obtained for VS<sub>4</sub>-CC@VS-3 at different  
27 scan rates is given in **Figure 14d**. These CV curves consist of broad redox peaks, arises due to  
28 the intercalation/deintercalation of [EMIM]<sup>+</sup>-ions, which represents that the SC electrode is  
29 pseudocapacitive in nature. The GCD curves obtained for VS<sub>4</sub>-CC@VS-3 at different current  
30 densities (1 to 10 mA/cm<sup>2</sup>) is given in **Figure 14e**. The charge/discharge cures shows that the  
31 SC electrode exhibited efficient electrochemical performance.

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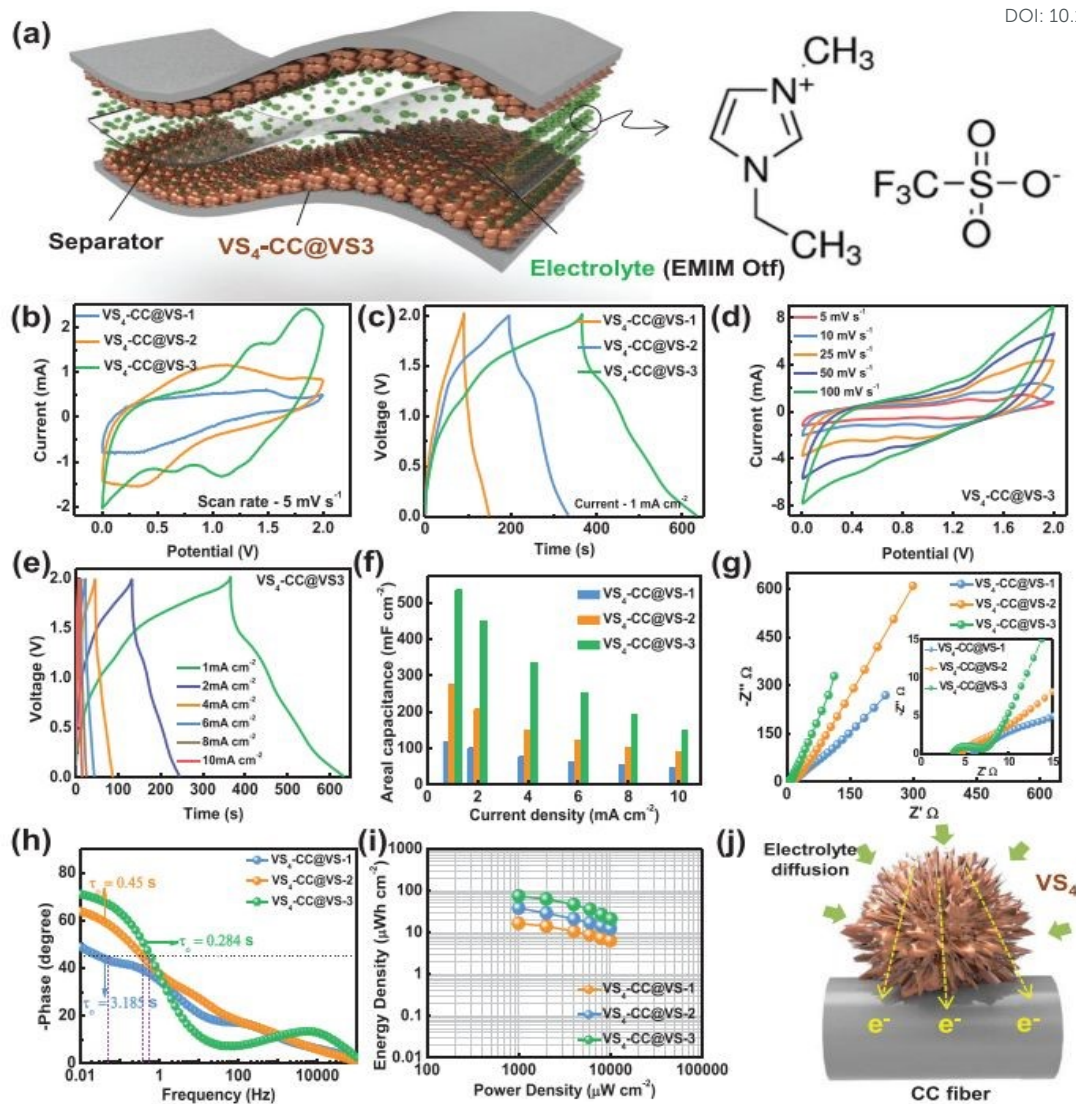




**Figure 13:** FESEM image of (a) VS<sub>4</sub>-CC@VS-1; b) VS<sub>4</sub>-CC@VS-2, and c) VS<sub>4</sub>-CC@VS-3 samples with various magnifications. Reproduced with permission from [56] Copyright (2020) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The area specific capacitance obtained for the three SC electrodes is calculated from the GCD curves measured at different current densities and plotted in **Figure 14f**. The SCs hold a maximum area specific capacitance of 119 mF/cm<sup>2</sup> for VS<sub>4</sub>-CC@VS-1, 277 mF/cm<sup>2</sup> for VS<sub>4</sub>-CC@VS-2 and 536 mF/cm<sup>2</sup> for VS<sub>4</sub>-CC@VS-3, from this it can be seen that the VS<sub>4</sub>-CC@VS-3 SC exhibited a superior performance when compared to that of the other two SCs. The VS<sub>4</sub>-CC@VS-3 SC possess area specific capacitances of 536, 452, 335, 254, 194, and 149 mF/cm<sup>2</sup> at a current density of x,y,..., respectively. This superior electrochemical characteristics of VS<sub>4</sub>-CC@VS-3 SC is due to the dense growth of VS<sub>4</sub> nanoflower on CF cloth which enabled large interaction area for the rapid diffusion of electrolyte-ions. The Nyquist plot (**Figure 14g**) and bode plot (**Figure 14h**) showed that the VS<sub>4</sub>-CC@VS-1, VS<sub>4</sub>-CC@VS-2, and VS<sub>4</sub>-CC@VS-3 SCs exhibited a series resistance of 4.629, 4.14, and 3.765 Ω cm<sup>2</sup>, respectively. Ragone plot of these three SCs (**Figure 14i**) revealed that the VS<sub>4</sub>-CC@VS-3 SC exhibited a high energy density of 28.6 Wh/kg at a corresponding power density of 9340 W/kg. This report envisages to design a binder-free electrode that facilitates a rapid diffusion of electrolyte ions thereby delivers high performance. A schematic representation of mechanism of binder-free VS<sub>4</sub>-CC@VS-3 SC electrode is depicted in **Figure 14j**.





**Figure 14:** (a) Pictorial representation of symmetric SC with ionic liquid electrolyte; (b) CVs of electrode at a scan rate of 5 mV/s; (c) GCD curve at 1 mA/cm<sup>2</sup> current density; (d) CV at different scan rates; (e) GCD at different current density; (f) variation of area specific capacitance at various current density; (g) Nyquist plot and (h) bode plot of device; (i) Ragone plot of symmetric device; (j) pictorial representation of mechanism of binder free electrode SC device with VS<sub>4</sub>-CC@VS-3. Reproduced with permission from [56] Copyright (2020) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

CF have prominent applications in energy fields due to its large surface area, large tolerance in temperature, reduced thermal expansion coefficient, high electrochemically active interfaces and a 1D pathway for the transportation of electrons. But the difficulty in synthesizing CNF-based SC electrodes in a green and cost-effective methods stand as a demerit for its further explorations. Li et al. [57] suggested a copolymerization approach where an oxygen-rich monomer named itaconic acid (IA) is introduced to molecular chain of PAN. This introduction does not produce any damage to the uniformity of trapezoidal structure formed in thermal stabilization approach. But it is found to create a large number of functional groups such as oxygen-containing functional groups, as shown in **Figure 15a,b**. It is found that the carbonization procedure led to a microporous structure by creating vacancy-effect in CNF. The

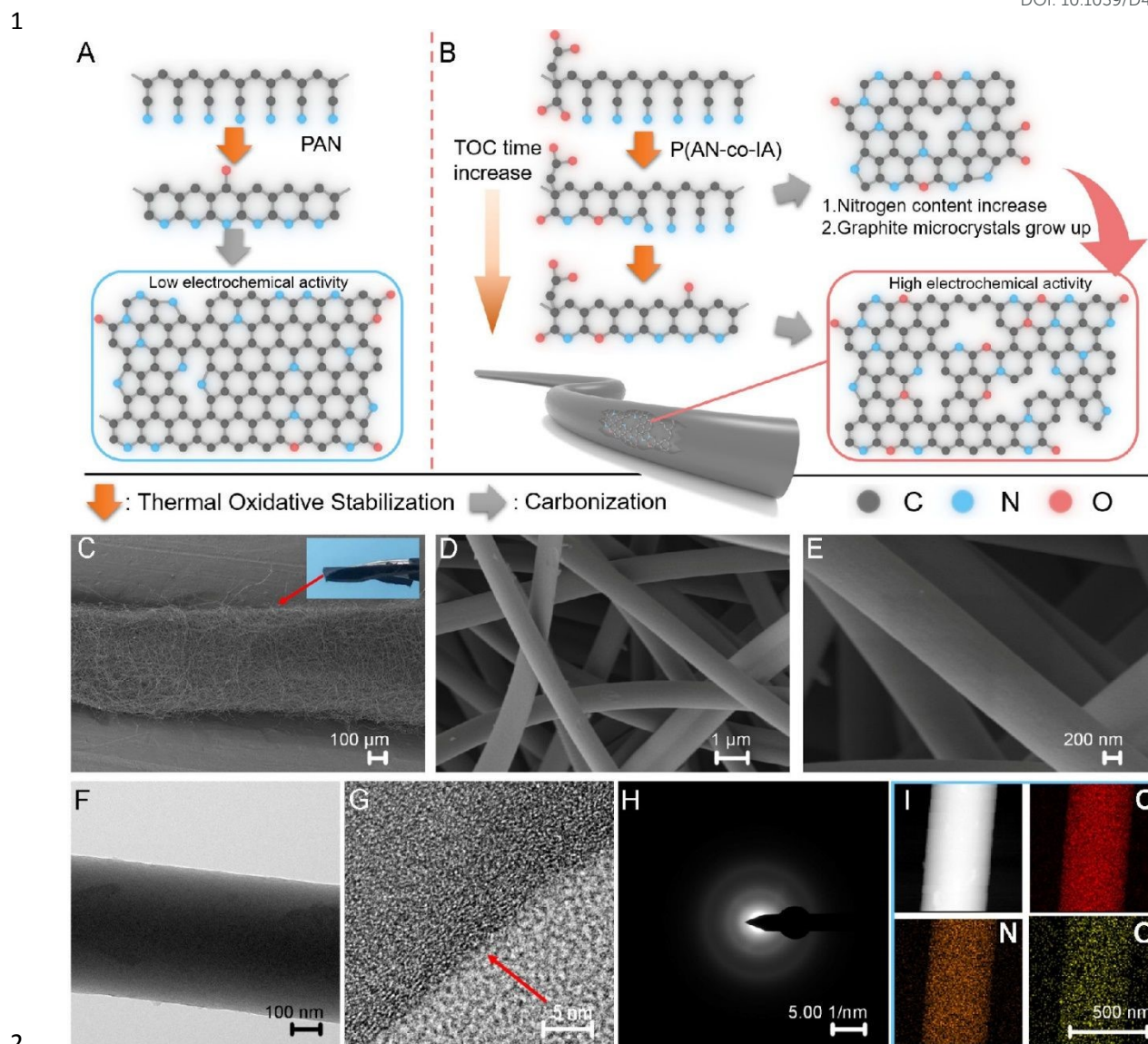




1 degradation of a segment increases by the substitution of N atom introducing higher redox  
2 activity to the material. After a stabilization period of 48 h, the prepared CNF membrane has  
3 received high flexibility and found stable even it is bent at a bending angle of 180° (inset image  
4 of **Figure 15c**). The SEM images of CNF obtained at different magnifications are depicted in  
5 **Figure 15c-e**. The HRTEM images of CNF exhibited a less graphitic structure, can be seen  
6 from **Figure 15f,g**. The selected area electron diffraction pattern (SAED) pattern which  
7 possesses a diffused rings shows an amorphous nature (**Figure 15h**). The elemental mapping  
8 analysis showed the even distribution of carbon, oxygen and nitrogen in the CNF (**Figure 15**  
9 **i**). The authors of this work fabricated a flexible symmetric SC using gel electrolyte and it is  
10 shown schematically shown in **Figure 16a**. The gel electrolyte exhibits low ionic conductivity,  
11 hence a small deviation in the CV curves can be observed from its normal rectangular shape  
12 but it still maintains a uniformity in symmetry even at a scan rate of 100 mV/s (**Figure 16b**).  
13 **Figure 16c** shows the CV curves obtained at different bending angles such as 0°, 90°, and 180°  
14 and no variation in the area under the curve was observed. This shows the excellent stability of  
15 the SC even at a severe bending of 180°. The GCD curves obtained for the solid-state SC is  
16 shown in **Figure 16d**, which represents a linearity in GCD curves with a symmetric triangular  
17 shape. The Ragone plot of assembled SC is depicted in **Figure 16e** exhibits an area power  
18 density of 2142  $\mu\text{W}/\text{cm}^2$  with a corresponding energy density of 23.8  $\mu\text{Wh}/\text{cm}^2$ .  
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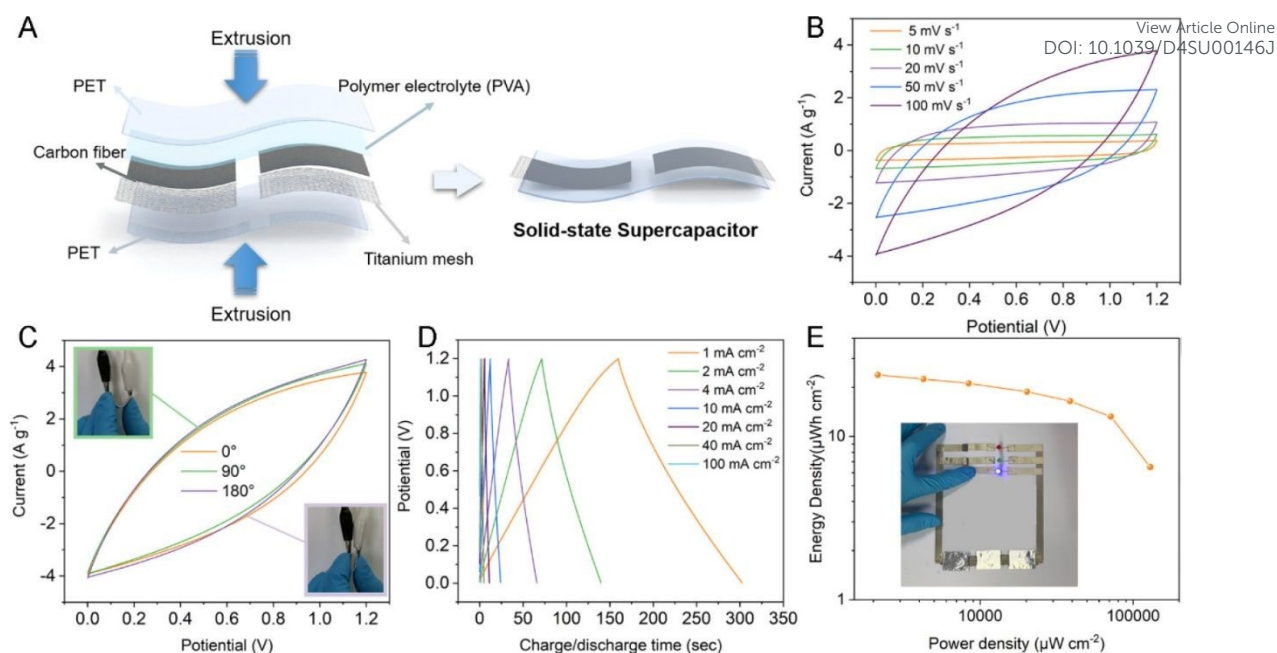
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**Figure 15:** (a) Pictorial representation of carbonization procedure of PAN; (b) image of PAN copolymer carbonization. When the cyclization of precursor increases, pre-nitrogen content and material graphitization also increase. SEM image (c-e) carbonized CNF and image of piece of CNF. HRTEM image of CNF (f, g), (h) SAED image; (i) electron loss spectroscopy (EELS) elemental mapping. Reproduced with permission from [57] Copyright (2021) American Chemical Society.

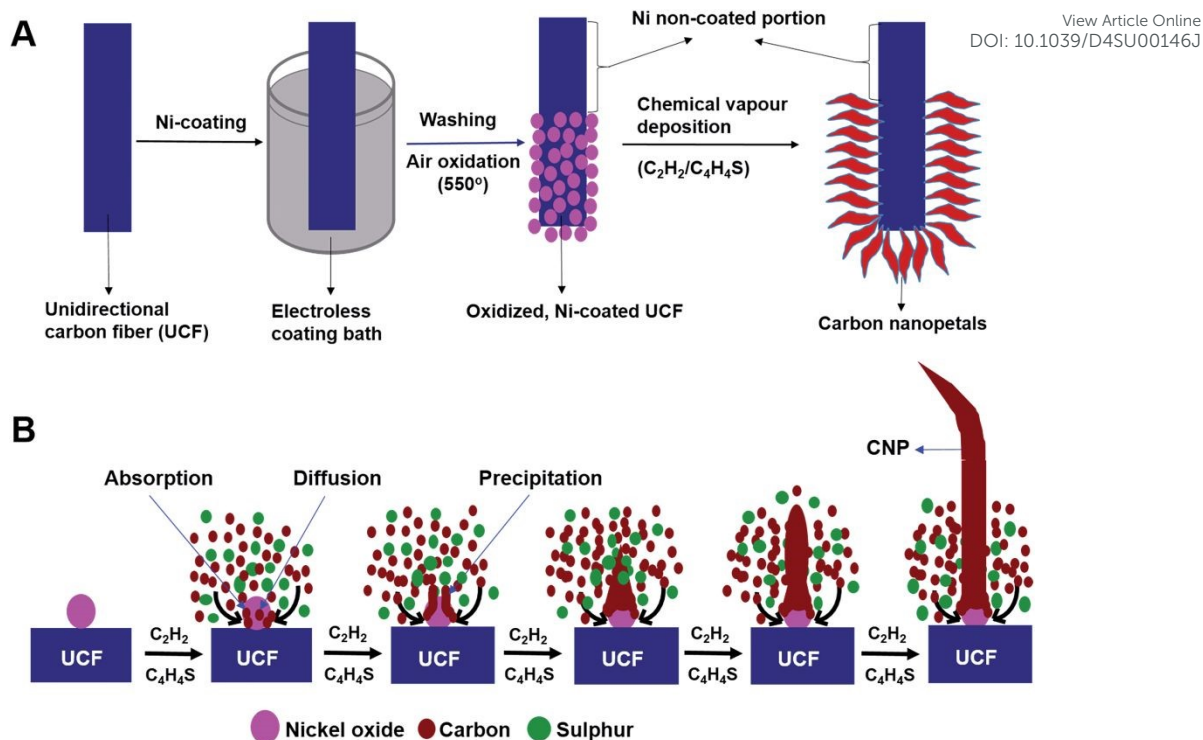




**Figure 16:** (a) Preparation of SC; (b) CV curve of device; (c) CV curve of device in different bending angles; (d) GCD curve; (e) Ragone plot with inset showing a blue LED constructed powered by the device. Reproduced with permission from [57] Copyright (2021) American Chemical Society.

A novel carbon nanostructure termed carbon nanopetals (CNPs) is reported in the literature [58]. The CNPs were grown over unidirectional CF (UCF) by CVD method and further used as a flexible electrode for SC application. The CNP/UCF hybrid material was further used as electrode-cum-current collector for the fabrication of a flexible SC. For the synthesis of CNPs, initially nickel is coated over UCF by electroless coating method. The electroless coating bath contains nickel sulphate hexahydrate, sodium hypophosphate, ammonium chloride, trisodium citrate and liquor ammonia. Firstly, UCF is dipped inside the electroless coating bath fixed at a temperature of 85°C under constant stirring for a duration of 10 minutes followed by rinsing it several times using ethanol and de-ionized water and subsequently dried at 85°C for 24 h. The UCF strands coated with nickel nanoparticles are further oxidized at a temperature of 550°C in air-bed reactor for 30 minutes to make nickel oxide nanoparticles. The proposed oxidized nickel-coated UCF is acted as a substrate to synthesize CNPs using catalytic CVD. During this process, oxidized, nickel-coated UCF is heated to a temperature of 500°C in a horizontal quartz furnace under continuous flow of N<sub>2</sub>. To avoid excess generation of oxides on nickel nanoparticles, H<sub>2</sub> is introduced at a flow rate of 100 mL/min for a duration of 15 minutes. The temperature is then increased to 700°C and introduced acetylene gas at a flow rate of 90 mL/minute for 15 min, by keeping fixed the N<sub>2</sub> flow at a rate of 200 mL/minute. Later, thiophene is introduced inside the CVD reactor simultaneously by heating a round bottom flask kept at a temperature of 80°C on the route of N<sub>2</sub> flow. The CNPs grown over UCF is collected after cooling down the CVD reactor to the room temperature under N<sub>2</sub> flow. The entire procedure involved in synthesis of CNPs over UCF is shown in **Figure 17a**. A proposed mechanism of growth executed for CNP over the UCF is depicted in **Figure 17b**. The CVD growth established for CNPs consists of four sequential procedures which involves transportation of mass and reaction in gas phase, dissociative absorption of carbon atom on the surfaces of nickel oxide nanoparticles, carbon atom diffusion over its surface and carbon atom precipitation from nickel oxide nanoparticles.



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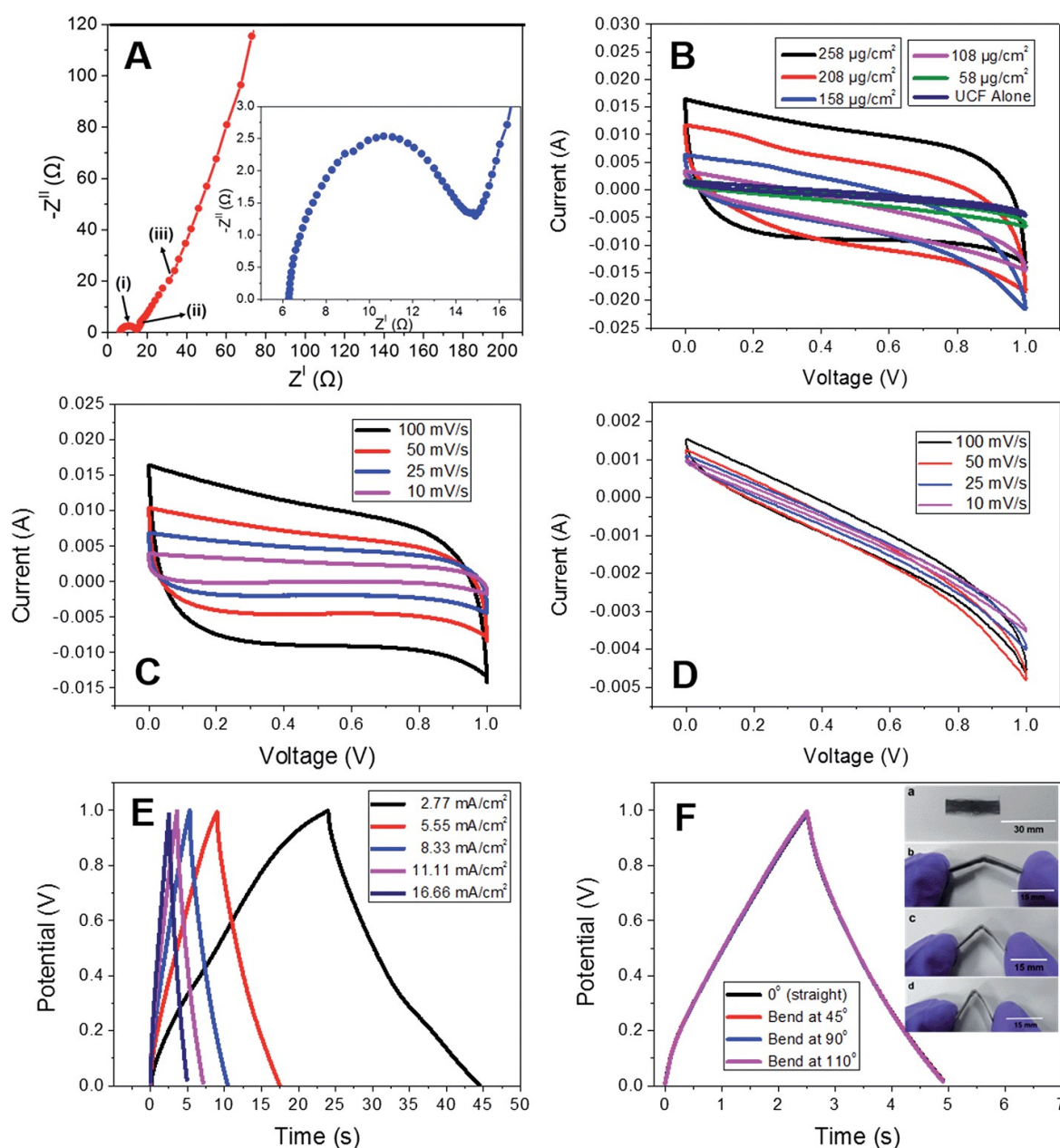
**Figure 17:** (a) Pictorial representation of procedures involved in the synthesis of CNPs on UCF, (b) mechanism of growth of CNPs on UCF. Reproduced with permission from [58] Copyright (2016) Royal Society of Chemistry.

The CNPs grown on UCF is further used as an electrode-active material for fabricating a SC. From the Nyquist plot (**Figure 18a**), it is found that the SC exhibits a bulk electrolyte resistance of about  $6.2 \Omega$ , and this smaller value of resistance indicates a high ionic conductivity possessed by the electrode-active material. The CV curves measured with a variation in the loading content of carbon nanopetals ( $258, 208, 158, 108,$  and  $58 \mu\text{g}/\text{cm}^2$ ) for the hybrid SC electrode (**Figure 18b**). The CV curves exhibited by CNP/UCF SC with the electrode having a CNP loading density of  $258 \mu\text{g}/\text{cm}^2$  at different scan rates is given in **Figure 18c**. The CV curves possess a near rectangular shape that representing the efficient double layer charge storage mechanism in accordance to the efficient propagation of charges through electrode-cum-current collector. To examine the electrochemical characteristics of pristine UCF SC electrode-active material, the CV analysis was performed in a two-electrode cell configuration at different scan rates and it is given in **Figure 18d**. From this analysis, it is clear that there exists only a slight contribution to charge storage introduced with pristine UCF. The GCD analysis of CNP/UCF SC electrode with respect to different current densities is given in **Figure 18e**. From the given analysis, it is clear that the SC possesses a high discharge capacitance of  $102.6 \text{ mF}$  at a current density of  $2.77 \text{ mA}/\text{cm}^2$  and  $69.9 \text{ mF}$  at a comparatively high current density of  $11.11 \text{ mA}/\text{cm}^2$ . The porous architecture of the SC electrode along with the CNP orientation helps in the rapid movement of electrolyte-ions thereby an accelerated charge transfer happened which leads to high-performance. To demonstrate the practical applicability of the CNP/SC in flexible electronic devices, the SC is undergone a bending test in which the CNP/UCF SC was bend at different bending angles (**Figure 18f**). The GCD curves obtained for the SC at different bending angles such as  $0^\circ, 45^\circ, 90^\circ,$  and  $110^\circ$  are depicted in **Figure 18f**. The bending test display no significant variation in the charge/discharge profiles, which represents the excellent flexibility of the SC. An areal capacitance of  $39.8 \text{ mF}/\text{cm}^2$  is obtained at  $0^\circ$  and it is found unaltered even at a severe bend of  $180^\circ$ . By increasing the loading content





1 of CNP, the CV curve consists large area under the curves where an area gets reduced upon  
 2 lowering the CNP content in the electrode. A volume specific energy density obtained for the  
 3 CNF/UCP SC is 0.753 mWh/cm<sup>3</sup> with a corresponding gravimetric energy density of 30 W  
 4 h/kg at a constant current density of 2.77 mA/cm<sup>2</sup>.

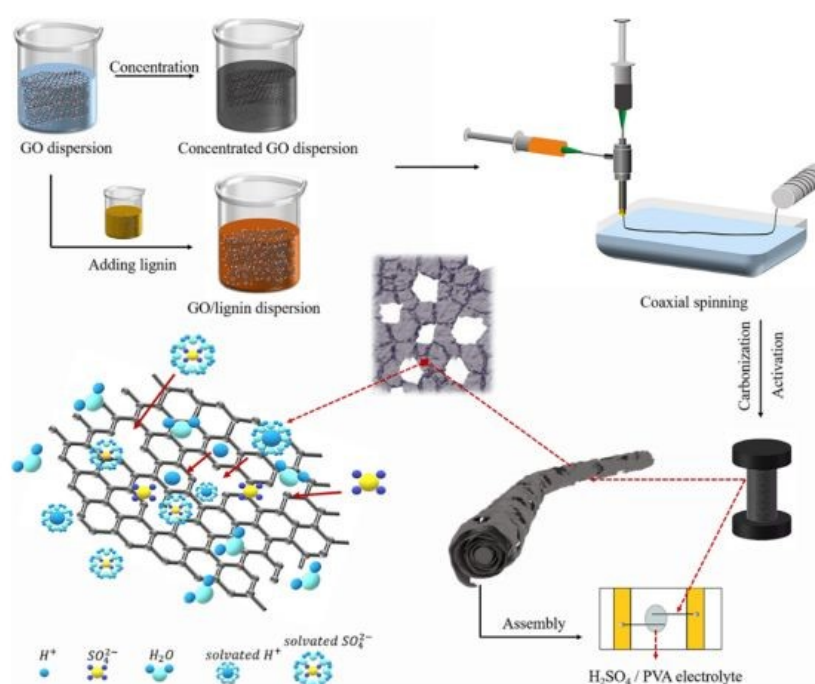


6  
 7  
 8 **Figure 18:** a) Nyquist plot (inset represents Nyquist in high frequency region); b) CV curve in  
 9 different loading density; c) CV curve for different scan rate having CNP loading density of  
 10 258  $\mu\text{g}/\text{cm}^2$  of CNP/UCF SC; d) CV curve of UCF at various scan rate. GCD curve at e) various  
 11 current density and f) various bending angles of CNP/UCF SC (inset shows the digital  
 12 photograph of CNP/UCF SC bent for 0° (a), 45° (b), 90° (c), and 110° (d)]. Reproduced with  
 13 permission from [58] Copyright (2016) Royal Society of Chemistry.

14  
 15 Carbon-based flexible SCs are promising candidates for powering up the smart textile wearable  
 16 electronics. But their reduced energy density hindering its industrial applications especially  
 17 due to the limitation of efficient synthesis approach for a highly conductive fiber electrode



1 exhibiting high specific capacitance. Hu et al. [59] developed a sustainable, cost-effective  
 2 approach in a scalable way to develop lignin-based carbon/graphene fiber (CG@GF) hybrid  
 3 with a porous structure and further used it as an electrode-active material for SC. This  
 4 environment-friendly approach has envisaged the large-scale preparation of CG@GF hybrids  
 5 for a variety of application including SC electrode preparation. A schematic representation of  
 6 CG@GF hybrid depicting the overall synthesis procedure of CG@GF hybrid and the CG@GF  
 7 SC is given in **Figure 19**. Here, the lignin powder is firstly dissolving in a 5 mL aqueous KOH  
 8 solution by fixing the KOH to lignin mass ratio as 2:1. KOH is added to the lignin solution in  
 9 order to introduce the dissolution of lignin in alkaline environment and to create a  
 10 homogeneously arranged spinning dope. Under 0% lignin, solvent is stand as water without  
 11 any KOH content. The as-prepared alkaline solution is added to the GO solution drop-wise and  
 12 the concentration was fixed to be 15 mg/mL. Later, the CG@GF hybrid fibers are synthesized  
 13 by coaxial wet spinning method.

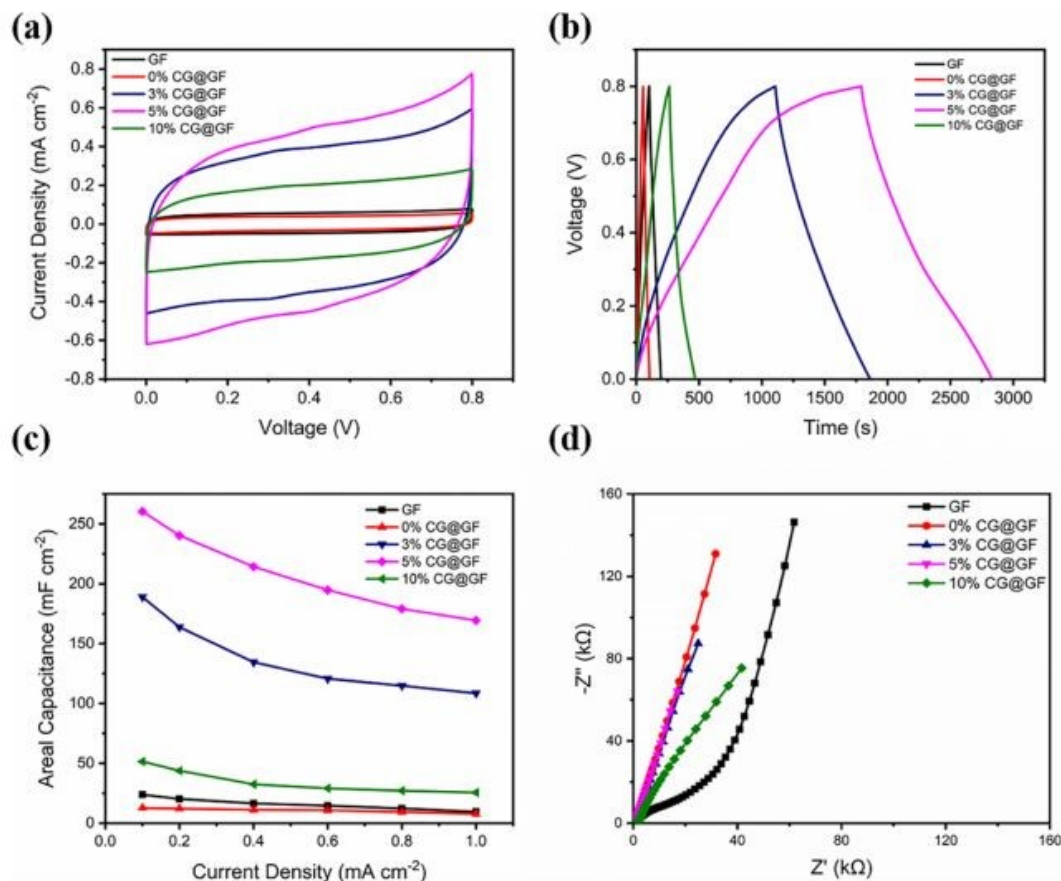


15  
 16  
 17 **Figure 19:** Pictorial representation of synthesis procedure of CG@GF electrode and  
 18 fabrication of flexible SC. Reproduced with permission from [59] Copyright (2021) American  
 19 Chemical Society.

20  
 21 The significance of carbon with lignin on the electrochemical performance in the CG@GF SC  
 22 electrode is evaluated by CV measurement and shown in **Figure 20a**. It can be observed from  
 23 the CV curves that that the CG@GF SC electrode exhibited a rectangular curve with a rapid  
 24 propagation of charges at a scan rate of 5 mV/s. Also, the coaxially wet spun fiber in a ratio of  
 25 0% CG@GF possessed a smaller area due to an increase in the fiber diameter. The GCD curves  
 26 of CG@GF hybrid-based fiber SC electrode (**Figure 20b**) shows an almost symmetric isosceles  
 27 with a triangular shaped correlation between the time and charge/discharge potential at a  
 28 current density of 0.1 mA/cm<sup>2</sup> within a potential window of 0 - 0.8 V. These features indicate  
 29 that the CG@GF hybrid-based fiber SC electrode holds efficient charge/discharge  
 30 characteristics. The area specific capacitance of CG@GF hybrid-based fiber SC electrode  
 31 calculated from GCD curve is given in **Figure 20c**. The pure graphene fiber electrode exhibited  
 32 an area specific capacitance of 23.9 mF/cm<sup>2</sup> at a current density of 0.1 mA/cm<sup>2</sup>. It is also



1 observed that with an increase in the current density from 0.1 to 1 mA/cm<sup>2</sup>, there exhibits a  
 2 retention of capacitance of wet-spun coaxial carbon-based fiber of 60%, 57%, 65%, and 49%  
 3 for 0%, 3%, 5%, and 10% CG@GF hybrid electrodes, respectively. The Nyquist plots show  
 4 that (**Figure 20d**) the wet spun fiber holds a large semi-circle at the high-frequency region,  
 5 depicting a high charge transfer resistance.  
 6



7  
 8  
 9 **Figure 20:** (a) CV curve with scan rate of 5 mV/s; (b) GCD curve at a current density  
 10 0.1mA/cm<sup>2</sup>; (c) area specific capacitance obtained from GCD curve in different current density;  
 11 (d) Nyquist plot of flexible SC. Reproduced with permission from [59] Copyright (2021)  
 12 American Chemical Society.

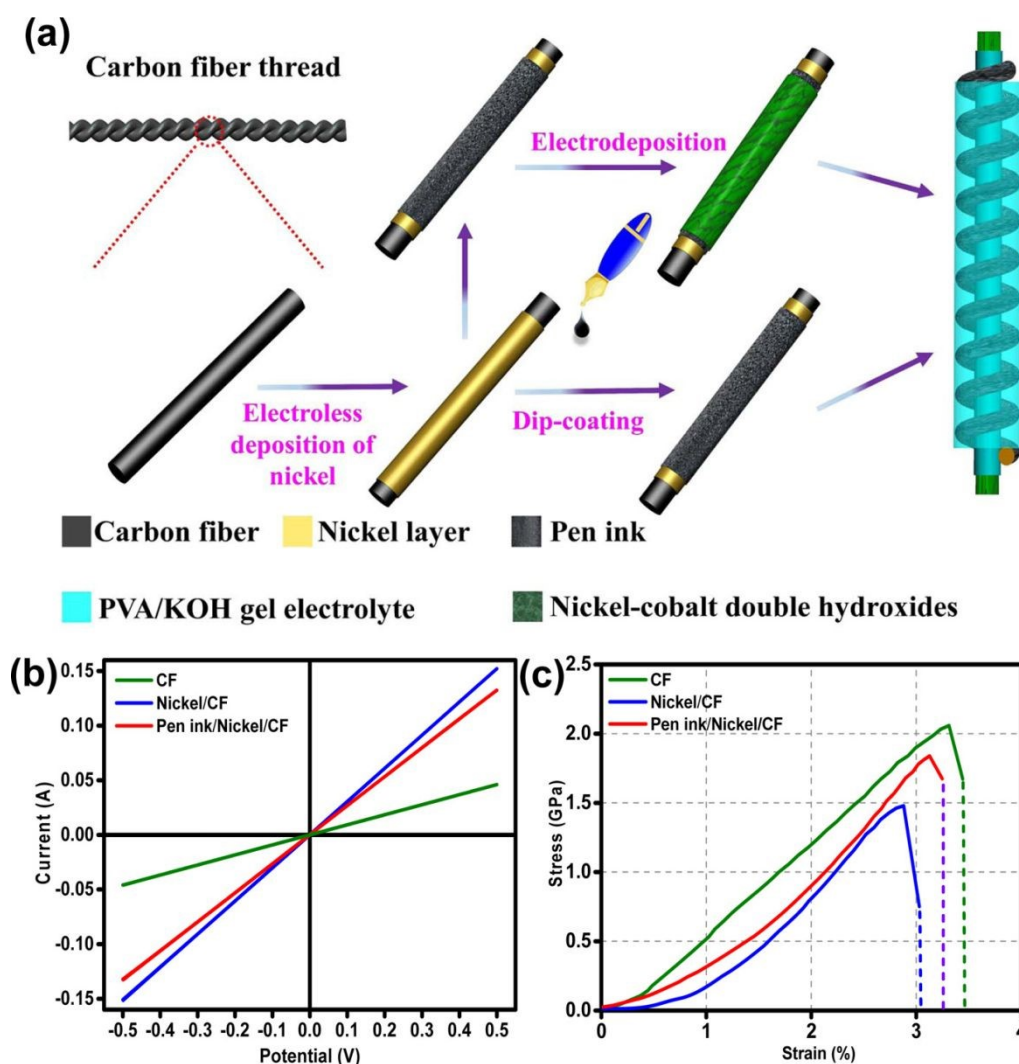
#### 14 4.2 Carbon Fibers/Layered Double Hydroxide Nanocomposite Electrodes

15 Layered double hydroxides are excellent candidates for SC electrode application due to their  
 16 pseudocapacitive charge storage. Layered nanostructured electrodes envisages the diffusion of  
 17 electrolyte-ions through it thereby an enhanced charge storage can be achieved. Gao et al. [60]  
 18 fabricated a flexible SC with nickel-cobalt double hydroxide (Ni-Co LDHS) using pen ink  
 19 electrodes constructed using a CF substrate. Fabrication of solid-state asymmetric SC with  
 20 these electrodes is depicted in **Figure 21a**. Here, a CF thread holding small diameter range of  
 21 200-400 μm is selected as the primary electrode due to its better stiffness, light-in-weight and  
 22 good conductivity. The electrical conductivity of CF thread is enhanced when it was coated  
 23 with a thin layer of nickel by electrodeposition technique. The resultant electrode possesses an  
 24 increase in the conductivity when compared to that of pristine CF, is evident from **Figure 21b**,  
 25 it increased by a factor of 3.3 and it is found to be lighter than corresponding pure metal yarns.  
 26 This is due to a thin deposition of nickel layer (about 820 nm) and it creates an improvement  
 27 in the mass of electrode. Also, there exist a reduction in tensile strength of the fabricated SC





1 electrode from 2.05 to 1.47 GPa, mainly due to adverse effect introduced by interaction of  
 2 surface carbon filament and deposited nickel atoms and the tensile test results are shown in  
 3 **Figure 21c**.

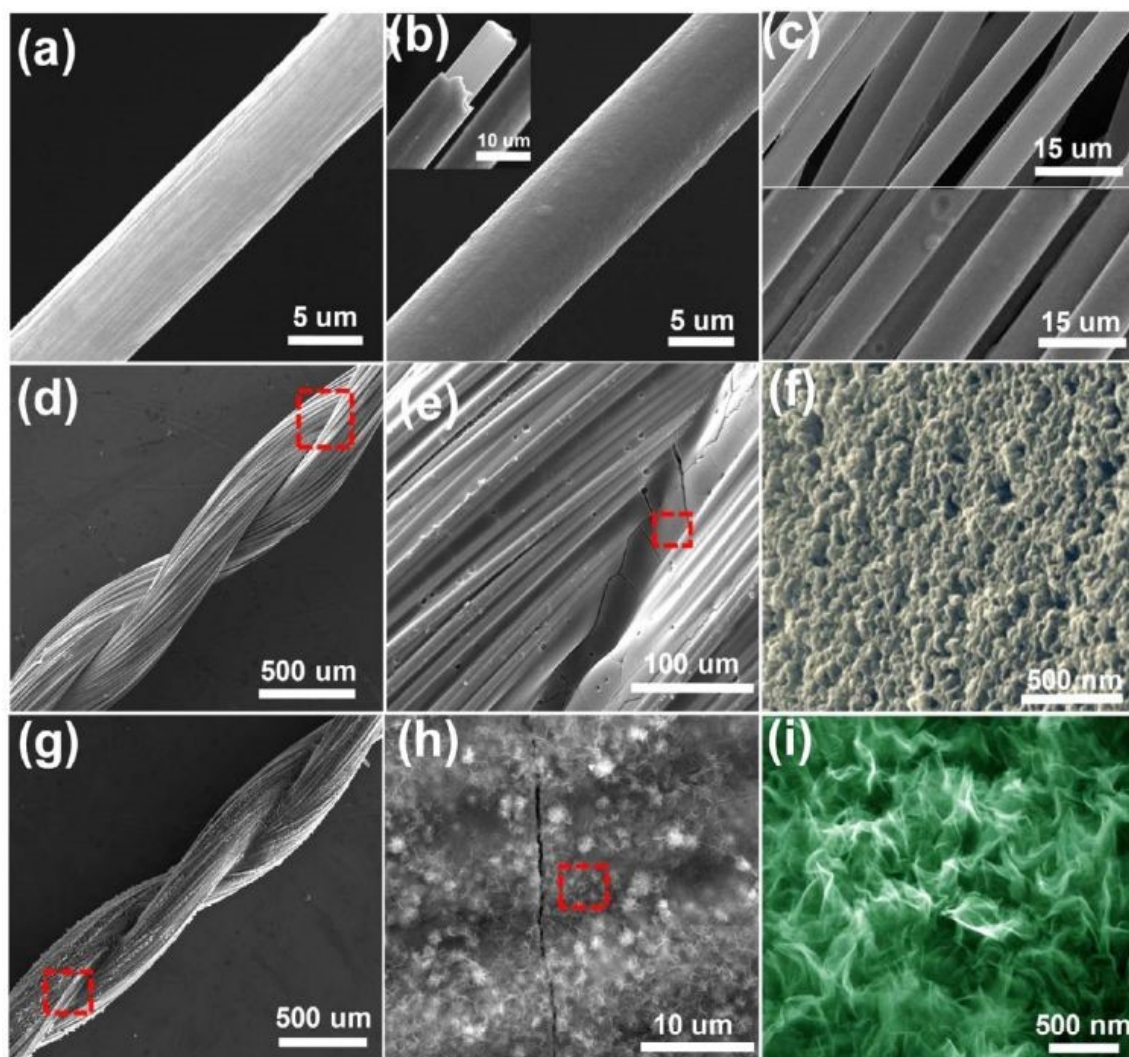


5  
6  
7 **Figure 21:** (a) Pictorial representation of fabrication process of flexible fiber-type solid-state  
 8 asymmetric device; (b) its conductivity, not two-electrode test; (c) analysis of tensile test.  
 9 Reproduced with permission from [60] Copyright (2017) American Chemical Society.

10  
11 The surface morphology of these fabricated hierarchical fiber electrodes is given in **Figure 22**.  
 12 A single CF filament with a thickness of 6.93  $\mu\text{m}$  holding a smooth surface can be viewed from  
 13 **Figure 22a** and this CF filament coated with a thin nickel layer having a thickness of 820 nm  
 14 is shown in **Figure 22b**. Because of the effective chemical penetration towards the core of CF,  
 15 nickel is going to deposit uniformly on CF thread bundle is given in **Figure 22c**. **Figure 22d**  
 16 and **e** confirms a uniform distribution of pen ink on nickel/CF thread. From the enlarged view  
 17 of pen ink film (**Figure 22f**), which represents a porous structure holding a ravine morphology  
 18 and helped in enhancing the surface area of the electrode nanostructure thereby an enhanced  
 19 electrochemical reaction to occur. The FESEM image corresponding to Ni-Co LDHS on the  
 20 substrate is shown in **Figure 22g**. In **Figure 22h**, we can find a thin transparent interconnected  
 21 network growing over the ink film, which creates a highly electrically conducting network that  
 22 consists of a large number of electroactive surface regions for the enhanced electrochemical



1 reaction to occur. The nanosheet microstructure having a rippled silk-like morphology is  
 2 observed from the high-magnification SEM image depicted in **Figure 22i**.  
 3



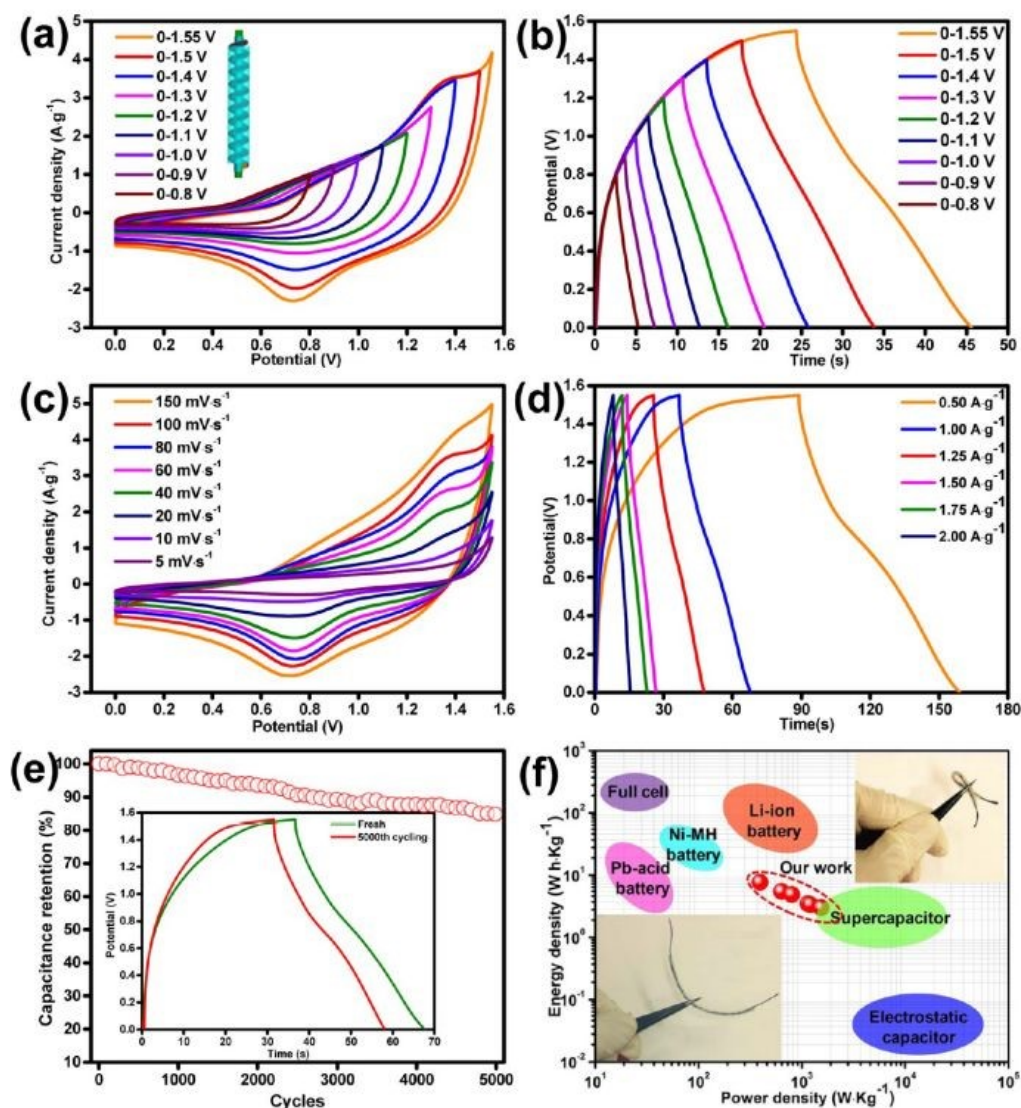
4  
 5  
 6 **Figure 22:** SEM image corresponds to (a) CF with a smooth surface; (b) CF uniformly coated  
 7 over nickel layer having a smooth surface; (c) top portion of CF bundle and bottom portion is  
 8 the CF bundle which was coated using Nickel; (d, e) Nickel/CF coated to a pen ink film; (f)  
 9 porous structure with ravine morphology of pen ink/nickel/CF; (g, h) Ni-Co LDHS creating a  
 10 uniform conductive network with ink film having porous nature and (i) SEM image with higher  
 11 magnification. Reproduced with permission from [60] Copyright (2017) American Chemical  
 12 Society.

13  
 14 An asymmetric SC was fabricated using the Ni-Co LDHS as the x electrode and yy as negative  
 15 electrode. The CV curves of the as-fabricated asymmetric SC at varying potential window of  
 16 0–0.8 V to 0–1.55 V is given in **Figure 23a**. The area under the curve is found to be increased  
 17 upon widening the potential window, which is obvious. The GCD curves of the as-fabricated  
 18 asymmetric SC at varying potential window of 0 - 0.8 V to 0 - 1.55 V is given in **Figure 23b**  
 19 and it can be seen that the SC work in a stable potential window of 0 - 1.55 V without any  
 20 significant potential drop. The CV curves of the as-fabricated asymmetric SC at different scan  
 21 rates such as 5 mV/s, 10, 20, 40, 60, 80, 100, and 150 mV/s within a potential window of 0 -  
 22 1.55 V is depicted in **Figure 23c**. These CV curves show that the redox-active electrodes with





1 an efficient reaction kinetics. The GCD measurements of the as-fabricated asymmetric SC at  
 2 different current densities are shown in **Figure 23d**, which indicates a hybrid charge storage  
 3 mechanism. The specific capacitance of the SC is found to be 22.94 F/g at a current density of  
 4 0.5 A/g and is found to decrease to 7.9 F/g when current density changed to 2 A/g. A high  
 5 capacitance retention of 86% was also observed for the SC during the cyclic study even after  
 6 5000 cycles (**Figure 23e**). The GCD curves at its first and after completing the cycling study  
 7 are depicted as an inset image of **Figure 23e**. The energy density and power density variation  
 8 of the SC in the form of Ragone plot is given in **Figure 23f**. From this plot, it can be seen that  
 9 with an increase in the current density from 0.5 to 2 A/g, there exists a reduction in specific  
 10 energy density from 7.66 Wh/kg to 3 Wh/kg.



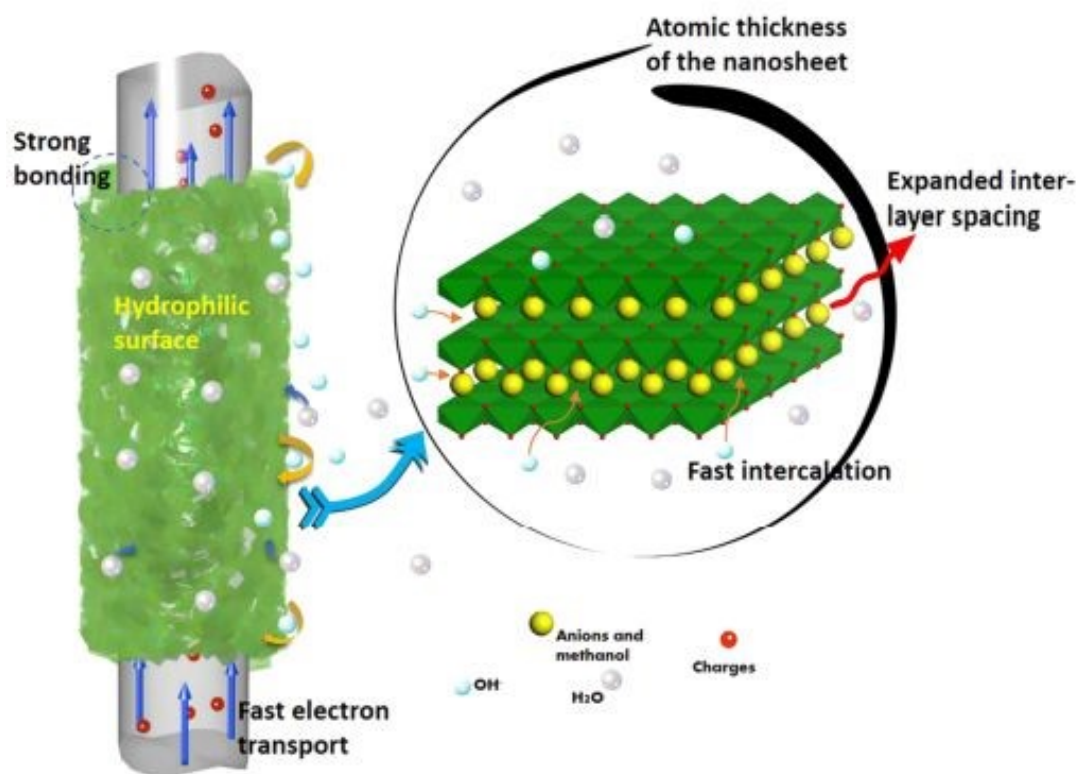
12  
 13  
 14 **Figure 23:** Electrochemical studies of fabricated asymmetric SC in KOH/PVA gel electrolyte  
 15 (a) CV curve at 100 mV/s scan rate; (b) GCD curve in various voltage window at 1.25 A/g  
 16 fixed current density; (c) CV curve with scan rate of 5-150 mV/s; (d) GCD curve in current  
 17 density of 0.5–2.0 A/g; (e) Cyclic stability analysis of device at current density of 1 A/g with  
 18 inset representing the GCD curve of device before and after 5000 cycles; (f) Ragone plot, inset  
 19 corresponding to the optical image of device. Reproduced with permission from [60] Copyright  
 20 (2017) American Chemical Society.

21





1 A solvothermal reaction was opted to synthesize Ni-Co LDHS nanosheets over CF cloth by Wang et al [61]. By using a complex 2-methylimidazole and methanol as solvent, the LDHS  
 2 nanosheet layer was prepared on CF that exhibited a growth in the (003) direction with an  
 3 expansion of interlayer spaces. This resulted in the formation of a 3D porous structure having  
 4 a thickness of 5 - 7 nm. The pictorial representation of charge storage mechanism of the SC  
 5 electrode is shown in **Figure 24**.  
 6  
 7



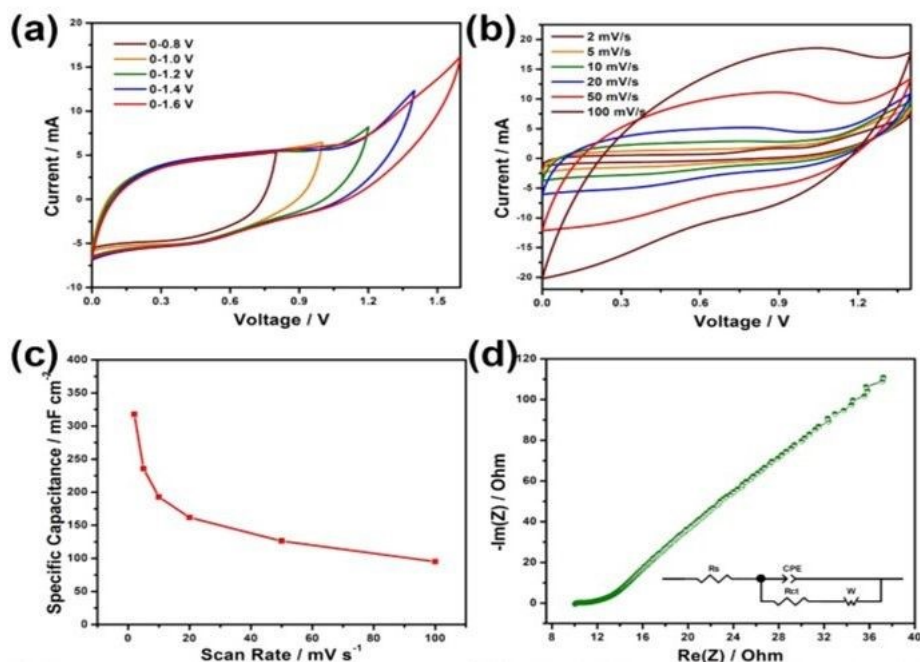
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10 **Figure 24:** Diagrammatic representation of charge storage mechanism in electrode material.  
 11 Reproduced with permission from [61] Copyright (2017) American Chemical Society.

12  
 13 A SC was fabricated using the Ni-Co LDHS as the x electrode and yy as negative electrode.  
 14 The CV curves of the as-fabricated SC at varying potential window of 0 - 0.8 V to 0 - 1.6 V is  
 15 given in **Figure 25a**. The SC could work within a potential window of 0 - 1.6 V without any  
 16 deterioration in its behavior but the authors selected a slightly lower potential window of 0 -  
 17 1.4 V. The CV curves of the as-fabricated SC at different scan rates within a potential window  
 18 of 0 – 1.4 V is given in **Figure 25b**. The specific capacitance of the SC was calculated at  
 19 different scan rates and plotted in **Figure 25c**. A maximum capacitance of 317.9 mF/cm<sup>2</sup> is  
 20 obtained for the SC at a lower scan rate of 2 mV/s and is found to decrease exponentially at  
 21 higher scan rates. The Nyquist plot of the SC shown in **Figure 25d** holds a series resistance of  
 22 10.15 Ω/cm<sup>2</sup> with a charge transfer resistance of 0.71 Ω/cm<sup>2</sup> representing its excellent  
 23 conductivity. The as-fabricated SC is found to be highly flexible when the bending test is  
 24 carried at different bending angles. The CV curves obtained at different bending angles from  
 25 15° to 180° showed no significant variation, which represents its excellent flexibility. Jagadale  
 26 et al. [62] reported the synthesis of CoAl LDHS on CF yarns using electrodeposition approach  
 27 and use it as electrode-active material for fabricating a solid-state SC. The solid-state SC was  
 28 fabricated using CoAl LDHS on CF yarns as electrode and KOH-PVA gel electrolyte. The



1 electrochemical performance of the solid-state SC is tested and an area specific capacitance of  
 2 about 195 mF/cm<sup>2</sup> and a volumetric energy density of 1.6 mWh/cm<sup>3</sup> were obtained.

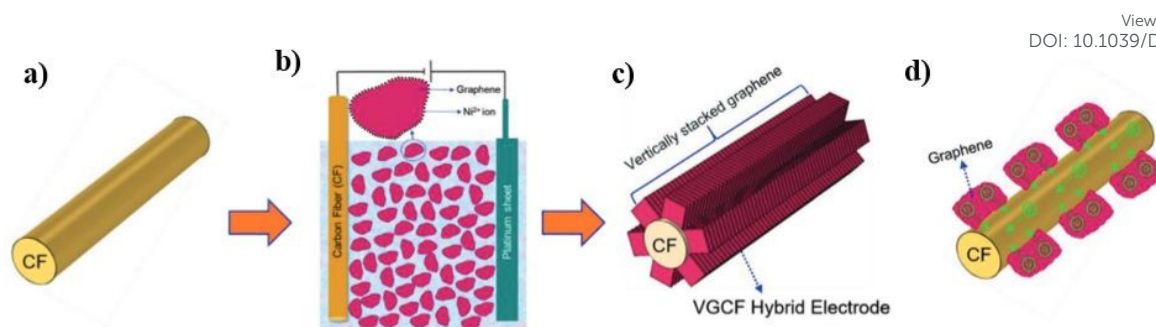


4  
 5  
 6 **Figure 25:** (a) CV curve of device at various voltage windows at a sweep rate 20 mV/s; (b)  
 7 CV; (c) specific capacitance at various sweep rates; (d) EIS spectrum. Reproduced with  
 8 permission from [61] Copyright (2017) American Chemical Society.

#### 10 4.3 Carbon Fibers/Carbon Nanostructures Nanocomposite Electrodes

11 Carbon-carbon nanocomposites are highly demanded for SC electrode application due to their  
 12 good electronic conductivity, good chemical and electrochemical stabilities, easy synthesis,  
 13 etc. Carbon nanostructures such as CNTs, graphene, CNPs, etc are highly exploited as  
 14 electrode-active materials for SC application in the recent past. Graphene-based SC electrodes  
 15 has demerit of restacking of graphene layers during the electrode preparation. This leads to the  
 16 closure of the pores available in the electrode nanostructure, which eventually deteriorates its  
 17 electrochemical performance. To avoid the restacking of graphene layers while employing it  
 18 as an electrode-active material for SC fabrication, a new strategy is reported to align graphene  
 19 sheets vertically on CF substrate [32]. This novel strategy is found to be a versatile method of  
 20 preparing graphene electrodes by the vertical attachment of graphene sheet to CF (VGCF)  
 21 thereby the specific surface area of graphene available for electrochemical reactions to occur  
 22 become enhanced. The VGCF hybrid electrode is synthesised using electrophoretic deposition  
 23 as given in **Figure 26a-c**, where CF having an average diameter of 6  $\mu\text{m}$  is applied as the  
 24 substrate for depositing graphene sheets. An electrophoretic deposition is performed whereby  
 25 the transportation of graphene sheets which are positively charged due to the adsorption of  
 26 nickel ions towards CF electrode. The electrophoretic deposition of graphene sheets is carry  
 27 forwarded by applied a DC potential of 50 V (**Figure 26b**) and a 3D VGCF hybrid electrode  
 28 is obtained (**Figure 26c**). The electron transport in the VGCF hybrid SC electrode is  
 29 schematically portraited in **Figure 26d**.





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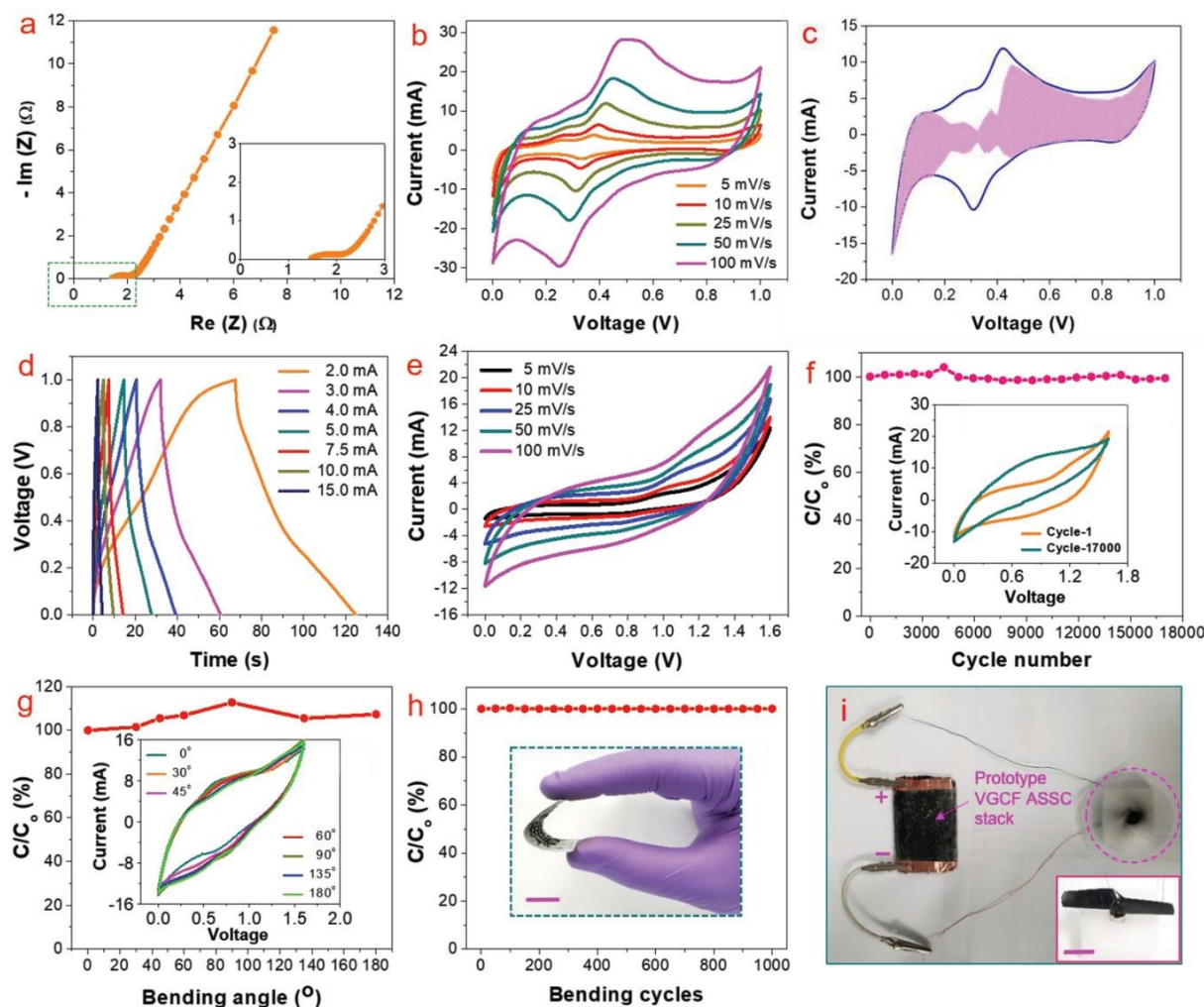
**Figure 26:** Pictorial representation of synthesis of VGCF electrode (a) CF substrate for electrophoretic deposition; (b) electrophoretic deposition with CF as negative electrode, Pt as positive electrode, and a bath consists of dispersion of graphene sheets in isopropyl alcohol with nickel nitrate hexahydrate; (c) VGCF hybrid after electrodeposition; (d) Pictorial representation of electron transport from graphene to CF. Reproduced with permission from [32] Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In order to analyse the application of this VGCF hybrid electrode material for industrial purposes, the authors of this work fabricated a symmetric SC using aqueous 1M  $\text{H}_3\text{PO}_4$  as electrolyte. Nyquist plot of the VGCF hybrid electrode is given in **Figure 27a** and the Nyquist plot at the high-frequency region is given as an inset image, which showed that the electrode exhibited a low electrolyte series resistance. The CV curves obtained for the VGCF hybrid SC (**Figure 27b**) showed that the hybrid electrode exhibits a redox-type charge storage induced by the presence of oxygen-containing surface functional groups on the graphene sheet as well as the  $\alpha\text{-Ni}(\text{OH})_2$ . The charge storage contribution from the surface-controlled and the diffusion-controlled mechanism is calculated by using Dunn's method and found that the electrode material has 70% surface-controlled and 30% diffusion-controlled charge storage, as depicted in **Figure 27c**. The GCD curves obtained for the VGCF hybrid SC shown in **Figure 27d** exhibited a charge/discharge profile with two slopes, this is due to the different charge storage mechanisms introduced by the electrode. The CV study performed within a potential window of 0 - 1.6 V (**Figure 27e**) depict the efficient charge storage capability of the SC. The VGCF hybrid SC exhibited a capacitance retention of 99.4% even after 17000 cycles (**Figure 27f**) and the inset CV curves show that there is no significant change in the area under the curve in the first cycle and the last cycle. The flexibility of the SC was analysed by bending it at different bending angles such as 30°, 45°, 60°, 90°, 135°, and 180° and from the CV curves (inset image), it is clear that the SC device has a capacitance retention of 100% even at a severe bend of 180° (**Figure 27g**). The SC is found to retain its capacitance even after completing 1000 bending cycles (**Figure 27h**). The inset image is the digital photograph at a bending angle of 90°. A device prototype of this fabricated SC which operating a toy drone propeller fan is given in **Figure 27i** and the running of the fan is given as an inset. In another work, a free-standing helically-coiled CNTs (HCNTs) grown on CF (HCNTF) is used as an electrode-cum-current collector for the fabrication of a flexible SC [63]. The authors of this work synthesized HCNTF hybrid by CVD method using thiophene as the defect induced catalyst for the growth of HCNTF. The flexibility of this SC is analysed by choosing the bending angles 0, 30, 60, 90, and 120°. The rate performance of fabricated electrode with HCNT density of 5.77 mg/cm<sup>3</sup> is verified by GCD measurements performed at various current densities. It is worth to note that the HCNTF hybrid electrode can be charged at a relatively higher current density of 8.33 mA/cm<sup>2</sup>. A solid-state SC was fabricated by using HCNTF hybrid electrode-cum-current collector and PVA/LiCl gel electrolyte. The SEM image (**Figure 28a**) shows a mesoporous





1 open network of HCNTs. A TEM image of a single strand of HCNT is depicted in **Figure 28b**.  
 2 The SAED pattern (**Figure 28c**) shows that the HCNT is not crystalline due to the defect-  
 3 induced growth. A schematic representation of the fabricated solid-state SC is given in **Figure**  
 4 **28d**. A digital image of SC module comprising of two similar solid-state HCNTF SCs  
 5 connected in series is shown in **Figure 28e** and this module is bent at an angle of  $180^\circ$  is shown  
 6 in **Figure 28f**. The practical application of this SC module in wearable electronic devices is  
 7 demonstrated by lighting-up an LED at its normal position (**Figure 28g**) and at a severe bend  
 8 of  $180^\circ$  (**Figure 28i**), which shows that no change in the light intensity.  
 9



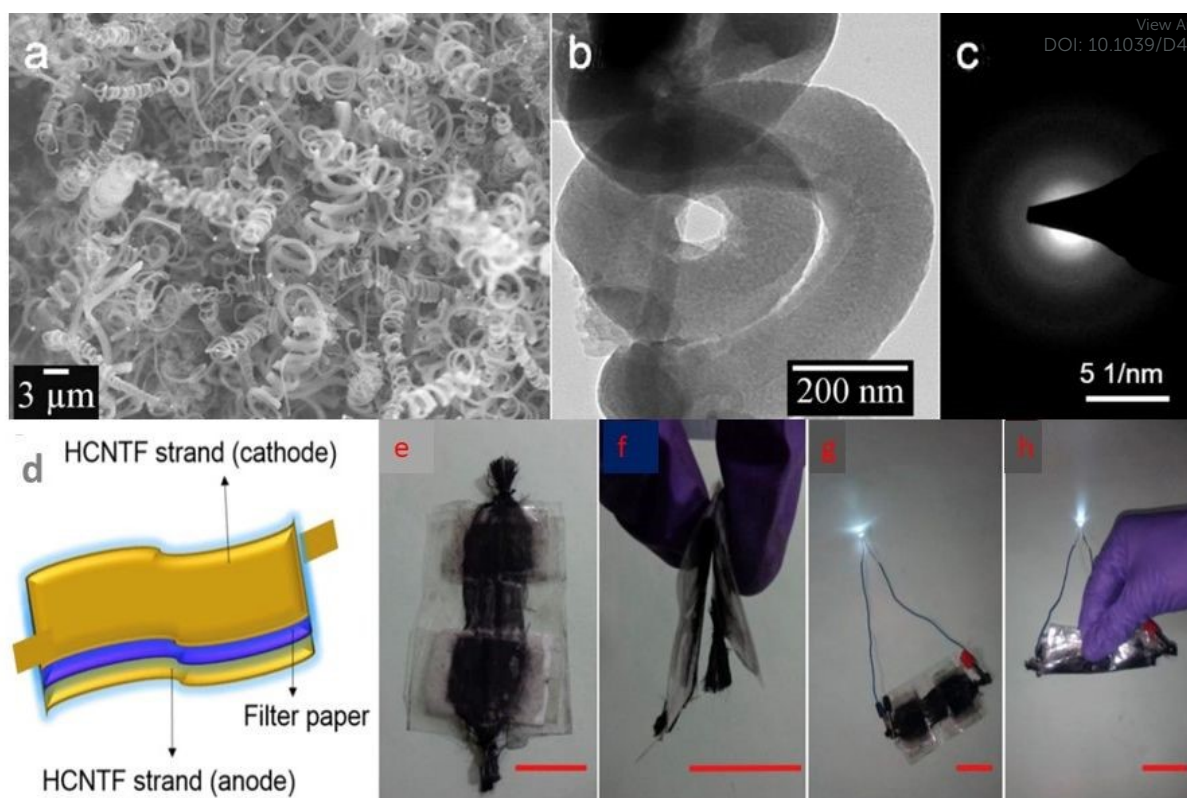
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12 **Figure 27:** Electrochemical analysis of VGCF SC (a) Nyquist plot (high resolution view of  
 13 high frequency region); (b) CV with different scan rates; (c) calculation of contribution of  
 14 capacitance at a scan rate of 25 mV/s; (d) GCD curve at various current density; (e) CV at  
 15 various scan rate ; (f) capacitance retention with cycle number for 17000 cycles; (g) capacitance  
 16 retention at various bending angle (inset is the CV at various bending angle at 100 mV/s scan  
 17 rate); (h) capacitance retention at 1000 bending cycle (inset is the digital photograph at an angle  
 18 of  $90^\circ$ ); (i) device prototype. Reproduced with permission from [32] Copyright (2019) WILEY-  
 19 VCH Verlag GmbH & Co. KGaA, Weinheim.

20





**Figure 28:** (a) SEM; (b) TEM; (c) SAED spectrum of HCNTF having HCNT density 5.77 mg/cm<sup>3</sup>; (d) Pictorial representation of fabricated device; (e) series connection of two solid state flexible HCNTFs; (f) bending of module at 180°; (g) discharging of module by LED; (h) discharging of module by a white LED with bending at 180°. Reproduced with permission from [63] Copyright (2016) Elsevier.

Yang et al. [64] developed a sandwich patterned reduced graphene oxide (rGO)/carboxylated multi-walled CNT (MWCNT) (RGO/cMWCNT) hybrid film and polypyrrole supported with CF paper (CFP/PPy) using vacuum infiltration method and electrochemical deposition. An asymmetric SC was fabricated using RGO/cMWCNT as negative electrode and CFP/PPy as positive electrode, and potassium polyacrylate/KCl gel electrolyte. This asymmetric SC exhibited an energy density of 28.6 W h/kg at a corresponding power density of 15.1 kW/kg at a working cell voltage of 1.6 V. The device holds a capacitance retention of 93% with long cycle life after 2000 cycles. Using a two-step solution process consisting of hydrothermal and chemical bath deposition, Liu et al. [65] synthesized SnO<sub>2</sub>@MO<sub>x</sub> heterostructure over CF cloth in order to fabricate a high-performance SC. This heterostructure possesses the features of good electronic conductivity of SnO<sub>2</sub> nanosheets as backbone for the deposition of MO<sub>x</sub>. The as-fabricated SC showed a higher discharge area specific capacitance of 980 mF/cm<sup>2</sup> at a current density of 1 mA/cm<sup>2</sup> along with an efficient rate capability of about 767 mF/cm<sup>2</sup> when tested at a comparatively higher current density of 20 mA/cm<sup>2</sup>. The SC hold an efficient cyclic stability of ~21.9% retention after completing 6000 cycles when performed at a current density of 1 mA/cm<sup>2</sup>. Feng et al. [66] synthesized MnO<sub>2</sub> tube-in-tube arrays supported over CF cloth using a facile template-assisted electrodeposition route. The solid-state SC fabricated with PVA/LiCl shows a high area specific capacitance of about 322 mF/cm<sup>2</sup> at a current density of 0.125 A/g. This SC exhibited a volumetric energy density of 0.073 mW h/cm<sup>3</sup> at a corresponding power density of 25W/kg along with a capacitance retention of 96.4% even after completing 2000 cycles. An asymmetric fiber-shaped SC in a weavable and flexible pattern using CF bundle@CNT-NiCo(OH)<sub>x</sub> (CF@CNC) as positive electrode and CF bundle



1 @activated carbon (CF@AC) as negative electrode was reported by Lu et al. [67]. In order to  
2 remove the demerits of the hydrophobic nature, reduced electrical conductivity and low surface  
3 area, a treatment with air plasma and modification with CNT is performed during the  
4 CF@CNC fabrication. This asymmetric SC exhibited an energy density of 0.84 mWh/cm<sup>3</sup>  
5 energy density at a corresponding power density of 19.1 mW/cm<sup>3</sup>. A high capacitance retention  
6 of 100% is also observed even after completing 8000 charge/discharge cycles. Using  
7 electrospinning and carbonization process on a CNF membrane, flexible  
8 polypyrrolone/polyimide composite (PBPICF) was prepared by Liu et al. [68]. For the  
9 preparation of PBPICF, polycarboxylic acid ammonium salt (PCAAS) and polyamic acid  
10 (PAA) is mixed in different proportions. The prepared nanofibers are exhibiting a network form  
11 structure having a uniformity in diameter of about 400-500 nm. Prepared PBPICF membrane  
12 hold an efficient flexibility and it can able to bent and fold without producing any break. This  
13 report shows that the prepared SC holds a specific capacitance of 172.44 F/g at a current density  
14 of 0.2 A/g. These results show that these binder free, flexible membrane is capable to fabricate  
15 a SC with good performance. Here the prepared PBPICF membrane have efficient power  
16 density value of 90 W/kg at 19.4 Wh/kg energy density with capacitance retention of 96% after  
17 10000 cycles at a current density of 1 A/g.

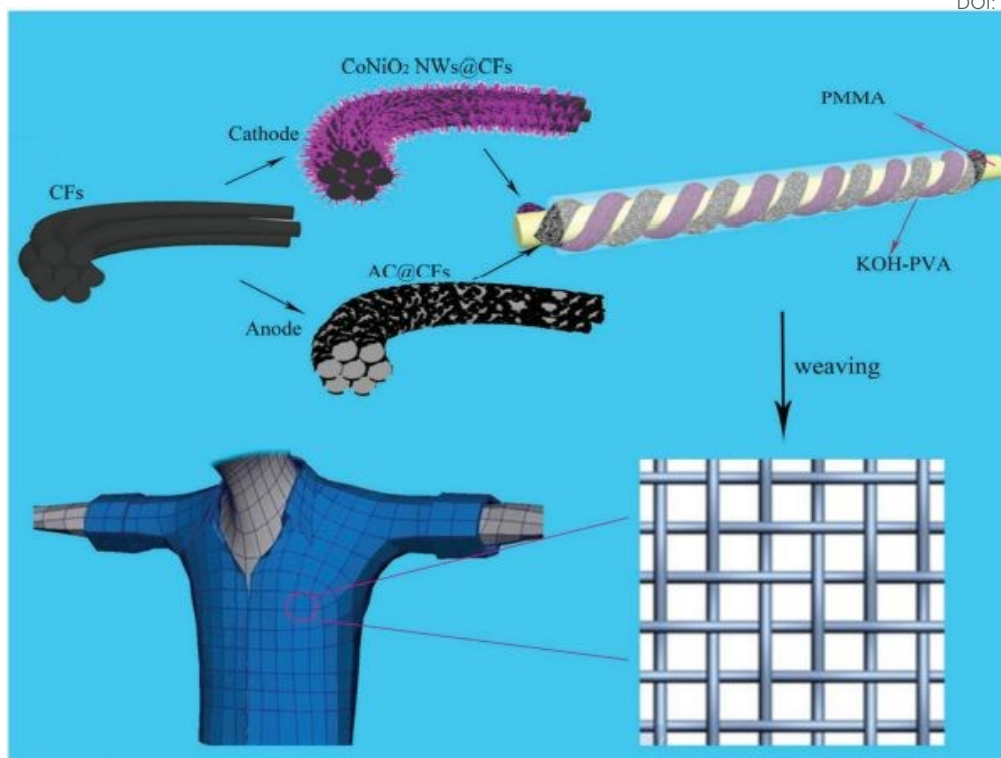
19 With the aid of a multi-step transformation procedure, Tong et al. [69] fabricated an elm-seed  
20 structured NiS<sub>2</sub> nanosheets on the surface of coal-based CF. Here, the silica/coal-based fiber is  
21 prepared by electrospinning a mixed solution consists of oxidized coal, polyvinyl alcohol and  
22 tetraethyl orthosilicate in water/N,N-dimethylformamide followed by carbonization. Due to the  
23 large surface area and novel structure, the as-prepared binder-free hybrid electrode for SC and  
24 this electrode exhibited a high value of specific capacitance of about 635.1 F/g at a current  
25 density of 1 A/g. Also, the SC electrode showed a capacitance retention of about 96.4% after  
26 5000 cycles. Ding et al. [70] fabricated a fiber electrode where acidified CF is modified by  
27 rGO/g-C<sub>3</sub>N<sub>4</sub>. The symmetric SC fabricated from this electrode exhibits an areal capacitance of  
28 61 mF/cm<sup>2</sup> with a capacitive retention of 90% after 5000 cycles. Using hydrothermal approach,  
29 Yu et al. [71] created a 3D nanostructure with combination of vertical polyaniline (PANI)  
30 nanowire array nitrogen plasma etched-carbon fiber cloth (eCFCs) in order to use it as an  
31 electrode for flexible SC. The flexible SC shows a higher specific capacitance of 1035 F/g at a  
32 current density of 1 A/g. It possesses an efficient capacitance retention of 88% even at a  
33 comparatively higher current density of 8 A/g with a long cyclic stability of 5000 cycles. The  
34 flexibility of assembled PANI/eCFC was evaluated at a fixed mechanical stress and its  
35 performance is evaluated. They observed that this assembled device has efficient flexibility  
36 and mechanical properties and it undergoes different bending angles. The proposed  
37 performance durability is relating to higher mechanical flexibility of electrode and it possess  
38 strong connection between nitrogen doped eCFC and PANI arrays, indicates their application  
39 in flexible electronics.

#### 41 4.4 Carbon Fibers-Based Wired Electrodes

42 Wired SCs have received tremendous hope in current era due to its rapid discharge capacity,  
43 flexibility, weavable structure, long cycle life and it can be easily be integrated with on-body  
44 wearable electronic devices. Ai et al. [72] fabricated a solid-state wired SC by using  
45 nanostructured CoNiO<sub>2</sub>@CF nanocomposite electrode and activated carbon@CF electrode  
46 having length greater than 1 m. A schematic representation of the fabrication of this asymmetric  
47 solid-state SC is given in **Figure 29**. Here, the anode and cathode fiber are twisted on a  
48 polymethylmethacrylate (PMMA) backbone using KOH-PVA gel electrolyte and PDMS layer  
49 as shell. The as-fabricated asymmetric SC exhibits efficient flexibility, wearability and  
50 toughness.





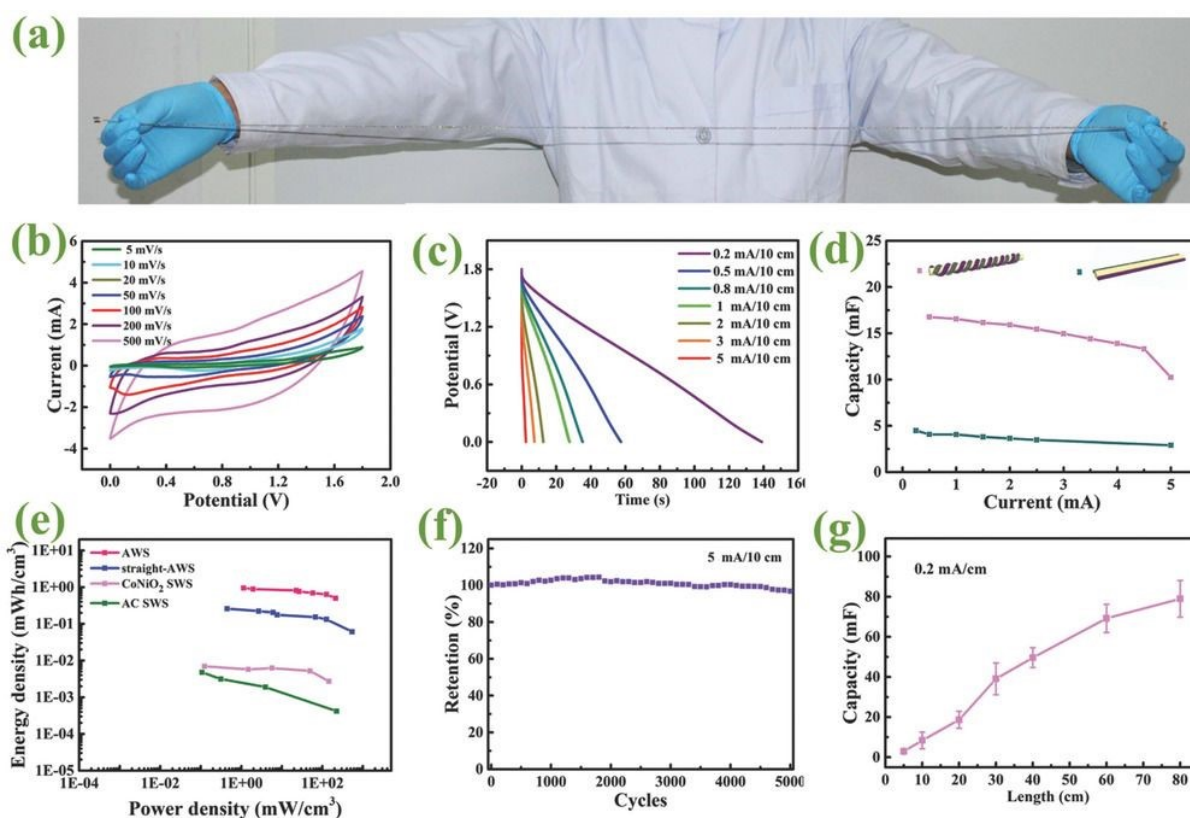


**Figure 29:** Pictorial representation of fabrication process of wired asymmetric SC. Reproduced with permission from [72] Copyright (2016) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The electrochemical characteristics of the asymmetric SC is analysed by taking a 10 nm length as given in **Figure 30a**. The CV measurements are carried out within a potential window 0 - 1.8 V and the CV curves (**Figure 30b**) obtained at different scan rates from 5 mV/s to 500 mV/s showed a quasi-rectangular nature. The discharge curves of the asymmetric SC within a potential window of 0 - 1.8 V is given in **Figure 30c**. The specific capacitances calculated from the discharge curves are 16.75, 16.55, 16.14, 15.91, 15.45, 14.95, 14.41, 13.89, 13.32, and 10.24 mF at different current densities such as 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mA, respectively (**Figure 30d**). The wire-shaped SC having an energy density of 0.95 mWh/cm<sup>3</sup> is obtained at a power density of 1.14 mW/cm<sup>3</sup> (**Figure 30e**) and the SC possesses a capacitance retention of about 97% after completing 5000 cycles (**Figure 30f**). The mean variation tendency for capacitance exhibited by the wired asymmetric SC is given in **Figure 30g**.



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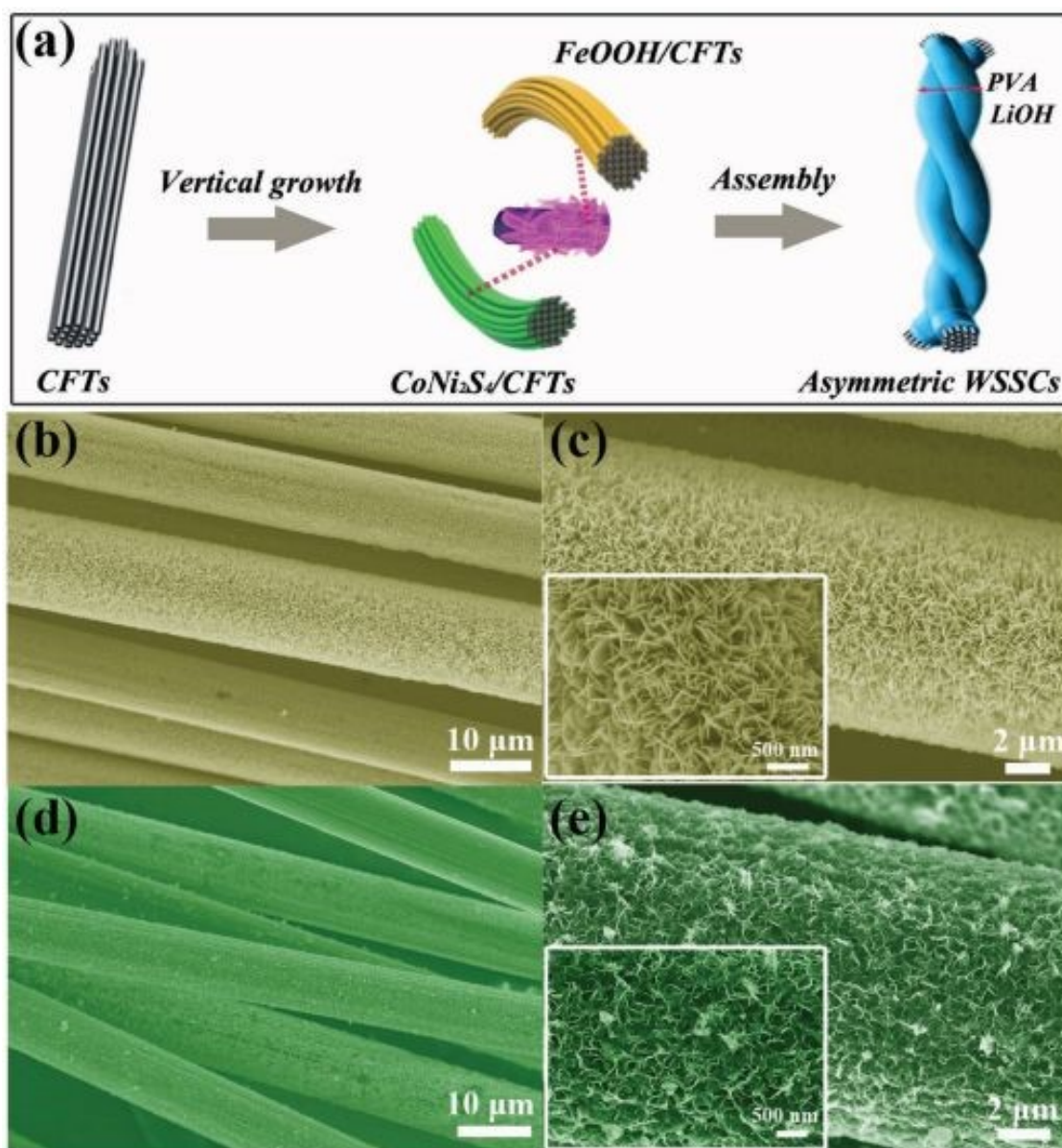
4 **Figure 30:** (a) Digital image of asymmetric wired SC with length 1.2 m; (b) CV and (c) GCD  
 5 curve of SC device; (d) capacitance comparison of spiral double-helix twisted asymmetric wire  
 6 supercapacitor with those of the straight twisted asymmetric wire supercapacitor; (e) Ragone  
 7 plot; (f) cyclic stability analysis; (g) change in capacitance of device with length condition  
 8 measured in similar condition. Reproduced with permission from [72] Copyright (2016)  
 9 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

10

11 Harvesting of wind power in association with SCs have received great attention due to their  
 12 sustainable energy conversion and storage features. The energy obtained from the wind  
 13 turbines can be easily be stored in a SC but a major requirement for the same is that the Sc  
 14 should exhibit high energy density. But the fabrication of a SC with high energy density and  
 15 reduced internal resistance is a tedious task. Shi et al. [73] developed a strategy to merge wind  
 16 driven generator (WDG) with an asymmetric wire-shaped SC (WSSC), where the WDG part  
 17 responsible for the conversion of energy and the asymmetric WSSC responsible for storing the  
 18 energy. Asymmetric WSSC was assembled using CoNi<sub>2</sub>S<sub>4</sub> nanosheets arrays and vertical  
 19 FeOOH coated to flexible CF tubes (CFTs) as a negative and positive yarn electrode,  
 20 respectively (**Figure 31a**). Here, the vertically aligned cross-linked porous network is  
 21 introduced by the electroactive nanosheet array is found suitable for diffusion of the ions as  
 22 well as transportation of charges. **Figure 31b** and **c** represents the FESEM images of  
 23 FeOOH/CFTs yarn electrode at different magnifications. Here, we can observe that the CFTs  
 24 are fully covered by the FeOOH (**Figure 31b**). In the case of high-magnification FESEM image  
 25 (**Figure 31c**), it can be seen that the vertically aligned FeOOH nanosheet with an average  
 26 thickness in the range of 20 nm is obtained. These nanosheets tend to be interconnecting to  
 27 each other without producing any agglomeration effect. In the case of CoNi<sub>2</sub>S<sub>4</sub>/CFTs yarn



1 electrode, a network architecture over CFT is introduced by a uniform construction of  $\text{CoNi}_2\text{S}_4$  New Article Online  
DOI: 10.1039/D4SU00146J  
2 nanosheet vertical arrays (**Figure 31d** and e).  
3



4  
5  
6 **Figure 31:** (a) Schematic diagram of an asymmetric WSSC. (b,c) FESEM images of  $\text{FeOOH}$ .  
7 (d,e) FESEM images of  $\text{CoNi}_2\text{S}_4$  vertical nanosheets grown over CF tubes. Reproduced with  
8 permission from [73] Copyright (2017) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.  
9

10 The electrochemical performances of as-fabricated SC for harvesting the wind energy were  
11 examined by consecutive experiments. The pictorial representation of an integrated system  
12 consists of miniaturized WDG, electronic regulator and two asymmetric WSSCs connected in  
13 series combination is depicted in **Figure 32a**. The output electric signal generated from the  
14 WDG is rectified by a regulator with 3 V output (**Figure 32b**) and there exist a conversion of  
15 alternating current to direct current of 600 mA, and the WSSC was charged steadily. Within 8  
16 s, the WSSC module is rapidly charged to 3 V. After completely charging WSSC module, it is  
17 discharged via a red LED is given in **Figure 32c**. This process is not only mentioning an  
18 effective method to harvest the wind power to charge the WSSC module but also indicating

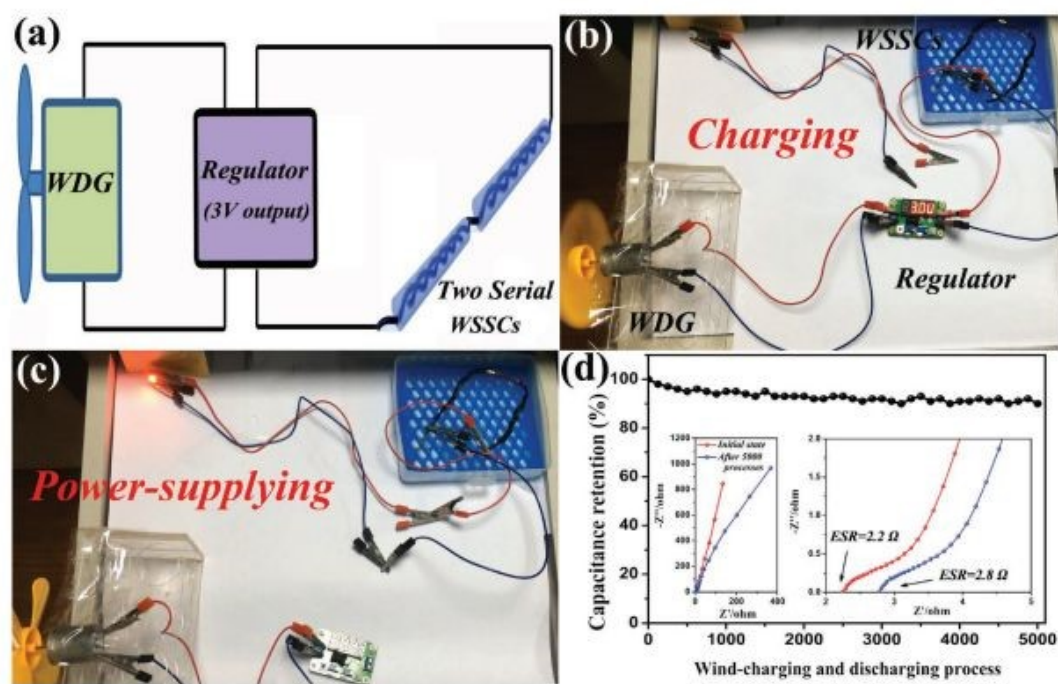




1 the fabrication of a WSSC with high energy density. After the completion of 5000  
 2 charging/discharging cycles, there is only a slight change in the capacitance observed, which  
 3 is clear from **Figure 32d**. After the cycling study, the electrochemical series resistance (ESR)  
 4 of the module is found to be increased slightly ( $2.8 \Omega$ ) whereas the ESR before the cycling was  
 5  $2.2 \Omega$  (inset of **Figure 32d**).

6 The preparation of a 3D nanoarchitecture over flexible current collector is a suitable  
 7 method for the fabrication of portable and wearable power source. Li et al. [74] developed a  
 8 flexible and efficient electrode with electrospun CF substrate possessing a hierarchical porous  
 9  $V_2O_5$  nanosheets by solvothermal method. The formation of a 3D network is clear from the  
 10 FESEM image given in **Figure 33a**. A cross-sectional view of the prepared electrospun CF  
 11 indicates that the substrate is holding a thickness of about  $87 \mu\text{m}$ , which is given as an inset  
 12 image in **Figure 33a**. An average diameter of around  $270 \text{ nm}$  is obtained for the electrospun  
 13 nanofiber and it possesses a smooth surface (**Figure 33b**). A uniform 1D hierarchical  
 14 architecture can be observed from the FESEM micrograph shown in the inset of **Figure 33c**.  
 15 From the enlarged view of this SEM image (**Figure 33c**), it is found that the 1D architecture is  
 16 composing of ultrathin sheet-like subunits which producing a uniform growth over the surface  
 17 of electrospun CF.

18



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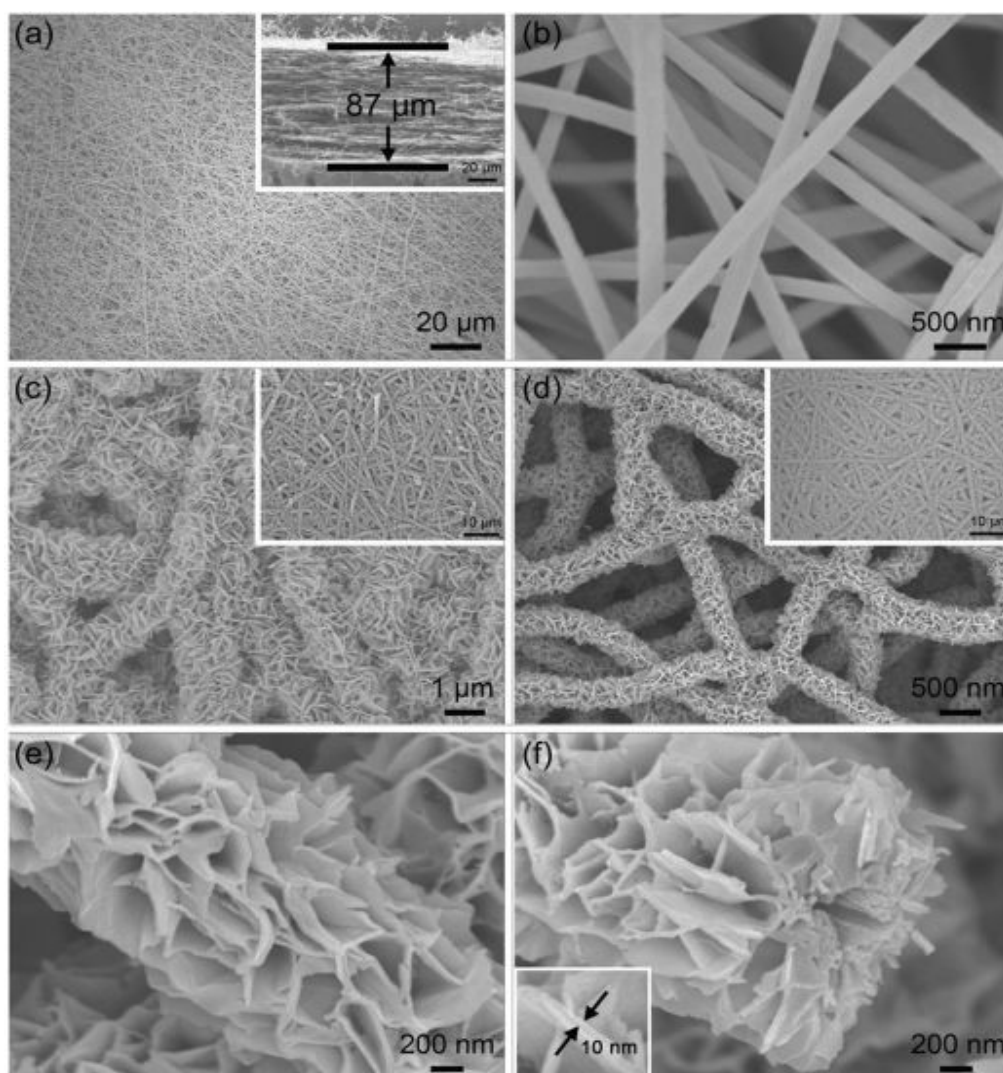
21 **Figure 32:** (a) A pictorial representation of the fabrication of wind-charging system, (b) real-  
 22 time picture of charging process in WSSCs by the harvesting of wind energy, (c) digital  
 23 photograph of lighting of red lamp with WSSCs after completely charging, (d) retention of  
 24 capacitance after wind-charging and discharging procedures. Inset representing the Nyquist  
 25 plot of device before and after 5000 cycles. Reproduced with permission from [73] Copyright  
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27

28 After a low temperature annealing in air, the V-O precursor is fully converted to a  $V_2O_5$   
 29 crystalline nanosheets. The CF is found to impart a robust support. The morphology of as-  
 30 prepared  $V_2O_5$  architecture is still maintained after the annealing procedure (**Figure 33d**). The  
 31 magnified images of  $V_2O_5$  architecture provided in **Figure 33e,f** shows a perpendicularly cross-  
 32 linked  $V_2O_5$  with porous structure, which exhibited a sheet-like morphology. It consists of an



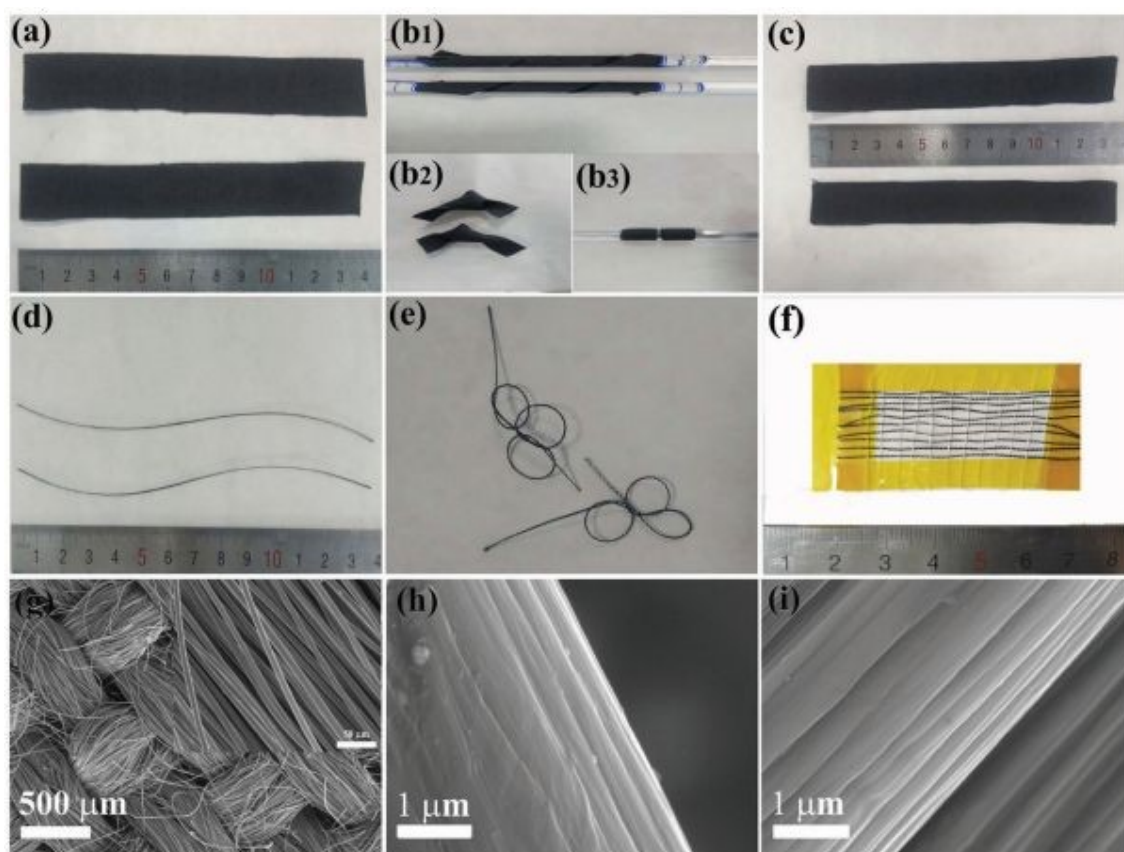
1 open space between the individual nanosheets, which helps in an easy penetration of  
 2 electrolyte-ions and hence it produces an efficient electrochemical performance while using it  
 3 as an electrode-active material in a SC. An asymmetric hybrid supercapacitor device is  
 4 assembled by using  $V_2O_5$ -electrospun CF as anode and electrospun freestanding CF as cathode.  
 5 The assembled hybrid SC hold an excellent cyclic stability of 10000 cycles with a decay of  
 6 10.7% capacitance after completing the cycling study. The SC possesses an excellent energy  
 7 density of 22.3 Wh/kg at a corresponding power density of 1500 W/kg and efficient mechanical  
 8 flexibility. The flexibility of SC was evaluated by bending it at different bending angles and  
 9 possessed excellent mechanical stability during the testing. The electrochemical characteristics  
 10 of this SC is maintained even after bending it for 200 times, which demonstrates prominent  
 11 mechanical robustness for practical applications. This study portraits an effective fabrication  
 12 of hybrid electrodes for flexible SCs.



14  
 15  
 16 **Figure 33:** FESEM image of (a,b) electrospun CF substrate in different magnifications (inset  
 17 image a) cross-sectional view of ECF)), (c) V-O precursor nanosheet array with inset as its  
 18 large areal view (d-f) crystallized  $V_2O_5$  in various magnification , inset of d) showing the large  
 19 areal view and inset of, (f) showing the nanosheet with magnified structure. Reproduced with  
 20 permission from [74] Copyright (2015) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



1 Textile energy storage systems utilizing the features of wearable electronics is rapidly growing  
 2 but the development of CF electrode with better capacitance to generate a higher energy density  
 3 and power density is still remains a challenge. Qin et al. [75] fabricated a carbon cloth (CC)  
 4 enriched by nitrogen/oxygen (N/O) possess a large surface area and accurate pore volume by  
 5 electrochemical oxidation approach. The CC electrochemically treated for a duration of 3  
 6 minutes (3-CC), pristine CMF bundles and electrochemically-treated CF bundles (3-CMF)  
 7 possess good mechanical strength and flexibility through the deformation test. The CC and 3-  
 8 CC did not undergo any breakage when it was wounded on a glass rod with a diameter of ~6  
 9 mm and unfolded it afterwards. The CC and 3-CC is found to withstand its original structure  
 10 (**Figure 34a-c**). The bare CF bundle and electrochemically-treated CF bundle was able to fold  
 11 onto a logo surface (**Figure 34d,e**) and it was weaved into a cloth with area ~1-5 cm<sup>2</sup> using  
 12 cotton threads (**Figure 34f**). The CMF bundle holding crossed warp and weft composed  
 13 possessed a diameter of ~400  $\mu\text{m}$  and it can be observed from the SEM image (**Figure 34g**).  
 14 After completing the oxidation procedure, the grooves over the surface and embossments are  
 15 found to be deeper and clear in comparison with the bare one (**Figure 34h,i**).  
 16



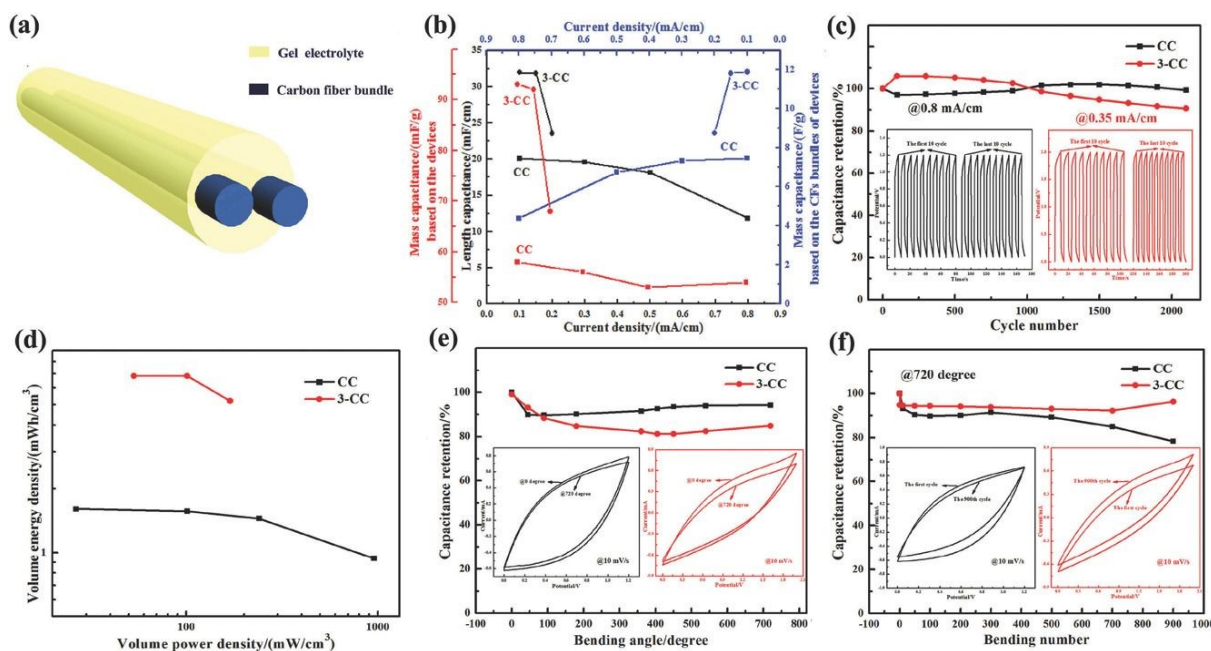
17  
 18  
 19 **Figure 34:** Morphological study of CF, CC and and 3-CC. (a) Optical images of CC (up) and  
 20 3-CC (down) before shape changing, b1, b3) wounded on glass rod, b2) kinked, (c) after shape  
 21 changing; (d) bundles of pristine CF (up) and CF with electrochemical treatment (down), (e  
 22 kinked; (f) weaved with white cotton threads; (g) SEM images of CC (the inset: its high  
 23 magnification image) and (h) of pristine CF fiber at high magnification and (i) with  
 24 electrochemical treatment. Reproduced with permission from [75] Copyright (2017) WILEY-  
 25 VCH Verlag GmbH & Co. KGaA, Weinheim.

26  
 27 The CC and 3-CC electrode-based fiber-shaped and fabric-based SCs were fabricated as shown  
 28 in **Figure 35a**. The fiber-shaped SC exhibited a higher capacitance of 32 mF/cm<sup>2</sup> than a SC





1 fabricated with CC (20 mF/cm) (**Figure 35b**). The cyclic stability analysis using GCD  
 2 measurement is given in **Figure 35c** from which it can be seen that the SC based on CC and 3-  
 3 CC electrodes exhibited a capacitance retention of 99% and 90%, respectively. These results  
 4 show that the SCs exhibit excellent cycling stability. The volumetric energy density of the SC  
 5 fabricated with 3-CC electrode is about 6.8 mWh/cm<sup>3</sup>, which is found to be greater than the  
 6 SC fabricated with CC electrode ( $\approx 1.6$  mWh/cm<sup>3</sup>), as given in **Figure 35d**. The SCs  
 7 maintained their capacitance while bending it to different bending angles, which indicates its  
 8 better stability for their implementation in wearable textile devices. The fiber-shaped SCs  
 9 fabricated with both 3-CC and CC electrodes retained its efficient electrochemical properties  
 10 while bending it for different cycle numbers, indicates the good flexibility. As an example,  
 11 about 94% and 85% capacitance value is maintained during bending of the SC fabricated with  
 12 CC and 3-CC electrodes, respectively (**Figure 35e**). In addition to this, there exists a  
 13 maintenance of capacitance hold by the SC fabricated with 3-CC electrode to  $\sim 97\%$  even after  
 14 completing 900 cycles kept at 720°, which is found to be higher than that of the SC fabricated  
 15 with CC electrode (about 79%), as shown in **Figure 35f**. These hierarchical nanostructured  
 16 electrodes contain large number of active-sites, which helps in enhancing the capacitance of  
 17 SCs.



19

20

21 **Figure 35:** Electrochemical analysis of two-fiber shaped SC with CC and 3-CC bundles (a)  
 22 schematic of fiber shaped SC; (b) rate calculation based upon GCD with various current  
 23 density; (c) cyclic stability; (d) ragone plot. Retention of capacitance with (e) bending in 0° and  
 24 720° (inset corresponds to CV before and after bending), (f) stability in bending at 720° (inset  
 25 representing the CV before and after bending). Reproduced with permission from [75]  
 26 Copyright (2017) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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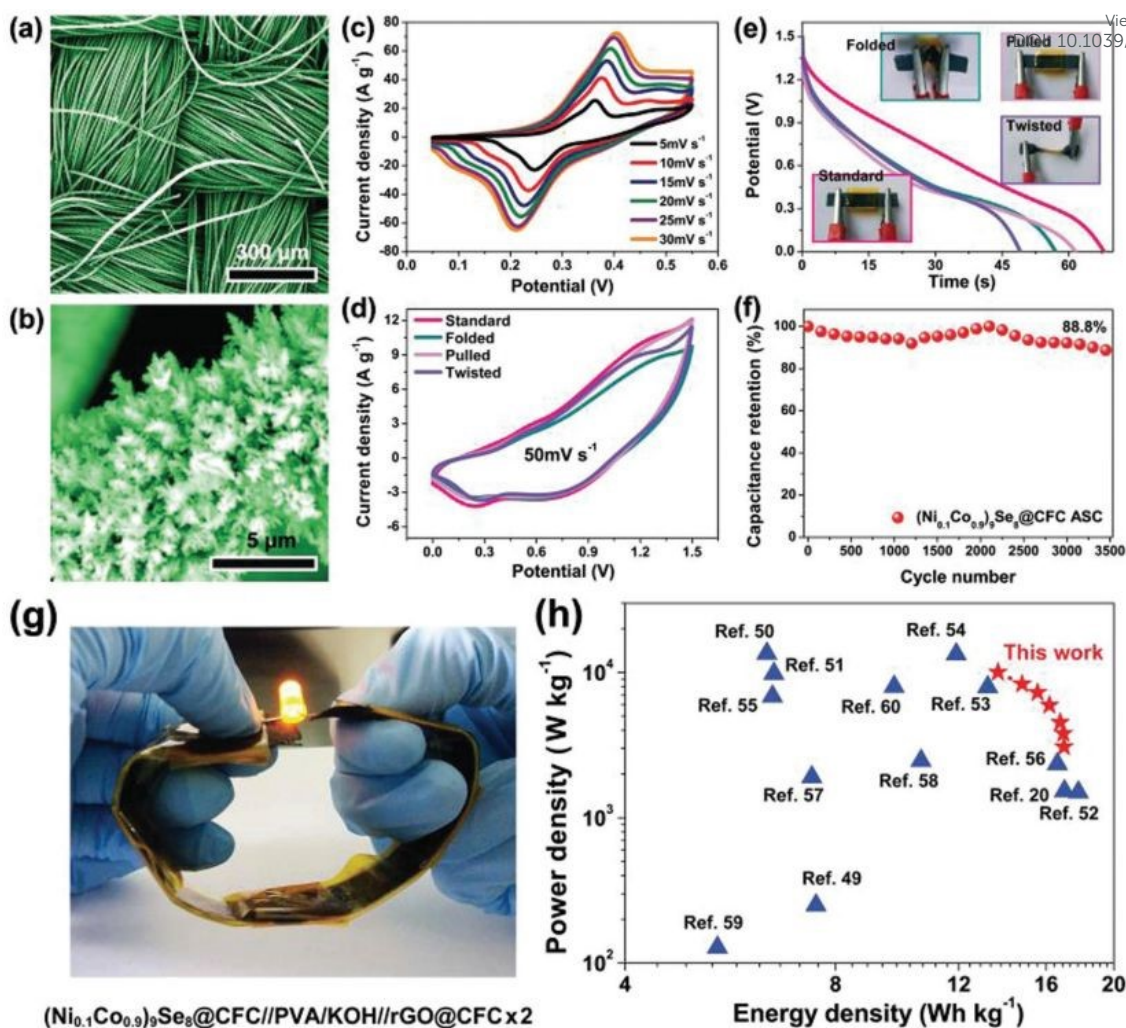
#### 28 4.5 Carbon Fibers-Based Hybrid Electrodes

29 Using in-situ growth method, Yang et al. [33] prepared (Ni<sub>x</sub>Co<sub>1-x</sub>)<sub>9</sub>Se<sub>8</sub> solid solution series on  
 30 CFC substrate. The (Ni<sub>0.1</sub>Co<sub>0.9</sub>)<sub>9</sub>Se<sub>8</sub> nanodendrite arrays were found to exhibit a dense growth  
 31 over the CFC substrate. Before initiating the growth, there exists a pre-treatment for the CFC



1 substrate by soaking it on nitric acid and sulfuric acid mixture to introduce a non-uniform  
2 surface, which is favourable for its growth. The SEM images given in **Figure 36a** and **b** show  
3 the surface morphology of the hierarchical 3D nano-dendrite arrays grown over the CFC  
4 substrate. The CV analysis of the SC electrode is performed in a three-electrode cell  
5 configuration at different scan rates such as 5, 10, 15, 20, 25, and 30 mV/s and the resultant  
6 CV curves are depicted in **Figure 36c**. The CV curve of the system is working in a potential  
7 window of 0.05-0.55 V and at a current density of 5 A/g it delivers a specific capacitance of  
8 about 591.1 F/g. The as-fabricated SC electrode can be stranded, folded, pulled, and twisted  
9 and the CV curves obtained in each state at a constant scan rate of 50 mV/s is shown in **Figure**  
10 **36d**. The CV curves are found to be identical in each procedure, which shows excellent  
11 flexibility. In the case of assembled device, the GCD measurements were repeated at these  
12 states (such as stranded, folded, pulled, and twisted) and the resultant discharge curves are  
13 depicted in **Figure 36e** and it can be seen that the discharge curves exhibited a deviation in  
14 various states. The asymmetric SC retained a capacitance retention of 88.8% after 3500 cycles  
15 (**Figure 36f**). An asymmetric SC was fabricated in a  
16  $(\text{Ni}_{0.1}\text{Co}_{0.9})_9\text{Se}_8@\text{CFC}/\text{PVA}/\text{KOH}/\text{GO}@\text{CFC}$  fashion and two such SCs are connected in  
17 series lighted-up an LED is given in **Figure 36g**. The asymmetric SC exhibited an energy  
18 density of 17 Wh/kg at a corresponding power density of 3.1 kW/kg and 13.7 Wh/kg at a  
19 corresponding power density of 10 kW/kg (**Figure 36h**) and these performance metrics shows  
20 that this asymmetric SC is capable to meet the growing demand in wearable electronics. Jost  
21 et al. [76] developed a textile SC with knitted-CF and activated carbon ink. This textile SC  
22 exhibited a specific capacitance of 0.51 F/cm<sup>2</sup> at a scan rate of 10 mV/s. The electrochemical  
23 performance of this textile SC is comparable with the standard activated-CF electrode in similar  
24 conditions with good flexibility.  
25





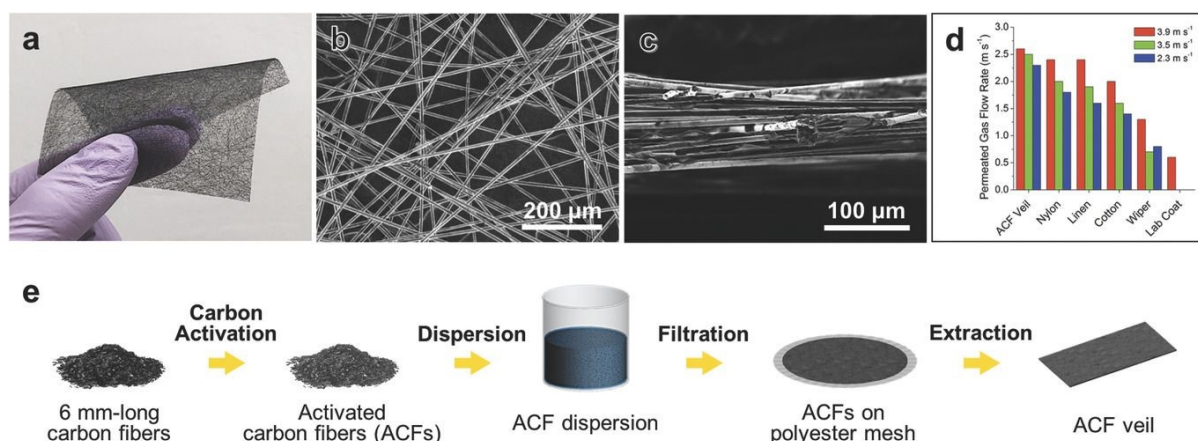
**Figure 36:** (a, b) SEM image of  $(\text{Ni}_{0.1}\text{Co}_{0.9})_9\text{Se}_8$  nanodendrite array grown over CFC; (c) CV and; (d) CV curve for a scan rate of 5  $\text{mV s}^{-1}$ ; (e) GCD curve at 1  $\text{A/g}$  of the asymmetric flexible SC in various bending conditions; (f) capacitance retention curve; (g) LED indicator lighted by two  $(\text{Ni}_{0.1}\text{Co}_{0.9})_9\text{Se}_8$ @CFC//PVA/KOH//rGO@CFC asymmetric supercapacitors connected in series (h) Ragone plot in comparison with other reports of nickel-cobalt sulfides and selenides. Reproduced with permission from [33] Copyright (2018) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

By employing ammonia activation and direct procedure of carbonization, Zhan et al. [77] synthesized blow spun activated CF and further used it as an electrode-active material to fabricate a flexible asymmetric hybrid SC. The salient features of this electrode such as highly conducting network, availability of doping with nitrogen, controlled pore structure and surface properties, helped in achieving good electrochemical performance. The asymmetric SC exhibited a high energy of 98  $\text{Wh/kg}$  and 9  $\text{Wh/kg}$  at a corresponding power density of 400  $\text{W/kg}$  and 34  $\text{kW/kg}$ , respectively. With the application of dipping-drying method, Zhang et al. [78] introduced CNT/ $\text{MnO}_2$  onto activated CF felt substrate. The fabricated flexible SC exhibited an area specific capacitance of 4148  $\text{mF/cm}^2$  with an energy density of 141  $\mu\text{Wh/cm}^2$  at a corresponding power density of 4466  $\mu\text{Wh/cm}^2$ . The flexibility of this SC was evaluated while bending it for 100 cycles, indicating its high flexibility. Zhou et al. [79] proposed an effective strategy to develop molten- $\text{NaNH}_2$  activated CF cloth for the fabrication of a flexible asymmetric SC. Here, a commercially available CF cloth is oxidized with the aid of wet-





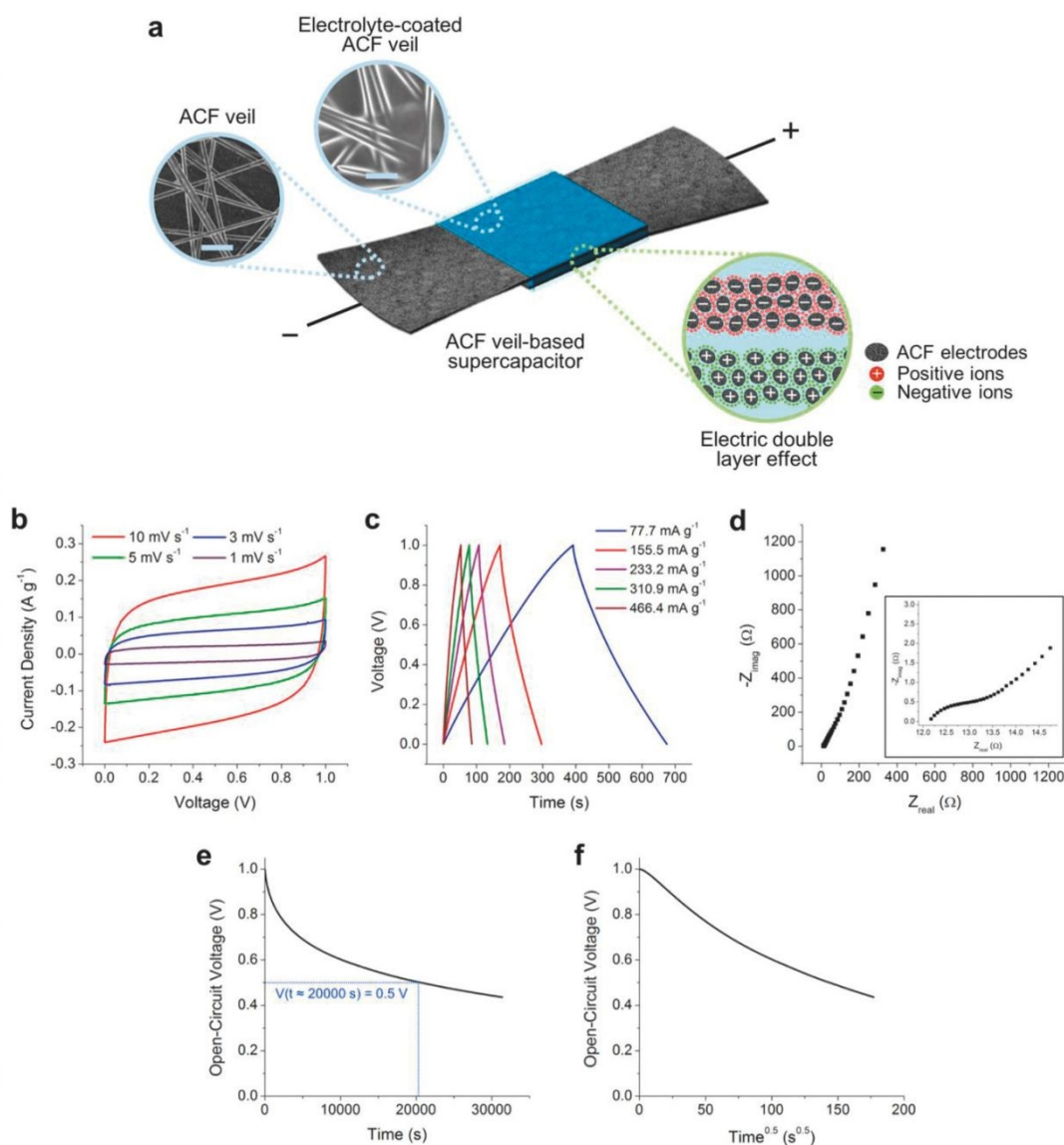
1 chemical approach and activated with molten- $\text{NaNH}_2$ . The as-prepared electrode-active  
 2 material holds many features such as efficient wettability, large surface area, good conductivity  
 3 and high mechanical strength. The SC electrode delivered a high area specific capacitance of  
 4  $744.5 \text{ mF/cm}^2$  at a current density of  $1 \text{ mA/cm}^2$  with a capacitive retention of 96.94% in 6 M  
 5 KOH after 10000 cycles. In another report, a flexible solid-state SC was fabricated using a free-  
 6 standing and porous nanohybrid aerogel containing carbon nanosphere fiber  
 7 (CNPf)/molybdenum disulfide ( $\text{MoS}_2$ )/rGO as electrodes and  $\text{H}_2\text{SO}_4$ /PVA gel electrolyte [80].  
 8 The CNPF/ $\text{MoS}_2$ /rGO SC electrode exhibited a specific capacitance of  $1144.3 \text{ F/g}$  at a scan  
 9 rate of  $2 \text{ mV/s}$ . A capacitance retention of 98% was obtained even after completing 10000  
 10 cycles at current density of  $5 \text{ mA/cm}^2$ . The CNPF/ $\text{MoS}_2$ /rGO SC electrode delivered an energy  
 11 density of  $57.5 \text{ } \mu\text{Wh/cm}^2$  at a corresponding power density of  $28.8 \text{ Wh/kg}$  along with good  
 12 bendability. Wei et al. [81] fabricated a hybrid Zn-ion SC using polypyrrole/p-  
 13 phenylenediamine/CF electrode. The as-fabricated hybrid SC delivered a large specific  
 14 capacity of about  $47.6 \text{ mAh/g}$  at a current density of  $0.2 \text{ A/g}$  and found to maintain a  
 15 capacitance of 85.4% immediately after 1000 cycles and 78.5% after completing 5000 cycles.  
 16 A coaxial fiber-type electrode was fabricated by Xu et al. [82] by wrapping carbon paper over  
 17 a  $\text{MnO}_2$ -modified nanoporous gold wire. The fabricated SC exhibited an area specific  
 18 capacitance of  $12 \text{ mF/cm}^2$  and an energy density of  $5.4 \text{ } \mu\text{Wh/cm}^2$  with a long cyclic stability.  
 19 With the aid of an in-situ growth for conductive wrapping mapproach, Tao et al. [83] fabricated  
 20 a polypyrrole/ $\text{MnO}_2$ /CF-based hybrid electrode. A SC fabricated with this hybrid electrode  
 21 structure exhibited a volume specific capacitance of  $69.3 \text{ F/cm}^3$  at a current density of  
 22  $0.1 \text{ A/cm}^3$ . Also, this SC delivered an energy density of  $6.16 \times 10^3 \text{ Wh/cm}^3$  at a corresponding  
 23 power density of  $0.04 \text{ W/cm}^3$ . In order to introduce an efficient durability and longer cycle life,  
 24 Shin et al. [84] fabricated a veil-based flexible SC electrode by using activated-CF (ACF). An  
 25 optical image of ACF veil is given as **Figure 37a** and it comprising of a porous network  
 26 structure of non-uniformly distributed ACF holding a thickness in the range of  $100 \text{ } \mu\text{m}$  (**Figure**  
 27 **37b** and **c**). The permeability of this electrode was examined and found that the permeability  
 28 of ACF veil electrode is almost the same to that of linen, cotton and nylon (**Figure 37d**)  
 29 represents its potential in wearable textile application. The synthesis procedure of ACF veil SC  
 30 electrode fabrication involve various steps including activation of carbon, dispersion, filtration  
 31 and extraction, as shown in **Figure 37e**.



33 **Figure 37:** (a) Optical image of ACF veil. SEM images, (b) top view, (c) side view, (d)  
 34 permeability of air in the network; (e) synthesis process of ACF veil. Reproduced with  
 35 permission from [84] Copyright (2018) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.  
 36  
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 38



1 The electrochemical performance evaluation of the ACF veil SC electrode is conducted in a  
 2 two-electrode cell configuration using PVA/H<sub>3</sub>PO<sub>4</sub> gel electrolyte, as shown in **Figure 38a**.  
 3 The CV (**Figure 38b**) and GCD (**Figure 38c**) measurements were also performed at different  
 4 scan rates such as 1, 3, 5, and 10 mV/s and at different current densities ranging from 77.7 to  
 5 466.4 mA/g, respectively, within a potential window of 1 V. The rectangular CV curves and  
 6 triangular GCD curves proved that the charge storage is by means of EDL formation. The  
 7 Nyquist plot obtained for the SC is depicted in **Figure 38d** from which it can be seen that at a  
 8 higher frequency region, a diffuse resistance is generated due to a slower ion diffusion. A rapid  
 9 reduction in open circuit voltage can also be observed in the prepared SC, where a 50% of  
 10 energy is conserved after a charging of 5.5 h (**Figure 38e**). The observed potential drop is  
 11 proportional to the square root of time (**Figure 38f**), which indicates the diffusion-controlled  
 12 ion concentration variation is prominent mechanism of self-discharge. In another study, Pan et  
 13 al. [85] reported the preparation of a flexible textile SC electrode based on CNT/PANI fiber  
 14 composite, which delivered a specific capacitance of 272.7 F/g. This composite electrode was  
 15 further integrated to generate an energy textile, it makes a conversion of solar energy toward  
 16 electrical energy other than storing and producing a photoelectric conversion and storage  
 17 efficiency of 2.1%.



19  
20



1 **Figure 38:** (a) Schematic representation of veil-based SC; (b) CV; (c) GCD; (d) Nyquist plot. View Article Online  
 2 Inset represents the high frequency region (e) reduction of OCV with time; (f) OCV with square  
 3 root of time. Reproduced with permission from [84] Copyright (2018). WILEY-VCH Verlag  
 4 GmbH & Co. KGaA, Weinheim. DOI: 10.1039/D4SU00146J








5  
 6 From the above discussion, it can be seen that CF can be used both as a substrate for  
 7 SC electrode as well as an electrode-active material to fabricate a SC. The prominent features  
 8 of CF such as flexibility and electrochemical stability, it can be considered as a suitable material  
 9 for the fabrication of flexible and wearable SC along with other electrode-active materials.  
 10 **Table 1** provides the salient features of CF-based SC reported in the literature.

11  
 12 **Table 1:** Salient features of CF-based SCs in the literature.

Sl. No.	Electrode Material	Synthesis Method	Major Observations	Ref.
1.	Coaxial MnO <sub>2</sub> -CNF cable mat	Electrodeposition	✚ Coin cell symmetric SC gives a specific capacitance of 47 F/g at 0.5 A/g in a potential window of 0 to 1.6V	[86]
2.	MnO <sub>2</sub> /CF hybrid fiber	Electrochemical deposition	✚ Solid state device shows a volumetric energy density 3.8 mWh/cm <sup>3</sup> at a power density 89 mW/cm <sup>3</sup> ✚ It possesses an efficient flexibility 85.8% capacitance retention after 10000 cycles	[87]
3.	Meso-macroporous nano-CF	Electrospun method	✚ Symmetric device with NCF having 138 F/g at 5 mV/s and 98 F/g at 100 mV/s	[88]
4.	Free-standing porous coaxial carbon nanofiber	Coaxial electrospinning and template method	✚ Energy density of 48.6±3 Wh/kg and power density 67.5±1 Wh/kg in a two-electrode system	[89]
5.	Polypyrrole-doped with dodecyl benzene sulfonate	Electrochemical deposition	✚ Energy density and power density of 1.20 mWh/cm <sup>3</sup> and 0.59 W/cm <sup>3</sup> at a discharge current density of 1.50 A/cm <sup>3</sup> using LiCl/PVA electrolyte	[90]
6.	Ni-Co selenide on CF paper	Selenization approach	✚ Symmetric SC device possesses volumetric capacitance of 14.55 F/cm <sup>3</sup> at 1 mA/cm <sup>2</sup> and 0.47 mWh/cm <sup>3</sup>	[91]













			volumetric energy density at 10 mA/cm <sup>2</sup>	View Article Online DOI: 10.1039/D4SU00146J
7.	CNT fiber/3D porous CNTs/PANI	Electrophoretic deposition and electrochemical polymerization	 Specific capacitance of 67.31 mF/cm <sup>2</sup> at 0.5 mA/cm <sup>2</sup> and it maintains a capacitance of 99.8% even bending it to 180° for 500 cycles	[92]
8.	MnO <sub>2</sub> with cotton derived carbon cloth	Pyrolysis treatment	 Area specific capacitance of 202 mF/cm <sup>2</sup> with area specific energy density 30.1 μWh/cm <sup>2</sup> at a power density of 0.15 mW/cm <sup>2</sup> . It shows a capacitance retention of 87.7% after 5000 cycles	[93]
9.	NiCo <sub>2</sub> O <sub>4</sub> @MnO <sub>2</sub> core shell	Hydrothermal deposition method	 Area specific capacitance of 1.55 F/cm <sup>2</sup> at 2 mA/cm <sup>2</sup> with higher energy density of 1.983 mWh/cm <sup>2</sup> at a power density of 1.72 mW/cm <sup>2</sup> having good stability over 8000 cycles at 50 mA/cm <sup>2</sup> current density	[94]
10.	NiCo layered double hydroxide	In-situ growth with substitution	 Flexible device holds a specific capacity of 1377 mC/cm <sup>2</sup> at 1 mA/cm <sup>2</sup> with 70% capacitance retention and 99% coulombic efficiency over 10000 cycles	[95]
11.	Hollow N-doped CF embedded with graphene nanosheet	Coaxial electrospinning and thermal treatment	 In a three-electrode system it delivers a specific capacitance of 249 F/g at 1 A/g with capacitance retention of 99% over 5000 cycles in a two-electrode arrangement	[96]
12.	BN co-doped CNTs grown over the surface of CF around carbon cloth	Single step pyrolysis based thermal chemical vapour deposition	 It delivers a volumetric capacitance of 21.4 F/cm <sup>3</sup> with 741.8 mWh/cm <sup>3</sup> energy density and 1 kW/cm <sup>3</sup> power density	[97]
13.	3D nanocomposite of CNTs-carbonized cotton fiber-PANI	Single step chemical vapour deposition	 Area specific capacitance of 3.1 F/cm <sup>2</sup> at 2 mA/cm <sup>2</sup> current density with a	[98]



				View Article Online DOI: 10.1039/D4SU00146J
			cyclic stability of 91% after 2000 cycles	
14.	CuCo <sub>2</sub> O <sub>4</sub> @Ni(OH) <sub>2</sub> /CFC	Simple step procedure	Asymmetric SC device gives a higher energy density 58.9 Wh/kg at a power density of 400 W/kg	[99]
15.	Ni <sub>3</sub> S <sub>2</sub> /polyaniline on CF	Electrodeposition and in-situ polymerization	Flexible asymmetric SC gives an energy density of 35.7 Wh/kg at a power density of 850 W/kg	[100]
16.	NiCo <sub>2</sub> S <sub>4</sub> nanotube grown over CF	Hydrothermal method	Asymmetric device gives energy density of 24.78 Wh/kg at a power density of 1770.13 W/kg	[101]
17.	NiCo <sub>2</sub> O <sub>4</sub> decorated PAN/lignin-based CF	Electrospinning, stabilization, carbonization followed by hydrothermal method	Asymmetric SC device gives a specific capacitance of 134.3 F/g at 1 A/g current density with an energy density of 47.75 Wh/kg at a power density of 799.53 W/kg	[102]
18.	Ni <sub>0.4</sub> Co <sub>0.6</sub> (OH) <sub>2</sub> grown over CF	Hydrothermal method	Symmetric solid-state SC delivers a specific capacitance of 1816 F/g at 1 A/g with a capacitance retention of 98.3% after 5000 cycles	[103]
19.	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> MXene/CF	Electrospinning of PAN	Gravimetric capacitance of 120 F/g at 2 mV/s with 98% capacitance retention after 10000 cycles	[104]
20.	Crystalline tetraaniline nanofiber deposited over oxidized CFC	Solution based self-assembly approach	Device delivers a capacitance retention of 99.97% after 10000 cycles in H <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> SO <sub>4</sub> /PVA electrolyte	[105]
21.	V <sub>2</sub> O <sub>5</sub> nanosheet assembled over 3D CF	Hydrothermal method	Freestanding asymmetric SC gives energy density of 0.928 mWh/cm <sup>3</sup> at 17.5 mW/cm <sup>3</sup> power density with a capacitance retention of 89.7% after 2000 cycles	[106]
22.	FeNiP@CoNi-LDH grown over carbon cloth	Hydrothermal and phosphorization treatment	Aqueous symmetric SC gives an energy density of 87.3 Wh/kg at power	[107]



			density of 408.8 W/kg with capacitance retention of 73.9% after 20000 cycles	View Article Online DOI: 10.1039/D4SU00146J
23.	2D 1T-MoS <sub>2</sub> /1D Cu(OH) <sub>2</sub> over CF paper	In-situ growth	 It exhibits an energy density of 0.13 mWh/cm <sup>2</sup> at a power density of 0.375 mW/cm <sup>2</sup> . The device holds 90.8% capacitance retention after 20000 cycles	[108]
24.	Polypyrrole@CF yarn electrode	Electrosynthesis	 It delivers a specific capacitance of 50.08 F/cm <sup>3</sup> with an energy density of 4.45 mWh/cm <sup>3</sup> and it maintains a capacitance retention of 89% after 5000 bending cycles	[109]
25.	Polyaniline/manganese hexacyanoferrate	Electrochemical co-polymerization method	 Specific capacitance of 730 F/g at 1 A/g current density with a capacitance retention of 85% after 1000 cycles	[110]
26.	Carbon nanofibers@polypyrrole@graphene film	Electrochemical deposition	 Specific capacitance of 336.2 F/g at 2 mV/s with capacitance retention of 98% after 2500 cycles	[111]
27.	Ultrathick CNT fiber	Sonochemical process	 Volumetric capacitance of 523.3 F/cm <sup>3</sup> with a flexibility of 98.4% at a bending angle 90°	[112]
28.	CF surface-grown over helical CNTs and polyaniline	Catalytic CVD and in-situ polymerization	 Specific capacitance of 439 F/g at 0.05A/g current density and capacitance retention of 95.4% over 500 cycles	[113]
29.	Micro-nano integrated core sheath CF electrode	Space confined hydrothermal method	 Volumetric capacitance of 27 F/cm <sup>3</sup> with energy density of 3.75 mWh/cm <sup>3</sup> and a power density of 612 mW/cm <sup>3</sup>	[114]
30.	MnO <sub>2</sub> nanograsses on porous CFC	Simple wet-chemical method	 Delivers an energy density of 841 μWh/cm <sup>2</sup> with a capacitance retention of 96% after 20000 cycles	[115]

1

2 **5. Future Perspectives**



1 CF-based flexible SCs are futuristic devices for widespread wearable electronic applications.  
2 The utilization of CF as a flexible substrate to a wearable SC is a facile way to use it for on-  
3 body applications. But one of the major demerits underlying with the use of CF in SC  
4 fabrication is depends upon its precursor hence the purity. Although CF is highly flexible at its  
5 virgin state, during various treatment processes, there is a high chance to reduce its flexibility,  
6 structural pattern, etc., thus it is very compulsory to optimize the experimental parameters  
7 before using it. Another parameter which depends upon the CF performance is the synthesis  
8 method adopted. An optimized concentration of precursor materials is necessary for the  
9 introduction of CF with a porous morphology to establish high performance in SC fabrication.  
10 The synthesis of CF in a low-cost approach is mandatory, such as synthesis from a biomass  
11 derived material where only a small number of reports based on synthesis of CF from biomass  
12 materials can be seen from the literature. The derivation of CF from biomass ingredients opens-  
13 up a facile pathway for its environment-friendly route. A widespread study on suitable  
14 biomaterial that are favourable to synthesis CF may open-up a facile and cost-effective  
15 approach to its large-scale synthesis. A long-term stability of CF-based electrode is a major  
16 criterion which depicts their durability in application. There exists a probability in reduction of  
17 stability hold by CNF due to restacking and other structural distortions, which hurdle their  
18 performance in long-run functioning. Another demerit of CNF is the less eco-friendly nature  
19 of synthesis hence the synthesis of CNF from less toxic materials is appreciated in the future,  
20 such as synthesis from biomass-based materials. By considering these features, CF can be used  
21 as a potential electrode candidate in the futuristic wearable supercapacitors with high flexibility  
22 and long cyclic stability.  
23

## 24 6. Summary

25 CF is considered a promising sustainable material for a variety of applications due to their high  
26 flexibility, ease in synthesis, good mechanical strength, etc. to name a few. In this review, we  
27 described the salient features of CF in order to use it in the preparation of SC electrodes. The  
28 various synthesis methods of CF were discussed by emphasizing the microstructure and surface  
29 morphology of the CF. The various precursors used for the CF synthesis was explained with  
30 uniqueness in obtaining a particular morphology. Further, the application of CF in flexible SC  
31 application was explained in detail with the help of literature data. Various synthetic methods  
32 such as drop-casting or spin-coating approaches were opted for the synthesis of flexible  
33 electrodes. The capability of CF-based SC for their easy integration with flexible and wearable  
34 electronic devices was examined with the help of various electrochemical analysis tools such  
35 as CV and GCD measurements performed at various bending angles and at different states such  
36 as folded, pulled, twisted, stranded, etc. We discussed the recent developments on the CF-based  
37 electrode-active materials for wearable SCs. CF-based electrode materials enabled excellent  
38 flexibility and electrochemical performance to the fabricated flexible SCs including symmetric  
39 and asymmetric SCs. The various synthetic approaches to prepare flexible electrodes using  
40 polymer-based solid-state gel electrolytes is discussed in detail. The CF-based electrode-active  
41 materials should be synthesized in a cost-effective, facile and eco-friendly manner in order to  
42 make it a sustainable material for the future. The preparation of CF-based hybrids or  
43 nanocomposites for SC electrode application helped in achieving high specific capacitance was  
44 included. The demonstration of CF-based SC electrodes in order to meet the requirements of  
45 flexible electronic device demonstrations such as in the field of telecommunication, health-  
46 monitoring systems, etc were also provided. The CF-based flexible SCs are highly  
47 recommended for flexible and miniaturized-devices to compete our daily life. A further  
48 development and utilization of CF-based wearable SCs is indeed for the sustainable on-body  
49 wearable devices in the future.  
50



## Conflicts of interest

The authors declare no conflict of interest.

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