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Plant Biomass Derived Multidimensional Nanostructured Materials: A Green Alternative for Energy Storage

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Abstract

Utilization of plant-based bioresources toward the exploration and development of novel nano materials for long-term sustainable energy storage could enhance cost competitiveness in terms of energy supply markets and reduction of environmental impacts, and meet the urgent need for green and sustainable development strategies. The latest research trend in energy storage is to focus on storage devices including supercapacitors (SC), lithium-ion batteries, fuel cells, and lead-acid batteries. SCs are attractive due to their superior performance in power and energy densities along with prolonged life cycle and easy operating conditions in applications such as electric vehicles, portable electronics as well as stationary electric grids. Since SCs are constructed by non-renewable and fossil resources, urgent alternative effective materials are the need of the hour. Multidimensional high porosity nanostructured carbon from renewable biomass sources could be a promising greener alternative as electrode materials for SC. In SCs, porous nanocarbon derived from biomass acts as conductive layer on the electrode surface. Electrical conductivity, accessibility of electrolyte, pore structure and shape, pore size distribution, along with high surface area play major roles on the specific capacitance of the SC. This review comprises the latest research platforms on biomass-derived multidimensional nano carbon electrode materials for energy storage devices specifically for SCs and their future outlook.

Keywords: Energy storage devices; Multidimensional nanomaterials; Plant biomass; Supercapacitors.

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1. Introduction

The drastic climate change is now recognized as a severe threat to the well-being of the world, particularly to the existential flora and fauna prevalent in the nature. A significant contributor to the climate change is the over-dependence of economic growth on fossil fuels based energy consumption.[1] To mitigate the change and to provide an effective alternative, the energy issue has to be addressed by having affordable, reliable, secure, clean and equitable energy supply. Future energy demand and supply, along with environmental and social context, are dependent on a slew of uncertainties that arise due to global economic and geopolitical situations and technological advancements. The path forward is shifting to renewable energy generated specifically from carbon neutral, biomass-derived materials, to ensure reduced Greenhouse Gas emissions and meet the future energy demands sustainably.[2]

Biomass derived energy has the potential to develop into an economical, greener alternative to coal and fossil fuels. At the same time, it seamlessly aligns with other renewable energy sources such as wind, solar, hydro, and geothermal. It has the potential to contribute significantly to all the energy generating sectors such as electrical power stations, automobile industry for societal needs, and also in domestic sectors for everyday energy consumption.[3] Sheridan C. predicts that post 2030, transportation sector will get more efficient by accommodating biofuels and electric vehicles, and slow down the use of the predominant fossil fuels. By 2050, the non-renewable energy sources' contribution to energy is predicted to go down from 66% to 38%, particularly the primary energy demand from coal, fossil fuels, and gas. Promising value-addition from plant-based bioresources has

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received extensive attention and has becomes a hot research topic globally due to their merits of renewability, unique micro-structure, and specific chemical composition.[4]

Electrochemical energy storage systems (EESSs) are crucial and integral part of our life because of our dependence on transportation vehicles and electronic gadgets. In addition, developing energy storage devices with lightweight, long lifespan and smaller size is the need due to the ubiquitous usage of smart and portable electronics. EESSs including 1) Supercapacitors, 2) Batteries: a) Lithium-ion batteries (LiIBs), b) Sodium-ion batteries (NaIBs) and c) Lithium-Sulphur batteries (LiSBs) have attracted enormous interest in research community. Wide range of electrochemical performances of high power/energy densities, high capacity, good safety and good cyclability are expected with these different classes of EESSs which are dependent on the electrode material. High performance EESSs can be achieved with development of novel nanostructured electrode materials with desirable properties such as large surface area, reduced ion diffusion, easy electrolyte accessibility. Amongst a variety of nanostructured materials, carbon nanomaterials attract attention due to their large surface area, cost effectivity, high conductivity and unique geometry.[5] Particle size reduction to nano level leads not only to tremendous increase in the availability of atoms on the surface but also decreases the core to surface distance for ion transport.[6] The applications of these electronic devices have broadened when we explore at nano level, such as zero, one, two, and three dimensions. There is a need for developing cutting edge electrochemical energy storage devices by overcoming current restrictions and thus substantially enhance the prominence of energy storage devices, such as batteries and supercapacitors (SC).

Plant-based biomass residues, which are available post-harvest, is severely under-utilized and the current practice is to burn them in open fields. This has become a significant contributor toward poor air quality. Several research groups are working on effects of crop residue burning on nutrient loss of soils. Sinha *et al*. investigated the rise in the levels of carcinogenic benzenoid compounds such as BTEX (benzene, toluene, ethyl benzene and xylene) along with trimethyl benzene on paddy reside burning in north western India.[7] Global atmospheric chemistry and physics is destructively affected by biomass fires. The air quality and climate are damagingly affected by organic aerosol formation and ozone due to the emittance of reactive compounds during the biomass fires.[8]

On a positive note, Vadlani enumerated the constructive use of lignocellulosic biomass, including agricultural and forest residues, toward production of sustainable bioenergy and advanced platform chemicals and polymers, which is a significant step in the right direction from the climate change mitigation perspective. Further, Vadlani *et al.* elucidated in detail the financing methods that can be executed to enable sustainable chemical bioenergy industries.[9–11] Biomass was utilised for sustainable energy production by several researchers across the globe for wide variety of applications spanning from biofuels,[12–14] chemicals,[15,16] enzymes,[17–19] and carbon dots[20] *etc*. through strategic pretreatment[10] techniques[21] for applications such as carbon dioxide (CO_2) capture,[22] hydrogen storage,[23] dye-sensitized solar cells,[24] water treatment,[25] and energy storage[26] due to its widespread availability, sustainability, renewable nature, unique structure, and low cost.

There are several reviews highlighting the nanoscale origin in energy devices,[27] bio-nanotechnology in high performance SC,[28] biomass derived carbon materials for SC,[29] application of nanomaterials in energy storage,[30] zero dimensional materials for various applications,[31] one-dimensional (1D), two-dimensional (2D)[32] and three-dimensional (3D) biomass derived materials for electrodes in SC,[33] doping,[34] design and principles of energy storage[35] and also latest trend of flexible energy devices.[36] Shao *et al*. reviewed the synthesis strategies for improving electrochemical performances using various dimensional nanomaterials for supercapacitors which include carbon sources from non-renewable sources.[37] Similarly, Du *et al*.[38] and Asyadi *et al.*[39] reviewed design and synthesis of transition metal oxides for supercapacitor applications in detail about the structure-property relationship. Yu *et al*. critically reviewed the recent advances in the design of electrode materials in zero to three dimensions for energy storage devices.[40] The effect of nanostructure on important properties of supercapacitors such as rate capability, specific capacitance and cycle stability were discussed. However, the materials considered in the review are non-renewable sources such as graphene, metal oxides, transition metals. Ma *et al*. reviewed electrode materials of different dimensions for high performance supercapacitors in transition metal oxides.[41] Biomass polymer such as xylose is used for capacitive deionization by pyrolysis with $KHCO_3$. Adsorption capacity of 16.29 mg per gram was observed through this novel strategy with low cost of preparation and superior desalination performance.[42] Li *et al.* substantially reviewed the consideration of biomass materials-based electrodes for electrical double layer capacitance (EDLC) supercapacitors. They were pragmatic about the feasibility of biomass materials with respect to specific surface area, pore diameter controlling, pore size structure resulting in poor EDLC performance.[43]

Lu *et al*. reviewed biomass polymers such as cellulose, hemi-cellulose and lignin derived materials for supercapacitor applications of various synthesis strategies such as activation and/or carbonization at various lab scale methods. Analysis of electrical conductivity, control over pore structure, surface functional groups for electrochemical enhancement was also discussed.[44] Wang *et al*. reviewed relationship between properties of supercapacitors to various species of biomass used for preparation of electrode materials and their influence on degree of graphitization, introducing heteroatoms, specific morphologies on electrochemical properties.[45] Data mining technologies such as artificial neural networks were employed to predict electrochemical properties of biomass derived electrode materials. Specifically to predict the structure performance relationship of biomass based supercapacitors and batteries;[46] different dimensions of biomass derived carbon materials for supercapacitors electrodes were also reviewed to utilise the inherently precise and uniform biological structures.[33] Supercapacitors with binder-free electrode materials or free-standing electrode materials from renewable sources were also reviewed.[47]

In our review, we comprehensively evaluate the renewable resources of carbon, including the origin of biomass usage, trends in energy production, principles of energy storage, and biomass derived multi-dimensional nanostructures for SC and next generation EESSs. The primary purpose of this review is to inform the scientific community regarding the appropriate properties of electrode materials and enhance the supercapacitors efficiency and performance. Novel nanoelectrode materials in 0, 1, 2, 3 dimensional materials from biomass derived carbons including overview of design, challenges and recent development of new electrode materials, are presented in this review along with their evaluation for potent electrochemical performance in supercapacitors.

Use of lignocellulosic biomass is associated with a number of opportunities as well as challenges. The beneficial characteristic of the lignocellulosic biomass is its unique components including carbohydrate polymers (cellulose and hemicellulose), lignin, and extractives which possess a wide range of applications.[21]

1.1 Structure of lignocellulosic biomass

Typical structure of lignocellulosic biomass comprising primarily cellulose, hemicellulose and lignin is depicted in Fig. 1. All three polymers assemble to form microfibrils, which are then bundled to form macrofibrils, thereby facilitating unique structural stability to the cell wall. Cellulose, a β-1,4 linked chain of glucose molecule, is the main component of lignocellulose. Resistance to degradation arises from the hydrogen bonds between polysaccharide layers. Hemicellulose, a polymer of 5- and 6- carbon sugars namely glucose, xylose, arabinose, galactose, and mannose are the second most abundant materials. Further, p-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S) are the three major phenolic compounds that constitute lignin. Polymerization of these polymers varies in different ratios depending on plants, wood tissues, and cell wall layers.[48]

1.2 Innovative way forward in energy sector

The first prerequisite for sustainable manufacturing is the availability of non-fossil sources of energy that are economical and renewable. Fig. 2 provides an intuitive road map that captures the recent developments in various energy technologies as potential replacements to the current non-renewable fossils.[49] In this context, it is paramount to explore the naturally available renewable sources of energy that are green and are efficient technologies for the energy production and assimilation. One of the keys to resolve this issue is to address the design and development of clean and sustainable energy through two important aspects namely:

i) Successful energy conversion from renewable sources.
ii) Advancements in reliable energy storage devices like SC and rechargeable batteries.

There is a need for storage strategies, since renewable energy sources are mostly intermittent due to cropping cycles. At the moment, widely used EESSs are secondary batteries. There is a limitation for use of batteries in energy storage due to low cyclability and short life span. This happens because during the charging and discharging process of the energy in batteries, the electrodes and electrolytes undergo

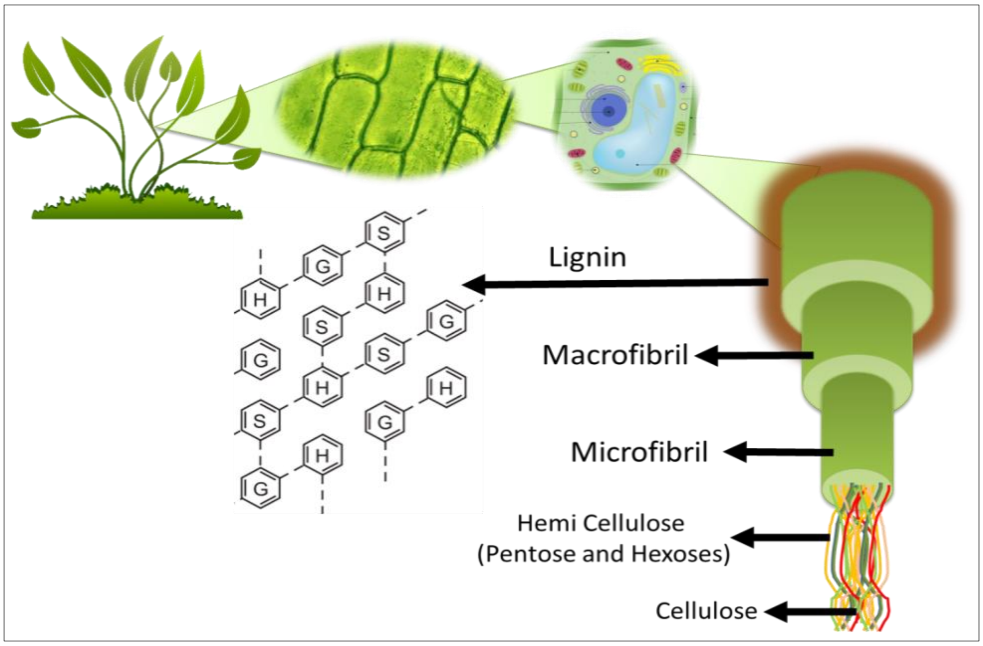

Fig. 1 Structure of lignocellulose: Cellulose, Hemicellulose and Lignin. Reproduced with the permission from [50], Copyright 2021 Elsevier Ltd.

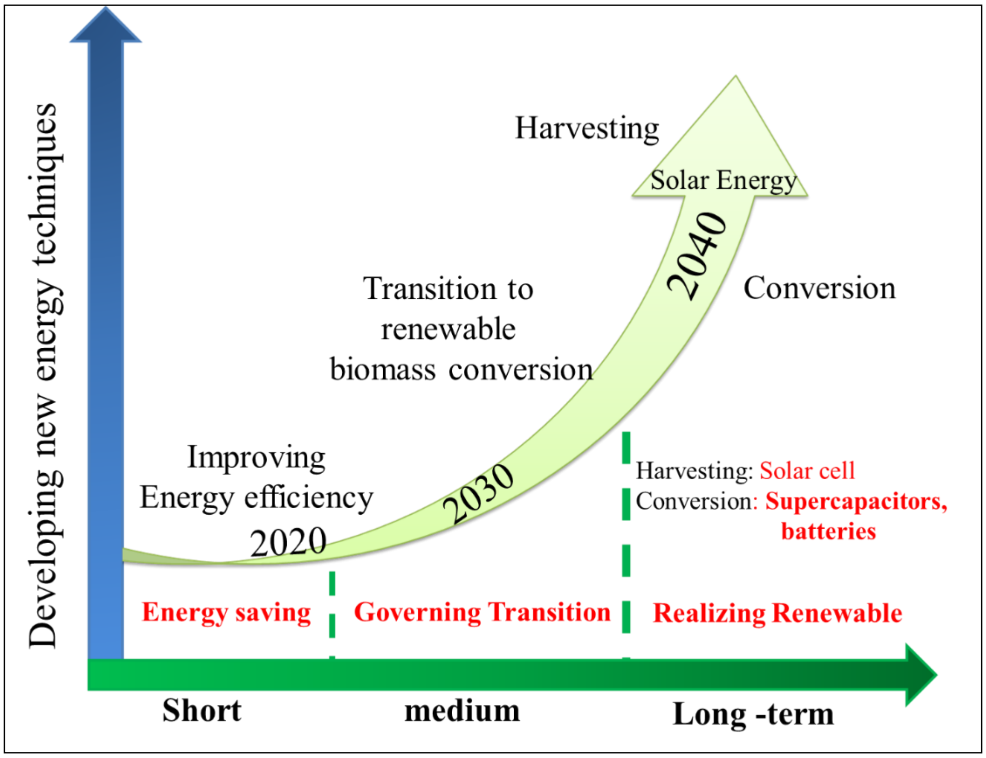

Fig. 2 Indicative roadmap of future energy scenario. Reproduced with the permission from [53] Copyright 2019 Elsevier Ltd.

physicochemical changes. SCs have divergent properties compared to batteries due to good cycling stability and high-power density; however, high cost, high effective series resistance, and low energy density limit their utility in energy storage. Lead acid and lithium-ion batteries have higher energy density over SC; however, in terms of long-life cycles, high power density, low safety concerns and high cyclability, the latter is more desirable and has gained prominence as novel energy systems. Performance comparison of various electrochemical storage systems are tabulated in Table 1. Thus, increasing the energy density of SCs has become the foci of many researchers. The three crucial components of SCs are: 1) electrode materials, 2) electrolytes, and 3) separators. Decreasing the equivalent series resistance (R) and increasing either or both operating voltage (V) and specific capacitance (C) will increase both energy density and power density. SC specific capacitance can be enhanced by optimising the already existing electrode materials or finding new materials with more suitable surface area, electrical conductivity, and interconnected porosity.

Energy is stored in SC based on dual capacitive behaviours:

1) **Electrical Double Layer Capacitance**: EDLC arises due to electrostatic interaction. The advantage of EDLC is that no swelling of electrode materials is experienced, and polarization resistance does not restrict electrochemical kinetics. Two nano porous electrodes connected to current collectors on each electrode store the energy. The discharge of accumulated charges from the electrode releases the energy stored as observed in Fig. 3. This stored energy is thus proportional to the number of charges stored, which in turn are dependent on the surface area of the electrode. For an electrode material to be a good candidate for supercapacitor application, it must have high surface area. Performance of SC can be

Table 1. Comparison of SCs with batteries and conventional capacitors.

Parameter	Conventional capacitor	Supercapacitors	Batteries
Power density	< 100,000 W kg^{-1}	< 10,000 W kg^{-1}	1000 W kg^{-1}
Energy density	< 0.1 W h kg $^{-1}$	1-10 W h kg^{-1}	30-40 W h kg^{-1}
Charge time	10^{-3} – 10^{-6}s	0.3-30 s	1-5 h
Voltage	6-800 V	2.3 V-2.75V/cell	1.2V-4.2V/cell
Discharging time	10^{-3} – 10^{-6}s	0.3-30 s	0.3-3 h
Life cycle	>500,000	>500,000	1000
Charging and discharging efficiency	95%	85-98%	70-85%
Operating temperature	-20-100 ℃	-40-85 ℃	-20-65 ℃
Form factor	Small to large	Small	Small to large
Weight	1 g to 10 kg	1 to 2 g	1 g to >10 kg

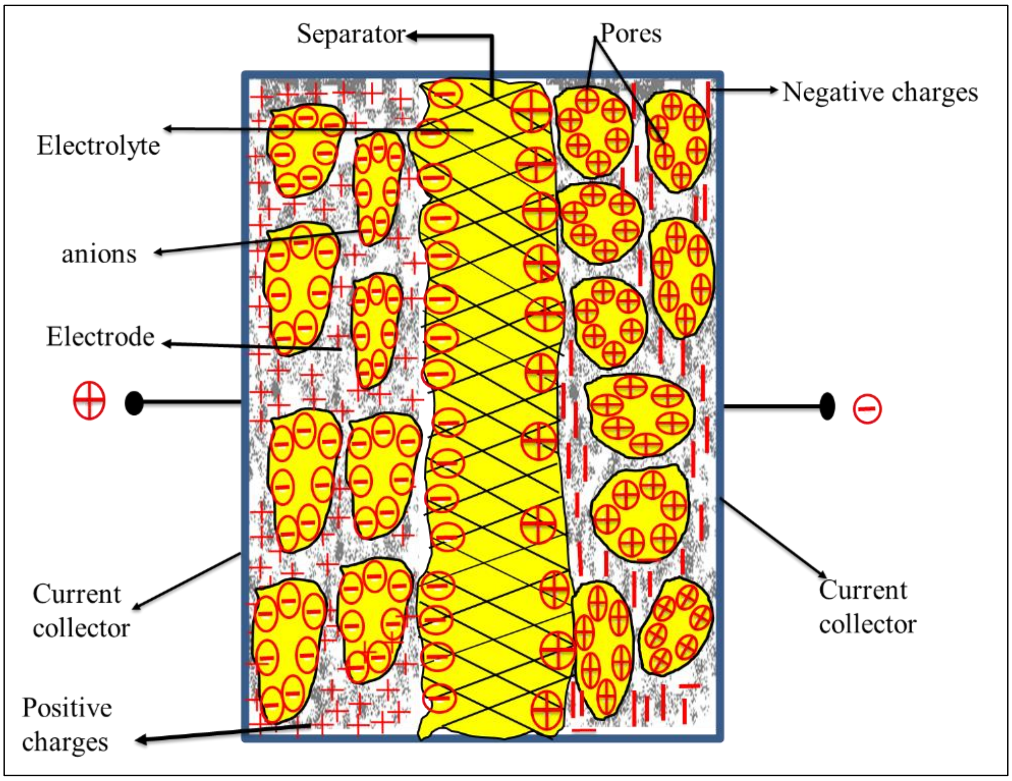

Fig. 3 Schematic representation of electrode interface in supercapacitor. Reproduced with the permission from [51] Copyright 2019 Elsevier Ltd.

enhanced through finding new materials for electrodes, exploring the behaviour of ions in the micro, macro and meso pores, and by strategically combining capacitive electrodes and faradaic electrodes to achieve hybrid systems.[52,53]

Rice husk carbonization through novel hydrothermal process was undertaken to synthesize manganese silicate composite nanostructures possessing excellent properties such as high specific surface area, electrolyte ions fast absorbance/desorbance, and electrolyte wettability. Further investigation of this composite material for supercapacitance gave EDLC of 108 F g^{-1} at 1 A g^{-1} and exceptional cycling behaviour after 8400 cycles at 82%. Flexible solid-state hybrid supercapacitor was assembled with manganese-silicon and nickel hydroxide.[54] Wheat straw derived biochar through microwave heating was explored to synthesize mesoporous carbon. Doping of oxygen containing chemical groups was observed through a series of post oxidation reactions between oxygen and active sites of porous carbon. High specific surface area of 1905 m^2 g^{-1} was observed with 21.6% of oxygen rich structures with well-balanced pore distribution of meso-/macropores (0.53 cm^3 g^{-1}) and abundant micropores (0.62 cm^3 g^{-1}). These superior characteristics resulted in high ELDC specific capacitance of 268.5 F g^{-1} at 0.5 A g^{-1} along with 81.2% high retention at 10 A g^{-1}. High power density of 7.2 kW kg^{-1} at 10 A g^{-1} and high energy density of 21.5 Wh kg^{-1} at 0.5 A g^{-1} was extracted from mesoporous high surface area carbon.[55]

2) **Pseudo capacitance**: It arises due to faradaic reactions involving reversible and fast electrochemical reactions. The electrolyte and electrode materials involve redox reactions between them. Electrons are the products of these redox reactions, which are transported between electrode and electrolyte interfaces.[56]

Application of electrode materials for SC needs careful choice of biomass materials because not all kinds of pores will be suitable. For better performance of SC, it was reported that micropores and mesopores are more helpful in charge transfer. Electrochemistry at nanoscale have significant impact on modern science and influences crucial research areas such as energy storage and conversion, environmental science, sensor development, and catalysis.

2. An overview of the electrochemical energy storage systems (EESSs)

Viable solutions for discovery of sustainable and economical energy alternatives against the background of rapidly declining fossil fuel reserves are available in this age of nanotechnology. Of late, rechargeable energy devices are gaining attention in the search for proficient EESSs. The EESSs were recently classified into three groups:

(1) Batteries
(2) Supercapacitors
(3) Hybrid systems

2.1 Design of the typical electrochemical cell

Typically, an EESS comprises of positive and negative electrodes connected to current collectors, separator, and electrolyte; all of these are encased in a cell. Electrons travel from one half-cell to other *via* the external circuit connected to electrodes that are dynamic part of EESSs. Transfer of ions in the cell occurs due to the electrolyte in numerous forms such as liquid, solid or gel. Preliminary energy storage device comprises of dielectric insulating material sandwiched between two parallel plates. In the recent technological trend, the electrolyte replaces the dielectric material in electrolytic based capacitors; as a consequence, resulting in superior charge due to the free mobile ions.

2.2 Chemistry and Physics of EESSs

A typical EESS consists of a cathode, an anode, a separator, electrolyte and current collectors. The energy storage mechanism depends on the type of device: EDLC and pseudo-capacitance for SC, lithium transformation/intercalation, alloying in LiIBs, and combination of both in hybrid capacitors. Adsorption of cations and anions electrostatically on the surface of electrodes decides the EDLC energy storage capacity. Charging process involves cations migrating to cathode and anions to anode independently. During discharging, ions are desorbed from anode or cathode and then migrate in opposite directions. EDLCs reaction process can be described as below:

$$E_A + A^- \rightleftharpoons E_A / A^- + e^- \tag{1}$$

$$E_C + C^+ \rightleftharpoons E_C / C^+ + e^- \tag{2}$$

where E_C and E_A are cathode and anode respectively; e^- is electron, C^+ and A^- are cation and anion. Activated carbon as electrode material of EDLCs usually possess high specific surface area, and capacitance of a single electrode is calculated using the following equation:

$$(C)=A\,(\varepsilon_r \varepsilon_0)\,/\,d \tag{3}$$

where ε_r and ε_0 are permittivity of electrolyte and vacuum respectively, C is capacitance of one electrode, A is specific surface area, d is distance between electrodes.

Redox reactions between electrode materials and electrolyte are the basis of faradaic pseudo-capacitance. It can be subdivided into three types: 1) reversible absorption of hydrogen ions, conducting polymer's protonation reaction, and transition metal oxide's redox reactions. In LiIBs, there are several energy storage mechanisms such as surface adsorption, interfacial interactions, alloying reactions, free radical reactions, conversion reactions, electrodeposition, phase transformations, and intercalation reactions.

The energy storage devices can be categorised into:

i) Based on electrolyte medium into: a) aqueous, and b) nonaqueous;
ii) Based on combination of electrode materials into: a) symmetric, and b) asymmetric systems.

2.3 Components of EESSs

Most common energy storage material is activated carbon. Activated carbon can serve not only as cathode but also as anode depending on the working potential. The capacitance of the EESSs is crucially affected by activated carbon's specific capacitance. Recently, modifying the surface structure and open framework structure was found to improve the capacitance. Electrostatic adsorption on the surface of activated carbon defines the charge storage capability. However, increase in the charge storage capacity cannot upsurge after a particular value irrespective of increase in surface area. This is due to reduction in the pore diameter for proper electrolyte permeation. Furthermore, decrease in skeletal density and decline in electric conductivity is observed with increase in porosity and specific surface area. The key to improving properties of activated carbon is in design and control of the pore size distribution and specific surface area.

Cathode and anode materials:

1) EDLCs: High surface area activated carbon employed as both cathode and anode materials.
2) Batteries: Lithium containing metal oxides and polyanionic compounds as cathodes and transition metal oxides and graphite as anode materials.
3) Hybrid capacitors: Activated carbon as anode material and cathode are lithium ions, which supports fast-intercalation.

Separator: A membrane separates the cathode and anode to prevent short circuits and electron conduction, while electrolyte movement is hindered due to small pore diameter of the separator. Research is underway to explore the relationship between electrochemical properties and pore diameter. Considering the usability and processability of separator, the membrane should meet the requirements such as:

1) Homogeneous pore size distribution and uniform thickness;
2) Separator should easily pass the electrolyte but insulate and isolate the electrode to prevent short circuits;
3) Storage of electrolyte and should have good wettability;
4) Thermal stability, dimensional stability, chemical stability in electrolyte and mechanical strength.;
5) Minimal resistance thus having perfect ion transportation.

Currently, the most used separator materials are cellulose and polypropylene. Separator can structurally be classified into a) single layer structure and b) hybrid structure where two or three layers are employed.

2.4 Supercapacitors (SC)

Supercapacitors, also called ultracapacitors or electrochemical capacitors, have two electrodes separated by an ion permeable separator and electrolyte through which electrodes are connected. EDLC or pseudo capacitance by faradaic charge transfer phenomenon *via* redox reactions occur at the electrode-electrolyte interface. Helmholtz double layers formed at this interface due to segregation of charges is the principle behind the charge accumulation in SC. Redox electrolytes are substituted in the latest SC for the electrolyte where redox active species are combined to allow faradaic electron transfer reactions. Porous membrane separator lies sandwiched between the electrodes and prevent electrical short circuits and immediate self-discharge. The need for separator is no more required when polymer or solid-state electrolytes are utilised. Transferring of electrons is feasible when current collectors are connected between battery terminals and electrodes. If metallic type conductive materials are used as electrode materials, which have high conductive nature, then there is no need for current collectors. Environmental effects and evaporation of electrolyte can be eliminated by using a casing, which also give mechanical strength to the EESSs.

The advantages are due to the fast charge/discharge rates (compared with rechargeable batteries) and long cycle life (millions of cycles), as well as a reasonable energy density (sometimes even close to batteries). Presently, commercial SC are mostly EDLCs because of their low cost and technical maturity. But the low energy density limits the practical application. In general, the energy density of EDLCs is less than 10 Wh kg^{-1}, and this value is less than 50 Wh kg^{-1} for pseudocapacitors. Substantial research has been undertaken to effectively improve the energy density.[57]

SCs are electrochemical energy sources with high energy storage capacity and faster power delivery with outstanding cycle life. In 1971, NEC (Japan) developed aqueous-electrolyte capacitors under the energy company SOHIO's licence for power saving units in electronics, and this application can be considered as the starting point for electrochemical capacitor use in commercial devices. Cordless tools such as electric cutters and screwdrivers use SCs, which can be fully charged and discharged in less than 2 minutes, are particularly suited for these applications.[58] New applications are emerging in mobile electronics, transportation (electronic cars, buses, trains, and in aerospace systems) and defence systems. The immediate operation of SC is seen in public transport system named as "CAPA buses" in Shanghai. "Sunwin" company brings out buses with SC which can charge to 50% in 30 seconds and 80 seconds to 100% at each bus stop with help of a pantograph like arm similar to tram.[59] In all of these applications, SC chiefly capture the power generated off the braking and releases this energy in assisting the acceleration.

Recently, Todorov reported the use of SC instead of battery in the "S Pen" of Samsung Galaxy Note 9 phone. This takes only 40 seconds for charging and can be used for up to 30 minutes.[60] This is largely attributed to their durability under various stress factors in combination with the surging popularity for the automatic technologies.[61] Further, SCs can be used for heavy-duty applications under extreme harsh environments like burst power and hybrid cold temperature forklifts and cranes. But the crucial trouble is their relative low energy density. The available SCs currently possess an energy density of <10 Wh kg^{-1}, which is significantly lower than the lithium-ion batteries that provide more than 180 Wh kg^{-1}. Hence even with so many merits, SC and lithium batteries still encounter many roadblocks for scale-up and subsequent commercialisation.

In this context, the research by industry and academia has gathered pace in the quest of enhancing the energy density of SCs through the development of modern electrodes, novel electrolytes that offer a wide operation voltage window, and an ingenious architecture of the device. The various criteria that are used for the evaluation of the materials as suitable SC electrodes are its price, specific capacitance, and electrolyte stability and cycling. About the specific capacitance, the key parameters to be determined include the specific surface area, pore size and geometry, and electronic and ionic conductivity. It should be noted that electrode material has a paramount impact on the electrocapacitive performance of SCs.[62]

SCs offer the distinctive advantage of high power density, high energy density, safety, and relatively a very long cycle life (>100, 000 cycles) making them promising alternatives for diverse applications in energy storage devices.[63] In the assessment of SCs, the two most fundamental properties are expressed as a plot of power against energy density, called a Ragone plot as shown in Fig. 4.[61] Ragone plot is specific energy *vs*. specific power for various energy storage devices. SCs are located between batteries/fuel cells and conventional dielectric capacitors. SCs have much higher power density despite lower energy density, making them favourable for applications in hybrid and electric motor-vehicles, smart grids, uninterruptible power supply, and different consumer electronic goods.[58]

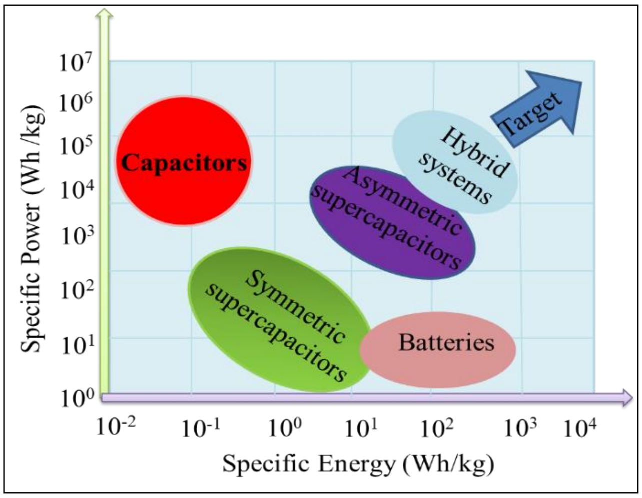

Fig. 4 Ragone plot of specific energy *vs*. specific power for various EESSs. Reproduced with the permission from [61] Copyright 2020, Springer Nature Limited.

Electrochemical performance calculation principle

To evaluate the electrochemical performance, specific capacitance is an important indicator and cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) are two most prominent methods. Cyclic voltammetry applies variable linear potential between the reference electrode and working electrode. Scan rate or sweep rate is the rate of change of voltage to record the instantaneous current response. The specific capacitance can be calculated with equation 1 from the CV curve. Where I is current in amperes, v is scanning rate (mV s^{-1}), m is mass in grams, V_1 is starting voltage and V_2 is ending voltage.[64]

$$C = \frac{\int_{U_2}^{U_1} \text{Ivdv}}{2vm\,(V_2 - V_1)} \tag{4}$$

The specific capacitance C_{sp} is calculated by the formula

$$C_{sp} = \frac{C}{m} \tag{5}$$

where C is measured capacitance and m is the mass of the active materials.

Relationship between scan rate and current is given by equation 6, which is sporadically used to distinguish batteries and electrochemical capacitors. The dominant mechanism for different values of b is given below:

Mechanism	b
Semi-infinite diffusion control	0.5
Electric Double Layer Capacitance	1

For the most part, the two mechanisms coexist, and each type of contribution can be separated. However, it is difficult to distinguish between EDLCs and PCs due to their similar time scales.

$$I = av^b \tag{6}$$

$$C = \frac{It}{mU} \tag{7}$$

Another method is galvanostatic charge–discharge testing (GCD). Potential-time curves are recorded at constant current. The weight capacitance based on the GCD curve can be calculated by equation (7), where I is the current (A) and t is the discharge time (s). Rate capacity can be assessed by selecting different currents, and cycle stability can be assessed by extending the time. Limited energy density (equation 8) is a challenge for supercapacitors, although EDLCs are the main commercialised EESSs. The challenge is to improve the amount of energy stored. Here C is the capacitance in Farad, V is cell voltage, and W is energy (watt hour).[65]

$$W = \left(\frac{1}{2}\right)\frac{CV^2}{3600} \tag{8}$$

2.5 Hybrid Supercapacitor

Hybrid EESSs have evolved during the recent pursuit for high energy density and power density electrochemical energy storage devices.[66] Combining supercapacitor property of outstanding power density along with battery property of high energy density into a single device is the origin of hybrid supercapacitors. In recent years, synergistic combination of metal oxides/hydroxides with biomass carbon-based materials has become the trend. Mono-, bi-, and trimetallic metal hydroxides and oxide composites with biomass-derived carbon for supercapacitor applications were reviewed.[67]

In these devices, one electrode from SC is combined with battery type materials to fabricate hybrid EESSs, termed as 'Supercapattery' (Supercapacitor + Battery). Supercapacitor electrode acts as source of power and battery acts as source of energy. This combination results in 'best of both worlds' scenario with high energy SCs or high cycle life and/or higher power battery. Efficiency of hybrid devices lies in between SC and battery but it opens up scope for more progress in ESSSs domain.[68] Schematic illustration of SC and lithium batteries are shown in Figs. 5(b, c) along with the charge storage mechanisms.

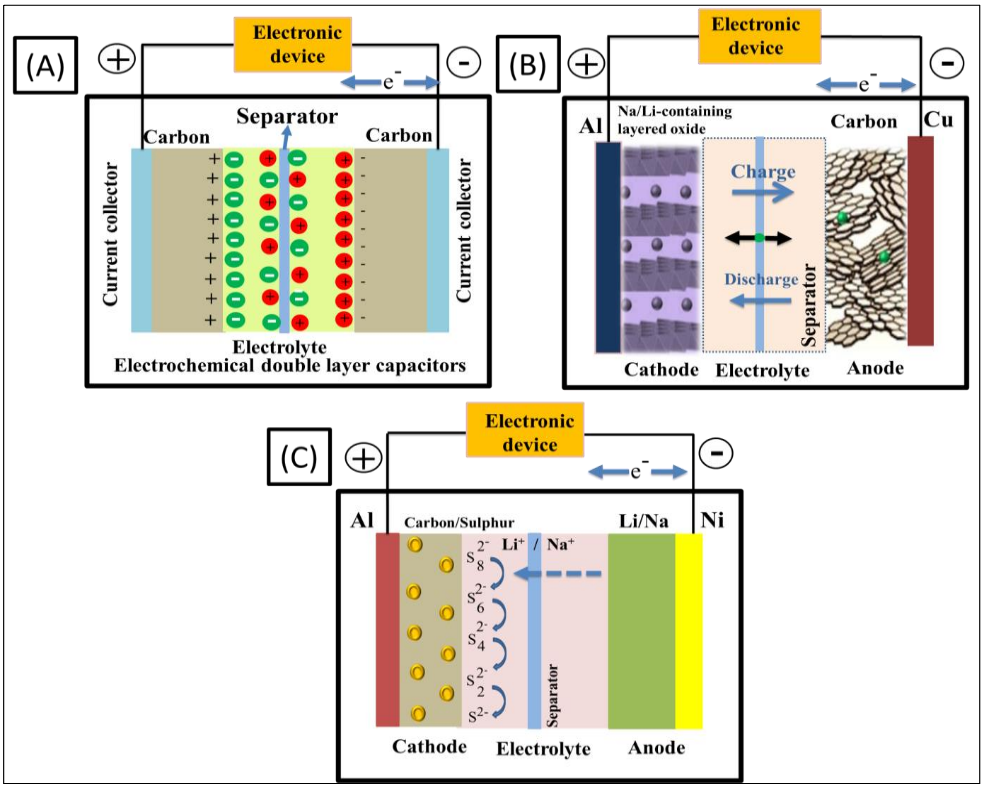

Fig. 5 Schematic illustrations of typical (a) supercapacitor of EDLC, (b) Li/Na-ion battery, and (c)Li/Na-S battery. Reproduced with the permission from [71] Copyright 2020, Springer-Verlag GmbH Germany.

2.6 Rechargeable Batteries

2.6.1 Lithium-ion batteries (LiIBs)

Batteries comprising a pair of electrodes and an electrolyte are another fascinating collection of EESSs. Working principle involves electrical energy being stored in the form of chemical bonds within electrolyte or positive-negative poles between them (Fig. 5). Energy harvested as direct current through redox reactions or in the case of lithium-ion batteries through insertion. A range of applications from automobile industry to microchips and stationary EESSs devices are powered continually by batteries. Large scale stationary storage devices essentially need long cycle life, high safety, cost-effectiveness and to a certain extent high energy density. These requirements demand for next generation EESSs alternatives. Due to less abundance and less economic viability, lithium-ion batteries can contribute only partly to substantial energy storage, which desire for extensive exploitation of renewable energy.

The full evolution of lithium-air batteries (LiABs) as potential and efficient use as EESSs need to resolve various scientific quarantines. It is well known that efficiency of LiABs depends on electrochemical reactions occurring on the surface of cathode. Therefore, for making competent LiABs, devices need novel cathodes with potential structure to tackle energy crisis and air pollution. With the continuous development of high-tech products such as portable devices and electric vehicles, expectation for the high performance of LIBs batteries keep rising.[57]

LiIBs sequentially supply electrochemical energy to electric vehicles and electronic devices *via* continuous redox reactions between positive and negative electrode materials by transfer of lithium ions. Energy density of LiIBs has been enhanced by applying various metal oxides for anode materials due to their high theoretical capacity. Sluggish lithium-ion diffusion pathways and poor electronic conductivity usually limit the rate performance of the electrodes. Meagre cycling performance is observed due to unstable solid electrolyte interface, structural disintegration and reduction in volume during lithiation and delithiation causes. Short lithium diffusion pathways and better contact with the electrolyte at interface are observed with nanostructures. Nano materials also significantly prevent the electrode materials from cracking and large volume variation buffering during cycling.

The next generation energy storage devices with high energy and power densities are possible when LiIBs are constructed with carbon based nanocomposites.[57] Cai *et al.* carbonized and performed KOH activation on Eichhornia crassipes into honeycomb-shaped structures for biochar synthesis and tested as anode materials for LIBs. Sara *et al.* reviewed advancements in nanostructured cathode materials, applications, and properties in rechargeable batteries. Synthesis mechanism together with structure and architecture of biologically inspired materials were investigated. Rechargeable batteries such as aluminium-ion batteries, zinc-ion batteries, potassium-ion batteries, sodium-ion batteries, lithium-sulphur batteries, lithium-oxygen batteries, lithium-ion batteries are illustrated in Fig. 6.[69] Various LiIBs synthesized from biomass derived nanomaterials are shown in Table 2.

2.6.2 Lithium-sulphur batteries (LiSBs)

Another promising energy storage device of next generation that are capturing attention with energy density and high theoretical capacity is LiS batteries (Fig. 5). The lithium sulphur storage mechanism involves multi-step complex processes with the overall reaction of $S_8 + 16\ Li^+ \rightarrow 8\ Li_2S$. It is noted that carbon electrode material displays low utilization efficiency and sluggish kinetics due to the insulating nature of the reduced product Li_2S. Furthermore, low columbic efficiency is observed due to the shuttling of polysulphide ions in electrolyte between cathode and anode produced during the process of charging and discharging. Additionally, cathode structure is damaged due to the variation in volume arising from the conversion between Li_2S and sulphur. These deliberated issues lead to poor rate, quick fading of capacitive behaviour and cycling performances.[5,70] Li *et al.* reviewed biomass derived carbon materials as host and separators in lithium-sulphur materials due to their low cost, environmental friendliness, strong chemisorption and tuneable chemical and physical properties apart from their diverse microstructure. In-depth discussion on impact of design, composition and structure on battery performance is discussed. Practical problems faced in industrial application of lithium-sulphur batteries are discussed.[71]

2.6.3 Sodium-ion batteries (NaIBs)

Sodium ion batteries make significant progress in a few decades as EESSs technology in renewable energy and smart grid applications. NaIBs have gathered considerable research attention due to the abundance, high energy density, low cost of sodium, economical resources, and elevated profusion. Sodium is chemically similar to lithium, which helps in understanding that NaIB technology had emerged from LiIBs technology. Ionic radius of 0.98 Å for Na^+ is bigger compared to Li^+ of 0.69 Å resulting in reaction kinetics being sluggish, reduced ion transport, extraction or insertion of Na/Na^+ with larger volume changes. The above-mentioned limitations cause sodium storage reversibility and less rate capability, which accelerates efforts to develop energy storage materials for SIBs with fast diffusion kinetics and high capacity. Carbon based materials are explored as anode materials for NaIBs due to their gained popularity. Amongst them, nanosized carbon composites find several advantages to enhance the performance of NaIBs, including: A) carbon nanomaterials provide large specific surface area and expand electrolyte and electrode contact area, B) fast diffusion kinetics of sodium ions, C) electrical transport is facilitated by direct channels of carbon nanomaterials, and D) long cycling performance, which hinders the pulverization and/or aggregation of active materials during the charging/discharging process and dodges the strain by sodium ions intercalation/deintercalation.[57]

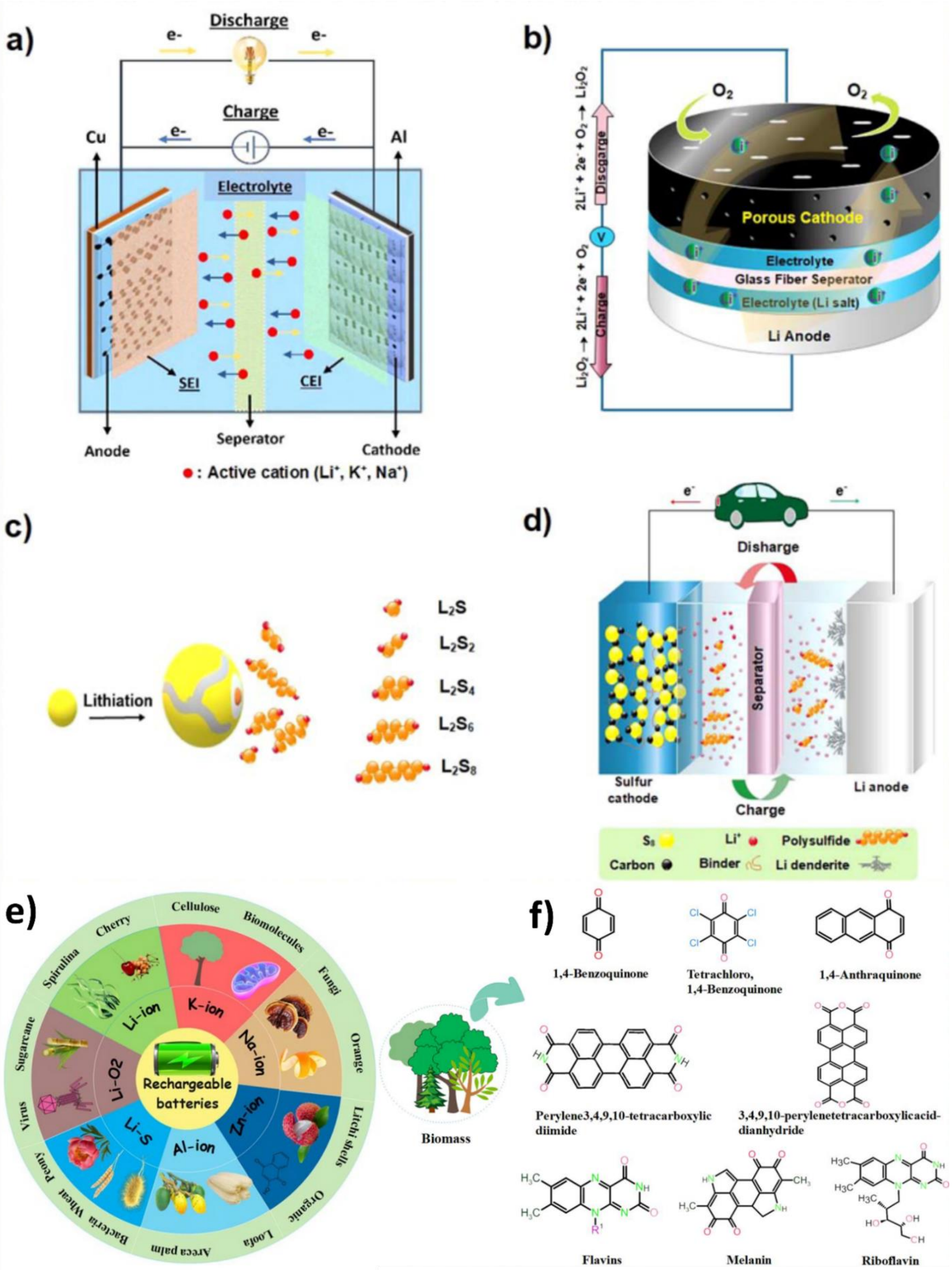

Fig. 6 Schematic diagrams of the primary structure and operating mechanism of secondary rechargeable batteries: a) Rocking-chair model (metal-ion batteries). (b) Lithium-air battery. (c) Volumetric expansion after lithiation in sulphur. (d) Lithium-sulphur battery. (SEI: solid electrolyte interphase, CEI: cathode electrolyte interphase). e) Schematic presentation of different bio-inspired materials utilized in cathode materials preparation for rechargeable batteries. f) Small organic molecules structures, which have been reported as electrode materials. Reproduced with the permission from [69], Copyright IOP Publishing.

Table 2. LIBs from biomass derived nanomaterials.

Biomass material	Synthesis and Activation	Surface area (m^2/g)	Capacitance	References
Eichhornia crassipes	KOH	278.56	697 $mAh\cdot g^{-1}$ at 50 $mA\ g^{-1}$	[44]
Wastewater -treatment algae	NaOH	-	358 $mAh\ g^{-1}$ at 0.1 $A\ g^{-1}$	[74]
chestnut shell fluff		-	1522.8 $mAh\ g^{-1}$ at 0.1 $A\ g^{-1}$	[75]
cornstalks	Delignification and calcination	-	454 $mAh\ g^{-1}$ at 3 $A\ g^{-1}$	[76]
Rice husk	HTC	243	218 $mAh\ g^{-1}$ at 0.375 $A\ g^{-1}$	[77]
Porous starch	Carbonization	192	805 $mAh\ g^{-1}$ at 0.1 $A\ g^{-1}$	[78]
Ginkgo leaves	Carbonization	504	505 $mAh\ g^{-1}$ at 0.1 C	[79]

3. Renewable Biomass for nanostructured electrode materials

3.1 Fabrication strategies of biomass derived nanostructures

One of the earliest uses of biomass for the generation of carbon materials was explored using the banana fibres by Subramanyam *et al*. These fibres were treated for the pore-formation *via* the chemical activation with $ZnCl_2$ and KOH that sought to enhance their surface area and consequently, their electrochemical performance when used as alternatives for the conventional electrical double-layers in the capacitor electrodes. They were even evaluated for their performance as a function of electrolyte. This was among the first reports to demonstrate the impact of increasing the specific surface area in the material because of the formation of pores.[72] Thereafter in 2008, the seminal work in the field was undertaken by Rufford *et al*. in the generation of activated carbon from the waste 'coffee grounds' by treatment with $ZnCl_2$. This study once again confirmed that the electrochemical performance was a direct consequence of the developed porosity, with a size distribution of both micro- and meso- pores of 2–4 nm wide. This study was one of the earliest reports to highlight the paradigm utility in biomass for the production of economic electrode materials for energy storage.[73] Mechanism of KOH activation is complex in nature to understand totally. However, some researchers suggested the KOH activation process is a synergistic process of physical and chemical activation, carbon lattice expansion by metallic K intercalation as illustrated in Fig. 7.

In the following year, the potential of the large aquatic systems was first reported, where Raymundo *et al*. studied a diverse family of seaweeds that are appropriate nano-carbon precursors in their chemical composition.[80] Depending on their origin, they led to oxygen enriched carbons or finely tuned well developed micro/mesoporous carbon. The former demonstrated excellent potential as supercapacitor electrodes in aqueous media, while the latter were directly applicable in the organic media. Most interestingly, these precursors always resulted in high-density materials, leading to very high volumetric capacitance. This increased their focus over activated carbon in the design of compact electrical sources of power sources for environmental remediation of water and air.[81]

Rufford *et al*. in 2010 reported the first significant use of sugarcane bagasse as a precursor for the generation of activated carbon for supercapacitor applications using chemical activation with $ZnCl_2$. The chemical activation was evaluated using TGA and the porosity extensively characterized. Their electrochemical performance was attributed to the high specific surface area.[82] Another promising study in the year elucidated the use of cassava peel as a precursor for activated carbon that combined both the physical and chemical activation. The results demonstrated the use of cassava peel waste as a potential cheap raw material for producing high performance activated carbon materials for EDLCs.[83]

One of the pioneering works by Nabais *et al*. in 2011 demonstrated the design of single step low-cost electrodes in monolithic shape for SC from coffee endocarp. Predominantly, even though microporous in their nanostructure, these

Fig. 7 Activation mechanism by the penetration of metallic K into the a) carbon lattices, the expansion of the lattices by the b) intercalated metallic K, and the removal of the intercalated K from the c) carbon matrix. Reproduced with the permission from [69], Copyright Royal Society of Chemistry.

materials showed a unique pattern of porosity formation.[84] Further, Wei *et al*. even explored the use of various raw materials ranging from cellulose, starch present in potato to the eucalyptus bark to obtain very high micro-porosity.[85] The first facile synthesis using the microwave route was successfully reported from the sugarcane bagasse *via* the chemical activation as an ionic-liquid supercapacitor. This study confirmed the capacitive performances in these carbons as a direct function of their pore sizes. Another interesting study was the preparation of granular carbon with high micro/meso porosity (V_{meso}/V_{total}) exceeding 75%, synthesized from the coconut shells in a facile one-step process combining steam and pyrolysis activation. They also evaluated the impact of variables like activation temperature, rate of water flow, and dwell time on the meso-porosity.[86]

Functional carbon with high specific surface area was fabricated *via* the one-step pyrolysis of dead plant leaves of neem and Ashoka, that elucidated the role of the composition and inherent constitution of the bio-source.[87] SC based on activated carbon obtained from various pollens, and the partially graphitized ginkgo-based activated carbon that was prepared from the ginkgo shells *via* pyrolysis, and KOH activation with cobalt nitrate as the graphitization catalyst, exhibited greater specific capacitance in ionic liquids compared to commercial graphene-based SC. Other notable developments were the high performance SC built using novel hetero-atom microporous carbon nano-plates prepared using regenerated silk fibroin,[88] and porous graphene-like nanosheets with very high specific surface area fabricated *via* simultaneous activation–graphitization route from waste coconut shells.[89] He *et al*. explored the use of peanut shell and rice husk *via* the one-step chemical activation assisted by microwave heating to produce mesoporous carbon.[90]

Jin *et al*. optimized activation time for the preparation of series of activated carbon fibres *via* the one-step carbonization and activation of wooden fibres. The pore size and morphology was successfully tuned by adjusting the levels of burn-off in order to study the effects of these parameters on specific capacitance and rate capability.[91] Very high surface area activated carbon was synthesized from pine cone petals by a chemical activation process,[92] while the low cost, high-performance activated carbon was fabricated from bean dregs that exhibited superior capacitive performance, and excellent cycle stability.[93] The use of agro-based derivatives as precursors was demonstrated by Hou *et al*. in their preparation of controlled micro/mesopores framework in 3D carbon possessing very high specific surface area from raw rice brans through KOH with promising applications in high-performance energy-storage devices.[94]

In 2015, Li *et al*. synthesised N-doped activated carbon *via* one-step carbonisation of eggplant[95] and Xu *et al*. synthesized dual S/N–doped activated carbon *via* chemical activation of broad beans.[96] The work of Jianhua *et al* demonstrated the utility of hierarchical porous nitrogen-doped carbon nanosheets synthesized by the one-step method from natural silk for high-performance as LiIBs and SC. These are even being touted as the next generation hybrid energy devices.[97]

Jiang *et al*. designed the fabrication of high-performance capacitors with 3D hierarchical porosity constituting all the three: macro (>50 nm), micro (<2 nm) and meso-pores (2–50 nm). This method essentially mixed the biomass with $KHCO_3$ that was subjected to pyrolysis that resulted in high specific surface area. Most importantly, they also demonstrated the applicability of 'leavening' for most biomass inclusive of starch, glucose, chitin,[98] cellulose, bamboo and rice straw.[99] The role of temperature and chemical activation agent[100] on the porosity and the structure of activated carbon was evaluated in the study conducted by Liu *et al*. in 2016.[101] Ground soybean was used for synthesis of hollow porous nanocarbon of pore size range 0.5–4 nm by HTC in H_2SO_4 followed by heating in furnace at 850 °C under inert atmosphere.[102] Cao *et al.* explored poplar saw dust to prepare nitrogen doped porous carbons (NPC) and NPC-polyaniline composites to achieve 362 F g^{-1} of supercapacitance in 6M KOH at 0.5 A g^{-1}.[103]

Thus, the extensive literature survey mentioned above inspires the quest for novel SC from biomass precursors possessing the important properties of large surface area, porosity in structure and significant electrical conductivity. The conversion processes of biomass to green carbon materials were achieved by physical activation, chemical activation, pyrolysis, HTC and other activation methods as shown in Fig. 8.

3.2 Additional factors affecting supercapacitance

Electrolytes: It comprises of solute dissolved in pure salt (for ionic liquids) or solvent and is one of the vital components of EESSs. Important roles of electrolyte in EESSs are: 1) formation of electric double layer in EDLC, 2) charge compensation on each electrode in EESSs cell is allowed due to the ionic conductivity, 3) participation in charge storage processes in pseudo capacitors. The performance of EESSs is greatly affected by electrolytes as a result. Cell voltages of 2.5 V to 2.8 V can be achieved with use of organic electrolytes. Acetonitrile is used as solvent for most of the organic electrolytes while others use propylene carbonate as solvent. Fig. 9 gives a bird eye view of the various electrolytes available for EESSs.

Aqueous electrolytes are less used compared to organic electrolytes in commercial EESSs due to limited cell voltage potential but widely reported mainly due to their ease of handling and are cost effective.[104] Ionic liquids and organic electrolytes on the other hand require controlled atmosphere conditions for complicated purification procedures without moisture. This distinguishing feature of aqueous electrolyte greatly eases the assembling and fabrication of EESSs. In nanocarbon electrodes with aqueous electrolytes, the specific capacitance is higher than nonaqueous electrolytes due to the higher dielectric constant and small solvated ions.[105]

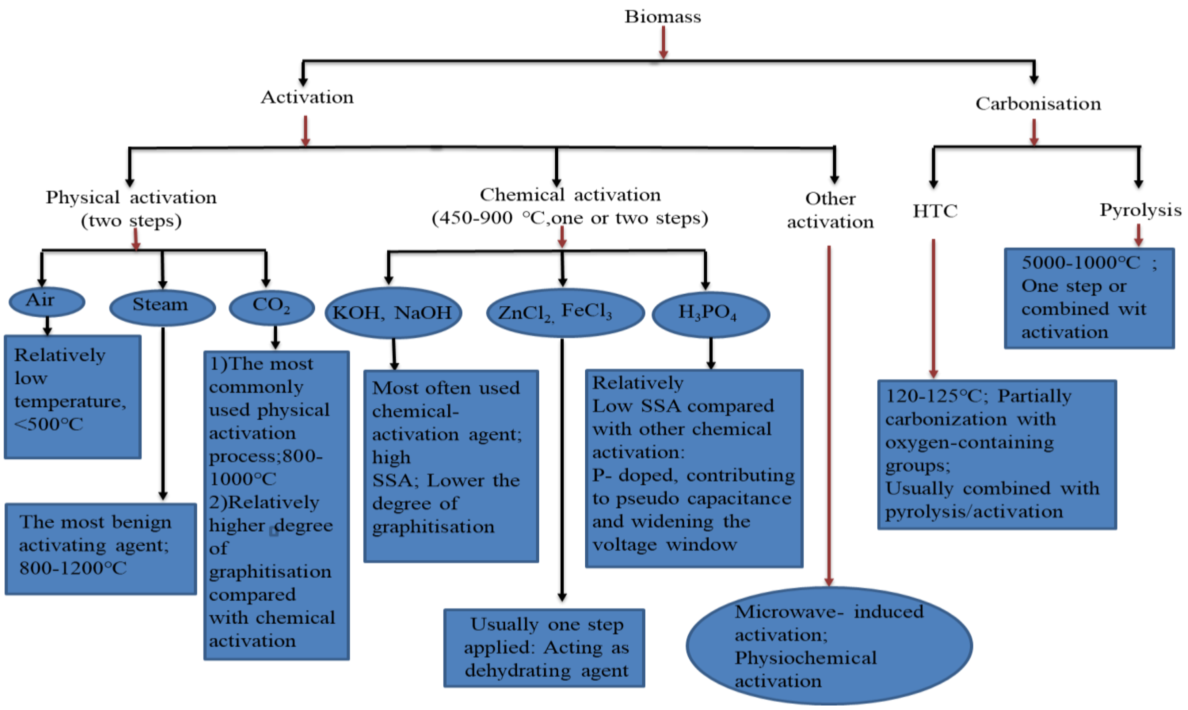

Fig. 8 Common methods for converting biomass to carbon materials with their respective advantages and disadvantages. Reproduced with the permission from [75], Copyright Royal Society of Chemistry

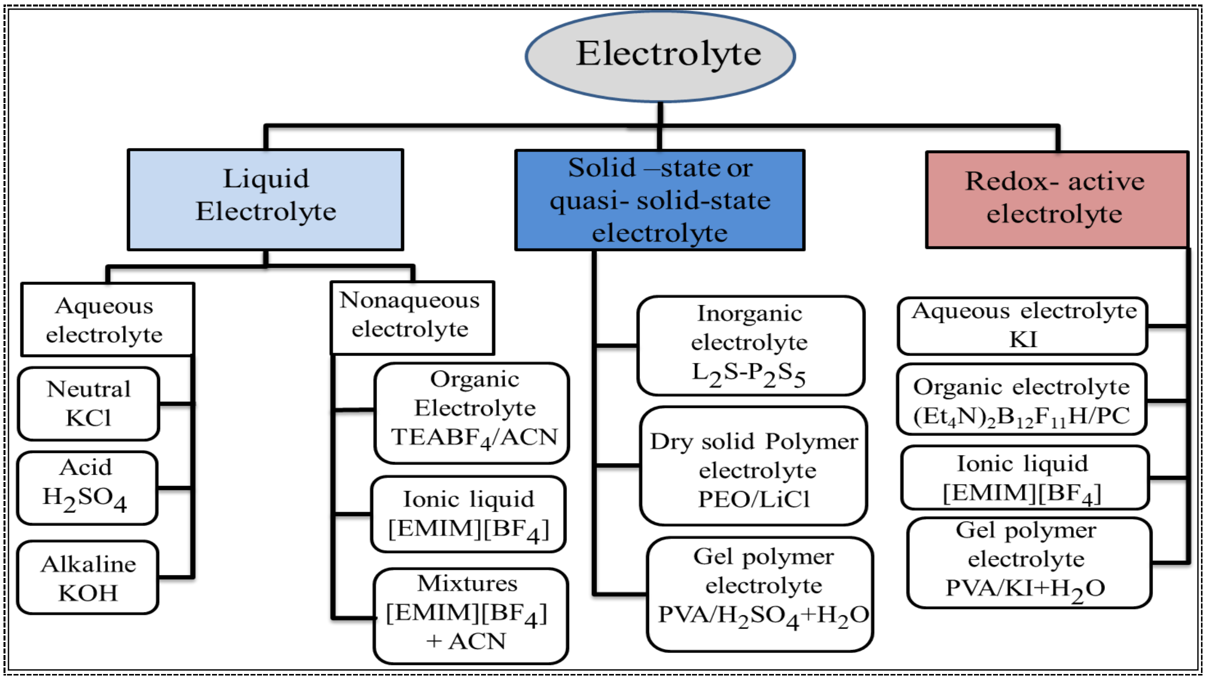

Fig. 9 Electrolytes classification for EESSs. Reproduced with the permission from [75], Copyright Royal Society of Chemistry.

4. Nanostructured electrode materials as supercapacitors

The extensive use of nanomaterials took several decades to emerge at the end of 20th century and in the early years of 21st century it gained wide prominence. Nanomaterials found applications in several broad domains ranging from medicine to microelectronics. In 2011, the EU gave a definition for nanomaterials as "*A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm.*" This definition does not greatly differ from the one given by the International Organization for Standardization (ISO): "*Material with any external dimension in the nanoscale or having internal structure in the nanoscale« with Nanoscale meaning; Size range from approximately 1 nm to 100 nm*".

One could naively think that the application of nanomaterials in the energy storage field may revolutionize the figures of merit for battery and supercapacitor performance in the second millennium. The reduction of particle size to nano level decreases the ions travelling distance from core to surface simultaneously increasing the ratio of atoms that reside at the surface. Although frequently omitted, nano size affects the redox potential values and changes the surface energy significantly.[6]

Electronic conductivity and ionic transport are often greatly improved with nanomaterials for SC. Fast ion diffusion resulting in high specific capacitance is achieved owing to filling up of all available intercalation sites in particle volume.

These features offer promising solution for high-power density and high-energy density storage devices when nanomaterials are employed for electrode materials which can endure high currents. Nanomaterials have limitations to be used in commercial devices as energy storage technology. Development for decades explored library of nanomaterials (Fig. 10) with different chemical compositions, shapes and morphologies such as:

1) 0 Dimension : Carbon dots and zero-dimensional nanoparticles
2) 1 Dimension: Nanotubes, nanowires, nanobelts
3) 2 Dimension: Nanosheets and nanoflakes
4) 3 Dimension: Porous nanonetworks

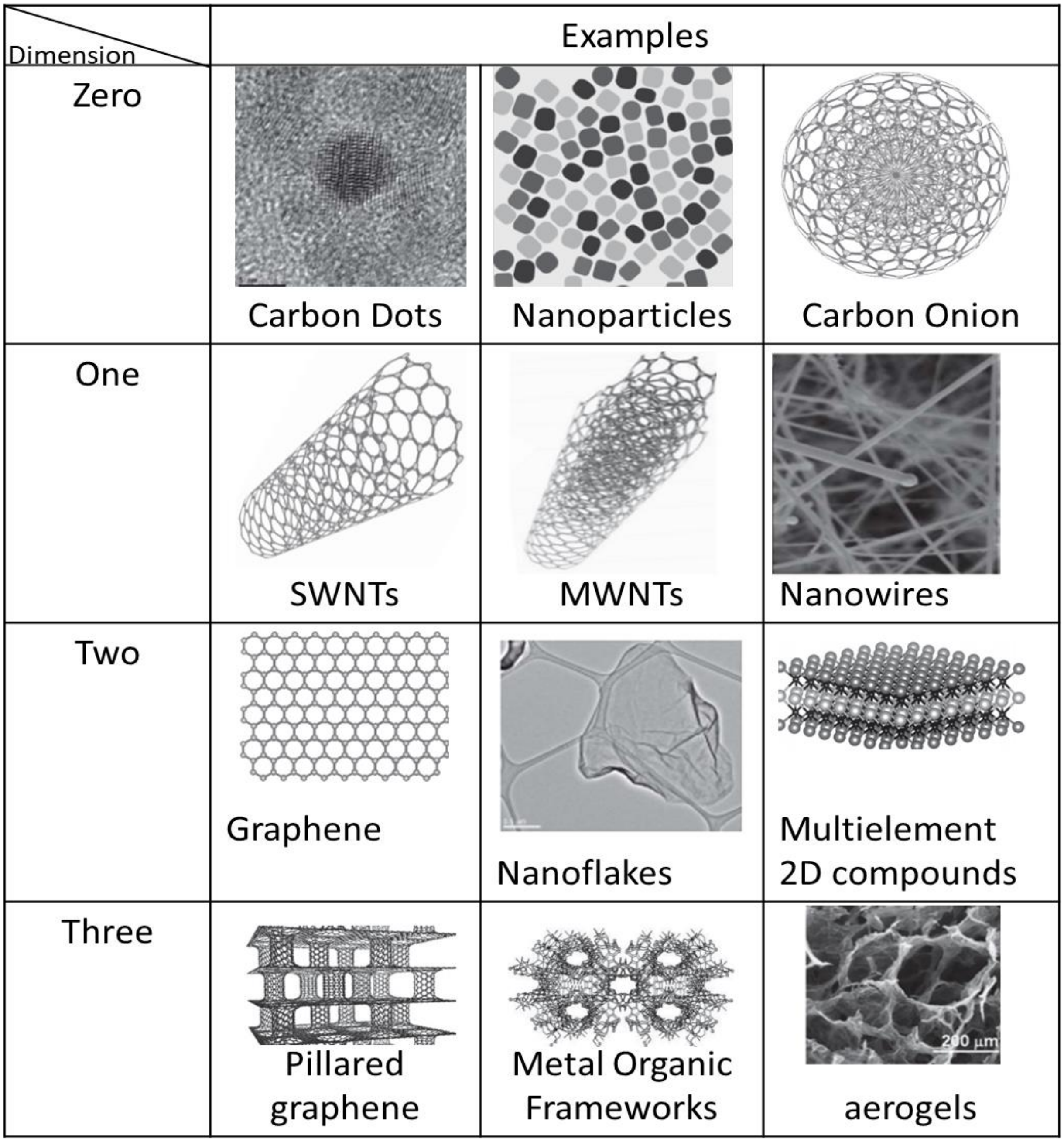

Fig. 10 Representative figure for zero, one, two and three dimensions in Nanocarbons available for EESSs. Reproduced with the permission from [30], Copyright 2018, Springer International Publishing AG.

Wearable and structural energy storage devices are achievable with nanotechnology because of available chemically diverse nanoscale building blocks but not with conventional materials. There are diverse aspects for achievements of nanomaterials in energy storage applications. The achievement of nanomaterials in energy storage applications has diverse aspects. For controlling the electrochemical performance and exploring various charge storage mechanisms such as pseudo capacitance, ion absorption, and diffusion limited intercalation processes, nano structuring is becoming a key process. Designing of high-power next generation energy storage devices is plausible with the development of latest high-performance materials with conductivity more than other conventional electrode materials and carbons such as transition metal carbides.

Challenges associated with large volume change characteristic of alloys and conversion materials can be avoided when hybrid nanoarchitectures are developed such as carbon-sulphur or carbon-silicon. Realizing and designing high power, high energy and long lasting energy storage devices can be a reality when nanoarchitecture electrodes and nanomaterials are employed.[106] Plant tissue morphology largely defines the nanopore size distribution of carbon nanostructures derived from biomass.

4.1 Nanomaterials as electrodes

Different materials such as porous materials, metal oxides, conducting polymers were investigated as electrode materials for SC. The performance of SC is defined by parameters such as high surface area and ideal pore size of the electrode material for a given electrolyte. Energy is stored on the surface of electrochemical storage devices which demands the high surface area as a precondition. Since carbon materials are available in different forms with variety of dimensions, as discussed in previous section, they are gaining more attention as perspective electrode materials. Table 3 elucidates the characteristics of the zero to three dimensional nanoparticles for EESSs. The electrochemical performance of the materials can be altered by adjusting the surface chemistry and microstructures of the carbon materials. Further, it is reported that electrodes made from activated carbon from biomass possess excellent properties such as low cost, high surface area, tailorable pore distribution, high thermal stability, high electrical conductivity, excellent corrosion resistance, reasonable compatibility to make composites with a number of materials.[56]

There are two mechanisms that interpret the energy storage in SCs: electric double-layer mechanism and the redox reaction mechanism. Consequently, this leads to the two variations of SCs: i) EDL capacitors (EDLCs) and ii) pseudo-capacitors. Activated carbon largely comprises the former kind of electrode materials, while metal oxides and conducting polymers constitute the latter. In general, the pseudocapacitive materials demonstrate higher specific capacitance *vis-a-vis* the EDL electrodes and therefore, always possess a bigger energy density. The recent class of carbon-based materials however exhibit better cycle stability and rate capability, making EDLCs operable at high charge and discharge rates over the lifetime of a million cycles. It is precisely this observation that has led to the emergence of an exponential research in carbon materials ranging from classic activated carbon to nanostructured carbons as advanced electrode materials for SCs to push up their energy densities.[107] Until now, there have been myriad raw materials used ranging from traditional coal, pitches, cokes, peat, lignite and graphite. Unfortunately, the reserves of graphite and petroleum coke derived activated carbon are limited and non-renewable. Therefore, it is an urgent need to develop sustainable alternatives by more

Table 3. Advantages and disadvantages of 0,1,2,3-dimension nanoparticles for EESSs.[44]

Dimensions	Advantages	Disadvantages
Zero	1) Small in all dimensions 2) Surfaces on all sites are accessible to electrolytes 3) No bulk solid-state diffusion 4) Can be integrated into multiple systems 5) Can be used in stable inks for printing	1) Agglomeration 2) Do not densify and form only low density non-uniform structures 3) Numerous points of contact lead to high resistance 3) Poor chemical stability
One	1) Mechanical reliability 2) Possibility to integrate with wearable devices 3) Porous flexible free-standing films	1) Low packing density; Cannot exhibit high volumetric performance 2) Low yield and high cost of synthesis 3) Diffusion pathways can be relatively long
Two	1) Open 2D channels for ion transport; all surface is accessible enabling fast charge storage 2) Compatible with flexible devices 3) Small nanoflakes can be used in inks for printing	1) Re-stacking 2) Low out-of-plane electronic and ionic conductivity 3) High cost of synthesis
Three	1) Can be used to create thick electrodes with large areal and volumetric storage properties	Design Stability Manufacturing

efficient, greener and cost-effective methods.[108] Taking the inspiration from nature's way of manufacturing carbon materials, which often possesses hierarchical structures with porous organisation and periodic pattern, led to the synthesis of advanced carbon materials with the desired properties for SCs using renewable biomass.

More importantly, biomass materials such as leaves, barks, and shells often possess complex organizations and intriguing microstructures, which can be inherited through well-designed synthesis strategies as illustrated in Fig. 6. Various biomass materials employed for making nano porous carbon through diverse activating agents and their respective surface area, pore size and supercapacitance properties, are depicted in Table 4. The interconnected structures formed an integrated 3D conductive network, which is beneficial for the fast electron transfer and ion migration. In addition, the micrometre-scale walls of veins can also accommodate the volumetric change during electrochemical reaction process. All these components synergistically worked together to ensure the conductivity, rich porosity and stability of the electrodes.[109] The modification in the surface texture and functionalization of the carbon materials is attainable *via* the appropriate activation agents and methods.

4.2 0D biomass nanocarbon materials

Zero dimensional nano carbons also called as carbon quantum dots (CQDs) or graphene quantum dots (GQDs) are highlighted in several reports for their wide variety of applications spanning from EESSs such as SC,[110] batteries such as metal-air batteries and fuel cells,[111] LiIBs,[112] NaIBs,[113] electrocatalytic water splitting,[114–116] biofuel cells,[117] along with applications such as optoelectronics,[118] sensing,[31] electrochemical biosensors,[119] photocatalysis,[120–122] bioimaging and biomedicine.[118,123]

CQDs obtained from biomass with excitation dependent emission have potential to serve as SC when mixed with reduced graphene oxide to form composite.[124] EESSs such as SC and batteries are tested using GQD/CQDs.[125] Higher pseudo-capacitance was observed when rich heteroatom containing function groups such as of oxygen and nitrogen, which offer greater number of active sites.[124]

The electrochemical property of CQDs is due to the interactions between the functional groups and carbogenic core that regulate the electron transfer. The electron transfer is facilitated by greater surface area and abundantly available edge sites.[141,142] Heteroatoms positively influence this interaction further.[143] Doping with elements such as boron,

Table 4. Biomass derived carbon nanomaterials for EESSs and their SC values.

Biomass material	Activation agents	Surface area (m^2/g)	Avg. Nanopore diameter (nm)	Capacitance	Electrolyte	References
Popla sawdust	KOH	2149	-	362 F g^{-1} @ 0.5 A g^{-1}	6M KOH	[103]
11Banana stem	KOH	567.3	1.205	479.2 F g^{-1} @ 1 mV s^{-1}	6M KOH	[126]
Banana stem	H_3PO_4	177.7	1.789	202.1 F g^{-1} @ 2 mV s^{-1}	6M KOH	
Corn cob	KOH	215.4	1.199	309.8 F g^{-1} @ 2 mV s^{-1}	6M KOH	[127]
Corncob	KOH			295.93 F g^{-1} @ 1 A g^{-1}		
Soybean	H_2SO_4	1077.6	0-50	143 F g^{-1} @ 1 A g^{-1}	6M KOH	[102]
Soybean	KOH	1749	0.7-9.2	243 F g^{-1}@ 0.5 A g^{-1}	6M KOH	[128]
Peanut shell	Na_2CO_3-K_2CO_3	408	-	154 F g^{-1} @ 0.5 A g^{-1}	1M H_2SO_4	[129]
Peanut shells	$ZnCl_2$	1549	1.8-4.2	333 F g^{-1} @ 0.5 A g^{-1}	1M H_2SO_4	[130]
Peanut shells	KOH, mechanical exfoliation	2070	2.1-5.4	186 F g^{-1} @ 0.5 A g^{-1}	1M H_2SO_4	[131]
Walnut shells		363	~ 2	42 F g^{-1} @ 0.5 A g^{-1}		
Almond shells		403	~ 2	78 F/g @ 0.5 A g^{-1}		
Starch	$Mg(NO_3)_2·6H_2O$	2300	100-200	229 F g^{-1} @ 1 A g^{-1}	6M KOH	[132]
Rice husk	HF	786	7.03-7.92	260 F g^{-1} @ 1 A g^{-1}	6M KOH	[133]
Rice Husk	H_2SO_4	1493	3.25	112 F g^{-1} @ 1 A g^{-1}	1M Na_2SO_4	[134]
Orange peels	H_3PO_4	640.3	90.22	275 F g^{-1} at 10mV s^{-1}	H_2SO_4	[135]
Cotton textile	NaF	450	-	977 F g^{-1} @ 2.5 A g^{-1}	6M KOH	[136]
Tobacco rods	KOH	1761-2115	2.3	286.6 F g^{-1} @ 0.5 A g^{-1}	6M KOH	[137]
Human hair	KOH	1306	< 3	340 F g^{-1} @ 1 A g^{-1}	6M KOH	[138]
Sugarcane bagasse	$ZnCl_2$	1465-1348	2.5-7.0	138 F g^{-1} @ 0.2 A g^{-1}	$EMImBF_4$	[139]
Lotus pollen	KOH	3037	-	185 F g^{-1} @ 1 A g^{-1}; (1 M $TEABF_4$ /AN) 207 F g^{-1} @ 1 A/g ($EMIMBF_4$)	1 M $TEABF_4$ /AN, $EMIMBF_4$	[87]
Neem leaves	No activation	1230	0.5-1, 2	400 F g^{-1} @ 0.5 A g^{-1}	1M H_2SO_4	[140]
Cotton stalk	H_3PO_4	1481	2-3	114 F g^{-1} @ 0.5 A g^{-1}		[9]

sulphur, nitrogen is reported to impart specific catalytic characteristics.[144] In GQDs, dislocation of sp_2 carbon weaken the transfer of electron if oxygenated functional groups are present on the base; while when present on the edges it is found to express catalytic attributes.[145,146]

In SC, GQDs aid to be ideal electrode materials. Electrophoretic deposition of GQD of 312 nm thickness was explored on interdigital gold electrode to fabricate symmetric micro-supercapacitor. Cyclic voltammetry curves of the device showed typical rectangular curves at high scan rates of 1000 V s^{-1} and small relaxation time constant displaying superior power response and ideal capacitive behaviour. Hydrothermal fabrication of hybrid nanocomposite is prepared with reduced graphene oxide and nitrogen doped biomass derived CQDs from waste leaves of cauliflower.[124] High pore volume (2.94 cm^3 g^{-1}) and large surface area (415 m^2 g^{-1}) was observed when CQDs prevent the restacking/aggregation of RGO sheets acting as intercalators. Higher pseudo-capacitance was observed additionally when more active sites on RGO/CDs were provided on addition of rich nitrogen functional groups. Maximum specific capacitance of 278 F g^{-1} and 165 F g^{-1} was observed at current densities of 0.2 A g^{-1} and 100 A g^{-1} with hybrid of RGO/CDs while retaining the rate capability of 59.5%. The galvanostatic charge/discharge study of this composite electrode material after 10,000 cycles showed high capacitance retention of 96.1% at 20 A g^{-1} current density. Heteroatom doping of RGO/CD with iodine (6.1 wt%) improved electrical conductivity on deoxygenation by reduction using hydroiodic acid vapour.[124]

Biomass derived hydrothermal carbon microspheres decorated with ternary metal sulphide nano-flakes were explored for superior energy and power densities as well as long term durability. Positive electrodes were biomass derived hydrothermal carbon spheres decorated with ternary zinc-cobalt sulphide nanosheet hierarchical microspheres. In addition, composites of pyrolyze polyaniline nanotubes (PPNTs) and iron oxide, receiving advantages from highly porous structure and modification of nitrogen as a heteroatom, were used as the negative electrodes in the fabricated asymmetric supercapacitors. The assembled Zn-Co-S@HTCSs//Fe_2O_3@PPNTs asymmetric supercapacitor with a broad potential window not only delivered superior energy density (85.12 Wh kg^{-1}) at a reasonable power density of 460 W kg^{-1} but also rendered reasonable cycle durability. The advanced asymmetric design together with encouraging results presented herein makes these supercapacitors immensely promising for high-performance electronics.[147]

Cauliflower leaf wastes were used to prepare green carbon dots *via* a one-step green synthetic technique. Subsequently one-step hydrothermal treatment was employed to fabricate composites of reduced graphene oxide (RGO) with carbon dots. These composites were tested for electrochemical performance by varying their mass ratios of carbon dots to RGO. Highest specific capacitance of 278 F g^{-1} at 0.2 A g^{-1} and 227 F g^{-1} at 2 mV s^{-1} were exhibited with 2:1 mass ratio of RGO to carbon dots. Important properties of composite materials such as surface area, pore volume, composition, proton diffusivity and electrical conductivity plays crucial role in offering excellent electrochemical properties.[124]

4.3 1D biomass nanocarbon materials

One of the most viable nanostructures identified for SC and also several other devices are 1D nanomaterials derived from biomass such as fibrous and tubular structures.[25,148] Here, dimensionality of carbon refers to: A) tubular structures such as willow catkins,[149] kapok,[150] cotton[151] or B) fibrous structures bacterial cellulose,[152] and ramie.[153] The most abundant, ideal building block with promising features on earth for renewable advanced energy storage system is cellulose, a biomass fibre. A few of the attractive properties include high specific surface area, high carbon content, useful mechanical properties, abundant surface chemical properties, abundant surface chemical properties, ease of processing and thermal stability.[154] Cai *et al*. performed electrospinning technique followed by deacetylation and pyrolysis of cellulose acetate solution to produce carbon nanofibers with nitrogen functionalization. Characterization of the obtained nanofibers revealed diameter in the range of 70–400 nm, nitrogen atoms doping in the structure giving high electrical conductivity of 5.9 S cm^{-1}, water contact angle of 24–40º displaying hydrophilicity. These results of the nanofibers make them ideal electrodes for advanced EESS applications.[155]

The second most abundant biopolymer worldwide after cellulose and by-product of paper and pulp industries is lignin. Berenguer *et al*. demonstrated that controlling porous interconnected carbon-lignin fibres was possible with suitable rate of heating during stabilization. Slow heating rate stabilized lignin from softening during the sequential carbonization to produce loose nanofibers. Faster heating rates in contrast led to partial softening during carbonization along with crosslinking at contact points between nanofibers. The crosslinking between fibres increased capacitance and enabled charge transfer.[156]

Hollow nanostructures of carbon derived from biomass can act as reservoirs for buffering ions to augment the charge storage in the interior surface along with reducing the diffusion path.[150] Until now, porous carbon nanomaterials are prepared from naturally available 1D hollow microstructures. Liu *et al*. synthesized carbon nanofibers by carbonization after pretreatment of the fibres in urea/NaOH solution. These nanofibers exhibited high EDLC of 22.17 F g^{-1} at current of 0.3 A g^{-1} along with good cycling stability at 2 A g^{-1} up to 6000 cycles, with loss of 4.6%. This was possible due to the well retained structures of fibres which allowed high charge accumulation by maximizing utilization of surface area and minimizing the electrons and electrolyte’s transfer/diffusion resistance.[157] More significantly, the biomass derived electrode materials have few unique features such as fabrication ease, abundantly available and low cost. These conclusions establish that for SC with rapid charge/discharge operations, 1D hollow carbon microtubular structures are advantageous as electrode materials.

4.4 2D biomass nanocarbon materials

2D nanocarbon materials have displayed countless potential in energy conversion and storage due to several advantages such as: A) long cycle stability: the internal free space and hierarchical pore structures in the nano carbon sheets help buffer the changes in volume during charging and discharging cycles,[102,104] B) ion transmission distance is shortened due to its unique ultrathin 2D layered structure with large lateral size of the carbon,[158,160] and C) higher specific capacitance is achieved due to the in-plane active sites and rich active surface edges facilitating the charge storage.[104]

Excellent supercapacitance is achieved currently with widely developed graphene as 2D nano carbon electrode materials that involve high cost and complex manufacturing processes. Biomass derived carbon nanomaterials are successfully prepared resembling graphene that are cost effective and renewable. The effective fabrication process and sustainable raw materials provide a great platform for electrode materials in 2D nanocarbon materials for EESSs.

Purkait *et al*. activated groundnut shell with KOH followed by mechanical exfoliation to prepare multi-layered graphene like nano carbon sheets. Large pore volume of 1.33 cm^3 g^{-1} and high specific surface area of 2070 m^2 g^{-1} were achieved with abundant mesopores and micropores in the graphene-like nanocarbon materials. The electrochemical cell was prepared in aqueous acidic electrolyte of 1 M H_2SO_4 without binder to achieve high power density of 37.5 kW kg^{-1} and high energy density of 58.13 W h kg^{-1}.[131]

Heteroatom doping can further improve the electrochemical performances; surface electrochemical properties can be adjusted along with controlling the property of electron acceptors or donors of carbon materials. Moreover, the supercapacitance can be boosted by heteroatom doping which enhances wettability, reduces the charge transfer resistance.[159] Biomass contains nitrogen, oxygen, phosphorous and sulphur along with carbon. It is understandable that pyrolysis of biomass yields carbon nanomaterials doped with these elements. Yan *et al*. explored carbonization of human hair to develop nitrogen doped nanocarbon while retaining the lamellar structure of human hair. High specific capacitance of 340 F g^{-1} at 1 A g^{-1} in aqueous 6 M KOH was achieved. Organic electrolyte of 1 M $LiPF_6$ exhibited 126 F g^{-1} of capacitance at 1 A g^{-1} current density.[138] This was achieved due to the high charge storage capacity of the nano carbon flakes with nitrogen doping.

Furthermore, flexible electrodes can be explored for using in wearable EESSs. Yu *et al.* explored flower petals for preparing activated carbon by simple thermal pyrolysis. The nano thickness (10–20 nm) of petals and wrinkled surfaces were attractive for ion storage along with flexible electrodes preparation. Great bending stability and maximum supercapacitance of 154 F g^{-1} was achieved with negligible decay of capacitance after 10 bending cycles.[160]

4. 5 3D biomass nanocarbon materials

It is well established that electrode material's supercapacitance depends on the microstructures upon exploring higher dimensional materials such as 3D, which enlarges the active surface area along with exposing certain facets of electrolyte.[161] In this view point, 3D structures shorten the diffusion pathways thus accelerating ion transfer, interconnected nano and micro pores provides good electrical contact, a requirement for high performance electrode materials design.[162] Thus, 3D microstructures enhance the electrochemical performances by tailor making the novel architectures synthesis and rational designing. Currently biomass-based materials are explored for synthesis of nano carbons with 3D structures. This approach not only precisely inherits 3D structure of the natural species but also reduces the raw materials cost. Flexible carbon films, aerogels, and hierarchical porous carbons in 3D architectures are explored using biomass as precursor material which prove excellent performances in supercapacitor applications.

Hierarchical porous carbon from biomass-based materials for 3D structures is explored by directly carbonizing corn husks post KOH pretreatment. KOH acts as an activating agent in the development of interconnected hierarchically porous network structure and promotes the breakdown of lignin and hemicellulose to separate cellulose. This cell structure of cellulose acts as a framework for interconnected macropores of 3D hierarchical porous carbon. This 3D porous carbon exhibits excellent supercapacitor properties with 356 F g^{-1}, good cycling stability of 95% after 2500 cycles, high energy density in aqueous electrolyte (Na_2SO_4) of 21 W h kg^{-1} and retention of 84.3% from 1 to 20 A g^{-1} displaying excellent rate capability.[163] In the future, pseudo materials are expected to combine with 3D based biomass porous carbon materials as a new nanocomposite to fulfil the rising energy demands for EESSs. For example, Fang *et al*. prepared nanowire arrays of PANI interconnected to porous carbon to achieve conductive pathways for electrolyte with shorter diffusion path. This composite materials in aqueous acidic electrolytes displayed specific capacitance of 1080 F g^{-1}.[164]

A carbon aerogel is another kind of porous carbon that gained attention due to its tuneable architecture, high conductivity, high porosity and large specific surface area, high power performances, high-rate capability and provide channels for free transportation of electrolyte ions. Aerogel preparation *via* traditional approach involves complex synthesis procedures along with expensive and harmful chemicals which limit their manufacturing in large scales.[165] Therefore, it is highly desirable to explore facile, low-cost, environmentally friendly approach to prepare the aerogels. Biomass was found to be a promising precursor to synthesise carbon aerogels because of its biodegradable nature.

Zu *et al*. synthesized aerogels by pyrolyzing cellulose followed by activation by CO_2 with high surface area. The synthesis process involved dissolution of cellulose in aqueous solution of NaOH, subsequently gelation, regeneration and CO_2 drying at supercritical temperature. This aerogel exhibited excellent electrochemical property for SC application due to the interconnected nano porous structure which provided efficient migration of electrolyte ions.[166] 3D porous hierarchical micro, meso and macro porous structures of carbon doped with nitrogen and oxygen were synthesized from kelp. Excellent capacitance of 669 mF cm^{-2} at 1 mA cm^{-2} ion transportation and storage in electrodes was improved with high specific surface area of 3D hierarchical porous structures. Excellent cyclic performance after 10,000 cycles with retention of 104% was exhibited by kelp derived carbon.[167]

Sorghum stem was carbonized and KOH activated to create high porous and surface area carbon. Capacitive deionization used to deionize water is explored to test the versatility of porous carbon derived from sorghum. Since both applications involve EDLC behaviour, the performance trend is similar for both capacitive deionization and

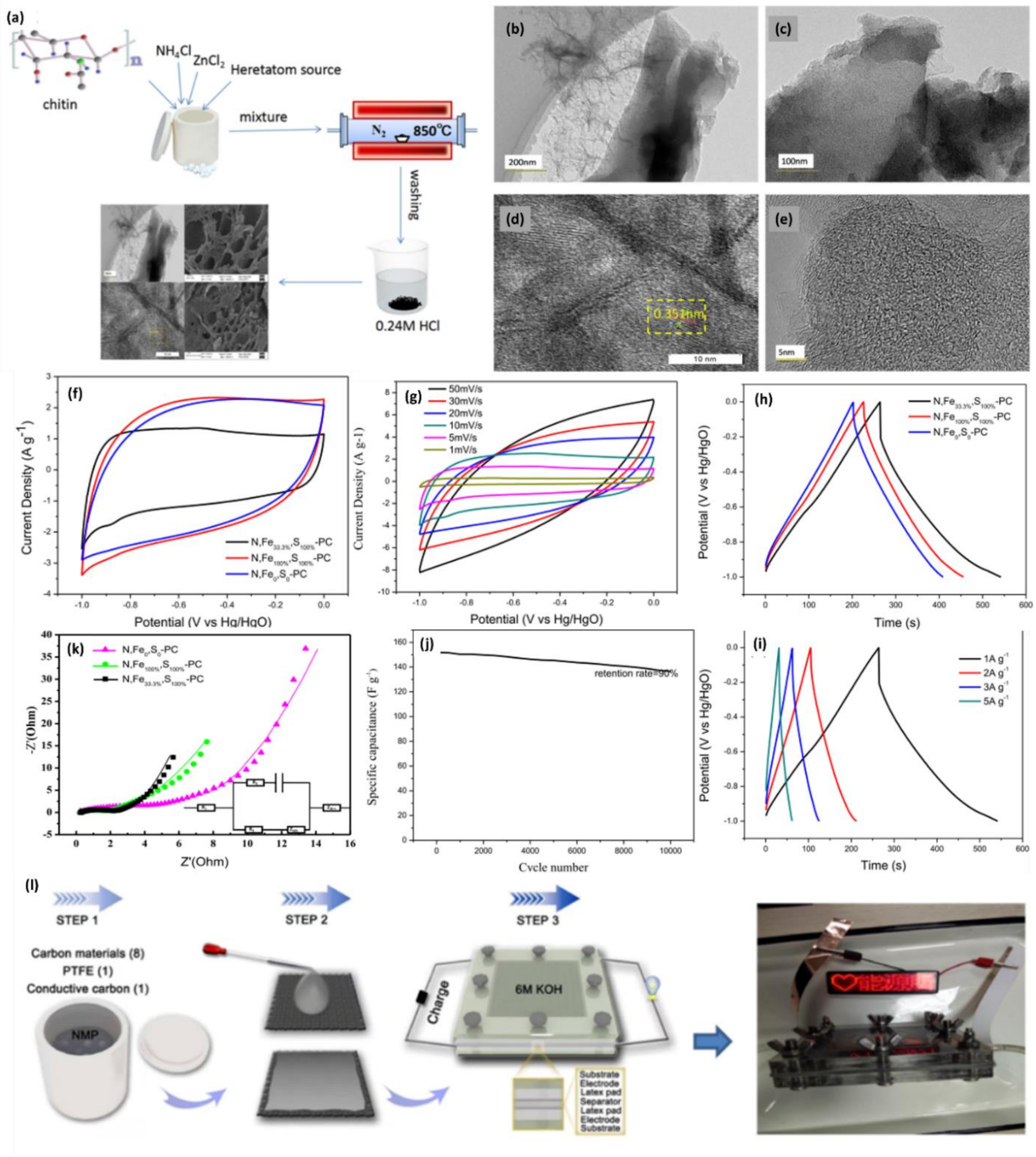

Fig. 11 a) Schematic showing the preparation process of N,Fe$_X$,S$_Y$-PC, (b–e) TEM image of N,Fe$_{33.3\%}$,S$_{100\%}$-PC, (f) CV curves of N,Fe$_0$,S$_0$-PC, N,Fe$_{100\%}$,S$_{100\%}$-PC and N,Fe$_{33.3\%}$,S$_{100\%}$-PC at a scan rate of 10 mV/s. (g) CV curves of N,Fe$_{33.3\%}$,S$_{100\%}$-PC, h) GCD curves of N,Fe$_0$,S$_0$-PC, N,Fe$_{100\%}$,S$_{100\%}$-PC, and N,Fe$_{33.3\%}$,S$_{100\%}$-PC at 1 A g^{-1}, i) GCD curves of N,Fe$_{33.3\%}$,S$_{100\%}$-PC, j) Nyquist plots and circuit, k) linear graph of N,Fe$_0$,S$_0$-PC, N,Fe$_{100\%}$,S$_{100\%}$-PC and N,Fe$_{33.3\%}$,S$_{100\%}$-PC. l) Scheme of assembling the supercapacitor. Reproduced with the permission from [98], Copyright 2021 Elsevier Ltd.

supercapacitance.[168] Nanoporous carbon was derived from jute by KOH chemical activation. High surface area of 2682 m^2g^{-1} was obtained with micropores and mesopores.[169]

Wang et al. synthesized heteroatom loaded porous carbon material (Fig. 11) from chitin which has abundant amide and hydroxyl groups. Sulphur, nitrogen, zinc and iron heteroatoms loading was done to prepare SC, which exhibited capacitance of 277.4 F g^{-1} at 1 A g^{-1}.[98] Wang *et al.* explored poplar saw dust biomass to synthesise nitrogen doped porous carbon (NPC) and its polyaniline composites (NPC/PANI) at 650 ºC, 700 ºC, 750 ºC and 800 ºC (Fig. 12) with KOH activation. Highest capacitance of 362 F g^{-1} was obtained at an optimized temperature of 750 ºC in 6M KOH. This occurred due to the suitable pore size distribution and high graphitization degree, which consequently, resulted in high surface area of 2149 m^2 g^{-1}.[103]

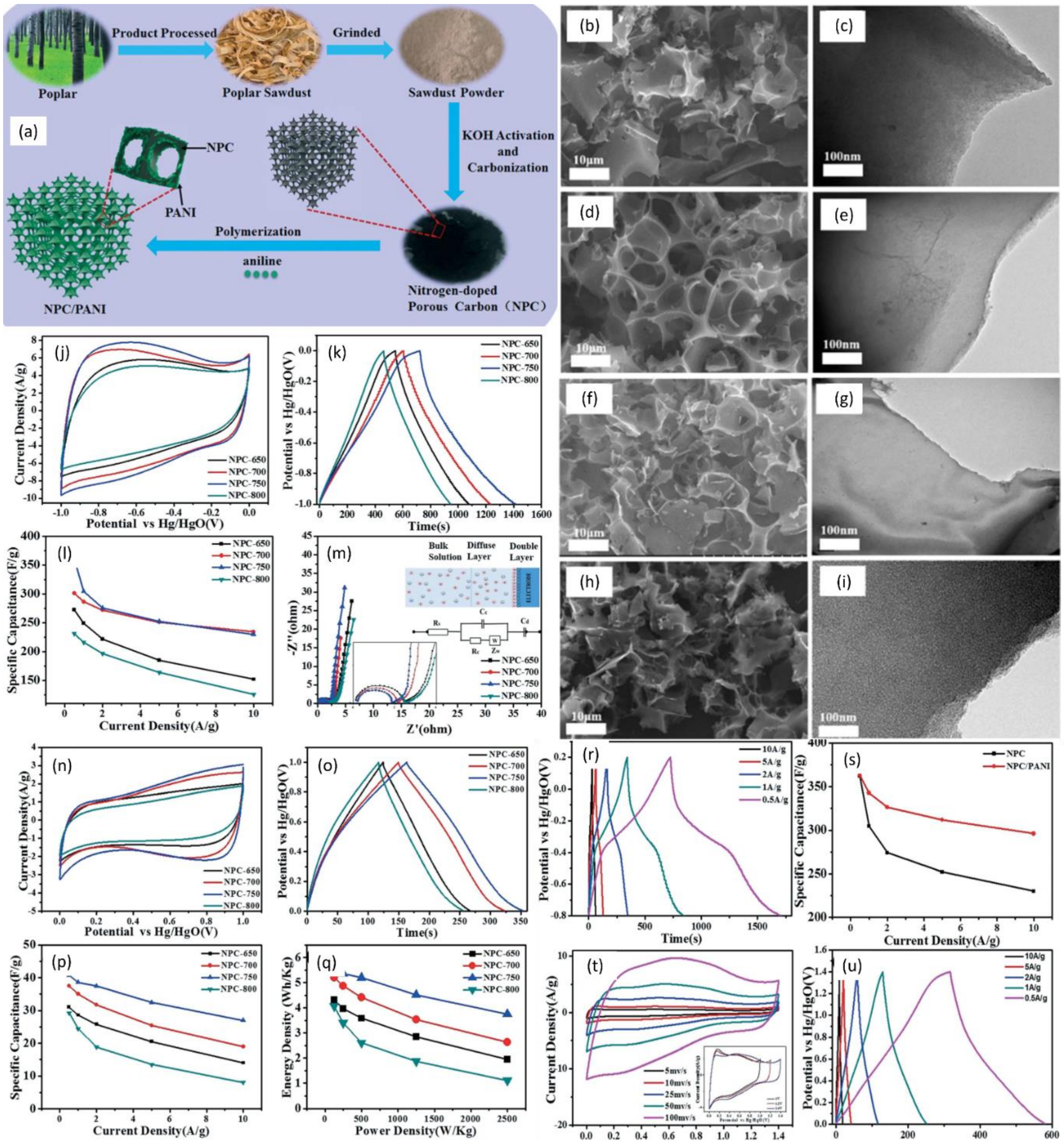

Fig. 12 (a) Scheme of poplar saw-dust derived NPC and NPC/PANI composites. (b-i) Morphologies of four poplar sawdust-derived NPCs. SEM images (b, d, f, h); TEM images (c, e, g, i): NPC-650 (b, c), NPC-700 (d, e), NPC-750 (f, g), NPC-800 (h, i). Electrochemical properties of four poplar sawdust-derived NPCs in three electrode setup: (j) CVs at scan rate of 25 mV s^{-1}, (k) GCD at a current density of 0.5 A g^{-1}, (l) Specific capacitance at different current densities, (m) Impedance plots and equivalent circuit model. Two-electrode setup: (n) CVs at scan rate of 25 mV s^{-1}, (o) GCD at current density of 0.5 A g^{-1} (p) Specific capacitance at different current densities, and (q) Ragone plot. (r) Galvanostatic charge–discharge of NPC/PANI at different current densities and (s) Specific capacitance at different current densities in a three-electrode setup. (t) Cyclic voltammograms curves at different potential window at 25 mV s^{-1} (inset). The CV curves at different scan rates and (u) GCD curves at different current densities of NPC/PANI in a two-electrode setup. Reproduced with the permission from [103], Copyright 2021 Elsevier Ltd.

5. Challenges and future outlook

Novel EESSs and conversion systems are emerging sustainable technologies which solve major outstanding challenges such as pollution remediation, GHG mitigation, global warming and rural empowerment. Further, innovative manufacturing led to reduced environmental footprints and cost. However, major challenges that hinder their deployment are high cost of electrodes, access scarcity, low energy density (SC), shortage of lithium (LiIBs), slow ORR rate at cathodes, slow reaction kinetics (NaIBs). Thus, it is a global imperative to find low-cost electrode materials with high performance without foregoing the electrocatalytic features and reduced noble metal usage.[170,171]

Novel biomass-based nano-porous carbon materials such as 0D, 1D, 2D and 3D are found promising in electrochemical conversion and energy conversion. This is because they offer excellent properties of energy and power densities equivalent to commercially available electrodes along with high surface area and rapid electron transfer.[175,176] However, the correlation between electrochemical performance and chemical composition, surface functional groups, microstructure and wettability of nano porous electrode materials is not well understood. An important challenge remains as to what are the requirements of raw biomass materials to attain easy-to-tune structures, suitable specific surface area along with high electrical conductivity.[58,172,173] Designing of sustainable and low cost electrode materials for EESSs are feasible with biomass derived nano porous carbon materials with high electrical conductivity combined with high surface area.[174] Nevertheless, increased porosity resulted in reduction in electrical conductivity.[180,181] Heteroatom doping with elements such as nitrogen, oxygen, boron, phosphorous, sulphur offer greater active sites for enhancing the electrochemical behaviour of the nanomaterials.

This review describes the work on the adoption of various plant-based bioresources for preparation of 0D, 1D, 2D and 3D nanostructures for EESSs such as SC and batteries. The electrochemical performance of 0-3D based materials and their mechanism has gathered much attention recently. However, the detailed mechanism of these nanomaterials in EESSs are yet to be understood in detail. Specifically, for 0D carbons, the Density Functional Theory applications looks like a promising strategy to address these hinderances. 0D materials have excellent photoluminescence and high quantum yields, but not explored for EESSs. Systemic investigation is required to understand the relationship between electrochemical performance and fluorescence.[177]

In general, 1D, 2D and 3D nanostructures from biomass carbon follow three main approaches to create porosity: 1) Chemical activation; 2) Physical activation; and 3) Hydrothermal treatment and subsequent activation. Relevant and prominent fabrication strategies and their advantages and disadvantages are provided in Table 5. Several reviews are published for SC detailing the carbon derived from biomass[152,178–182] and it is difficult to draw a simple relationship between pore size distribution and the kind of biomass used. This void in understanding is due to: A) Biomass morphology is heterogeneous (cellulose, hemicellulose, lignin) leading to activation agent diffusion which varies along the materials; and B) During activation, complex chemical reactions occur simultaneously. While these methods are under investigation, it is observed that micropores in large amount increase the capacitance and surface area, which is the most effective pathway to boost

Table 5. Advantages and disadvantages of various synthesis strategies to prepare biomass derived carbon nanomaterials.

No.	Fabrication strategies	Advantages	Disadvantages
Carbonization	Pyrolysis	Single step or combined with activation	500-1000 ºC
	HTC	Partial carbonization with oxygen containing groups, combination with pyrolysis and activation.	120-250 ºC
Physical activation	Air	Relatively low temperature	<500 ºC
	Steam	The most benign activating agent	800-1200 ºC
	CO_2	Relatively higher degree of graphitization compared to chemical	
Chemical activation	KOH, NaOH	Most often used chemical activation agent, High specific surface area	Lower degree of graphitization
	$ZnCl_3$, $FeCl_3$	Usually one step applied, acting as dehydrating agent	
	H_3PO_4	Phosphorous doped, contributing to pseudo-capacitance and widening the voltage window.	

energy density of EESSs.[59,188] A small amount of mesopores (~2–10 nm) in the carbon materials improve the kinetics at high current density and facilitate ion diffusion to deliver high power density. Another important structural feature is shape of the pore, but there is lack of numerical models to predict the pore structures.[183]

Plant tissue morphology is a primary factor in deciding the pore size distribution of the activated carbon from biomass. A recent study focussing on pyrolyzing various plant organs at 800 °C finds that the stems and leaves of lotus have different microporosity, which strongly depends on the morphology of the organs of the plant.[184] A study on ternary system comprising of cellulose, hemicellulose and lignin to produce biochars observes that 2D structures are produced from lignin, an aromatic compound, and 3D structures are derived from cellulose and hemicellulose.[185,186] Future strategies should aim to develop nanomaterials with controlled geometry and smart assembly. Since the limitation of biomass derived carbon is related to surface area, which affects the electrolyte interaction. It causes agglomeration and also parasitic reaction during the first cycle, which is called first cycle reversibility.[106] For industrial scale development of biomass-based carbon nanomaterials, there are a few difficulties to consider. Firstly, irregular morphology of biomass posing difficulty in precise tuning of shape and structure, thus limiting rate performance and power density. Effects of pore size, surface area and chemistry of biomass derived energy storage remain unknown to large extent. Another big challenge to investigate is ion diffusion process in hierarchical structure. To address the issues mentioned, changes in research direction towards structural design of supercapacitors and synthesis strategies are needed. Thirdly, controlling the properties of biomass derived nanomaterials synthesized with various methods from wide range of biomass precursors is required. With continuous research on biomass derived multidimensional carbon nanomaterials, great opportunities will open for renewable energy conversion and storage.[44]

6. Summary

A sustainable society requires great efforts to develop novel methods for producing enhanced materials towards transition to green energy pathway. Recycling importance, biodegradability of the products manufactured, and environmental impacts of our current technological solutions need critical valuation through life cycle assessment. Biodegradable electronic materials are achievable with biomass. Tremendous advances in energy storage have already been achieved through bio-based inventions. There are a variety of biomass precursors with chemical and structural diversity (such as agricultural by-products, biomass wastes, industry by-products) to produce promising results on high performance EESSs, but unfortunately reproducibility is hardly achieved.

The increasing demand for biofuels to reduce GHG emissions is expected to yield copious amounts of bio-related compounds which may lead to by-product classification. This is needed for economic viability in bio-refinery concept. This is due to the current studies lacking systemic correlation of physico-chemical characteristics of precursors with electrochemical performance[108,187,188] From our point of view, fabrication strategies, the use of activating agents, electrolytes, the dimensionality of the nanocarbon, and a combination of these factors will have great effect to produce EESSs.

In conclusion, nano-structured carbon materials produced by tailored synthetic routes along with knowledge of biomass precursors will be conducive to establish sustainable EESSs.

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Conflict of interest

There are no conflicts to declare.

Supporting information

Not applicable.

References

[1] H. H. Mardhiah, H. C. Ong, H. H. Masjuki, S. Lim, H. V. Lee, *Renewable and Sustainable Energy Reviews*, 2017, **67**, 1225-1236, doi: 10.1016/j.rser.2016.09.036.

[2] K. C. Swain, *Journal of Fundamentals of Renewable Energy and Applications*, 2014, **4**, 1-4, doi: 10.4172/2090-4541.1000129.

[3] A. Zervos, C. Lins, J. Muth, RE-Thinking 2050: A 100% Renewable Energy Vision for the European Union, 2010.

[4] C. Sheridan, *Nature Biotechnology*, 2013, **31**, 870-873, doi: 10.1038/nbt.2704.

[5] C. Shi, K. A. Owusu, X. Xu, T. Zhu, G. Zhang, W. Yang, L. Mai, *Small*, 2019, **15**, 1902348, doi: 10.1002/smll.201902348.

[6] M. R. Palacín, P. Simon, J. M. Tarascon, *Acta Chimica Slovenica*, 2016, 417-423, doi: 10.17344/acsi.2016.2314.

[7] C. Sarkar, V. Kumar, V. Sinha, *Current Science*, 2013, **104**, 1703-1709.

[8] V. Kumar, B. P. Chandra, V. Sinha, *Scientific Reports*, 2018, **8**, 1–15, doi: 10.1038/s41598-017-19139-3.

[9] P. V. Vadlani, *Green Energy to Sustainability: Strategies for Global Industries*, 2020, 569-586, doi: 10.1002/9781119152057.ch23.

[10] Y. N. Guragain, P. V. Vadlani, *Clean Technologies*, 2021, **3**, 243-259, doi: 10.3390/cleantechnol3010014.

[11] S. K. Lohan, H. S. Jat, A. K. Yadav, H. S. Sidhu, M. L. Jat, M. Choudhary, J. K. Peter, P. C. Sharma, *Renewable and Sustainable Energy Reviews*, 2018, **81**, 693-706, doi:

10.1016/j.rser.2017.08.057.

[12] Y. N. Guragain, K. P. Bastola, R. L. Madl, P. V. Vadlani, *BioEnergy Research*, 2016, **9**, 643-655, doi: 10.1007/s12155-015-9706-y.

[13] Y. N. Guragain, A. I. Herrera, P. V. Vadlani, O. Prakash, *Natural Product Communications*, 2015, **10**, 1934578X1501000, doi: 10.1177/1934578x1501000141.

[14] Y. N. Guragain, K. M. Ganesh, S. Bansal, R. Sai Sathish, N. Rao, P. V. Vadlani, *Industrial Crops and Products*, 2014, **61**, 1-8, doi: 10.1016/j.indcrop.2014.06.014.

[15] Y. Zhang, P. V. Vadlani, *Journal of Bioscience and Bioengineering*, 2015, **119**, 694–699, doi: 10.1016/J.JBIOSC.2014.10.027.

[16] Y. N. Guragain, P. Srinivasa Rao, P. V. Vara Prasad, P. V. Vadlani, *Applied Biochemistry and Biotechnology*, 2017, **183**, 1093-1110, doi: 10.1007/s12010-017-2486-4.

[17] S. P. Thota, P. K. Badiya, S. Yerram, P. V. Vadlani, M. Pandey, N. R. Golakoti, S. K. Belliraj, R. B. Dandamudi, S. S. Ramamurthy, *Renewable Energy*, 2017, **103**, 766-773, doi: 10.1016/j.renene.2016.11.010.

[18] S. P. Thota, P. K. Badiya, S. K. Belliraj, Y. N. Guragain, P. V. Vadlani, M. Pandey, R. B. Dandamudi, S. S. Ramamurthy, *Journal of Sustainable Bioenergy Systems*, 2018, **8**, 1–19, doi: 10.4236/jsbs.2018.83004.

[19] P. K. Badiya, S. P. Thota, S. Yerram, P. V. Vadlani, P. Vedantam, S. S. Ramamurthy, N. R. Golakoti, R. Sharma, B. S. V. Kumar, *Journal of Technology Innovations in Renewable Energy*, 2018, **7**, 7-18, doi: 10.6000/1929-6002.2018.07.02.

[20] S. P. Thota, S. M. Thota, S. Srimadh Bhagavatham, K. Sai Manoj, V. S. Sai Muthukumar, S. Venketesh, P. V. Vadlani, S. K. Belliraj, *IET Nanobiotechnology*, 2018, **12**, 127-132, doi: 10.1049/iet-nbt.2017.0038.

[21] Y. N. Guragain, D. Wang, P. V. Vadlani, *Renewable Energy*, 2016, **96**, 832-842, doi: 10.1016/j.renene.2016.04.099.

[22] A. Ganesan, M. M. Shaijumon, *Microporous and Mesoporous Materials*, 2016, **220**, 21-27, doi: 10.1016/j.micromeso.2015.08.021.

[23] N. Balahmar, A. C. Mitchell, R. Mokaya, *Advanced Energy Materials*, 2015, 5, 1500867, doi: 10.1002/aenm.201500867.

[24] L. Wang, Y. Shi, Y. Wang, H. Zhang, H. Zhou, Y. Wei, S. Tao, T. Ma, *Chemical Communications*, 2014, **50**, 1701, doi: 10.1039/c3cc47163b.

[25] Q. Ma, Y. Yu, M. Sindoro, A. G. Fane, R. Wang, H. Zhang, *Advanced Materials*, 2017, **29**, 1605361, doi: 10.1002/adma.201605361.

[26] C. Wang, X. Wang, H. Lu, H. Li, X. S. Zhao, *Carbon*, 2018, **140**, 139-147, doi: 10.1016/j.carbon.2018.08.032.

[27] P. R. Bueno, *Journal of Power Sources*, 2019, **414**, 420–434, doi: 10.1016/j.jpowsour.2019.01.010.

[28] Y. Zhang, X. Liu, S. Wang, L. Li, S. Dou, *Advanced Energy Materials*, 2017, **7**, 1700592, doi: 10.1002/aenm.201700592.

[29] T. K. Enock, C. K. King'ondu, A. Pogrebnoi, Y. A. C. Jande, C. K. King, A. Pogrebnoi, Y. Abeid, C. Jande, C. K. King'ondu, A. Pogrebnoi, Y. A. C. Jande, *International Journal of Electrochemistry*, 2017, **2017**, 1–14, doi: 10.1155/2017/6453420.

[30] M. Notarianni, J. Liu, K. Vernon, N. Motta, *Beilstein Journal of Nanotechnology*, 2016, **7**, 149-196, doi: 10.3762/bjnano.7.17.

[31] M. Ozhukil Valappil, V. K. Pillai, S. Alwarappan, *Applied Materials Today*, 2017, **9**, 350-371, doi: 10.1016/j.apmt.2017.09.002.

[32] J. Nan, X. Guo, J. Xiao, X. Li, W. Chen, W. Wu, H. Liu, Y. Wang, M. Wu, G. Wang, *Small*, 2021, **17**, 1902085, doi: 10.1002/smll.201902085.

[33] Z. Bi, Q. Kong, Y. Cao, G. Sun, F. Su, X. Wei, X. Li, A. Ahmad, L. Xie, C.-M. Chen, *Journal of Materials Chemistry A*, 2019, **7**, 16028-16045, doi: 10.1039/c9ta04436a.

[34] I. Y. Jeon, H. J. Noh, J. B. Baek, *Chemistry-An Asian Journal*, 2020, **15**, 2282-2293, doi: 10.1002/asia.201901318.

[35] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z. X. Shen, *Advanced Science*, 2018, **5**, 1700322, doi: 10.1002/advs.201700322.

[36] T. Lv, M. Liu, D. Zhu, L. Gan, T. Chen, *Advanced Materials*, 2018, **30**, 1–17, doi: 10.1002/adma.201705489.

[37] F. Ran, X. Yang, L. Shao, *Advanced Composites and Hybrid Materials*, 2018, **1**, 32-55, doi: 10.1007/s42114-017-0021-2.

[38] Y. Ma, X. Xie, W. Yang, Z. Yu, X. Sun, Y. Zhang, X. Yang, H. Kimura, C. Hou, Z. Guo, W. Du, *Advanced Composites and Hybrid Materials*, 2021, **4**, 906-924, doi: 10.1007/s42114-021-00358-2.

[39] M. A. Azam, N. S. N. Ramli, N. A. N. M. Nor, T. I. T. Nawi, *International Journal of Energy Research*, 2021, **45**, 8335-8346, doi: 10.1002/er.6377.

[40] Z. Yu, L. Tetard, L. Zhai, J. Thomas, *Energy & Environmental Science*, 2015, **8**, 702-730, doi: 10.1039/c4ee03229b.

[41] Y. Ma, X. Xie, W. Yang, Z. Yu, X. Sun, Y. Zhang, X. Yang, H. Kimura, C. Hou, Z. Guo, W. Du, *Advanced Composites and Hybrid Materials*, 2021, **4**, 906-924, doi: 10.1007/s42114-021-00358-2.

[42] T. Lu, Y. Liu, X. Xu, L. Pan, A. A. Alothman, J. Shapter, Y. Wang, Y. Yamauchi, *Separation and Purification Technology*, 2021, **256**, 117771, doi: 10.1016/j.seppur.2020.117771.

[43] T. Li, R. Ma, J. Lin, Y. Hu, P. Zhang, S. Sun, L. Fang, *International Journal of Energy Research*, 2020, **44**, 2426-2454, doi: 10.1002/er.5061.

[44] H. Lu, X. S. Zhao, *Sustainable Energy & Fuels*, 2017, **1**, 1265-1281, doi: 10.1039/c7se00099e.

[45] J. Wang, X. Zhang, Z. Li, Y. Ma, L. Ma, *Journal of Power Sources*, 2020, **451**, 227794, doi: 10.1016/j.jpowsour.2020.227794.

[46] C. Senthil, C. W. Lee, *Renewable and Sustainable Energy Reviews*, 2021, **137**, 110464, doi: 10.1016/j.rser.2020.110464.

[47] Y. Wang, Q. Qu, S. Gao, G. Tang, K. Liu, S. He, C. Huang, *Carbon*, 2019, **155**, 706-726, doi: 10.1016/j.carbon.2019.09.018.

[48] E. M. Rubin, *Nature*, 2008, **454**, 841-845, doi: 10.1038/nature07190.

[49] G. Centi, S. Perathoner, *ChemSusChem*, 2010, **3**, 195-208, doi: 10.1002/cssc.200900289.

[50] Z. Zhou, D. Liu, X. Zhao, *Renewable and Sustainable Energy Reviews*, 2021, **146**, 111169, doi:

10.1016/j.rser.2021.111169.

[51] V. V. N. Obreja, *Physica E: Low-dimensional Systems and Nanostructures*, 2008, **40**, 2596–2605, doi: 10.1016/J.PHYSE.2007.09.044.

[52] S. Najib, E. Erdem, *Nanoscale Advances*, 2019, **1**, 2817-2827, doi: 10.1039/c9na00345b.

[53] D. Gielen, F. Boshell, D. Saygin, M. D. Bazilian, N. Wagner, R. Gorini, *Energy Strategy Reviews*, 2019, **24**, 38-50, doi: 10.1016/j.esr.2019.01.006.

[54] H. Jiang, Y. Zhang, C. Wang, Q. Wang, C. Meng, J. Wang, *Inorganic Chemistry Frontiers*, 2019, **6**, 2788-2800, doi: 10.1039/c9qi00766k.

[55] W. Chen, X. Wang, C. Liu, M. Luo, P. Yang, X. Zhou, *Waste Management*, 2020, **102**, 330-339, doi: 10.1016/j.wasman.2019.10.058.

[56] T. K. Enock, C. K. King'ondu, A. Pogrebnoi, Y. A. C. Jande, *Materials Today Energy*, 2017, **5**, 126-137, doi: 10.1016/j.mtener.2017.06.006.

[57] Y. Wang, P. Yang, L. Zheng, X. Shi, H. Zheng, *Energy Storage Materials*, 2020, **26**, 349-370, doi: 10.1016/j.ensm.2019.11.006.

[58] P. Simon, Y. Gogotsi, *Nature Materials*, 2008, **7**, 845-854, doi: 10.1038/nmat2297.

[59] D. Lamd, Supercapacitors to charge Galaxy Note 9's S Pen: What is it and how does it work?- Technology News, Firstpost, can be found under https://www.firstpost.com/tech/science/supercapacitors-to-charge-galaxy-note-9s-s-pen-what-is-it-and-how-does-it-work-5010721.html, 2018.

[60] N. Todorov, "The Galaxy Note 9 S Pen has a clever rapid-charging "battery" with one tiny flaw," can be found under https://www.phonearena.com/news/Galaxy-Note-9-S-Pen-battery-super-capacitor_id107622, 2018.

[61] W. Gu, G. Yushin, *Wiley Interdisciplinary Reviews: Energy and Environment*, 2014, **3**, 424-473, doi: 10.1002/wene.102.

[62] Z. Gao, Y. Zhang, N. Song, X. Li, *Materials Research Letters*, 2017, **5**, 69-88, doi: 10.1080/21663831.2016.1250834.

[63] L. L. Zhang, X. S. Zhao, *Chemical Society Reviews*, 2009, **38**, 2520, doi: 10.1039/b813846j.

[64] A. Allagui, T. J. Freeborn, A. S. Elwakil, B. J. Maundy, *Scientific Reports*, 2016, **6**, 38568, doi: 10.1038/srep38568.

[65] W. G. Pell, B. E. Conway, *Journal of Power Sources*, 2001, **96**, 57-67, doi: 10.1016/s0378-7753(00)00682-0.

[66] S. S. Patil, T. S. Bhat, A. M. Teli, S. A. Beknalkar, S. B. Dhavale, M. M. Faras, M. M. Karanjkar, P. S. Patil, *Engineering Science*, 2020, **12**, 38-51, doi:10.30919/es8d1140.

[66] S. S. Patil, T. S. Bhat, A. M. Teli, S. A. Beknalkar, S. B. Dhavale, M. M. Faras, M. M. Karanjkar, P. S. Patil, *Engineered Science*, 2020, **12**, 38–51, doi: 10.30919/es8d1140.

[67] J. G. Ruiz-Montoya, L. V. Quispe-Garrido, J. C. Calderón Gómez, A. M. Baena-Moncada, J. M. Gonçalves, *Sustainable Energy & Fuels*, 2021, **5**, 5332-5365, doi: 10.1039/d1se01170g.

[68] K. Khan, A. K. Tareen, M. Aslam, A. Mahmood, Q. Khan, Y. Zhang, Z. Ouyang, Z. Guo, H. Zhang, *Progress in Solid State Chemistry*, 2020, **58**, 100254, doi: 10.1016/j.progsolidstchem.2019.100254.

[69] S. Pakseresht, D. Kuruahmet, A. Guler, S. O. Duman, H. Gungor, B. Cetinkaya, G. S. Martynkova, *Journal of the Electrochemical Society*, 2022, **169**, 010534, doi: 10.1149/1945-7111/ac4843.

[70] A. Ganesan, A. Varzi, S. Passerini, M. M. Shaijumon, *Electrochimica Acta*, 2016, **214**, 129-138, doi: 10.1016/j.electacta.2016.08.030.

[71] Q. Li, Y. Liu, Y. Wang, Y. Chen, X. Guo, Z. Wu, B. Zhong, *Ionics*, 2020, **26**, 4765-4781, doi: 10.1007/s11581-020-03694-3.

[72] V. Subramanian, C. Luo, A. M. Stephan, K. S. Nahm, S. Thomas, B. Wei, *The Journal of Physical Chemistry C*, 2007, **111**, 7527-7531, doi: 10.1021/jp067009t.

[73] T. E. Rufford, D. Hulicova-Jurcakova, Z. Zhu, G. Q. Lu, *Electrochemistry Communications*, 2008, **10**, 1594-1597, doi: 10.1016/j.elecom.2008.08.022.

[74] J. Yu, T. Tang, F. Cheng, D. Huang, J. L. Martin, C. E. Brewer, R. L. Grimm, M. Zhou, H. Luo, *Materials Today Energy*, 2021, **19**, 100580, doi: 10.1016/j.mtener.2020.100580.

[75] G. Xia, X. Li, J. He, Y. Wang, Y. Gu, L. Liu, J. Huang, P. Dong, J. Duan, D. Wang, Y. Zhang, Y. Zhang, *Ceramics International*, 2021, **47**, 20948-20955, doi: 10.1016/j.ceramint.2021.04.093.

[76] S. Wang, C. Xiao, Y. Xing, H. Xu, S. Zhang, *Journal of Materials Chemistry A*, 2015, **3**, 6742-6747, doi: 10.1039/C5TA00050E.

[77] L. Wang, Z. Schnepp, M. M. Titirici, *Journal of Materials Chemistry A*, 2013, **1**, 5269, doi: 10.1039/c3ta10650k.

[78] C. Yu, M. Chen, X. Li, C. Zhao, L. He, J. Qiu, *Journal of Materials Chemistry A*, 2015, **3**, 5054-5059, doi: 10.1039/c4ta07019d.

[79] J. Ou, L. Yang, X. Xi, *Chinese Journal of Chemistry*, 2016, **34**, 727-732, doi: 10.1002/cjoc.201600095.

[80] T. E. Rufford, D. Hulicova-Jurcakova, Z. Zhu, G. Q. Lu, *Electrochemistry Communications*, 2008, **10**, 1594-1597, doi: 10.1016/j.elecom.2008.08.022.

[81] E. Raymundo-Piñero, M. Cadek, F. Béguin, *Advanced Functional Materials*, 2009, **19**, 1032-1039, doi: 10.1002/adfm.200801057.

[82] T. E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu, G. Q. Lu, *Journal of Power Sources*, 2010, **195**, 912-918, doi: 10.1016/j.jpowsour.2009.08.048.

[83] A. E. Ismanto, S. Wang, F. E. Soetaredjo, S. Ismadji, *Bioresource Technology*, 2010, **101**, 3534-3540, doi: 10.1016/j.biortech.2009.12.123.

[84] J. M. Valente Nabais, J. G. Teixeira, I. Almeida, *Bioresource Technology*, 2011, **102**, 2781-2787, doi: 10.1016/j.biortech.2010.11.083.

[85] L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya, G. Yushin, *Advanced Energy Materials*, 2011, **1**, 356-361, doi: 10.1002/aenm.201100019.

[86] J. Mi, X.-R. Wang, R.-J. Fan, W.-H. Qu, W.-C. Li, *Energy & Fuels*, 2012, **26**, 5321-5329, doi: 10.1021/ef3009234.

[87] L. Zhang, F. Zhang, X. Yang, K. Leng, Y. Huang, Y. Chen, *Small*, 2013, **9**, 1342-1347, doi: 10.1002/smll.201202943.

[88] L. Jiang, J. Yan, L. Hao, R. Xue, G. Sun, B. Yi, *Carbon*, 2013,

56, 146-154, doi: 10.1016/j.carbon.2012.12.085.

[89] L. Sun, C. Tian, M. Li, X. Meng, L. Wang, R. Wang, J. Yin, H. Fu, *Journal of Materials Chemistry A*, 2013, **1**, 6462, doi: 10.1039/c3ta10897j.

[90] X. He, P. Ling, J. Qiu, M. Yu, X. Zhang, C. Yu, M. Zheng, *Journal of Power Sources*, 2013, **240**, 109-113, doi: 10.1016/j.jpowsour.2013.03.174.

[91] Z. Jin, X. Yan, Y. Yu, G. Zhao, *Journal of Material Chemistry A*, 2014, **2**, 11706-11715, doi: 10.1039/c4ta01413h.

[92] K. Karthikeyan, S. Amaresh, S. N. Lee, X. Sun, V. Aravindan, Y.-G. Lee, Y. S. Lee, *ChemSusChem*, 2014, **7**, 1435-1442, doi: 10.1002/cssc.201301262.

[93] C. Ruan, K. Ai, L. Lu, *RSC Advances*, 2014, **4**, 30887, doi: 10.1039/c4ra04470c.

[94] P. Hao, Z. Zhao, Y. Leng, J. Tian, Y. Sang, R. I. Boughton, C. P. Wong, H. Liu, B. Yang, *Nano Energy*, 2015, **15**, 9-23, doi: 10.1016/j.nanoen.2015.02.035.

[95] Z. Li, W. Lv, C. Zhang, B. Li, F. Kang, Q.-H. Yang, *Carbon*, 2015, **92**, 11-14, doi: 10.1016/j.carbon.2015.02.054.

[96] G. Xu, J. Han, B. Ding, P. Nie, J. Pan, H. Dou, H. Li, X. Zhang, *Green Chemistry*, 2015, **17**, 1668-1674, doi: 10.1039/c4gc02185a.

[97] J. Hou, C. Cao, F. Idrees, X. Ma, *ACS Nano*, 2015, **9**, 2556-2564, doi: 10.1021/nn506394r.

[98] J. Wang, Y. Xu, M. Yan, B. Ren, X. Dong, J. Miao, L. Zhang, X. Zhao, Z. Liu, *Biomass and Bioenergy*, 2022, **156**, 106301, doi: 10.1016/j.biombioe.2021.106301.

[99] J. Deng, T. Xiong, F. Xu, M. Li, C. Han, Y. Gong, H. Wang, Y. Wang, *Green Chemistry*, 2015, **17**, 4053-4060, doi: 10.1039/c5gc00523j.

[100] J. Wang, S. Kaskel, *Journal of Materials Chemistry*, 2012, **22**, 23710–23725, doi: 10.1039/c2jm34066f.

[101] C. Liu, G. Han, Y. Chang, Y. Xiao, M. Li, W. Zhou, D. Fu, W. Hou, *ChemElectroChem*, 2016, **3**, 323-331, doi: 10.1002/celc.201500376.

[102] S. Wang, W. Sun, D.-S. Yang, F. Yang, *Materials Today Energy*, 2019, **13**, 50-55, doi: 10.1016/j.mtener.2019.04.015.

[103] X. Wang, X. Zeng, D. Cao, *Engineered Science*, 2018, **1**, 55–63, doi: 10.30919/es.180325.

[104] Y. He, X. Zhuang, C. Lei, L. Lei, Y. Hou, Y. Mai, X. Feng, *Nano Today*, 2019, **24**, 103-119, doi: 10.1016/j.nantod.2018.12.004.

[105] B. E. Conway, W. G. Pell, *Journal of Solid State Electrochemistry*, 2003, **7**, 637-644, doi: 10.1007/s10008-003-0395-7.

[106] E. Pomerantseva, F. Bonaccorso, X. Feng, Y. Cui, Y. Gogotsi, *Science*, 2019, 366, eaan8285, doi: 10.1126/science.aan8285.

[107] Z. Yu, L. Tetard, L. Zhai, J. Thomas, *Energy & Environmental Science*, 2015, **8**, 702-730, doi: 10.1039/c4ee03229b.

[108] G. P. Robertson, S. K. Hamilton, B. L. Barham, B. E. Dale, R. C. Izaurralde, R. D. Jackson, D. A. Landis, S. M. Swinton, K. D. Thelen, J. M. Tiedje, *Science*, 2017, **356**, eaal2324, doi: 10.1126/science.aal2324.

[109] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X. W. Low, *Advanced materials*, 2012, **24**, 5166-5180, doi: 10.1002/adma.201202146.

[110] X. Zhao, M. Li, H. Dong, Y. Liu, H. Hu, Y. Cai, Y. Liang, Y. Xiao, M. Zheng, *ChemSusChem*, 2017, **10**, 2626-2634, doi: 10.1002/cssc.201700474.

[111] J. Liu, S. Zhao, C. Li, M. Yang, Y. Yang, Y. Liu, Y. Lifshitz, S.-T. Lee, Z. Kang, *Advanced Energy Materials*, 2016, **6**, 1502039, doi: 10.1002/aenm.201502039.

[112] C. Zhu, D. Chao, J. Sun, I. M. Bacho, Z. Fan, C. F. Ng, X. Xia, H. Huang, H. Zhang, Z. X. Shen, G. Ding, H. J. Fan, *Advanced Materials Interfaces*, 2015, **2**, 1400499, doi: 10.1002/admi.201400499.

[113] D. Chao, C. Zhu, X. Xia, J. Liu, X. Zhang, J. Wang, P. Liang, J. Lin, H. Zhang, Z. X. Shen, H. J. Fan, *Nano Letters*, 2015, **15**, 565–573, doi: 10.1021/nl504038s.

[114] A. Datta, S. Kapri, S. Bhattacharyya, *Journal of Materials Chemistry A*, 2016, **4**, 14614-14624, doi: 10.1039/c6ta04737h.

[115] P. P. Bag, G. P. Singh, S. Singha, G. Roymahapatra, *Engineered Science*, 2020, **13**, 1–10, doi: 10.30919/es8d1166.

[116] J.-X. Wu, P. P. Bag, Y.-T. Xu, L. Gong, C.-T. He, X.-M. Chen, J.-P. Zhang, *Advanced Materials*, 2021, **33**, 2007368, doi: 10.1002/adma.202007368.

[117] G. Wu, Y. Gao, D. Zhao, P. Ling, F. Gao, *ACS Applied Materials & Interfaces*, 2017, **9**, 40978-40986, doi: 10.1021/acsami.7b12295.

[118] F. Yuan, S. Li, Z. Fan, X. Meng, L. Fan, S. Yang, *Nano Today*, 2016, **11**, 565-586, doi: 10.1016/j.nantod.2016.08.006.

[119] A. Muthurasu, V. Ganesh, *Applied Biochemistry and Biotechnology*, 2014, **174**, 945-959, doi: 10.1007/s12010-014-1019-7.

[120] M. Han, S. Zhu, S. Lu, Y. Song, T. Feng, S. Tao, J. Liu, B. Yang, *Nano Today*, 2018, **19**, 201-218, doi: 10.1016/j.nantod.2018.02.008.

[121] P. P. Bag, P. Sahoo, Designing metal-organic frameworks based photocatalyst for specific photocatalytic reactions: a crystal engineering approach, *Green photocatalysts for energy and environmental process*, Springer, Cham, 2020, 141–186, doi: 10.1007/978-3-030-17638-9_6.

[122] P. P. Bag, X.-S. Wang, P. Sahoo, J. Xiong, R. Cao, *Catalysis Science & Technology*, 2017, **7**, 5113-5119, doi: 10.1039/c7cy01254c.

[123] D. Iannazzo, I. Ziccarelli, A. Pistone, *Journal of Materials Chemistry B*, 2017, **5**, 6471-6489, doi: 10.1039/c7tb00747g.

[124] V. C. Hoang, L. H. Nguyen, V. G. Gomes, *Journal of Electroanalytical Chemistry*, 2019, **832**, 87-96, doi: 10.1016/j.jelechem.2018.10.050.

[125] W. Li, Y. Liu, M. Wu, X. Feng, S. A. T. Redfern, Y. Shang, X. Yong, T. Feng, K. Wu, Z. Liu, B. Li, Z. Chen, J. S. Tse, S. Lu, B. Yang, *Advanced Materials*, 2018, **30**, 1800676, doi: 10.1002/adma.201800676.

[126] S. Ghosh, R. Santhosh, S. Jeniffer, V. Raghavan, G. Jacob, K. Nanaji, P. Kollu, S. K. Jeong, A. N. Grace, *Scientific Reports*, 2019, **9**, 16315, doi: 10.1038/s41598-019-52006-x.

[127] Z. Sun, K. Qu, J. Li, S. Yang, B. Yuan, Z. Huang, Z. Guo,

Advanced Composites and Hybrid Materials, 2021, **4**, 1413-1424, doi: 10.1007/s42114-021-00352-8.

[128] G. Lin, R. Ma, Y. Zhou, Q. Liu, X. Dong, J. Wang, *Electrochimica Acta*, 2018, **261**, 49-57, doi: 10.1016/j.electacta.2017.12.107.

[129] H. Yin, B. Lu, Y. Xu, D. Tang, X. Mao, W. Xiao, D. Wang, A. N. Alshawabkeh, *Environmental Science & Technology*, 2014, **48**, 8101-8108, doi: 10.1021/es501739v.

[130] Z. Xiao, W. Chen, K. Liu, P. Cui, D. Zhan, *International Journal of Electrochemical Society*, 2018, **13**, 5370–5381, doi: 10.20964/2018.06.54.

[131] T. Purkait, G. Singh, M. Singh, D. Kumar, R. S. Dey, *Scientific Reports*, 2017, **7**, 15239, doi: 10.1038/s41598-017-15463-w.

[132] J. Cao, C. Zhu, Y. Aoki, H. Habazaki, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 7292-7303, doi: 10.1021/acssuschemeng.7b04459.

[133] Y. Huang, J. He, Y. Luan, Y. Jiang, S. Guo, X. Zhang, C. Tian, B. Jiang, *RSC Advances*, 2017, **7**, 10385-10390, doi: 10.1039/c6ra27788h.

[134] A. Ganesan, R. Mukherjee, J. Raj, M. M. Shaijumon, *Journal of Porous Materials*, 2014, **21**, 839-847, doi: 10.1007/s10934-014-9833-4.

[135] M. Dhelipan, A. Arunchander, A. K. Sahu, D. Kalpana, *Journal of Saudi Chemical Society*, 2017, **21**, 487-494, doi: 10.1016/j.jscs.2016.12.003.

[136] Z. Gao, C. Bumgardner, N. Song, Y. Zhang, J. Li, X. Li, *Nature Communications*, 2016, **7**, 11586, doi: 10.1038/ncomms11586.

[137] Y.-Q. Zhao, M. Lu, P.-Y. Tao, Y.-J. Zhang, X.-T. Gong, Z. Yang, G.-Q. Zhang, H.-L. Li, *Journal of Power Sources*, 2016, **307**, 391-400, doi: 10.1016/j.jpowsour.2016.01.020.

[138] W. Qian, F. Sun, Y. Xu, L. Qiu, C. Liu, S. Wang, F. Yan, *Energy & Environmental Science*, 2014, **7**, 379-386, doi: 10.1039/c3ee43111h.

[139] W.-J. Si, X.-Z. Wu, W. Xing, J. Zhou, S.-P. Zhuo, *Journal of Inorganic Materials*, 2011, **26**, 107-113, doi: 10.3724/sp.j.1077.2010.10376.

[140] M. Biswal, A. Banerjee, M. Deo, S. Ogale, *Energy & Environmental Science*, 2013, **6**, 1249, doi: 10.1039/c3ee22325f.

[141] M. Chen, X. Kang, T. Wumaier, J. Dou, B. Gao, Y. Han, G. Xu, Z. Liu, L. Zhang, *Journal of Solid State Electrochemistry*, 2013, **17**, 1005-1012, doi: 10.1007/s10008-012-1946-6.

[142] J. Zhang, F. Zhang, Y. Yang, S. Guo, J. Zhang, *ACS Omega*, 2017, **2**, 7293-7298, doi: 10.1021/acsomega.7b00908.

[143] X. T. Zheng, A. Ananthanarayanan, K. Q. Luo, P. Chen, *Small*, 2015, **11**, 1620-1636, doi: 10.1002/smll.201402648.

[144] T. van Tam, S. G. Kang, K. F. Babu, E.-S. Oh, S. G. Lee, W. M. Choi, *Journal of Materials Chemistry A*, 2017, **5**, 10537-10543, doi: 10.1039/c7ta01485f.

[145] Y. Zhang, C. Wu, X. Zhou, X. Wu, Y. Yang, H. Wu, S. Guo, J. Zhang, *Nanoscale*, 2013, **5**, 1816, doi: 10.1039/c3nr33954h.

[146] H. Sun, N. Gao, K. Dong, J. Ren, X. Qu, *ACS Nano*, 2014, **8**, 6202-6210, doi: 10.1021/nn501640q.

[147] F. Hekmat, H. Hosseini, S. Shahrokhian, H. E. Unalan, *Energy Storage Materials*, 2020, **25**, 621-635, doi: 10.1016/j.ensm.2019.09.022.

[148] Q. Wei, F. Xiong, S. Tan, L. Huang, E. H. Lan, B. Dunn, L. Mai, *Advanced Materials*, 2017, **29**, 1602300, doi: 10.1002/adma.201602300.

[149] Y. Li, G. Wang, T. Wei, Z. Fan, P. Yan, *Nano Energy*, 2016, **19**, 165-175, doi: 10.1016/j.nanoen.2015.10.038.

[150] Y. Cao, L. Xie, G. Sun, F. Su, Q.-Q. Kong, F. Li, W. Ma, J. Shi, D. Jiang, C. Lu, C.-M. Chen, *Sustainable Energy & Fuels*, 2018, **2**, 455-465, doi: 10.1039/c7se00481h.

[151] Z. Shi, L. Xing, Y. Liu, Y. Gao, J. Liu, *Carbon*, 2018, **129**, 819-825, doi: 10.1016/j.carbon.2017.12.105.

[152] X. Hao, J. Wang, B. Ding, Y. Wang, Z. Chang, H. Dou, X. Zhang, *Journal of Power Sources*, 2017, **352**, 34-41, doi: 10.1016/j.jpowsour.2017.03.088.

[153] Q. Jiang, Z. Zhang, S. Yin, Z. Guo, S. Wang, C. Feng, *Applied Surface Science*, 2016, **379**, 73-82, doi: 10.1016/j.apsusc.2016.03.204.

[154] W. Chen, H. Yu, S.-Y. Lee, T. Wei, J. Li, Z. Fan, *Chemical Society Reviews*, 2018, **47**, 2837-2872, doi: 10.1039/c7cs00790f.

[155] J. Cai, H. Niu, H. Wang, H. Shao, J. Fang, J. He, H. Xiong, C. Ma, T. Lin, *Journal of Power Sources*, 2016, **324**, 302-308, doi: 10.1016/j.jpowsour.2016.05.070.

[156] R. Berenguer, F. J. García-Mateos, R. Ruiz-Rosas, D. Cazorla-Amorós, E. Morallón, J. Rodríguez-Mirasol, T. Cordero, *Green Chemistry*, 2016, **18**, 1506-1515, doi: 10.1039/c5gc02409a.

[157] Y. Liu, Z. Shi, Y. Gao, W. An, Z. Cao, J. Liu, *ACS Applied Materials & Interfaces*, 2016, **8**, 28283-28290, doi: 10.1021/acsami.5b11558.

[158] Y. Hou, M. Qiu, T. Zhang, X. Zhuang, C.-S. Kim, C. Yuan, X. Feng, *Advanced Materials*, 2017, **29**, 1701589, doi: 10.1002/adma.201701589.

[159] H. Jin, J. Li, Y. Yuan, J. Wang, J. Lu, S. Wang, *Advanced Energy Materials*, 2018, **8**, 1801007, doi: 10.1002/aenm.201801007.

[160] X. Yu, Y. Wang, L. Li, H. Li, Y. Shang, *Scientific Reports*, 2017, **7**, 1–8, doi: 10.1038/srep45378.

[161] C. Wang, Y. Xiong, H. Wang, C. Jin, Q. Sun, *Journal of Materials Chemistry A*, 2017, **5**, 15759-15770, doi: 10.1039/c7ta04178k.

[162] Y. Zhang, Z. Hu, Y. Liang, Y. Yang, N. An, Z. Li, H. Wu, *Journal of Materials Chemistry A*, 2015, **3**, 15057-15067, doi: 10.1039/c5ta02479j.

[163] S. Song, F. Ma, G. Wu, D. Ma, W. Geng, J. Wan, *Journal of Materials Chemistry A*, 2015, **3**, 18154–18162, doi: 10.1039/c5ta04721h.

[164] P. Yu, Z. Zhang, L. Zheng, F. Teng, L. Hu, X. Fang, *Advanced Energy Materials*, 2016, **6**, 1601111, doi: 10.1002/aenm.201601111.

[165] X. Xu, J. Zhou, D. H. Nagaraju, L. Jiang, V. R. Marinov, G. Lubineau, H. N. Alshareef, M. Oh, Flexible, *Advanced Functional Materials*, 2015, **25**, 3193-3202, doi: 10.1002/adfm.201500538.

[166] G. Zu, J. Shen, L. Zou, F. Wang, X. Wang, Y. Zhang, X.

Yao, *Carbon*, 2016, **99**, 203-211, doi: 10.1016/j.carbon.2015.11.079.
[167] Y. Zhang, H. Jiang, Q. Wang, J. Zheng, C. Meng, *Applied Surface Science*, 2018, **447**, 876-885, doi: 10.1016/j.apsusc.2018.04.061.
[168] M. Kim, H. Lim, X. Xu, M. S. A. Hossain, J. Na, N. N. Awaludin, J. Shah, L. K. Shrestha, K. Ariga, A. K. Nanjundan, D. J. Martin, J. G. Shapter, Y. Yamauchi, *Microporous and Mesoporous Materials*, 2021, **312**, 110757, doi: 10.1016/j.micromeso.2020.110757.
[169] J. H. Khan, F. Marpaung, C. Young, J. Lin, M. T. Islam, S. M. Alsheri, T. Ahamad, N. Alhokbany, K. Ariga, L. K. Shrestha, Y. Yamauchi, K. C.-W. Wu, M. S. A. Hossain, J. Kim, *Microporous and Mesoporous Materials*, 2019, **274**, 251-256, doi: 10.1016/j.micromeso.2018.07.050.
[170] R. Thangavel, K. Kaliyappan, H. V. Ramasamy, X. Sun, Y.-S. Lee, *ChemSusChem*, 2017, **10**, 2805-2815, doi: 10.1002/cssc.201700492.
[171] A. B. Fuertes, M. Sevilla, *ChemSusChem*, 2015, **8**, 1049-1057, doi: 10.1002/cssc.201403267.
[172] D.-W. Wang, F. Li, M. Liu, G. Lu, H.-M. Cheng, *Angewandte Chemie International Edition*, 2008, **47**, 373-376, doi: 10.1002/anie.200702721.
[173] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, *Advanced Materials*, 2014, **26**, 2219-2251, doi: 10.1002/adma.201304137.
[174] G. A. Ferrero, A. B. Fuertes, M. Sevilla, *Scientific Reports*, 2015, **5**, 16618, doi: 10.1038/srep16618.
[175] H. Wang, Z. Xu, A. Kohandehghan, Z. Li, K. Cui, X. Tan, T. J. Stephenson, C. K. King'Ondu, C. M. B. Holt, B. C. Olsen, J. K. Tak, D. Harfield, A. O. Anyia, D. Mitlin, *ACS Nano*, 2013, **7**, 5131–5141, doi: 10.1021/nn400731g.
[176] E. Raymundo-Piñero, K. Kierzek, J. Machnikowski, F. Béguin, *Carbon*, 2006, **44**, 2498-2507, doi: 10.1016/j.carbon.2006.05.022.
[177] V. C. Hoang, K. Dave, V. G. Gomes, *Nano Energy*, 2019, **66**, 104093, doi: 10.1016/j.nanoen.2019.104093.
[178] P. Cheng, T. Li, H. Yu, L. Zhi, Z. Liu, Z. Lei, *The Journal of Physical Chemistry C*, 2016, **120**, 2079-2086, doi: 10.1021/acs.jpcc.5b11280.
[179] L. Li, Q. Zhong, N. D. Kim, G. Ruan, Y. Yang, C. Gao, H. Fei, Y. Li, Y. Ji, J. M. Tour, *Carbon*, 2016, **105**, 260-267, doi: 10.1016/j.carbon.2016.04.031.
[180] Y. Li, Q. Zhang, J. Zhang, L. Jin, X. Zhao, T. Xu, *Scientific Reports*, 2015, **5**, 14155, doi: 10.1038/srep14155.
[181] P. Yadav, A. Basu, A. Suryawanshi, O. Game, S. Ogale, *Advanced Materials Interfaces*, 2016, **3**, 1600057, doi: 10.1002/admi.201600057.
[182] J. Chmiola, G. Yushin, R. Dash, Y. Gogotsi, *Journal of Power Sources*, 2006, **158**, 765-772, doi: 10.1016/j.jpowsour.2005.09.008.
[183] N. Jäckel, M. Rodner, A. Schreiber, J. Jeongwook, M. Zeiger, M. Aslan, D. Weingarth, V. Presser, *Journal of Power Sources*, 2016, **326**, 660-671, doi: 10.1016/j.jpowsour.2016.03.015.
[184] Y. Zhang, S. Liu, X. Zheng, X. Wang, Y. Xu, H. Tang, F. Kang, Q.-H. Yang, J. Luo, *Advanced Functional Materials*, 2017, **27**, 1604687, doi: 10.1002/adfm.201604687.
[185] J. Deng, T. Xiong, H. Wang, A. Zheng, Y. Wang, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 3750-3756, doi: 10.1021/acssuschemeng.6b00388.
[186] S. Herou, P. Schlee, A. B. Jorge, M. Titirici, *Current Opinion in Green and Sustainable Chemistry*, 2018, **9**, 18-24, doi: 10.1016/j.cogsc.2017.10.005.
[187] A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Science*, 2014, **344**, e1246843, doi: 10.1126/science.1246843.
[188] A. G. Pandolfo, A. F. Hollenkamp, *Journal of Power Sources*, 2006, **157**, 11-27, doi: 10.1016/j.jpowsour.2006.02.065.

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