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## Recent progress in carbon-based materials for supercapacitor electrodes: a review

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**Recent progress in carbon-based materials for supercapacitor electrodes: a review**

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**Abstract**

Increased energy consumption stimulates the development of various energy types. As a result, the storage of these different types of energy becomes a key issue. Supercapacitors, as one important energy storage device, have gained much attention and owned a wide range of applications by taking advantages of micro-size, light-weight, high-power density and long cycle life. From this perspective, numerous studies, especially on electrode materials, have been reported and great progress in the advancement in both the fundamental and applied fields of supercapacitor has been achieved. Herein, a review of recent progress in carbon materials for supercapacitor electrodes is presented. First, the two mechanisms of supercapacitors are briefly introduced. Then, research on carbon-based material electrodes for supercapacitor in recent years are summarized, including different dimensional carbon-based materials and bio-mass derived carbon materials. The characteristics and fabrication methods of these materials and their performance as capacitor electrodes are discussed. On the basis of

these materials, many supercapacitor devices have been developed. Therefore, in the third part, the supercapacitor devices based on these carbon materials are summarized. A brief overview of two types of conventional supercapacitor according to the charge storage mechanism is compiled, including their development process, the merits or withdraws, and the principle of expanding the potential range. Additionally, another fast-developed capacitor, hybrid ion capacitors (HICs) as a good compromise between battery and supercapacitor are also discussed. Finally, the future aspects and challenges on the carbon-based materials as supercapacitor electrodes are proposed.

### **Keywords**

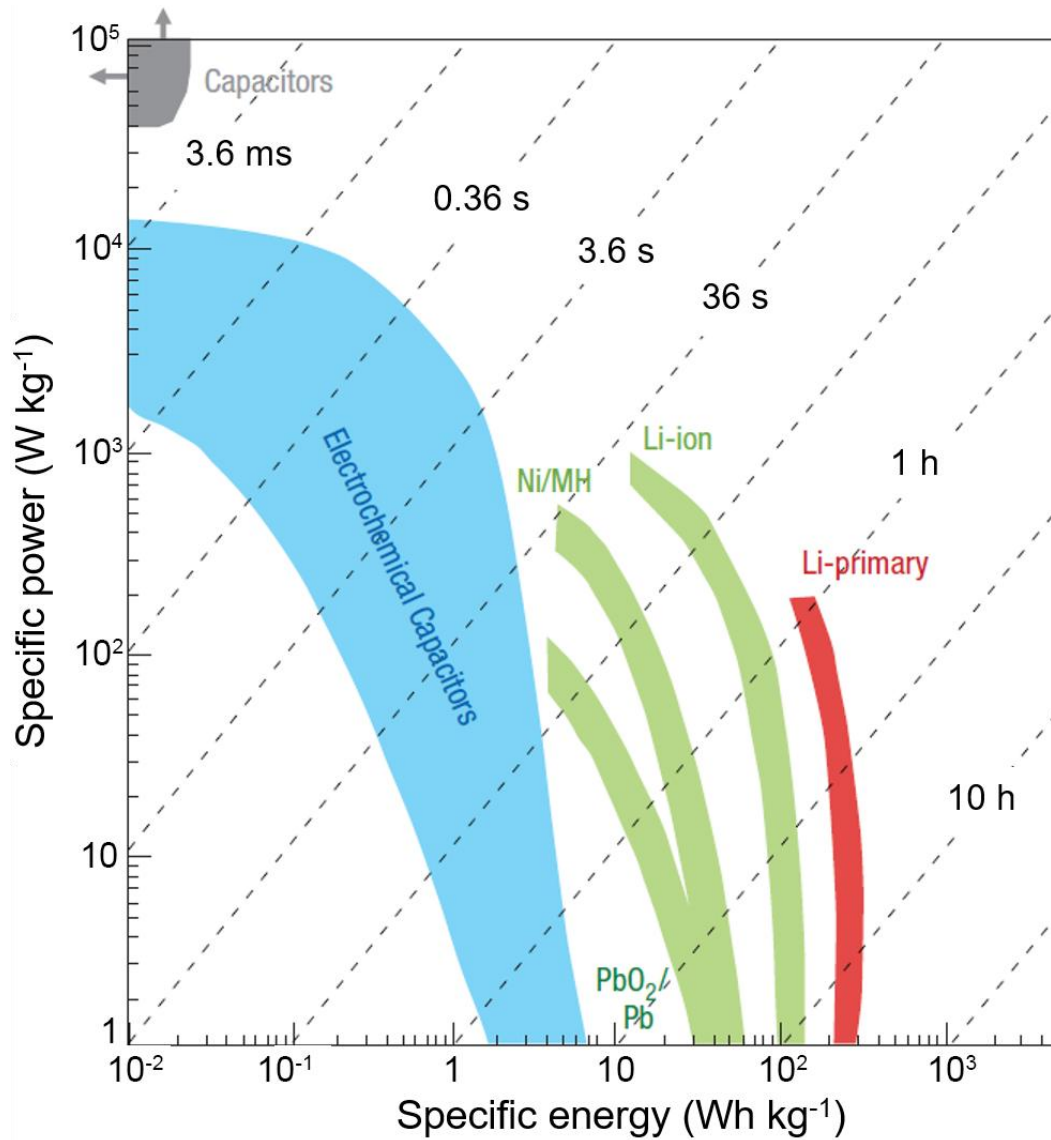
supercapacitor; energy storage; carbon-based materials; electrode

### **1. Introduction**

Increased energy consumption along with the progress in the economic development brought severe pollution which was a serious threat to human health and environment security. The paradox between the dependence on energy of human being and the combustion of fossil fuels motivates the development of utilization of various energies, such as solar energy, wind energy, tidal energy, and nuclear energy, etc. Therefore, the storage of different types of energy became a key issue [1-4]. To evaluate the most relevant storage solution, it is necessary to consider the lifetime, reliability, storage capacity, cost, and environmental impact. Implementing the efficient and economic energy storage in the power infrastructure can bring great benefits to the power industry and human beings. Energy as a state variable is typically categorized into chemical, electrical, mechanical, radiant, thermal, nuclear, or relativistic. Both short term storage (only a few hours) and long-term storage (a few months) are essential in most applications. According to the final energy, there are electric energy storage and non-electric energy storage. Electric energy storage systems accept and return the stored energy as electric power, although they may store the energy in another form. Supercapacitor and battery, as two main electric energy storage systems, have been widely applied in different fields ranging from portable electric devices to smart grid [5-7]. Compared with battery, supercapacitor possesses high-power density and long cycle life (>100,000 cycles) which ensure the fast charging/discharging speed and almost no

maintenance charge [8-10].

The comparison of specific power *v. s.* specific energy among different energy storage systems is presented in the Ragone plot (**Fig. 1**) [11]. It clearly shows that supercapacitor plays an important role in terms of high specific power and relatively high specific energy. With the advantages of micro-size and light-weight, **supercapacitor** can be used as power supplies for various portable electric devices like smart phone, notebook etc. In hybrid electric vehicles, **supercapacitor** can meet the requirements of high-power output for the short-term acceleration and high capacity for temporary energy storage equipment during braking, which save energy and avoid batteries suffering high frequency fast charge/discharge cycles [2,8]. In this case, **supercapacitor** is acting as a bridge for power/energy difference between high power output (capacitor) and high energy storage (batteries), and has the potential to play an important role in future large-scale hybrid energy systems.



**Figure 1.** Ragone plot of specific power v. s. specific energy for various energy devices [11] (©Springer Nature 2008).

Generally, energy density and power density are two important parameters to measure the performance of energy storage devices, which can be calculated by Eq. (1) and (2), respectively [8,11,12]:

$$E_d = \frac{1}{2} CV^2 \quad (1)$$

$$P_d = \frac{V^2}{4R_s} \quad (2)$$

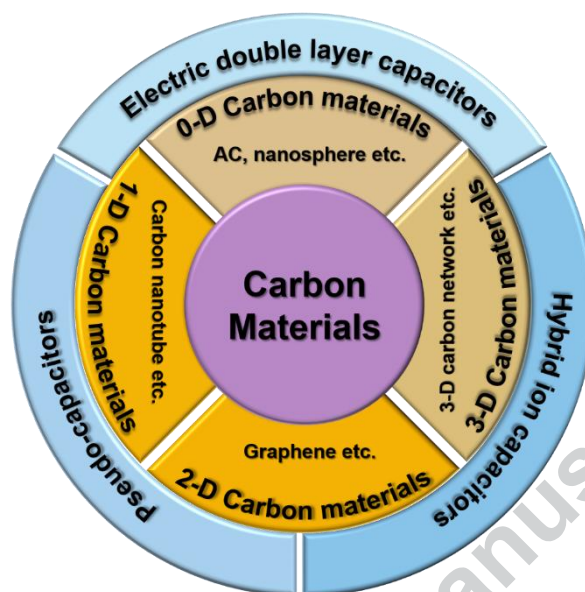
where  $E_d$  and  $P_d$  are energy density and power density, respectively,  $C$  is capacitance,  $V$  is operating voltage window, and  $R_s$  is the equivalent series resistance (ERS) of two electrodes.

According to these two equations,  $C$ ,  $V$ , and  $R_s$  are three key factors affecting  $E_d$  and  $P_d$ . In **supercapacitor**, the capacitance largely depends on the electrode material, while the voltage is influenced by both electrode and electrolyte. However, ERS has more influence factors, such as the inner resistance of electrode and electrolyte, the resistance during charge transfer, and the contact of electrode materials with collectors etc. Hence, for the best performance of supercapacitor, it must simultaneously possess a high capacitance, a high voltage and a low resistance.

Among all factors, electrode materials play the most important role in determining the performance of supercapacitor. Normally, the selection of electrode materials is based on different mechanisms of charge storage. For supercapacitor, the mechanism can be divided into two types, i.e. electric double layer capacitors (EDLCs) and pseudo-capacitors [13]. Thus, the electrode materials of supercapacitor can be categorized into three types [1,14]: (1) carbon materials, (2) conductive polymers, and (3) metal oxides/hydroxides. **Among them, carbon-based materials are the most widely studied and applied for industrialization of batteries and capacitors. Carbon-based materials have the following advantages [1,13,15]: (1) abundance, (2) relatively low-cost, (3) easy for manufacturing, (4) non-toxicity, (5) higher specific surface area, (6) good mechanical property, (7) good electronic conductivity, (8) high chemical stability, and (9) wide working temperature range.**

In the past decade, many reviews on capacitor electrode materials have been published [1,3,8,12,16]. These articles mainly reviewed the carbon-based materials on the structure design properties and applications of individual classification of carbon electrodes, such as CNTs, graphene, C/metal oxides, and so on. As the development of modern electronics, supercapacitor devices are highly demanded. Therefore, it is necessary to deeply understand and thoroughly summarize the recent progress and development of carbon-based materials for supercapacitor electrodes and devices. There are mainly three parts in this review as shown in **Fig. 2**. (i) The mechanism of two types of conventional supercapacitors; (ii) A brief introduction of recent research on carbon materials for supercapacitor electrodes, including carbon-based materials in different dimensions; and (iii) Applications of carbon-based material in supercapacitor devices in recent years. Finally, challenges and future perspectives

are provided based on the present development of carbon-based materials for supercapacitor electrodes and devices.



**Figure 2.** The overview picture of the content of the article.

## 2. Mechanism of supercapacitors

### 2.1 Electric double layer capacitors

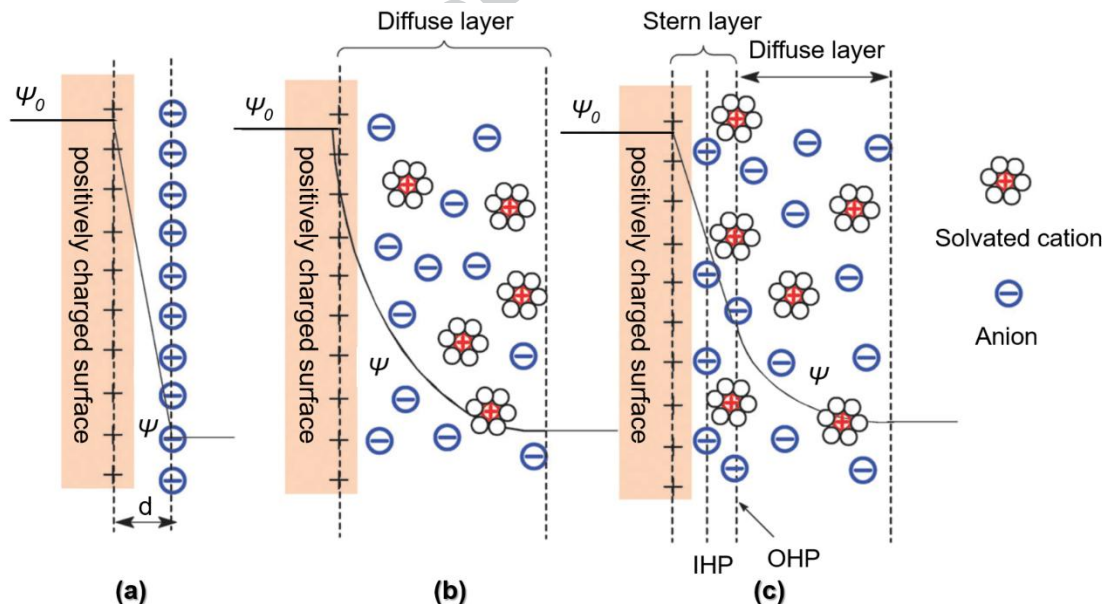
The concept and model of EDL were first built by von Helmholtz who thoroughly investigated colloidal suspension in 1853 [17]. This model described that two layers of electrically opposite charges formed at electrode/electrolyte interface and were divided in one atomic distance, which was quite similar to that of traditional capacitor. Then, this simple EDL model was modified by Gouy and Chapman [18,19]. The Gouy-Chapman model treated both cations and anions as a continuous distribution in electrolyte, which formed diffuse layer under thermal motion drive. In consideration of ions which were not rigidly attached to the surface, the amount of the distribution of opposite ionic charges in the electrolyte surrounding the charged solid was equal. The thickness of the diffuse layer was partially depended on the kinetic energy of the ions. However, this model led to an over estimation of EDL capacitance, because the capacitance that appeared along two different separated charges was inversely proportional to the distance between them, hence a huge capacitance value would be obtained when point charge ions came close to the electrode surface. Later, the Gouy-Chapman model was further modified by Stern by combining Helmholtz model with Gouy-Chapman model



[20]. He recognized two regions for charges distribution—the stern layer and the diffuse layer. In the Stern layer, charges (usually hydrated) were very strongly absorbed on the electrode, which consisted of specifically absorbed charges (SACs) and non-specifically absorbed countercharges (nSACs). While the IHP and OHP represented SACs and nSACs, respectively. The EDL models demonstrate that charges are stored at the electrode/electrolyte interface through electrostatic adsorption while no charge transfer occurs within electrode/electrolyte interfaces during charge/discharge processes. Benefiting from the physical electrostatic processes, the charge/discharge processes of EDLCs completes rapidly, which can respond to potential changes immediately. The capacitance of EDLCs electrode can be calculated by the following equation [8]:

$$C = \frac{\epsilon_r \epsilon_0}{d} A \quad (3)$$

where  $\epsilon_r$  and  $\epsilon_0$  are relative permittivity and permittivity in vacuum,  $A$  is the effective contact area between electrode and electrolyte, and  $d$  is the thickness of EDL. The development of the above three modeling mechanisms for EDL was reviewed by Zhang and Zhao, as illustrated in **Fig. 3** [8].

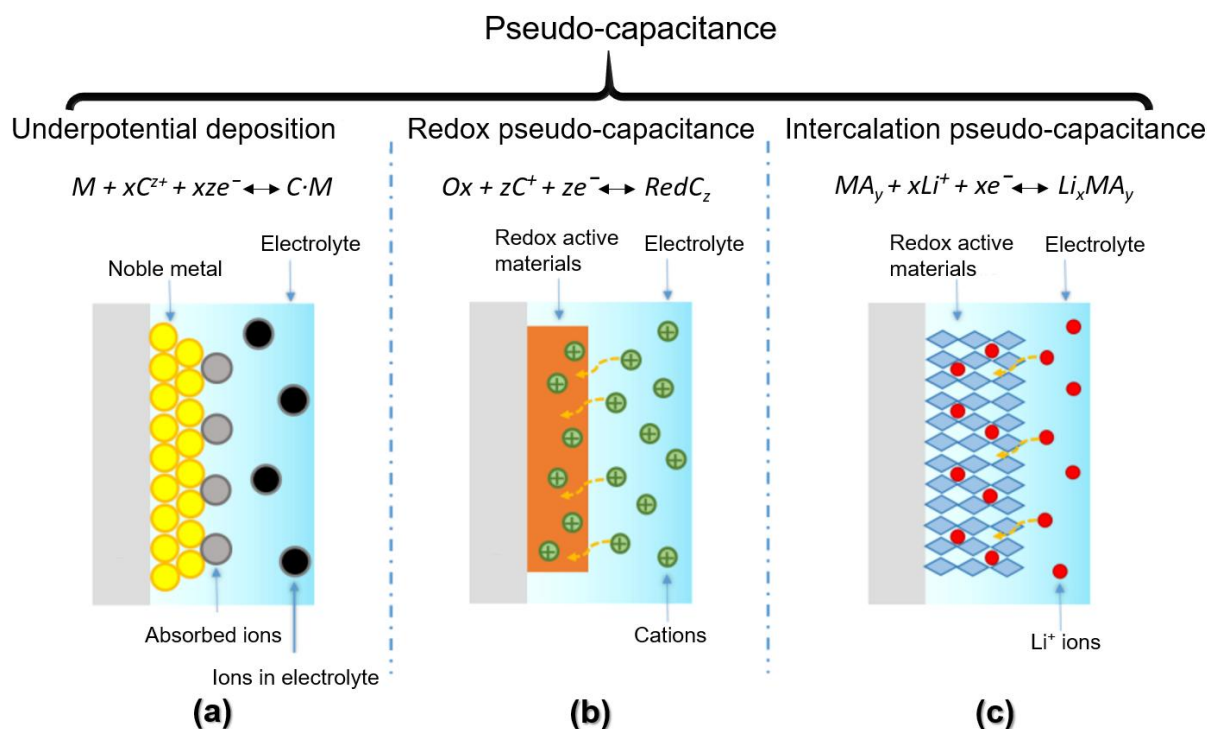


**Figure 3.** Models of EDLCs: (a) the Helmholtz model, (b) the Gouy-Chapman model, and (c) the Stern model, where  $\Psi_0$  is electrode potential,  $\Psi$  is potential at electrode/electrolyte interface,  $d$  is Helmholtz distance, IHP and OHP are abbreviation of inner and outer Helmholtz plane, respectively. [8] (©The Royal Society of Chemistry 2009).

## 2.2 Pseudo-capacitors

In contrast to EDL, pseudo-capacitance is driven by the thermodynamic factor and attributed to charges acceptance ( $\Delta q$ ) and changes in potential ( $\Delta U$ ) [8]. The main electrochemical signature is that pseudo-capacitors electrode materials has Faraday process, i.e., redox reaction, during the charge/discharge processes, which means valence state changes with charge/discharge processes [21,22].

The mechanisms of charge storage in pseudo-capacitors are illustrated in **Fig. 4** [23]. Under potential deposition is a process in which the atoms are adsorbed on noble metals with an electrodeposition potential less negative than that of equilibrium potential for cation reduction. Redox pseudo-capacitance arises from redox reactions. These reactions are accompanied by cations being adsorbed on the surface of the electrode material, resulting in reversible and rapid charge transfer at the electrolyte/electrode interface [11]. Pseudo-capacitance can also deliver from cations insertion/extraction in tunnels or layers of crystalline materials. The crystal can remain electrically neutral during insertion/extraction. In some way, the intercalation pseudo-capacitance can be considered as “transitional” behavior between Li-ion battery and supercapacitor [24]. The pseudo-capacitance electrode can perform a very higher capacitance than EDL electrodes do, however, they suffer from poor electrical conductivity and cycling stability.



**Figure 4.** Schematics of charge storage in pseudo-capacitors: (a) underpotential deposition, (b) redox reactions, (c) ion insertion/extraction [23] (©American Chemical Society 2018).

### 3. Carbon materials

Carbon materials come from a wide range of sources. Variety of natural materials, such as coal, crude oil, or biomass, can be used as precursor of carbon-based materials. When they come to nanoscale, their properties change greatly. With regard to carbon materials, different dimensions of carbon nanostructure give carbon-based materials different properties, such as light, heat, and electricity etc. Therefore, this section will be discussed according to various carbon nanostructures with different dimensions.

#### 3.1 Zero-dimensional carbon material

Zero-dimensional (0-D) carbon materials refer to sphere-shaped carbon particles with an aspect ratio of  $\sim 1$ . 0-D carbon materials mainly include activated carbon (AC), carbon nanosphere, and **mesoporous** carbon. 0-D carbon materials possess a very large specific surface area (hundreds to thousands  $\text{m}^2 \text{g}^{-1}$ ) with tunable pore size and distribution, which are critical factors that govern the performance of supercapacitor.

An ideal pore structure should have the feature of hierarchical pore structure, which contains **macropores** ( $>50 \text{ nm}$ ) for infiltration of electrolyte, **mesopores** ( $2\text{--}50 \text{ nm}$ ) as the

place for ion transport, and micropores (<2 nm) for charge storage [25]. Migration of ions in micropores depends on the size of the solvated molecules and pore diameter [26]. In other words, when the size of the solvent molecules and solvated ions is smaller than the pore size, it is difficult for ions to break the energy barrier and access to the pores [27]. Hence, although the increase of micropores can increase the specific surface area, it does not necessarily contribute to the increase of specific capacitance ( $C_s$ ). On the contrary, mesoporous is more conducive to the rapid transfer of ions, resulting in the improvement of electrochemical properties [28,29]. In addition, the pore size distribution is another thing needed to be taken into account. Pore structure with a narrow distribution can reduce the ion transport length, which improves the electrode kinetics [25]. Thus, the optimal performance is based on a reasonable pore size and distribution.

Normally, 0-D carbon materials are produced from carbon-rich precursors by either physical (thermal) activation at high temperature (700-1200 °C) with H<sub>2</sub>O, CO<sub>2</sub> and air, or chemical activation with a lower temperature (600-800 °C) with H<sub>3</sub>PO<sub>4</sub>, KOH, ZnCl<sub>2</sub> etc. [30]. Previous reports showed that AC employed as electrode exhibited specific capacitance of 100-300 F g<sup>-1</sup> [31-35]. In addition, carbon nanosphere can be synthesized by the template method or the hydrothermal method. Yang *et al.* [36] prepared carbon nanosphere by using F108 (PEO<sub>132</sub>-PPO<sub>50</sub>-PEO<sub>132</sub>) as the structure direct agent. **After carbonization and KOH activation, the products presented the highest specific capacitance of ~147 F g<sup>-1</sup> in 6 M KOH electrolytes and 97.5% capacitance retention over 10000 cycles.** Li *et al.* [37] fabricated carbon nanospheres by hydrothermal method with the highest specific capacitance of 207 F g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte, and high rate capability (181 F g<sup>-1</sup> at a current density of 10 A g<sup>-1</sup>). Moreover, a series of studies have reported the preparations of carbon microspheres from glucose or glucose derivatives as supercapacitor electrodes. These microspheres have a specific capacitance of 200-400 F g<sup>-1</sup> in aqueous electrolyte [38-41].

### 3.2 One-dimensional carbon material

**0-D carbon nanoparticles, especially AC, have been widely used as electrode materials, where electrons are delivered either via hopping through trap states of adjacent nanoparticles**

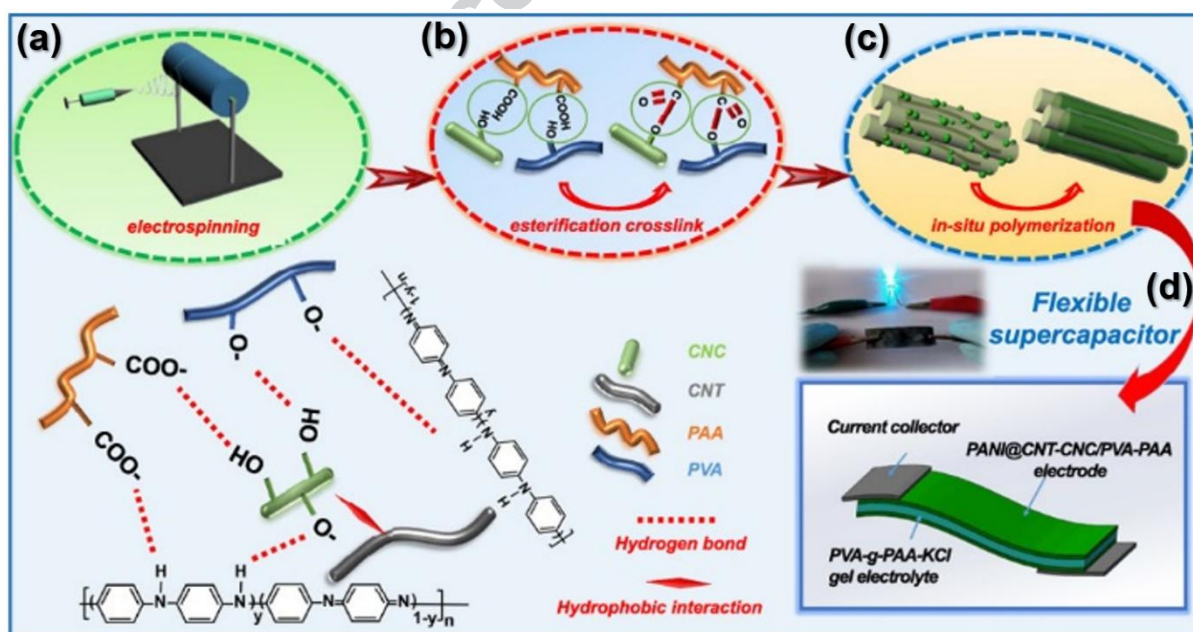
or via diffusive movement within the extended states, which is slowed by the (de)trapping processes [42-44]. The limited continuity among carbon nanoparticles is not beneficial to the improvement of electrical conductivity, so as to reduce the power density. Compared with 0-D carbon nanoparticles, one-dimensional (1-D) carbon materials are promising candidates for supercapacitor electrodes due to their long 1-D nanostructure, which helps forming a consecutive network for the charge transport [12].

Carbon nanotubes (CNTs), the most typical 1-D carbon material, exhibited a much higher conductivity than AC. CNTs can be categorized to single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) and can be produced by arc-discharge method, chemical vapor deposition (CVD), pyrolysis of hydrocarbons, and pulsed laser vaporization [3,13,45]. Since its discovery, CNTs have received great attention for their potential applications in energy storage [46,47]. Previous research reported that pure CNTs possessed specific capacitance in a range of 20-100 F g<sup>-1</sup> in aqueous electrolyte [48-52]. The limited capacitance may be ascribed to the hydrophobic property and the limited specific surface area. After surface treatment by acid or base, the specific capacitance of CNTs still remains around 100 F g<sup>-1</sup> [3]. In addition, it was proved that entangled CNTs did not perform as well as aligned CNTs in fast ions transfer, due to the irregular porosity and the high entanglement [53].

Carbon nanofibers (CNFs) are another typical 1-D carbon material which can be prepared by chemical vapor methods [54-57] or simple electro-spun technology [58-61]. Like other carbon materials, the pore size distribution and pore volume of CNFs can be activated by physical or chemical methods [59,62-65]. Recently, a large number of researches on CNFs as electrode materials by the electrospinning technology have been reported. Jiang *et al.* [66] prepared a CNF electrode followed by ZnCl<sub>2</sub> activation. The as-prepared CNFs material exhibited the highest specific capacitance of 214 F g<sup>-1</sup> at 1.0 A g<sup>-1</sup> in acidic electrolyte and showed excellent cycling stability in alkaline electrolyte (97.3% after 60,000 cycles). Liu *et al.* [67] developed a facile and green method for the preparation of CNF from the perylene diimide derivative. This CNF showed a specific capacitance of 192 F g<sup>-1</sup> at the current density of 1 A g<sup>-1</sup> in 2 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Interestingly, the specific capacitance increased

with the cycling test, reaching  $226 \text{ F g}^{-1}$  after 1000 cycles at  $4 \text{ A g}^{-1}$ .

In nature, a lot of fibrous biomass, including cotton, flax, ramie, wood, have been utilized as precursors for the preparation of 1-D carbon electrodes. Cellulose is the most basic component of these biomass [68]. Due to abundant carbon reserve, rich active chemical groups, excellent mechanical property, and high specific surface area, cellulose becomes currently the most widely studied and used fiber-like material in energy storage systems [16,69-71]. So far, a series of research on cellulose-derived CNFs as electrode materials have been reported. These CNFs were obtained by electrospinning technology and owned a specific capacitance in a range of  $150\text{--}280 \text{ F g}^{-1}$  in aqueous electrolyte [72-77]. Also, Han *et al.* [78] used cellulose nanocrystals (CNCs) to develop a nanofiber composite by combining electrospinning technology and in-situ polymerization. **Fig. 5** illustrates the synthesise routine of this composite. By taking advantage of intermolecular esterification cross-linking, the composite membrane presented excellent mechanical strength, and thermal stability. **The supercapacitor assembled by as-prepared materials showed a specific capacitance of  $155.5 \text{ F g}^{-1}$  in  $2 \text{ M H}_2\text{SO}_4$  electrolyte and a high capacitance retention of 92, 90, and 89% after long-life cycles under flat, bending, and twisting form, respectively.**

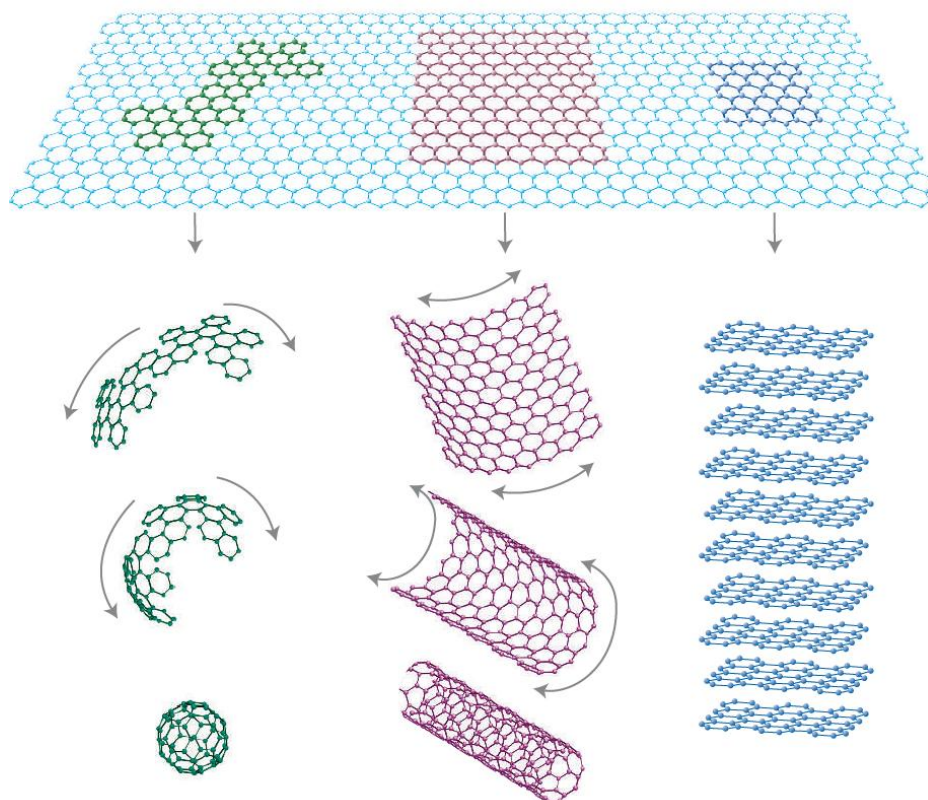


**Figure 5.** Schematic diagram of the preparation process of nano-cellulose membrane with core-shell structure. (a) nano-cellulose membrane was prepared by electrospinning from

PVA/PAA/CNTs/CNC solution. (b) the membrane was thermally cross-linked to form ester bonds. (c) the core-shell structure was constructed by in-situ polymerization of aniline. (d) the core-shell membrane was used as flexible electrode for the assembly of device to lighten a LED) [78] (©American Chemical Society 2019).

### 3.3 Two-dimensional carbon material

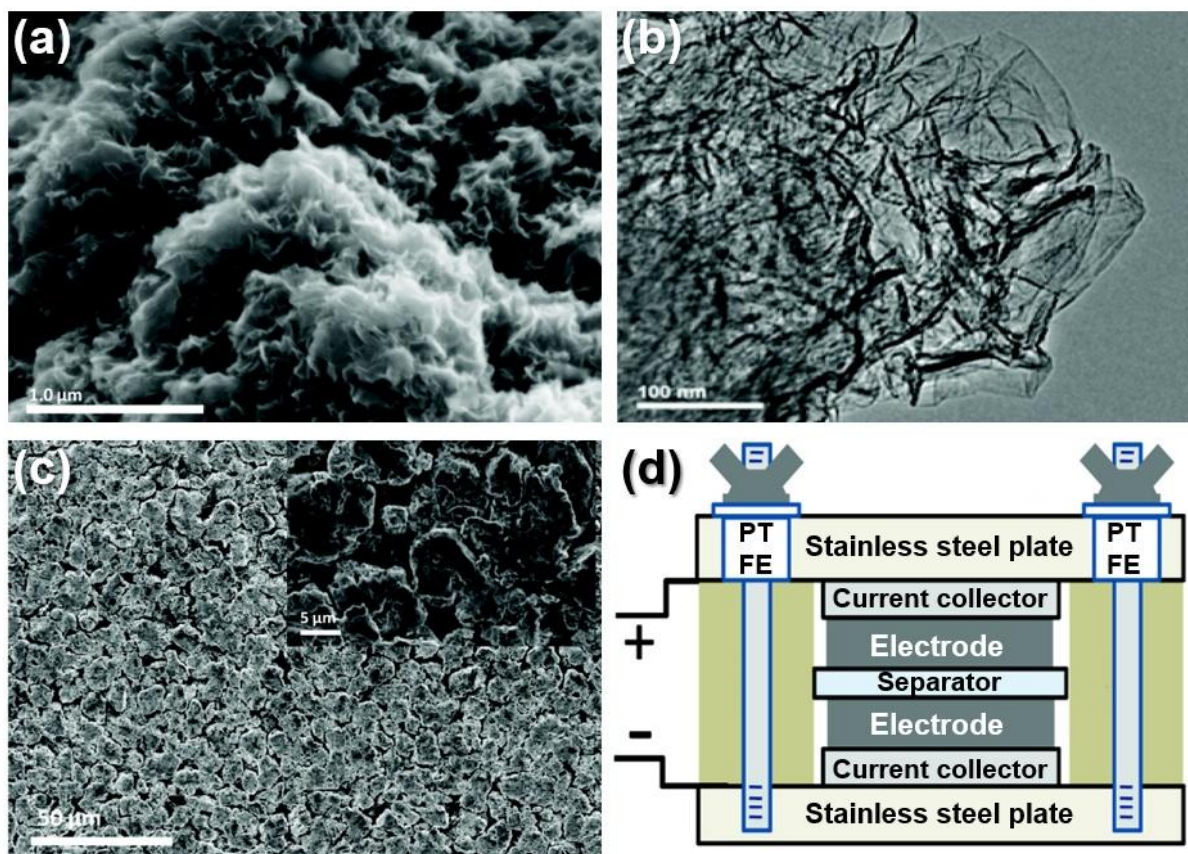
**Graphene**, a typical two-dimensional (2-D) carbon material, is a one-atom-thick 2-D mono layer consisted of sp<sup>2</sup>-hybrid carbon. As shown in **Fig. 6**, graphene is considered as the basic constituent material of carbon materials in other dimensions which can be twisted into 0-D carbon nanocages (fullerenes), rolled into 1-D carbon nanotubes or stacked into three-dimensional (3-D) graphite [79]. Owing to this unique structural feature, graphene owns a series of intrinsic virtues in both chemical and physical aspects, such as strong mechanical strength ( $\sim 1$  TPa), excellent mass and heat transfer capability, extremely high light transmittance ( $\sim 97\%$ ) and large surface area ( $2675 \text{ m}^2 \text{ g}^{-1}$ ), which may match or even exceed that of single-walled or multi-walled carbon nanotubes [80]. Several approaches have been utilized to prepare graphene, including CVD, mechanical stripping, solvent spalling, and reduction of graphene oxide (GO) [80,81].



**Figure. 6** Diagram of graphene as the basic structure for all other dimensional carbon material [79] (©Springer Nature 2007).

Excellent electric conductivity ensures that graphene can be used in energy storage devices [81]. Ruoff's group [82] first explored graphene-based supercapacitor system utilizing chemically modified graphene. As shown in **Fig. 7**, although GO sheets could disperse in water evenly, the graphene agglomerated into particles with a size of approximately 15-25  $\mu\text{m}$  in diameter during reduction progress. **Due to the relatively high specific surface area, the graphene electrode still remained a specific capacitance of 135 F g<sup>-1</sup> in KOH electrolyte.** However, the aggregation of GO sheets is irreversible [83]. Thus, improving the dispersion of GO sheets in solution is the key issue to convert GO sheets to graphene sheets by solution reduction method. To avoid severe stacking of GO sheets, **Chen's group [84] prepared graphene sheets by gas-based hydrazine reduction. A maximum specific capacitance of 205 F g<sup>-1</sup> in aqueous electrolyte was obtained.**





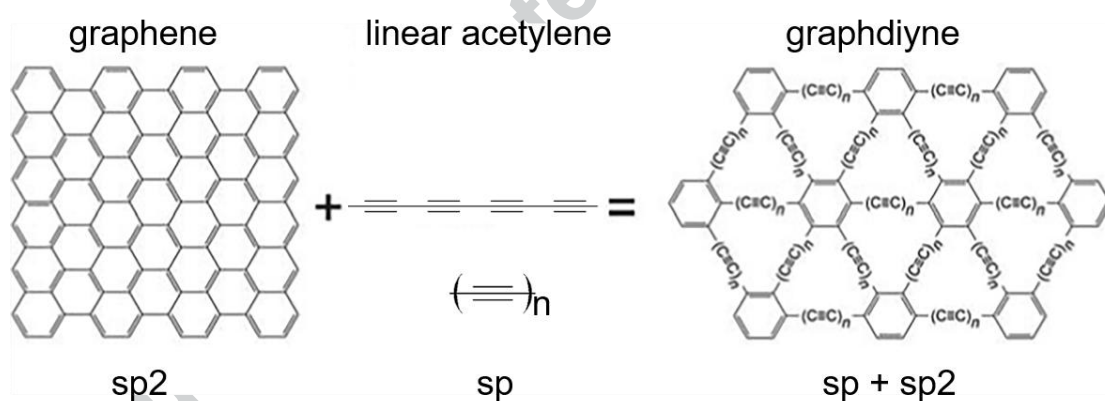
**Figure 7.** SEM (a) and TEM (b) images of individual graphene particle, respectively, (c) SEM image of graphene electrode, and (d) scheme of graphene-based supercapacitor [82] (©The American Chemical Society 2008).

The dispersion of GO sheets is not the only factor which affects the performance of supercapacitor based on graphene. The interlayer distance of graphene is another factor which has influence on the performance of supercapacitor. Lin *et al.* [85] prepared the interlayer distance-enlarged graphene by intercalation of hexadecyl trimethyl ammonium bromide and ionic liquids. It was found that the interlayer distance increased from 0.41 nm to 2.51 nm, resulting in the improvement of specific capacitance (43 to 141 F g<sup>-1</sup>). In addition, Romano *et al.* [86] developed a wet-jet milling (WJM) method to peel single/few layered graphene from graphite, possessing an industrial-scaled production rate (0.5 kg/Day).

Recently, Taniya *et al.* [87] prepared few-layered graphene by carbonizing peanut shell and activating with KOH. **The as-prepared carbon nanosheets owned a high specific surface area of 2070 m<sup>2</sup> g<sup>-1</sup> and a high specific capacitance of 186 F g<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte.** Gao *et al.* [88] prepared two different types of 2-D carbon nanosheets from cornstalk by

simple carbonization. The cornstalk pith derived- and cornstalk skin derived- nanosheets were named as P-carbon and S-carbon, respectively. It was found that P-carbon possessed a graphene-like nanosheets structure, while S-carbon showed a thicker planar morphology. The pore size distribution demonstrated that mesopores of P-carbon and S-carbon were concentrated on 2.12 and 12.24 nm, respectively. Thus, P-carbon exhibited a better specific surface area (805.17 to 332.07 m<sup>2</sup> g<sup>-1</sup>) and a superior specific capacitance (116 to 69 F g<sup>-1</sup> in 6 M KOH electrolyte).

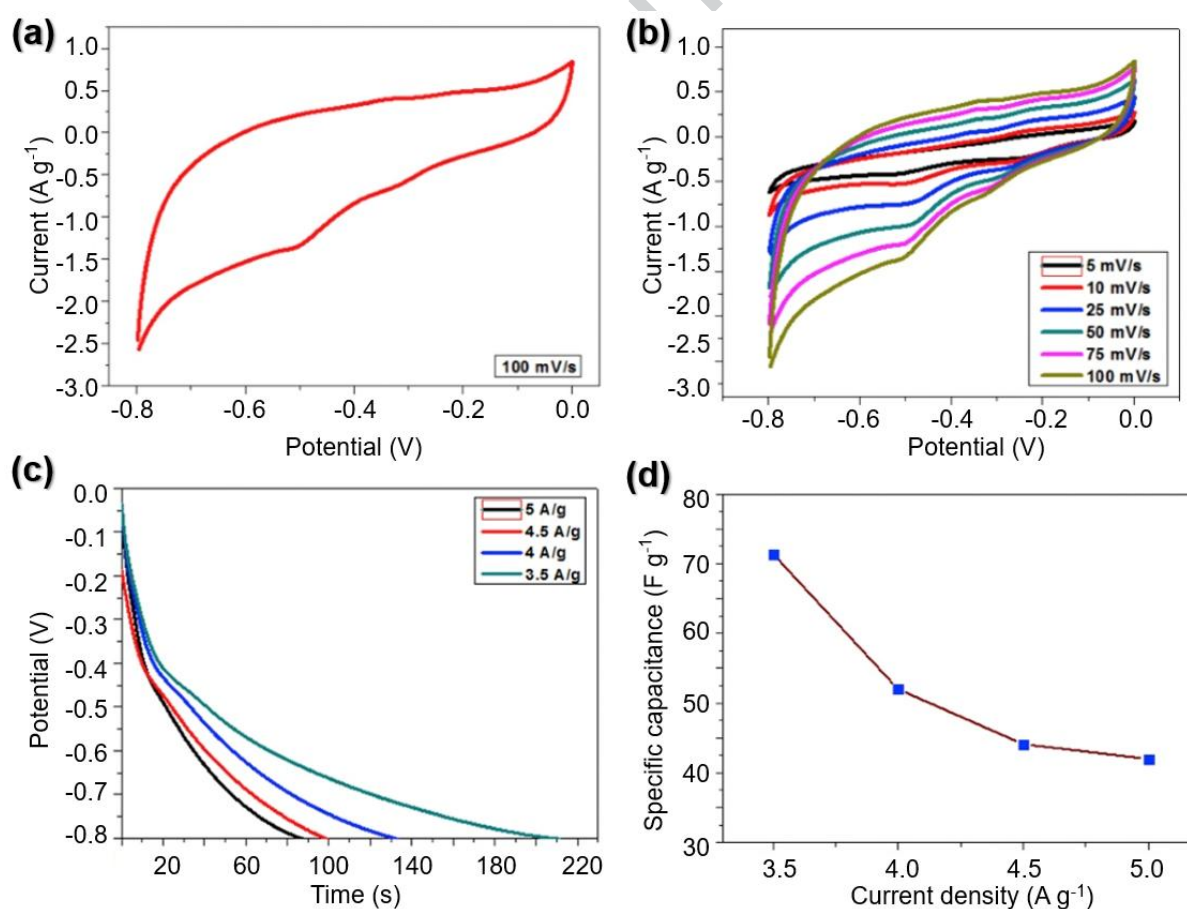
It is worth noting that **graphdiyne** (GDY) is a series of brand new 2-D carbon materials formed by the connection of sp and sp<sup>2</sup> hybrid carbon (**Fig. 8**) [89]. The existence of sp hybrid carbon gives graphene a completely different structure from other carbon materials, resulting in totally different properties. **For example, sp and sp<sup>2</sup> hybrid carbon enable GDY to exhibit high chemical activity and stable physical properties.** Under external stimulation, the activity of c-c triple bond may expand the chemical properties of carbon materials (light, magnet, and electricity).



**Figure 8.** Illustration of graphene to graphdiyne: aromatic groups linked by linear acetylene. (graphdiyne contains both sp and sp<sup>2</sup> hybrid carbon) [89] (©The Royal Society of Chemistry 2012).

Moreover, enriched  $\pi$ -conjugated systems bring good theoretical conductivity and fast charge transfer [90]. These features guarantee GDY has the potential to be applied in better fabrication for high-performance electronic devices. The typical synthesis routines of GDY can be divided into dry chemical method and wet chemical method [91]. Kim and co-workers [92] first studied supercapacitors with the use of GDY as electrode. **The GDY electrodes**

delivered a specific capacitance of  $71.4 \text{ F g}^{-1}$  at a current density of  $3.5 \text{ A g}^{-1}$  in  $\text{Na}_2\text{SO}_4$  electrolyte. The shapes of CV curves suggested that both EDLC and faradaic reactions contributed to the overall capacitance (**Fig. 9**). Li's group also studied GDY-based supercapacitor systems. GDY with various N content were obtained through the reaction between different precursors with tetrabutylammonium fluoride [93]. Interestingly, the sample without N-doping delivered a maximum specific capacitance of  $250 \text{ F g}^{-1}$  in  $7 \text{ M KOH}$  electrolyte. XPS spectrum implied that the existence of N element increased the band gap of GDY and indicated that the N-doping strategy was effective to tune the band gap for the on-demand requirements, which may widely extend the application of GDY. In the following work, Li's group [94] first developed a moderate and superfast method for the growth of ultrafine GDY nanochain on arbitrary substrates. The as-prepared GDY electrode was applied as the self-standing electrode with high areal capacitance of  $134.2 \text{ F g}^{-1}$  in  $7 \text{ M KOH}$  electrolyte and robust cycle stability.



**Figure 9.** (a) CV curve of graphdiyne electrode at 100 mV/s, (b) CV curves of graphdiyne

electrode at different scan rate, (c) discharge curves at different current density, (d) rate capacitance of graphdiyne electrode [92] (©Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. 2015)

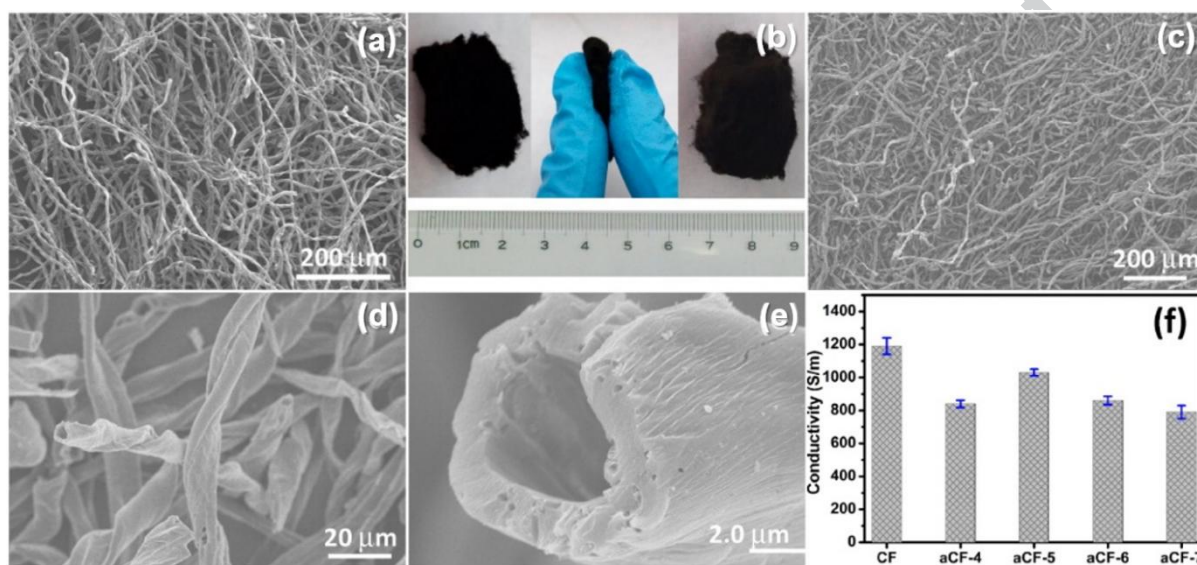
### 3.4 Three-dimensional carbon material

As we know, microstructures of electrode materials play an important role in performances of energy storage systems [95-98]. With increasing in dimensionality, more percentage of active surface are contacted with electrolyte, which will efficiently improve electrochemical properties of electrode materials. From this point of view, three-dimensional (3-D) structure with well-interconnected pores not only offers continuous channels to guarantee good contact with electrolyte, but also accelerates the charge transfer by reducing the diffusion pathways [16,98-102].

Usually, 3-D carbon materials are grown on a flexible substrate such as metal-foam or polymer substrate by CVD, hydrothermal method, or template method [103-105]. Despite substrate can offer the electrode mechanical property that gives electrode self-standing ability, the use of substrates especially metal-foam increases the weight of devices, which hinders the improvement in the gravimetric specific energy and gravimetric specific power. Thus, 3-D carbon nanostructures without substrates are promising candidates for high performance supercapacitor. Ciszewski *et al.* [106] prepared resorcinol-formaldehyde-based carbon aerogels and modified with graphene, GO and CNT, respectively. It demonstrated that the introduction of graphene-like structured mass within traditional carbon aerogel greatly enhanced specific capacitance. The specific capacitance of CNT-, graphene- and GO-modified aerogel was 326, 227, and 244 F g<sup>-1</sup>, respectively in 6 M KOH electrolyte. Wang *et al.* [107] prepared N, O-rich carbon aerogel from polyimide gel after carbonization and activation. As a result, the sample exhibited a high capacitance of 386 F g<sup>-1</sup> at 1 A g<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Furthermore, the sample delivered an outstanding rate capacitance, the capacitance could remain 150 F g<sup>-1</sup> at 100 A g<sup>-1</sup>.

Compared to previous 3-D carbon nanostructured materials, biomass has obvious advantages in preparing 3-D carbon materials, which benefits from preservation of the original structure of biomass after carbonization [108,109]. For example, Lei's group [110]

prepared a flexible carbon fiber aerogel (CFA) by simply carbonizing and activating natural cotton with KOH. The CFA presented an interleaved network structure with high conductivity (**Fig. 10**). The specific surface area was various with the amount of KOH, which was in a range of 1536 to 2436  $\text{m}^2 \text{g}^{-1}$ . Due to the distinct structural advantage of CFA electrode, it exhibited a specific capacitance of  $283 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  in 6 M KOH electrolyte and possessed a high capacitance retention of  $\sim 80\%$  ( $224 \text{ F g}^{-1}$ ) when the current density up to  $100 \text{ A g}^{-1}$ .



**Figure 10.** (a) SEM image of CFA, (b) Photograph of CFA after activation, (c-e) SEM images of CFA after activation with different magnifications, (f) conductivity of CFA activated with different KOH ratio [110] (©American Chemical Society 2016).

## 4. Supercapacitor

Supercapacitor can be categorized to EDLCs or pseudo-capacitors due to the mechanism or can be divided into symmetric or asymmetric supercapacitor according to the electrochemical activity of electrode materials. To evaluate the performance of electrode materials, it is not sufficient to test the electrode. It is necessary to assemble devices with these electrode materials. In this section, we will briefly summarize the application of carbon materials in devices based on the capacitor mechanism in recent years.

### 4.1 Conventional supercapacitor

#### 4.1.1 Electric double layer capacitors

Although the mechanism of the EDL was recognized since the beginning of 20th

century, the first patent for electrochemical capacitors was not applied until 1954 [111]. It described an EDLC device containing two porous carbon electrodes immersed in  $\text{NH}_4\text{Cl}$  or  $\text{H}_2\text{SO}_4$  electrolyte. The device delivered a capacitance of 6 F at 1.5 V. After that, an EDLC device with multi cell units was developed by Rightmire at Standard Oil Company of Ohio (SOHIO) [112]. The device performed a storage capacity of 4-10 Wh per pound and could be charged to 6 V. SOHIO did not commercialize their invention, but licensed the technology to NEC, who finally marketed it to provide backup power for clock chips or CMOS. With the rapid increase in market demand, more and more studies on EDLCs have been reported. Some researches on aqueous/non-aqueous EDLCs in recent years are listed in **Table 1**.

**Table 1.** A brief overview of EDLC devices in aqueous/non-aqueous electrolyte in recent years

Electrode	Electrolyte	Voltage/V	Specific capacitance/F g <sup>-1</sup>	Cycle life	Ref.
AC//AC	6 M KOH	0.9	66.8 at 0.1A g <sup>-1</sup>	93% after 1000 cycles	[113]
	2 M KCl	0.9	62.1 at 0.1A g <sup>-1</sup>	94% after 1000 cycles	
AC//AC	0.5 M K <sub>2</sub> SO <sub>4</sub>	1.7	42.8 at 0.1A g <sup>-1</sup>	96% after 1000 cycles	[114]
	1.5 M Na <sub>2</sub> SO <sub>4</sub>	1.0	93.1 at 0.005 A g <sup>-1</sup>	–	
AC//AC	1 M Na <sub>2</sub> SO <sub>4</sub>	0.6	113 at 0.3 A g <sup>-1</sup>	100% after 5000 cycles	[115]
S-CB//S-CB	6 M KOH	1.0	120 at 1 A g <sup>-1</sup>	92.6% after 10000 cycles	[116]
CNT-MC//CNT-MC	3 M H <sub>2</sub> SO <sub>4</sub>	0.8	237 at 1 A g <sup>-1</sup>	92% after 20000 cycles	[117]
CNF//CNF	1 M Na <sub>2</sub> SO <sub>4</sub>	0.8	69.3 at 50 mV s <sup>-1</sup>	2000 cycles	[118]
	6 M KOH	0.8	88.1 at 50 mV s <sup>-1</sup>	2000 cycles	
GnP//GnP	1 M Na <sub>2</sub> SO <sub>4</sub>	1.0	92 at 0.1 A g <sup>-1</sup>	–	[119]
	1 M Et <sub>4</sub> NBF <sub>4</sub>	2.0	76 at 0.1 A g <sup>-1</sup>	–	
CMK-3//CMK-3	NaClO <sub>4</sub> in EC/DMC (1:1 vol/vol)	3.0	78 at 0.2 A g <sup>-1</sup>	–	[120]
CMK-8//CMK-8		3.0	66 at 0.2 A g <sup>-1</sup>	–	

It can be seen that both the aqueous and non-aqueous EDLCs are limited by the specific capacitance of the device, which is ascribed to the inherent properties of the pure carbon materials. Also, due to the finite conductivity and incomplete utilization of active sites, the specific capacitance of EDLCs has generally been limited to 100-250 F g<sup>-1</sup> [121]. In case of aqueous EDLCs, the operating voltage (~1 V) is another critical factor which affects the performance of devices. The decomposition of H<sub>2</sub>O is 1.23 V, which greatly hinders the performance of aqueous EDLCs [122]. In addition, non-aqueous EDLCs performs a slightly less specific capacitance than aqueous EDLCs because the molecular size of organic electrolytes is larger than aqueous electrolytes. Previous studies implied that the pore size of 0.4-0.7 nm was adequate to aqueous electrolytes, while the pore size of 0.8 nm was suitable for organic electrolytes [123,124]. As a result, the commercial EDLCs electrodes can only reach an  $E_d$  in a range of 3–10 Wh kg<sup>-1</sup>.

#### 4.1.2 Pseudo-capacitors

The first material found to exhibit pseudo-capacitance is RuO<sub>2</sub> [125]. Despite the faradaic nature of the charge storage in RuO<sub>2</sub> thin film, the cycle voltammogram of RuO<sub>2</sub> showed a rectangular-like shape, which demonstrated a typical capacitive behavior. Subsequent study improved the capacitance of RuO<sub>2</sub> over 700 F g<sup>-1</sup> by preparing hydrous RuO<sub>2</sub> with porous nanoscale structure [126,127]. Although the high-cost was a barrier to the application of RuO<sub>2</sub>, the discovery of pseudo-capacitance expanded the approach to enhance the capacitance of electrode materials.

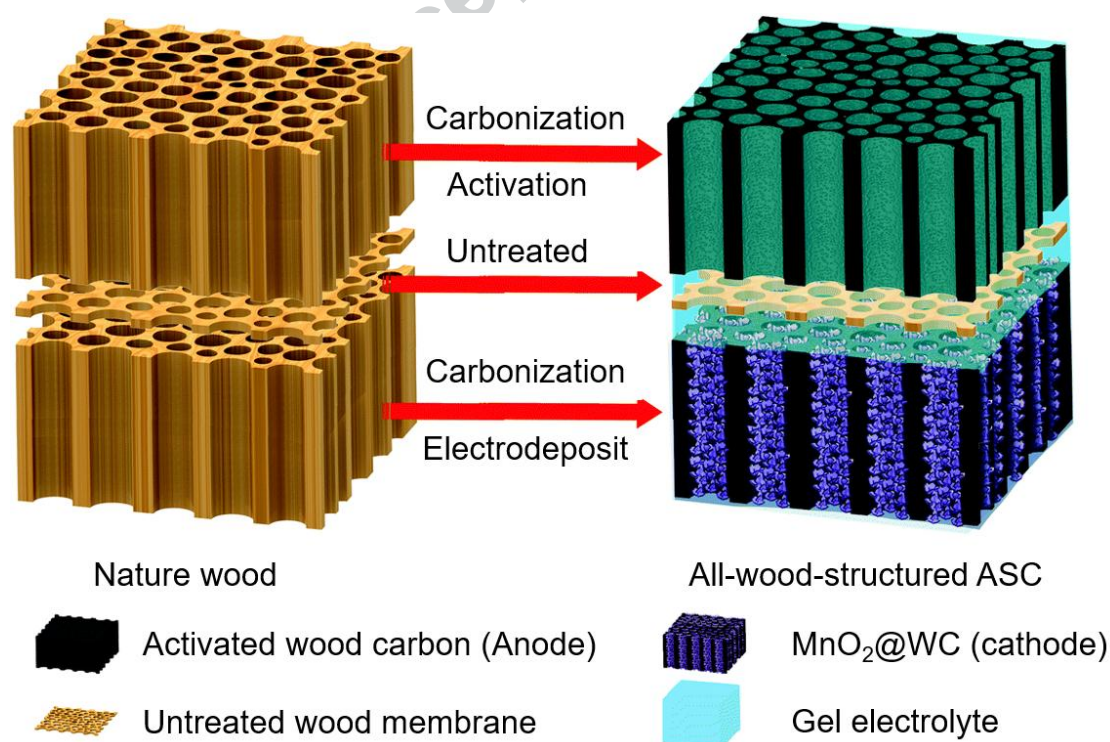
Typically, heteroatoms-doping is one of the most common way to introduce pseudo-capacitance to enlarge the charge capability of carbon material. It has been proved that mono, dual or multi heteroatom-doping (N, B, S, F, Cl, Si, Ti, etc.) could improve the electrochemical activity because it opened the intrinsic band gap and offered more active sites [128]. Usually, heteroatom-doped carbon materials can be synthesized in a variety of ways, such as CVD [129], pyrolysis with hetero precursor [130-132], self-doping [133-136] etc. These as-prepared electrode materials exhibited a specific capacitance of 150-500 F g<sup>-1</sup> in aqueous/organic electrolyte. However, these methods either have complex production processes, or utilize petroleum products as raw materials, which limits the industrial



production. To avoid these problems, it is a wise choice to use heteroatom-rich biomass or biomass waste as raw material. Recently, Jiang *et al.* [137] prepared N-doped porous carbon materials (NPCMs) using the wheat straw by carbonization and activation with KCl/ZnCl<sub>2</sub>. The NPCMs delivered an excellent specific capacitance of ~224 F g<sup>-1</sup> in 6 M KOH electrolyte and an outstanding cycle stability (capacitance maintained 91.6% after 10000 cycles). Cai *et al.* [138] reported the synthesis of N-doped carbons from *enteromorpha prolifera* by hydrothermal carbonization. After optimizing parameters, the as-prepared N-doped carbon achieved a specific capacitance of 200 F g<sup>-1</sup> at 1 A g<sup>-1</sup> in 6 M KOH electrolyte. The symmetric device showed a good cycle stability (capacitance retention of 96% after 10000 cycles at 10 A g<sup>-1</sup>).

Hybridizing with metal oxide/metal hydroxide is another important way to increase the specific capacitance of electrode materials. Many studies on carbon metal oxide/metal hydroxide composites have been reported, such as C/MnO<sub>2</sub> [139,140], C/Co<sub>3</sub>O<sub>4</sub> [141-143], C/CoOOH [144] etc. MnO<sub>2</sub> has been considered as the most promising candidate for electrode materials due to low cost and easy manufacturing. C/MnO<sub>2</sub> composite can be easily prepared by redox reaction between carbon and KMnO<sub>4</sub> [145,146], electrodeposition [147,148], template method [149] etc. Since the early report by Lee and Goodenough in 1999 [150], C/MnO<sub>2</sub> has attracted widespread concern and large number of research on C/MnO<sub>2</sub> for supercapacitor electrode has been reported, including mesoporous carbon/MnO<sub>2</sub> [151], CNT/MnO<sub>2</sub> [152,153], graphene/MnO<sub>2</sub> [154,155], CNF/MnO<sub>2</sub> [156,157] etc. These composites delivered a specific capacitance in a range of 270-642 F g<sup>-1</sup> with a long cycle life. Besides, biomass can also be good host for preparing C/MnO<sub>2</sub> electrode in aqueous electrolyte. He *et al.* [158] prepared a self-standing C/MnO<sub>2</sub> electrode by flax-derived carbon cloth reacted with KMnO<sub>4</sub>. The specific capacitance of electrode (in terms of MnO<sub>2</sub>) reached 684 F g<sup>-1</sup> at 2 A g<sup>-1</sup> and still retained 269 F g<sup>-1</sup> at 300 A g<sup>-1</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte, indicating the outstanding electrochemical performance of the carbon cloth/MnO<sub>2</sub>. Hu' group [159] developed wood-derived carbon/MnO<sub>2</sub> (MnO<sub>2</sub>/WC) electrode by electrodeposition (**Fig. 11**). MnO<sub>2</sub>/WC electrode performed a maximum specific capacitance of 176.8 F g<sup>-1</sup> (calculated based on the mass of MnO<sub>2</sub>) in 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. When assembled in

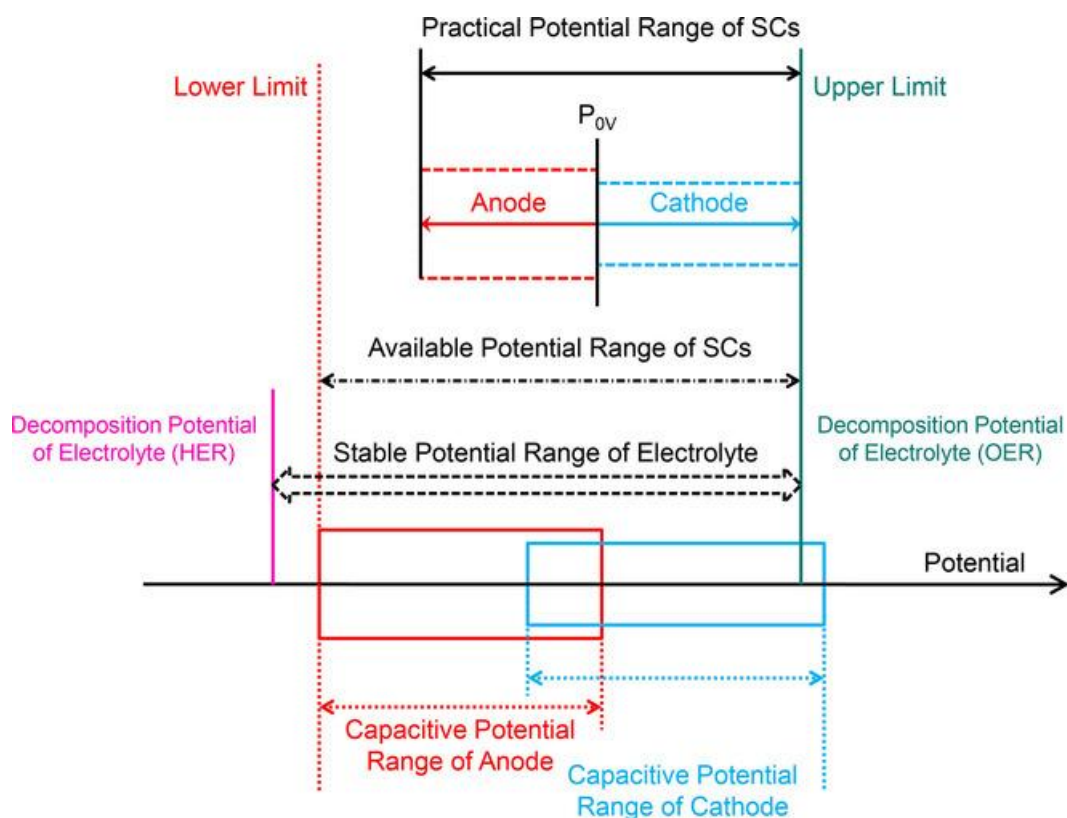
asymmetric device, an excellent areal capacitance of  $3600 \text{ mF cm}^{-2}$  at  $1 \text{ mA cm}^{-2}$  can be achieved, with a high energy density of  $1.6 \text{ mWh cm}^{-2}$  and a long lifetime (over 10 000 cycles). These studies establish a platform for low-cost, facile and large-scale fabrication for self-standing pseudo-capacitance electrode materials. Ni compounds such as NiO,  $\text{NiCo}_2\text{S}_4$ , etc. have also received extensive attention due to their extremely high theoretical specific capacities [160-162]. Yi's group [163] demonstrated design and simple preparation of mesoporous  $\text{NiCo}_2\text{O}_4@\text{MnO}_2$  nanoneedle arrays on a conductive nickel foam. Benefits from the high surface area and their unique architecture,  $\text{NiCo}_2\text{O}_4@\text{MnO}_2$  composite electrodes exhibited excellent electrochemical performance. The initial specific capacitance of composite electrode was  $1001 \text{ F g}^{-1}$  at current density of  $15 \text{ A g}^{-1}$  in 3 M KOH electrolyte and maintained  $736 \text{ F g}^{-1}$  after 10000 cycles. In fact, transition metal compounds (TMCs) usually suffer severe cycle attenuation due to poor conductivity. The same group reported the synthesis of a novel ternary composites, porous spherical  $\text{NiO}@\text{NiMoO}_4@\text{PPy}$  nanoarchitecture, for high performance supercapacitor [164]. The PPy-modified composite electrode exhibited significant improvement in cycling performance with a high specific capacitance retention of 77.1% even after 30,000 cycles.



**Figure 11.** Scheme of the design and construction of the all-wood-based supercapacitor (WC

means wood carbon) [159] (©The Royal Society of Chemistry 2017).

**Fig. 12** illustrates the correlation among factors that affect the potential range of supercapacitor. As illustrated, the available potential range is the result of synergy between the potential range of the electrode and the stable voltage range of the electrolyte [165,166]. For electrode materials, the potential range refers to a range that guarantee electrodes perform reversible charge/discharge processes without causing electrode material decomposition. The range depends on the electrochemical activity of materials, especially for materials with a pseudo-capacitance behavior. A reference electrode ( $P_{0V}$ ) can be used to detect the potential variation between cathode and anode.  $P_{0V}$  is considered as a core parameter for determining the electrode potential ranges and is defined as the potential which device are operated at 0 V [166-168].  $P_{0V}$  represents the full discharge of the cathode and anode, which means that when a certain pole reaches the limit of the possible range, the voltage range is determined. Therefore, finding suitable  $P_{0V}$  is critical for adjusting the potential range [169]. Further, in aqueous system, the overpotentials for the evolution of  $H_2$  and  $O_2$  should be taken into account during the selection of electrode for extending potential range [170-173]. Thus, building asymmetric supercapacitor systems to expand the operating voltage for higher performance is necessary.



**Figure 12.** Scheme of the correlation among the potential range of supercapacitor [169]

(©Wiley- VCH Verlag GmbH & Co. KGaA, Weinheim 2018).

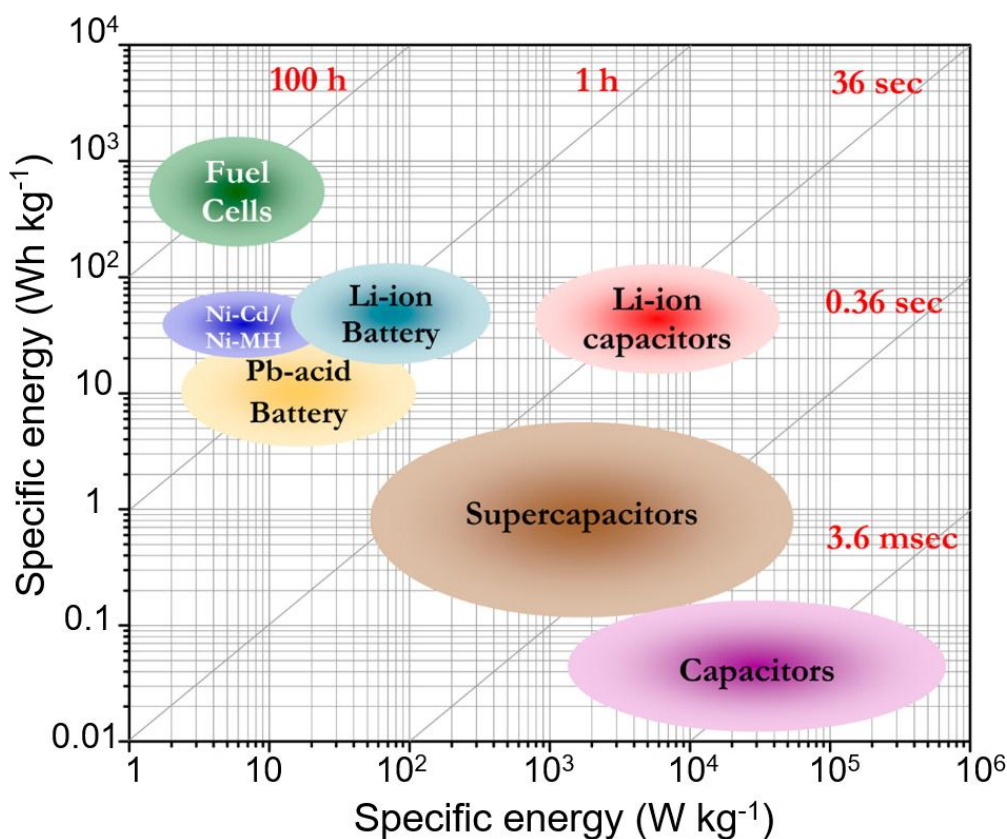
**Table 2** lists some typical asymmetric supercapacitors based on carbon/metal oxide or metal hydroxides ( $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$  etc.). It can be seen that it is effective to expand the working voltage window of the device by constructing asymmetric supercapacitors, which brings an increase in both  $E_d$  and  $P_d$ . However, these composites in the above reports show far less specific capacitance than the theoretical capacitance in three-electrode test. This is due to the poor electrical conductivity of metal oxides/metal hydroxides, which makes electron transport blocked, resulting in insufficiently utilizing of specific capacity during charge/discharge progress. To alleviate these problems, most researches have focused on designing metal oxide microstructures, reducing metal oxide size, or hybridizing [174-176]. The specific capacitance was increased to some value by these methods, but still less than the theoretical value. Till now, improving the specific capacitance of materials (close to the theoretical value) still challenging.

**Table 2.** Some aqueous asymmetric supercapacitors in recent years.

Positive electrode	Negative electrode	Voltage/V	Specific capacitance/ F g <sup>-1</sup>	Maximum $E_d/Wh\ kg^{-1}$	@ $P_d/W\ kg^{-1}$	Cycle life	Ref.
MnO <sub>2</sub> @SBA-C	FeOOH@SBA-C	2.0	70.9 at 0.1 A g <sup>-1</sup>	39.4	500	82.7% after 5000 cycles	[177]
CNF/PEDOT/MnO <sub>2</sub>	PCNFs	1.6	1061 at 0.6 A g <sup>-1</sup>	60.5	700	104.6% after 5000 cycles	[178]
Fe <sub>2</sub> O <sub>3</sub> /MnO <sub>2</sub>	rGO/Fe <sub>2</sub> O <sub>3</sub>	2.3	61.3 at 1 A g <sup>-1</sup>	57	333	88.9% after 10000 cycles	[179]
NiO/MnO <sub>2</sub> @CFC	AC	1.7	–	20.87	850	92% after 1000 cycles	[180]
TiO <sub>2</sub> @MnO <sub>2</sub>	SWCNT	2.2	111.5 at 1 A g <sup>-1</sup>	62	1000	–	[181]
CNFs/PEDOT/MnO <sub>2</sub>	AC	1.6	148.1 at 0.3 A g <sup>-1</sup>	49.4	224.02	81.6% after 8000 cycles	[182]
DPC/Co <sub>3</sub> O <sub>4</sub>	AC	1.7	60.76 at 1 A g <sup>-1</sup>	21.1	790	–	[183]
C/Co <sub>3</sub> O <sub>4</sub>	AC	1.6	99.8 at 1 A g <sup>-1</sup>	35.08	630	94.2% after 5000 cycles	[184]
C/Co <sub>3</sub> O <sub>4</sub>	AC	1.5	446.5 at 2 A g <sup>-1</sup>	68.17	549	87.92% after 10000 cycles	[185]
GLF/NiO	GLF	1.5	152 at 1 A g <sup>-1</sup>	47.6	750	83.6% after 6000 cycles	[186]
3-D Graphene/NiO	AC	1.6	34.4 at 1 A g <sup>-1</sup>	12.3	815.3	74.6% after 5000 cycles	[187]
NiO/D-rGO	Bi <sub>2</sub> O <sub>3</sub>	1.6	62 at 3 A g <sup>-1</sup>	43.7	4799	89.5% after 5000 cycles	[188]

## 4.2 Hybrid capacitors

There are two main types of reversible electrochemical energy storage devices: secondary batteries and electrochemical capacitors (EDLCs and pseudo-capacitors). The former provides a high  $E_d$ , while the latter offers a high  $P_d$  with long cycle-life. For instance, commercial lithium ion batteries (LIBs) deliver a specific  $E_d$  up to  $200 \text{ Wh kg}^{-1}$ , but with a maximum  $P_d$  being below  $350 \text{ W kg}^{-1}$ . In contrast, commercial electrochemical capacitors possess  $P_d$  reaching  $10 \text{ kW kg}^{-1}$ , but with an  $E_d$  less than  $5 \text{ Wh kg}^{-1}$ . Therefore, a new goal of next-generation electric energy storage devices is to provide high energy and high power concomitantly in a single system [189-191]. In this case, the concept of a hybrid ion capacitors (HICs) was proposed and HICs are named for their structure. In HICs, two electrodes are composed of a battery material and a supercapacitor material, respectively. **Fig. 13** illustrates the comparison of specific energy *v. s.* specific power for electrochemical energy storage methods, including lithium ion capacitors (LICs) which is a representative of HICs. Benefiting from their structure, the HICs is a good compromise between the battery and the **supercapacitor** in terms of energy supply, offering battery-like energy with supercapacitor-like power. One important potential application of HICs is regenerative braking. Regenerative braking energy from trains, different types of vehicles represents a huge potential market. Besides, UPS, voltage sag compensation, smart grids, and energy recovery systems in industrial machinery are all worth noticing [192]. However, due to the limitations in existing energy storage technologies, this market has not been fully developed, which accelerates the research on HICs [193].



**Figure 13.** Ragone diagram of energy storage with different electrochemical energy storage methods [192] (©American Chemical Society 2014).

#### 4.2.1 Lithium/Sodium ion capacitor

The mechanism of LIBs provides support for the construction of HICs. In LIBs, lithium ions can be inserted (extracted) into (out of) the graphite anode, which facilitates the selection of electrode materials. **Table 3** compiles some representative samples of various carbon-based materials employed for LICs or sodium ion capacitors (NICs).

The majority of carbon-based materials are non-graphite structure and highly porous carbon. Since the radius of sodium ions is larger than that of lithium ions (0.102 nm to 0.076 nm), it is very difficult for sodium ions to be embedded in graphite [194,195]. Moreover, heteroatoms-doped carbon and TMCs can also be employed for the storage of Li<sup>+</sup> /Na<sup>+</sup> . Overall, the choice of electrode materials for LICs/NICs is diverse and requires more extensive research.

**Table 3.** A summary of carbon-based LICs/NICs

Anode	Cathode	Type	Voltage/V	Maximum $E_d/\text{Wh kg}^{-1}@P_d/\text{W kg}^{-1}$		Cycle life	Ref.
graphite	AC	LIC	3.5	145.8	65	65% after 10000 cycles	[196]
N-doped C	AC	LIC	2	28.5	348	97% after 5000 cycles	[197]
Hard carbon	Bio-derived carbon	LIC	2.5	121	300	81% after 8000 cycles	[198]
		NIC	2.3	82	~300	60% after 8000 cycles	
N,O-doped C	HPC-800	LIC	4.0	184	200	70% after 10 000 cycles	[199]
Ti3C2/TiO2/rGO	LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub>	LIC	3.2	165	260	83% after 700 cycles	[200]
Soft carbon	AC	NIC	3.6	110	245	71% after 1000 cycles	[201]
N-doped disordered C	AC nanosheet	NIC	4	111	67	81% after 5000 cycles	[202]
Peanut-skin derived C	Peanut-skin derived C	NIC	1.5	112	67	85% after 3000 cycles	[203]
Na <sub>2</sub> Ti <sub>7</sub> O <sub>15</sub> /graphene	AC	NIC	3.7	82.7	97.5	90% after 10000 cycles	[204]
Sn <sub>4</sub> P <sub>3</sub>	AC	NIC	1.6	45	40	94% after 6000 cycles	[205]



#### 4.2.2 Other ion capacitor

LIBs and sodium-ion batteries have many shortcomings, such as limited lithium reserves, difficulty in embedding sodium ions into graphite, the use of flammable organic electrolytes, etc. These issues lead to research on new types of ion batteries, including  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ , and  $Zn^{2+}$  [206-212]. Based on these ion storage mechanisms, hybrid ion capacitors name after these cations have naturally attracted attention, especially multivalent ions. Compared with energy storage system on univalent ion, the multivalent ion-based energy storage system possesses some advantages, such as fast charge transfer kinetics and higher capacity and energy density [213]. Among these multivalent ions,  $Zn^{2+}$  and  $Al^{3+}$  have attracted intensive attention because of their small ionic radius, abundant reserves, high volumetric capacity, and the ability to use aqueous electrolytes [214]. Some HICs based on multivalent ions (MHICs) are summarized in **Table 4**. These HICs show excellent performance, indicating that the design of devices based on multivalent ions is effective. In addition, it is worth noting that various materials are proven to be available for constructing MHICs, whereas only a few studies on AIC, MgIC and CaIC have been reported.

**Table 4.** A brief overview for construction and performance of ZICs and AICs

Cathode	Anode	Type	Voltage/V	Maximum $E_d/Wh\ kg^{-1}@P_d/W\ kg^{-1}$		Cycle life	Ref.
MnO <sub>2</sub>	AC	ZIC	2.0	34.8	~60	93.4% after 5000 cycles	[215]
coconut shell-derived AC	Zn foil	ZIC	1.8	52.7	1725	91% after 20000 cycles	[216]
AC	Zn	ZIC	1.6	84	65	91% after 10000 cycles	[217]
AC	MoO <sub>3</sub> @PPy	AIC	1.5	28	460	93% after 1800 cycles	[218]
AC	CuFe-PBA	AIC	1.0	55 F g <sup>-1</sup> (only provide specific capacitance)		90% after 1000 cycles	[219]
AC	Mg foil	MgIC	1.6	90 F g <sup>-1</sup> (only provide specific capacitance)		79% after 4500 cycles	[220]
AC	Ca foil	CaIC	3.2	92 mAh g <sup>-1</sup> (only provide specific capacity)		84% after 1000 cycles	[221]

## 5. Conclusion and perspective

The scale of global market for supercapacitor reached \$470 million in 2010. By 2020, the supercapacitor market is expected to be \$3.5 billion, which will cover 5% of the battery market [12]. Due to the increasing market, it will further stimulate the study and development of supercapacitors. In our opinion, future research on carbon-based material as supercapacitor electrodes can be carried out in the following aspects.

(i) EDLCs generally possesses fast charge/discharge processes with long cycle-life. However, they are still limited by the relatively low specific capacitance, incomplete utilization of active sites, and relatively narrow operating voltage, which significantly affect the  $E_d$  and  $P_d$ . To obtain high  $E_d$  and high  $P_d$ , the future development of supercapacitors involves the novel design of carbon-based composite materials, e.g. carbon combined with pseudocapacitive materials because such composite materials are beneficial to expand the operating voltage and improve the capacitance of capacitor devices. Among pseudocapacitive materials, TMCs are often limited by their high charge transfer resistance from poor electrical conductivity and structure pulverization during cycling. Thus, the rational design in nanostructure of both carbon materials and TMCs to promote electrochemical kinetics and reduce the charge transfer resistance is still a big challenge. For example, uniform pore size distribution of porous carbon will reduce the ion transport length while suitable pore size will improve contact with electrolyte and ion migration (**Section 3.1**). Also, combining TMCs with conductive polymers can simultaneously improve the electrical conductivity and protect TMCs from structure damage and dissolution in the electrolyte.

(ii) Flexible carbon-based supercapacitor devices are highly required for the expansion of the electronic product market. The fabrication to the flexible devices includes flexible packaging and the preparation of flexible electrodes.

Packaging improvements are equally important to the success of qualified flexible energy storage systems. The development of a thinner, moisture-impermeable, flexible package that prevents electrolyte from flowing out of energy storage systems will help increase its volumetric energy density and make them more compatible. Current sealing plastics based on polydimethylsiloxane (PDMS) or other stretchable elastomers can meet the requirement on

mechanical properties, however, are limited by moisture permeability. The development of stretchable inorganic coatings, which can be deposited on stretchable elastomers, will help reduce the penetration of moisture into energy storage systems. Flexible electrodes based on paper, textiles, sponges, etc., can be achieved by vacuum suction filtration, printing technology, electrospinning technology, CVD, and electrochemical deposition. The stretchable electrodes can be realized by coating the electrode materials on stretchable substrates or embedding them in stretchable substrates. However, under strain, especially under severe strain, the electrochemical performance of flexible devices tends to be greatly compromised. Therefore, it is still a challenge to guarantee the electrochemical performance of flexible devices under ultimate strain.

(iii) Supercapacitor devices in harsh conditions such as high temperature, low temperatures, strong acid and strong base are highly required in some extreme environments. The key points for such devices will be focus on the development of novel electrodes, electrolytes, separators and binders. Compared with the normal operating temperature, at high temperatures, the electrochemical reaction is faster and the pseudocapacitor behavior is more obvious, which puts forward the requirements for the structure stability of the electrode materials. In addition, at high temperatures, the electrode may peel off from the current collector due to the failure of the binder, resulting in performance degradation. While the wettability of the electrode material to the electrolyte will become worse at extremely cold temperatures, and the electrochemical reaction is slow or even stops. Hence, the selection and structural design of new electrode materials to meet the needs of normal operation under extreme conditions is very necessary. Additionally, molecular design to achieve high performance electrolytes, separators and binders could be a suitable path in the future. For example, ionic liquids and antifreeze agents could be good options for electrolytes in ultralow temperatures while high performance polymers such as polyimides (PI) could be the ideal candidate for separators and binders.

(iv) There are still challenges to the way of industrial production of novel electrode materials. (1) One factor restricting the industrialization of new materials in supercapacitors is the high cost and energy consumption, which mainly occur during the carbonization and

the activation process of the material. Therefore, it is necessary to develop new procedure to simplify the above process. (2) Blade coating is the most commonly used process for depositing electrode slurry in large-scale production. However, it is difficult to achieve electrodes with ultrathin thickness and special patterns by this process. The developing technologies, such as screen printing, 3-D printing, and inkjet printing etc., could be the ideal options to realize such electrodes. (3) It is still necessary to develop test standards for supercapacitors in industrial and laboratory experiments.

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