

Recent Advances in Materials for Supercapacitors

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Abstract

The fluctuating availability of energy sources has encouraged the development of energy storage devices such as supercapacitors. Supercapacitors are good electrochemical energy storage materials that have demonstrated promising efficiencies in diverse applications. They are able to release high power at low energy operating conditions. In this article, we introduce basic knowledge on supercapacitors, their different classifications, and their relevance to material development. We outline the progress made on diverse materials adopted in improving the performance, charge retention, and stability of supercapacitive materials. Finally, we discuss the different methods utilised in obtaining highly stable supercapacitors.

Keywords: supercapacitor; energy storage; electrochemistry; specific capacitance; efficiency; charge retention

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1 Introduction

Great attention has been channelled into developing sustainable energy resources to curb the effects of global warming and other harmful environmental issues [1], [2]. The demand for sustainable and highly efficient energy storage devices has become a necessity for energy storage to occur [3]–[9]. Supercapacitors are energy storing devices that possess unique qualities [10], [11] such as long cyclic stability, less weight, long charge–discharge cycles, non-poisonous, safe operations, and increased power density [12]. They require less maintenance practices [13] and are simple to operate. They are durable, relatively affordable [14], and able to store and release electrical energy at a high speed [15]. Supercapacitors are able to release high power at low energy operating conditions [16]. They store charges at the interface between the electrode and electrolyte and have an electrolyte separating two conducting plates. The transport of ions and electrons occur independent of each other [17]. Their energy storage principle led to the classification of supercapacitors into electrochemical double-layer capacitors (EDLCs) and pseudo-supercapacitors [12], [18] as illustrated in Figures 1a and 1b and outlined in Table 1.

EDLCs adopt an electrostatic charge storage mechanism at the surface [19] and entail the electrode material absorbing and releasing ions during the charging and discharging processes [20]–[22]. The two ionic layers get either adsorbed or desorbed at the interface between the electrode and electrolyte. Pseudosupercapacitors store charges through faradaic processes such as redox reactions with a small time constant [23], [24]. They exhibit more capacitance and energy density values than EDLCs [25]. To increase the electrode performance, large masses should be loaded, and highly reversible surface reactions, stability at the interface, improved energy and power densities, wider potential windows, and chemically stable electrolytes should be adopted [17].

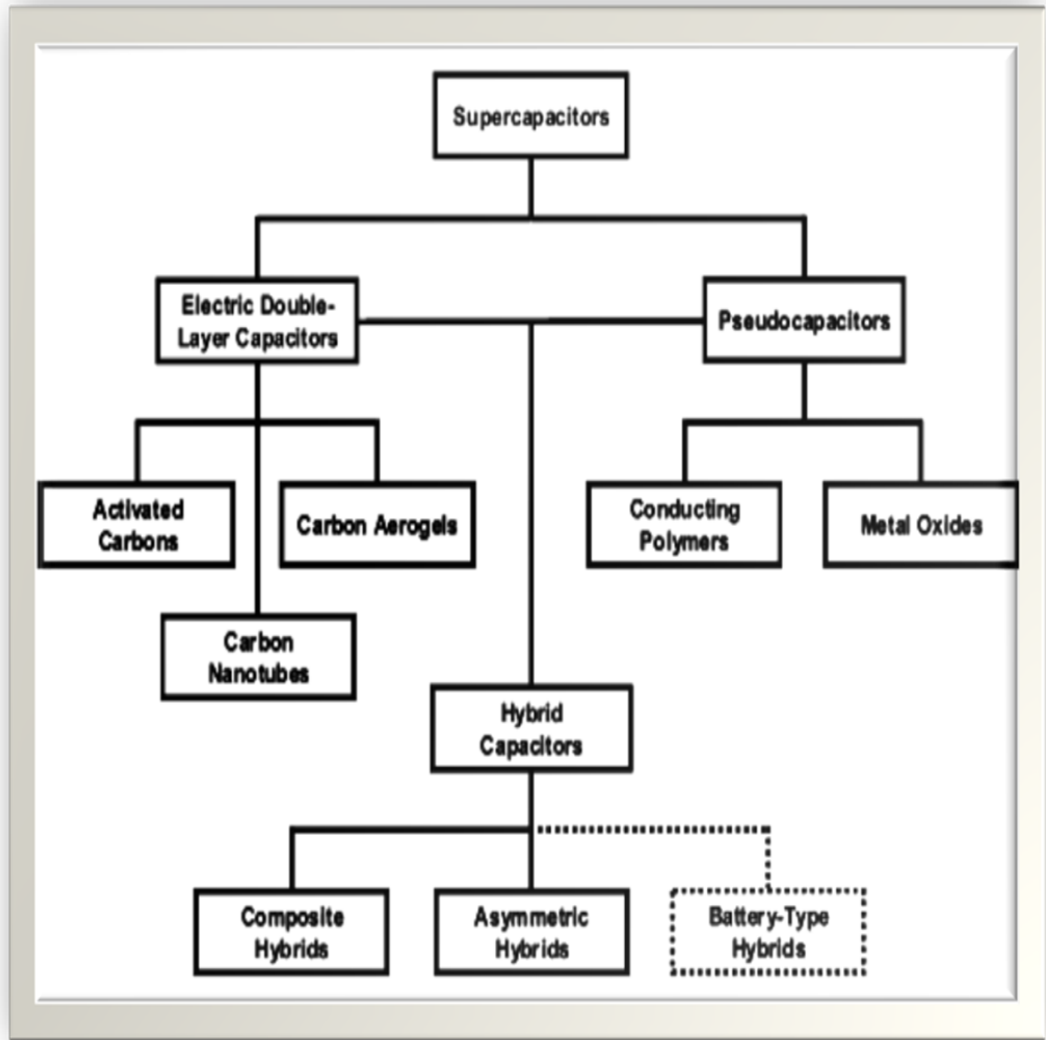


Figure 1a: Schematic diagram showing the various classifications of supercapacitors based on fabrication material used

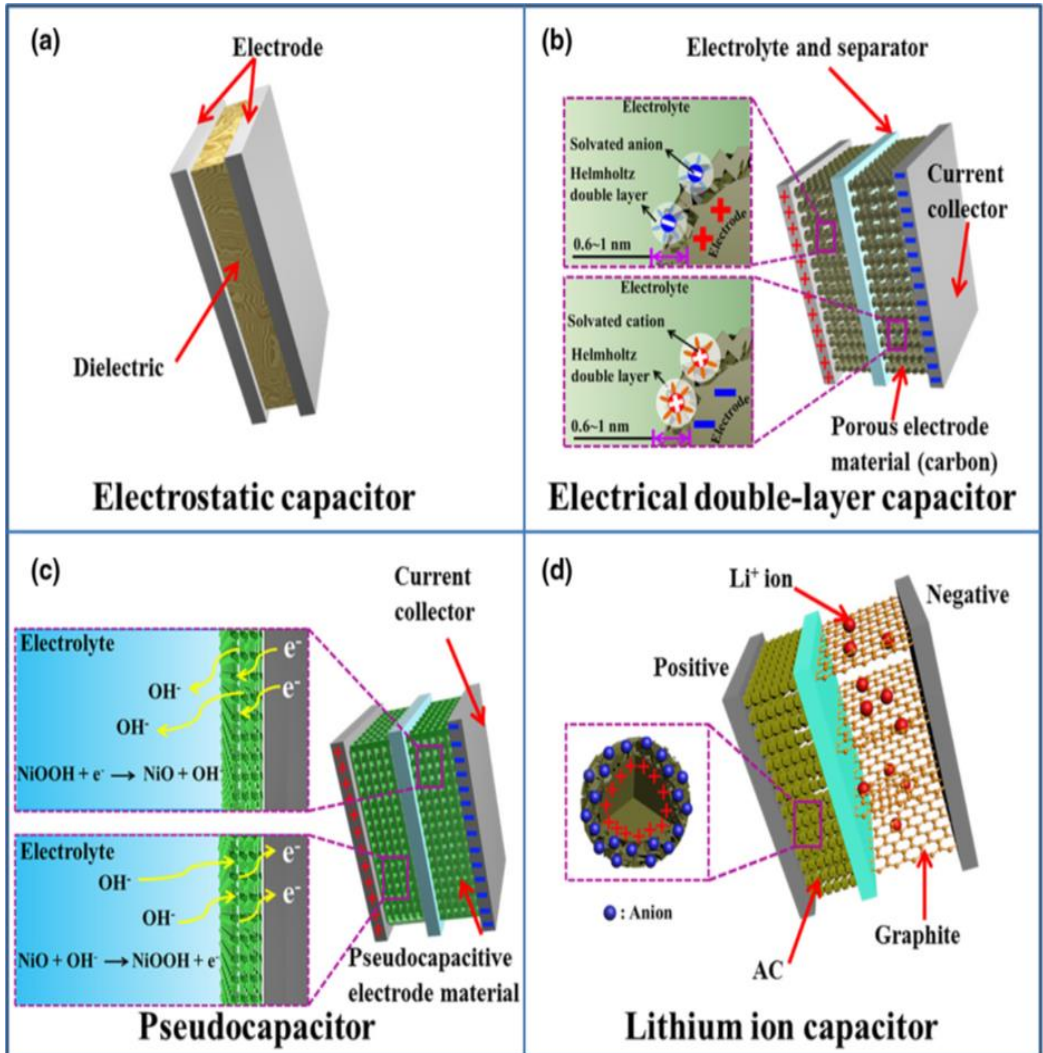


Figure 1b: Diagrams showing the various classifications of supercapacitors based on charge storage mechanism [17]

Table 1: Supercapacitor types, electrode materials, charge storage mechanism, and merits [26]

Types of supercapacitor	Electrode material	Charge storage mechanism	Merits/shortcomings
Electrochemical double-layer capacitor	Carbon	Electrochemical double layer, non-faradaic process	Good cycling stability, low specific capacitance, low energy density
Pseudocapacitor	Redox metal oxide or redox polymer	Redox reaction, faradaic process	High specific capacitance, relatively high energy density, relatively low-rate capability
	Asymmetric hybrid	Anode: pseudocapacitance materials; cathode: carbon	High energy density, high power density, and good cycle ability
Hybrid capacitor	Symmetric composite hybrid	Redox metal oxide/carbon or redox polymer/carbon	High energy density, moderate cost, and moderate stability
	Battery-like hybrid	Anode: Li insertion material; cathode: carbon	High energy density, high cost, and requires electrode material capacity match

Low energy density is a major challenge facing supercapacitors [27]–[32]. Energy density gives the quantity of energy stored per unit mass, whereas power density measures the amount of power released per unit mass. To elevate energy density values, the capacitance and voltage values of the cell can be increased by optimising the interface between the electrolyte and active material [33]. The composition and structure of electrode materials are tunable in modifying their electrochemical and physical characteristics. New electrode materials with high transport mobility of ions should be designed [34], [35]. Inorganic nanoparticles embedded into polymer matrix are a good way of minimising loss, reducing cost, improving the low energy density and efficiency of the charge-to-discharge rate of supercapacitors [36]. This causes optimisation of the device as the energy storing ability of the supercapacitor gets increased. The performance of supercapacitors can be estimated using the capacitance through cyclic voltammetry (CV) and galvanostatic charge–discharge methods [17]. The CV scan operates with a linear changing potential applied between the reference and working electrodes to get the specific capacitance and current response values [37]. Supercapacitors have numerous applications such as in hybrid vehicles, portable electronic devices, transport systems, missile developers, memory backup devices, brake pads, and emergency doors [33], [38], [39].

Our prime aim of this review is to study analytically ways of enhancing the energy and power densities of various supercapacitors with the purpose of using them as a primary power source in electronic gadgets and empowering them to efficiently substitute batteries in our contemporary society.

2 Advanced Materials for Supercapacitors

2.1 Metal Organic Frameworks

Metal organic frameworks (MOFs) have demonstrated outstanding performance in different electrochemical energy storage or conversion devices such as fuel cells, supercapacitors and batteries [40], [41]. They have a very wide area of surface, diverse shapes, modifiable structures and different sizes [42]. They also exhibit high specific capacitance, stable cycles and a porous structure [43]. The structural make-up of MOFs leads to diverse classifications such as porous coordination networks (PCN), two-dimensional MOFs (2D-MOFs), entangled MOFs, and emerging MOFs. PCNs have several topologies, simple preparation processes, different structural build-ups, flexible cavities, and vast application areas [44]–[47]. The hybrid system of electrode shown in Figure 2 gives a capacitance of $1\,710\text{ mF/cm}^2$ at a current density of 0.4 mA/cm^2 [48]. Solvothermally prepared Ni/Mn-MOF electrode yielded 67.7% charge retention, increased electrolyte permeation, and specific capacitance of 531.5 F/g [40].

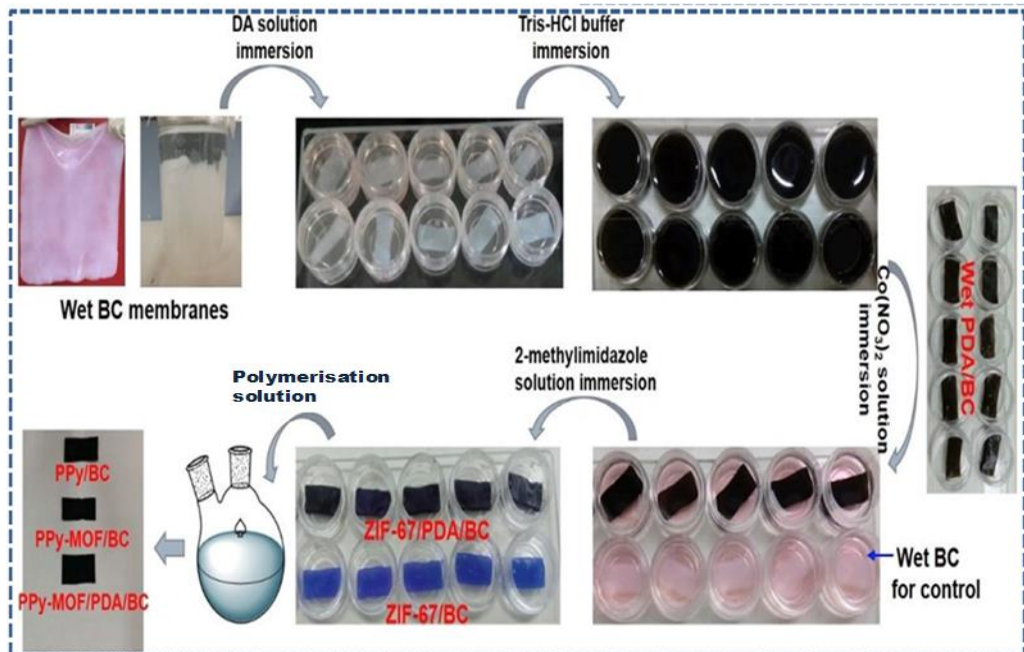


Figure 2: Schematic diagram of membrane electrodes for metal organic frameworks [48]

MOFs doped with nickel and manganese have served as good electrode materials for supercapacitors [12], [49]. Gravimetric and normalised capacitance values of 111 Fg^{-1} and $18 \mu\text{F}/\text{cm}^2$ with high charge retention and good porous surface to enhance energy storage in supercapacitors are shown in Figure 3. Amorphous manganese oxide and its composites are abundant, of green nature, affordable, and of great electrochemical behaviour [50]. Reddy and Reddy synthesised manganese oxide at 400°C via the sol-gel technique [51]. High specific capacitance of 110 F/g , stability over 800 cycles, and amorphous structure were obtained. Replacing the electrolyte (sodium chloride and potassium chloride) with sodium sulfate yielded no capacitive behaviour. Xu et al. synthesised manganese oxide electrodes that are thermally stable with a wide area of surface and narrow pore sizes [52].

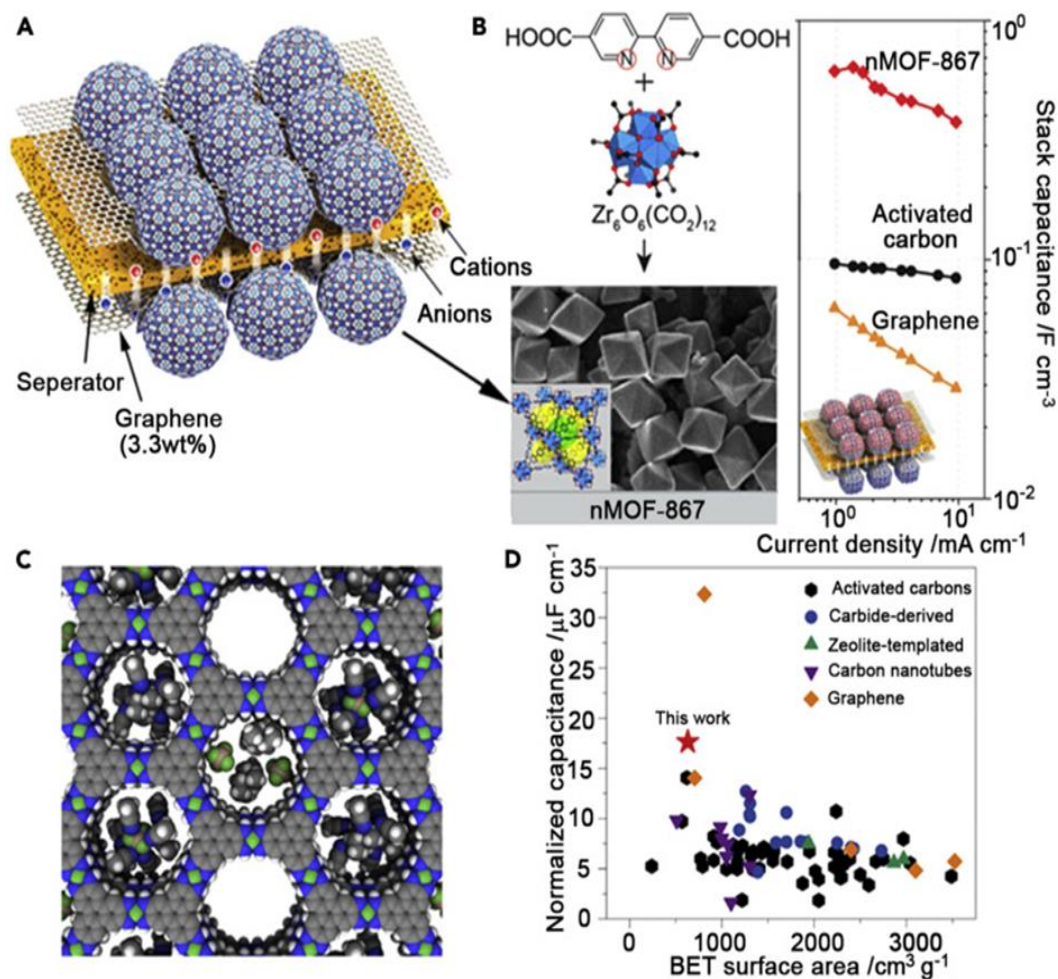


Figure 3: Experimental results for metal oxide fluorides as electrode materials [12]

Hu et al. synthesised nanocomposite of $\text{MnO}_x/\text{MnOOH}$ via the pulse galvanostatic technique [53]. The materials exhibited a better electrochemical property with a specific capacitance of 1 659 F/g at a current density of 2 A/g. The synthesis and formation processes for the composite development are illustrated in Figure 4.

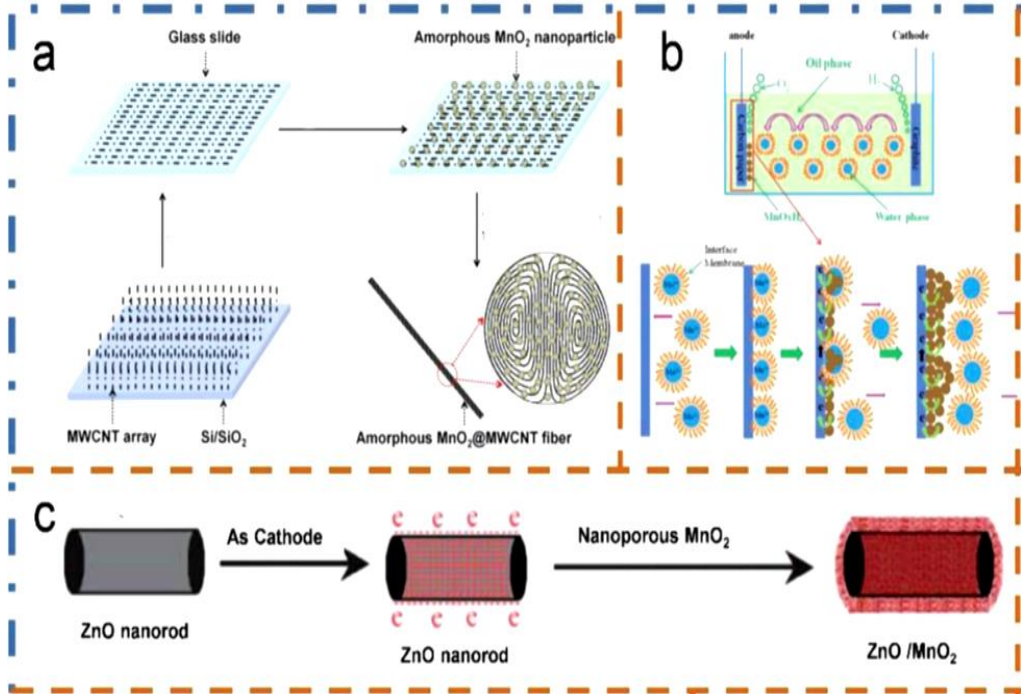


Figure 4: Schematic on the synthesis procedures carried out in the MnO_2 composite preparation [53]

2.2 Green Materials

Using green energy has been on the increase to curb environmental pollution and enhance sustainability [17]. Green materials such as residues from agriculture, animal waste, microbial organisms, and other accumulations from the surroundings have been recently implored in developing active electrodes for supercapacitors [54]. These green materials which are rich in carbon have excellent features such as high porosity, wide area of surface, and are highly electrically conductive, mechanically strong, and easy to process [55], [56]. Their porous nature supports transportation of ions and increased capacity for storing charges. These materials can be harnessed and recycled to eliminate the negative effects of toxicity on the environment [54]. Carbon materials made from biomass (plant-based matter, animal dung, microorganisms) have proved to be good energy storage materials because they are environmentally friendly and naturally abundant [57]. They also have structures with porosity that encourages ion absorption and charge storage.

The morphology of carbon-based biomass materials is a function of the amount of carbon (graphene) incorporated into the host matrix. The electrochemical feature and performance of such an electrode can be predicted using data mining technology [57]. Introducing some degree of graphitisation is a means of enhancing electrochemical performance, minimising resistance internally, and increasing power output and carrier mobility [58]. Graphitisation can be achieved through thermal pyrolysis and catalyst introduction. Top-down and bottom-up approaches can be adopted to get binder-free carbon materials from biomass [59]. Some of the biomass-derived carbon precursors are represented in Figure 5. Upgrading biomass materials by introducing cellulosic residue (hemp) via hydrothermal carbonisation is a good way of developing cheap and sustainable energy [60]. The use of green materials produces clean energy with increased charge retention and high specific capacitance values [61].

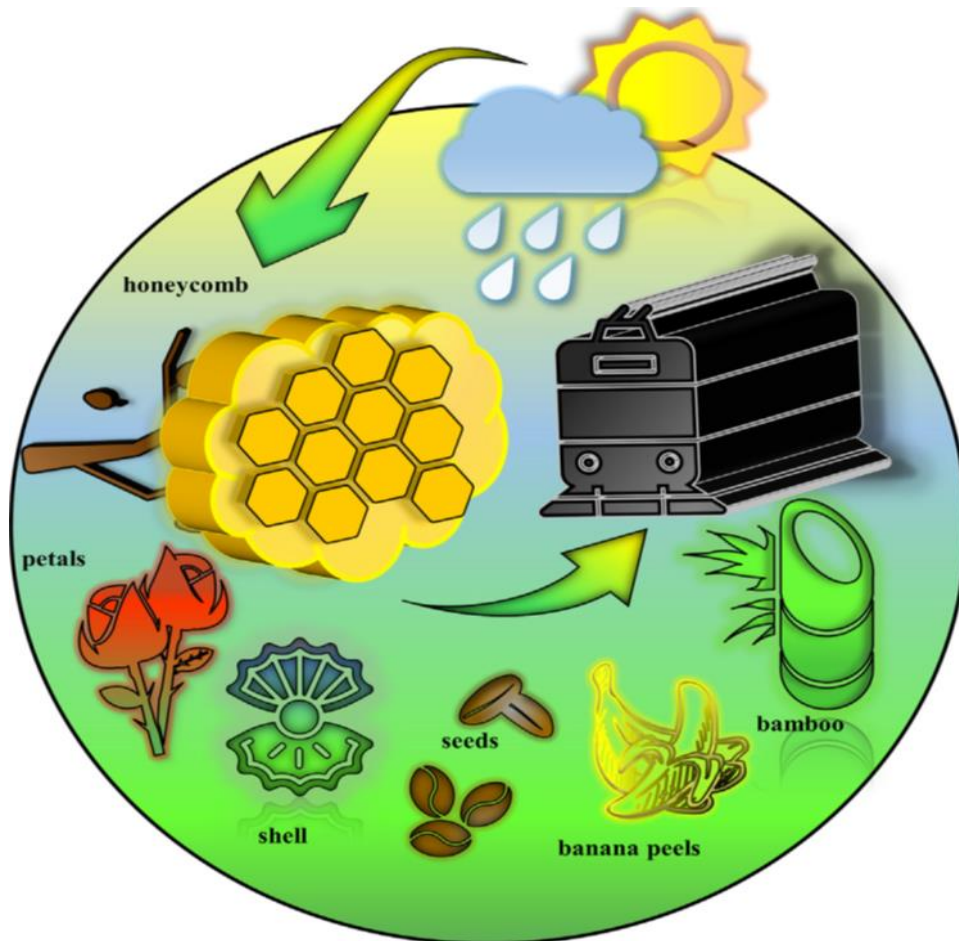


Figure 5: Schematic diagram showing diverse carbon precursors for biomass-derived materials [59]

Biomass materials are very abundant, relatively cheap, eco-friendly and renewable energy sources. Plant-based biomass is made of ligno-cellulose and comprises the seeds, flowers, fruits, stems and leaves of plants. The lignin acts as a good electrode precursor material for supercapacitors [62]. Biomass obtained from microorganisms involves bacterial cellulose as precursor material. The growth process as seen in Figure 6 involves forming a three-dimensional network of microorganisms upon synthesis by diverse means. This stacked network was synthesised via hydrothermal and carbonisation techniques with high charge storage ability exhibited [63].

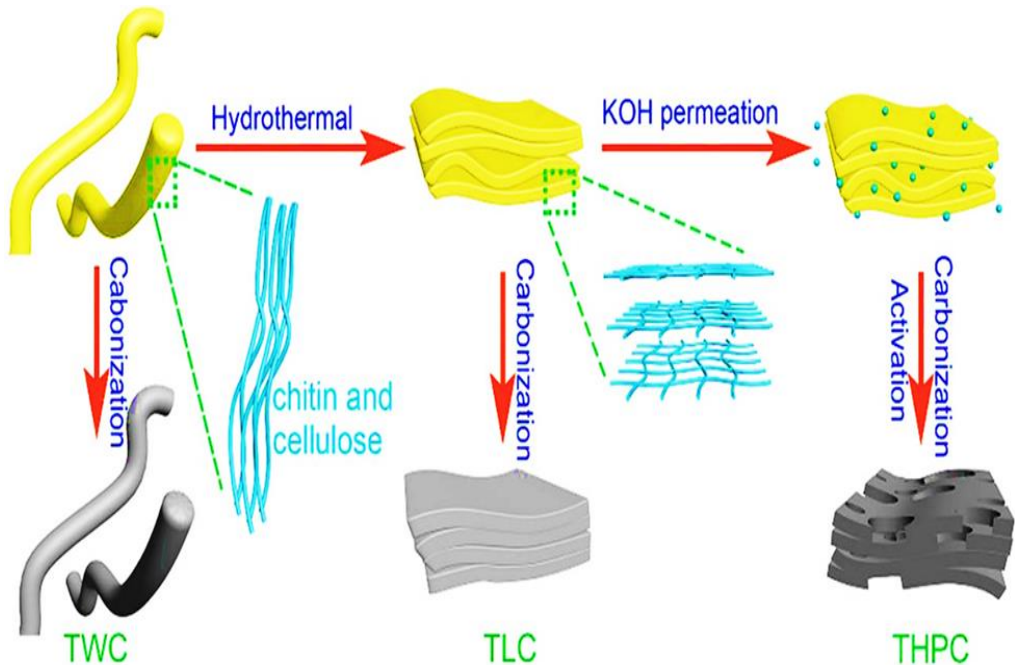


Figure 6: Schematic representation of the preparation procedures in forming stacks of carbon sheets [63]

Wang et al. adopted biomass cornstalk under ambient temperature using neutral salt as activating reagents [64] as shown in Figure 7. Neutral salts such as sodium chloride and potassium chloride minimised burning of the cornstalk and increased the concentration of chloride ions [64]. The chloride ions aided tissue etching and porous structure formation. The synthesised corn stalk recorded a thickness of approximately 4.6 mm, a wide specific surface area of 1 588 m²/g, specific capacitance of 407 F/g, and charge retention of about 2×10^4 cycles.

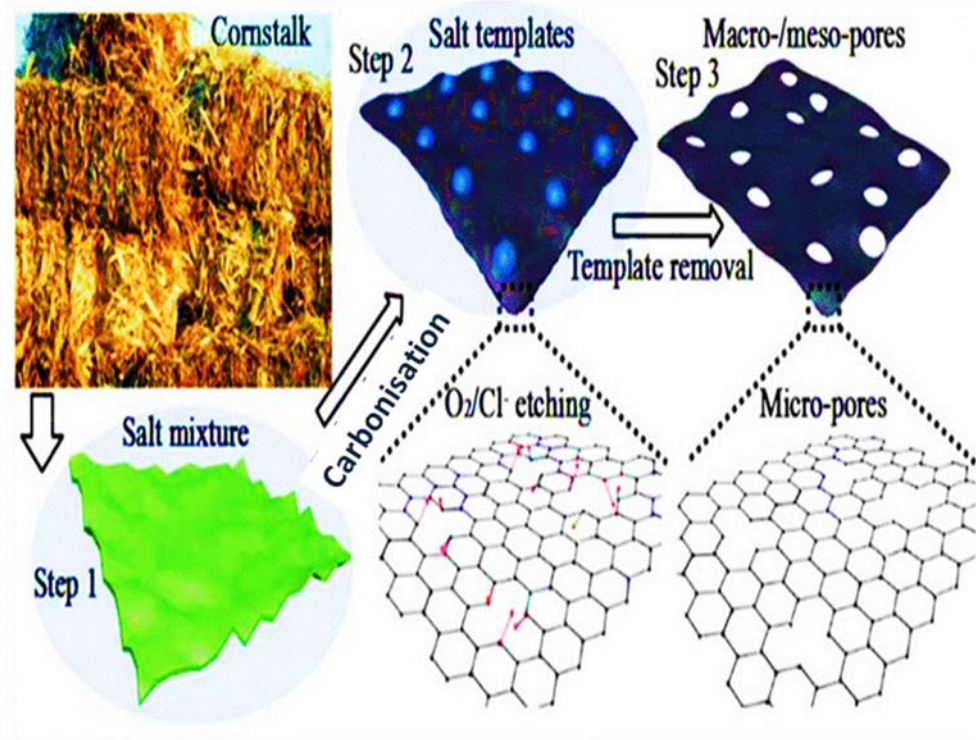


Figure 7: Schematic on cornstalk structure when exposed to ambient air [64]

2.3 Nanofibers

Nanofibers are desirable in supercapacitors because they exhibit increased electrochemical characteristics and can be easily integrated into flexible and conductive materials [14]. Cellulose-based nanofibers are biodegradable, thermally stable, mechanically strong, and exhibit a high surface area, porous nature and flexible structure [65]. Fibrous electrodes enhance ionic transport and increase the electrochemical performance of supercapacitors. Electrolytes made of cellulose perform dual functions as electrolytes and separators [65].

2.4 Carbon Materials

Supercapacitor electrodes made of carbon aid self-healing activities of supercapacitors [66]. These self-healers strengthen the structure and electrical performing ability when it undergoes mechanical faults [12]. Carbon nanotubes (CNTs) exhibit a wide area of surface, and are less dense, chemically stable, and electrically conductive [67] with great physicochemical features [68], [69]. Multi-walled CNTs have reduced the density of mass and greater power density than single-walled CNT. They have different molecular networks bonded by hydrogen force that exhibit self-cleaning features as shown in

Figure 8. This feature links the cut surfaces at the edges when damage occurs and still retains the capacitive properties of the carbon material.

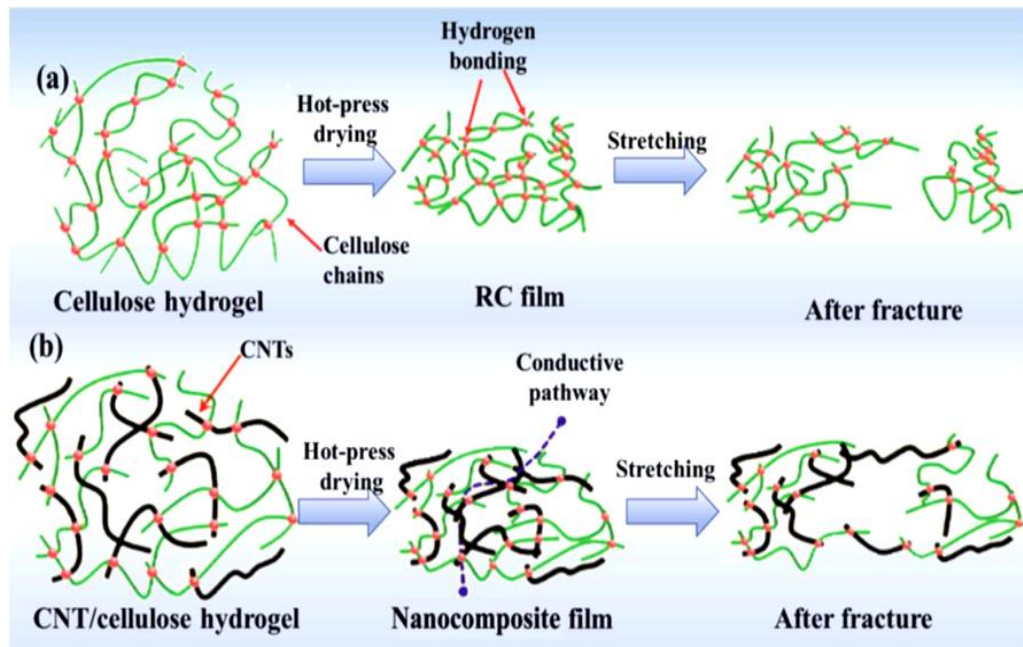


Figure 8: Schematic illustration of (a) reduced carbon and (b) nanocomposite of CNT [70]

Electrolytes with self-healing attribute have conductive ions that are created through cross-linking of hydrogen bonds. Such electrolytes have excellent performance when compared to other non-carbon materials. Graphene-based polymers are also useful electrodes in pseudocapacitors and double-layer capacitors [16]. Carbon materials can be integrated into cellulose matrix to improve the electrical conductivity [70], [71]. Carbon matrix has high conductivity and stability with small specific capacitance values. The soluble template method was used to synthesise salty seaweed as a carbon precursor in supercapacitors [72]. The soluble method is a water-soluble method that is good for controlling the carbon structure as it yields carbon materials with reduced surface energy. Figure 9 shows that introducing the template elevated the surface energy of the synthesised material. The carbon electrode was rich in oxygen with surface pores and specific capacitance of 324.3 F/g in 1 M of sulfuric acid [72].

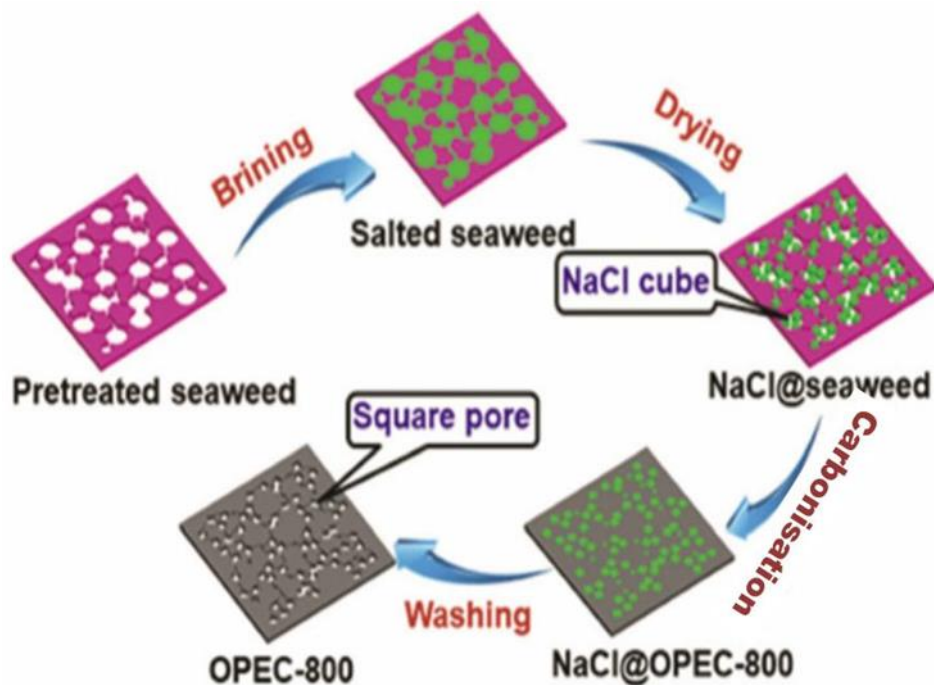


Figure 9: Schematic on the fabrication of carbon materials by the soluble template method [72]

2.5 Hybrid Nanocomposites

Hybrid supercapacitor materials have dual characteristics of electric double-layer capacitors and pseudocapacitors [26]. This gives them better energy density, high power density, and better efficiency [73]. Redox reaction and non-faradaic charge-to-discharge reaction occur at each end of the electrode. Nanocomposites of cellulose and carbon can be designed to be good electrodes in supercapacitors [72], [74]. Hybrid nanocomposites generated from biomass are useful for synthesising carbon materials that would be incorporated into designing advanced capacitors of electric double-layer and hybrid nature [75]. The reflux method has been used to fabricate nanocomposite of reduced graphene oxide/lanthanum oxide by loading the lanthanum oxide onto the reduced graphene oxide sheets [76]. Upon assembling the sheets into a button-type approach as seen in Figure 10, the current density of 0.1 A/g yielded specific capacitance of 156.25 F/g, stable cycles, high charge retention, and efficiency. The hybrid composite of MnS/Co₃S₄ prepared by the ion exchange method recorded specific capacitance of 627 F/g, charge retention at 73.5%, and 93.1% of stable cycles [77]. Nanocomposite of strontium ferrite and graphene synthesised by hydrothermal technique yielded specific capacitance of 681.2 F/g and retained 95% of the initial charge [78]. T_{i3}C₂TX/PEDOT nanocomposite retained 96.5% of its initial charge and recorded specific capacitance,

energy density, and power density of 564 F/g, 6.34 Wh/kg, and 4 077 W/kg respectively [79]. Composite of nickel cobalt sulfide and CNTs encountered high redox activity and excellent conductivity [80]. The composite was an essential component in enhancing the performance and stability of supercapacitors and other energy storage devices [81]–[83].

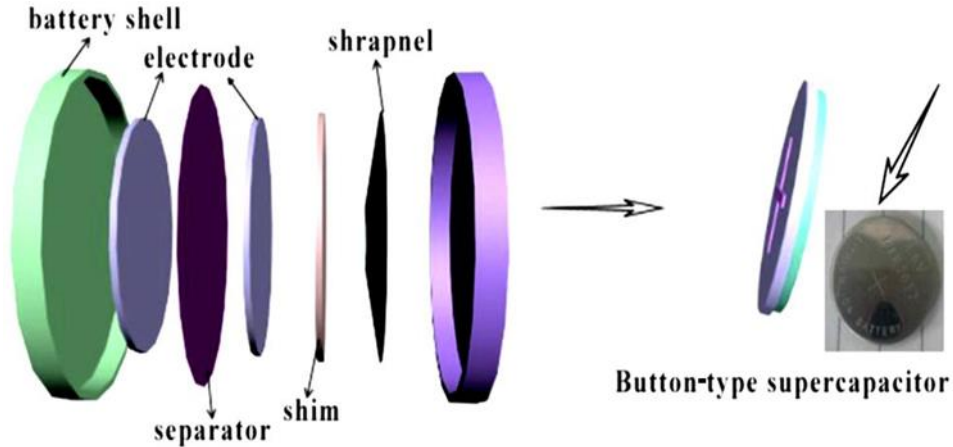


Figure 10: Schematic showing the button-type assembly method [76]

2.6 Metal Oxides

2.6.1 Nickel-Based Materials

Nickel-based materials are good electrodes useful for pseudocapacitive and supercapacitive purposes owing to their elevated theoretical specific capacitance value, affordability, thermal stability, chemical stability, and environmental safeness [17], [84], [85]. These materials usually have capacitance values from 500 F/g to 2 500 F/g. The electrochemical property of nickel-based materials is evident from the peaks of the cyclic voltammograms [86]. Nickel-based materials such as nickel oxide and nickel hydroxide are good supercapacitive materials that usually perform better with potassium hydroxide as electrolyte, exhibit high capacitance value, are affordable, and have minimal environmental hazards [31], [87]. Resin spheres were used to design different nickel oxide layers so that the rate of calcinations and concentration of ions can be regulated [88]. This layered structure was thermally induced from the forces of adhesion and contraction. Abdalla et al. obtained area and gravimetric capacitances of 3.28 F/cm² and 245.3 F/g respectively upon synthesising nanotubes of nickel oxide [89]. Nickel hydroxide usually exists in the alpha or beta phase with the alpha phase exhibiting more capacitance values [90]. Facile co-precipitation and ultrasonication techniques have been adopted in preparing an ink of nickel hydroxide [91]. Specific capacitance of 1 000 F/g was obtained with potential application in supercapacitive electrode devices.

Incorporating nickel-based materials with elements such as carbon, copper, iron, manganese and molybdenum is a great way of increasing their stability and specific capacitance [92], [93]. Carbon materials moderate particle growth, limit the formation of agglomerates, encourage charge transport, and mediate changes in volume during the cyclic tests [94]. Materials such as graphene [95], carbon aerogels, reduced graphene oxide, carbon quantum dots, and CNT are commonly used [96], [97]. Copper is also efficient in forming composites with nickel-based materials because it is affordable, available, highly active, very conductive, and exhibits great physiochemical features [98], [99]. Iron has high specific capacitance value and great electrochemical performance [100]. The morphology and composition of manganese can be easily tuned to yield better electrochemical results [101]. The porous nature of molybdenum enhances charge storage [102], [103]. The specific capacitances of supercapacitive electrode materials are a function of the scan rate, electrolyte, and current density. Decorating nickel oxide quantum dots with graphene nanoflakes resulted in a capacitance of 1 181.1 F/g and current density of 42 Ag⁻¹ [104]. Nickel hydroxide deposited on CNT by chemical vapour deposition technique yielded specific and areal capacitances of 3 300 F/g and 16 F/cm² respectively [105], [106]. Chen et al. processed nickel-cobalt-oxide (NiCo₂O₄) by depositing the material on carbon surface as illustrated in Figure 11. The obtained capacitance value was 2 367 F/g while the cyclic voltammograms were rectangular in shape with no prominent redox peak [107]. The high capacitance value obtained was attributed to the introduction of nickel nanoparticles [108].

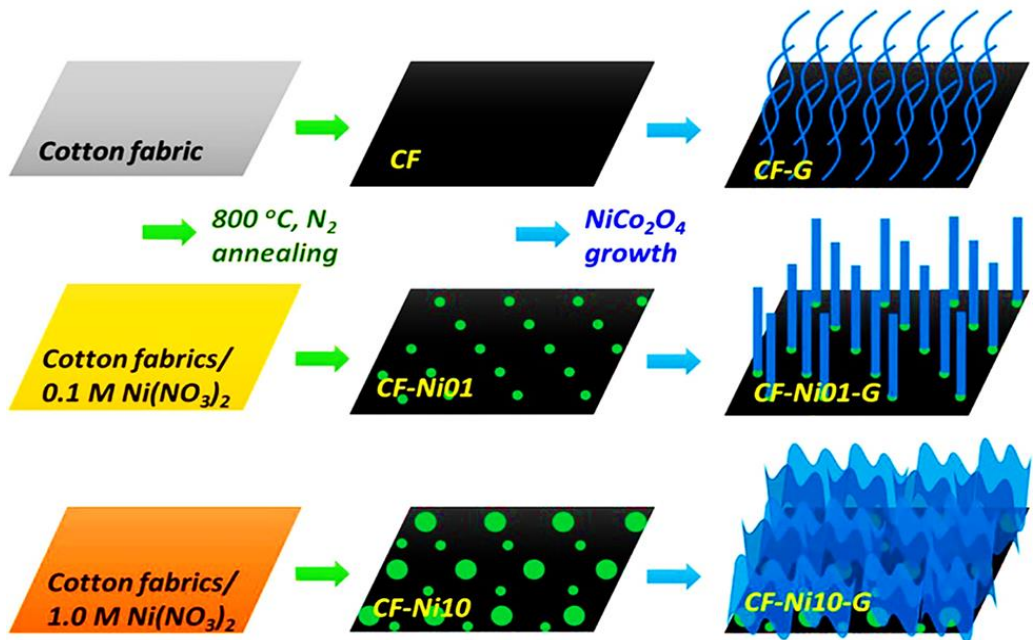


Figure 11: Synthesis processes of NiCo₂O₄ on carbon substrate [107]

2.6.2 Cobalt-Based Materials

Cobalt oxide (Co_3O_4) is a very prominent electrode material for supercapacitors owing to their attractive properties such as high conductivity and good cyclic stability. The literature study revealed that the cobalt oxide thin films have been deposited using chemical bath deposition [16], successive ionic layer adsorption and reaction (SILAR), spray pyrolysis, chemical vapour deposition, spin coating, and pulsed-laser deposition methods [92]–[96]. Various reports have shown that capacitance of Co_3O_4 electrode resulted from the electric double-layer capacitance and pseudocapacitance, which encouraged the usage as supercapacitor electrodes materials [38], [109].

2.6.3 Manganese-Based Materials

Manganese (Mn) exists in various oxidation states. The highest stable oxidation states include Mn (II) and Mn (IV). Mn (II) transforms to MnO when there is abundant oxygen while Mn (IV) changes to MnO_2 and Mn_2O_3 . However, MnO_2 possesses α , β , γ , and δ type polymorphs. Various advantages of manganese-based materials include cheapness, small toxicity, availability and environmental friendliness. In interaction with electrolytic solutions, MnO , MnO_2 and Mn_2O_3 form various oxidation states leading to their high specific capacitance nature. Nevertheless, low electrical conductivities and big volume variations witnessed and reported by many scholars on the course of electrochemical processes using manganese-based materials lead to low rate performance and cyclic instability [97]. The consequence of low rate performance and cyclic instability reduces specific capacitances of manganese oxides based supercapacitors, which prompted scientists to develop new strategies such as the addition of carbon materials and the formation of composites to increase their electrical conductivities, create volume buffers to reduce interior strains and enhance their performances.

2.6.4 Metal/Carbon-Based Materials

Carbon materials in recent uses include fullerenes, graphene and CNTs. These carbon materials are synthesised in the form of materials such as of carbon nano-rod or wire, carbon nano-shell, and nano-cage [98]. Fullerenes contain nanomaterial that is spherical whereas CNTs are tubular in shape as shown in Figure 12. Numerous carbon-based materials such as porous carbon, graphene, carbon fibre, CNT, and carbon network are widely used as supercapacitor electrodes material owing to their high specific surface area, high electronic conductivity, high chemical stability, availability and low cost [99]. In addition, the flexible solid-state supercapacitors based on carbon materials with long cycle life, high power density, environmental friendliness, and safety afford a promising option for energy storage applications [100].

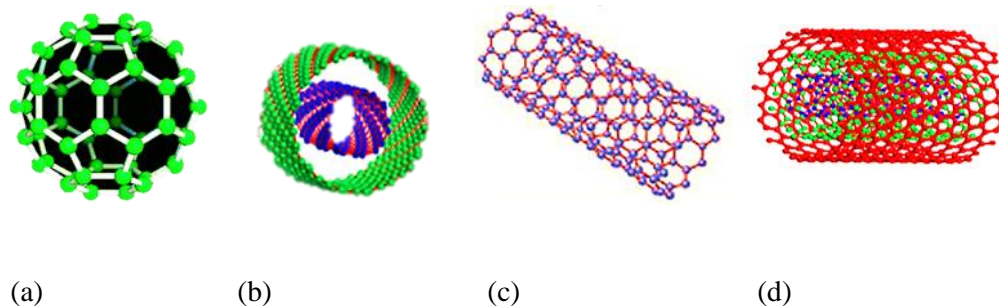


Figure 12: (a) Fullerenes (b) CNTs (c) Wrapped graphene (d) Multi-wall CNTs

Metal oxides/carbon-based composites are currently used for supercapacitor electrodes because they possess better characteristics and performance [110]–[114]. The synergistic effects between these metal oxides and carbon materials produce electrodes with better performance.

2.7 Metal Sulfides

Metal sulfides are useful electrodes that are abundant, affordable, good electrochemical features, and with easy production mechanisms [115]. The merits, demerits and future prospective for metal sulfides are outlined in Figure 13. Metal sulfides, especially transition metal sulfides, are good materials for asymmetric supercapacitors because they are electronically and electrically conductive, undergo redox reversible reactions, and have improved electrochemical performance [116]. Metal sulfides could be non-layered or layered (comprising different layered atoms held together by covalent bonds). The charge transport processes of layered metal sulfides are controlled by the interlayer spacing. Nickel/manganese-sulfide nanoparticles were obtained from Ni/Mn-MOF-74 material via hydrothermal technique for use as supercapacitor electrode [117]. High cyclic performance of 84% and specific capacitance of 2 510 F/g analysed at 1 A/g were obtained. The two-step solvothermal technique was adopted in fabricating multiple composite of $\text{Fe}_{0.92}\text{Co}_{0.08}@\text{NiS}/\text{NiO}$ material [118]. The material exhibited a lamellar structure which created more room for efficient electron mobility and better electrochemical feature. Energy density, specific capacitance, and charge retention of 38.2 Wh/kg, 1 868 F/g at 1 A/g, and 85.3% were recorded after 500 cycles. The fabricated electrodes would be useful in ultracapacitor devices. The synthesis method employed determines the extent of conduction and volume change occurring in metal sulfides [115]. Introducing MOFs and MXene to metal sulfides increases their hydrophilic and conductive nature. In a bid to improving the supercapacitive nature of metal sulfides, the interlayer spacing should be increased, non-corrosive ionic electrolyte be used, and different synthesis methods be adopted in improving the material performance [115].

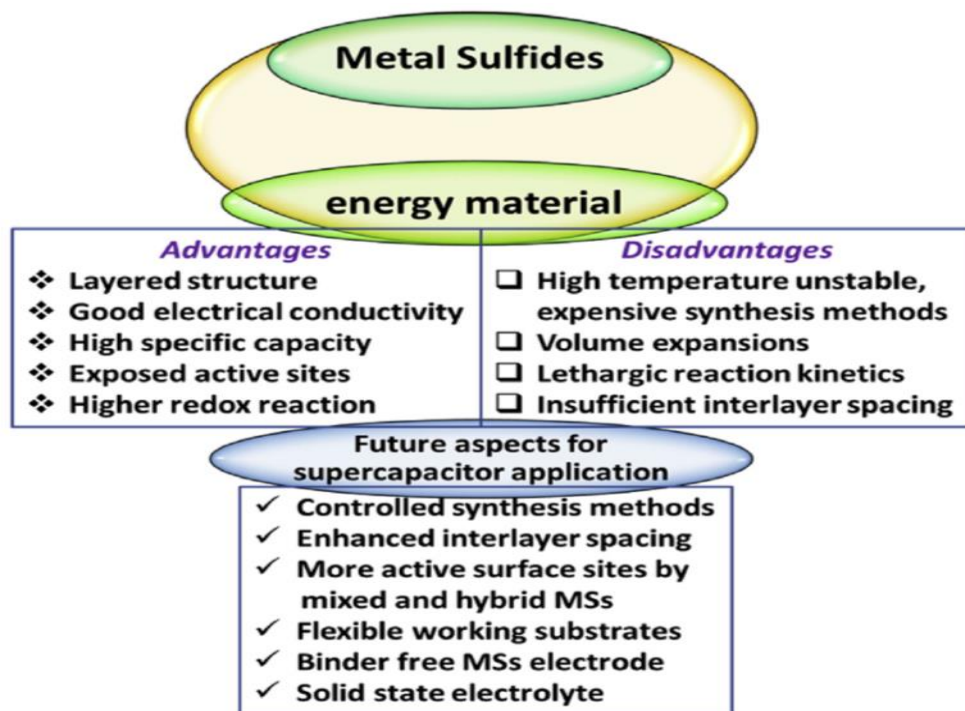


Figure 13: Illustration of the advantages, disadvantages and future aspects of metal sulfides for use in supercapacitors [115]

2.8 Metal Phosphides

Metal phosphides have been considered to be good electrodes because they are relatively cheap and have high metalloid features [119]. Despite their reduced cyclic stability and low energy density, they exhibit excellent electrical conductivity and increased capacity theoretically [120]. The facile potentiostatic technique was adopted in synthesising $\text{Ni}_{0.5}\text{Co}_{0.5}\text{P}$ nanosheet as a binder-free cathode in hybrid supercapacitors [121]. Energy density of 45.2 Wh/kg was delivered at a power density of 800 W/kg and 86.7% charge retention after 10^4 cycles. Electrodeposition and phosphorisation methods were used in synthesising arrays of Fe-Co-Ni-P nanosheet on carbon substrate as shown in Figure 14 [120]. The synergy between the elemental ions led to increased electrical conduction, a wide area of surface, increased redox sites, and specific capacity of 593 C/g.

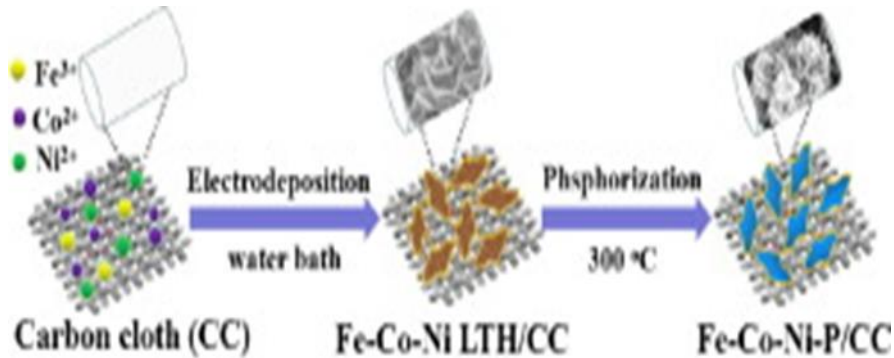


Figure 14: Stages of preparation for the Fe-Co-Ni-P electrode [120]

CoP-Mn₃P nanoclusters were formed by the hydrothermal technique [122]. The heterojunction formed at the interface led to accelerated electron mobility and increased electrode conductivity. Energy density, power density, and specific capacitance values of 46.4 Wh/kg, 800 W/kg, and 2 714 F/g were obtained. One-step phosphorisation was used to synthesise binder-free NiCoP@P-rGO materials hydrothermally for supercapacitor use [119]. The electrode revealed hollow nanohorns in their morphology as seen in Figure 15, charge retention of 72% after 10 000 cycles, specific capacitance of 2 384 F/g, enhanced power density of 8.82 kW, and energy density of 39.7 Wh/kg. The electrodes could be practically applied in electrochemical supercapacitors.

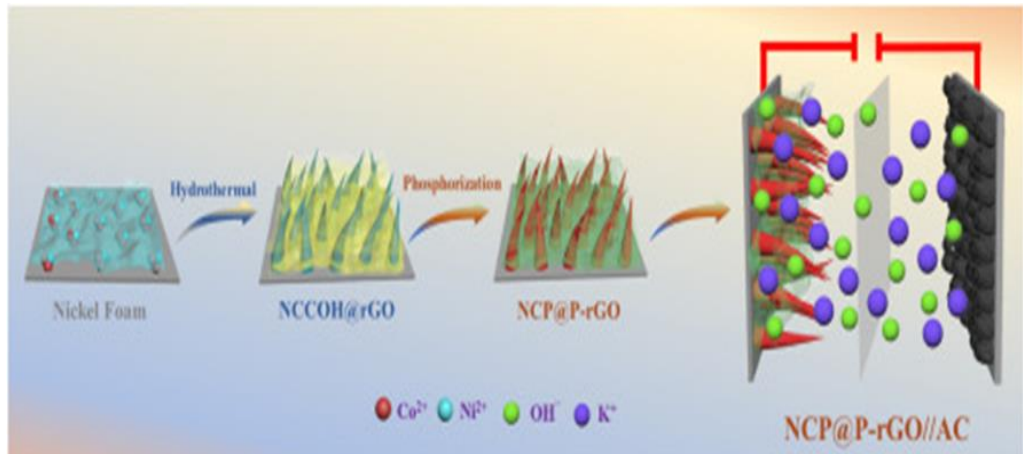


Figure 15: Fabricated NiCoP@P-rGO electrode showing nanohorned morphology and encapsulated into supercapacitor device [119]

The two-step hydrothermal technique accompanied by the phosphorisation process was used in preparing nickel phosphide decorated with nitrogen-doped carbon quantum dots and cobalt oxide for use in energy storage systems [123]. Enhanced electrochemical property, ultracapacitance of 2 088 F/g and energy density of 53.5 Wh/kg were obtained. Binder-free carbon nanofibers@nickel phosphide nanoparticles were prepared via chemical vapour deposition for performance alleviation in supercapacitors as illustrated in Figure 16 [124]. The electrodes exhibited a wide area of surface, enhanced conductivity, specific capacitance of 59.3 mF/cm², energy density of 27.4 Wh/kg, and charge retention of 95% after numerous charge and discharge cycles. Integrating chemical vapour deposited one-dimensional carbon nanofibers with redox electrolyte enhance charge retention, specific capacitance, and energy densities of supercapacitors [124].

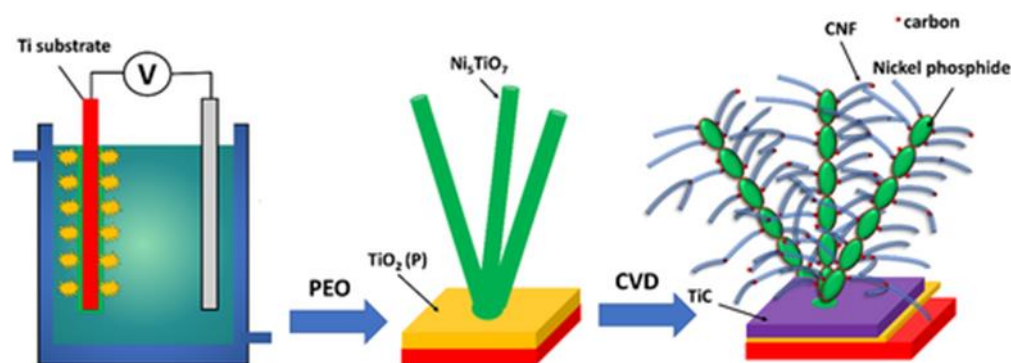


Figure 16: Preparation stages for the CNFs@nickel phosphide nanoparticles on a titanium substrate [124]

3 Conclusion

This work encompasses a mini-review on the use of advanced materials in supercapacitors. We highlighted differences between the various classifications of supercapacitors: EDLCs, pseudocapacitors and hybrid capacitors. We discussed useful advanced materials geared towards improving the charge storage capacity of solar cell devices.

The electrochemical performance, specific capacitance, and stability of supercapacitive materials can be enhanced through modification with suitable materials such as MOFs, green materials, nanofibers, carbon materials, hybrid nanocomposites, nickel-based materials, metal sulfides and metal phosphides. The effects of surface area and porous surfaces should be studied to improve the performance of supercapacitors. Other efficient fabrication methods should be researched. In conclusion, this review should be properly studied to elucidate harmful synthesis practices and encourage sustainable energy development.

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