Doped carbon nanofibers as electrode for supercapacitors

El-Refaie S. Kenawy 1, Sherif Kandil 2, Sherine N. Khattab 3, Mohamed G. Al-Tamami 1, *, Amany A. Abdelbar 1

1 Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt.
2 Material Science-Institute of Graduate Studies and Research, Alexandria, Egypt.
3 Chemistry Department, Faculty of Science, Alexandria University, Alexandria, 21321, Egypt.

* Correspondence Address:
Mohamed G. Al-Tamami: Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt, E.mail address: mohamed152492@science.tanta.edu.eg.

KEYWORDS: Nanofiber, Doped carbon, Electrospinning, Pyrolysis, Ultrasonication.

ABSTRACT: The electrochemical characteristics of supercapacitors can be greatly improved by using heteroatom-doped (N, P, S, and O) carbon materials as electrodes. Enhancing pseudo-capacitance, raising electrical conductivity, wettability, and elevating metal ion reversible storage capacity and rate capability are all facilitated by heteroatom doping. Heteroatom-based Due to its lightweight and three-dimensional structure, and transition metal-doped carbon nanofiber can be generated by electrospinning and employed as an electrode for high performance flexible supercapacitors (SCs).

Extremely high mechanical stability and a wide range of capacitance and mechanical strengths are provided by the large concentration of distinct heteroatoms in the doped electrode of supercapacitors. There are differences in the characteristics and conductivity of each heteroatom-doped carbon nanofiber electrode. The performance of supercapacitors depends on the atoms that are doped to give the electrode. In this review, we provide examples of several doped carbon nanofiber types and the attributes they confer on the electrode.

1. INTRODUCTION

It is necessary to create new materials in order to get increased power and energy density. For this reason, energy-storage gadgets like supercapacitors and batteries are gaining popularity all over the world. Inventive materials are necessary for these gadgets. Materials for energy storage are also necessary for the use of renewable energy sources and for the flexible, affordable, and clean use of energy [1, 2]. High performance electrochemical supercapacitors (SCs) are one of the most promising energy storage technologies. Supercapacitors (SCs) are distinguished by a long lifespan, quick charging and discharging, high power capacity, little sensitivity to temperature changes, and nontoxicity in nature. Ordinary capacitors and batteries have low energy capacity and restricted energy storage [3-6]. Despite the fact that research on SCs significantly advanced the previous year, scientists are still working to increase the material's energy density while preserving its high energy output so that SCs may be employed as major energy sources [7, 8].

Depending on the kind of charge-storage mechanism, SCs are divided into three categories: pseudo capacitors, electrolytic double-layer capacitors (EDLCs) and hydride capacitors. Because of the extra charges that are transported within the allotted potential, pseudo capacities have larger capacitances than EDLC-type devices; nevertheless, because of active material degradation brought on by Faradic interactions, pseudo capacities often have a shorter life cycle. [9]. Materials for pseudo-electrodes that are commonly utilized are metal oxides and conductive polymers because of their fast, reversible oxidation reactions, cost-effectiveness, ease of processing, and relatively longer periodic stability [10, 11].

The configuration of SCs consists of two electrodes and an electrolyte in a sandwich structure as shown in (Figure. 1). Electroactive materials can be used to create electrode materials with enhanced electrochemical performance in a straightforward, economical, and environmentally friendly manner [12].

The two primary charge storage methods used by SCs are (i) charge adsorption and (ii) oxidation-reduction reactions linked to chemical shifts. carbon-based compounds with exceptional chemical stability and electrical conductivity, such as graphene, dopant carbon, and carbon nanotubes. They usually function as SCs electrode materials in the first mechanism, which produces a high energy density and extended cycle life, but a flat energy density.
Conductive polymers with oxides and hydroxides of transition metals, it functions normally in the second mechanism, showing weak cycle stability but a high energy density. Because constant oxidation and reduction in electrode materials distorts their microstructure Relationships [13,14]. Carbon-based is Due to their large interlayer distance, chemical stability, high ion storage capacity, and conductivities, supercapacitor electrode materials include graphene, expanded graphite, and amorphous carbon. One dimensional carbon nanofiber smaller than 1 mm can be produced by modifying these carbonaceous materials. Because they are lighter and more portable, they are perfect for usage as supercapacitor processing components in mobile devices like laptops and cell phones as well as electric cars. [15-17].

Carbon Nanofibers (CNFs) have a fibrous, cylindrical, and cup-stacked structure that can produce a quantum effect at the nanoscale. The sheets of graphene that formed "cones" or "cups" are layered in several layers to create the carbon nanofiber. Carbon nanofibers (CNs) exhibit exceptional mechanical pliability, chemical stability, elevated porosity, vast surface area, and electrical conductivity [18]. More active cargo storage sites and a higher surface area to volume ratio can be produced by manufacturing CNFs in thin, foldable electrodes with highly desired surface imperfections. Additionally, the catalyst's homogeneous porosity structure minimizes the amount of mass reactant that is transferred from solution to the catalyst's active sites. Because of this, carbon nanofibers can be used at greater power rates and with faster ion transport [19]. Doping CNFs is one of the techniques used to form electrodes in supercapacitors, which is the most promising, effective, and long-lasting. Electron-capped CNFs with a distinct nanostructure Conductive polymers or heteroatoms enable the complete realization of the usage of active pseudo capacitors in some versions [20-22].

The use of carbon nanofiber in supercapacitors has been the subject of several reviews [23-30]. However, there is no review specifically on doped carbon nanofiber for supercapacitor applications. As a result, a critical study of the potential of doped carbon nanofiber for supercapacitor applications would be beneficial. This review discusses the benefits of doped carbon nanofiber for supercapacitor applications and how to improve them using various techniques. These techniques' benefits and drawbacks are also reviewed and discussed. Since they have long lengths, tiny diameters and pores, and a high surface area per unit volume, the electrospun nanofibers used in supercapacitors are of interest to both industry and science. These properties make them a great matrix or template for creating different hierarchical nanostructures for use as sensors, catalysts, remediation, and energy storage applications. It is believed that electrospun nanofiber electrodes are a great option for a variety of high-efficiency electrochemical energy storage devices. Based on the charge storage mechanisms of SC electrodes, electrospun nanomaterials can be broadly classified into three types: metal oxide nanofiber materials and their hybrid materials, metal capacitive conducting polymers, and electrochemical double-layer capacitive carbon nanofiber-based materials. The primary focus of emphasis is the relationship between the compositions, nanostructures, and electrochemical characteristics of the electrospun nanomaterials for each material class [31].

2. **Non-metal doped CNF (Carbon nanofiber doped by Heteroatom)**

One efficient way to modify the electron donor properties of carbon nanomaterials and, in turn, adjust the surface's electrical and chemical performance is to engineer them by replacing some of their atoms with heteroatoms, such as nitrogen (N), phosphorus (P), boron (B), sulfur (S), iodine (I), and so forth.
Because of its enormous potential in energy storage systems, heteroatom-doped nanostructured carbon materials have attracted a lot of attention. It is well known that there are many possible applications for three-dimensional designs. Flexible hierarchically porous carbon polyhedral embedded with carbon nanofibers doped by N and S (NSCPCNF) were generated by electrospinning metal-organic frameworks ZIF-67 and thiourea, combined with polycrylonitrile precursor and carbonization as shown in (Figure 2).

Due to the increased specific surface area, enhanced charge transfer capability, and pseudo-capacitance contributions from N, S double doping, the NSCPCNF thus obtained exhibits a much higher energy density of 396 F g⁻¹ at a current density of 1 A g⁻¹ and shows a high specific capacity of 1 mol L⁻¹ H₂SO₄ electrolyte (three-electrode mode) as ECNFs (192 F g⁻¹). More importantly, a flexible supercapacitor (FSC) constructed with NSCPCNF electrodes exhibits a high specific capacitance of 103 F g⁻¹ at a current density of 0.5 A g⁻¹ (two-electrode mode), and a 14.3 Wh kg⁻¹. It has a high energy density and achieves a power density of 250 W kg⁻¹ at kg, which outperforms most of the reported ECNFs based FSCs, and it also exhibits a high capacitance retention (107% of the initial value after 3000 charge-discharge cycles) and superior bending stability (Figure 3 and 4) [32].

Figure 2. Diagrammatic representation of the FSC structure and NSCPCNF preparation.

Figure 3. The electrochemical properties of NSCPCNF, PANC, and CPCNF: Nyquist plots (a), CV curves at a scan rate of 10 mV s⁻¹ (b), GCD curves at a current density of 1 A g⁻¹ (c), specific capacitances at various current densities (d), inset of (a) shows Magnified Nyquist charts in the high frequency region.
By pyrolyzing bacterial cellulose that has been submerged in $\text{H}_3\text{PO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{H}_3\text{BO}_3/\text{H}_3\text{PO}_4$ aqueous solution, respectively, 3D P-doped, N, P co-doped, and B, P co-doped carbon nanofiber networks are successfully created.

Additionally, the N, P-co-doped carbon nanofibers demonstrate good supercapacitive behavior in their prepared state [33].

The special ZIF-8-incorporated 3D nitrogen and boron co-doped carbon nanofiber electrode outperformed PAN-based carbon nanofiber supercapacitor electrodes in terms of specific capacitance, producing a high value of 295 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$ when evaluated as a binder-free supercapacitor electrode. The novel electrode demonstrated exceptional cyclic stability, with 94.5 percent capacitance retention, even after 10,000 charge-discharge cycles.

It demonstrated high-rate capability. The B and N doped carbon nanofiber electrode’s enormous surface area, mesoporous structure, and excellent wettability are responsible for its superior electrochemical performance (Figure 5) [34].
2.1. N-Doped Carbon Nanofiber as electrode for Supercapacitors

In contrast to the most widely used N-containing carbon materials, nitrogen-doped porous carbon nanofiber, a different kind of hybrid nanofiber for supercapacitors, shows a lot of promise as an effective electrode material for supercapacitors with favorable electrochemical performance, or a comparatively high specific capacity, excellent rate performance, and cycling stability. The electrical conductivity suffers with increasing porosity due to the incompatibility of conductive routes or oxygen-containing functional groups, which significantly reduces the power capacity even if the majority of porous materials show substantial capacitances, Development of carbon materials with large surface area, energy density, particular conductivity qualities, and, of course, long cycle life is therefore required [35]. N-doped nanofibers (also known as N-CNFs) are 100–150 nm in diameter, and they cross over to create a porous conductive network. Better electrochemical performance is demonstrated by N-CNFs/CC arrays than by CNFs/CCs because of their increased conductivity and increased structural stability. N-doped carbon nanofibers (NCNFs) that have a high doping N content of 13.8% are synthetic-size, showing high reversible capacity (248 mA g\(^{-1}\) at 25 mA g\(^{-1}\), excellent rate capability (104 and 101 mA g\(^{-1}\) at 10 mA g\(^{-1}\), respectively), and great spinnability (4000 cycles) as the anode substances in half the cells. Electrical-Polymerization of pyrrole followed by carbonization Polypyrrole (PPy) is an easy-to-reproduce synthetic route for obtaining N-doped carbon arrays integrated by N-CNFs/CC arrays because of their improved conductivity and increased structural stability. N-doped carbon nanofibers (NCNFs) that have a high doping N content of 13.8% are synthetic-size, showing high reversible capacity (248 mA g\(^{-1}\) at 25 mA g\(^{-1}\), excellent rate capability (104 and 101 mA g\(^{-1}\) at 10 mA g\(^{-1}\), respectively), and great spinnability (4000 cycles) as the anode substances in half the cells. Electrical-Polymerization of pyrrole followed by carbonization Polypyrrole (PPy) is an easy-to-reproduce synthetic route for obtaining N-doped carbon arrays integrated into the conductor substrates. This new approach requires equipment cost but also allows precise control of the exact properties and surface functions of carbon (i.e., surface groups containing nitrogen and oxygen) by changing carbonation temperature.

Controlling the surface characteristics, or the pores' size and makeup of heterogeneous atoms, is essential to improving capacitance and performance rate for N-doped carbon matrices, according to our thorough surface study. Furthermore, we show that the newly created carbon

---

**Figure 5.** The electrochemical performances of the 3D-BN-CNF-ZF900 were measured in a three-electrode system using 2 M KOH as the electrolyte. The measurements included: (a) CV curves at various scan rates ranging from 5 to 100 mV s\(^{-1}\); (b) GCD curves at various current densities ranging from 0.5 to 5 A g\(^{-1}\); and (c) a cyclic stability test conducted at 5 A g\(^{-1}\) where the capacitance retention percentage was computed every 200 cycles. The inset displays (d) Nyquist plots before and after 10,000 cycles, as well as GCD curves at 0.5 A g\(^{-1}\). The Nyquist plot magnified in the high frequency area is shown in the inset.
array can be used as a large surface, conductive substrate for different materials with pseudo-capacity. Using this carbon group, a Ni(OH)₂ electrode was created as a model system and evaluated for use as a false electrode. The Ni(OH)₂ electrode's gravitational and area capacitances were found to be superior to other Ni(OH)₂ electrodes in the literature. Numerous benefits of the N-doped carbon group are responsible for this outstanding performance: (1) a large surface area that permits the loading of numerous electroactive materials in the form of a thin, uniform film; (2) high electrical conductivity that facilitates quick electron transfer; and (3) a porous structure that makes it simple for electrolytes to reach the surface of electroactive materials [36,37].

PANI (Polyaniline) has several great benefits, making it a good contender as a material for making potent supercapacitors. Researchers have realized the potential of electrospun PANI thanks to recent studies on electrospun PANI nanofiber webs electrodes, three-dimensional porous PANI/polyacrylonitrile core-shell, sandwiched symmetric supercapacitors made of flexible PANI/carbonized polyimide, PANI/GO/PVDF, hollow-structured PANI, and PANI/vanadium pentoxide as asymmetric supercapacitors. A study on using PANI nanofiber webs as electrode materials for supercapacitors was started by Chaudhari and his associates. They suggested fabricating high aspect ratio PANI (>50) by electrospinning a polymeric blend of PANI and polyethylene oxide because direct processing of PANI by electrospinning is a challenging undertaking (PEO). A homogeneous slurry was made with 75 weight percent PANI, 15 weight percent carbon black, 10 weight percent polyvinylidene fluoride, and a few drops of N-methyl pyrrolidinone for the purpose of making electrodes. After that, the resulting slurry was applied to a graphite substrate, which was used as a current collector. The performance of electrospun nanofibers synthesized in organic (1 M LiClO₄ in propylene carbonate (PC)) and aqueous (1 M H₂SO₄) electrolytes is compared with PANI powder. In comparison to PANI powder (208 F g⁻¹), a PANI nanofiber web has a greater specific capacitance (267 F g⁻¹) at a current density of 0.35 A g⁻¹. PANI nanofiber webs offer a specific capacitance of 230 F g⁻¹ at the 1000th cycle and exhibit superior stable performance as compared to PANI powder. In fact, after 1000 cycles, over 86% of its initial capacitance is still there; in contrast, the PANI powder’s capacitance retention is only 48%. According to this observation, PANI nanofiber webs have higher cycle stability than PANI powder. In the instance of PANI nanofiber webs, reduced individual impedance values were also observed, indicating the existence of electroactive sites necessary for the charge transfer reaction and counterion diffusion. The characteristics of PANI nanofibers generated by electrospinning were found to make them a promising choice for use as an electrode material in high performance supercapacitors [38].

2.2. S- Doped Carbon nanofiber as electrode of Supercapacitors

Production of S-doped carbon with a well-planned and controllable porous structure for energy storage and conversion has advanced significantly. The structural flaws of S-doped carbon have been the subject of several attempts and extensive research efforts to enhance its electrochemical performance for SCs. To create a well-ordered intermediate composite, natural sulfur or compounds containing sulfur are thermally processed using templates. This is followed by carbonization at a high temperature (>500 °C). During the post-treatment process, sulfur atoms are grafted to the original carbon via heat polymerization, oxidation processes, and replacement reactions. For the preparation of S-doped carbon, numerous drying techniques exist. To make S-doped carbon, for instance, dried carbon is simply exposed, without the use of a solvent, to a sulfur-atom-rich gas environment at high temperatures, followed by cooling. In typically, though, carbon is impregnated for a few minutes in sulfur-containing chemical solutions before being dried and heated for the wet modification. Likewise, in a few minutes in sulfur-containing chemical solutions before being dried and heated for the wet modification. Additionally, sulfur-based functional groups’ electrochemical activity improves redox processes, increasing the specific capacitance of carbon-based materials [39].

The doping of sulfur minimizes both the formation of undesirable pores and pore shrinking. Due to the presence of mesopores carbon and high sulfur content, the 1.4 V symmetric SC demonstrated exceptional SC performance, delivering a high specific capacitance (≈137 F g⁻¹) and exhibiting good energy (≈9 Wh kg⁻¹) and power (≈687 W kg⁻¹) density in H₂SO₄ electrolyte at a current density of 1.0 A g⁻¹. S-doped AC structures thus perform better in 6 m KOH electrolyte than in 1 m H₂SO₄ electrolyte in terms of specific capacitance and, consequently, energy density when comparing the two electrolytes. Sulfur's presence in the tiny pores of nanocarbons produces positive charges that attract anions and improve electrode-electrolyte interactions at the EEI [40].

2.3. P-Doped Carbon Nanofiber electrode for Supercapacitors

Production of S-doped carbon with a well-planned and controllable porous structure for energy storage and conversion has advanced significantly. The structural flaws of S-doped carbon have been the subject of several attempts and extensive research efforts to enhance its electrochemical performance for SCs. To create a well-ordered intermediate composite, natural sulfur or compounds containing sulfur are thermally processed using templates. This is followed by carbonization at a high temperature (>500 °C). During the post-treatment process, sulfur atoms are grafted to the original carbon via heat polymerization, oxidation processes, and replacement reactions. For the preparation of S-doped carbon, numerous drying techniques exist. To make S-doped carbon, for instance, dried carbon is simply exposed, without the use of a solvent, to a sulfur-atom-rich gas environment at high temperatures, followed by cooling. In typically, though, carbon is impregnated for a few minutes in sulfur-containing chemical solutions before being dried and heated for the wet modification.
Doped carbon nanofibers as electrode for supercapacitors

The conversion of carbon from substrate materials pyrolysis of the atmosphere (as NH₃), and/or modification of the precursor of TM are the primary methods of optimizing the catalytic performance of TM-N-C catalysts. The electrical stimulation activity of the TM-N-C catalysts was found to exhibit the following sequence in both acidic and alkaline solutions: Fe > Co > Cu > Mn > Ni. Transition metal doped carbon nanofiber can be used as an electrode for supercapacitors and this metal is Ni. The Ni-doped PANI exhibits a unique electrochemical property, namely a specific capacitance of 370 F g⁻¹ at 0.5 A g⁻¹, which is superior to that of the other synthesized materials. This property allows for improved rate capability and sustained cycling performance. The traditional approach is not followed in this case. This material is a potential candidate for use as an electrode material in supercapacitor applications because of its intriguing features, which are the result of a well-organized and doped nanostucture.

We synthesized nickel-carbon nanofibers by an electrospinning procedure. Polyacrylonitrile (PAN) solution in dimethylformamide (DMF) with Ni salt, Ni(CH₃COO)₂, was prepared in order to electrospinning Ni/C composite nanofibers. Several concentrations of nickel salt were used in the polymer solution. To study the effect of Ni quantity on the properties of Ni/C nanofibers, especially the pore diameter and surface area. A solution containing 8 wt% PAN was prepared in DMF. The solution was in the ultrasonic bath for 4.5 hours at 70°C. Moreover, designers in order to spend two more hours at 70°C, a small amount of metallic salt, Ni(CH₃COO)₂, was added and mixed again in the ultrasonic bath. The amount of Ni(CH₃COO)₂ added to the same PAN/DMF solution was varied, yielding four distinct mixtures. The mixed solutions were electrospun one by one, resulting in four different precursor fibers. These fibers are heat treated and carbonized up to 1400°C. Four nanocomposite Ni/C nanofibers with different amounts of N [47,48].

4. Different synthesis methods

4.1. Synthesis by Electrospinning method
The technique of electrospinning, which Reneker revived in the 1990s, is a group of fiber-forming technologies where the production of fibers is regulated by electrostatic forces. It has been successful in spinning nanofibers in the submicron range from a variety of polymeric melts and solutions. The structure and morphological properties of polymeric nanofibers have been the subject of much research, but the electrohydrodynamic of the electro-spinning process is not well documented in the public domain. The electrospinning process has been used to spin polymers with desirable chemical, mechanical, and electrical properties such as high conductivity, high chemical resistance, and high tensile strength into ultrafine fibers. Electrostatic forces and the polymer’s viscoelastic behavior both have an impact on how nanofibers are produced by the electrospinning process. The structure and properties of electrospun nanofibers are influenced by process parameters such as solution feed rate, applied voltage, nozzle-collector distance, and spinning environment, as well as material characteristics such as solution concentration, viscosity, surface tension, conductivity, and solvent Vapour pressure. The characteristics of fibers as a function of process and material parameters have been the subject of extensive research. A thorough explanation of how process and material factors effect on the structure and features of nanofibers is given. An alternative to electrospinning, electrospinning relies on the application of an electric field force to a polymer solution or melt. Fibers can solidify when the electrified jet is stretched during electrospinning to counteract the electrostatic repulsions between the surface charges and solvent
evaporations [49]. Polymer alloys, both organic and synthetic, as well as polymers having functional nanoparticles integrated into them, can all be processed via electrospinning. Multifunctional qualities for a wide range of applications are made possible by the special benefits of electrospinning.

A metallic or plastic syringe, a collector, and a high-voltage DC or AC power supply make up the basic electrospinning setup. The syringe is going to hold the polymer solution. When a high voltage is supplied, the polymer solution drop at the syringe’s tip will become polarized, and the induced charges will spread across the surface. The charged polymer will accelerate toward the collector due to the high electrostatic field. The phrase “electrohydrodynamic jetting” refers to the use of electrostatic forces inside the electrospinning process to supplement or replace the traditional mechanical forces (such as hydrostatic and pneumatic) used to produce the jet and reduce fiber size. The collector often functions well as an electric conductor to balance the charge carried by nanofibers. However, the charge on the nanofibers can be partially neutralized by airborne ions from corona discharges, which allows the nanofibers to be collected on separate collectors or even on the surface of liquid. By observing, theories about electrospinning can be separated into three categories. The following phenomena were seen during the electrospinning process: (1) fluid charging theories; (2) Taylor Cone Theory theories on liquid droplets under high voltage; and (3) instability theories on jets in flight.

The process of creating charges in the syringe’s fluid is known as fluid charging. High electric field polarization is usually the cause of this. The process of electrospinning between positive and negative potentials is called induction charging [50]. When this happens, the fluid’s ion mobility causes free electrons, ions, or ion pairs to form double layers as charge carriers. The mobility of ions in the fluid determines the double layer thickness when there is no flow; ions may be convincing away from the electrode and the double layer continuously replenished in the presence of flow. In general, inductive charging is possible for fluids with conductivities on the order of 10-2 S/m. Higher Voltage Liquid Droplet—Taylor’s Cone Theory G. I. Taylor developed the Taylor Cone theory in 1964 to explain how small-volume liquid deforms under a strong electric field [51](1). When an electric field comes into contact with a liquid that conducts electricity, a small volume of the liquid can take on a stable shape because the surface tension and electric forces are in equilibrium in the cases of inviscid, Newtonian, and viscoelastic liquids (if the potential is not too large). (2) The liquid body takes on a conical shape with a half angle of 49.3° (a whole angle of 98.6°) as the voltage is increased to the critical potential, and any further rise will shatter the equilibrium. In flight-thinning and instability theories, these are known as the Taylor Cone Jets. When charged jets blasted out of the Taylor Cone, researchers studying electrospinning observed that the jets typically traveled in a nearly straight line before bending into a convoluted path where electrical forces stretched and thinned them by significant ratios. Numerous theoretical studies have been conducted in light of those events. The charged jets released from the Taylor cone during the electrospinning process will go through in almost a straight line before twisting into a convoluted path [52]. The syringe tip and collector are separated by a very tiny distance, which can be as little as 3 mm or 500 mm, in a novel method of controlling the fiber direction using near-field electrospinning (NFE) (the almost straight line before the intricate journey). It is imperative to take note of three crucial aspects while conducting the NFE procedure. A) To use the stable liquid jets’ region for fiber direction control, there must be 500 mm to 3 mm between the syringe tip and the collector. B) Similar to traditional electrospinning, the applied voltage is lowered due to the short distance and the electrical field intensity is kept within the 107 V/m range. Identical to a dip pen, discrete droplets of the polymer solution should be given by dipping the electrode into the solution and then pulling it out again [53].

Electrospun nanomaterial electrodes for solar cells (SCs): This method of creating more types of nanomaterials involves electrospinning combined with post-processing steps like solvothermal, chemical Vapour deposition (CVD), electrodeposition, and high-temperature calcination. Three primary categories comprise electrospun nanomaterials produced by electrospinning and ensuing chemical or thermal post-treatments: carbon nanofibers (CNFs), carbon-free fibers (CFF-based fibers), and carbon-free fibers represented by transition metal oxides.

4.2. Pyrolysis-Based Synthesis

When organic waste is thermally treated, pyrolysis across a wide spectrum is frequently used to create carbon nanostructures. Based on the growing size, medium, and physio-chemical properties, the method of nanoparticle growth dictates the functional distribution of nanoparticles. Growth of carbon nanostructures is a difficult process where temperature, catalyst type, and precursor type have a major influence. Modern advances in nanomaterial growth methods have created new avenues for the manufacturing of carbon-based nanomaterials on a commercial scale. The approaches that use organic waste that is high in hydrocarbons as a feed source are the most promising. Different pyrolysis procedures are described in relation to the production of carbon-based nanomaterials, notably carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphene (G) [54].

CNFs were synthesized by the pyrolysis method. The Si (100) substrates, measuring 10 mm by 10 mm, were cleaned with an ultrasonic cleaner in acetone, then rinsed with deionized water and finally dried with a nitrogen blower. The quartz boat, which was then positioned in the middle of the quartz tube, was used to hold the substrates. One end of the quartz tube was fitted with the spray nozzle, while the other end was fitted with the gas bubbler. N2 gas was used to extract air from the quartz tube. In a precursor container, 2% ferrocene was combined with turpentine oil. The furnace was given the time it needed to reach the desired temperatures of between 650 and 800 °C before permitting the mixture of ferrocene and turpentine oil to enter the quartz tube. The cock was opened when the furnace reached the desired temperature to let the mixture of turpentine oil and ferrocene pass through. The boiling point of turpentine oil is 170 °C, while the sublimation temperature of ferrocene is 175 °C. By means of the spray nozzle, nitrogen gas flow was kept going to atomize the liquid. The liquid was kept moving at a rate of 3–4 droplets per minute so that in 60 minutes, fluids might be sprayed. The furnace was turned off after deposition and permitted to cool [55].
4.3. Creation using Ultrasonication

After eight hours of ultrasonication, carbonization and electrospinning were performed. In contrast to what would have been obtained otherwise (230 nm, 1010 S/m, and correspondingly 105 F/g), the sample's diameter, electrical conductivity, and specific capacitance were purportedly enhanced by the addition of carbon nanotubes (6%), ultrasonication, and carbon nanofiber produced from cellulose at 145 F/g. Ultrasonication is a synthetic method for material degradation that combines an ultrasonic wave with a liquid medium, such as solvents or polymer melts, with a frequency greater than 20 kHz. Due to the high energy density of ultrasonic waves, they can expand and compress in a liquid medium to produce negative pressure. Thus, a well-dispersed carbon nanofiber is produced by reducing the aggregation of carbon nanofiber particles. High dispersion carbon nanofiber has reportedly been shown to increase mechanical strength. But it was discovered that using ultrasonication on biomass to create carbon nanofibers is still a relatively novel technique [56-58]. Ultrasonication is frequently used to disperse nanoparticles into base fluids and break up agglomerates. The available literature contains only a small number of studies on the effects of sonication on nanofluid characteristics. The impact of sonication on the thermal conductivity and viscosity of 0.5 weight percent carbon nanotubes in an ethylene glycol-based nanofluid is investigated. The related impacts on the lengths of carbon nanotubes and agglomeration sizes are seen. It was shown that the thermal conductivity of the nanofluids increased nonlinearly with increasing sonication time/energy, peaking at 1,355 minutes of sonication time with a 23% augmentation. However, at a sonication time of 40 minutes, the viscosity of nanofluids reaches its peak; after 1,355 minutes of sonication, the viscosity starts to drop and eventually approaches that of pure base fluid. Additionally, it has been found that the sonication procedure reduces the length of carbon nanotubes as well as agglomeration sizes. Over the current experimental range, the reduction in agglomeration size is more significant than the reduction in carbon nanotube length. Therefore, in order to get the highest increase in heat conductivity and the lowest increase in viscosity which could affect application prolonged sonication is employed [59].

4.4. Synthesis via Hydrothermal Process

Compared to pyrolysis, hydrothermal treatment has a lower starting temperature but a longer holding period (>8 h), which results in higher power consumption. In comparison to electrospinning, hydrothermal provides bacterial cellulose that has undergone treatment. To create carbon nanofiber, maintain a temperature of 180 °C for 12 hours. Additionally, it was shown that hydrothermal might potentially be a successful method for doping bacterial cellulose with heteroatoms, as putting more active sites on its surface will make it better. The carbon nanofiber's capacitive properties [60]. Reportedly, the N-doped bacterial cellulose-derived carbon nanofiber obtained by hydrothermal treatment measured 10 nm in diameter and 254 F/g in capacitance, compared to 20 nm and 77 F/g in capacitance produced through pyrolysis treatment. It has been proven that carbon nanofiber with better characteristics can be produced through hydrothermal treatment for use in energy storage applications. [61,62]. Carbon nanofibers undergo hydrothermal treatment at 180 °C, which reduces the oxygen and hydrogen content of the fibers through hydrolysis [63].

4.5. Synthesis using the Method of Floating Catheter

CNFs are generated using the floating catalyst method, which has the potential to be used in industrial engineering and has high productivity because it is continuous production. Several experimental parameters, including sulfur additives, the feedstock’s evaporation temperature (T), and the amount of hydrogen flow, have been tested. Carbon nanofiber growth has clear effects. Transmission electron microscopy was used to investigate the materials. It is shown that filamentous carbon can be produced from feedstock with just the right quantity of sulfur. Additionally, Tbw is an important component in the creation of carbon nanofibers. A low Tbw is required to produce carbon nanofibers that are straighter and thinner, and 230C was required. In the floating catalyst approach, the rate of hydrogen flow also has a significant impact, and the impact of hydrogen is a challenging issue. Because it can continuously gather products and has a wide range of potential uses, the floating catalyst approach is more productive than the seeded one. The primary filaments also referred to as catalytically produced filaments that make up the VGCFs created using the floating catalyst approach are covered in different layers of pyrocyanogen with reduced graphitization. Additionally, it is demonstrated that smaller-diameter VGCFs are stiffer than larger-diameter ones [64-67].

4.6. Synthesis and purification of SCNFs (Specific For S_Type Super capacitors)

On a ceramic boat placed in the second heating zone of the CVD, 100 mg of the used catalyst was dispersed. 1.5 g of sulfur powder (in a ceramic boat) was introduced to the first heating zone of the catalyst after acetylene gas was broken down on it to form SCNFs. While the Sulfur container temperature in the first zone was raised from ambient temperature to 200 °C in an argon atmosphere, the second zone’s temperature was raised to 600 °C. The second zone’s temperature was then maintained constant during the SCNF’s development stage. The sulfur container’s (first zone) temperature was then raised to 550 °C. For this stage, acetylene (150 mL/min) was used in place of the 50% argon flow for 45 minutes. The substrates were then gradually cooled to room temperature in an argon environment using SCNFs [68].

5. Conclusion

Supercapacitors are regarded as one of the most significant objectives that nations are attempting to achieve in the modern day because of their significance in offering several energy sources when utilized. They are employed in many facets of daily life. They are thought to be the most significant method of energy storage at current time, making it one of the most significant uses that could become more prevalent in this field in the future. Supercapacitors are rapidly charging and are available in the majority of countries worldwide. Numerous examples of this kind of application have already reached the market and are altering our perception of energy storage. It might be some time before a standalone, commercially feasible supercapacitor battery is realized. Carbon nanofiber electrodes can perform better through doping by different atoms and metal oxides; Different atoms have...
different effects when combined with carbon nanofibers as the electrode in supercapacitors. Carbon nanofiber electrode can be produced by using different methods, but electrospinning is the best way to produce it. The process of electrospinning is a simple, flexible, and rapid technological advance that has the potential to create materials with varying porosity and fiber types in addition to producing nonwoven nanofibers with desirable qualities like a high surface area to volume ratio. These intriguing characteristics make a promising method appear to be electrospinning.

References


[37] Zhang, R.; Tu, Q.; Li, X.; Sun, X.; Liu, X.; Chen, L. Template-free preparation of α-Ni(OH)₂ nanosphere as high-performance electrode material for advanced supercapacitor. Nanomaterials. 2022, 12, 2216.


[49] Ozden, E.; Menceloglu, Y. Z.; Papila, M. Engineering chemistry of electrospun nanofibers and interfaces in nanocomposites for superior mechanical properties. ACS applied materials & interfaces. 2010, 2, 1788-1793.


