Carbon-based supercapacitors for efficient energy storage

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ABSTRACT

The advancement of modern electronic devices depends strongly on the highly efficient energy sources possessing high energy density and power density. In this regard, supercapacitors show great promise. Due to the unique hierarchical structure, excellent electrical and mechanical properties, and high specific surface area, carbon nanomaterials (particularly, carbon nanotubes, graphene, mesoporous carbon and their hybrids) have been widely investigated as efficient electrode materials in supercapacitors. This review article summarizes progress in high-performance supercapacitors based on carbon nanomaterials with an emphasis on the design and fabrication of electrode structures and elucidation of charge-storage mechanisms. Recent developments on carbon-based flexible and stretchable supercapacitors for various potential applications, including integrated energy sources, self-powered sensors and wearable electronics, are also discussed.

Keywords: electric double-layer supercapacitors, pseudocapacitors, hybrid supercapacitors, carbon nanotube (CNT), graphene, flexible and wearable electronics

INTRODUCTION

The ever increasing consumption of fossil fuels and their soaring price have caused serious concerns about the fast depletion of existing fossil-fuel reserves and the associated alarming greenhouse-gas emissions and pollutions in air and on soil. Therefore, it is important to develop environment friendly energy-generation and storage technologies. In particular, there has recently been intensive attention on the advancement of energy-storage devices, including electrochemical supercapacitors and batteries [1–7]. Compared to batteries, electrochemical supercapacitors (ESCs) are capable of providing 100–1000 times higher power density, but with 3–30 times lower energy density [8]. As a consequence, ESCs are particularly useful for high power bursts, for example for accelerating/breaking high-speed transportation systems. Moreover, ESCs can sustain up to millions of charge/discharge cycles via the electric double-layer charge storage free from chemical reactions. In contrast, batteries suffer from volumetric modulation and swelling of active materials in the electrodes due to the excessive redox reactions during charge/discharge cycles [8]. As far as the safety issues are concerned, therefore, supercapacitors are much more reliable than batteries. In order to minimize/avoid possible decomposition of the electrolyte, however, the operating voltage for ESCs must be low as compared to batteries. Nevertheless, a high operating voltage is desirable for ESCs with a high energy density, and hence an optimized operating voltage is essential for high-performance ESCs.

In an electrochemical supercapacitor, two electrodes are kept apart by a separator between them (Fig. 1). These two electrodes are identical for a symmetric supercapacitor (Fig. 1a), but different for an asymmetric supercapacitor (Fig. 1b and c). The separator is generally ion-permeable, but also electrically insulating, soaked with electrolytes to allow ionic charge transfer between the electrodes. Polymer or paper separators are often used with organic electrolytes while ceramic or glass-fiber separators are preferred for aqueous electrolytes [8,9]. Depending on the ways in which energy is stored, ESCs can be divided into electric double-layer capacitors (EDLCs), in which charge storage occurs at the interfaces between the electrolyte and electrodes (Fig. 1a), and pseudocapacitors (PCs), involving reversible and fast Faradaic redox reactions for charge storage.
Figure 1. Schematic representation of (a) electrical double-layer capacitor (EDLC), (b) pseudocapacitor (PC) and (c) hybrid supercapacitor (HSC).

storage (Fig. 1b). When a supercapacitor stores charges by matching the capacitive carbon electrode with either a pseudocapacitive or lithium-insertion electrode (Fig. 1c), it is then called a hybrid supercapacitor (HSC). Owing to their availability in large quantities at a relatively low cost, unique hierarchal structures with a large surface/interface area and excellent electrical/electrochemical/mechanical properties, nanoporous and/or mesoporous carbon materials are useful as the electrode materials in all types of ESCs.

Along with the recent rapid development of flexible/wearable electronics, there is an urgent need for integrated power sources based on flexible and even stretchable electrodes. Consequently, flexible and stretchable fiber-shaped or very thin supercapacitors (SCs) have recently attracted a great deal of interest [10]. In this context, carbon nanotubes (CNTs) and graphene with a high mechanical stability and excellent bending strength have been reported to be ideal electrode materials for flexible and stretchable ESCs. Thus, carbon nanomaterials have been widely investigated for developing new electrode materials in various ESCs for efficient energy storage. A huge amount of literature on carbon-based ESCs has been produced, with the number of publications still rapidly increasing every year. A timely review on such a rapidly growing field of such significance is highly desirable. The aim of this article is to provide a timely, concise and critical review by summarizing recent important progress on the topic and presenting critical issues related to the material/electrode design and the elucidation of energy-storage mechanisms. Through such a critical review, our understanding of carbon-based electrode materials for energy storage will significantly increase, as will insights for the future development.

CARBON NANOMATERIALS

Conventional carbon materials are divided into three forms: diamond, graphite and amorphous carbon [1]. Their properties vary depending on the arrangement of carbon atoms. For example, diamond is hard and rigid due to its special diamond cubic crystal structure with sigma bonding between sp3 hybridized carbon molecules. Having a layered structure with strong covalent bonding between sp2 hybridized carbon atoms in the plane of individual layers and weak van der Waals interactions between adjacent layers, graphite is soft. The recent development of nanoscience and nanotechnology has opened up a new frontier in carbon materials research by creating new graphitic carbon nanomaterials with multi-dimensions, including dimension-less (0D) fullerene, one-dimensional (1D) carbon nanotubes (CNTs) [11–19] and two-dimensional (2D) graphene [20–31]. Fullerene C60 has a soccer-ball-like structure containing 20 carbon hexagons with 12 carbon pentagons formed into a cage of truncated icosahedrons. Fullerene C60 is a perfect electron acceptor, which has been widely used in solar cells for charge separation. Due to its intractability, low electrical conductivity and small surface area, fullerene has been rarely used for energy storage with respect to other carbon nanomaterials. So far, CNTs [2,32–42], graphene [29,43–73], mesoporous carbon [74–80] and their hybrids [81–94] have been widely studied as supercapacitor electrodes because of their excellent electrical conductivity, high specific surface area, outstanding electrochemical activity and the ease with which they can be functionalized into multidimensional and multifunctional structures with excellent electrical and mechanical properties.

APPLICATION OF CARBON NANOMATERIALS IN SUPERCAPACITORS

Current research and development on energy-storage devices have been mainly focused on supercapacitors, lithium-ion batteries and other related batteries. Compared with batteries, supercapacitors possess higher power density, longer cyclic stability, higher Coulombic efficiency and shorter period for
full charge–discharge cycles. Thus, supercapacitors, particularly those based on carbon CNTs, graphene and mesoporous carbon electrodes, have gained increasing popularity as one of the most important energy-storage devices.

**EDLCs**

Similarly to traditional capacitors, EDLCs also store energy through charge separation, which leads to double-layer capacitance. Unlike a traditional capacitor, however, an EDLC contains two separated charge layers at the interfaces of electrolyte with positive electrode and negative electrode, respectively. The separation between electrical double layers in an EDLC is much smaller than that in a conventional capacitor, leading to a several orders of magnitude higher specific capacitance for the EDLC. Since there is no chemical reaction involved and the transport of ions in the electrolyte solution or electrons through the electrodes is responsible for charge storage, EDLCs can be fully charged or discharged within a short time with a high power density. Ideally, EDLCs require electrode materials with a high specific surface area and excellent electrical conductivity, which can be fulfilled especially by CNTs and graphene.

**CNTs in EDLCs**

CNTs, with and without compositing with other electrode materials, are highly suitable for supercapacitor electrodes. The reported specific surface area of pure CNTs is in between 120 and 500 m$^2$/g with the specific capacitance ranging from 2 F/g to 200 F/g [2,32–34]. Using single-walled carbon nanotubes (SWNTs) as the electrode materials, a specific capacitance, power density and energy density up to 180 F/g, 20 kW/kg and 7 Wh/kg, respectively, have been reported [35,36]. The specific surface area can be enhanced by activating the CNT walls and/or tips. For example, Pan et al. have improved the specific surface area of SWNTs from 46.8 m$^2$/g to 109.4 m$^2$/g through electrochemical activation, leading to a three-times increase in the specific capacitance [37]. Hata and coworkers have reported a specific surface area of 1300 m$^2$/g for highly pure SWNTs [38]. Using organic electrolyte (1 M Et$_4$NBF$_4$/propylene carbonate) to ensure a high voltage of 4 V, these authors have reported an energy density as high as 94 Wh/kg (or 47 Wh/L) and a power density up to 210 kW/kg (or 105 kW/L).

CNT diameters play a key role in controlling the intrinsic surface area. It was reported that the specific surface area of multiwall carbon nanotubes (MWNTs) with outer diameter of 10–20 nm and inner diameter of 2–5 nm varied from 128 to 411 m$^2$/g with increasing diameters, and the MWNTs exhibited the highest specific capacitance of 80 F/g in 6 M KOH electrolyte [39]. So far, many of the reported EDLCs based on pure CNTs showed high-rate capabilities and cyclic stabilities, together with rectangular cyclic voltammograms and symmetric triangular galvanostatic charge–discharge profiles, indicating high performance for charge storage.

Apart from improving the specific surface area, much effort has been made to improve the electrical conductivity and increase the active sites on CNTs. Heteroatom doping has been demonstrated to be an important and efficient technique for these purposes. For instance, nitrogen-doped (N-doped) CNTs were synthesized by in-situ polymerization of aniline monomers on CNTs, followed by carbonization of polyaniline (PANI)-coated CNTs [40]. In this study, the N-doping level was controlled by adjusting the amount of aniline used, leading to a highest specific capacitance of 205 F/g in 6 M KOH electrolyte—a much higher value than 10 F/g for the pristine CNTs, at 8.64% (by mass) nitrogen doping. Moreover, 97.1% of the initial capacitance was maintained after 1000 cycles. Recently, Gueon and Moon prepared N-doped CNT-based spherical particles by emulsion-assisted evaporation of hexadecane, followed by N-doping using melamine [41]. A specific capacitance of 215 F/g was achieved at a current density of 0.2 A/g—3.1 times the enhancement as compared to that of the pristine CNTs. The observed performance improvement was attributed to the combination of more active sites with a higher electrical conductivity induced by N-doping. Interestingly, N-doped aligned CNT arrays have also been synthesized and systematically characterized for their application in supercapacitors [42]. It was found that the supercapacitor performance at a low scan rate was highly dependent on the pyridinic nitrogen content in N-doped CNTs due to the net charges induced onto the neighboring carbon atoms through protonation of the pyridinic nitrogen.

**Graphene in EDLCs**

Having the basic carbon lattice structure similar to CNTs with all carbon atoms exposed at the surface, the single-atom-thick 2D graphene sheets show similar electrical and other properties to CNTs, but with an even larger specific surface area [1,2]. Like CNTs, therefore, graphene sheets have also been extensively studied as electrode materials in ESCs. The availability of graphene oxide (GO) by acid
oxidation of graphite [43–45], followed by chemical reduction [29,43–45], provides an effective approach for low-cost mass production of reduced graphene oxide (RGO), which can directly be used as EDLC electrode materials. In this regard, Stoller et al. used hydrazine hydrate as the reducing reagent to produce RGO from GO [29]. The resultant RGO exhibited a specific capacitance of 135 F/g and specific surface area of 705 m²/g [29], which is much lower than the theoretic value of 2630 m²/g, presumably due to RGO aggregation. To minimize the RGO aggregation, Chen and coworkers synthesized graphene with mesoporous structure through thermal exfoliation of RGO at 1050 °C to produce a specific capacitance up to 150 F/g in 30% KOH aqueous solution [46]. Microwave irradiation in vacuum can reduce the reduction temperature required for thermal exfoliation, as demonstrated by Lv et al. [47]. These authors decreased the exfoliation temperature down to 200 °C with a concomitant increase in the specific capacitance up to 264 F/g [47]. By using microwave radiation to assist the exfoliation process, Zhu et al. also effectively deducted the exfoliation time to as short as 1 min and the produced graphene could still exhibit specific capacitance of 191 F/g in 5 M KOH [48].

For conventional graphene and RGO electrodes, electrolyte ions can only transfer charges between graphene sheets, which inevitably leads to a much longer ion-transport path with respect to ions transferring through the graphene sheets (Fig. 2). To address this issue, Xu et al. synthesized holy graphene sheets, which allow ions to pass through the holes with a minimized transport path while still maintaining the electron-transport efficiency [49]. As a result, their hierarchical structuring three-dimensional (3D) holy graphene electrode exhibited both high gravimetric and volumetric specific capacitances of 298 F/g and 212 F/cm³, respectively. Moreover, the energy density for a corresponding fully packaged supercapacitor is as high as 35 Wh/kg (49 Wh/L), which is sufficient to bridge the gap between supercapacitors and batteries.

Similarly to CNTs, surface activation can also be used to improve the specific capacitance of graphene electrodes without a detrimental effect on the electrical conductivity. Of particular interest, Ruoff and coworkers obtained a dramatically improved specific surface area up to 3100 m²/g by activating exfoliated GO with KOH [50], which is even higher than the theoretically predicted specific surface area of monolayer graphene (2630 m²/g) and attributable to the presence of a 3D network containing pores with sizes of 1–10 nm. In another study, the same group activated RGO films to produce graphene films of a specific capacitance of 120 F/g at high current density of 10 A/g with corresponding energy density and power density of 26 Wh/kg and 500 kW/kg, respectively [51]. Later, they further improved the specific surface area up to 3290 m²/g by designing a mesoporous structure integrated with macroporous scaffolds [52]. As a result, specific capacitance of 174 F/g (100 F/cm³) was achieved with energy density and power density of 74 Wh/kg and 338 kW/kg, respectively.

Doping graphene with hetero atoms can also improve its electrical/electrochemical properties for energy storage and many other applications [53]. Indeed, Jeong et al. synthesized N-doped graphene through a simple plasma process [54], and the N-doped graphene thus produced was found to exhibit a specific capacitance of 280 F/g, which is four times higher than that of the corresponding undoped pristine graphene. This is because N-doping can introduce charge-transferring sites through doping-induced charge modulation and improve electrical conductivity of graphene, and hence the improved specific capacitance, along with an enhanced power density of $8 \times 10^5$ W/kg and energy density of 48 Wh/kg. N-doped graphene can also be synthesized through hydrothermal reduction of GO with nitrogen containing chemicals [55]. The resultant 3D N-doped graphene framework has a very low density of 2.1 mg/cm³ with a high specific capacitance of 484 F/g in 1 M LiClO₄ electrolyte and maintains 415 F/g capacitance after 1000 cycles at a high

Figure 2. Schematic illustration of the graphene and holy graphene foams. (a, b) Initial 3D macroporous (a) graphene foam and (b) holy graphene foam. (c, d) Compressed films of the (c) graphene foam and (d) holy graphene foam. (e, f) A closed-up view of (e) graphene and (f) holy graphene films. The arrows highlighted the ion transport pathway. Reproduced with permission from ref. [49]. Copyright of Macmillan Publishers Ltd (2014).
current density of 100 A/g [55]. Similarly, doping graphene with other elements, such as boron, phosphorous and/or co-doping with N and P or B and N, has also been demonstrated to significantly improve their energy-storage performance [56,57].

Graphene-based self-assembled 3D structures (such as hydrogels and aerogels) have recently emerged as electrode materials for supercapacitors due to their high porosity, low density and excellent adsorption capacity [58–60]. The detailed synthetic processes and properties of graphene hydrogels and aerogels have been reviewed in references [58–60]. Briefly, in an aqueous solution of GO, the van der Waals attractions from the basal planes of GO sheets and the electrostatic repulsions from the functional groups of GO sheets are balanced each other to maintain the well-dispersed state of GO sheets. While this balance is lost, gelation of the GO dispersion takes place, leading to the formation of 3D GO hydrogels that can be further reduced or functionalized to produce 3D graphene-based architectures [61–63]. Different techniques have been used to produce graphene hydrogels, such as hydrothermal reduction [61], chemical reduction [63], cross-linking agent (including metal ions [64], biomolecules [65], polymers [66] etc.), sol-gel reaction [67], freeze-drying [68] and so on. Similarly to hydrogels, graphene aerogels are made through replacing the solution part with a gas [69–70]. There have been numerous studies on graphene aerogels for supercapacitor applications. Such successful efforts have been summarized in Table 1. For assemblies of graphene hydrogels, aerogels or organogels [71], their overall conductivities are generally poor.

As the graphene-based nanostructured carbon materials often offer low density, in most cases, the volumetric energy densities of carbon-based supercapacitors are low, which hinders their practical application. Yang et al. and Yoon et al. have demonstrated graphene-based highly packed supercapacitors with volumetric energy density of 59.9 Wh/L and specific capacitance of 171 F/cm³, respectively [72,73]. However, much more effort must be made in improving the volumetric energy density.

**Mesoporous carbon in EDLCs**

Activated carbon has been widely used as electrodes in energy-storage devices because of their easy synthesis, low cost and acceptable electrical conductivity. However, these advantages are hindered by its low effective specific surface area due to the presence of randomly connected micropores with size less than 2 nm that are hardly accessible by electrolyte ions [2]. To address this issue, mesoporous carbon of a larger pore diameter (2–50 nm) was explored as a supercapacitor electrode with a high specific surface area, fast ion-transport pathway and high power density. As an example, mesoporous carbon synthesized through carbonization of poly(vinyl alcohol) and inorganic salt mixture exhibited a specific capacitance of 180 F/g in aqueous H₂SO₄ electrolyte [74]. However, the volumetric specific capacitance, energy density and power density of mesoporous carbon electrodes could be influenced directly by the mesoporous size and content. A balanced population of mesopores and micropores is desirable for efficient electrochemical energy storage [75,76].

As discussed above, the size and shape of the pores in mesoporous carbon can be well controlled through various synthetic techniques [77]. When mesoporous carbon is produced as an ordered mesoporous carbon (OMC) with homogeneously distributed pores of regular size, it can facilitate charge storage and transport, and hence both the capacitance and rate capability can be improved. Highly OMCs with pore sizes of 2.8 nm (C-1) and 8 nm (C-2) have been synthesized using SBA-16 silica with mesostructured templates and polyfurfuryl alcohol as the carbon source [77]. The resultant OMCs, both C-1 and C-2 with a specific surface area of 1880 and 1510 m²/g, respectively, were tested as supercapacitor electrodes in different electrolytes. It was evident that the highest specific capacitance reached up to 205 F/g by the C-1 with a pore diameter of 2.8 nm whereas the C-2 with a pore diameter of 8 nm exhibited better stability while increasing the rate.

For mesoporous carbons, activation can also be performed to introduce micropores. For instance, Xia et al. activated mesoporous carbon with CO₂ at 950 °C, which introduced micropores into the mesoporous carbon to improve the specific capacitance up to 223 F/g from 115 F/g in 6 M KOH [78]. The observed enhancement in specific capacitance can be attributable to the formation of hierarchical pores with a high specific surface area (2749 m²/g) and the well-balanced populations of micropores and mesopores. Recently, production of mesoporous carbon through carbonization of non-conventional materials, like biomass, are becoming more and more popular. For example, N-doped mesoporous carbon has been prepared by a one-step method of pyrolysing the mixture of milk powder and potassium hydroxide without using any template. The N-doped mesoporous carbon (NMPC) showed a specific surface area of 2145.5 m²/g and a pore volume of 1.25 cm³/g. As a supercapacitor electrode material, the NMPC, with 2.5% N dopant, exhibited a specific capacitance of 396.5 F/g at 0.2 A/g in 6 M H₂SO₄ and stable capacitance retention of 95.9% after 2000 cycles at 50 mV/s [79]. Furthermore, the shape and
Table 1. Carbon nanomaterials in electrical double-layer capacitors (EDLCs).

| Electrode                          | Electrolyte                                      | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|------------------------------------|-------------------------------------------------|----------------------|---------------|---------------|----------------------|------|
| (i) Carbon nanotube (CNT)          |                                                 |                      |               |               |                      |      |
| CNT (functionalized by –OH and –COOH) | 0.075 M Hydroquinone (HQ) into 1 M H₂SO₄ aqueous | 3199 F/g at 5 mV/s   | –             | –             | 70% after 350 cycles | 32   |
| PEDOT/MWCNT                        | 1 M LiClO₄                                      | 79 F/g               | 5000 W/kg     | –             | 85% after 1000 cycles | 33   |
| PTFE/PANI-CNT                      | 30% KOH in H₂O                                  | 163 F/g at 0.1 A/g   | –             | –             | –                    | 34   |
| C tubes                            | 0.5 mol/l H₂SO₄                                 | 315 F/g at 0.35 V    | –             | –             | –                    | 37   |
| SWNT                               | 1 M Et₄NBF₄/propylene carbonate                 | 160 F/g at 24 kW/kg  | 17 Wh/kg      | –             | 96.4% after 1000 cycles | 38   |
| MWCNT                              | 6 mol/1 KOH                                     | 80–135 F/g           | –             | –             | –                    | 39   |
| N-doped (8.64 wt.%) carbon shell and a CNT-core | 6 mol/1 KOH                                | 205 F/g              | –             | –             | 97.1% after 1000 cycles | 40   |
| Spherical particles of N-doped CNT | 1 M H₂SO₄                                      | 215 F/g at 0.2 A/g   | –             | –             | 99% after 1500 cycles | 41   |
| (ii) Graphene                      |                                                 |                      |               |               |                      |      |
| rGO                                | 1-butyl-3-methylimidazolium hexafluorophosphate (BMIIPF₆) | 348 F/g at 0.2 A/g | –             | –             | 120% after 3000 cycles at 10 mV/s | 43   |
| Graphene hydrogel                  | 5 M KOH                                         | 220 F/g at 1 A/g     | 30 kW/kg      | 5.7 Wh/kg     | 92% after 2000 cycles | 44   |
| rGO by Na₂CO₃                      | 6 M KOH                                         | 228 F/g at 5 mA/cm²  | –             | –             | –                    | 45   |
| Graphene sheets                    | 30 wt.% KOH in H₂O                              | 150 F/g at 0.1 A/g   | –             | –             | 100% up to 500 cycles | 46   |
| Exfoliated rGO                     | 30 wt.% KOH in H₂O                              | 264 F/g at 0.1 A/g   | –             | –             | 97% after 100 cycles  | 47   |
| MW assisted rGO                    | 5 M KOH                                         | 191 F/g at 0.15 A/g  | –             | –             | 9% reduction at 0.6 A/g | 48   |
| Hollow graphene                    | 1-ethyl-3-methylimidazolium tetrafluoroborate/acetonitrile (EMIMBF₄/AN) | 298 F/g at 1 A/g | 1000          | 35 Wh/kg     | –                    | 49   |
| Exfoliated rGO                     | 1-ethyl-3-methylimidazolium tetrafluoroborate/acetonitrile (EMIMBF₄/AN) | 166 F/g at 5.7 A/g | 250 kW/kg     | 70 Wh/kg     | 97% after 10 000 cycles | 50   |
| rGO (KOH activated)                | Tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile | 120 F/g | 500 kW/kg | 26 Wh/kg | 95% after 2000 cycles | 51   |
| Electrode                                | Electrolyte                                                                 | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|-----------------------------------------|------------------------------------------------------------------------------|----------------------|---------------|----------------|----------------------|------|
| Graphene made porous carbon             | 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][TFSI] and Acetonitrile in 1:1 ratio | 174 F/g at 4.1 A/g current | 338 kW/kg     | 74 Wh/kg       | 94% after 1000 cycles | 52   |
| N-doped graphene                        | 1 M tetraethylammoniumtetrafluoroborate (TEA BF4)                            | 280 F/g at 20 A/g current in 6 M KOH | 800 kW/kg     | 48 Wh/kg       | 99.8% after 230 000 cycles | 53   |
| N-doped (5.86 at.%) graphene hydrogel   | 6 M KOH                                                                      | 308 F/g at 3 A/g current | –             | –              | 92% after 1200 cycles | 54   |
| 3D N-doped graphene                     | 1 M LiClO4                                                                  | 484 F/g at 1 A/g and 415 at 100 A/g current | ~10 kW/kg | ~5.5 Wh/kg | 95% after 4500 cycles | 55   |
| B-doped rGO                             | 6 M KOH solution                                                            | 200 F/g at 0.1 A/g current | ~10 kW/kg | ~5.5 Wh/kg | 95% after 4500 cycles | 56   |
| N/P doped rGO                           | 6 M KOH solution                                                            | 165 F/g at 0.1 A/g current | –             | –              | 80% after 2000 cycles at 0.5 A/g | 57   |
| Graphene hydrogel (hydrothermal)        |                                                                              | 175 F/g at 10 mV/s | –             | –              | –                    | 61   |
| 4.38% (at.) N-graphene hydrogel (hydrogel) | 5 M KOH                                                                    | 131 F/g at 80 A/g current | 144 kW/kg     | 4.5 Wh/kg     | 95.2% after 4000 cycles at 100 A/g | 62   |
| Graphene aerogel (3D printed)           | 3 M KOH                                                                      | 4.76 F/g at 0.4 A/g current | 4.08 kW/kg     | 0.26 Wh/kg     | ~95.5% after 10 000 cycles at 200 mV/s | 69   |
| Graphene aerogel                        | 0.5 M H2SO4                                                                 | 325 F/g at 1 A/g | 7 kW/kg       | 45 Wh/kg       | ~98% after 5000 cycles | 70   |
| 2D microporous covalent triazine-based framework | Solvent-free ionic liquid EMIMBF4                                               | 151.3 F/g at 0.1 A/g current | 10 kW/kg | ~42 Wh/kg | 85% after 10 000 cycles at 10 A/g | 71   |
| (iii) Mesoporous carbon                  |                                                                              |                      |               |               |                      |      |
| Porous carbon (Surface area (S BET) = 1300 m²/g, pore diameter (D P) = 5–15 nm) | 2 M H2SO4 1 M (C2H5)4NBF4 in acetonitrile | 0.14 F/m² | 0.075 F/m² (at 1 mA/cm²) | 2600 W/kg | 1 Wh/kg | 85% at 100 mA/cm² | 74   |
| Porous carbon (S BET = 1600 m²/g, D P = 0.6–1.1 nm) | 1.5 M (C2H5)4NBF4 in acetonitrile | 100–140 F/g at 1 mA/cm² | – | – | 100% up to 100 mA/cm² | 75   |
| Porous Carbon (S BET = 1880 m²/g, D P = 2.8 nm) | 6 M KOH | 205 F/g at 1 mV/s | – | – | 86.8% after 3000 cycles at 500 mA/g | 77   |
Table 1. Continued.

| Electrode                              | Electrolyte          | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|----------------------------------------|----------------------|----------------------|---------------|----------------|----------------------|------|
| Porous carbon (S BET = 2749 m²/g, D p = 3–4 nm) | 6 M KOH              | 223 F/g at 2 mV/s    | –             | –              | 73% at 50 mV/s       | 78   |
| N-doped (2.5 at.%) mesoporous carbon (S BET = 2145.5 m²/g, D p = 0.8–2.5 nm) | 6 M H₂SO₄            | 396.5 F/g at 0.2 A/g | –             | –              | 95.9% after 2000 cycles at 50 mV/s | 79   |
| (iv) Hybrid carbon nanomaterials       |                      |                      |               |                |                      |      |
| Graphene/carbon black                  | 6 M KOH              | 175 F/g at 10 mV/s   | –             | –              | 98.9% after 6000 cycles (200 mV/s) | 81   |
| Porous carbon/rGO (S BET = 1496 m²/g, D p = 1.4–3.5 nm) | 6 M KOH              | 171 F/g at 10 mV/s scan | 4.2 kW/kg     | 3.3 Wh/kg      | 74% at 0.1 A/g       | 82   |
| rGO/CNT                                | 0.1 M sodium phosphate buffered saline (PBS) | 140 F/g at 0.1 A/g current | –             | –              | 64.3% at 100 A/g     | 83   |
| Graphene/CNT                           | 1 M H₂SO₄            | 124 F/g at 0.1 V/s   | –             | –              | 95% at 1 V/s         | 85   |
| Graphene/CNT fiber                     | Poly(vinyl alcohol) /H₃PO₄ (1:1, mass) | 31.5 F/g at 0.04 A/g current | –             | –              | 100% after 5000 cycles | 86   |
| SWNT/N-doped rGO fiber                 | PVA/H₂PO₄, 1 M H₂SO₄ | 300 F/g at 26.7 mA/cm², 1085 mW/cm³, 6.3 Wh/cm³ | 73.5 mA/cm³   | 250 mW/cm³      | 93% after 10 000 Cycles at 10 000 cycles | 87   |
| 3D N-doped graphene/CNT                | 6 M KOH              | 180 F/g at 0.5 A/g current | –             | –              | 96% after 3000 cycles | 88   |
| Freestanding graphene hydrogel/carbon fiber composite | 1 M Na₂SO₄ | 150.2 F/g at 1 A/g current | –             | –              | 97.9% after 2000 cycles | 89   |

structure of pores of mesoporous carbon have also been explored to improve the electrochemical performance [80].

**Hybrid carbon nanomaterials in EDLCs**

Carbon nanomaterials with distinct structures can be combined to exhibit synergetic effects for electrochemical performance. For example, carbon black has been used to separate graphene sheets to produce 3D hybrid materials with minimized aggregation of graphene, leading to a high specific capacitance of 175 F/g at 10 mV/s scan rate in 6 M KOH electrolyte [81]. In other work, mesoporous carbon spheres were sandwiched between graphene sheets and the resulting 3D structure exhibited a specific capacitance of 171 F/g at the same 10 mV/s scan rate in 6 M KOH [82]. More interestingly, CNTs were intercalated between graphene sheets to retain the specific surface area of graphene by minimizing its aggregation [83]. The π–π interaction between graphene and CNTs can also improve electrical conductivity and mechanical strength [84]. Just like GO to disperse CNTs in solvents [83], oxidized CNTs have been used to form composites with graphene [85]. In this context, Yu and Dai produced hybrid films of CNT and graphene interconnected network with well-defined nanoporous [85], which exhibited a specific capacitance of 120 F/g in 1 M H₂SO₄ electrolyte and an almost rectangular cyclic voltammogram even at a 1-V/s scan rate. Sun et al. reported other interesting work [86], in which graphene
sheets were intercalated between CNTs in aligned CNT fiber. Although the resultant hybrid fiber exhibited a specific capacitance of only 31.5 F/g, it was much higher than that of the pure CNT fiber (5.83 F/g). By using a modified hydrothermal micro-reactor, Yu et al. produced a continued CNT and graphene hybrid fiber with well-defined mesoporous structures [87], which showed a specific surface area as high as 396 m²/g with an electrical conductivity of 102 S/cm. The corresponding fiber-shaped supercapacitor showed a volumetric specific capacitance of 305 F/cm³ at 26.7 mA/cm³ current density and a volumetric energy density of 6.3 mWh/cm³, which is comparable to the energy density of a 4 V–0.5 mAh thin-film lithium-ion battery. Furthermore, a 3D N-doped CNT/graphene network was also synthesized through hydrothermal treatment and freeze-drying, followed by carbonizing GO and the pristine CNT mixture in the presence of pyrrole [88]. The resultant hybrid carbon fiber showed high electrochemical performance, especially capacitance retention of 96% after 3000 cycles [88]. In case of self-assembled carbon-composite material [89–94], freestanding 3D graphene hydrogel and carbon nanofiber composite material demonstrated 150.2 F/g specific capacitance at 1-A/g current with 97.8% capacitance retention after 2000 cycles [89]. Carbon nanofiber and nanotube network was also synthesized from conjugated polymer for electrochemical energy storage [90]. Table 1 summarizes carbon-based electrical double-layer supercapacitors (EDLCs).

**Pseudocapacitors (PCs)**

Pseudocapacitors store energy through reversible Faradaic charge transfer, which involves fast and reversible electrochemical redox reactions on the interface between the electrodes and electrolyte. As such, the specific capacitance of a pseudocapacitor is often higher than that of an EDLC, as is the energy density. As the redox reactions occur on the electrode surface, a high specific surface area and high electrical conductivity are essential for electrodes in a high-performance PC. Therefore, carbon nanomaterials, including CNTs, graphene, mesoporous carbon and their hybrids, have also been used as the substrate to load active materials and/or current collector to ensure high capacitance and fast charge transfer for electrodes in high-performance PCs.

**CNTs in pseudocapacitors**

CNTs have been used in pseudocapacitors in either a functionalized form or composited with other active components, such as conductive polymers and metal oxides. CNTs can be functionalized through chemical or electrochemical methods. The most common way to functionalize CNTs is acid oxidation (e.g., a mixture of concentrated sulfuric acid and nitric acid) to introduce surface carboxyl groups [95]. Through acid oxidation, the specific capacitance of CNTs can be increased by 3.2 times due to the increased hydrophilicity of the electrodes in aqueous electrolytes and the introduction of pseudocapacitance. Treatment of CNTs with NaOH solution at 80°C, followed by ultrasonication in H₂SO₄/HNO₃ solution, can also improve the specific capacitance from 28 F/g for the pristine CNTs to 85 F/g for the functionalized CNTs [32]. However, the oxidation treatments inevitably induced defects to degrade the CNT structure and reduce the electrical conductivity. Therefore, a delicate balance between the electrode performance and its structure integrity is important for high-performance pseudocapacitors (i.e., PCs).

Conducting polymers possessing good electrical conductivities and redox activities often exhibit high specific capacitances when they are composited with CNTs. In this regard, Bai et al. increased the energy density of a CNT-based PC by four times, up to 11.3 Wh/kg, by compositing poly (3,4-ethylenedioxythiophene) (PEDOT) homogeneously onto the CNT electrode through in-situ polymerization [96]. Similarly, polypyrrole (PPy)/CNT composite electrodes have been also synthesized to yield a specific capacitance of 165 F/g in 1 M KCl solution [97]. Compared with PEDOT and PPy, PANI possesses a higher theoretical specific capacitance [98], which was confirmed by a high specific capacitance of 501.8 F/g reported for flexible PANI/SWNT composite films synthesized through in-situ electrochemical polymerization (Fig. 3) [99]. Subsequent electrodegradation further increased the specific capacitance to 706.7 F/g by forming charge transfer channels via selective dissolution of polycrystalline and off-lying disordered PANIs. Because PANI changes its color during the charge–discharge process, PANI/CNT composites have been used for high-performance (308.4 F/g in PVA/H₃PO₄) smart supercapacitors with highly reversible chromatic transitions during charge–discharge processes for monitoring the energy-storage status by the PANI color changes [100].

Metal oxides and hydroxides are two other important classes of active electrode materials for pseudocapacitors. Compared to conductive polymers, metal oxides and hydroxides often exhibit a better electrochemical stability but lower electrical conductivity. For metal oxides and hydroxides to
be used in high-performance pseudocapacitors, the corresponding metals must possess two or more oxidation states, which can coexist and inter-transfer freely. Examples include RuO$_2$, MnO$_2$, NiO, V$_2$O$_5$, Fe$_3$O$_4$, Co$_3$O$_4$, TiO$_2$, SnO$_2$, Mn$_3$O$_4$ and Ni(OH)$_2$ [101–108]. In the metal oxide and CNT composite electrodes, CNTs can not only provide the high electrical conductivity and large specific surface area for efficiently loading the active materials, but also effectively restrict the volumetric change of metal oxides or hydroxides caused by the cyclic charge–discharge processes [106]. As RuO$_2$ has three oxidation states and a wide operation potential window, RuO$_2$/CNTs have become a typical composite electrode material for pseudocapacitors. The specific capacitance of RuO$_2$ with a large surface area can reach up to 1170 F/g in 0.5 M H$_2$SO$_4$ electrolyte [108]. Reddy and Ramaprabhu have synthesized RuO$_2$/CNT, TiO$_2$/CNT, SnO$_2$/CNT composites by chemical reduction of corresponding salts to functionalize CNTs and demonstrated the highest capacitance of 160 F/g for the TiO$_2$/CNT [107]. On the other hand, MnO$_2$ possesses a high theoretical specific capacitance of 1370 F/g [109] and has been electrochemically deposited onto chemical vapor deposition (CVD)-grown CNT arrays to exhibit a specific capacitance of 642 F/g in 0.2 M Na$_2$SO$_4$ electrolyte [110]. Very high charge/discharge stability of up to 10 000 cycles can be obtained using MnO$_2$/CNT composite electrodes [111]. Furthermore, flexible and wearable supercapacitors based on MnO$_2$/CNT composite fibers prepared by electrochemical deposition of MnO$_2$ on aligned CNT fibers were demonstrated to show a specific capacitance of 3.707 mF/cm$^2$ [112].

Graphene in pseudocapacitors

Just like metal oxide and CNT electrodes, graphene with a high specific surface area and high electrical conductivity has also been composited with other active materials, including conductive polymers, metal oxides and hydroxides, as electrodes for pseudocapacitors [113–119]. Indeed, PANI/GO composites have been synthesized through in-situ polymerization of aniline into PANI on GO [113]. Depending on the mass ratio of PANI to GO, performance of the PANI/GO electrode varied and the highest specific capacitance of 746 F/g has been
achieved at a PANI/GO mass ratio of 200/1. Like a pure PANI electrode, however, the PANI/GO composite electrode showed very poor electrochemical cyclic stability, with a retention rate of only 20% after 500 cycles. Increased electrochemical cyclic stability could be achieved by increasing the portion of GO in the PANI/GO composite and a 73% retention rate was obtained at the PANI/GO ratio of 23/1. By growing vertically aligned PANI nanowires on GO substrate (Fig. 4a) [114], the morphology of PANI and the mass ratio of PANI to GO can be well controlled to produce a specific capacitance as high as 555 F/g in 1 M H₂SO₄ at 0.2 A/g with a 92% retention rate after 2000 cycles at 1 A/g. Yan et al. also synthesized a PANI/graphene composite with PANI nanoparticles (2 nm) uniformly decorated on the graphene flakes (Fig. 4b) [115]. In this work, graphene not only acted as a support material to offer active sites for the nucleation of PANI, but also provided a better electron-transfer path, leading to a specific capacitance of 1046 F/g in 6 M KOH at a 1-mV/s scan rate, energy density of 39 Wh/kg and power density of 70 kW/kg. To further improve the performance, graphene sheets with more active nucleation sites were prepared by unzipping CNTs to produce graphene nanoribbons with a specific capacitance of 340 F/g and a retention rate of 90% after 4200 charge–discharge cycles [116]. More interestingly, an even higher specific capacitance of 989 F/g in 6 M KOH electrolyte was obtained when cobalt was introduced into PANI/graphene composites through polymerizing aniline in the presence of both cobalt and graphene [117].

3D PANI/graphene composite hydrogel was also synthesized as a freestanding film to prepare flexible supercapacitors without binders [118,119], which exhibited excellent energy-storage properties as well as outstanding flexibilities for portable electronic devices. More recently, a simple and cost-effective method was reported to produce graphene/polystyrene sulfonic acid-graft-aniline (Gr/S-g-A) nanocomposite through direct exfoliation of graphite using S-g-A as a surfactant [120]. The Gr/S-g-A composite electrode was demonstrated to exhibit a superior specific capacitance of 767 F/g at 0.5 A/g current density in 0.1 M Bu₄NPF₆/acetonitrile electrolyte with 92% capacitance retention after 5000 cycles. The corresponding supercapacitor showed an energy density of 208.8 Wh/kg and a power density of 347.8 W/kg [120].

In addition to PANI, polypyrrole (PPy) has also been composited with graphene simply by directly mixing PPy with RGO [121]. The PPy/graphene composite thus produced showed a specific capacitance of 400 F/g in 2 M H₂SO₄ at a current density of 0.3 A/g. PPy/GO composite was also synthesized through in-situ chemically polymerizing pyrrole monomers in the presence of FeCl₃ to improve uniformity of the composite, and hence a slightly improved specific capacitance of 421.42 F/g in 0.1 M KCl electrolyte [122]. By substituting FeCl₃ with ammonium persulfate dissolved in citric acid, the specific capacitance was further improved to 728 F/g at 0.5 A/g current density with a retention rate of 93% after 1000 cycles [123]. Similarly to PANI, PPy can also be assembled with GO into layer-by-layer composites through the electrostatic interaction [124]. However, the electrochemical performance of PPy/GO composite is not promising due to the poor electrical property of GO.
Through electrochemical polymerization of pyrrole monomer and simultaneous electrostatic deposition, Zhao et al. also synthesized 3D PPy/graphene composites [125]. The resulting 3D PPy/graphene composite foam exhibited a specific capacitance of 350 F/g at a current density of 1.5 A/g with no change in the initial capacitance even after 1000 cycles. In another attempt, PPy/graphene composite films were prepared through electrochemical polymerization of PPy on graphene pre-deposited electrodes. Films were prepared through electrochemical polymerization onto a Ti substrate [126], leading to a specific capacitance of 1510 F/g (or 151 mF/cm²), or 151 F/cm³ in 0.1 M LiClO₄ electrolyte at the 10-mV/s scan rate. This ultrahigh specific capacitance was attributed to the porous structure, effective utilization of the pores and the large specific surface area for rapid redox reactions during the charge-discharge process in the pseudocapacitor.

As is the case for CNTs, metal oxides or hydroxides can also be composites with graphene-based nanomaterials to improve the pseudocapacitance. In this context, MnO₂/GO composite with MnO₂ nanoneedles deposited on the GO was synthesized through the chemical reaction of KMnO₄ and MnCl₂ in water/isopropyl alcohol mixture in the presence of GO [127]. The as-synthesized MnO₂/GO composite exhibited a specific capacitance of 216 F/g and a retention of 84.1% after 1000 cycles. By perpendicularly grafting polymer brushes, polyelectrolytes, onto the GO sheets prior to loading of MnO₂ nanoparticles, MnO₂/GO composite with uniformly distributed MnO₂ on the GO substrate was prepared, which showed an improved specific capacity of 372 F/g in 1 M Li₂SO₄ at 0.5A/g current density and an increased retention rate of 92% after 4000 cycles [128]. Alternatively, MnO₂/GO composite with porous structure has also been synthesized with the aid of microwave irradiation [129,130] to exhibit a specific capacitance of 310 F/g at a 2 mV/s scan rate and 228 F/g at a high scan rate of 500 mV/s. Besides, Mn₃O₄/graphene composite was also prepared to show a specific capacitance of 271.5 F/g at 0.1 A/g and 180 F/g at even a high current density of 10 A/g with no obvious decay of capacitance even after 20 000 cycles [131]. A filtration technique was also developed for preparing freestanding Mn₃O₄/graphene composite film as the electrode [132]. With regard to carbon-supported metal oxide PCs, Vanadium phosphates (VOPO₄)/graphene composites with vertically aligned porous 3D structure obtained through an ice-templated self-assembly process showed a 527.9-F/g gravimetric capacitance at 0.5-A/g current density with 85% capacitance retention after 5000 cycles at a 100-mV/s scan rate in 6 M KOH electrolyte—promising supercapacitive performance [133].

RuO₂, a highly active metal oxide for redox reactions, has also been composed with graphene as electrodes in pseudocapacitors. RuO₂/graphene composite was synthesized most commonly through a sol-gel technique, followed by annealing, to exhibit a specific capacitance of 570 F/g in 1 M H₂SO₄ and a retention rate of 97.9% after 1000 cycles [134]. This method could effectively reduce the aggregation of both RuO₂ nanoparticles and graphene sheets by separating graphene sheets with the grafted RuO₂ nanoparticles. An energy density up to 20.1 Wh/kg at 0.1-A/g current density was achieved, which remained at 4.3 Wh/kg when the power density approached 10 kW/kg.

Cobalt oxide is another kind of metal oxide that can demonstrate rapid and reversible redox reactions during the charge-discharge process in pseudocapacitors. For example, Co₃O₄/graphene composite was synthesized via a chemical reaction of cobalt nitrate with urea in GO suspension under microwave irradiation to exhibit a specific capacitance of 243.2 F/g in 6 M KOH [135]. Co₃O₄/graphene composite can also be synthesized by a hydrothermal method, followed by calcination to improve the electrochemical performance [136]. Morphology of the resultant Co₃O₄/graphene composite depends strongly on the ratio of Co₃O₄ to graphene. At a 7% mass ratio of graphene, Co₃O₄ nanofibers homogeneously grew on the graphene sheets, leading to improved specific capacitances of 667.9 and 385.1 F/g at the current densities of 1.25 and 12.5 A/g, respectively. Besides, Co₃O₄ and Co(OH)₂ could also be composed with graphene to prepare pseudocapacitor electrodes. In particular, a sheet-on-sheet-structured Co(OH)₂/graphene composite was synthesized through a one-step in-situ hydrothermal method to exhibit a specific capacitance of 540 F/g at a high current density of 10 A/g [137]. Increased specific capacitances with charge-discharge cycles were observed for both the Co₃O₄/graphene and Co(OH)₂/graphene composites, attributable to a gradual activation of the active materials wrapped up by graphene during the initial charge-discharge cycling [136].

Apart from Mn, Ru and Co oxides, oxides of other metals with multiple valences, such as Ni, Fe, Ti and Zn, have also been under research focus as alternative electrode materials that can be composed with graphene to further improve pseudocapacitive performance [138–142]. For instance, hexagonal nanoplates of single-crystal Ni(OH)₂ have been grown on lightly oxidized conductive graphene sheets using an in-situ synthesis technique [138]. The resultant composite exhibited an...
ultrahigh specific capacitance of 1335 F/g in 1 M KOH at a current density of 2.8 A/g with a remarkably high-rate capability of 953 F/g at 45.7 A/g and an excellent cycling stability (94.3% specific capacitance retained after 3000 cycles).

Self-assembled graphene-based structures, such as hydrogels and aerogels, were also extensively utilized for pseudocapacitor electrode applications [143]. In particular, Zhang et al. recently developed a plasma treatment approach to fabricate 3D N-doped graphene aerogel/Fe3O4 nanostructures, which showed a specific capacitance of 386 F/g in 6 M KOH electrolyte with a 97% retention rate after 1000 cycles [144]. In-situ growth of active materials on a graphene substrate can achieve high energy-storage properties because of the intimate interactions and efficient charge transfer between active nanomaterials and the conductive graphene substrate. Among other self-assembled graphene-based 3D structures, graphene hydrogels modified with different oxygen-containing groups using hydroquinones [145], MnO2/graphene hydrogel composites [146,147], graphene hydrogels modified with 2-aminoantraquinone [148], RuO2/reduced graphene-oxide hydrogels [149], freestanding polyaniline/reduced graphene-oxide composite hydrogels [150] and single-crystalline Fe3O4 nanoparticles directly grown on graphene hydrogels [151] have been studied. Details of their supercapacitive performance have been summarized in Table 2. Self-assembled porous graphene networks synthesized from various organic chemicals have also been used for supercapacitor applications. These structures are generally called organogels [152–155]. However, more studies are needed for better understanding the mechanism of charge storage in such organogels for improving their performance as efficient supercapacitor electrodes.

Similarly to EDLCs, it is highly desirable to improve the volumetric capacitance of graphene-based PCs for practical applications. In this context, Xu et al. recently reported a PC fabricated using a PANI and graphene composite monolith, which demonstrated 802 F/cm³ volumetric capacitance at 54% PANI loading and 66% of the capacitance was maintained when the current density increased by 100 times [156].

**Mesoporous carbon in pseudocapacitors**

Mesoporous carbon with functional groups can act as efficient pseudocapacitor electrodes. The use of strong activation reagents, such as sulfuric acid, nitric acid and ammonium persulfate, to activate mesoporous carbons can not only introduce micro-pores, but also introduce various functional groups with additional pseudocapacitance. For example, OMC activated by nitric acid possesses small-sized mesopores as well as functional groups, including –OH, –COOH and/or –C=O, and showed improvement in specific capacitance from 117 to 295 F/g at a 10-mV/s scan rate in aqueous alkali electrolyte [157]. By pyrolysing the iron fumarate metal organic frameworks, Wang et al. recently adopted a simple and scalable technique to synthesize porous carbon nanorods (Fe3O4-DCN) supported by 3D kenaf stem-derived macroporous carbon (KSPC) for high-performance supercapacitors [158]. The 3D-KSPC/Fe3O4-DCN was employed as an efficient electrode in supercapacitors to exhibit a high specific capacitance of 285.4 F/g in 2 M KOH at 1-A/g current density with the capacitance remaining at 220.5 F/g even after 5000 cycles at 2 A/g. Mesoporous carbon has also been composited with other active materials, including conductive polymers and metal oxides, as electrode materials in pseudocapacitors, as exemplified by PANI nanowires grown onto bimodal mesoporous carbon via chemical polymerization [159]. The resultant PANI/mesoporous carbon composite exhibited a specific capacitance of 517 F/g in 1 M H2SO4 and a retention rate of 91.5% after 1000 cycles due to the combination of the outstanding electrochemical properties of PANI and hierarchical porous structures of mesoporous carbon.

In the case of N-doped carbon (NC), previous studies suggested that four different types of nitrogen (pyrrolic N, pyridinic N, quaternary N/graphitic N and N oxides of pyridinic N) can be introduced into NCs, depending on the heat-treatment temperature and nitrogen sources [160,161]. Since conventional synthetic methods cannot produce NC with a single N component (e.g. pyrrolic N, pyridinic N or quaternary N/graphitic N), it is very difficult to determine the real role of different N-functional groups. NCs are reported to demonstrate not only double-layer capacitance, but also pseudocapacitance [51,162]. The mechanism of pseudocapacitance in NCs has yet been confirmed, although some preliminary studies have indicated that the presence of nitrogen atoms on the edges of graphene sheets (e.g. pyridinic N) played a crucial role [160].

**Hybrid carbon nanomaterials in pseudocapacitors**

As mentioned earlier, different carbon nanomaterials can be combined together to exhibit a synergetic effect. For pseudocapacitors, CNT and graphene have also been composited with PANI via in-situ polymerization [163]. The resultant
Table 2. Carbon nanomaterials in pseudocapacitors (PCs).

| Electrode | Electrolyte | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|-----------|-------------|----------------------|---------------|---------------|----------------------|------|
| (i) Carbon nanotube (CNT) | Poly(3,4-ethylenedioxythiophene) or PEDOT/MWCNT | 1 M LiClO 4 | 79 F/g at 1 A/g current | 5 kW/kg | 11.3 Wh/kg | 85% after 1000 cycles | 96 |
| | Polypyrrrole-coated MWCNT | 1 M KCl | 165 F/g at 0.5 mA/cm² current | – | – | 100% after 1000 cycles | 97 |
| | Polyaniline (PANI)/SWNT | 0.5 M H₂SO₄ | 706.7 F/g at 5 mV/s | – | – | – | 99 |
| | PANI/aligned CNT | PVA/H₃PO₄ (1:0.85, mass) | 308.4 F/g at | – | – | 73.9% | 100 |
| | RuO₂/MWCNT, TiO₂/MWCNT, SnO₂/MWCNT | 1 M H₂SO₄ | 138 F/g, 160 F/g, 93 F/g at 2 mV/s | 500 W/kg | 36.8, 40.2, 25 Wh/kg | – | 107 |
| | RuO₂/CNT | 0.5 M H₂SO₄ | 1170 F/g at 10 mV/s | – | – | 82% at 400 mV/s | 108 |
| | MnO₂/CNT | 0.2 M Na₂SO₄ | 642 F/g at 10 mV/s | – | – | 100% up to 700 cycles | 111 |
| | MnO₂/CNT | 1 M Na₂SO₄ | 201 F/g at 1 A/g current | 600 W/kg | 13.3 Wh/kg | 100% up to 10 000 cycles at 1 A/g | 112 |
| (ii) Graphene | GO-doped polyaniline (PANI) | 1 M H₂SO₄ | 531 F/g at 0.2 A/g current | – | – | – | 113 |
| | PANI nanowire/GO | 1 M H₂SO₄ | 555 F/g at 0.2 A/g current | – | – | 92% after 2000 cycles at 1 A/g | 114 |
| | Graphene sheet/PANI | 6 M KOH | 1046 F/g at 1 mV/s | 70 kW/kg | 39 Wh/kg | – | 115 |
| | PANI nanorods/graphene nanoribbon | 1 M H₂SO₄ | 340 F/g | 3.15 kW/kg, 9.47 kW/kg | 7.56 Wh/kg, 4.01 Wh/kg | 90% after 4200 cycles | 116 |
| | Co-PANI/graphene | 6 M KOH | 989 F/g at 2 mV/s | 1.581 kW/kg | 352 Wh/kg | 79% after 1000 cycles | 117 |
| | 3D graphene/PANI hydrogel | 6 M KOH | 334 F/g at 3 A/g current | – | – | 57% after 5000 cycles | 118 |
| | PANI/graphene | 1 M H₂SO₄ | 375.2 F/g at 0.5 A/g current | 1 kW/kg | 30.34 Wh/kg | 90.7% after 500 cycles at 3 A/g | 119 |
| | Graphene/poly(styrenesulfonyl acid-graft-aniline) | 0.1 M Bu₄NPF₆/acetonitrile | 767 F/g at 0.5 A/g current | 0.35 kW/kg | 208.8 Wh/kg | 92% after 5000 cycles | 120 |
| | Graphene/polypyrrole (PPy) nanotubes | 2 M H₂SO₄ | 400 F/g at 0.3 A/g current | – | – | 88% after 200 cycles at 1.5 A/g | 121 |
| Electrode                          | Electrolyte     | Specific capacitance | Power density | Energy density | Retention capability | Ref.  |
|----------------------------------|-----------------|----------------------|---------------|----------------|-----------------------|-------|
| PPy/GO                           | 0.1 M KCl       | 421.4 F/g at 2 mA current | –            | –              | –                    | 122   |
| Graphene/PPy nanowires           | 1 M KCl         | 728 F/g at 0.5 A/g current | –            | –              | 93% after 1000 cycles | 123   |
| Pillared GO/PPy                   | 2 M H2SO4       | 510 F/g at 0.3 A/g current | –            | –              | 70% after 1000 cycles at 5A/g | 124   |
| PPy/3D graphene foam             | 3 M NaClO4      | 350 F/g at 1.5 A/g current | –            | –              | 100% after 1000 cycles | 125   |
| PPy/Graphene                     | 0.1 M LiClO4    | 1510 F/g at 10 mV/s | 3 kW/kg | 5.7 Wh/kg | Stable up to 25 cycles | 126   |
| GO/MnO2 needles                   | 1 M Na2SO4      | 216 F/g at 0.15 A/g current | –            | –              | 84.1% after 1000 cycles at 0.2 A/g | 127   |
| Amorphous MnO2/GO                | 1 M Li2SO4      | 372 F/g at 0.5 A/g current | –            | –              | 92% after 4000 cycles at 0.5 A/g | 128   |
| MnO2/porous graphene             | 1 M H2SO4       | 256 F/g at 0.25A/g current | 24.5 kW/kg | 20.8 Wh/kg | 87.7% after 1000 cycles | 129   |
| MnO2/graphene                     | 1 M Na2SO4      | 310 F/g at 2 mV/s | –            | –              | 88% at 100 mV/s | 130   |
| Mn3O4/graphene sheets            | 6 M KOH         | 271.5 F/g at 0.1 A/g current | –            | –              | 100% after 20,000 cycles | 131   |
| Mn3O4/graphene paper             | Potassium polyacrylate (PAAK)/KCl | 321.5 F/g at 0.5 A/g current | –            | –              | – | 132   |
| 3D VOPO4/graphene                | 6 M KOH         | 527.9 F/g at 0.5 A/g current | –            | –              | 85% after 5000 cycles at 100 mV/s | 133   |
| RuO2/Graphene sheets             | 1 M H2SO4       | 570 F/g at 1 mV/s | 10 kW/kg | 20.1 Wh/kg | 97.9% after 1000 cycles at 1 A/g | 134   |
| Co3O4/graphene sheets            | 6 M KOH         | 243.2 F/g at 10 mV/s | –            | –              | 95.6% after 2000 cycles at 200 mV/s | 135   |
| Co3O4 nanoplates/graphene sheets | 2 M KOH         | 667.9 F/g at 1.25 A/g current | –            | –              | 81.3% after 1000 cycles | 136   |
| Co(OH)2/graphene sheet layers    | 1 M KOH         | 622 F/g at 2 A/g current | 15.8 kW/kg | 86.6 Wh/kg | 80% after 10,000 cycles at 10 A/g | 139   |
| Ni(OH)2/graphene                 | 1 M KOH         | 1335 F/g at 2.8 A/g current | 10 kW/kg | 37 Wh/kg | 100% after 2000 cycles at 28.6 A/g | 140   |
### Table 2. Continued.

| Electrode                        | Electrolyte | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|----------------------------------|-------------|----------------------|---------------|----------------|----------------------|------|
| $\alpha$-Fe$_2$O$_3$ nanotubes/rGO | 0.1 M K$_2$SO$_4$ | 181 F/g at 3A/g current | –             | –              | 108% after 2000 cycles at 5A/g | 141  |
| TiO$_2$/graphene                 | 1 M KOH     | 84 F/g at 10 mV/s    | –             | –              | 87.5% after 1000 cycles at 2 A/g | 142  |
| ZnO/graphene                     | 1 M KOH     | 62.2 F/g             | 8.1 kW/kg     | –              | 94.9% after 200 cycles | 143  |
| Fe$_3$O$_4$/N-doped graphene aerogel | 6 M KOH | 386 F/g at 5 mV/s | –             | –              | 153% after 1000 cycles | 144  |
| Graphene hydrogel functionalized using hydroquinones | 1 M H$_2$SO$_4$ | 441 F/g at 1 A/g current | –             | –              | 86% after 10000 cycles at 10 A/g | 145  |
| MnO$_2$/graphene hydrogel        | 1 M KOH     | 445.7 F/g at 0.5 A/g current | 6.4 kW/kg ~18 Wh/kg | 82.4% after 5000 cycles at 50 mV/s | 146  |
| MnO$_2$/rGO hydrogel and aerogel | 1 M Na$_2$SO$_4$ | 242 F/g at 1 A/g current | 0.82 kW/kg    | 212 Wh/kg      | 89.6% after 1000 cycles | 147  |
| Graphene hydrogel modified by 2-aminoanthraquinone | 1 M H$_2$SO$_4$ | 258 F/g at 0.3 A/g current | –             | –              | Slightly increased after 2000 cycles at 10 A/g | 148  |
| 15% RuO$_2$/rGO hydrogel         | 1 M H$_2$SO$_4$ | 345 F/g at 1 A/g current | –             | –              | 100% after 2000 cycles at 1 A/g | 149  |
| PANI/graphene hydrogel           | 1 M H$_2$SO$_4$ and 1 M H$_2$SO$_4$ + 0.4 M Hydroquinone | 223.82 and 580.52 F/g at 0.4 A/g current | 2.637 kW/l | 13.2 Wh/l | 87.5 and 70% after 5000 cycles at 10 A/g | 150  |
| Single-crystal Fe$_3$O$_4$/graphene hydrogel | 1 M KOH | 908 F/g at 2 A/g current | –             | –              | 69% at 50 A/g | 151  |
| Graphene organogel               | 1 M propylene carbonate in tetraethylammonium tetrafluoroborate | 140 F/g at 1 A/g | 16.3 kW/kg | 15.4 Wh/kg | 64.3% at 30 A/g | 152  |
| Polyethyleneimine-induced coagulated graphene-oxide nanosheets from the dispersion (iii) Mesoporous carbon | 6 M KOH | 46.3 mF/cm$^2$ at 0.1 A/g | –             | –              | 98% after 1000 cycles at 10 A/g | 153  |
| Oxygen/porous carbon ($S_{\text{BET}} = 578$ m$^2$/g, $D_p = 2.2, 5.3$ nm) | 6 M KOH | 295 F/g at 10 mV/s | –             | –              | 100% after 500 cycles at 10 mV/s | 157  |
| Fe$_3$O$_4$/porous carbon nanorods ($S_{\text{BET}} = 25.7$ m$^2$/g, $D_p = 14.9$ nm) | 2 M KOH | 285.4 F/g at 1 A/g current | –             | –              | 104% after 5000 cycles at 2 A/g | 158  |
| PANI nanowire/porous carbon ($S_{\text{BET}} = 599$ m$^2$/g, $D_p = 2.4, 5$ nm) | 1 M H$_2$SO$_4$ | 517 F/g at 0.1 A/g current | –             | –              | 91.5% after 1000 cycles at 0.5 A/g | 159  |
Table 2. Continued.

| Electrode                  | Electrolyte | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|---------------------------|-------------|----------------------|---------------|---------------|----------------------|------|
| (iv) Hybrid carbon nanomaterial |             |                      |               |               |                      |      |
| Graphene sheet/CNT/PANI   | 6 M KOH     | 1035 F/g at 1 mV/s scan | 94% after 1000 cycles at 200 mV/s | 163 |
| N-doped porous carbon/MWCNT (SBET = 1270 m²/g, Dp = 2.8 nm) | 1 M H₂SO₄ | 262 F/g at 0.5 A/g current | 164 |
| PANI-graphene/CNT         | 1 M KCl     | 271 F/g at 0.3 A/g current | 165 |
| Graphene-MnO₂/CNT         | 1 M Na₂SO₄/ polyvinylpyrrolidone (PVP) | 486.6 F/g at 1 A/g current | ∼1.7 kW/kg | 15 Wh/kg | 92.8% after 800 cycles at 1 A/g | 166 |
| Cobalt chloride carbonate hydroxide nanowire/AC | 1 M KOH | 1737 F/g at 2.5 mA/cm² current | 29.03 Wh/kg | 168 |
| Patronite (VS₄)/SWNT/rGO  | 0.5 M K₂SO₄ | 558.7 F/g at 1 A/g current | 13.85 kW/kg | 174.6 Wh/kg | 97% after 1000 cycles | 169 |
| PANI/GO/graphene          | 2 M H₂SO₄  | 793.7 F/g at 1 A/g current | 50.2 Wh/kg | 170 |
| Ni(OH)₂-graphene/CNT      | 2 M KOH     | 1065 F/g at 22.1 A/g current | 35 Wh/kg | 171 |

PANI/CNT/graphene composite showed a specific capacitance as high as 1035 F/g in 6 M KOH electrolyte at a 1-mV/s scan rate, which is comparable with that of PANI/graphene (1046 F/g) and higher than that of PANI/CNT (780 F/g) or pure PANI (780 F/g). Moreover, 94% of the initial capacitance was maintained after 1000 cycles, though the corresponding retention rates for the PANI/graphene and PANI/CNT composites were only about 52% and 67%, respectively. Similarly, various efforts have also been made to explore other ternary composites (e.g., metal oxide/CNT/graphene, conductive polymer/metal oxide/graphene, N-doped microporous carbon/CNT) [164–167]. Of particular interest, cobalt chloride carbonate hydroxide nanowire arrays (CCCH NWAs) with an average length of 8 mm were synthesized on a Ni foam surface via a simple hydrothermal process to show a specific capacitance as high as 1737 F/g in 1 M KOH at 2.5 mA/cm², and angood cycling stability with a capacitance retention of 87.3% after 2000 cycles at a current density of 7.5 mA/cm². An asymmetric supercapacitor based on CCCH NWAs as positive and activated carbon as negative electrodes exhibited an energy density of 29.1 Wh/kg and a power density of 100 W/kg with a good stability over a wide voltage range of 0–1.6 V [168]. Patronite (VS₄) has also been demonstrated to perform well in combination with SWNT and rGO to show a specific capacitance of 558.7 F/g in 0.5 M K₂SO₄ at 1-A/g current density in 0.5 M K₂SO₄ electrolyte and to deliver an energy density of 174.6 Wh/kg with a power density of 13.85 kW/kg [169]. Recently, the combination of both GO and pristine graphene with PANI has led to a specific capacitance of 793.7 F/g in 2 M H₂SO₄ at a 1-A/g current density [170]. This symmetric supercapacitor has exhibited an energy density of 50.2 Wh/kg at a power density of 2.14 kW/kg, attributable to the synergistic effects of the individual ingredient. A graphene and CNT stacked structure has also been conceived for supercapacitor applications [171,172]. Table 2 summarizes carbon-based pseudocapacitors.
Carbon-based hybrid supercapacitors

Hybrid supercapacitors (HSCs) are mainly introduced to bridge the gap between ESCs that have high power but low energy and batteries that have high energy but low power. Actually, in most cases, HSC consists of a capacitive carbon electrode matched with either a pseudocapacitive or a lithium-insertion electrode (Fig. 1) [173–176]. In HSCs, the combination of the Faradaic intercalation on cathode and non-Faradaic surface reaction on anode (Fig. 1c) provides an opportunity to achieve both high energy and power densities even without compromising the cycling stability and affordability.

The reported carbon-based electrodes so far used for the cathode in HSCs are graphite, CNTs, graphene, activated carbon (AC), 3D mesoporous carbons and different metal oxide or polymer-based carbon composites [177]. 3D graphene/MnO2 composite has a maximum specific capacitance of 1145 F/g, which is about 83% of the theoretical capacitance at a mass loading of 13% of MnO2 [178]. On the other hand, HSCs were fabricated using a Fe3O4 nanoparticle/graphene composite by a simple solvothermal method (Fig. 5). Fe3O4/graphene-based half-cell exhibited a high reversible specific capacity exceeding 1000 mAh/g at a current density of 90 mA/g with an excellent rate of capability and cycle stability [179]. When this composite was assembled in a Li-ion-based (LiPF6) HSC, energy densities of 204–65 Wh/kg and power densities from 55 to 4600 W/kg were achieved [179]. Besides, Lim et al. reported HSCs based on a mesoporous Nb2O5/carbon-composite anode and AC (MSP-20) cathode, showing excellent energy and power densities of 74 Wh/kg and 18 510 W/kg (at 15 Wh/kg), respectively, with a capacity retention rate of 90% at 1000 mA/g after 1000 cycles in the mixture electrolyte of LiPF6 (1.0 M)/ethylene carbonate and dimethyl carbonate (1:1 volume ratio) [180]. Li et al. reported a hybrid-type supercapacitor based on N-doped AC, which showed high material-level energy densities of 230 Wh/kg with a power density of 1747 W/kg and a capacity retention of 76.3% after 8000 cycles [181].

Carbon-based bendable supercapacitors (film-/fiber-shaped)

Along with the recent development of flexible and wearable electronics, flexible and wearable SCs, in either a thin film or fiber-shaped (coating, fabric/cloth, paper, textile, etc.), have attracted increasing attention as advanced power sources. Due to their large surface area, excellent mechanical and electrical properties, and high electrochemical stability, carbon nanomaterials are also promising as electrode materials for flexible supercapacitors (FSCs). In this context, Chen et al. produced flexible and transparent supercapacitors based on In2O3 nanowire/CNT heterogeneous films, and observed an increase in specific capacitance up to 64 F/g with increasing numbers of In2O3 nanowires (up to 0.007 mg) dispersed on the CNT films [182]. In another study, a 2-mm-thick film-based FSC made of MnO2 nanosheet-decorated carbon nanofiber electrodes was demonstrated to show a gravimetric capacitance of 142 F/g at a slow scan rate (∼10 mV/s) when the electrode was interfaced with PVA-H4SiW12O40·nH2O [183]. Other materials used for the electrode in FSCs include TiO2/MWNT/PEDOT composited carbon fibers [184] and various carbon papers made of fibers,
aerogel and nanotubes [185]. Liu et al. fabricated highly flexible porous films of carbon nanofibers (P-CNFs) by an electro-spinning technique combined with a Co ion-assistant acid corrosion process [186]. The resultant fibers have high conductivity and outstanding mechanical flexibility, with little change in their resistance under repeated bending many times, even up to 180°. The P-CNF electrode showed a specific capacitance of 104.5 F/g in 0.5 M H2SO4 at 0.2 A/g current, effectively improved cycling stability and 94% retention of specific capacitance after 2000 charging/discharging cycles, along with a retention rate of 89.4% capacitance after 500 bending cycles [186]. These remarkable performances are attributable to the high graphitization degree and the unique hierarchical pore structures of P-CNF [186].

A low processing cost for flexible electrode manufacturing is always desirable. Du et al. developed a low-cost, flexible and high-performance hybrid electrode based on a MnO2 nanotube (NT) and CNT composite film obtained through a vacuum-filtering method [187]. Due to the ultra-long 1D nanotube morphology, the synergetic effects between pseudocapacitive MnO2-NTs and conductive CNTs, the hierarchical porous structure of the freestanding film and the high mass loading of MnO2 (4 mg/cm2), the resultant MnO2-NT/CNT electrodes showed excellent mechanical and electrochemical performance with a volumetric capacitance of 5.1 F/cm3 in the polyvinyl alcohol (PVA)/LiCl gel electrolyte, a high energy density of 0.45 mWh/cm3 for the entire FSC volume and the retention of capacitance about 105% of the initial capacitance after 6000 cycles due to a self-activation effect. As shown in Fig. 6, these SCs can be integrated in wearable electronic devices as flexible power that can drive watches and light emitting diodes (LEDs).

Flexible supercapacitors have also been fabricated from conducting polymers with and without compositing with other electrode materials (e.g., CNTs, graphene). PANI, PPy and PEDOT possess high specific capacitances of 1284, 480 and 210 F/g, respectively [188]. PPy is a popular polymer electrode material for FSCs due to its high environmental stability, excellent redox activity and easy availability. Moreover, the electrochemical properties of PPy can further be enhanced by compositing with CNTs, graphene or their hybrid/composites. Recently, Yesi et al. prepared films of CNT-PPy core–shell composite by growing CNTs directly on carbon cloth (CC) as a skeleton, followed by electropolymerization of PPy on the CNTs [189]. The direct fabrication of CNT-PPy on the flexible CC electrode increased the interfacial conductance and the ion transport between the electrode and electrolyte. The PPy/CNT-CC electrode thus prepared exhibited 1038 F/g gravimetric capacitance per active mass of PPy and up to 486.1 F/g per active mass of the PPy/CNT composite, with excellent mechanical flexibility and cycle stability up to 10 000 cycles with 18% capacitance reduction. At the same time, the corresponding asymmetric supercapacitor (PPy/CNT-CC/CNT-CC) showed a maximum power density of 10 962 W/kg and energy density of 3.9 Wh/kg at 1.4-V potential.

For most solid-state supercapacitors based on freestanding graphene materials, the specific capacitance ranges from 80 to 135 F/g, while the corresponding theoretical value should be around 550 F/g. The observed difference is most probably due to the restacking of graphene sheets, and hence reduced active surface area of the graphene-based electrodes [187]. To overcome the π–π restacking of graphene sheets, numerous attempts have been made to control the electrode structure into, for example, porous 3D graphene hydrogels on Ni foam by CVD or freeze-drying GO. Mitchell et al. have further proposed a strategy to produce hierarchical and flexible nanosheets of NiCo2O4-graphene-oxide composite on nickel foam by using electrochemical deposition [190], which exhibited a specific capacitance of 1078 F/g in 3 M KOH electrolyte at 1-mA discharge current and a relatively poor cyclic stability (almost 45% reduction over 500 cycles). In another attempt to reduce the restacking of graphene layers in a 3D graphene electrode, Li et al. fabricated a solid-state asymmetric supercapacitor (ASC) based on flexible electrodes [191]. In this
case, the positive electrode was made from densely packed graphene sheets with intercalated Ni(OH)₂ nanoplates to give a gravimetric capacitance of 573 F/g and volumetric capacitance of 655 F/cm³ in 1 M KOH electrolyte at 0.2 A/g current density, excellent rate capability and cycling stability. On the other hand, the negative electrode was fabricated with CNT layers stacked in between highly dense graphene sheets. The asymmetric supercapacitor exhibited an energy density of 18 Wh/kg and power density of 850 W/kg at 1-A/g current density. When the current density increased up to 20 A/g, the corresponding energy density remained at 6.4 Wh/kg with a high power density of 17 kW/kg. Bending the device up to 180° caused no influence on the electrochemical performance [191]. With the aim to improve the specific capacitance in film-based FSCs, complex and hybrid structures like CNT/graphene and Mn₃O₄ nanoparticles/graphene paper electrodes with a polymer gel electrolyte of potassium polyacrylate (PAAK)/KCl were conceived and specific capacitance of 72.6 F/g at 0.5 A/g current was obtained [132].

As is the case for conventional ESCs discussed above, composites of CNT/graphene and conducting polymers have also been widely used in FSCs. In particular, Wang et al. recently synthesized polycrylic acid/PANI composites enhanced by nitrogen-doped graphene (NG) (NG-PAA/PANI) [192] and demonstrated that the CC electrodes containing 32 wt.% PANI and 1.3 wt.% NG showed a high capacitance of 521 F/g in 1 M H₂SO₄ electrolyte at 0.5 A/g (Fig. 7). A symmetric supercapacitor fabricated from 20 wt.% PANI-CC electrodes exhibited four times higher capacitance of 68 F/g at 1 A/g than the previously-reported SCs based on flexible PANI-CNT composites. The NG-PAA/PANI electrode retained the full capacitance over large bending angles with an energy density of 5.8 Wh/kg, a power density of 1.1 kW/kg, a superior rate capability of 81% at 10 A/g and long-term electrochemical stability (83.2% retention after 2000 cycles) [192]. By incorporating graphene and CNTs with PPy, Aphale et al. fabricated freestanding hybrid electrodes to show a specific capacitance of 453 F/g in 1 M H₂SO₄ at 5 mV/s scan rate (Fig. 8) [193]. Furthermore, the hybrid electrode demonstrated an ultrahigh energy density of 62.96 Wh/kg at a power density of 566.66 W/kg. Four such SCs assembled in a series successfully lit up a 2.2 V LED.

For the fiber-based FSCs, a wearable, fiber-shaped and all-solid-state asymmetric FSC was recently fabricated with a 1.5-V operating voltage using ultrathin MnO₂ nanosheets on carbon fibers as the positive electrode and graphene on carbon fibers as the negative electrode [194], leading to an energy density of 27.2 Wh/kg and power density of 979.7 W/kg. These values are higher than the latest reported for MnO₂-based asymmetric or symmetric supercapacitors, including MnO₂ nanotubes/activated graphene (22.5 Wh/kg at 146.2 W/kg) [195], MnO₂ nanoflowers/Bi₂O₃ nanoflowers (11.3 Wh/kg at 352.6 W/kg) [196], graphene foam (GF)-CNT-MnO₂/GF-CNT-PPy (22.8 Wh/kg at 860 W/kg) [197], 3D...
Figure 8. Fabrication and characterization of hybrid electrode. (a) Schematic representing the fabrication process of the nanocomposite electrodes. (b) Illustration of hybrid nanocomposite film forming a unique interface where graphene and CNT are embedded in situ during polymerization of PPy. (c, d) Optical image of the actual freestanding film on the graphite substrate with ~2 cm × 2 cm area. (e) Cross-sectional SEM micrograph showing layered formation of the polypyrrole film. (f) Layers of graphene-CNT coated with PPy during polymerization forming a nanocomposite PCG film. Reproduced with permission from ref. [193]. Copyright of Macmillan Publishers Ltd (2016).

graphene-MnO₂/3D graphene-MnO₂ (6.8 Wh/Kg at 62 W/Kg) [198], multilayer MnO₂-GO/porous carbon (energy density of 46.7 Wh/kg at power density of 100 W/kg) [199], 3D MnO₂/graphene hydrogel (21.2 Wh/kg at 0.82 kW/kg) [200] and 2D planar MnO₂/graphene (17 Wh/kg at 2.52 kW/kg) [201]. Moreover, this fiber-shaped asymmetric FSC further displayed sufficiently good bendability and mechanical stability for being connected in parallel and woven into cotton textiles (Fig. 9). By integrating this asymmetric FSC with a nanowire-based photodetector into a self-powered nanodevice, the fiber-shaped asymmetric FSC could efficiently power a photo detector without any requirement for an external bias [194].

Using a silica capillary column as a hydrothermal micro-reactor as depicted in Fig. 10 [202], Yu and coworkers demonstrated a large-scale manufacturing method for continuously producing carbon microfibers with a unique hierarchical structure composed of an interconnected network of CNTs with interposed nitrogen-doped reduced graphene-oxide sheets. The resultant carbon fiber electrode showed an electrical conductivity of 102 S/cm, volumetric capacity of 305 F/cm³ in sulfuric acid (measured at 73.5 mA/cm² in a three-electrode cell) and 300 F/cm³ in polyvinyl alcohol (PVA)/H₃PO₄ electrolyte (measured at 26.7 mA/cm³ in a two-electrode cell). The full micro-supercapacitor with PVA/H₃PO₄ gel electrolyte, free from binder, current collector and separator, has a volumetric energy density of 6.3 mWh/cm³, which is comparable to that of 4 V–500 mAh thin-film lithium battery while maintaining a power density more than two orders of magnitude higher than that of batteries as well as a long cycle life. This fiber-based, all-solid-state micro-supercapacitor was further successfully interfaced into miniaturized flexible devices to power a TiO₂-based ultraviolet photodetector and a light-emitting diode (Fig. 10). Another type of cable/wire-shaped flexible SC, as presented in Fig. 11, was fabricated on a stainless-steel wire using hydrothermal rGO nanosheets [203]. In redox additive electrolyte (PVA/H₃PO₄/Na₂MoO₄), this flexible SC exhibited a maximum length capacitance and energy density of 18.75 mF/cm (areal capacitance of 38.2 mF/cm²) and 2.6 mWh/cm (areal energy density of 5.3 mWh/cm²), respectively. The flexibility and stability of the above FSC device have also been investigated and three serially connected devices could be used to light up the green and blue LEDs (Fig. 11) [203]. A similar attempt has been made to demonstrate an rGO-based wearable SC on Cu wire [204]. While recent progress in FSCs is summarized above, interested readers are referred to some earlier review articles on flexible SCs related
Carbon-based stretchable and twistable supercapacitors (film-/fiber-shaped)

Along with the FSCs described above, stretchable and twistable FSCs are needed for advanced electronics, including polymer-based self-powered sensors, polymer light-emitting diodes, polymer solar cells and active matrix displays, to name a few [196]. As well as early reports on stretchable SCs, buckled SWNT/polydimethylsiloxane (PDMS) electrodes have drawn considerable attention, as they could show a strain up to 140% without any change in resistance [206,207]. The use of crumpled graphene papers reduced the cost and complexity for fabricating stretchable and high-performance electrodes for SCs [208,209]. The crumpled-graphene-paper-based electrode demonstrated high stretchability up to 300% linear strain and 800% aerial strain with a high specific capacitance of 196 F/g in H3PO4-PVA electrolyte and reliability up to 1000 stretch/relax cycles [208].

In addition, Kim et al. have reported a delamination-free stretchable supercapacitor, in which all the component layers were prepared with a single matrix composed of an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and a polymer, poly(vinylidene fluoride-hexafluoropropylene), as an electrolyte and a supporting layer, respectively, in the stretchable supercapacitor [210]. The electrode layer was fabricated by incorporating CNTs in the common (polymer) matrix with all the layers being seamlessly fused into one body by dissolving the surface of the composite with acetone. The operational cell voltage was as high as 3 V due to the use of ionic liquid-based gel electrolytes. Specific electrode capacitance and areal cell capacitance were 67.2 F/g and 12.7 F/cm2, respectively. The standard deviations of the capacitance were only ±2.1% and ±1.4%, respectively, after 500 cycles of the lateral and radial stretches at 0.5 strain.

Polypyrrole (PPy)-coated MnO2 nanoparticles were deposited onto CNT-based textile supercapacitor electrodes, which increases by 38% the electrochemical energy storage of MnO2/CNT-based flexible (13% bend) and stretchable (21% tensile strain) supercapacitors (Fig. 12) [211]. A specific capacitance of 461 F/g in H3PO4-PVA electrolyte was reported at 0.2-A/g current density, which was attributed to the delamination prevention of MnO2 nanoparticles by PPy coating. Furthermore, the capacitance retention was 96.2% even after 750 000 bending (13%) cycles [211].

A thin SWNT film and a honeycomb PDMS structure have been utilized as electrode materials and stretchable substrate supports for fabricating stretchable micro-supercapacitors (MSC) [212]. An array of 4 × 4 MSCs showed that the maximum strain in the MSC regions was almost 5 orders of magnitude lower than that the applied strain (of about 150%), and the device capacity remained same even at 150% stretch. Yun and coworkers constructed a stretchable MSC of practical significance, where a stretchable patterned graphene gas sensor driven by integrated micro-supercapacitor array on
Figure 10. (a) Schematic of the fiber synthesis process by injecting a homogeneous solution containing acid oxidized SWNTs, GO and EDA through a pump into a flexible silica capillary column, followed by in-situ thermal treatment in an oven at 220 °C for 6 h before a continuous fiber was pushed into a water reservoir by a pressurized nitrogen flow. (b) Photograph of the as-prepared fibers collected in water. (c) A dry fiber with diameter of ∼50 mm and length of ∼0.5 m (∼20 inches). (d) Planar structures obtained by bending fibers. (e) Compressed and stretched fiber springs. (f) A knitted textile fabricated from fibers. All scale bars: 0.5 cm. (g) Schematic of a micro-SC constructed using two fiber-3 electrodes on a polyester (PET) substrate. (h) Capacitance retention after 1000 cycles up to 90° bending angle. Inset: Photograph of a bent micro-SC. (i) Current response assembly of the ultraviolet photodetector based on the TiO2 nanorod array powered by the micro-SC. Reproduced with permission from ref. [202]. Copyright of Macmillan Publishers Ltd (2014).

the same deformable substrate, as demonstrated in Fig. 13 [213]. The patterned MSCs, which consisted of PANI-wrapped multiwalled carbon nanotubes (MWNTs) and an ion-gel electrolyte of poly(ethylene glycol)diacrylate and 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulfonyl) imide, exhibited excellent electrochemical performance under a uniaxial strain of 50% and a biaxial strain of 40%; their initial performance (capacitance of 6.1 F/cm³ at 5-mA/cm³ current) characteristics were retained even after 1000 cycles of repetitive uniaxial (50%) and biaxial (40%) stretching. Moreover, the patterned graphene sensor successfully detected NO2 gas for longer than 50 min via integration with MSCs using the serpentine interconnections even under uniaxial stretching by 50%. Such a hybrid combination of SCs with other practical electronic devices is highly desirable for near-term...
applications. However, much more attention must be given to further improving capacitive storage capability in flexible and stretchable supercapacitors. Buckled CNT film was also investigated for stretchable electrodes in SCs, as shown in Fig. 14a–c [214]. A comparative study between PANI composites of buckled CNT with and without nitric acid treatment revealed that acid-treated buckled CNT@PANI electrodes exhibited a higher specific capacitance of 1147.12 mF/cm² in H₃PO₄-PVA electrolyte at 10 mV/s [214]. This observation can be correlated with the formation of better interfacial bonding between acid-treated CNTs and PANI. The acid-treated electrode also showed an energy
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(a) Schematic illustration of the fabrication of polypyrrole−MnO2-coated textile supercapacitor. (b) Schematic for bending test was performed on polypyrrole−MnO2-coated supercapacitor. (c) Cyclic voltammetry of supercapacitor under 13% bending strain. Reproduced with permission from ref. [211]. Copyright of American Chemical Society (2015).

density from 31.56 to 50.98 μWh/cm² with power density changing from 2.294 to 28.404 mW/cm² at the scan rate of 10–200 mV/s. The corresponding supercapacitor sustained an omnidirectional strain of 200%.

In the case of fiber-shaped stretchable and twistable SCs, recently, yarn-based SCs have been demonstrated, which consist of core–shell-structured coiled electrodes with pseudocapacitive CNT-cores and MnO2-shells, as shown in Fig. 14d and e [215]. The linear and volumetric capacitances of the coiled yarn were determined to be 2.72 mF/cm and 34.6 F/cm³, respectively. Interestingly, around 84% of its static capacitance was retained after being reversibly stretched by 37.5% strain, while 96.3% dynamic capacitance was maintained during 20% strain deformation despite the extremely high strain rate of 6%/s. The yarn supercapacitors exhibited 95% or 98.8% capacitance retentions after many stretching/releasing or charge/discharge cycles [215]. Stretchable coaxial fiber-shaped SCs have also been fabricated using CNT sheets wrapped on an elastic fiber using a polymer gel sandwiched between the two coaxial CNT layers as the electrolyte and separator as well [216,217].

Transparent SCs have also become important for various optoelectronic applications. Indeed, transparent energy-storage devices are highly desirable for automobile/building windows or personal electronics with high aesthetic appeal. In this regard, a simple dry press transfer technique has been used to transfer thin SWNT films to transparent substrates to prepare transparent and flexible EDLCs with a transparency of 92% at 550 nm and high transparency over visible light and near infrared (NIR) wavelengths [218]. The resultant films showed an extremely high mass specific capacitance of 178 F/g (which is 482 F/g when calculated per mass of carbon) in PVA/H3PO4 electrolyte and area specific capacitance of 552 μF/cm² compared to other reported carbon-based flexible and transparent EDLCs [219]. The films were also highly stable in terms of specific capacitance over 10 000 loading cycles [218]. Chen et al. also fabricated graphene-based transparent and flexible SCs [209], which are attractive for various portable electronic devices. Table 3 summarizes carbon-based flexible, stretchable, wearable as well as transparent supercapacitors.

The advantages of using carbon materials for supercapacitor electrodes lay in the facts that they are highly conductive, binder-free and flexible with a large surface area and excellent properties intrinsically associated with different carbon allotropes. Carbon materials are Earth-abundant and environmentally friendly with respect to metal- or polymer-based electrode materials. Through using flexible carbon materials in supercapacitors, it would be possible to reduce the unnecessary use of metal foils (such as Al) as the current collector. It is also possible to eliminate polymer-binders or other conductive additives. Therefore, the use of carbon materials can propel the flexible supercapacitors to be lighter, portable and more easily manufactured. For many practical applications, however, their efficiencies still need to be improved by combining flexible carbon materials with pseudocapacitive materials (such as, metal oxides and polymers).
Figure 13. (a) Schematic definition of the biaxial strain $\varepsilon_{\text{biaxial}}$. (b) Optical microscope image of the MSC array (left) and the strain distribution estimated by FEM analysis (right) under a biaxial strain of 40%. (c) Optical images (left) and the results obtained from FEM analysis (right) of a serpentine interconnection in various uniaxial stretching states. The cross-sectional view shown is for a strain of 50%. Reproduced with permission from ref. [213]. Copyright of Elsevier (2016).

Carbon-based ultrafast supercapacitors for ac-line filtering

Alternating current (ac)-line filtering by using ultrafast supercapacitors is essential for domestic power usage in order to remove undesired high-frequency noises. ac electricity has a frequency of either 50 or 60 Hz. The combination of various nonlinear loads from different electronic devices in domestic requirements, portable electronics, automobiles and medical appliances often induces higher-order harmonics ($>120$ Hz) of the basic generating frequency [220]. In order to protect electronic devices from such voltage ripples, aluminum electrolyte capacitors (AECs) are used for ac-line filtering [221–223]. However, AECs have low specific capacitance, and hence occupy a large space and volume in electronic circuits. In this regard, supercapacitors, possessing specific capacitance of 2–5 orders higher in magnitude than that of AECs, could be used for effective ac-line filtering with very negligible occupied space or volume in capacitive components [224,225]. A supercapacitor generally acts like a resistor at 120 Hz after being introduced into transmission lines [223]. The typical resistor–capacitor (RC) time constant for a supercapacitor is around 1 s, associated with the high electrochemical series resistance and microporous structure of supercapacitor electrodes, which is far too long to be useful for the common application of 120-Hz filtering ($\sim 8.3$ ms period)—indicating the necessity for smoothing the leftover ac ripples in most line-powered electronics [226]. This is mainly because of the fact that unsuitable pore structures of supercapacitor electrodes impede high-rate ion diffusions or their high resistances restrict efficient charge transfer [227]. Thus, the design and fabrication of highly conductive electrodes with optimized micro-/nano-architectures for facile electron/ion transportations can improve the performance for ac-line filtering. Thus, high-surface-area materials with less inherent porosity have been studied for such applications.

Among a variety of other electrode materials, including onion-like carbon [228] and CNTs [229,230], carbide-derived carbon [231], metal oxides [232], polymers [233] and mesoporous carbons [225], utilized to improve related rate capability for ac-line filtering, graphene-based materials and graphene/CNT hybrid structures have recently emerged to be promising over conventional carbon materials because of their superior electrical conductivity and high specific surface area [227,234,235]. Graphene and porous carbon composites have also been demonstrated to be excellent ac-line filters, though their energy-storage capabilities still need to be improved [236].
Figure 14. (a) SEM images of buckled structures formed in CNT films at 50% omnidirectional prestrain. (b) Digital images of buckled CNT film at various stretching states. (c) Specific capacitance variation for CNT/PANI SCs with scan rate. Reproduced with permission from ref. [214]. Copyright of American Chemical Society (2016). (d) Schematic illustration for the complete solid-state coiled supercapacitor, which comprises two symmetric MnO₂/CNT core-shell-coiled electrodes and gel electrolyte. (e) Stress loading/unloading curves of the hybrid MnO₂/CNT coiled electrode with tensile strains from 20% to 40%. Reproduced with permission from ref. [215]. Copyright of Wiley (2016).

Lim et al. recently demonstrated that the substitutional pyridinic nitrogen dopant sites in carbon nanotubes can selectively initiate the unzipping of CNT side walls at a relatively low electrochemical potential (0.6 V) [235]. The resultant nanostructures consisting of partially zipped and/or unzipped graphene nanoribbons wrapping around carbon nanotube cores maintain the intact 2D crystallinity with well-defined atomic configuration at the unzipped edges (Fig. 15). The synergistic interaction between the large surface area and robust electrical connectivity of the unique nanoarchitecture led to ultrahigh-power supercapacitor performance, which can serve for ac filtering with the record high-rate capability of 85° (very close to that of AECs, 83.9°) of phase angle at 120 Hz. Lin et al. also fabricated a 3D graphene/CNT carpet (G/CNTC)-based micro-supercapacitor on nickel electrodes [237]. The G/CNTC showed an 81.5° phase angle at a 120-Hz frequency. However, much work still needs to be done in order to realize supercapacitors having both ac-line-filtering capability and excellent charge-storage capability for practical applications.

**SUMMARY AND PERSPECTIVES**

Carbon nanomaterials, including 1D CNTs, 2D graphene, 3D mesoporous carbon and their composites with conductive polymers or metal oxides, have been widely used as electrodes in supercapacitors, such as EDLCs, PCs and HSCs. Generally speaking, pure carbon nanomaterials without any functional groups are useful as EDLC-electrodes because of their high specific surface area and excellent electrical conductivity. The advantages of EDLC include its high-rate capability and outstanding cyclic stability (e.g. retention of 95%~100% after 1000~10 000 cycles). The specific capacitance for pure carbon nanomaterials in EDLC has been demonstrated to be in the range of 10~300 F/g. For carbon-composite nanomaterials, the specific capacitance can be increased by one order of magnitude: generally 100~1000 F/g. By compositing carbon nanomaterials with other materials having pseudo-capacitances (e.g. conducting polymers, metal oxides or hydroxyls), therefore, the energy density can be largely improved, but their rate capability and cyclic stability may decrease to 60~90% after 1000 cycles.

Numerous recent efforts have been made to improve the electrochemical performance of the supercapacitors based on carbon nanomaterials by improving their specific capacitance, energy density, power density, rate capability and/or cyclic stability. The design and development of advanced 3D electrode structures and compositing carbon nanomaterials with other active materials have been demonstrated to be effective approaches to high-performance carbon-based SCs. Hybrid supercapacitors can fill the gap between a supercapacitor and a
Table 3. Carbon nanomaterials in flexible, stretchable, wearable and transparent supercapacitors.

| Electrode | Electrolyte | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|-----------|-------------|----------------------|---------------|---------------|----------------------|------|
| (i) Flexible | | | | | | |
| CNT-graphene/MnO$_2$-graphene (flexibility: bendable and twistable) | Potassium polyacrylate (PAAK)/KCl | 72.6 F/g at 0.5 A/g | 22.9 Wh/kg | 86% after 10 000 cycles at 10 mV/s | 132 |
| MnO$_2$/carbon nanofiber | PVA-KOH, PVA-H$_2$SiW$_{12}$O$_{40}$-nH$_2$O | 100 F/g, 142 F/g at 5 mV/s scan | – | – | 60%, 28% at 100 mV/s | 183 |
| TiO$_2$/MWCNT | 1 M H$_2$SO$_4$ | 36.8 F/g at 20 mV/s scan | – | – | 184 |
| Porous carbon nanofibers (flexibility: no degradation after 100 times complete bending) | 0.5 M H$_2$SO$_4$ | 104.5 F/g at 0.2 A/g current | 3.22 Wh/kg | 94% after 2000 cycles at 1 A/g | 186 |
| MnO$_2$ nanotune/CNT (flexibility: no degradation on bend and twist) | Polyvinyl alcohol (PVA)/LiCl | 29.3 F/g at 0.5 mA/cm$^2$ current | 0.45 mWh/cm$^3$ | 105% after 6000 cycles at 1.2 mA/cm$^2$ | 187 |
| CNT (core)/PPy(shell) (flexibility: no degradation after 20 bending cycles) | 0.5 M H$_2$SO$_4$ | 48.61 F/g at 1.25 A/g current | 3.9 Wh/kg | 82% after 10 000 cycles at 8 A/g | 189 |
| NiCo$_2$O$_4$-GO (flexibility: no degradation up to 180° bending and complete twisting) | 3 M KOH | 1078 F/g at 1 mA current | – | – | ~58% after 100 cycles at 3 mA | 190 |
| Ni(OH)$_2$/dense stack of graphene sheets (flexibility: no degradation up to 180° bending) | 1 M KOH | 573 F/g at 0.2 A/g current | 8.5 kW/kg | 9 Wh/kg | 89% after 2000 cycles | 191 |
| N-doped graphene–polyacrylic acid (PAA)/PANI (flexibility: no degradation up to 135° bending) | 1 M H$_2$SO$_4$, H$_2$SO$_4$-PVA | 521 F/g at 0.5 A/g current | 1.1 kW/kg | 5.8 Wh/kg | 83.2% after 2000 cycles at 1 A/g | 192 |
| PPy/CNT-graphene (flexibility: not demonstrated) | 1 M H$_2$SO$_4$ | 453 F/g at 5 mV/s scan | 566.66 W/kg | 62.96 Wh/kg | – | 193 |
| rGO coated on stainless-steel wire (flexibility: no degradation after 180° bending) | PVA/H$_3$PO$_4$/Na$_2$MoO$_4$ polymer gel | 38.2 mF/cm$^2$ at 0.5 mA current | 5.3 microWh/cm$^2$ | 63.7 microW/cm$^2$ | 100% after 2500 cycles | 203 |
| (ii) Flexible and wearable | | | | | | |
| MnO$_2$ sheets/carbon fiber (flexibility: highly flexible wire without any degradation on bending) | PVA-LiCl | 634.5 F/g at 2.5 A/g current | 979.7 W/kg | 27.2 Wh/kg | 95.2% after 3000 cycles at 20 A/g | 194 |
| SWNT/N-doped rGO fiber (flexibility: 97% of capacitance retention after 1000 times bending at 90°) | 1 M H$_2$SO$_4$ | 305 F/cm$^3$ at 26.7 mA/cm$^3$ current | 1.085 W/cm$^3$ | 6.3 mWh/cm$^3$ | 93% after 10 000 cycles at 250 mA cm$^{-3}$ | 202 |
| Graphene aerogel on Cu wire (flexibility: 99% of capacitance retention after 1000 times bending at 160°) | Polyvinylpyrrolidone (PVP) | 12.5 F/cm at 5 mV/s scan | – | – | 95% after 10 000 cycles at 1 A/g | 204 |
| Electrode                                      | Electrolyte                           | Specific capacitance | Power density | Energy density       | Retention capability | Ref.  |
|-----------------------------------------------|---------------------------------------|----------------------|---------------|----------------------|----------------------|-------|
| Buckled SWNT macrofilm (no degradation after 30% strain) | 1 M Et4NBF4/propylene carbonate       | 54 F/g at 1 A/g current | 1 kW/kg       | ~3.5 Wh/kg           | 96.3% after 1000 cycles with 30% strain at 1 A/g | 206   |
| SWNT/polydimethylsiloxane (PDMS) (can sustain 120% strain) | H2SO4-polyvinyl alcohol (PVA)         | 53 F/g at 10 A/g current with 120% strain | 32 kW/kg      | –                    | 100% after 1000 cycles under 120% strain | 207   |
| Crumpled graphene hydrogel (can sustain 300% linear and 800% areal strain) | H3PO4-PVA                             | 166–196 F/g at 1 A/g current | –            | 30 Wh/kg under 300% axial strain | 95% after 1000 stretching cycles with 200% strain | 208   |
| Double-walled CNT/poly(vinylidene fluoride-hexafluoropropylene (can sustain 50% lateral strain) | 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide | 67.2 F/g at 2.5 A/g current | 3.7 kW/kg | 20.3 Wh/kg with 50% lateral strain | 97.9% after 500 cycles of 50% lateral strain | 210   |
| PPy-MnO2/CNT textile (can sustain 21% tensile and 13% bending strains) | H3PO4-PVA                             | 461 F/g at 0.2 A/g current | 22.1 kW/kg | 31.1 Wh/kg           | 96.2% after 750 000 bending (13%) cycles | 211   |
| SWNT/honeycomb PDMS (can sustain 150% stretch) | H3PO4-PVA                             | 3.3 F/cm² at 10 V/s scan | –            | –                    | 100% after 150% stretch | 212   |
| PANI/MWCNT (can sustain 50% uniaxial strain and 40% biaxial strain) | poly(ethylene glycol) diacrylate/ Et4NBF4 | 6.1 F/cm³ at 5 mA/cm³ current | 3 mW/cm³ | 3.2 mWh/cm³          | Within 95% up to 1000 cycles of 50% uniaxial strain | 213   |
| Buckled CNT/PANI (can sustain 200% strain) | H3PO4-PVA                             | 364.6 F/g at 10 mV/s scan. | 2.34 to 30.04 mW/cm² | 30.2 to 54.6 μWh/cm² | 96.9% after 20 stretching cycles | 214   |
| MnO2-CNT (shell)/nylon (core) (can sustain 150% strain) | PVA-LiCl                               | 5.4 mF/cm (linear), 40.9 mF/cm² (areal) | 66.9 μW/cm² | 2.6 μWh/cm²          | 87.8% with 17.1% strain for 0–120% strain cycles | 215   |
| CNT sheets coated on elastic fiber (can sustain up to 75% strain) | H3PO4-PVA                             | 41.4 F/g at 0.1 A/g current | 421 W/kg     | 0.363 Wh/kg          | 95% after 100 stretching cycles at 75% strain | 216   |
| PEDOT-PSS/CNT/Elastic wires (can sustain up to 350% strain) | H3PO4-PVA                             | 122.8 F/g at 0.5 A/g current | –            | –                    | 106% after 100 stretching cycles with 200% strain | 217   |
| In2O3 nanowire/CNT (~60% transparent at 600 nm and flexible) | 1 MLiClO4                              | 64 F/g at 0.5 A/g | 7.48 kW/kg | 1.29 Wh/kg           | 82.8% after 500 cycles at 0.5 A/g | 182   |

**Table 3. Continued.**
Table 3. Continued.

| Electrode                                      | Electrolyte       | Specific capacitance | Power density | Energy density | Retention capability | Ref. |
|------------------------------------------------|-------------------|----------------------|---------------|-----------------|----------------------|------|
| Wrinkled graphene (57% transparent at 550 nm, can sustain bending and 40% strain) | PVA/H₃PO₄/H₂O     | 7.6 F/g at 1 V/s scan | –             | –               | 100% after 100 cycles with bending or 40% strain | 209  |
| SWNT (92% transparent at 550 nm and flexible up to 180°) | PVA/H₃PO₄        | 178 F/g at 0.53 A/g current | –             | –               | 100% up to 10 000 cycles | 218  |

Flexible, stretchable and even transparent supercapacitors are also very important for the next generation of wearable electronics. Although compositing graphene and CNT with appropriate conducting polymers has been demonstrated to be an effective approach towards SCs with excellent flexibility and strain resistance while retaining their electrochemical performance, conducting polymers often lose their inherent electrical properties in composites.

As can be seen from the above discussions, great progress has been achieved in the development of carbon-based supercapacitors, including EDLCs, PCs and HSCs in either traditional or flexible, stretchable and even transparent forms. Compared with batteries, SCs possess a high power density, short charging time, good discharge/charge cyclability and broad-temperature-range applicability. These advantages make SCs useful for various potential applications, including hybrid electric vehicles, renewable-energy-storage gadgets and portable electronics. However, there are still some challenges that need to be addressed to further improve the performance of carbon-based electrodes.

First, carbon is well known to have a lower specific capacitance as compared to other pseudocapacitive materials, such as metal oxide and conducting polymers. Therefore, the carbon content, nature of heteroatom dopant(s), if any, and its crystallinity or connectivity of a carbon network within composite electrodes must be well understood in order to obtain high electrode performance. Second, it is also essential to further improve electrolytes and separators for efficient charge storage as well as high-rate capability and cycling stability. Third, SCs with excellent ac-line-filtering capability still need to be developed to bring advanced SC technologies to the marketplace for various practical applications, ranging from self-powered wearable optoelectronics to electrical vehicles. Finally, the energy and power densities of
SCs need to be further improved while their weight, volume and cost to be further reduced.

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