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REVIEW

Carbon nano-materials (CNMs) derived from biomass for energy storage applications: a review

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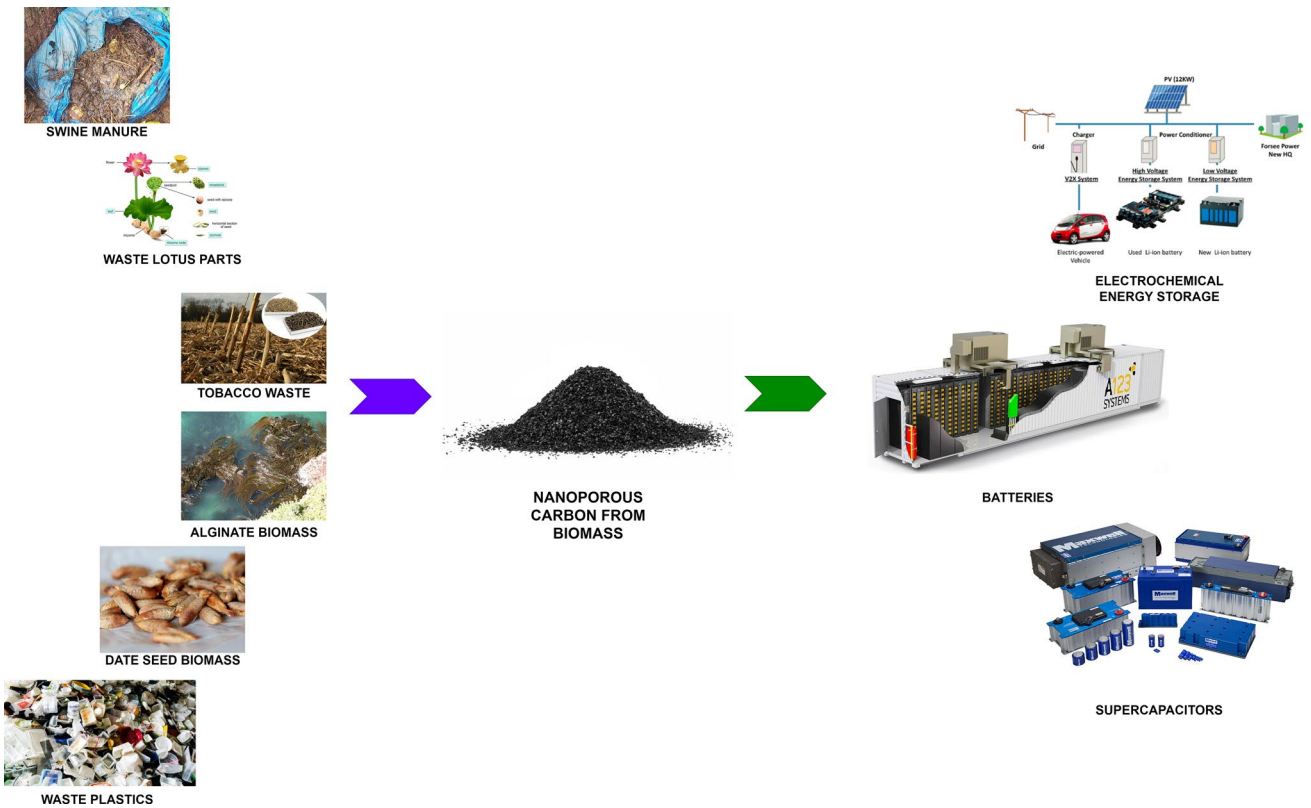
Abstract

In today's world, carbon-based materials research is much wider wherein, it requires a lot of processing techniques to manufacture or synthesize. Moreover, the processing methods through which the carbon-based materials are derived from synthetic sources are of high cost. Processing of such hierarchical porous carbon materials (PCMs) was slightly complex and only very few methods render carbon nano-materials (CNMs) with high specific surface area. Once it is processed, which paves a path to versatile applications. CNMs derived from biological sources are widespread and their application spectrum is also very wide. This review focuses on biomass-derived CNMs from various plant sources for its versatile applications. The major thrust areas of energy storage include batteries, super-capacitors, and fuel cells which are described in this article. Meanwhile, the challenges faced during the processing of biomass-derived CNMs and their future prospects are also discussed comprehensively.

Graphical abstract



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Keywords Biomass · Carbon nano-materials · Nanoporous carbon · Energy storage · Batteries · Super-capacitors

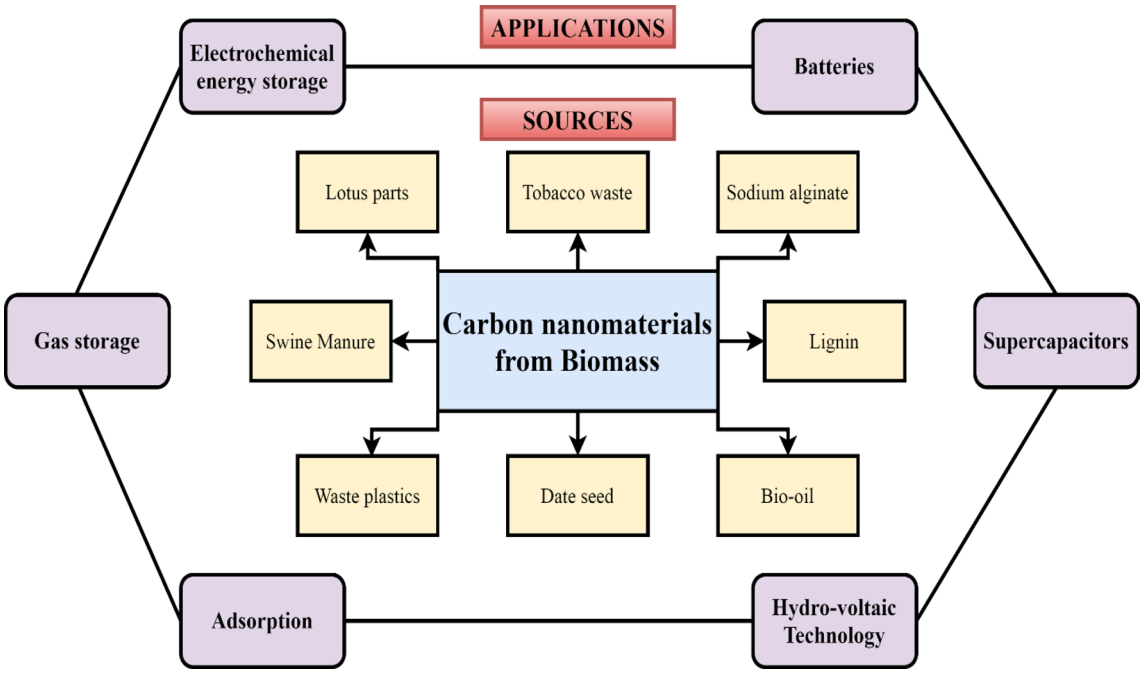
1 Introduction

In the global scenario, the shortage of fossil fuels is alarmingly rising which communicates the shear need for the generation of electricity from green sources and storing them properly. Prevailing energy storage systems have almost reached the theoretical energy storage limitation and the development of alternative and next-generation sources for storage of energy is very important these days. Renewable energy technologies have been desperately required for prospective energy generation, and storage, as well as usefulness because of the fast growth of the international budget, the ever-increasing residents, as well as the excessive consumption of decomposing plants and animals. So as to make efficient utilization of renewable energy from solar, wind, geothermic, waves, as well as biomass energy, a variety of energy transformation and storing knowledge have indeed been established, including super-capacitors, fuel cells, compressed hydrogen, as well as batteries [1]. When it comes to the efficiency of storing electrical energy systems, the constructional characteristics of the electrodes perform a significant part in defining how well these storing electrical energy systems can function [2–4]. Accordingly, focus has been given on the growth of the electrode materials as well as the accomplishment of superior performance with these electrochemical devices.

Electrode materials must ideally be derived from natural sources in an easy, low-cost, as well as naturally benign manner, with tunable structures, enhanced void fraction, appealable interface surface, as well as dynamic clusters. This is due to the fact that renewable resources have positive effects on both the environment as well as the economy. CNMs, which were among those that were exploited, garnered a lot of interest as well as presented some great promising areas of ecological prevention, capture of energy, as well as application of green and sustainable technologies. Because of their unique physico-chemical characteristics, unique carbon materials like fullerene, graphene, graphdiyne, as well as carbon nano-tubes (CNTs) have garnered an excessive contract of attention in the past few years in the disciplines of energy storage [5–7]. They have a high specific surface area, a high electrical conductivity, superior chemical stability, tunable porosity, as well as enriched electro-active sites. However, the production of these CNMs requires the use of precursors derived from fossil fuels (including carbolic acid, hydrocarbon), as well as energy-intensive artificial procedures (including gas-phase precursors and laser extirpation), which is both harmful to the atmosphere and expensive [6–8].

In spite of the fact that all these strategies have reached a mature stage of knowledge at the top scale, they have not yet been prepared for commercial purposes because the artificial measures that are required are so complicated [9, 10]. As a result, it is of the greatest status to develop measures for producing CNMs that are more productive, less harmful to the environment, and more cost-effective. In addition to fossil fuels, biomass is yet another kind of source that can be converted into CNMs. In contrast to fossil fuels, biomass seems to be a material that is either derived from plants or is based on plants. It is obtained through the earth and is produced by means of CO_2 and H_2O through a procedure called photo-synthesis. According to a summary that was done in the year 2017, the cumulative quantity of biomass transversely all taxonomic groups in the world is approximately 550 Gt on dry weight, and approximately 80% is composed of agriculture [11, 12]. Using thermo-chemical conversion in the existence of an inactive troposphere, biomass, which is a resource that is both renewable and non-renewable, could be transferred into an outcome called biochar that resembles charcoal [13, 14]. While H_2, O_2, N_2, and N are primarily designed into air even during conversion, C is transformed into lightweight black residue (biochar) [15, 16].

Biochar is not to be confused with carbon black or activated carbon, both of which are primarily derived from resources that are not renewable (for example, coal or petroleum-depended products). Comparisons are made regarding their starting materials, carbon content, methods of preparation, and characteristics. Amorphous and porous best describe activated carbons and biochar, respectively. However, in contrast to activated carbons derived from fossil fuels as well as carbon black, biochar is produced in a manner that is environmentally friendly and contains a high concentration of functional groups [17–19]. Carbons derived from biomass provide a variety of advantages, including the following: (i) it is a by-product of thermal conversions of biomass materials to produce bio-oil, making it both the best possible profit as well as plentiful; (ii) stable in both physical and chemical mode [20]; (iii) it acquires numerous different variety of surface dynamic sector (for example, distinct O_2-containing or N_2-containing dynamic sectors), where it could be adapted using distinct feedstock or thermochemical situations [21]; (iv) it is essentially absorbent or organized, which allows encouraging customizable transport properties; and (v) because of these characteristics, biomass-derived carbon is quickly becoming a sought-after



Scheme 1 Flow of this review

material in a variety of application fields, such as soil remediation, catalysis, energy storage, and also as an absorbent for various pollutants [22]. However, use of a typical top-down approach makes it difficult to control the structures and characteristics of the material, such as its multi-scale morphology, porosity, and surface chemistry, which restricts the applications for which it can be used. Therefore, the correct activation and modification are necessary to improve the performance of carbon obtained from biomass in subsequent applications [23].

After decades of investigation, important implementing strategies have been applied to renewable biomass to make progress in the production of carbon that is derived from biomass. This advancement comes after decades of research. In addition, an extensive variety of renewable, biological materials have been utilized to synthesize CNMs via conversion of biomass into an intermediate liquid product with activation as well as alteration processes, which has resulted in the production of absorbent carbon or low-dimensional allotropes of carbon with enhanced void space, an abundance of dynamic nature, organized absorbent construction, as well as outstanding conductivity [24, 25]. As a result of these benefits, carbon derived from biomass are being looked at as potentially useful electrode materials for a wide variety of electrochemical energy storage and conversion systems, such as fuel cells [26], super-capacitors [27], potassium batteries [28], lithium batteries [29], as well as sodium batteries [30]. Because of the rapid advancement in this area, which is not only essential and also immediate to examine and make comparisons of their fabrication methods, characteristics, applications, as well as accomplishments in electrochemical energy storage technologies. However, the majority of the recently published literature reviews do not provide an organized opening to the techniques of biomass-derived carbons. These reviews also fail to provide a thorough discussion upon that assessment of the relationships between structures of these carbons as well as their characteristics [31–33]. In addition, comparative studies of the correlations between the physio-chemical properties of carbons based on biomass and their electrochemical performance are extremely uncommon [34, 35]. In related literature reviews, comprehensive evaluations as well as perspectives that cross disciplinary boundaries of viable energy storage systems, such as super-capacitors, batteries, as well as fuel cells, are still uncommon [18, 36, 37]. Hence, it could be noted that biomass-derived CNMs are gaining high importance owing to numerous advantages. In line with all the above facts, the current review focuses on the CNMs derived from biomass and biomaterials along with the state-of-the-art applications of such materials. Scheme 1 shows the flow of the review along with the contents.

2 CNMs from biomass

PCMs derived from biomass have witnessed an edge over synthetic carbon sources owing to their sustainability, cheap, and eco-friendliness. Biomass-derived CNMs were proven

to possess high specific surface area, porosity, pore size distribution, and good surface morphology on par with the CNMs derived from synthetic sources. It is become increasingly difficult to find low-cost energy for manufacturing in this modern age of rapid technological development since the industrial revolution. As fossil fuels have increasingly been used in various fields, the amount of greenhouse gas emissions have steadily increased. Scientific advancements have been made even though the Paris Agreement was signed in 2015 to reduce CO_2 emissions, which also account for the majority of greenhouse gas emissions. CCS (carbon capture, utilization, and storage) advancements, which can transform CO_2 from the air into high-value-added substances, have been gaining consideration. Since the double covalent bonds between the atoms of carbon and oxygen in CO_2 make it remarkably stable, various methods of CO_2 conversion have been developed. These include super-critical transformation, electrochemical transformation, metal-based transformation, and CO_2 transformation utilizing inorganic substances [38–40]. Energy exhaustion and contamination have drawn people's care in recent decades and encouraged them to investigate new, more environmentally friendly energy storage and conversion innovations. To achieve the maximum amount of energy, high-capacity super-capacitors have been widely studied. However, their excellent performance is largely dependent on the growth of novel electrode materials. To produce great-performance high-carbon materials, the conditions in which they are produced must be extremely harsh. To face the increasing request for high-performance carbon materials while minimizing environmental impact, new methods must be developed. Its biodegradability, abundance of raw materials, and low cost make biomass an important precursor to carbon-based materials. High-performance sustainable materials like porous carbons made from biomass have gained consideration due to their advantages, such as high porosity, large definite surface area, and high graphitization degree [41–43].

Despite the fact that numerous studies and summaries have been published on PCMs derived from biomass, there is still room for improvement and additions. New classifications are made for the generation methods of biomass-derived PCMs for super-capacitors. For elevated biomass-based PCMs, design methods and strategies are examined. Advanced super-capacitors can benefit from biomass-based PCMs. These materials face a variety of challenges and opportunities in the future. New discoveries and practical applications of biomass-derived CNMs are expected to be stimulated and promoted in the area of more energy storage and transformation through the use of elevated properties in the field of super-capacitors [44–46]. Research into new, environmentally friendly as well as effective electrodes for energy storage devices is encouraged by the ongoing need for clean energy implementation. As pioneer electrodes for energy storage, PCMs were established due to their own inherently diverse structures, ecological helpfulness, low price, and widespread affordability for manufacturing on a large scale [47–49]. When biomass is thermo-chemically converted to produce biochar, a renewable and environmentally friendly forum for the readiness of numerous workable CNMs (graphene) is provided. Electrochemical energy storage devices such as super-capacitors were built extensively because of their versatile physico-chemical properties [50, 51]. Methods for preparing biomass-derived CNMs are summarized in this review. Focus has been given to the literature based on the last half decade. Very recent literature were used to consolidate that the sources of biomass from the CNMs can be derived. Though there are many other biomass sources, the most recent literature were given utmost concentration. Such CNMs have a great potential for use in various energy storage devices such as super-capacitor electrodes. The characteristics associated with their ability to store charge are explored in detail along with the associated challenges and prospects in various journal articles and patents. The forthcoming section deals with the attributes of CNMs derived from different biomass sources.

2.1 Carbon from swine manure

Swine manure (SM) is an effective by-product of swine operation which is normally used as a fertilizer for crop production. Yet, these manures have low carbon content owing to the presence of more nitrogen. By suitably processing these manures with high carbon-containing substrates and increasing their surface area, these manures can be used for the production of CNMs [52, 53]. In some research works, SM-activated carbon (SMAC) was produced using a normal in situ technique that combined potassium hydroxide excitation with pyrolysis and used SM as a forerunner. Simplified metal does not remove natural metal oxides but instead makes full use of them as in situ templates. It was found that different pickling stages during pyrolysis and activation affected the effects of in situ layouts and the structural properties of SMACs. Surface areas ranging from 876 to 2321 m^2/g showed superior structural properties for SMACs. A combination of the activation effect of SiO_2 and CaO as pore supports, MgO as a catalyst for carbon decomposition, and MgO as activation support explains these outcomes. A charge transfer resistance of 278 F/g at 0.5 A/g and a power output of 24.62 Wh/kg at 450 W/kg for SMAC-related synchronous super-capacitors are among the best electrochemical performances of SMAC, with a retaining rate of 96.2% beyond 10,000 cycles. A practical method for making super-capacitor's biomass carbon electrodes at a low cost and with high efficiency was also explored by various researchers [54, 55]. Figure 1 denotes the entire process cycle through which the biochar and AC were used to synthesize CNMs

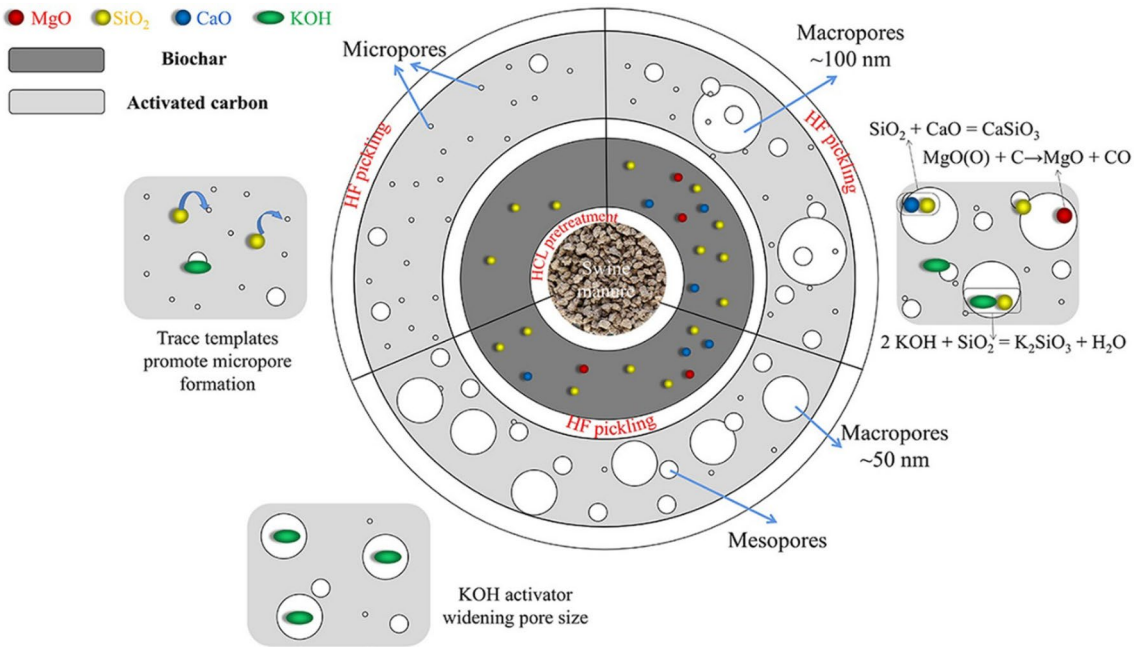


Fig. 1 Process flowchart of carbon production (Reproduced with permission from [54], Copyright Elsevier, 2022)

for energy storage applications. From the figure it could be understood that the carbon atom derived from a biomass using suitable activators had porous structure which can be more suitable for the energy storage applications [54].

2.2 Carbon from waste lotus parts

Lotus plant parts such as the leaf, floral, fruit and vegetables, and stalks are reported as a replaced forerunner of the readiness of lotus carbon (LC) materials in a simple, low-cost, and environmentally friendly way. There were four different types of PCMs derived from the lotus plant: leaf carbon, flower carbon, fruit carbon, and stem carbon. Numerous techniques, including electron microscopy and spectroscopy, BET-surface area analysis, and X-ray diffraction (XRD) were used to characterize the LC materials after they had been synthesized [55]. The permeability of LC components and the presence of heterocyclic rings in the LC materials were confirmed using these techniques. Because of its mesoporous structure, LC materials could be used in super-capacitors. Acquired LC has a coercivity of 160 F/g in relating to 1 M sulphuric acid minerals, a percentage achievement of 52% retaining from 0.01 to 5.0 A/g, and better repeatability of 95%. For high-performance supercapacitors, the highly permeable carbon derived from lotus fruit could be an ideal electrode material. Figure 2 shows the process of synthesizing various CNMs from lotus parts. Various parts of the lotus plants were initially collected, dried, and burnt in an argon atmosphere at 800 ℃ to obtain mesoporous carbon. The obtained CNMs were characterized for their attributes [56].

2.3 CNMs from tobacco waste

Biochar obtained from tobacco waste can be used to generate CNMs through direct carbonization. It was stated in various works of literature that out of 2.2×10^6 tons of tobacco planted, 1.2×10^6 tons of tobacco stem wastes were generated. This could act as a major source of biomass. Due to the high potassium content and low calorific value, tobacco wastes cannot be majorly used to produce biofuels or bio-oils but recycling of tobacco results in various advantages [57, 58]. There is a huge quantity of waste produced from tobacco manufacturing which includes tobacco trunks, stocks, and leaves. An important issue is to enhance the importance of waste derived from industry and agriculture. These biodegradable wastes can be reprocessed into CNMs with good electrical properties using this method. Tobacco waste biomass was carbonized in a single step to produce biochar. The specific capacitance of tobacco stems (305.92 F/g), stalks (328.07 F/g), and leaves (272.48 F/g) at 1 A/g was measured using a three-electrode structure and a six mole KOH electrolyte. An exploration into the benefit of nicotine waste to make lower, eco-friendly, and high-performance resources for electrochemical redox energy storage technologies have been introduced [59, 60].

Few experiments focused on determining the energy yield of biochar obtained from tobacco biomass. It was stated in the study that the energy yield of tobacco biomass was as

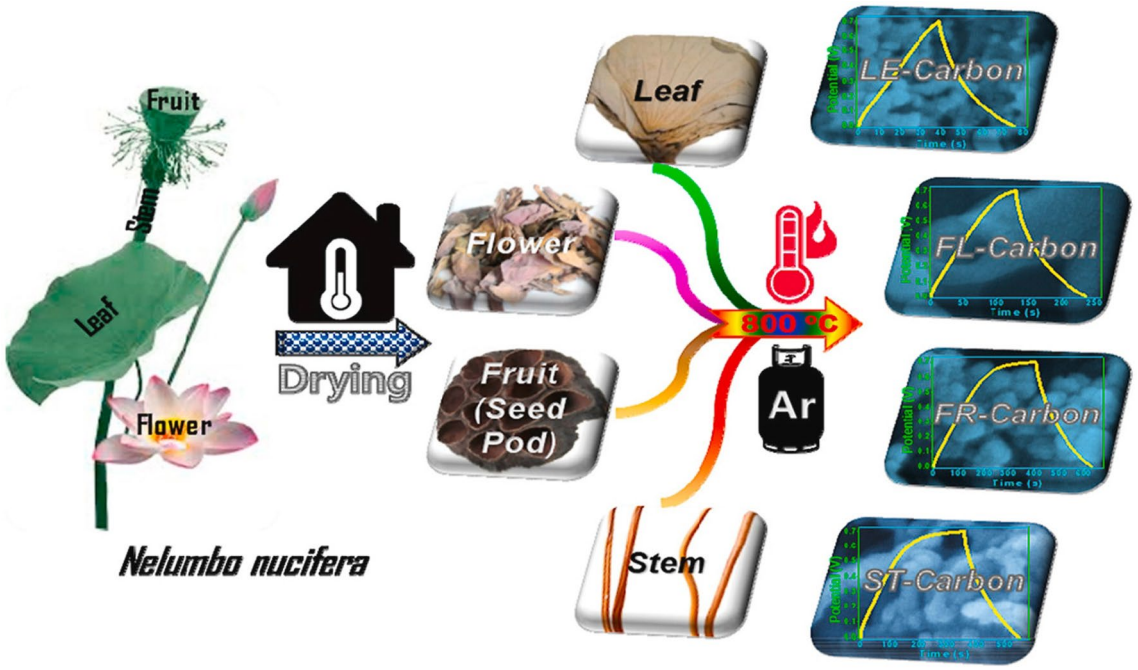


Fig. 2 PCMs from lotus parts (Reproduced with permission from [56], Copyright Elsevier, 2022)

high as 275 GJ/h.yr which was on par with the energy yields of biochar obtained from timber and wood biomass. Such tobacco biomass can be used to prepare biochar which could store methane and hydrogen at higher rates [61]. Few other experimenters dealt with the preparation of nano-materials for super-capacitor application from tobacco stalk wastes. High-temperature carbon was obtained by processing the tobacco stalks using the high-pressure hydrothermal method and the obtained biochar was activated using KOH after which the surface area of the obtained CNM was adjusted. As a result, the specific surface area of the carbon increased and possessed a large porosity. It was stated in a study that the pseudo-capacitance of the material was induced by the oxygenated groups and this enhanced the wettability of the material making it suitable for electrochemical storage applications. Retention of capacitance was 92.7% after 5000 cycles which was on par with other equivalent materials. Figure 3 shows the schematic of the process used to convert tobacco wastes into biochar and use it for energy storage applications. Tobacco stalks were separated, dried, and ball milled to obtain uniform sized powders. The milled powders were subjected to hydrothermal and KOH activation to obtain porous carbon material. They can be potentially used in supercapacitor-based applications [62].

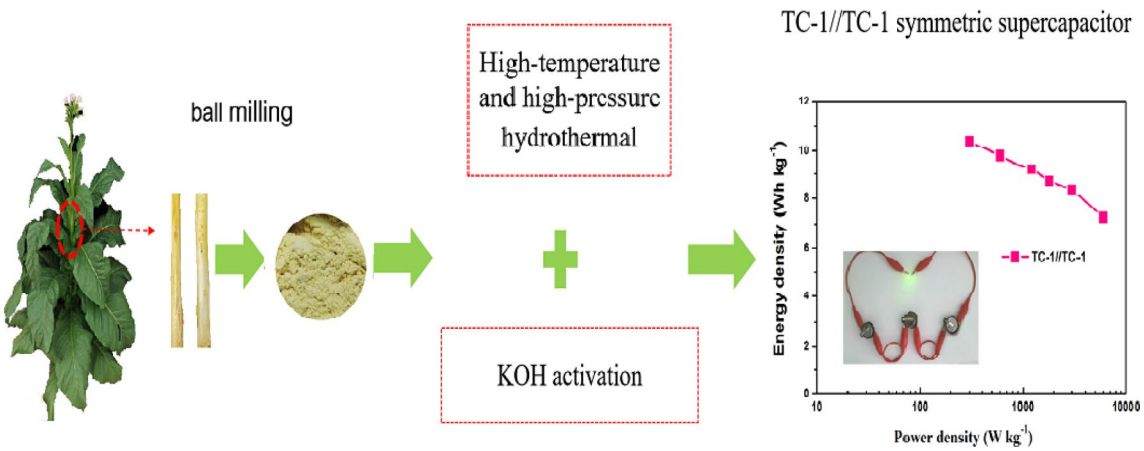


Fig. 3 Process to obtain tobacco biomass-based biochar (Reproduced from [62], Copyright MDPI, 2021)

2.4 Sodium alginate-based nanoporous carbon

Sodium alginate (SA) is a polysaccharide carbohydrate derived through seaweed that is both environmentally friendly and inexpensive. Since its molecular structure and molecular weight are easy to determine and can be easily controlled in the manufacturing process, SA is a promising carbon precursor due to these advantages. However, little research has been done on the mechanism by which SA carbonizes. Using SA pyrolysis, the mechanism of carbon a major post-translational modification of collagen, replacement of hetero-atoms in the graphitic structure, are investigated. Then a method was developed to produce a stable interconnected porous carbon made from SA-derived carbon using a self-template. This method yields materials with a maximum of 17.6% of oxygen content and a high specific surface area (384.4 m^2/g). SA-derived porous carbon in Zn-ion hybrid capacitors (ZICs) instruments produces superior energy densities of 78.35 Wh/kg at 160 and 5120 W/kg, respectively, at the power densities. For the first time, the carbonization process of sodium thickening agent was thoroughly explained and the potential of SA-based carbon in ZICs was thoroughly examined. The mode of carbon skeleton cross-linking, heteroatom doping, and defect generation in the SA pyrolysis process have been clarified. The SA-derived porous carbon was synthesized using a self-template and self-activation technique. Under power densities of 160 and 5120 W/kg, ZICs deliver greater energy densities of 78.35 and 35.56 Wh/kg [63].

Few researchers fabricated mesoporous carbon 3D hierarchical structures derived from SA biomass and used them as a substrate material in electrochemical sensors. The carbon was coated on a glassy carbon electrode and it was used as a substrate. Over the substrate, hydroquinone, resorcinol, and catechol were coated to measure the electrochemical performance. It was noted from the results that the SA biomass-derived carbon performed much better in electrochemical sensing [64]. In some other experiments, NCMs was derived from SA biomass using the zinc chloride activation method with zinc oxide as a template. From the results, it was noted that the alginate-derived carbon rendered better super-capacitance properties with an energy density of 16 Wh/kg. This novel triple synthesis method was proven to develop highly porous nanostructured carbon which could be readily used for power and energy storage [65]. Figure 4 shows the synthesis and reaction of nanoporous carbon from SA biomass. Zn–SA hydrogel were prepared from nano-ZnO and SA precursors through drop-wise condensation in an HCl medium. The hydrogels were converted into nano-aerogels using freeze drying process and the obtained aerogels were carbonized and washed to result in ZnO–SA-based CNMs [65].

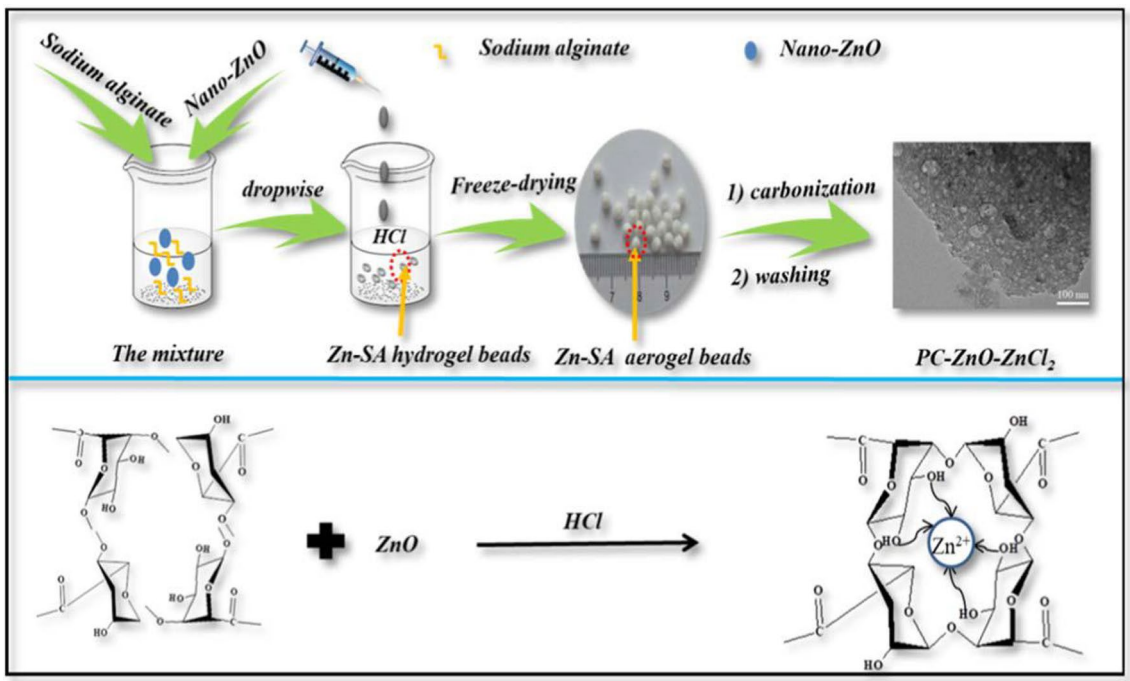


Fig. 4 Synthesis of porous carbon from alginate biomass (Reproduced with permission from [65], Copyright IOP Science, 2020)

2.5 Lignin-based carbon

Lignin-derived carbon materials have seen an uptick in interest in the last few years due to an increasing need for electrical storage materials. Thermo-chemical conversion of lignin, a readily available renewable carbon source, can produce a wide range of developed carbon materials with tunability pesticide, functional, physical, electrical, and chemical characteristics. It is important to keep in mind that lignin partitioning from plant biomass has an impact on the decomposition chemistry and the properties of the carbon materials formed as a result of the multifariousness of methoxylated derivatives of benzene, concentration, inter-unit linkages, and chemical reaction [66]. Finding a new, cost-effective method of fractionating lignin and cellulose from feedstock is critical to increasing the efficiency and lowering the environmental impact of lignocellulosic biomass for biofuels. Lignin was extracted from walnut and peach endocarps with the help of a deep eutectic solvent (DES). Lignin was extracted at maximum yields and cleanliness during enzymatic hydrolysis of plum and walnut endocarps that had been pre-treated with the DES. Derived lignin from DES pre-treated endocarp biomass had meaningfully lower molecular weights than raw lignin. The native endocarp lignins had a dominant G-unit and were of the SGH type. Isolated lignin was more thermally stable after DES pretreatment reduced the S and H-units, which resulted in a rise in compressed G-units [67]. A pyrolysis system was used at the initial period to link back pyrolysis composition, and dioxide material properties. As temperatures rose from 100 to 600 °C (2, 20, 40 °C/min), the entire product dividends, including volatiles as well as solid products, were monitored. The results showed that the pyrolysis conditions changed the reaction, which in turn altered the output and characteristics of the consequent carbon materials. The properties including permeability, chemical composition, and surface characteristics were all significantly influenced by both heat and heating systems rates during the lignin slow pyrolysis.

The complex organic polymers, cottonwood, pine plant, and industrial lignin obtained from kraft pulp, were subjected to the same conditions for the production of AC. More surface area and mesopore volume contributed to just a bigger electrochemical capacitor in the cotton wood-derived ACs than in the black spruce lignin-derived ACs. All lignin-derived ACs contained oxygen-contaminated dynamic groups, which were involved in the redox response, and therefore resulted to an extra pseudo-capacitance. The results recommend the construction and proportion of lignin are major parameters affecting the construction of holes and the ionic conductivity of the extracted carbon materials by defining the carbonization parameters [68]. After 100 cycles at 0.72 A/g as a negative electrode in a half-cell lithium-ion battery (LIB) test, a 3D, interrelated carbon/silicon nano-particles composite was demonstrated to possess an elevated beginning specific capacity of 2932 mAh/g and a maintaining capacity of 1760 mAh/g. It is discovered that C/Si NPs have been most usually connected via the Si–O-C instead of a direct Si–C bond, a characteristic that alleviates mechanical degradation from the volume change of Si, as well as a sound electronic conductivity for improved electrochemical effectiveness [69, 70].

2.6 Porous carbon from bio-oils

Large amounts of bio-oil produced by biomass pyrolysis were used as a carbon source for the production of carbon-based super-capacitor electrode materials. AC from the huge bio-oil-derived carbon source was compared to the synthesized carbon materials' high porosity, crystalline structure, as well as external texture structural unit. Electrochemical measurements in 2D and 3D electrode systems were used to assess the performance of the prepared carbon materials. Using a NaOH/heavy bio-oil carbon catalyst ratio of 3:1, a study discovered that carbon prepared with this ratio had the largest surface area and the largest total volume of pore space. There were specific capacitances for the metal electrode and two electrodes, respectively, in the three-electrode system for the single metal electrode. In addition, at a power density of 300 W/kg, the energy content of the adjacent super-capacitor was 12.95 Wh/kg. According to this study, heavy bio-oil can be used to make new AC electrode materials [71].

Few experiments were carried out for deriving bio-oil from biomass and plastic waste to produce CNTs through the catalytic co-pyrolysis process. The influence of the ratio of feedstock on the production of CNTs was assessed. Biomass was added with varying concentrations of polyethylene and it was noted from the results that the diameter and density of CNTs enhanced with the addition of polyethylene. But at lower polyethylene ratios, due to the deficient hydrocarbon bonds, low-density porous CNTs were formed. These CNTs can be readily employed in various energy storage applications [72]. In a few other experiments, AC was produced from corncob biomass-based bio-oil and was derived using wood vinegar and phosphoric acid activators. It was noted that highly PCM resulted at high activation temperatures and a higher specific surface area was obtained for carbon when derived with phosphoric acid as an activator. Such high surface area carbon was tested for hydrogen storage in the work and the specific capacitance of the AC was found to be higher [73].

2.7 AC from date-seed biomass and waste plastics

Various experimental trials were made to derive AC from agricultural biomass. Carbon derived from organic materials

with high lignocellulosic content was found to be more porous than the carbon derived from other sources. Shells and seeds of fruits and vegetables were proven to be the most reliable source of such porous carbon [74]. Accordingly, low-cost carbon material can be easily prepared without the use of a catalyst and produce impressive results with excellent mechanical power and energy from fruit seeds. Accurate measurements of AC were made by atomic absorption, scanning electron microscopy, Raman and laser diffraction and chemical methods to categorize the materials before they were crushed in a planetary crusher. There was an excellent specific capacitance of 528 F/g and high specific energy of 36.22 Wh/kg for the triple resource, as well as impact resistance for 10,000 charge–discharge cycles at 10 A-G1 with capacitors return rate of 89% [75].

The problem of plastic waste has grown to be a serious one for the environment, and as a result, more people are taking notice. Degradation, recycling, and upcycling have all been explored as treatment options for this waste, as the possibility of converting it into new, higher-value products. Plastic waste-derived carbon materials (PWCMs) have practical applications in the fields of energy generated from natural resources and maintainable ecological practices. PWCM preparation and application advancements were reviewed. These techniques include anoxic pyrolysis, catalytic and pressure carbonization, flash joule heating, microwave conversion, etc. An emphasis on property-performance correlation is placed on a wide range of applications, including green energy storage and generation (such as batteries and super-capacitors) as well as viable ecological concepts (pollutant adsorption and degradation, solar evaporation, and CO_2 capture) of PWCMs and PWCMs-based composites. Additionally, the continued improvements of PWCMs are also discussed. It is suggested that, PWCMs can be used for more advanced applications and to encourage the composting of plastic waste in the future [76]. Figure 5 shows the various waste plastic sources from which highly porous carbon can be derived. Table 1 enlists various sources of biomass from which CNMs were derived along with their proximity analysis values.

3 Applications of CNMs derived from biomass

Energy storage devices manufactured through conventional fossil fuels are facing a faster depletion of resources and it is high time to find an alternative green approach and materials for energy storage applications as pointed out by many of the previous studies. Utilization of synthetic process for the derivation of CNMs is depleting at a rapid rate due to the accumulation of CO_2 which overloads the carbon cycle and challenges the ecosystem of the earth. Moreover, CNMs derived through sustainable methods and sources possess better chemical and thermal stability, better chemical functionalization and promotes mass production. Deriving porous and

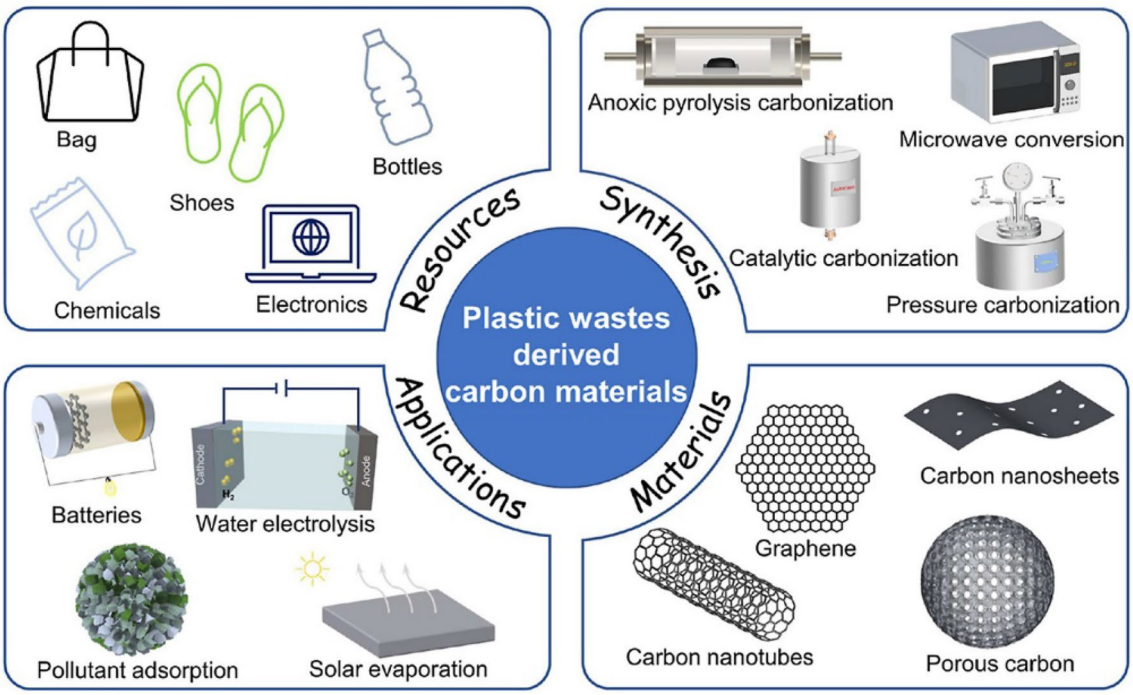


Fig. 5 CNMs from plastic wastes (Reproduced from [76], Copyright Elsevier, 2022)

Table 1 Contents of CNMs derived from biomass

S. No	Biomass	Processing method	Biochar yield (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Ref
1	Sewage sludge	Pyrolysis	60.36	31.85	54.08	7.81	35.18	5.45	15.66	5.53	[80]
2	Blackbutt wood	In situ pyrolysis	84.8	1.8	79.6	19.0	49	6.62	44.22	0.32	[81]
3	Microalgae	Hydrothermal liquefaction	75.3	3.3	65.3	24.9	46.4	7.0	31.7	6.4	[82]
4	Camillia Oleifera shells	Hydrothermal carbonization and pyrolysis	80.5	22.0	74.71	3.41	47.22	5.45	46.75	0.44	[83]
5	Poplar wood	Hydrothermal carbonization	81.5	1.2	82.1	17.22	48.7	6.7	43.7	0.12	[84]
6	Wheat stem	In situ pyrolysis (carbon arrestor)	75.6	11.1	71.4	17.8	46.5	6.5	45.7	0.21	[81]
7	Pinewood	Fast pyrolysis	78.6	2.4	71.6	19.4	49.0	6.2	42.6	0.11	[85]
8	Timothy grass	Fast pyrolysis	83.8	3.7	78.3	12.5	43.5	6.2	45.5	1.4	[86]
9	Pruned plum	–	76.85	2.2	69.74	21.1	–	–	–	–	[87]
10	Cotton stalk	Steam gasification	70.11	2.82	66.3	18.75	44.3	5.56	46.5	0.67	[88]
11	Rice husk	Gasification	69.99	16.31	67.71	16.01	41.77	5.16	36.31	0.31	[89]
12	Pinewood	Slow pyrolysis	89.9	0.4	78.0	22.2	54.1	5.8	38.81	–	[90]
13	Cattle manure	Slow pyrolysis	58.5	–	–	–	51.3	4.6	45.1	–	[91]
14	Wheat straw	Slow pyrolysis	94.9	8.2	76.4	23.8	50.2	6.3	37.75	–	[92]
15	Tobacco stalk	Hydrothermal carbonization	80.1	46.5	15.8	3.06	5.9	0.21	–	–	[93]
16	Green garden waste	Slow pyrolysis	98.3	3.8	78.5	25.5	53.3	6.4	44.1	–	[94]
17	Sewage sludge	Fast pyrolysis	63.2	74.2	–	–	17.5	0.8	33.2	–	[95]
18	Dry algae	Slow pyrolysis	72.9	30.1	46.5	70.1	62.1	7.5	38.1	–	[96]
19	Corncob	Fast pyrolysis	95.5	1.1	84.6	15.7	49	5.6	43.8	0.5	[97]
20	Cocopeat	Pyrolysis	62.9	15.7	14.3	67.25	84.4	2.88	11.67	1.02	[98]
21	Solid municipal waste	Low-temperature carbonization	50.6	7.6	77.8	14.6	–	–	–	–	[99]
22	Spain sewage sludge	Fast pyrolysis	52	32.4	59.2	8.4	55.27	7.78	25.84	9.75	[100]
23	Pine needles	Slow pyrolysis	57.57	7.20	38.64	54.16	84.19	4.37	7.57	3.88	[101]
24	Poultry litter	Pyrolysis	54.3	16.9	74.3	8.8	65.9	–	68.4	–	[102]
25	Municipal solid waste	Pyrolysis	75.4	6.2	15.1	78.2	70.4	8.1	13.7	1.3	[103]
26	Pecan shell	High-temperature pyrolysis	53	5.2	9.7	–	91.2	1.6	1.2	0.6	[104]
27	Conocarpus waste	Hydrothermal carbonization	23.19	8.56	–	–	84.97	34.05	17.45	1.4	[105]
28	Wood mixture	Pyrolysis	73.82	12	8.3	46.3	68.1	1.5	–	0.4	[106]

Table 1 (continued)

S. No	Biomass	Processing method	Biochar yield (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Ref
29	Orange peel	Pyrolysis	35.22	8.3	–	–	74.8	1.6	13.4	1.8	[107]

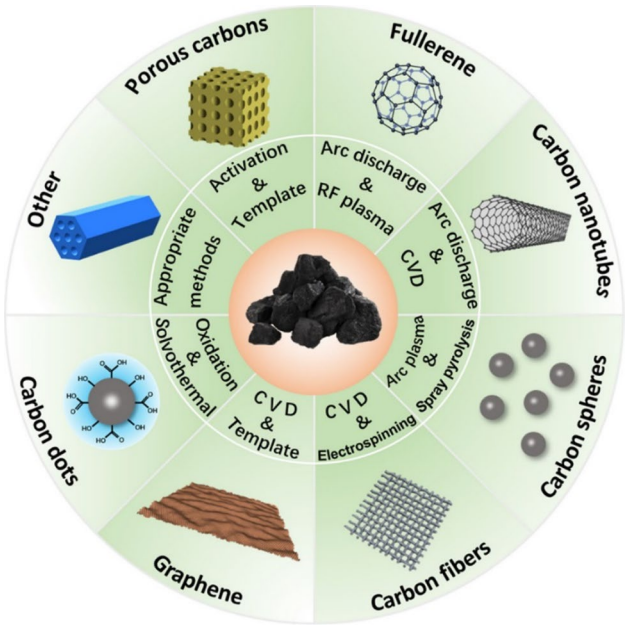


Fig. 6 Perspectives of CNMs produced based on coal (Reproduced with permission from [79], Copyright Elsevier, 2022)

intrinsically active carbon from biomass has been the order of the day which contributes greatly for building sustainable energy storage devices [77, 78]. Aromatic units and hydroaromatic groups make up the 3D cross-linked network construction of coal. Derivatives of coal have a lot of potential resources for synthesizing dynamic carbon resources because of their unique molecular properties. Coal-based carbon materials (CCMs) have made significant strides in recent years, including fullerenes, CNTs, and a variety of other porous and fullerene-based carbon materials, as well as monolayer carbon atoms. Various studies on CCM alteration approaches are critical for fine tuning the characteristic of the CCMs in light of their own intended appliances. It is possible that, the creation of coal-based workable carbon materials for super-capacitors storage and catalysis, composite materials, and environmental conservation (Fig. 6) [79].

Polybenzoxazines, a category of increased thermosets with nitrogen functionality and molecular design flexibility, are attractive precursors for heteroatom-doped carbon structures. In polybenzoxazine thermosets, carbonization has been used to build intelligent and engineered carbon materials, which has opened up a new avenue of exciting applications. For heteroatom-doped CNMs, poly benzoxazines can be a source of interesting morphologies and tailor-made properties if the right precursors are used and the right synthetic strategy is employed. It has been described how to achieve specific dimensionality and pore architecture as well as how to select the right precursor for carbonization to obtain greater char yield as well as significant heteroatom content. Carbon

structures obtained from poly benzoxazine, in CO_2 absorption, energy storage, catalysis, and adsorption have been described in terms of structure–performance relation [108].Figure. 7 explains the synthesis of non-porous carbon from polybenzoxazines along with the life cycle of such NCMs in energy storage applications.

Few authors tried to experiment with the non-porous carbon derived from polybenzoxazines precursors with nitrogen and phosphorous co-doped melamine polyphosphate for its possible application in the electrode for super-capacitors. It was stated that the co-doping of nitrogen and phosphorous enhanced the performance of the resulting electrodes in terms of pseudo-capacitance, electrical conductivity, and cyclic stability. Co-doping of nitrogen with polybenzoxazine enhances the specific capacitance and electrical conductivity of the carbon while phosphorous doping enhanced its cyclic stability. Such property-rich non-porous carbon can be used in advanced super-capacitors [109]. In few experiments, nitrogen-doped mesoporous carbon was synthesized from polybenzoxazines with different activation temperatures. Since activation temperature plays a significant role in producing porous carbon, studies were made with different activation temperatures. It was stated that higher activation temperatures rendered highly porous carbon suitable for super-capacitor applications and such carbons possessed high degree of graphitization and high meso- or macro-pores for rendering high specific surface area suitable for energy storage applications [110].

3.1 Electrochemical energy storage applications

In light of the environmental damage and the energy disaster, the collection and use of renewable energy, including solar or wind, is now imperative. When it comes to storing this energy, electrochemical energy storage (EES) devices have received a great deal of attention from researchers. For this, the electrode materials are critical, and CNMs have emerged as the most promising contenders to their distinct and noteworthy advantages. The electrochemical functioning of EES is heavily influenced by the electrode material's structure and controllable synthesis [111]. As active materials, conductive additives, and buffering frameworks, the major element of EES systems is CNMs. The implementation of this model of functional CNMs based on a thorough understanding of structure–property relationships is required to encounter the demands of rapidly expanding marketplaces for EES, particularly for E-vehicles and grid energy storage. Dimensionality differences, as well as hybridizing of carbon substances, take an important part in enhancing the electrochemical nature of EES devices. For electrodes, this forum looks at how to manipulate the dimensionality of functional carbon materials by transitioning between transitional and matching phases and then integrating those phases. Carbon-based electrodes' kinetics optimization, electron transfer acceleration, mechanical stability, as well as thermal dissipation during the charging/discharging performance can all be improved through dimensionality modification. Carbon-based electrode materials with a wide

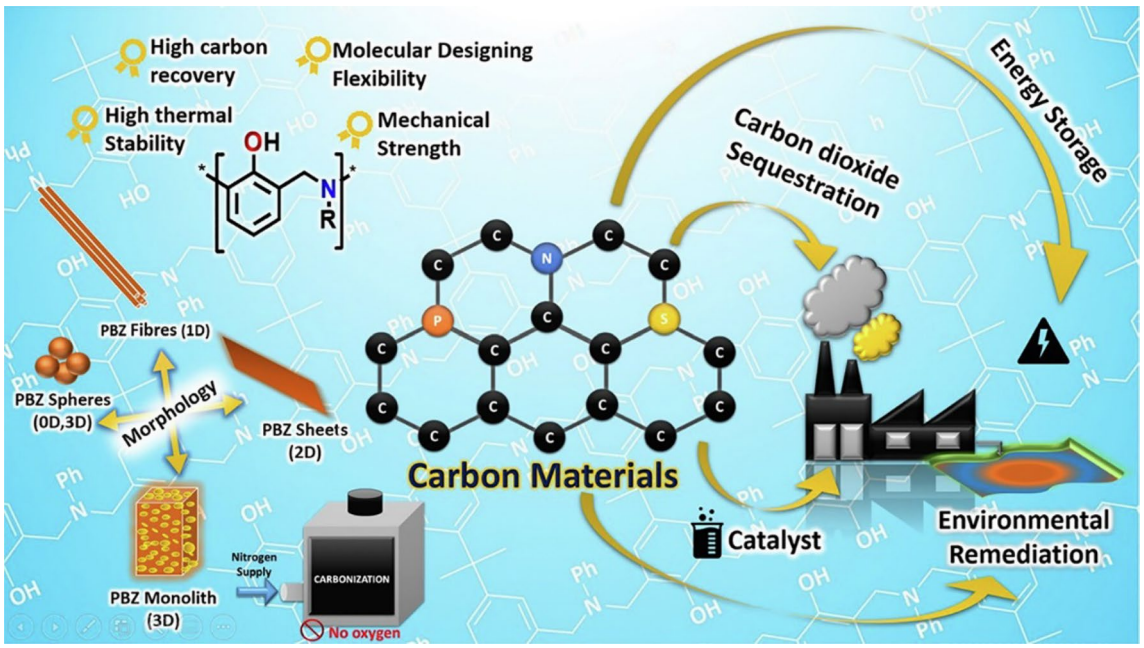


Fig. 7 Carbon from polybezoxazine for energy storage (Reproduced with permission from [108], Copyright Elsevier, 2022)

range of dimensionality variations can be used to create EES devices that are both safe and high-performing, and the optimized energy deployments that arise from these developments can be guided by the accomplishments [112, 113].

Various literatures focused on bringing out the EES performance of CNMs based on their dimensionality function. Carbon-dependent electrodes in rechargeable battery packs can be improved by manipulating functional carbon materials to change the dimensions of the electrochemical reaction space and charge delivery channels as well as thermal conductive framework, which have a direct impact on their overall performance. Uninstalling bulk carbon substances or generating basic carbon units, for example, allows the benefits of each dimension to be better leveraged for building suitable electrochemical reaction areas [114]. Adaptable interfaces for charge delivery or stress relief can be created by matching the dimensionality of carbon as well as non-carbon materials. When diverse carbon compounds are combined in a controlled manner to enhance ion transport, mechanical stability, and homogenous heat distribution, the advantages of each material can be harnessed to its full potential as illustrated in Fig. 8. It was stated in the experimental studies that the dimensional manipulation of carbon and non-carbon materials results in adaptable interfaces for the delivery of charge and relieving of stresses. Hybrid dimensional manipulation results in various advantages such as high thermal distribution, rapid ion diffusion, and higher mechanical stability [115, 116].

Carbon in electrode material can be custom-dimensioned to provide greater bulk capacity, rapid charging, as well as maximum thermal protection in EES devices in the future as illustrated in Fig. 9. Such carbon-based materials derived from various biomass sources will have smaller but effective reaction spaces, dense thermal conductivity links, and dynamic electrical linking structures [114].

3.2 Batteries

Production, storing, and utilization of the maximum useful arrangement of electrical energy by existing and supportable protocols are the issues in today's rapidly evolving society. This crisis has prompted rapid developments in batteries, super-capacitors, and fuel cells as EES devices. Fuel cells and batteries have maximum energy fluidity with high installation cost, volume, minimum power, and limited span duration being significant constraints. Fuel cells and batteries have a higher energy density than batteries. When it comes to uninterrupted power supply systems, super-capacitors currently serve as supporting or secondary devices in between these batteries and traditional capacitors. It is still possible to find super-capacitors with a wide range of unique properties like light weight and portability as well as a long cycle life and low maintenance [117, 118].

Nano-composite materials with increased energy density have been developed to replace first-generation super-capacitors. Because of this, super-capacitors can be successfully combined with high-energy battery materials without compromising their repeated operation significantly. It is, thus, possible to achieve better electrochemical performances using a new concept known as super-capatteries (super-capacitors + batteries), which combines the advantages of both batteries and electrochemical capacitors as energy storage mechanisms. Researchers are also working to find ways to design devices more cheaply without sacrificing device performance. With a focus on the earth, configuration,

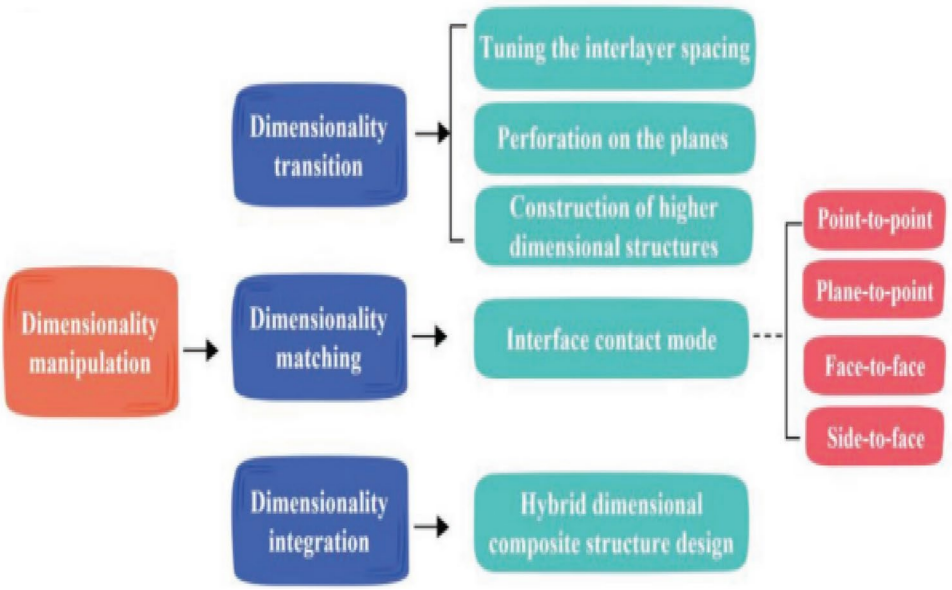


Fig. 8 Dimensionality manipulation of carbon materials (Reproduced with permission from [114], Copyright John Wiley & Sons, 2022)

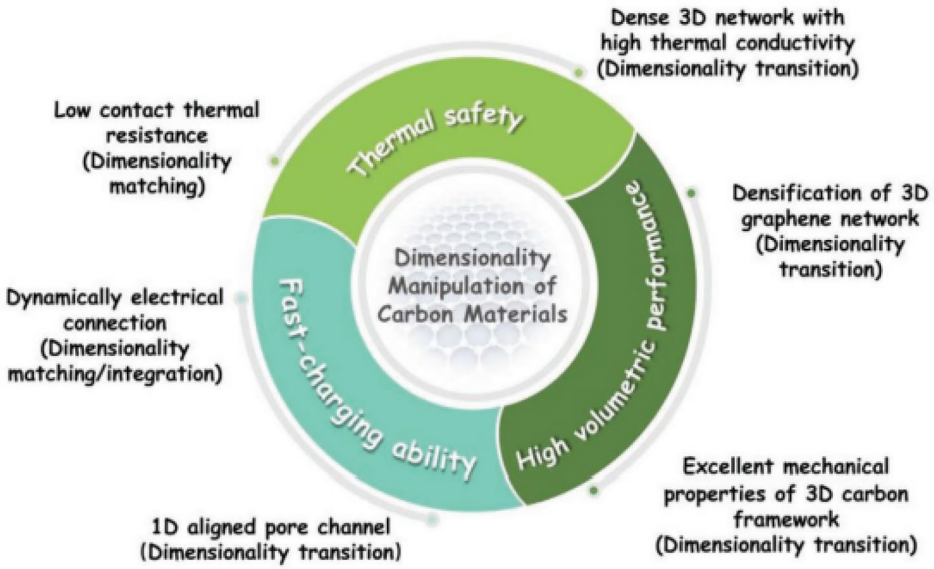


Fig. 9 Future outlook of dimensionality manipulation (Reproduced with permission from [114], Copyright John Wiley & Sons, 2022)

electrical and constructional design of electrolytes, and cell manufacturing with other involved factors which will help to enhance the entire electrochemical device behavior [119], the improvements of super-capacitor technology were discussed by various researchers.

3.2.1 Potassium ion batteries

Due to the abundant availability of potassium and sodium on the earth's crust, potassium ion batteries (PIBs) are considered to be affordable and sustainable battery technologies when compared with LIBs. Anodes of PIBs based on carbon materials show great promise owing to their elevated conductivity, structural stability as well as an abundance of natural resources [120, 121]. It was stated in various research works that carbon materials can be used in PIBs only if the interlayer spacing is increased as well as absorption sites are increased. C–S–C bonds could indeed substantially increase interlayer spacing between carbon materials as well as alter the nitrogen-doping layout in graphene layers. At 0.1 A/g, the sodium-doped nitrogen-based carbon materials show an ultrahigh capacity of 578 mA/hg after 200 cycles with edge-N doping of 87.9% and 0.41 nm interlayer spacing. After 10,000 cycles, they have an ultra-long-life span of 249 mA/hg at 5 A/g with a capacity loss of 0.024% per cycle, which is a significant improvement over the previous design. C–S–C bonds, according to theoretical calculations, can expand interfacial interaction measuring of graphitic layers as well as collaborate with edge-N atoms to enhance the K^+ adsorption capacity of carbon materials [122].

In few experiments, waste sorghum stalks were used to derive the nitrogen/oxygen-doped hard carbon (NOHC) using simple large-scale carbonization methods for their possible applications in PIBs. It was stated from the experimental results that hard carbon exhibited enhanced interlayer space and highly porous structures which easily enabled the more active ion pathways for the insertion and extraction of potassium ions. This in turn resulted in electrodes with high cycling ability and reversible capacity. Such electrodes can be considered as low-cost and sustainable alternatives for their application in commercial PIBs [123]. Figure 10 shows the schematic process of deriving NOHC from waste biomass of sorghum stalks. Some experimenters prepared carbon nanofibers (CNFs) for PIB electrodes from polypyrrole nanofibers through direct carbonization.

From the experimental results, it was observed that nitrogen-doped CNFs exhibited better electrochemical performance for PIBs application when compared with other materials. The influence of pyridine and pyrrolic dopants was found to be high when compared with conventional nitrogen dopants. It was also observed that the nitrogen-doped CNFs exhibited high potassium ion storage with maximum reversibility and polypyrrole usage that opened up an avenue for the production of disordered carbon materials also which is going to be the future of energy storage materials [124].

3.2.2 Lithium-based batteries

Next-generation high-energy–density batteries could use anodes made of lithium (Li) metal. Dendrites form during the plating or stripping of Li metal, resulting in a shorter lifespan and potential safety issues. Dendrite growth has been suppressed as well as the steady electrolyte stages have been regulated using a variety of approaches. The Li metal has been stabilized using carbon materials which are light, good conductors, have high porosity, chemical

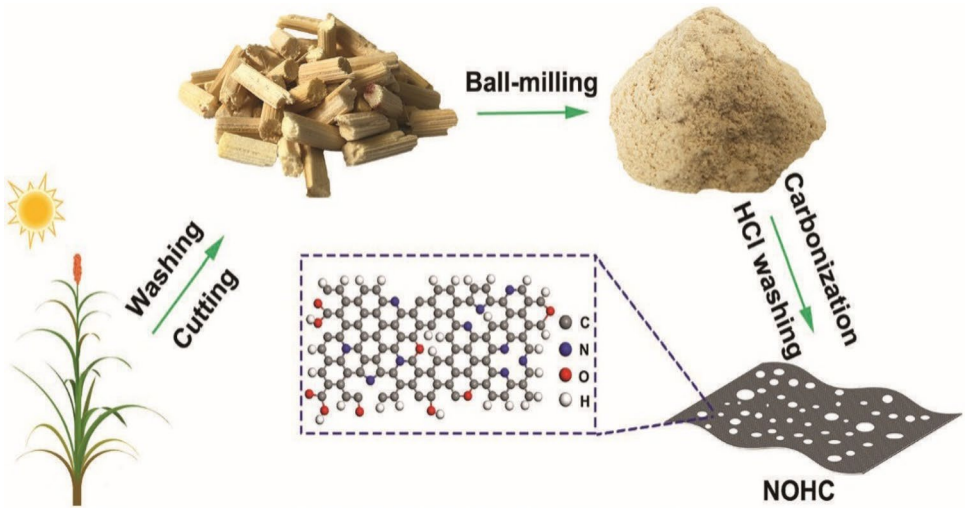


Fig. 10 Synthesis of carbon from waste sorghum stalk biomass (Reproduced from [123], Copyright John Wiley & Sons, 2020)

characteristics, and are physically stable. There have been substantial improvements in carbon-based materials to use as servers, enhancers, and covering layers for Li metal batteries (LMBs). The development of carbon-based materials for LMBs along with the shape and compositional properties of varied carbon materials were studied in various literature works [125, 126]. Because of the widespread use of LIBs, fires are on the rise, resulting in unspeakable devastation in terms of human life and property. In the case of LIB fire and explosion, thermal runaway is the primary cause, and carbon materials play a significant role in enhancing the safety of LIBs through their fire retardance capability. When it comes to battery safety and electrochemical properties, carbon materials were summarized in the first place. Following that, the parts of individual elements in the thermal runway and the procedure were presented, and the significance of carbon materials was emphasized. Carbon electrode materials' improvement measures were analyzed, and the impact on LIB security was examined. It was stated that the broadly utilized carbon materials have a significant impact on battery thermal hazards because of their importance in thermal runaway processing [127, 128].

Some bottlenecks in the commercialization path of lithium–sulfur (Li–S) batteries are a promising candidate for next-generation energy storage devices. Sulfur and its products have a low electrical and ionic conductivity, which makes them difficult to use, cycle, and maintain, as well as a poor Coulombic efficiency because of the disintegration and mobility of polysulfide anion, instability sturdy electrolyte dispersed phase and cytoskeletal expansion on photo anode, and lower density in both cathodes and anions. There has been a great deal of interest in hierarchical PCMs as a way to avoid the above issues in Li–S batteries because of their high specific surface area, large volume of pores, and good chemical stability. For Li–S batteries, recent advances in the development and implementation of PCMs, including sulfur cathodes, interlayers, and lithium anodes, are presented. Hierarchical porous carbon structures (permeability quantity, surface charge, pores' degree of doping, and heteroatom doping) are linked to the electrochemical performance of Li–S batteries [129–131].

Iron phosphate is the potential candidate material for the production of porous carbon used in LIBs. Its low cost, long lifespan, and high level of safety make it a popular cathode material for LIBs. Its inability to perform well at low temperatures makes it unsuitable for use in colder climates. This problem could be alleviated by combining $LiFePO_4$ with carbon materials, which have outstanding electronic and ionic conductivity. After briefly introducing the low-temperature fade mechanism of $LiFePO_4$ cells, the manufacturing steps, construction as well as electrochemical behavior of carbon-modified $LiFePO_4$ materials focus on carbon coatings, different carbon conductive fillers, and nano-carbon modifications. A low-temperature material can be created by combining $LiFePO_4$ with carbon and then coating it with carbon. Other conductive additives, including graphene-based materials, have a huge capability for use in low-temperature $LiFePO_4$ batteries. There is also a discussion of the difficulties that come across and the potential upcoming developments of mentioned composites [132, 133].

At low temperatures, LIBs with $LiFePO_4$, as the cathode's capacity drops precipitously, make them unsuitable for use in colder climates. Many factors influence the less heat effect of LIBs as an electrochemical system: (i) cathodic and anodic kinetics, (ii) liquid electrolyte conductivity at low temperatures, (iii) interconnect among electrode materials, (iv) LIB architecture, and (v) charge/discharge protocol. LIBs are complex electrochemical systems. Low-temperature LIBs use a variety of carbon materials, all of which have important roles. Few points are focused primarily on the use of carbon parts to enhance the kinetics of low-temperature applications of LIBs. Carbon-based materials have

two primary functions: (i) optimization of the carbon coating: the kinetic models of $LiFePO_4$ materials can be greatly enhanced by applying a carbon coating with outstanding electronic and ionic permeability. Sugar, organic acids, and polymeric materials are preferable carbon sources to single carbon sources. (ii) The use of CNTs with high electron conductivity and division string framed carbon black with high electrolyte surface charges can help improve low-temperature performance, even more CNTs could indeed enhance the kinetic model of $LiFePO_4$ materials when grown in situ [134, 135].

LIBs with a cathode made of $LiFePO_4$ will be the subject of further investigation to improve their low-temperature performance. First, let us take a look at some of the low-temperature performance that can be improved by selecting the right anode material. Modern techniques for improving the anode's low-temperature performance include surface treatment/coating, doping to extend the distance between layers, and the use of fine-particle graphite. Micro- and nano-pores can be created in particles by oxidation and fluorination on the surface. Li^+ transport and interface resistance can be further improved using a porous structure [136]. Generally speaking, surface coating relates to hard carbon coating. Because of the huge surface range, coating hard carbon with graphite is beneficial to transport Li^+, which improves the reduced productivity of LIBs. Li^+ transport may also be impeded by a tiny surface range in graphite. B, P, and other essentials can be incorporated into graphite during preparation to improve the layer remoteness, which improves Li^+ embolism and de-interaction, which enhances the low-temperature behavior of graphite. Larger particles have a lengthier dispersal route and lower heat nature than smaller ones. It is, therefore, possible to improve minimal heat behavior using graphite with a smaller granular size [137, 138].

Carbon coating, fresh conductive extracts, and nanocarbon materials will all be used to improve the low-temperature and high-rate achievement of $LiFePO_4$ as cathode resources. Second, electrolyte vs. Li^+'s interface transfer properties are influenced by the electrolyte as well as the droplet transfer process. Electrolytes with reduced melting and low-viscosity cleaning agents are beneficial for enhancing the liquid phase transfer of Li^+ at cold temperatures. Non-polar solvents can be used as diluents in high-concentration electrolytes to decrease their stickiness and enhance Li^+ transfer in liquid phases. This includes local high-concentration electrolytes. This energy barrier is determined by the coordination of Li^+ with oil droplets and anions in solvation structures for interfacial transport of solvated Li^+. De-solvation energy of Li^+ can be reduced and speeded up by utilizing low-polarity thinners as the primary thinners, low-polarity/nonpolar organic solvent as co-solvents, and ionic flavors to speed up Li^+ transfer between electrodes, it is important to adjust interaction of a solvent with the dissolved solute nature and introduce mineral extracts to produce anion/additive generated metabolic stage on electrode surfaces [67, 139]. Charge/discharge protocol and thermal management system: the lower output achievement of LIBs with $LiFePO_4$ as the cathode can be enhanced by optimizing the thermal storage system and the charge/discharge method in addition to the cell's own electrochemical characteristics. The tiny distance among single cells in the battery pack leads to an irregular rate of heat dispersion, which eventually results in irregular heat flux and a reduction in aggregate battery pack performance. The battery pack's inconsistency will be exacerbated at low temperatures. A superior heat management design means that the rechargeable battery will always operate within a sensible range of heat, which is beneficial to the battery's performance and extends the battery pack life [140].

Cell capacity and life are significantly reduced at low temperatures due to the weak vibrant effectiveness of LIBs as well as a sharp increase in electrochemical impedance, which results in a large polarization during charging or discharging. Lithium dendrites may form during charging, resulting in a significant loss of capacity. Consequently, the battery's swelling can be increased with decreased battery damage through the optimization of the charge/discharge procedure to decrease polarization during the charge and discharge process. Low-temperature performance is also influenced by the battery's architecture [141, 142]. LIBs with higher capacities may generate more heat during charging and discharging, resulting in improved low-temperature performance. Self-heating batteries have been shown to quickly warm up the battery, and thus improve LIB low-temperature performance in related research. The vibrational features of LIBs evaluate their low-temperature performance as an intricate electrochemical system. To fulfill the essential criteria of LIBs in cold regions, CNMs would be fully utilized [143, 144].

3.3 CNMs in super-capacitors

The demand for high-performance super-capacitors is increasing every day as fossil fuels are consumed and science and technology advance. Because of high specific power, long cycle stability, and quick charge/discharge rates, super-capacitors are becoming increasingly popular as energy storage devices. Researchers working on energy storage devices, such as super-capacitors, have taken notice of the availability of low-cost active electrode materials. For electrochemical double-layer capacitors, carbon-based electrode materials have proven to be excellent because of their extraordinary chemical and physical properties as well as their low cost. Graphene-based materials were particularly effective in super-capacitors, with

a life cycle of 3,35,000 cycles. Exceptional and critical properties of conducting polymers include metal-like conduction and the ability to switch back and forth between oxidation and reduction states [145]. Various experimental investigations focused on the development of new materials for super-capacitors, such as mashed metal oxides and metal sulphurised. Because metal oxide electrodes (Co_3O_4, MnO_2, WO_3, NiO, and TiO_2) make up the majority of super-capacitors' construction, their steadiness and retaining are exceptional (up to 94%). The specific capacitance of metal sulfidee materials, such as $CoNi_2S_4$ and Ni_3S_2, has reached 3296 F/g currently. Super-capacitors outperformed standard capacitors in terms of energy density and were, therefore, used in high-density storage devices. The stability and retention of super-capacitor electrodes, which are primarily constructed of metal oxides (CoO_4, MnO_2, WO_3, NiO_2, and TiO_2) are excellent (up to 94%). Carbon-based materials and conducting polymers, as well as metal oxides and metal sulfide amalgams, are currently the focus of the investigation [146–148].

CNMs with hetero-atoms regulation and hierarchical system, notable pore volume, outstanding permeability with good sustainable development are encouraging energy materials for super-capacitors. The multi-faceted shape controllable carbon materials were designed and synthesized using watermelon rind as a carbon source by activation method. Indeed, the carbon materials showing a variety of 3D hierarchical honeycomb nanoporous carbon nanostructures, 2D carbon prototypes, and 1D syringe porous carbon bars with/without various doped morphometric categorizations were developed. For 879.18 m^2g^{-1}, the carbon-based energy material had a large specific area, and the adaptable electrode had an excellent areal capacitance of 2245 F/cm^2 at 1 mA/cm^2. Finally, the adaptable synchronous detector has cycling stability of 99.5% after 20,000 cycles and an enhanced energy-specific gravity of 0.12 mWh.cm^2 with a battery capacity of 0.52 mWh.cm^2. This provides a simple and long-lasting method for synthesizing highly energetic components for capacitors [149, 150].

The PCMs have pore structures that can range in size from molecular to nano-scale to micro-scale. Aside from catalysis and adsorption, these materials have shown great promise in hydrogen storage and energy storage due to their outstanding physiological and biological properties, such as their high surface-to-volume ratio, lightweight, and high chemical stability. When it comes to super-capacitors, PCMs are an excellent choice for electrode material. PCMs can be prepared in a variety of ways, but stimulation is the commonly used method. It is possible to categorize activation methods into bodily stimulation, organic stimulation, and self-activation based on the stimulator utilized in the process. Following the activation process, the capacitance performance of PCMs is summarized. Pore optimization and the impact of pore structure on PCM capacitance performance are also addressed [151, 152].

Many experimental trials were carried out in zinc-ion hybrid super-capacitors (ZHSCs) for energy storage applications. It has been widely discussed that ZHSCs have high power density, long life span, low cost, and environmental protection, but their low energy density is due to the decreased specific capacitance of carbon electrode materials. Zinc-based metal–organic frameworks are used here to synthesize zinc and nitrogen co-doped PCMs by binding two ligands. Due to the zinc and nitrogen co-doping, excellent pore structure, and high specific surface area, the carbon materials obtained have outstanding electrochemical characteristics with high specific capacitance and cycling stability. A 252.2 F/g specific capacitance, a 113.49 Wh/kg energy density, outstanding cycle stability, and excellent rate performance are all demonstrated by ZHSCs constructed using a zinc and nitrogen co-doped porous carbon cathode and a zinc metal anode. At a current density of 10 A/g for 10,000 cycles, the super-capacitor's capacity retention rate was 97%. Using 2D nanomaterials in the design of porous carbon electrodes is an attractive option [153, 154].

3.4 Hydro-voltaic technology

Hydro-voltaic technology is a state-of-the-art technology through which the generation of electricity has become possible with the interaction through nano-structured materials such as nanoporous carbon, graphene, and graphene derivates. This technology can be used directly to harvest fresh water from different environments which also reduces global problems. Hydro-voltaic technology has the potential to retrieve energy from a natural source more effectively [155, 156]. Carbon black and PCM are most commonly used materials in hydro-voltaic devices because of their low cost and long-term availability. Various studies were carried out on geothermal voltaic transformation processes giving a small summary of the latest developments in hydro-voltaic device development. Hydro-voltaic devices were also examined for their effectiveness, as well as their potential future use in a range of domains, including sensors, power supply, water recycling, and desalination. Few issues remained to be addressed, as well as some ideas for moving forward with the progress of this new technology [157, 158]. Figure 11 shows the schematic of hydro-voltaic technology where the freshwater generation is done by a hydro-voltaic generator built using nanoporous carbon materials (NCMs).

3.5 Adsorption and energy conversion applications

2D PCMs have attracted a great deal of attention in recent years because of their own distinctive morphological features, properties, and promising applications. Their unique

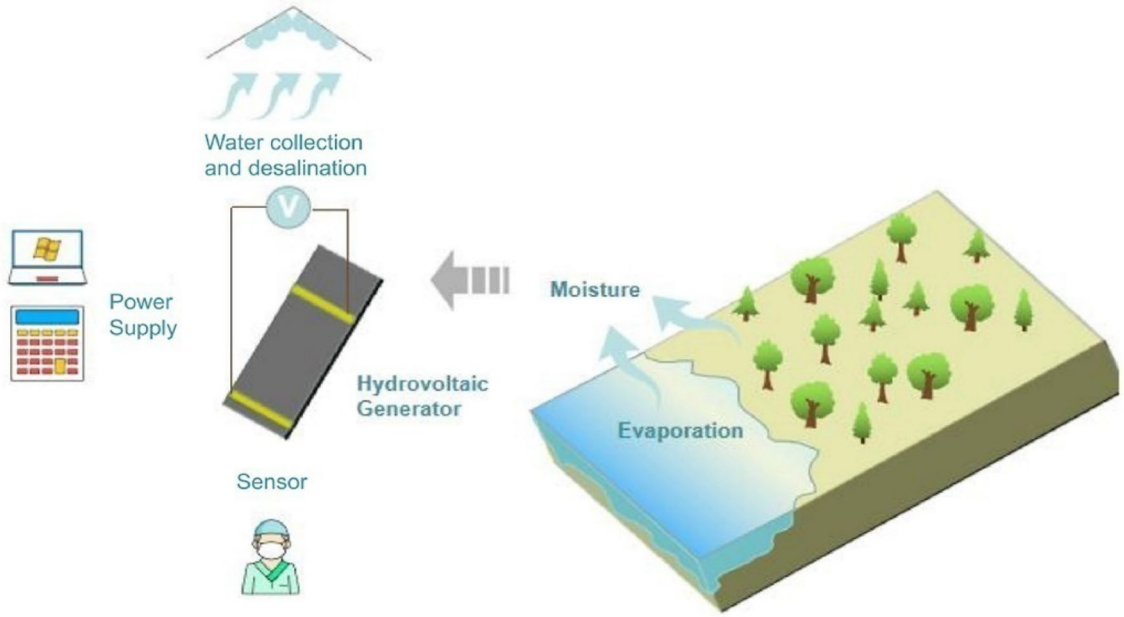


Fig. 11 Hydro-voltaic technology (Reproduced with permission from [157], Copyright Elsevier, 2022)

combination of 2D and porous properties, as well as their nano-scale thickness and large surface area make these materials ideal for a variety of energy-related applications such as thermal storage, catalysts, adsorption, and even energy storage. Since the explosion in graphene research, 2D PCMs have been particularly studied [117]. These materials' porous structures, which are significantly influenced by numerous synthetic measures, are the most important factors in determining their intended use.

Synthetic methodologies for 2D PCMs are the important porosity regulatory features highlighted for an individual technique. Li–S batteries, super-capacitors, lithium/sodium/potassium ion batteries, and heterogeneous catalysis are just a few of the energy storage and conversion devices that make use of these materials [159]. Method of heating plays a significant role in producing porous carbon structures suitable for LIBs and super-capacitor applications. Making PCMs involves a variety of heating methods, one of which is microwave irradiation.

In this method, the dielectric materials absorb the microwaves that kindle the translational and rotational motions of molecules through dipolar momentum. This results in the breakage of intermolecular bonding and the generation of new bonds along with the exothermic reaction of heat releasing. As an adsorbent or anode content in energy storage devices such as super-capacitors and LIBs, microwave-heated activated carbon is an excellent choice. For better understanding of the microwave-aided carbonization, activation, and rejuvenation of expanded activated carbon, accurate data of temperature measurement during microwave heating deem necessary which opens avenues for future works for developing activated carbons for energy adsorption applications [160, 161].

Various researchers investigated the thermo-physical attributes of magnesium nitrate hexahydrate (MNH), a salt hydrate, using carbon materials of various shapes and sizes. MNH/carbon composites were prepared by melting a variety of carbon fillers into the matrix, such as carbon spheres, multi-walled carbon nano-tubes (MWCNTs), mesoporous carbon, graphene nano-platelets (GNPs), and nano-graphite (NG). To examine the homogenous distribution of carbon materials in the MNH matrix, scanning electron microscopy (SEM) analysis was performed. The connection between carbon materials and MNH in MNH–carbon composites was studied using Fourier transform infra-red (FTIR) spectroscopy analysis. The thermo-gravimetric analysis (TGA) confirmed the cyclic stability of the composites developed. The addition of MWCNTs, GNPs, and NG at a 0.5 wt. % mass fraction significantly increased the thermal conductivity of MNH by 100%, 82.5%, 72.5%, and 65%. Adding carbon materials to composites improves their phase change properties while reducing the super-cooling effect, according to differential scanning calorimetry (DSC) results. The heat transfer properties of able to prepare MNH-carbon composites were evaluated using a traditional heating system to examine their practical viability. The MNH–carbon composite was found to have the greatest impact on charging time reduction. To conclude, a photovoltaic thermal energy storage system using an indigenously constructed

immediate solar water heating system employed the finest MNH–carbon composite with the greatest heat capacity and stability and the least amount of super-cooling [162–164].

3.6 Gas storage applications

When it comes to energy storage, cost includes the cost of raw materials and the ease of dispensation techniques. Coal samples from lignite, bitumen, and anthracite were used to produce oxygen-dynamic sector carbon materials. Tg-MS measurements and DFT calculations show that oxygen functional groups such as quinones, carboxylic anhydrides, and lactones are more easily formed close to defects than other functional groups. The lowest metamorphic-grade brown-coal-obtained carbon has cycling stability of 259.7 mAh/g after 50 cycles at 0.03 A/g, the best among these micron-sized coal-based carbons. At different scanning rates, in situ Raman and sinusoidal chronoamperometry curves reveal high stability and a large portion of sodium memory capabilities from surface active sites that are highly stable. Anode materials for SIBs can be made from coal-based carbon components as described by many earlier researchers [165, 166].

It was common practice to use NCMs in commercial adsorbents because of the maximum specific surface area and important bulk of micro-pores. The transformation of a combination of composites (furfural, hydroquinone, and urotropine) into an NCM, which has characteristics appropriate for adhesion of atoms and gas storing purposes, via alkaline stimulationwas investigated [167]. The surface area of the developed NCM is around 2722 m^2/g, and the volume of the pores is around 1.08 cm^3/g, which means that about 80% of the pores are narrow micro-pores. For the storage of methane (CH_4), the NCM's density is a critical factor, as is the thickness of the material. For a monolith NCM, the texture properties of the powdered NCM were slightly altered after it was compacted 2.5 times. Adsorbents synthesized for CH_4 adsorption were tested, and they performed well. At 10 MPa and 298 K, the powdered NCM had the maximum CH_4 adsorption capacity, with a value of 14.3 mmol/g, while the monolithic NCM's value drops to 13.3 mmol/g at uniform pressure after compaction. A total of 336 cm^3 of bulk CH_4 biosorbent ability has been attained at 10 MPa and 298 K for the NCM monolith. These excellent CH_4 adsorption characteristics of the new sorbent could be used in the adsorbed natural gas (ANG) techniques to improve energy storage and efficiency [168]. Table 2 shows the measured specific surface area, specific capacitance, and current and voltage density for various CNMs derived from biomass that was experimented for energy storage applications.

4 Challenges and future prospects

Biomass wastes obtained from dry leaves, outer shells of fruits, plant stalks, seeds, and roots can be effectively used as a biosource for the production of CNMs. The main advantage of using these wastes as CNMs precursors is that they are easily available, low in toxicity, sustainable, renewable and recyclable, and harmless to the environment. In most cases, recycling of the biomass may not be feasible as they loss their strength after many cycles of utilization and as per most of the literature, it is advisable to convert them into CNMs through suitable process. Moreover, recycling becomes feasible only when those biomasses were converted into some products such as lignocellulosic-biomass-based polymer composites. Instead, conversion of such biomass into CNMs was proven to be much more effective in variety of applications [224, 225]. Despite the cost of processing of CNMs from biomass, their advantageous porous microstructure and presence of large quantities of micro constituents like lignin and cellulose facilitate the effective rendering of CNMs for energy storage applications. Processing cost is relatively cheaper for mass production of CNMs from the biomass when compared with small-scale production. Since the biomass-derived CNMs possess large ion diffusion distance and easy electrolyte penetration, they render longer service life when compared with CNMs derived from synthetic sources. This clearly justifies the large cost of production of CNMs from the biomass [226, 227].

Many laboratory-scale experiments were carried out to assess the requisite properties of biomass-derived CNMs for their suitability in various energy storage applications [23, 71]. Yet, to accomplish a full-scale commercial implementation of these biomass-derived CNMs in energy storage devices, a few hurdles are to be overcome. Activation of carbon materials is done only using synthetic chemicals and this cannot be made using natural materials. Hence, this method demands a huge quantity of chemicals to be used which in turn retards the environmental friendliness of the biomass and increases the cost of the process. Chemical residues also reduce the porosity of the CNMs making them unsuitable for energy storage applications. In a few of the studies stated in earlier sections, manipulation of pore size of carbon was mentioned. But with some activation methods like KOH activation, pore geometry and size of the hierarchical PCMs cannot be easily manipulated. To obtain PCMs with high specific surface area and pore geometry, better electrolyte wettability, and enhanced electrical conductivity heteroatom doping have to be done which is again a complicated process [52, 133, 228, 229].

All the tests and evaluations stated above were only at the laboratory scale and the performance of PCMs

Table 2 Electrochemical properties of biomass-derived CNMs for energy storage applications

S. No	Biomass source	Electrolyte/ activation method	Specific surface area (m^2/g)	Specific capacitance (F/g)	Current density (A/g) or voltage density (mV/s)	Ref
1	Sunflower seed shells	Potassium hydroxide (KOH)	2599	310	0.25 A/g	[169]
2	Ant	KOH	2652	354	0.1 A/g	[170]
3	Garlic skin	KOH	2820	429	0.51 A/g	[171]
4	Sodium lignosulfonate	KOH	1869.2	371	0.49 A/g	[172]
5	Corn straw	KOH	1661	328	0.22 A/g	[173]
6	Sugarcane bagasse	Sulfuric acid	1940	299	1.1 A/g	[174]
7	Chitin	KOH	1000	110	1000 mV/s	[175]
8	Zuccini plant	KOH	186	348	2.1 mV/s	[176]
9	Kapok wood dust	Boron fluoride and polycarbonate	1601	142	1 A/g	[177]
10	Salvia splendens plant	KOH	1053	296	1 A/g	[178]
11	Walnut shell	KOH	3579	331	0.1 A/g	[179]
12	Shrimp shells	KOH	1948	323	0.5 A/g	[180]
13	Popcorn residue	KOH	3300	289	90 A/g	[181]
14	Ants	KOH	2651	578	1 A/g	[182]
15	Bagasse	KOH	1893	269	2 mV/s	[183]
16	Chitosan powder	KOH	2910	377	1 A/g	[184]
17	Rape pollen	KOH	2490	291	0.5 A/g	[185]
18	Cyclodextrin	KOH	662	323	0.5 A/g	[186]
19	Gelatin	KOH	394	360	0.1 A/g	[187]
20	Waste flour	KOH	1315	475	0.5 A/g	[188]
21	Red algae	KOH	4038	337	1.1 A/g	[189]
22	Waste newspapers	KOH	2814	310	1.2 A/g	[190]
23	Coconut shells	K_2CO_3	1508	92.15	0.2 A/g	[191]
24	Celtuce leaves	KOH	3405	420	0.6 A/g	[192]
25	Cornstalks	NaCl, KCl	1589	410	1 A/g	[193]
26	Wheat straw	$CaCl_2$	893	277	0.2 A/g	[194]
27	Lotus leaf waste	KOH	2490	378	1 A/g	[195]
28	Bougainvillea flower wastes	KOH	851	460	2.31 A/g	[196]
29	Tremella waste	KOH	1098	298	0.5 A/g	[197]
30	Egg yolk	KOH	–	550	1 A/g	[198]
31	Fish scale	KOH	965	308	1 A/g	[199]
32	Keratin fibers (Chinese)	KOH	1310	338	1 A/g	[200]
33	Cotton stalk	KOH	1968	255	0.21 A/g	[201]
34	Lotus stem	–	1611	175	0.49 A/g	[202]
35	Rice straw	KOH	1120	338	1.1 A/g	[203]
36	Lotus receptacle	KOH	1018	338	0.5 A/g	[204]
37	Rose petals	KOH	1913	210	0.5 A/g	[205]
38	Perilla frutescens	KOH	654	272	0.51 A/g	[206]
39	Macadamia shells	KOH	2810	232	1 A/g	[207]
40	Rice husk	KOH	3121	318	0.12 A/g	[208]
41	Banana fibers	$ZnCl_2$	1098	75	0.51 A/g	[209]
42	Waste coffee beans	$ZnCl_2$	1020	369	5 A/g	[210]
43	Coconut kernels	KOH	1201	175	–	[192]
44	Sunflower seed shell	KOH	1236	145	10 A/g	[211]
45	Cotton stalk	H_2PO_4	1482	115	2 A/g	[212]
46	Sugarcane bagasse	$ZnCl_2$	1789	301	1.5 A/g	[213]
47	Sorghum pith	NaOH	36	321	10.1 A/g	[214]
48	Coffee bean shells	$ZnCl_2$	843	160	1.1 A/g	[215]

Table 2 (continued)

S. No	Biomass source	Electrolyte/ activation method	Specific surface area (m^2/g)	Specific capacitance (F/g)	Current density (A/g) or voltage density (mV/s)	Ref
49	Waste Corn grains	KOH	3421	260	–	[216]
50	Waste neem leaves (Shed)	KOH	1232	401	0.5 A/g	[217]
51	Tobacco rods	KOH	–	287	–	[218]
52	Pistachio shells	KOH/CO_2	781	2148	–	[219]
53	Water hyacinth waste	$ZnCl_2$	1310	275	7.31 A/g	[220]
54	Bamboo wastes	Steam	1026	61	–	[221]
55	Brussel sprouts	KOH	2411	256	–	[222]
56	Recycled paper	KOH	–	418	–	[223]

derived from biomass has to be assessed in real-time which demands highly accurate and large-scale research and process protocols starting from the precursor materials. In the current scenario, the life cycle of the CNMs and the energy storage devices at the industrial scale must have low impacts on waste generation by having sufficient reclaiming and recycling policies. Stringent life cycle assessment (LCA) methods for electrochemical devices may expand the scope of commercialization of bio-based devices [35, 230–232]. By building a sustainable energy storage system with biomass feedstocks as carbon precursors, reduced utilization of non-environmentally friendly chemicals, metals and reusing the materials will alone render a truly bio-based energy storage system. Sustainable electrochemical devices can be built only when the concept of green chemistry and technology were applied during the material production and system manufacturing which ultimately contributes largely to the circular

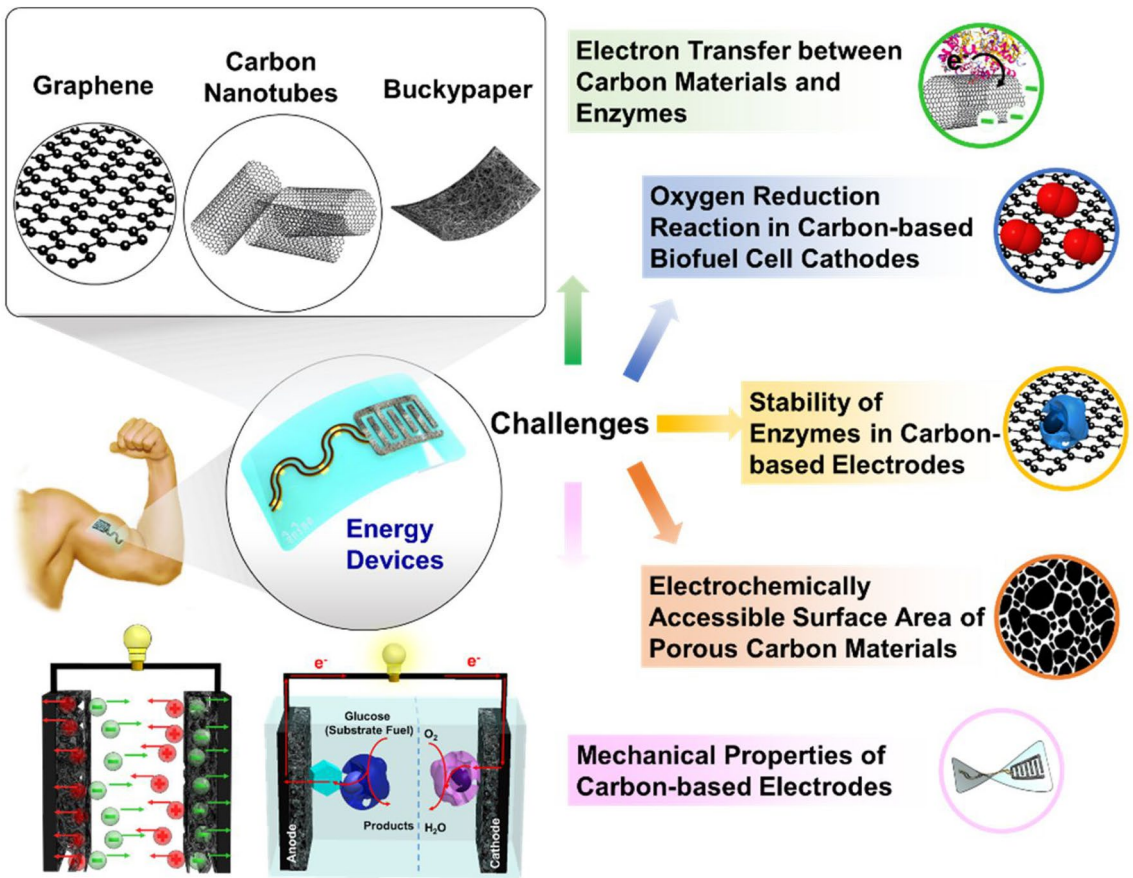


Fig. 12 Challenges faced in full-scale implementation of biomass-derived CNMs (Reproduced from [235], Copyrights 2019, MDPI)

economy [233, 234]. Figure 12 graphically depicts the challenges involved in full-scale implementation of biomass-derived CNMs in energy storage applications like supercapacitors and wearable electronic devices.

In general, future scope is assessed based on the research articles, industries bulletins, forums of scientific communities, and the patent landscape. Here patent landscape has been chosen as a metric to forecast the future scope of biomass-derived CNMs because of its immediacy in database updates when compared with other databases. A patent landscape analysis usually describes the analysis of patent data to describe the scientific, industrial, and technological trends. Landscape analysis can be carried out for a single industry, geographical region or a technological trend [236, 237]. Figure 13 depicts the number of patents filed in the utilization of CNMs for energy storage applications. It could be seen from the figure that a total of 14,129 patents were filed. The figure also reveals that USA dominates in this technology followed by China. Researchers want to work on this domain, looking for research collaboration in cross-countries. The major applicant is "LG Chem Ltd." with a filing count of 583 patents and no other players are able to compete. As an individual player, "Mr. Aruna Zhamu" dominates with a patent filing count of 140. Researchers aim for this company and this collaborator might have good scope for their research. Intentional patent classification (IPC) code plays a pivotal role for the researchers to converge their search with the aid of H01M is quite dominative. Growth in this technology is clearly depicted by the number of patents filed over the years, which has shown continuous progression.

Figure 14 depicts the number of patents filed using carbon-based materials derived from biomass used in energy storage applications. A total of 18 patents were filed in this field with various inventions heading toward the process and techniques adopted for the utilization of biomass for deriving CNMs and their application in energy storage devices. The figure also reveals that the USA dominates in this technology followed by Canada. Researchers aspiring to work in this domain and looking for research collaboration can look to these countries. The major applicant is "Aemerge LLC" with a filing count of 3 patents, none of the other players are unable to compete. As an individual player "Mr. Christopher R. Swartz" with a patent filing count of 2. Researchers aim for this company and this collaborator might have good scope for their research. IPC codes of C01B, H01G, and H01M are quite dominative to converge these searches. Growth in this technology is clearly depicted by the number of patents filed over the years, which has shown to progress.

A lot of patents were filed by various countries, industries, and researchers around the globe encompassing the biomass-derived CNMs as stated in the above analysis. Few Chinese researchers filed a patent to claim the novelty of the preparation method of energy storage electrode material from CNMs derived from the biomass pyrolysis oil. A novel hydrogenation and carbonization method was carried out by the researchers for preparing CNMs and, thus, the electrode material. Another researcher filed a patent claiming

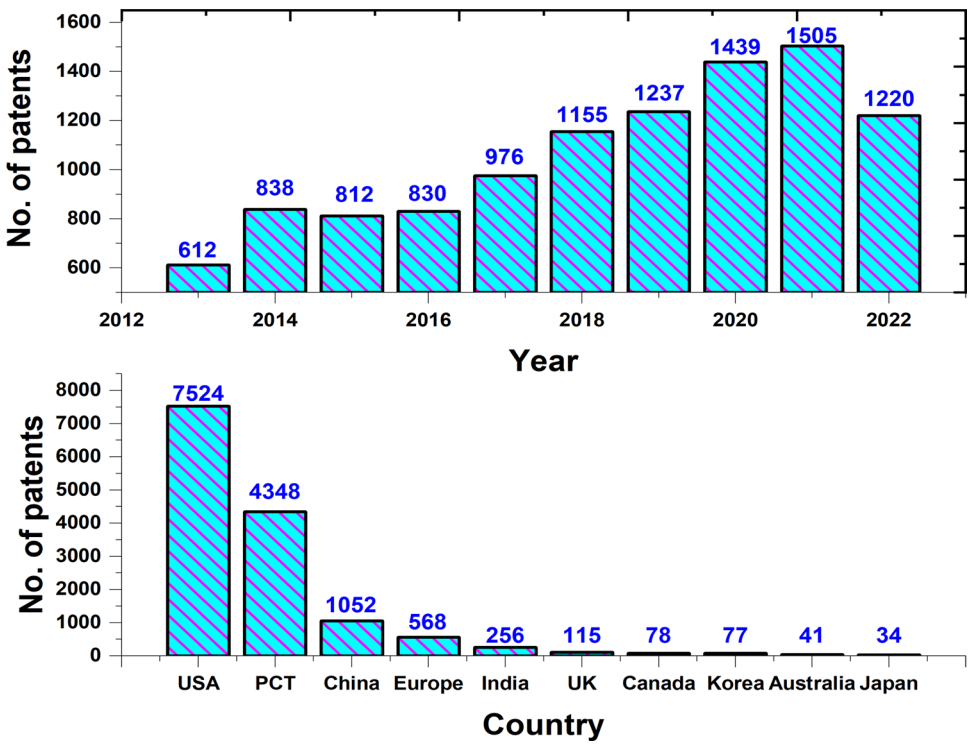


Fig. 13 Patent landscape for use of carbon materials in energy storage

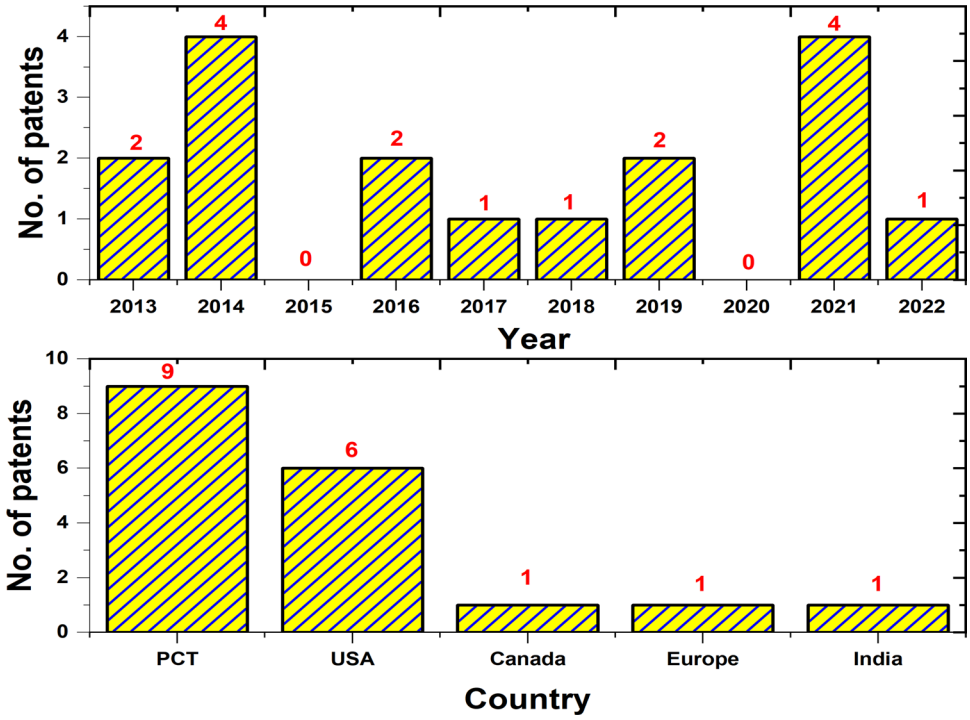


Fig. 14 Patent landscape for biomass-derived carbon material in energy storage

the novelty of the process involved in converting bamboo into bamboo charcoal for its use in energy storage devices. This patent was also a process-oriented patent and the claims were made on the carbonization, hydrogenation, and transformation process used to obtain CNMs from bamboo biomass. Hence, it could be observed that the technology involved in deriving CNMs have played a major role in the patents filed on biomass-derived CNMs [238, 239]. However, data regarding the implementation of the patents into a technology by an industry cannot be much obtained. But this trend clearly shows that the biomass-derived CNMs will clearly dominate the energy storage industries in near future.

5 Conclusion

Current-day energy storage requirements are fast changing owing to the increase in energy demand for electronic and electrical appliances which require faster power delivery and a high quantum of energy storage. CNMs are more prevalent in development of energy storage devices such as batteries, super-capacitors, electrochemical storage, energy conversion, and absorption applications. Yet, currently, carbon-based materials are derived from fossil fuel precursors with complex processing, high energy requirements, and high cost of production. Biomass could serve as potential alternative precursor materials for deriving NCMs which are considered to be highly sustainable, abundantly available, cheaper, and promising microstructures. Even though the current energy storage markets are dominated by super-capacitors, batteries, and other storage devices made of non-renewable synthetic sources-derived carbon-based materials, the future of these energy storage systems lies in the hands of NCMs derived from biomass so that they effectively act as alternatives for synthetic graphite in batteries and synthetic activated carbon in super-capacitors. The focus of this review is on various biomass sources from which NCM has been derived using various activation and modification techniques. Owing to the diverse modification and processing techniques, the resulting carbon materials had effective pore size distribution, porosity, pore dimensions, enhanced specific surface area, and modified surface morphology to accommodate an increase in pseudo-capacitance, cyclic and chemical stability, electrical and thermal conductivity. This review clearly portrays the microstructure and other physical properties along with the electrochemical performances of biomass-derived carbon materials for advanced energy storage and other functional applications from a multi-disciplinary point of view. Alongside, the use of such carbon materials in energy conversion, absorption, and gas storage applications has also been highlighted. From the literature, it could be readily concluded that biomass-derived CNMs will undoubtedly pave way for a sustainable future for energy storage devices which also brings reforms in the circular economy and structure of energy consumption. More rigorous research can be accelerated in this field so that the changes in these technologies become highly inevitable in the future.

Data availability All data collected or analysed during this review are included in this article.

Declarations

Conflict of interest All authors declare that they have no conflicts of interest.

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