

## ADVANCING SUPERCAPACITOR PERFORMANCE: A COMPREHENSIVE REVIEW OF ELECTROCHEMICAL CONVERSION OF COCONUT SHELLS INTO ACTIVATED CARBON NANOFIBERS

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### ABSTRACT

This assessment provides a comprehensive evaluation of the limitations associated with the application of supercapacitors, along with the imperative to enhance their functionality. Following this, the advantages of Electrochemical Double Layer Capacitors (EDLC) are discussed in comparison to other types utilized in supercapacitor contexts. The transformation of coconut shells into carbon nanofibers is extensively investigated through various methodologies, highlighting both their benefits and limitations. It becomes evident that the current utilization of coconut shells has not yet achieved optimal sustainability or viability for energy storage purposes. Nevertheless, coconut shells offer a widely available and sustainable resource that can be converted into Activated Carbon nanofibers for energy storage applications. Diverse techniques have been employed to produce these ACB nanofibers, each targeting specific objectives including improved energy density, adaptable diameter, reduced energy consumption, and faster charging times. Despite these accomplishments, it is evident that numerous significant properties of carbon nanofibers derived from coconut shells remain unexplored, leading to substantial knowledge gaps that must be addressed for each technique. Therefore, further research is warranted to advance the comprehension of key parameters associated with various methods, ultimately facilitating the development of highly desirable carbon nanofibers sourced from coconut shells and catering to the requirements of sustainable energy storage applications.

**Keywords:** Supercapacitor, Coconut shell, Electrochemical Double Layer Capacitors (EDLC), nanofiber, Energy storage, ACB.

### INTRODUCTION

#### The Multifaceted Potential and Obstacles Facing Supercapacitors in Various Industries Worldwide

A substantial quantity of energy has been extensively utilized by humans across diverse applications, notably in the realm of transportation (Bucher *et al.*, 2018), electricity for household appliances (Ozawa *et al.*, 2018), industrialization (Wu *et al.*, 2017), and urbanization (Nastasi *et al.*, 2017). Energy can be derived from sustainable sources, including renewable options such as solar, wind, marine tidal, biomass, and geothermal, as well as non-renewable alternatives like nuclear power and fossil fuels, such as petroleum oil, natural gas, and coal. Among these, fossil fuels are currently the most widely utilized resource for global energy production. However, the energy obtained from fossil fuels is insufficient to meet the increasing global energy demands.

This deficiency is attributable to the amplification in worldwide energy demand, inadvertently triggering a surge in global warming concerns (Wu *et al.*, 2017). According to Hatfield-Dodds *et al.* (2017), a recent projection forecasts a substantial rise of 53% in fossil fuel extraction, translating to an anticipated increase from 14 billion tonnes in 2015 to approximately 22 billion tonnes by 2050. This projected surge coincides with an estimated 65% growth in global energy demands, expected to climb from 524 exajoules (EJ) in 2015 to 864 EJ by 2040 (Kambo *et al.*, 2015). The comprehensive utilization of fossil fuels is anticipated to lead to the exhaustion of non-renewable reservoirs within the Earth's crust, given that the pace of fossil fuel extraction surpasses the natural rate of fossil fuel generation by a factor of 10,000 (Hussein *et al.*, 2015).

Furthermore, the process of converting fossil fuels into usable energy releases a variety of greenhouse gases (GHGs) such as carbon dioxide,

methane, nitrous oxide, sulfur oxides, nitrogen oxides, and harmful pollutants like fly ash, dioxins, and furans. These emissions pose a significant threat, as they have the potential to contaminate both the atmosphere and aquatic environments, contributing to and exacerbating the phenomena of global warming and climate change (Sims *et al.*, 2003; Mokhtar *et al.*, 2014). In response to these pressing concerns, numerous international conferences have taken place, including the G7 Leaders' Declaration Summit and the United Nations Summit. These gatherings serve a critical purpose by emphasizing the importance of sustainable development and encouraging a commitment to optimal strategies for managing natural resources (Hatfield-Dodds *et al.*, 2017). In light of the pressing global challenges associated with fossil fuel dependency, concerted efforts must be directed towards developing advanced technologies for harnessing renewable energy sources. This strategic shift is crucial to reduce our reliance on fossil fuels and ensure a sustainable energy future. Renewable energy sources are characterized by their sustainability, cleanliness, and minimal environmental impact. A multitude of research endeavors have been undertaken to enhance the efficiency and output of renewable energy generation, contributing to the advancement of sustainable development goals (Wang *et al.*, 2018). Nonetheless, renewable energy encounters a constraint in its ability to be directly transported and delivered to end-users. Upon generation, renewable energy necessitates conversion into electricity and subsequent storage within energy retention systems (Dell *et al.*, 2001). Denholm *et al.* (2006) ascertained that enhancements in energy storage mechanisms carry significance in optimizing the capacity for storing renewable energy. In the current context, advancements have led to the development of energy storage devices, exemplified by high-energy/power density supercapacitors with extended operational lifespans, designed specifically to retain renewable energy (Purushothaman *et al.*, 2017; Dong *et al.*, 2018; Lee *et al.*, 2018). Hence, comprehensive research efforts concerning supercapacitor technologies should be undertaken to enhance the storage capabilities of renewable energy, thereby addressing the challenge posed by the escalating global energy requirements.

In a general sense, the optimal elemental substance for supercapacitor apparatus should originate from a straightforward, economically viable, and ecologically sustainable synthesis process. These advantageous attributes can be sourced from coconut shells, primarily due to their abundant availability as a renewable resource. Moreover, coconut shells exhibit the advantage of minimal greenhouse gas emissions and the feasibility of uncomplicated synthesis procedures. Up to the present, investigations have been conducted that assess the potential utility of materials derived from coconut shells for supercapacitor applications. (Zhang *et al.*, 2016), and coconut shell-derived nanomaterials (Yao *et al.*, 2015), for use in electrochemical energy storage. As a result, a considered examination of the potential viability of utilizing carbon nanofibers derived from coconut shells for supercapacitor implementation was deemed valuable. This analysis provides a comprehensive overview of the merits inherent in Electric Double-Layer Capacitors (EDLCs) compared to alternative options in supercapacitor contexts. Furthermore, it delves into the enhancements achieved through diverse techniques in the conversion of coconut shell materials into carbon nanofibers. The strengths and constraints associated with these methods are thoroughly evaluated and subject to discussion within this appraisal.

### **Exploring the Capacitive Properties of Nanofibers Derived from Coconut Shells for Superconductive Electrodes**

Several types of carbon-based materials, such as expanded graphite, graphene, and amorphous carbon, have been demonstrated to be effective as electrode materials due to their advantageous properties in supercapacitors due to their notable attributes such as elevated ion storage capabilities, robust chemical stability, commendable electrical conductivities (Li *et al.*, 2010; Zhang *et al.*, 2016; Tang *et al.*, 2017), and large interlayer distance (Kong *et al.*, 2017). These carbonaceous substances have the potential to undergo alteration, resulting in the formation of one-dimensional activated nanofibers sourced from coconut shells, characterized by dimensions below 1 millimeter (Faccini *et al.*, 2015), this variation is

not only significantly lighter than alternative materials, offering improved weight efficiency for devices, but also demonstrates strong potential for integration in supercapacitor manufacturing, making it particularly well-suited for electric vehicles and portable electronics like laptops and mobile phones (Zhang *et al.*, 2016; Kong *et al.*, 2017). The nanofibers derived from coconut shells exhibit a fibrous, cylindrical configuration marked by cup-stacked structures that induce a quantum effect at the nanoscale. These nanofibers originate from graphene sheets that take on a multi-layered arrangement characterized by "conical" or "cupped" formations (Kaur *et al.*, 2018). Consensus was reached regarding the correlation wherein a diminutive quantum effect results in the contraction of electronic wave functions, consequently leading to heightened electronegative absorption in carbon nanofibers (Babitha *et al.*, 2017). This augments the stability, mechanical characteristics, thermal attributes, light reflectivity, and electrically conductive nature of the carbon nanofiber (Jazaeri, *et al.*, 2011; Hussein *et al.*, 2015; Zhou *et al.*, 2016). Compared to carbon nanotubes, which tend to clump together (agglomerate) due to strong Van der Waals forces, coconut nanofibers exhibit excellent dispersibility in solution. This superior dispersion not only simplifies processing but also contributes to enhanced mechanical strength (Gao *et al.*, 2007). As a result, the viability of employing coconut shell nanofiber across various applications is heightened. Intriguingly, the transformation of coconut shell nanofiber into foldable and thin-film electrodes introduces valuable surface irregularities, leading to an expanded surface area-to-volume ratio and an augmented number of active sites for charge storage (Zhang *et al.*, 2016). Carbon nanofiber has additionally been engineered to adopt a consistent porous arrangement, thereby mitigating the mass transfer of reactants between the solution and the active catalytic sites (Chung *et al.*, 2018). Consequently, carbon nanofibers are enabled to facilitate expedited ionic transport and an elevated rate of capacity. A recent investigation serves as an illustrative example, wherein porous carbon nanofibers were employed as a catalyst substrate to enhance the performance of  $\text{TiO}_2$  photocatalysts (Chung *et al.*, 2018). The substantial porosity of the coconut shell nanofiber has

engendered a diminished Fermi level discrepancy between the carbon nanofiber and  $\text{TiO}_2$ , consequently facilitating the transmission of electrons from the conductive band of  $\text{TiO}_2$  to the carbon nanofiber. This characteristic further renders coconut shell nanofibers suitable for a diverse range of applications, including but not limited to air and water filtration. (Thavas *et al.*, 2008), catalyst support (Bezeme *et al.*, 2006), biodetector (Vamvakaki *et al.*, 2006), electrical interfaces with neural systems (Nguyen *et al.*, 2006), electrochemical point probe (Guillorn *et al.*, 2002), and gated field emitter (Guillorn *et al.*, 2001). Hence, it can be inferred that the attributes of materials currently employed as electrodes in supercapacitors exhibit constraints, thus necessitating continued enhancements. Driven by the limitations of existing materials, researchers have turned their attention to exploring the potential of coconut shell materials in the development of supercapacitor electrodes.

### **Harnessing Coconut Shells for Sustainable Energy Storage: A Promising Biomaterial Approach**

A coconut shell is the hard, outer covering of a coconut fruit. It is typically brown and has a rough, fibrous texture. Coconut shells are often used to make various products such as bowls, utensils, and handicrafts due to their durable and natural properties. Additionally, they can be used as fuel, as a source of charcoal, and as a material for landscaping and gardening (Veluchamy *et al.*, 2023). It achieves a state of being 'carbon neutral' since the carbon dioxide emissions resulting from the synthesis and application processes originating from biomass do not disrupt the environment, as the released carbon dioxide is subsequently reclaimed through the process of photosynthesis (Zhao *et al.*, 2010). This quality renders them applicable within sectors such as the food, construction, and textile industries (Klass *et al.*, 2004). In recent times, there has been a notable surge in research efforts focused on crafting energy storage electrodes using readily accessible coconut shells (Xu *et al.*, 2015). Coconut shell emerges as a pragmatic substitute capable of bridging the gap that currently exists within the domain of electrode materials. This proposition stems from its origin as a renewable organic entity, widespread availability, environmentally

harmonious characteristics, commendable cycling durability, and relatively reduced material expenses when contrasted with metals and synthetic polymers (Peng *et al.*, 2013). Nevertheless, it has been documented that the energy storage application of coconut shell-derived electrodes exhibits a lower energy density in comparison to the presently employed materials (Deng *et al.*, 2016). In a bid to surmount this constraint, endeavors have been undertaken to modify the configuration of the coconut shell by reshaping it into a one-dimensional structure through the creation of carbon nanofibers. Research has revealed that carbon nanofibers originating from coconut shells can achieve an energy storage capacity of up to 791 F/g across a range of diameters, some as diminutive as 10 nm. This energy storage capacity surpasses that of three-dimensional structures (Yang *et al.*, 2015). This phenomenon arises because nanofibers derived from coconut possess a more expansive specific surface area compared to materials adopting three-dimensional structures. This enlarged surface area augments the conveyance of charged ions during energy storage. The compositional nature of coconut shells, specifically the presence of cellulose, allows for the facile production of nano-sized fibers. This is due to the structure of cellulose, which includes elemental fibrils (2-5 nm in diameter) interconnected by labile  $\beta$ -1-4 linkages and hydrogen bonds. (Xie *et al.*, 2016). Cellulose's strength and rigidity come from these linkages. Various methods, like pyrolysis, can break these down (Kim *et al.*, 2017), hydrothermal treatment (Deng *et al.*, 2017), ultrasonication (Li *et al.*, 2016), and solvent extraction (Yang, *et al.* 2015), have been utilized to disrupt these linkages, aiming to generate carbon nanofibers with distinct surface configurations.

### **Unlocking the Potential of Coconut Shells and Other Biomass as Precursors for Activated Carbon Nanofiber Synthesis**

#### ***Evaluating the Pros and Cons of Present-Day Materials for Implementing Supercapacitors***

Conventional electrical energy storage devices, such as batteries, typically employ electrodes in contact with an electrolyte solution. During operation, these devices store electrical energy through electrochemical reactions occurring at a

designated voltage level (Luo *et al.*, 2015). A wide range of materials, including metals, transition metals, synthetic polymers, and graphite, are commonly used as active components in supercapacitor electrodes. Particularly, metals and transition metals demonstrate impressive energy storage capabilities. Nevertheless, the environmental risks associated with these materials have emerged as a significant impediment to both sustainable advancement and safety considerations (Wang *et al.*, 2016). Electrodes containing metals like lead and ruthenium are composed of substances that possess toxic attributes (Yang *et al.*, 2017; Sharma *et al.*, 2018). These substances have the potential to accumulate in the human body over time, potentially leading to the development of kidney diseases (Rajput *et al.*, 2017), disorders affecting mitochondria, known as mitochondrial diseases, impact cellular energy production and can give rise to a variety of health issues (Alston *et al.*, 2017), resulting in adverse outcomes including mortality (Servais *et al.*, 2017). Conversely, polymer materials exhibit notable energy storage capacities; however, their suitability as electrodes is compromised by their limited lifespan throughout their usage (Alston *et al.*, 2017). This arises from the expansion, contraction, and excessive oxidation of polymers triggered by pseudocapacitive reactions. Polymer electrode performance is limited due to an unfavorable lifecycle resulting from enlargement, contraction, and excessive oxidation during pseudocapacitive reactions, which negatively impact their elevated energy storage capabilities (Sivakkumar *et al.*, 2007; Wang *et al.*, 2016). Graphite's versatility makes it valuable in electrodes. It can be used in its natural form or modified into one-dimensional structures like graphene or carbon nanotubes. These structural changes promote rapid electron mobility, leading to significantly enhanced electrical conductivity (Wu *et al.*, 2012). Nevertheless, graphite is not a renewable resource, and its production involves intricate synthesis procedures (Wang *et al.*, 2016). While creating electrodes, the phenomenon of aggregation commonly emerges, disrupting the movement of charged ions within the electrode structure. Consequently, this impairment diminishes the electrochemical efficiency of the energy storage devices (Wei *et al.*, 2016). To

produce one-dimensional graphene with high expense and significant energy consumption, methods including chemical vapor deposition (Zhao *et al.*, 2010), arc discharge (Cheng *et al.*, 2017), and laser assistance (Wei *et al.*, 2013) are commonly applied. Specifically, chemical vapor deposition stands out among these approaches in synthesizing costly and energy-demanding one-dimensional graphene structures. Consequently, it can be inferred that the existing properties of materials employed in supercapacitor electrodes exhibit limitations, necessitating further enhancements. These gaps have consequently spurred the impetus for the advancement of supercapacitor electrodes through the utilization of coconut shell materials.

### **Enhancing the Properties of pulverized Carbon Nanofibers Derived from Coconut Shells through Doping and Co-Doping Techniques**

Doping constitutes a procedure capable of enhancing the electrical characteristics of a material through the introduction of a novel element, referred to as a dopant, possessing desired attributes, in the material's structure. This novel element can originate from metallic sources such as sodium (He *et al.*, 2017), lithium (Parthasarathy *et al.*, 2001), zinc (Liu *et al.*, 2006), and non-metals such as nitrogen (Maldonado *et al.*, 2005), phosphorus (Kim *et al.*, 2003), and sulphur (Paraknowitsch *et al.*, 2013). The process of doping coconut shell-derived carbon nanofibers induces the creation of imperfections and pores on the nanofiber's surface. This attribute is advantageous in the development of materials designated for supercapacitor device electrodes. A key feature of good energy storage is a highly porous surface. This allows the electrolyte, which carries ions, to reach more areas and gives the active material space to expand and contract as the battery cycles. This, in turn, improves the battery's performance (Zhang *et al.*, 2014). The introduction of dopants into coconut shell nanofibers additionally contributes an abundance of electrons, facilitating robust pi-electron delocalization. This enhancement serves to elevate the electrical conductivity and catalytic efficacy of the activated coconut shell nanofibers (Shao *et al.*, 2008). Non-metallic dopants like boron and phosphorus have the potential to

enhance pseudocapacitive behavior by generating a more expansive surface area conducive to energy storage through faradaic reactions. Conversely, doping with hydrophilic dopants such as nitrogen can enhance dispersibility within aqueous environments (Shao *et al.*, 2008). Research findings indicate that supercapacitors featuring electrodes composed of coconut shell-derived carbon nanofibers doped with polymer (polyaniline) and carbon nanotubes can attain notable specific capacitances, reaching values as high as 791 F/g (Yang *et al.*, 2015). This phenomenon can be attributed to the enhanced characteristics conferred by carbon nanotubes (such as elevated surface area, remarkable chemical stability, and reduced electrical resistance) and polyaniline (which exhibits high electrical conductivity), (Yang *et al.*, 2015). Remarkably, the doped carbon nanofibers derived from biomass (specifically coconut shells) can store energy surpassing 791 F/g (Wu *et al.*, 2023). Exceeding the energy storage capacity of electrodes constructed from non-organic materials like graphene, which achieves approximately 117 F/g (Vivekanand *et al.*, 2008), ruthenium (200 F/g) (Miller *et al.*, 1997), cobalt (475 F/g) (Tao *et al.*, 2007), nickel (153 F/g) (Li *et al.*, 2013), and manganese (482 F/g) (Prasad *et al.*, 2004). Doping coconut shell-derived carbon nanofibers with nitrogen results in an augmentation of their specific surface area. Research findings indicate that nitrogen-doped carbon nanofibers produced from bacterial cellulose exhibit a substantial specific surface area of 916 m<sup>2</sup>/g, alongside noteworthy stability, retaining 94% of current density after a chronoamperometry period of 20,000 s (Liang *et al.*, 2015). It is intriguing to note that certain dopants, including iron, nitrogen, boron, and phosphorus, can be sourced naturally from biomass residues such as agricultural and aquaculture wastes (Tang *et al.*, 2017). Hence, employing biomass residues enriched with naturally occurring dopants to produce carbon nanofibers presents a secure and economically viable alternative when contrasted with the utilization of commercially sourced dopants. Illustrations of this approach include the utilization of palm kernel shells (containing 3 wt% iron) and chitin from seafood shells (comprising 6.9 wt% nitrogen). The resultant carbon

nanofibers exhibit a diminutive diameter (ranging from 30 to 300 nm) and an exceptionally elevated specific surface area (reaching up to 1000 m<sup>2</sup>/g) (Che *et al.*, 2009; Duan *et al.*, 2016). Consequently, it has been disclosed that employing a doping

strategy can yield coconut shell-derived carbon nanofibers endowed with advantageous attributes, including a notable specific area, a porous surface, and a reduced diameter size.

**Table 1:** Showing coconut shell with varying activating temperature, chemical agent, acting temperature, activating gas, surface area, pore volume, pore type discharged capacity and heating rate.

BIOMASS	ACTIVATION METHOD	CHEMICAL AGENT	DOPED	ACTIVATING TEMP.	ACTIVATING GAS	SURF. AREA (m <sup>2</sup> /g)	PORE. VOL (cm <sup>3</sup> /g)	PORE TYPE	Discharge cap. (WAh/g)	Heating Rate °C/min	REFERENCES
C.SHELL	Pyrolysis	KOH	NO	750	N <sub>2</sub>	2258.7	2.25	MP	1150	3	(Liu. <i>et al.</i> , 2015)
C.SHELL	Pyrolysis	KOH	NO	750	N <sub>2</sub>	365	0.148	MP	----	20	(Purnomo <i>et al.</i> , 2018)
C.SHELL	Physical	CO <sub>2</sub> /Steam	NO	700	N <sub>2</sub>	----	-----	----	----	10	(Chandana <i>et al.</i> , 2019)
C.SHELL	Hydrothermal	H <sub>3</sub> PO <sub>4</sub>	NO	750	N <sub>2</sub>	2000	-----	MiP	----	20	(Quesada-Plata, <i>et al.</i> 2016)
C.SHELL	Pyrolysis	ZnCl <sub>2</sub>	NO	700	----	1874	1.21	-----	54.7	---	(Sun <i>et al.</i> , 2013)
C.SHELL	Steam	Steam/F	NO	30	----	-----	-----	-----	----	---	(Halder <i>et al.</i> , 2016)
C.SHELL	Pyrolysis	H <sub>2</sub> SO <sub>4</sub> /KOH	NO	600	----	-----	-----	-----	46.94	---	(Zaini <i>et al.</i> , 2023)
C.SHELL	Pyrolysis	KH <sub>2</sub> PO <sub>4</sub> /FeCl <sub>3</sub>	YES	-----	----	760.5	0.4	-----	-----	---	(Zhong <i>et al.</i> , 2019)
C.SHELL	Pyr/MW	-----	NO	550	-----	0.4042	0.0058	-----	----	---	(Nuryana, <i>et al.</i> , 2020)
C.SHELL	-----	-----	NO	500	N <sub>2</sub>	1.224	0.003	-----	-----	---	(Pang <i>et al.</i> , 2021)
C.SHELL	Pyrolysis	----	NO	600	N <sub>2</sub>	25.3	0.026	-----	----	---	(Wang <i>et al.</i> , 2021)
C.SHELL	Pyrolysis	----	NO	300 500	---	308	0.15	-----	----	---	(Samsudin, <i>et al.</i> 2019)
C.SHELL	Pyrolysis	-----	NO	400-500	----	13	0.021	-----	----	---	(Solanki, <i>et al.</i> 2017)
C.SHELL	Steam	H <sub>3</sub> PO <sub>4</sub>	NO	900	N <sub>2</sub>	447	0.31	MiP	----	---	(Li <i>et al.</i> , 2023)
C.SHELL	Pyrolysis	KOH/HCl	NO	450	----	312	----	----	----	10	(Vighnesha <i>et al.</i> , 2018)
C.SHELL	Hydrothermal	KOH	NO	800	N <sub>2</sub>	1567	----	----	49.9	5	(Lee <i>et al.</i> , 2021)
C.SHELL	Pyrolysis	KOH	NO	500	N <sub>2</sub>	2410	----	---	----	---	(Deng <i>et al.</i> , 2022)

**Table 2:** Activated carbon surface modification/treatment with liquid acid.

Biomass	Acid	% wt (%)	Ratio	Te mp. °C	Time (hr)	BET (cm <sup>2</sup> /g)	Pore Vol. (cm <sup>3</sup> /g)	Capacitance (F/g)	References
Oil Shales	HNO <sub>3</sub>	5	-----	175	-----	-----	-----	-----	(Ashtari, M. 2016)
Cassava peel	HNO <sub>3</sub>	65	1:1	65	4	1186	0.343	264	(Ismanto <i>et al.</i> , 2010)
Cassava peel	H <sub>2</sub> SO <sub>4</sub>	98	1:1	65	4	1336	0.501	210	(Ismanto <i>et al.</i> , 2010)
Cassava peel	H <sub>2</sub> O <sub>2</sub>	30	1:1	65	4	1276	0.569	240	(Ismanto <i>et al.</i> , 2010)
Palm Shell	HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	(30 mL) 66 + 98(10 mL)	1:1	100	12	1306	0.81	182	(Togibasa <i>et al.</i> , 2023)
Sago waste	HNO <sub>3</sub>	65	1:1	110	24	730	0.49	----	(Yue <i>et al.</i> , 2019)
Sago Waste	H <sub>2</sub> SO <sub>4</sub>	98	1:1	110	24	853	0.58	----	(Yue <i>et al.</i> , 2019)
Sago waste	H <sub>2</sub> O <sub>2</sub>	30	1:1	110	24	605	0.39	----	(Yue <i>et al.</i> , 2019)
Waste Tea	HNO <sub>3</sub>	3.33	1	90	2	1060	0.8085	100	(Gürten İnal <i>et al.</i> , 2020)
Waste Tea	HNO <sub>3</sub>	10	1	90	2	901	0.6368	88	(Gürten İnal <i>et al.</i> , 2020)
Waste Tea	HNO <sub>3</sub>	20	1	90	2	644	0.4380	49	(Gürten İnal <i>et al.</i> , 2020)
Waste Tea	HNO <sub>3</sub>	40	1	90	2	524	0.2855	7	(Gürten İnal <i>et al.</i> , 2020)

**Table 3:** Activated carbon surface modification/treatment with liquid acid.

Biomass	Acid	% wt (%)	Ratio	Te mp. °C	Time (hr)	BET (cm <sup>2</sup> /g)	Pore Vol. (cm <sup>3</sup> /g)	Capacitance (F/g)	References
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Activated coconut shells are a valuable material used in adsorption and filtration processes. Tables 1, 2 and 3 investigate methods for creating these activated shells, highlighting how researchers can tailor the material's properties by adjusting the activation process.

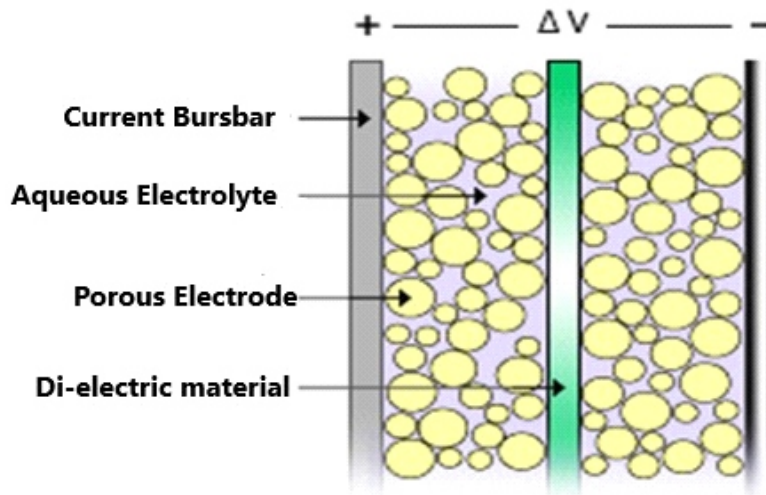
The tables explore various activation methods, including pyrolysis, physical activation, surface modification and chemical activation using agents like  $ZnCl_2$  and  $H_3PO_4$ . These processes significantly increase the surface area of the coconut shells, a key factor in adsorption, from a range of  $1.224 \text{ m}^2/\text{g}$  to  $365 \text{ m}^2/\text{g}$ . Additionally, activation creates pores within the material, impacting its ability to store and transport fluids. The pore volume varies between  $0.003 \text{ cm}^3/\text{g}$  and  $2.25 \text{ cm}^3/\text{g}$ . It's important to note that different studies may use varying conditions (temperature, heating rate) to achieve these results. The effects of different liquid acid treatments on activated carbon made from biomass sources, such as palm shells and cassava peel, are examined in Tables 2 and 3. Researchers experimented with different concentrations, temperatures, and treatment durations of three distinct acids: hydrogen peroxide, sulfuric acid, and nitric acid. The main discovery is that the activated carbon's qualities are greatly enhanced by acid treatment. The material's pore volume and surface area are both increased by the treatment. When nitric acid was applied to cassava peel, for instance, the surface area increased significantly in comparison to the untreated sample. Because of this improved characteristic, treated activated carbon performs better in filtration and adsorption applications.

### Comparing the Benefits of EDLCs to Alternative Supercapacitor Technologies

Supercapacitors can be categorized into three main types based on their taxonomy: Electrochemical Double-Layer Capacitors, Pseudo capacitors, and Hybrid capacitors. Each type is distinguished by its specific charge storage mechanism, which can be described as non-Faradaic, Faradaic, or a combination of the two.

Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between the electrode and electrolyte. In contrast, non-faradaic mechanisms do not rely on chemical reactions and instead involve the distribution of charges on surfaces through physical processes that do not involve the formation or breaking of chemical bonds. EDLCs (Figure 1) are constructed from two carbon-based electrodes, an electrolyte, and a separator. Like conventional capacitors, EDLCs store charge electrostatically, or non-faradaically, and there is no transfer of charge between electrode and electrolyte which makes it more reliable compared to other types of supercapacitors. Electric Double-Layer Capacitors (EDLCs) leverage an electrochemical mechanism centered around a dual-layer of charge for energy storage. Upon the application of voltage, charge accumulates on the surfaces of the electrodes. Through the innate attraction between dissimilar charges, ions within the electrolyte solution migrate through the separator and into the pores of the electrode with an opposing charge. Notably, the electrodes are meticulously designed to prevent the recombination of these ions. As a result, a double-layer of charge manifests at each electrode. This phenomenon, synergized with an amplified surface area and a diminished inter-electrode distance, empowers EDLCs to achieve heightened energy densities when compared to conventional capacitors (Signorelli *et al.*, 2006). Consequently, there is no transfer of charge between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities. EDLCs generally operate with stable performance characteristics for a great many charge-discharge cycles. Sequel to their cycling stability, EDLCs are well suited for applications that involve non-user serviceable locations, such as deep sea or mountain environments (Dhara, 2017).

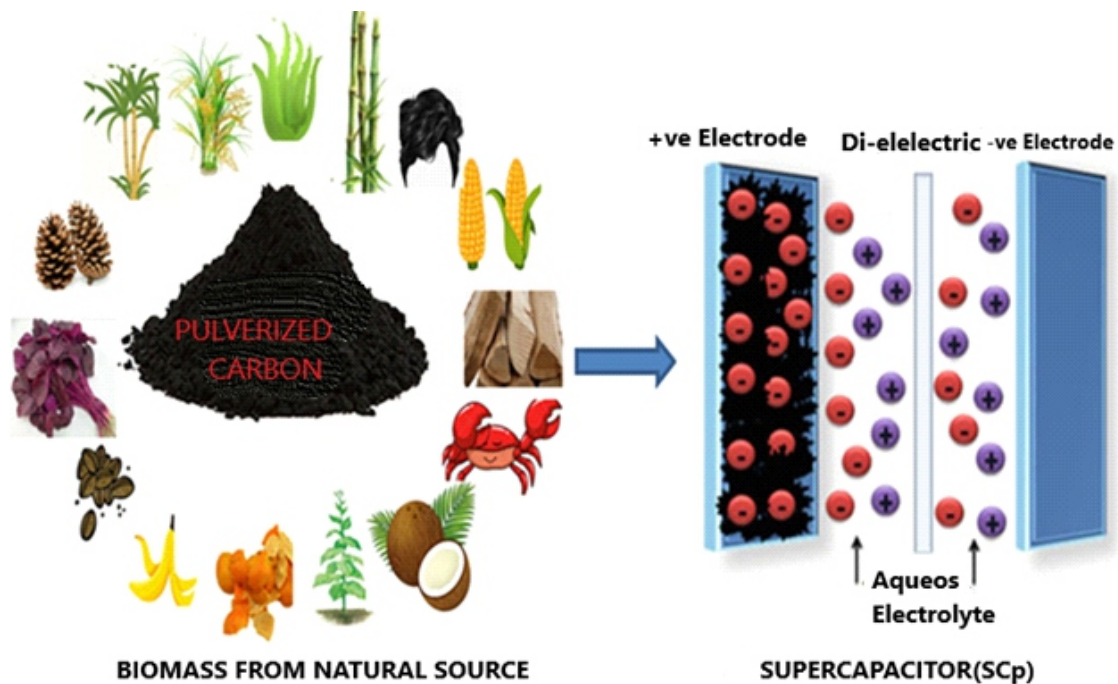




**Figure 1:** A typical supercapacitor showing major materials components such as activated carbon electrodes, electrolyte, and separator.

The internal components and operation of a supercapacitor are illustrated in Figure 1. The two activated carbon electrodes are essential for storing electrical energy because of their enormous surface area and carbon-based makeup. The separator, a thin membrane that serves as a traffic cop, divides these electrodes. It prevents a direct electrical connection that could short-circuit the device while allowing ions, which are

necessary for the energy storage process, to freely move within the electrolyte solution that fills the gap between the electrodes. While preventing any unintended chemical reactions with the electrodes, the electrolyte itself conducts electricity. Supercapacitors may store and release electrical energy through electrostatic processes with efficiency thanks to the well-coordinated.



**Figure 2:** Various Biomass used in both physical and chemical pulverization as a precursor for Supercapacitor.

Images of biomass used to produce activated carbon are shown in Figure 2, which offers information about the sources of the materials. Various plant materials, such as woodchips, sawdust, nutshells (including coconut shells), bamboo, grasses, and even agricultural waste, such as organic materials like animal dung, algae, or seaweed, are included in these pictures. This invariably create a porous route in the super capacitor applications.

The operational attributes of an EDLC can be fine-tuned by modifying its electrolyte composition. EDLCs have the option of employing either aqueous or organic electrolytes. Aqueous electrolytes like KOH generally exhibit reduced Equivalent Series Resistance (ESR) and minimal prerequisites for pore size in comparison to organic electrolytes such as acetonitrile. However, it's important to note that aqueous electrolytes also tend to have lower breakdown voltages. Consequently, the choice of electrolyte is often contingent upon the specific application of the supercapacitor. While the nature of the electrolyte is of great importance in supercapacitor design, the subclasses of EDLCs are distinguished primarily by the form of carbon they use as an electrode material. Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxide (Thomas *et al.*, 2014).

### **EMERGING METHODOLOGIES FOR PRODUCING CARBON NANOFIBERS FROM SOURCES LIKE COCONUT SHELL AND OTHER BIOMASS MATERIALS ARE GAINING PROMINENCE**

Various methodologies are utilized to synthesize coconut shell nanofibers, including pyrolysis, hydrothermal treatment, ultrasonication, and electrospinning.

#### **Pyrolysis**

Pyrolysis stands as a prospective method for converting waste materials via a thermochemical conversion process conducted within an inert atmosphere, where oxygen is excluded. This process results in the generation of char, liquid oil,

and gaseous products (Wan *et al.*, 2016; Nam *et al.*, 2018). The resulting char product can serve as activated carbon, while the liquid oil and gaseous byproducts can be utilized as fuel sources for power generation, given their reported high energy content (Lam *et al.*, 2017; Wan *et al.*, 2018). The pyrolysis procedure can be fine-tuned to enhance the yield of specific products by adjusting key process parameters like pyrolysis temperature and residence time (Lam *et al.*, 2018; Liew *et al.*, 2018). Pyrolysis can also serve as a method for generating cross-linked carbon nanofibers (Wu *et al.*, 2013). Nevertheless, pyrolysis entails substantial energy consumption, necessitating operation at elevated temperatures reaching up to 900 °C (Lam *et al.*, 2016). Throughout the pyrolysis process, intricate organic structures comprising biomass progress through a sequence of decomposition stages. This sequence commences with the liberation of moisture and subsequently advances to the breakdown of hemicellulose, cellulose, and lignin components (Yang *et al.*, 2007). Research findings indicate that hemicellulose is the first to break down, between 220 and 315 degrees Celsius (Yang *et al.*, 2007). Then, at higher temperatures, cellulose decomposes between 315 and 400 degrees Celsius, followed by lignin at the most extreme temperature, around 900 degrees Celsius. Notably, an intriguing observation emerges: a substantial carbon nanofiber yield (reaching up to 75 wt%) can be achieved within a brief processing timeframe (approximately 1 h), eliminating the necessity for a stabilization phase. (Bernd *et al.*, 2017; Wu *et al.*, 2013). This phenomenon arises due to the nature of pyrolysis, where cellulose undergoes an endothermic reaction and hemicellulose and lignin engage in exothermic reactions. These reactions possess the capability to cleave the chemical bonds within the functional groups of biomass compounds (Yang *et al.*, 2007). Utilizing pyrolysis within an inert argon atmosphere at a temperature of 700 °C, bacterial cellulose has been transformed into carbon nanofibers characterized by a remarkably diminutive diameter of 20 nm and an exceptionally low density of 4 mg cm<sup>-3</sup> (Wu *et al.*, 2012). The outcomes observed have contributed to the noteworthy electrical conductivity of the carbon nanofibers, reaching 20.6 S/m. This outcome implies that carbon nanofibers

fabricated through pyrolysis techniques hold significant promise for utilization as electrodes within energy storage devices.

This is achieved through a technique termed "microwave pyrolysis," which combines conventional pyrolysis with microwave irradiation (Zhang *et al.*, 2018). The utilization of microwave pyrolysis resulted in the formation of hollow carbon nanofibers characterized by lengths spanning from 1400 to 5000 nm (Zhang *et al.*, 2018). The unique hollow structure of the carbon nanofibers produced by microwave pyrolysis can

be explained by two key factors: hot spots and pressure. Microwaves create "hot spots" within the biochar, which act like tiny furnaces, breaking down the pine nut shells (pyrolysis). Additionally, during this process, the shells experience high internal pressure compared to their surroundings. This pressure forces volatile materials out through tiny pores like air bubbles rising in water. These escaping components leave behind the hollow, nanofiber tips that we see in the final product. Figure 3 below illustrates the process for a full pyrolysis route from precursor to activated carbon.



**Figure 3:** Schematic diagram describing nanofiber formation using pyrolysis technique.

### Hydrothermal Treatment

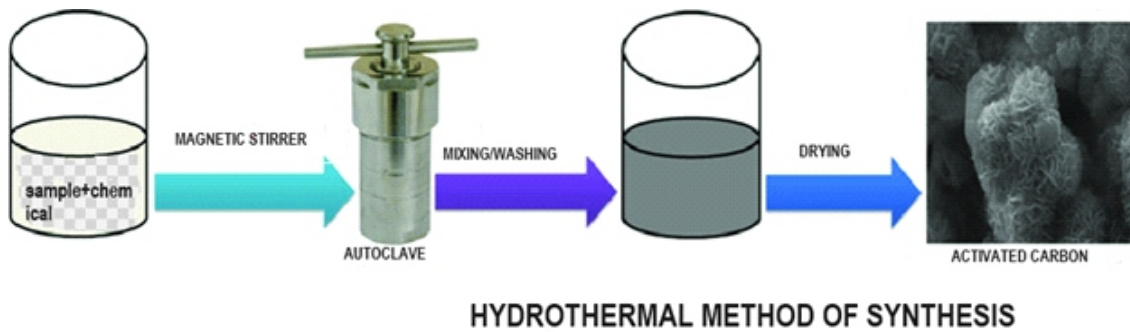
Hydrothermal treatment encompasses a thermochemical conversion process wherein biomass undergoes transformation in the presence of subcritical water (Funke *et al.*, 2010; Yan *et al.*, 2017). Subcritical water denotes water existing in a state within the temperature range of 100 to 374 °C and under pressures exceeding 1 MPa. (Ramos *et al.*, 2002). Through hydrothermal treatment at a subcritical water temperature of 180 °C, the oxygen and hydrogen content of carbon nanofibers is reduced via hydrolysis (Funke *et al.*, 2010). Water in hydrothermal treatment serves as a catalytic medium, dissociating into H<sup>+</sup> and OH<sup>-</sup> ions, generating reactive free radicals capable of breaking down bonds like hydrogen, ether, and ester bonds that constitute the complex structure of biomass. Despite hydrothermal treatment's advantage of lower processing temperatures

compared to pyrolysis, it necessitates a prolonged holding time exceeding 8 h, leading to increased electricity consumption as opposed to the electrospinning process (Deng *et al.*, 2017). Hydrothermal treatment has been successfully applied to bacterial cellulose at a relatively mild temperature of 180 °C for 12 h, resulting in the production of carbon nanofibers. Intriguingly, this treatment approach has demonstrated its efficacy in introducing heteroatoms to bacterial cellulose, thereby generating more active sites on its surface. This augmentation subsequently enhances the capacitive behavior of the resulting carbon nanofibers.

Research outcomes indicate that the N-doped bacterial cellulose-derived carbon nanofibers achieved through hydrothermal treatment exhibit a smaller diameter and a higher specific

capacitance in comparison to those derived from pyrolysis treatment. Specifically, these nanofibers attain a diameter of 10 nm and a capacitance of 254 F/g, surpassing the 20 nm diameter and 77 F/g capacitance exhibited by bacterial cellulose carbon nanofibers synthesized via pyrolysis (Chen

*et al.*, 2013). The findings affirm that hydrothermal treatment can yield carbon nanofibers endowed with enhanced properties suitable for utilization in energy storage applications. Figure 4 below illustrates the process for a full hydrothermal route from precursor to activated carbon.



**Figure 4:** Schematic diagram describing nanofiber formation using hydrothermal technique.

### Ultrasonication

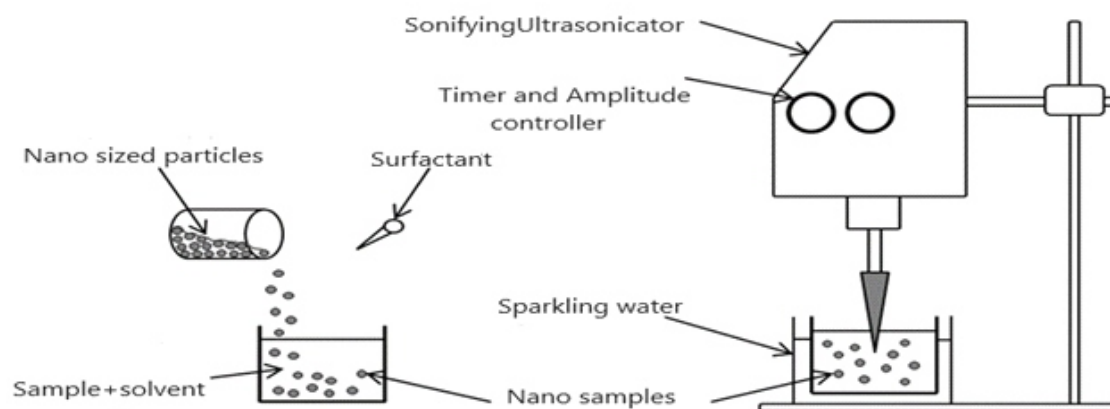
By treating biomass, it is possible to obtain micro-sized cellulose fibers through the elimination of hemicellulose and lignin. Ultrasonication, on the other hand, is a synthesis method employed for material degradation, utilizing ultrasonic waves with frequencies surpassing 20 kHz, combined with a liquid medium like solvents or polymer melts (Huang *et al.*, 2012; Tajik, *et al.*, 2012). Ultrasonic waves possess a significant energy density, capable of inducing expansions and compressions that lead to the generation of negative pressure within a liquid medium. This process effectively mitigates particle agglomeration within carbon nanofibers, resulting in the production of uniformly dispersed carbon nanofibers (He *et al.*, 2006; Mujuru *et al.*, 2012). Research has indicated that carbon nanofibers exhibiting a high degree of dispersion can yield enhancements in their mechanical strength (He *et al.*, 2006). Nevertheless, the utilization of ultrasonication on biomass for carbon nanofiber production remains a relatively novel technique, and the available studies on this approach are limited. Notably, oil palm empty fruit bunches and wood powder have been subject to modification employing a combination of chemical treatment and ultrasonication. This treatment strategy yielded fiber sizes of 83 nm and 30 nm for oil palm empty fruit bunches and wood powder, respectively (Chen *et al.*, 2011; Kojima *et al.*, 2018). The process of ultrasonication can be employed to transform the micro-sized fibers into

individualized nanofibers. This is achieved by disrupting the strong hydrogen bonding and mitigating fiber agglomeration through the application of ultrasonic energy (Kojima *et al.*, 2018). A recent investigation was conducted by (Deng *et al.*, 2018), in a recent study, researchers undertook an experiment involving a blend of commercial biomass cellulose and multi-walled carbon nanotubes, subjecting them to an ultrasonication process lasting 8 h. This was subsequently followed by electrospinning and carbonization procedures. The study's authors asserted that the incorporation of carbon nanotubes (at a concentration of 6%) coupled with ultrasonication resulted in significant improvements in the diameter, electrical conductivity, and specific capacitance of the resultant cellulose-derived carbon nanofibers. Specifically, the diameter increased to 100 nm, electrical conductivity rose to 1255 S/m, and the specific capacitance elevated to 145 F/g, compared to conditions without ultrasonication (where the values were 230 nm, 1010 S/m, and 105 F/g, respectively).

The presence of multi-walled carbon nanotubes helped in creating smaller carbon nanofibers by reducing the energy required (activation energy) for a key step in the process. This lower energy (from 230 to 180 units) made it easier to break specific bonds (C=O and C-O) in the cellulose during a stage called carbonization, leading to the formation of narrower carbon nanofibers (Deng

*et al.*, 2018). Consequently, the study unveiled that achieving effective dispersion between cellulose and multi-walled carbon nanotubes through ultrasonication has the potential to enhance the properties of carbon nanofibers intended for energy storage applications. Nonetheless, it should be noted that prolonged ultrasonication

beyond the optimal duration may lead to structural impairment of the carbon nanofiber and a subsequent reduction in its mechanical strength. Figure 5 below illustrates the process for a full ultrasonic route from precursor to activated carbon.



**Figure 5:** Schematic diagram describing nanofiber formation using ultrasonication technique.

### Electrospinning

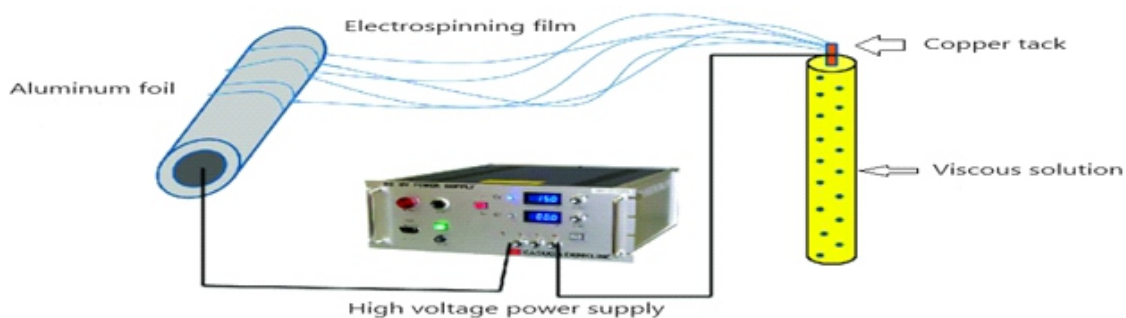
Electrospinning serves as an efficient technique to produce coconut shell nanofibers, yielding diameters below 100 nm (Matthews *et al.*, 2002). The typical process entails the utilization of a voltage supply, a capillary tube, and a metal collector (Huang *et al.*, 2003). To create carbon nanofibers derived from coconut shell, the initial step involves subjecting the coconut shell material to chemical treatment to yield coconut fiber. This coconut fiber is subsequently combined with a polymer solution and introduced into a capillary tube. During the electrospinning procedure, the surface tension of the fiber solution (characterized by fiber diameter sizes greater than 10  $\mu\text{m}$ ) is controlled within the capillary tube (Doshi *et al.*, 1995). Upon exposure to an electric field, the surface of the fiber solution undergoes electric charging, which subsequently triggers instability and charge repulsion dynamics between the fiber solution and the surface tension present within the capillary tube (Huang *et al.*, 2003). Subsequently, when the electric field attains its critical intensity, the fiber solution is expelled from the spinneret, generating a stream of fiber solution. This stream experiences a sequence of events, including instability, elongation, and evaporation as it nears the metal collector. Ultimately, this process culminates in the

formation of an interlinked network comprised of small, elongated, and slender nanofibers (Huang *et al.*, 2003). The diameter of the coconut-based nanofibers can be readily tuned through the manipulation of parameters such as the applied voltage, solution flow rate, molecular weight, and the spatial separation between the nozzle and the metal collector (Theron *et al.*, 2004). Nevertheless, the acquisition of these nanofibers can only be achieved at a notably low electrospinning rate of 25 mL/h. (Matthews *et al.*, 2002). Subsequently, the generated nanofibers undergo a stabilization process via carbonization carried out at elevated temperatures surpassing 600  $^{\circ}\text{C}$ , leading to the creation of coconut-derived carbon nanofibers (Show *et al.*, 2012). Scholars have extensively investigated the integration of coconut shell in conjunction with polymers like polyethylene oxide, resulting in the generation of activated coconut shell nanofibers exhibiting an interconnected web architecture. This web structure serves as a continuous conduit for ion transportation, thereby enhancing the overall energy storage performance. Additionally, the incorporation of polymers contributes to an enhancement in the viscosity and spinnability of the fiber solution throughout the electrospinning procedure (Lai *et al.*, 2014). An additional investigation conducted by a different group of

researchers (Tao *et al.*, 2018), this study exhibited the production of carbon nanofibers derived from coconut shell, featuring a diameter of 100 nm. Lignin and polyvinyl alcohol (PVA) were employed in the fabrication process. Remarkably, an elevated lignin/PVA weight ratio was associated with the formation of carbon nanofibers characterized by reduced diameter and heightened specific surface area. Consequently, these alterations led to an enhanced specific capacitance reaching up to 64 F/g. This effect was observed through electrospinning utilizing waste material.

In an independent investigation, walnut shell material underwent liquefaction through the utilization of phenol for 1 h. This was followed by

subsequent resinification utilizing formaldehyde, carried out for 2 h. Subsequently, the liquefied solution was combined with polyvinyl alcohol before engaging in the electrospinning process. This addition of polyvinyl alcohol served to enhance the solution's fluidic properties and its electro-spinnability, ultimately leading to the production of carbon nanofibers with smaller diameters, ranging from a minimum of 287 nm. (Tao *et al.*, 2018). The characteristics of coconut shell-derived carbon nanofibers acquired through the process of electrospinning can be augmented by incorporating polymers into the fabrication process. Figure 6 below illustrates the process for a full electrospinning route from precursor to activated carbon.



**Figure 6:** Schematic diagram describing nanofiber formation using electrospinning technique.

**Table 4:** Various techniques used in coconut nanofiber synthesis.

<i>Criteria</i>	<i>Pyrolysis</i>	<i>Hydrothermal treatment</i>	<i>Ultra sonification</i>	<i>Electrospinning</i>
<b>Operational time</b>	Small	Extended	Small	Extended
<b>Fabricating temperature</b>	High	Minimal	Minimal	Minimal
<b>Liquid infusion</b>	No	Solvent polymer solution	Solvent polymer solution	Solvent polymer solution
<b>Medium yield of carbon nanofiber</b>	High	Low	High	Low
<b>Diameter adjustment</b>	Hard	Rigid	Rigid	Rigid
<b>Pretreatment</b>	Chemical treatment	No	Chemical treatment	Chemical treatment
<b>Post treatment</b>	Nil	Nil	Carbonization present	Nil

Table 4 unlocks the secrets behind creating coconut nanofibers, microscopic fibers with valuable properties. Choosing the right technique depends on the desired outcome. For instance, pyrolysis and electrospinning are fast, low-temperature methods offering a high yield of nanofibers, though with limited diameter control. Hydrothermal treatment and ultra-sonication, while slower and requiring higher temperatures, also offer a high yield but with less control over diameter. Electrospinning, however, allows some control over diameter but produces a lower yield.

## CONCLUSION

While there have been several studies on supercapacitors, the use of coconut shells as a source of carbon nanofiber for supercapacitor applications has only recently gained attention. Nonetheless, there remains a scarcity of comprehensive knowledge concerning the transformation of coconut shells into carbon nanofibers, impeding the expansion of supercapacitor applications using this resource. Presently, a deficiency exists in comprehending the intricacies of the structure inherent to carbon nanofibers derived from coconut shells, as well as the technical insights essential for enhancing supercapacitor devices fashioned from this substance. Multiple methodologies have been devised for generating carbon nanofibers from coconut shells; however, each approach possesses its distinct advantages and limitations. There's still work to be done in perfecting the process of using coconut shells for supercapacitors. It's important to remember that the coconut itself (how old it is, what kind it is, how it was grown) can significantly affect how well the final carbon nanofiber electrodes store energy.

Considering the significant promise that carbon nanofibers hold in elevating the energy storage capabilities of supercapacitors, it is imperative to conduct additional research aimed at fine-tuning the diverse attributes of carbon nanofibers derived from coconut shells. Moreover, efforts must be directed towards upscaling the production methodologies to a level suitable for commercial applications. The ultimate achievement in this endeavor hinges on our adeptness in enhancing production techniques and cultivating a comprehensive understanding of

the fundamental properties intrinsic to coconut shell-derived carbon nanofibers.

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## CONFLICT OF INTEREST

Authors declare that there is no conflict of interest.

## AUTHORS' CONTRIBUTIONS

A.I.I. Conceptualization, Methodology (Material Science Physicist), reviewing and editing turnitin, G.B. and S.P.

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