Functional graphene film macroscopic assemblies for flexible supercapacitor application

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Abstract. The ever-increasing demand for flexible/wearable electronic devices has stimulated the rapid development of flexible supercapacitors with enhanced electrochemical performance and mechanical flexibility. Graphene-based materials are promising candidates for high-performance flexible supercapacitor electrodes due to their large surface area, high conductivity, low weight and superior mechanical flexibility. In this review, after a brief introduction, we mainly discuss different strategies to enhance performances of graphene-based electrode in recent years. Their fabrication process and electrochemical performances are discussed and compared. Then two types of flexible supercapacitors, namely, fiber-type supercapacitor and micro-supercapacitor, are also discussed in detail. We also present our point of view in our discussion.

1. Introduction

1.1. Supercapacitor

Supercapacitors, also known as ultracapacitors, as a form of energy carriers, have the ability to charge or discharge within seconds despite its huge capacitance. In addition, its extremely long life cycle (100 000 cycles) and simple structure also account for its increasing attention. Despite of the disadvantage of low specific energy density compared with other energy carriers such as lithium batteries, its advantages apparently outweigh its disadvantages.

There’re two types of supercapacitors. As shown in Figure 1, traditional supercapacitors have a double layer structure, with a positive and a negative electrode separated by a insulating separator and the rest full of iron- conducting electrolyte. Electrode is the key component of a supercapacitor. This double-layer supercapacitor depends on its electrodes’ large surface area to store energy though what we call a non-Faraday process where none chemical reaction happens. Thus the capacitance of supercapacitors rests heavily on the surface area of the electrode.

Another type is pseudo-capacitors which store energy through the surface chemical reactions. This mechanism resembles the Faraday process happened in the well-documented Li-batteries. That some redox-active materials use fast, reversible redox reactions at the surface of active materials is also known as the pseudocapacitance. Due to the introduction of chemical reactions, it’s estimated that it can increase the capacitance to 10~100 times but with a shortened life cycle.
1.2. Graphene

A wide range of electrode materials have been explored within last decades. Generally, they fall in three categories which are carbon-based materials, conductive polymers and transition metal oxide. Carbon-based materials like carbon hydrogel, carbon nano-tubes and graphene are extensively studied in double-layer capacitors. MnO2 and RuO2 are typical examples of conductive metal oxide. Conductive polymers such as PPY(polypyrrole) and PPT(polythiophene) are also used as electrode materials.

Graphene, first reported by Novoselov and his co-workers at the University of Manchester, was structurally characterized as a 2D sheet of carbon atoms arranged in a hexagonal configuration with atoms bonded by sp2 bonds. It’s unique properties including a large specific surface area\(^1\) (2630 m\(^2\) g\(^{-1}\)), high conductivity\(^2\), good chemical and thermal stability\(^3\), wide potential window\(^4\), and excellent mechanical flexibility\(^5\) have attracted world-wide attention. The capacitance of a perfect double-layer graphene was outstandingly estimated up to be \(\sim 550 \text{ F g}^{-1}\) as long as the entire surface area was utilized\(^6\). However, facts often fall short of dreams. These surprising characteristics are prone to defects, which are inevitable during the producing process.

A variety of methods were developed to produce graphene including mechanical exfoliation\(^7\), epitaxial growth\(^8\) and chemical vapor deposition\(^9\) (CVD), reduction of graphene oxide. Mechanical exfoliation method has a low efficiency and thus unsuitable for mass production. Epitaxial growth method was operated under a high temperature in vacuum. Despite the high quality of its yields, its use was limited in labs. CVD method also produce high-quality graphene, like epitaxial growth method, its high cost sets the upper limits for its mass production. In comparison, the mass production was achieved by the reduction of GO (graphene oxide). As the now widely-used precursor of graphene, GO can be easily produced though a modified Hummer’s method\(^10\). When its key components, sulfuric acid and potassium permanganate\(^10, 24, 25\), are mixed together around 55\(^\circ\)C, a strongly oxidizing species (Mn2O7) was created. When graphite is exposed to it, a series of micro-detonation occurred to functionalize the carbon surface\(^26\). Heavily oxygenated GO sheets possess the maximum quantities of hydroxyl and epoxy groups bound on the basal planes in addition to partial carboxyl groups located at the edges\(^83\) Although the reduced GO(RGO/rGO) only have a mediocre quality due to the defects (residual oxygen-containing groups, vacancy, edges and deformation), this method permits continuous large-scale production and effective functionalization for further enhancement\(^11\). Different reducing agents like hydrazine hydrate\(^151\), hydroquinone\(^152\), dimethylhydrazine\(^153\), ascorbic acid\(^154\) and sodium borohydride\(^155, 156\) have been used to obtain graphene from graphite oxide precursor. The type of reducing agent and solvent always play a major role deciding the effective surface area and agglomeration of graphene sheets, which leads to better capacitive performance.

Figure 1. Typical structure of supercapacitors
Here, it’s worth noting that Kaner et al. used a standard LightScribe DVD optical drive to do the direct laser reduction of graphite oxide films to graphene. The produced films are mechanically robust, showing high electrical conductivity (1738 S m⁻¹) and specific surface area (1520 m² g⁻¹), and thus can be directly used in the construction of supercapacitors without the need for binders or current collectors. More recently, Tour et al. further improved this technique and used Teflon to produce fluorinated graphene (FG) without other fluorine source. The laser is part of a commercial laser cutting/scriving system that is found in most machine shops and, therefore, is a readily accessible tool. This laser-induced reduction is a highly advanced technique that is also compatible with commercial mass production.

Figure 2. Formation FG from Teflon. (a) Reaction scheme for the synthesis of FG. The apparatus is adapted from their previous work. The pressure (~3 atm) and the gas flow (~50 sccm) are controlled by the valve at the outlet. The forming powders were collected in the chamber. (b) High-resolution C 1s XPS of FG and Teflon. The peak position is corrected by the covalent CF₂ bond at 292.5 eV. (c) High-resolution F 1s XPS spectra of FG and Teflon. (d) Raman spectra of FG, and Teflon.

2. Graphene-based electrode materials

2.1. Activated graphene

Graphene was recognized as a highly promising material to construct a electrode of a double-layer supercapacitor for its large surface areas as aforementioned. Notwithstanding, graphene sheets are inclined to aggregate or re-stack through π-π stacking forces or vander Waals attractions between nanosheets which will unavoidably lead to a decrease of the capacitance of graphene sheets. In recent years, efforts have been dedicated to resolve this problem. As a replacement of pure graphene, activated graphene was deemed more suitable for electrode materials. R S Ruoff12 first reported that the specific surface area can be largely enhanced after chemical activation by KOH. An ultrahigh surface area up to 3100 m² g⁻¹ can be obtained, which provides a specific capacitance of 200 F g⁻¹ at 0.7 A g⁻¹ and a capacitance retention of 93.5% at 3.5 A g⁻¹. It’s believed that by going under the activation process, mesopores that can provide more surface area and thus entails superior supercapacitor performances, are introduced into a 2D lamellas structure13. Other chemical activation process was also explored. The H3PO4-activated graphene by Lei et al’14. has a surface area of 1145 m² g⁻¹ and a pore volume of 0.81 cm³ g⁻¹, which brings a capacitance of 204 F g⁻¹ at 0.2 A g⁻¹ and a capacitance retention of 68.6% at 30 A g⁻¹. Physical activation by CO2 was explored by Park et al15. His team managed to prepare graphene, which hosts a high capacitance of 278 F g⁻¹ at 5 mV s⁻¹ and a retention of 88.5% at 100 mV s⁻¹, with trimodal pore system through CO2 activation. Xia13 and his co-worker concluded that adjusting KOH/GO mass ratio or CO2 activation time can seriously affect the pore geometry and surface characteristics. Under optimal activation conditions, the KOH-activated graphene appeared as 2D lamellas with a bimodal micro-mesopore distribution and an ultrahigh...
specific surface area of 2518 m² g⁻¹, which gave a specific capacitance of 261 F g⁻¹ at 1 mV s⁻¹ and a capacitance retention of 98.5% at 5 A g⁻¹ after 1000 cycles. Comparatively, CO₂-activated graphene showed 3D curly morphology with a hierarchical micromeso-macroporous structure and an ultra-large pore volume of 3.08 cm³ g⁻¹, where an excellent rate capability of 86.1% from 0.5 to 10 A g⁻¹ could be implemented.

2.2. Graphene foams and sponges

According to energy storage mechanism for supercapacitors, pore size distribution, pore shape and structure play a key role in electrochemical performances of supercapacitors. Typically, macroporous cores can serve as ion-buffering reservoirs, mesoporous walls have a smaller ion-transport resistance and micropores allows for charge accommodation with a localized graphitic structure for enhanced electric conductivity.

Graphene-based foams and sponges in which 3D interconnected networks exhibit great potential for a wide range of applications due to its unique properties such as low weight, high porosity, large surface area and stable mechanical, thermal, electrical characteristics. Wang’s group and Zhang’s group first introduced an effective preparation of freestanding graphene foam based on a sacrificial template of low-cost Ni foam. After using CH₄ or ethanol as the carbon source for a CVD method, the prepared graphene showed a high conductivity because of the void of apparent defects. A patented method used a metal foam framework to fabricate 3D graphene foam. By implementing a chemical bath, the metal foam framework is removed from a uniform distributed metal and graphene composite, leaving a highly porous graphene structure which is measured to have a surface area of at least 500 m² g⁻¹. Chen’s group reported a ‘leavening’ method reduced graphene oxide foams. Leavening is process often used in baking to produce more chewable and porous breads by the means of adding steam or gas. In their experiment, they employed hydrazine vapor to initiate chemical reduction of GO with rapid evolution of gaseous species. SEM analysis clearly indicates the formation of a porous network with size ranging from sub-micrometers to micrometers. They own its porous structure to the rapid evolution of gaseous species (such as CO₂ and H₂O) during the chemical reduction process.

Normally, a GO sponge is derived from a hydrogel after undergoing a freeze drying or a critical point drying. The high solubility and hydrophilic edges of the formed GO allow it to be well dispersed at high concentrations. At a concentration of 1 to 15 mg ml⁻¹, the well dispersed GO solution can be directly reduced and freeze dried to form GO sponges. Instead of adopting a chemical reduction which may cause collapse of the sponge, the GO sponge can be reduced in high temperature in dry argon environment. Template guided growth method, a well-defined procedure, can also be used as an effective way to create graphene sponges. As shown in Figure 3, Cheng’s group adopted a CVD method, using methane as the carbon source, to deposit graphene sheets on a delicately prepared template of Ni foam. Then, Ni template was etched away via a hot 3 M HCL under the presence of a sacrificial PMMA layer to prevent the collapse of graphene network. After etching away Ni template, the PMMA was gradually removed by placing the CVD-G sponge in hot acetone, which was then evaporated to result in a high surface area graphene monolith (850 m² g⁻¹ by a BET analysis). Their as-prepared GF/PDMS composites showed high electrical conductivity and can withstand deformation to some extent. The results are shown in Figure 3. Without any assistance of various substrates, Liu’s group employed a simple method to fabricate graphene sponges via a vacuum centrifugal evaporating system. At a low temperature, the GO sheets are likely to form their network via van der Waals force during water evaporation due to the outward centrifugal force that is more dominant than the upward evaporation force. The as-prepared reduced GO-sponges showed a good elastic property by SEM analysis when bent to a large degree by a pincette and soon recovered to its original configuration.
Figure 3. a~f. schematic illustration of the synthesis of GF/PDMS composite. g. Electrical-resistance variation of a composite at a bend radius up to 2.5 mm in the first bend cycle. h. Electrical-resistance change of a composite when bending to a radius of 0.8 mm and then straightening for each cycle. c. Electrical-resistance change of a composite after 50% stretching and then releasing for each cycle. In each cycle, the composite was gradually stretched to a strain of 50% and then released to zero strain with the same stretching rate of 0.5 mm min\(^{-1}\). d. Electrical-resistance variation of the composite as a function of uniaxial tensile strain until fracture. The inset shows the stretching process.

2.3. Graphene hydrogels and aerogels

Graphene hydrogels or aerogels has a unique configuration that retains the excellent intrinsic properties of graphene sheets, holds large surface area, high electrical conductivity and excellent mechanical strength. Moreover, the realistic capacitance can be improved by facilitating charge transfer through the abundant porous framework. Shi19 and his group reported the early work on preparation of the graphene hydrogel through a facile treatment of GO suspension via a hydrothermal process. The specific capacitance of the graphene hydrogel supercapacitor can reach 175 F g\(^{-1}\) at a scan rate of 10 mV s\(^{-1}\). Jiang’s group33 used a mild and time-saving method to prepare graphene hydrogel. A hydrothermal reduction of GO with glucose as assistant enabled these binder-free graphene-hydrogel-glucose materials to have an admirable electrochemical performance and good cycling stability. The specific capacitance is up to 384.6 F g\(^{-1}\) at the current density of 1 A g\(^{-1}\) and still retains 88% after 5000 cycles at a scan rate of 100 mV s\(^{-1}\). In order to save time and huge amount of reducing agent, Liu et al.34 recently introduced a facile and effective method to prepare reduced-graphene-hydrogels through a hydrothermal process under the presence of trace amount of benzenediol. They believe benzenediol acts not only as a reducing agent to restore the conjugated
structure but also as a structure modifier to prevent the aggregation. Their as-prepared supercapacitor have specific capacitance of about 253 \( \text{F g}^{-1} \) at 1 mV s\(^{-1}\) and retained 98.1\% of the initial capacitance after 10,000 charging/discharging cycles. Banda et al.\(^{35}\) demonstrated a simple one-step procedure to produce highly reduced graphene hydrogels using hydrazine monohydrate as the reducing agent. When tested in aqueous supercapacitors, a capacitance of 123 \( \text{F g}^{-1} \) at 100 A g\(^{-1}\) could be achieved and an excellent cycling ability was observed with 93\% capacitance retention after cycling for 2000 cycles at a high current density of 100 A g\(^{-1}\). Yang’s group\(^{18}\) revealed a novel evaporation-induced drying method to remove water from graphene hydrogels, which resulted in a high density graphene aerogel with a volumetric capacitance as high as 376 \( \text{F cm}^{-3} \).

2.4. Graphene incorporated with spacers

Among numerous strategies\(^{41-48}\) developed to prevent the aggregation of graphene sheets, ‘spacers’ is one of the most cited and often used strategies. Wang et al.\(^{158}\) reported that by introducing inexpensive carbon black into the layered graphene assembly, the restacking of graphene sheets could be greatly mitigated. As a result of effective ionic and electronic transport, their pillared GP electrodes exhibits a more than 700\% improvement over the original GP electrode at a fast scan rate of 500 mV s\(^{-1}\). The specific capacitance of the pillared graphene paper is 138 \( \text{F g}^{-1} \) in aqueous electrolytes with only a negligible (3.85\% and 4.35\%) degradation of the specific capacitance after 2000 cycles. As shown in Figure 4, Cheng et al.\(^{41}\) successfully proved that ice could be utilized as spacers. Inspired by the freeze-drying process that a substance is first frozen and then water is removed by sublimation under vacuum, they created GO aerogels with a three-dimensional porous network structure during crystallization of absorbed water molecules of individual GO sheet. The as-formed GO aerogel with a porous structure was in situ converted into a graphene aerogel. When tested in a K\(3\text{Fe (CN)}_6\)-KOH
redox-electrolyte at a current density of 20 mA cm\(^{-2}\), they obtained a capacitance value of 1624 mF cm\(^{-2}\). It is known that GO surface contains multiple functional groups such as hydroxyl, epoxy groups on the basal plane and carboxylic groups along the edge\textsuperscript{42,43}, which provide the graphene sheets with versatile functionalization abilities. Yue et al. took advantage of these abundant functional groups to prevent the aggregation of graphene sheets. P-phenylenediamine (PPD), serving as a spacer, was covalently functionalized onto GO nanosheets through the reaction between amine groups of PPD and the epoxy groups on the basal plane of GO. The modified graphene sheet is capable of delivering a much higher specific capacitance and energy density of 282.33 F g\(^{-1}\) and 39.24 W h kg\(^{-1}\), respectively at a discharge current of 0.75 mA. The resultant electrode also displays excellent electrochemical stability of 92.82\% after 1000 charge-discharge cycles. In the same vein, Yu et al.\textsuperscript{45} used Diethylene glycol (DEG) to decorate the surface of GO sheets to alleviate the re-stacking process and reduce them into 3D highly porous graphene sheets. In the meantime, the oxygen-containing groups on DEG led to favorable wetting properties for electrolyte solution to fully utilize the large surface of graphene sheets. Based on such composite electrode material, a specific capacitance up to 237.8 F g\(^{-1}\) was achieved at 0.1 A g\(^{-1}\) and no obvious decline in capacity was observed after 2000 charge/discharge cycles. Analogously, Park et al.\textsuperscript{46} used a supermolecular approach to functionalize GO with Nafion, known as an amphiphilic molecule. Nafion not only serves as a spacer to prevent the aggregation but also increases wetting properties between electrodes and electrolyte. As a result, the interconnected functionalized GO provides smooth pathways for fast iron transport. An all-solid-state flexible supercapacitor was fabricated and the specific capacitance of the functionalized RGO was measured to be 118.5 F g\(^{-1}\), about two times higher than the 62.3 F g\(^{-1}\) reported for unadulterated RGO. Furthermore, their as-prepared supercapacitor showed great mechanical flexibility when CV curves remained almost the same rectangular shape and specific capacitance during the bending test. It's worth pointing out that Liu et al.\textsuperscript{40} demonstrated a strategy to make a folded structured graphene paper by mechanically pressing a graphene aerogel. The wrinkles and curves, after experiencing a fast deformation under pressure, were transformed into folds to prevent the restacking of graphene sheets. The resultant graphene paper showed a specific capacitance of 172 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\) and an excellent cycling stability of retaining 99\% capacitance over 5000 cycles at 20 A g\(^{-1}\).

2.5. Graphene/pseudo-capacitive material composites

As previously mentioned, supercapacitors based on graphene could achieve an electrical double layer capacitance as high as 550 F g\(^{-1}\), if their entire surface area is used. The actual observed gravimetric specific capacitance is usually lower than 300 F g\(^{-1}\), which leads to lower energy density. Pseudo-capacitive materials, which include transition metal oxides and conducting polymers such as RuO\textsubscript{2}50–253, Fe\textsubscript{3}O\textsubscript{4}54–55, CuO56, NiO57–59, MnO\textsubscript{2}60–65, Co\textsubscript{3}O\textsubscript{4}66–68, Ni(OH)\textsubscript{2}69, 270, polyaniline (PANi)\textsuperscript{71–74}, polypyrrole (PPy)\textsuperscript{75}, and polythiophene (PT)\textsuperscript{76–78} et al., have attracted researchers attention for its higher capacitance than graphene. However, these materials often suffer from particle aggregation, poor electrical conductivities (especially for metal oxides), inherent rigidity and structural degradation, leading to low power density, poor cycling stability and marginal flexibility\textsuperscript{49} and thus are unfit for supercapacitor of high performances. Since graphene possesses a large surface area, high electrical conductivity, light-weight, and flexibility, it won’t be strange for researchers to combine these pseudo-capacitive materials with graphene nanosheets, serving as structured scaffolds, to obtain a even higher capacitance, stability and mechanical flexibility.

2.5.1. Graphene/conducting polymers composites

PANi is widely used as a conducting polymer\textsuperscript{79} in electrodes to enhance the electrochemical performances of carbon materials for its apparent advantages such as low production cost, well-defined synthesis and high capacitance. Cheng et al.\textsuperscript{80} prepared graphene/PANi composite through a combination of flow-directed assembly and in situ anodic electropolymerization. The resultant composite has a favorable flexibility and electrochemical activity and exhibits relatively high gravimetric capacitance of 233 F g\(^{-1}\) and volumetric capacitance of 135 F cm\(^{-3}\) due to the PANi
deposited on the graphene surface. In contrast, Wu et al. [81] also used an in situ anodic electropolymerization to achieve a homogeneously dispersed PANi in graphene/PANI composites. The aniline monomer was first mixed with graphene oxide sheets in aqueous solution by sonication to form a homogeneous suspension before oxidation and reduction. They reported their highest specific capacitance to be 480 F g⁻¹ at a current density of 0.1 A g⁻¹. Shi et al. [73] prepared free-standing flexible graphene/PANI composite via a vacuum filtration approach. The composite showed a layered structure caused by the flow-assembly effect of graphene sheets during filtration and has a high specific surface area. A symmetric supercapacitor was prepared and tested. The results suggested a high capacitance of 155 F g⁻¹ and a good stability of a 94% retention after 800 charge/discharge cycles. Yu et al. [82] demonstrated a simple one-step reduction-assembly for the preparation of flexible graphene paper with ordered microstructure on a large scale. The subsequent graphene-PANI paper, formed by electropolymerization of PANI nanorod arrays on the above graphene paper, exhibits high specific capacitance and high cycling stability when tested in a supercapacitor. Most graphene/PANI composites only utilized edged carboxyl groups to bond aniline, leaving the ample basal oxygenated groups intact. Aiming to fully tap the basal oxygenated groups into use, Liu et al. firstly converted the epoxide groups (-O-) on the basal plane of the GO sheets into hydroxyl groups (-OH) via a ring-opening reaction catalyzed by concentrated hydrobromic acid (HBr). [84] Figure 5 a illustrates their route. An esterification reaction was then followed by the introduction of oxalic acid (HOOC-COOH) interacting with the -OH groups to achieve carboxylation of the GO sheets (CFGO). The resultant converted graphene sheets shows high affinity to the amine nitrogens of the polymerized PANi chain and thus facilitates the formation of a stable, orderly composite structure. As Figure 5 b–d suggested, the CFGO/PANI composite exhibits the largest capacity up to 525 F g⁻¹.

![Figure 5. a. Schematic illustration of GO/PANI construction. Dotted arrow route: referenced method; solid arrow route: applied in their work. b–d. Electrochemical behaviors of PANI, GO/PANI, CFG/PANI, and CFGO/PANI electrodes in 1.0 mol L⁻¹ H₂SO₄ solution. (b)CV with scan rate 10 mV s⁻¹, (c) GCD with current density 0.3 A g⁻¹, (d) EIS with sweep frequency 10⁵–0.001 Hz.](image-url)
Different from these researches mentioned above that mainly tried to integrate PANi and 2D graphene sheets, other researchers also aimed to combine PANi with 3D graphene hydrogels or foams to achieve a higher specific capacitance. Dong et al. first synthesized 3D graphene foam through a CVD method using nickel foam as a substrate. Then PANi was integrated into 3D graphene foam through in-situ polymerization of aniline monomer under acid condition to produce free-standing graphene/PANi hybrids. The electrochemical measurements showed that the graphene foam/PANi hybrids electrodes exhibit a high specific capacitance (346 F g\(^{-1}\)) and a good cycling stability (retained 71% of its initial capacitance after 120 cycles). Wang et al. developed a facile and scale-up printing method to fabricate a new type of flexible and lightweight paper electrode. A 3D graphene loaded PANi material was first prepared and was coated on free-standing graphene by a well-controlled full inject printing method. The printing technique through well-controlled ejection of graphene ink droplets from nozzles onto various substrates not only provides the capability of printing films in controlled geometries and at specific locations on various substrates but also enables the manufacture of large-area flexible devices at low cost. An all-solid-state symmetric supercapacitor device based on this as-prepared material showed acceptable energy density (24.02 Wh kg\(^{-1}\)), remarkable flexibility (less than 2% change after 180° bending for 100 times) and high cycling performance (retained 85.6% of the initial capacitance after 5000 cycles).

Other conducting polymers such as PPy and PT are also extensively studied. Zhang et al. designed graphene-hollow PPy nanostructures by inserting PPy hollow spheres between graphene layers. Based on the synergistic effects of reduced graphite oxide and PPy, the nanocomposites exhibited enhanced electrochemical performance. The specific capacitance rose to as high as 500 F g\(^{-1}\) with a charging-discharging current density of 5 A g\(^{-1}\). Tsai et al. have demonstrated that GO can be incorporated in GO/PPy composite by an electropolymerization method and be further reduced by a direct electrochemical reduction to produce a highly compression-tolerant foam. Qu et al. developed a strategy to form a hydrogel that rationally combined 3D graphene with PPy which achieved a remarkable compression tolerance. Robust 3D PPy-G foam was formed by pre-mixing Py monomer with GO for hydrothermal production of Py-containing 3D graphene, followed by direct electropolymerization. They ascribed the excellent electrochemical properties (424 F g\(^{-1}\)) to the large surface area provided by RGO to charge separation and pseudocapacitance of PPy to the overall energy storage. During compression and electrochemical tests, the as-synthesized foam showed only small plastic deformation (10% of volume reduction) after compression at a set strain of ε = 50% for 200 cycles and did not alter specific capacitance significantly even up to 1000 cycles. Undercoated Py has a low conductivity, very low potentials (below -2.0 V vs. Ag|Ag\(^{+}\)) and thus is very unstable to oxygen and water. By substituting at the 3-position of the thiophene ring with phenyl, ethyl or alkoxy groups, the stability can be tremendously improved. A further approach is to add electron withdrawing groups to these substituents. These Py derivatives which have a lower band-gap include PEDOT, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3-(4-fluorophenyl)thiophene)(PFPT), poly(3-(3,4-difluorophenyl)thiophene)(MPFT) and poly(1-cyano-2-(2-(3,4-ethylenedioxythiophenyl)-1-(2-thienyl)vinylene) (ThCNVEDT) et al. PEDOT has attracted much attention for its good electrical conductivity and large pseudo-capacitance, which may be attributed to its low redox potential and fast redox reactions. Ram et al. synthesized a PEDOT/graphene nanocomposite through an oxidative polymerization technique. The PEDOT deposited on graphene surface improved its electrochemical performances and achieved a high capacitance of 350 F g\(^{-1}\). Lehtimaki et al. prepared PEDOT/GO composites by electrooxidation of EDOT in ionic liquid (BMIMBF4) onto flexible electrode substrates. After deposition, incorporated GO was reduced to rGO by a rapid electrochemical method of repetitive cathodic potential cycling, without using any reducing reagents. Figure 6 a–d shows SEM images of PEDOT/GO (a) and PEDOT/rGO (b) composite films. Compared with aqueous electrolyte, ionic liquids have excellent properties such as high ionic conductivity and a wide electrochemical potential window (5 V for BMIMBF4), which enables exhaustiveness of the reduction process. When they compared two different polymerization method, shown in Figure 6 e, cyclic voltammetry (CV) method was found to
be superior to potentiostatic polymerization for the growth of PEDOT/GO films. When tested in symmetric supercapacitors, it demonstrated a good capacitive properties as well as cycling stability.

Figure 6. a–d. SEM images of PEDOT/GO (a) and PEDOT/rGO (b) composite films with 1000× magnification. Images (c) and (d) show the cross section with 500× magnification. e. CVs in BMIMBF4 at 50 mV s⁻¹ of PEDOT/GO composite films electropolymerized using the CV method (solid line) and the constant potential method at 1.0 V (dashed line).

2.5.2. Graphene/transitional metal oxides composites
In addition to conducting polymers, transitional metal oxides are also considered to be promising pseudo-capacitor materials. By going under Faraday reactions, these redox-active materials can significantly enhance the capacitance of supercapacitors. Among different metal oxides, manganese dioxide (MnO₂), a traditional battery material, has received tremendous attention as a promising electrode material with great potential in light of its abundance on earth, environmentally-friendly nature, and large theoretical specific capacitance (1370 F g⁻¹). However, the widespread use of MnO₂ electrode materials has been plagued with its poor conductivity which inevitably leads to poor electrochemical performances. To alleviate this problem, many scientists have tried to integrate highly conductive materials like graphene with MnO₂ to improve their performances. Different steps or kinds of preparation of MnO₂/graphene composites can result in very disparate morphology or distribution of MnO₂ nanoparticles and thus influence the resultant electrode materials severely. Cheng et al. prepared a MnO₂ nanowire/graphene composite by solution-phrase assembly of MnO₂ nanowire and graphene.95 An asymmetric supercapacitor was prepared and tested, which exhibits a high power density of 5000 W kg⁻¹ and acceptable cycling retention rate of 79% after 1000 cycles. Fan et al. also
prepared MnO2/graphene composites through a facile and rapid microwave irradiation method using a household microwave oven. The specific capacitance of the composite was measured to be 310 F g⁻¹ at 2 mV s⁻¹. After 1500 cycles, the capacitance of this electrode only decreases by 4.6% of initial capacitance indicating excellent electrochemical stability. Zhu’s group employed a different reacting system of an isopropyl alcohol-water solution to prepare MnO2/graphene composites. They believe the reacting system is beneficial for the oriented growth of the crystal species to form 1D MnO2, resulting in the exfoliation of GO sheets. The resultant needle-like MnO2 crystals enables such composites to possess good electrochemical behaviors. Cui and his group used an electrodeposition method to deposit MnO2 nanoparticles onto graphene nanosheets. After a simple solution-based exfoliation process to coat highly porous textile fibers with graphene nanosheets, an ensuing controlled deposition of MnO2 was carried out. The prepared graphene/MnO2 hybrid achieved a good capacitance of 315 F g⁻¹ at scan rate of 2 mV s⁻¹. Tests of their as-prepared asymmetric supercapacitor revealed a high power density of 110 kW kg⁻¹, an energy density of 12.5 Wh kg⁻¹ and excellent cycling performance of 95% capacitance retention over 5000 cycles. Naderi et al. achieved a uniform dispersion of MnO2 by a sonochemical method. By irradiating a mixture of MnSO4, KBrO3 and nitrogen-doped reduced graphene (NRGO) with high-intensity ultrasound radiation of 480 W cm⁻² input power and working frequency of 24 kHz, they prepared a MnO2/NRGO nanocomposite that exhibits a high specific capacitance of 522 F g⁻¹ at 2 mV s⁻¹.

Similarly, when combined with MnO2 nanoparticles, 3D porous graphene structure also showed enhanced electrochemical performances. Chen et al. developed a simple hydrothermal approach to deposit MnO2 on the surface of graphene foam. By adjusting acidity of the solution, the morphology of MnO2 could be controlled. The resultant 3D hybrid has a high specific capacitance of 560 F g⁻¹ at the current density of 0.2 A g⁻¹. Ge et al. used a low-cost ‘dip and dry’ process, which is compatible with mass production, to fabricate MnO2/graphene nanostructured sponges with good performances. Patil et al. used an easy solution-growth method to synthesize 1D-MnO2 nanofibers on graphene foam. Synergistic cooperation between graphene foam and 1D-MnO2 nanofibers is believed to be accountable for the observed ultrahigh specific capacitance of 670 F g⁻¹. He et al. reported a type of MnO2-coated freestanding and flexible 3D graphene network, which has acceptable specific capacitance of 130 F g⁻¹, through a electrodeposition method. Li et al. created a facile and scalable spraying method to fabricate 3D multilayer porous MnO2/RGO/Ni foam composite electrode. The synergistic effect between the RGO nanosheets and MnO2 nanoparticles lead to an enhanced capacitive performance of 267 F g⁻¹at 0.25 A g⁻¹. They attribute the enhanced capacitive performance to the interconnected RGO nanosheets scaffolds, which serve as conducting networks and provide ion-transport channels, and the MnO2 nanoparticles firmly embedded into the inter-space of RGO nanosheets as spacers.

Besides the incorporation of MnO2, many other metal oxides are also studied with enthusiasm to increase the capacitive performances of supercapacitors. Nonetheless, an obvious decline in volume can be witnessed when it comes to the total amount of papers published on these metal oxides. Wu et al. attached RuO2 particles onto the surface of graphene sheets through a sol-gel process and low-temperature annealing. Despite of high cost of fabrication, the RuO2/graphene sheets showed high specific capacitance of 570 F g⁻¹. A flexible supercapacitor was prepared based on this composite and electrochemical tests suggested high energy density (20.1 Wh kg⁻¹) and excellent stability of 97.9% retention after 1000 cycles. Xiang et al. deposited Co3O4 on RGO during hydrothermal processing to yield a RGO/Co3O4 composite which, in their experiment, showed strengthened specific capacitance of 472 F g⁻¹ at a scan rate of 2 mV s⁻¹. Similarity, Dong et al. Fabricated 3D Co3O4/graphene foam through a hydrothermal procedure, which delivered high specific capacitance of 1100 F g⁻¹ at a current density of 10 A g⁻¹. Purushothaman et al. prepared a RGO/CuO composite via a hydrothermal method. The composite showed good specific capacitance of 326 F g⁻¹ and, notably, no measureable degradation in electrochemical performance even after 1500 cycles. In addition, Dai’s group reported a two-step method in which a single-crystalline thin nanoplates of Ni(OH)2 are selectively and directly grown on graphene. The resultant composites
showed ultrahigh specific capacitance of 1335 F g\(^{-1}\) at a current density of 2.8 A g\(^{-1}\). Li et al. grew Fe\(_3\)O\(_4\) nanoparticles on RGO through a simple hydrothermal process under the presence of glucose which not only binds Fe\(_3\)O\(_4\) nanoparticles and graphene together, but also reduces GO to RGO simultaneously.\(^{115}\) Figure 7 h shows their preparing process. The composite showed improved specific capacitance of 241 F g\(^{-1}\) at 1 A g\(^{-1}\) (Figure 7 f–g). It is noted that the rGO and Fe\(_3\)O\(_4\) has a synergistic effect in the formation and remain of this unique structure. On one hand, the wrinkle-structured rGO (Figure 7 A–E) provides large area and improves the dispersion of Fe\(_3\)O\(_4\) NPs. On the other hand, Fe\(_3\)O\(_4\) can inhibit the agglomeration of rGO during the reaction. Benefiting from this effect, the unique structure can facilitate the electron transport and retain their active surface areas required for the charge storage, further boosting the accessible capacity of the Fe\(_3\)O\(_4\)/rGO electrode. Zhao et al. performed an experiment that homogeneously anchored Fe\(_2\)O\(_3\) particles onto n-doped graphene sheets. The specific capacitance of the resultant material is up to 260.1 F g\(^{-1}\) and the retention rate (over 82.5\%) is also acceptable.\(^{116}\)

Figure 7. A–E. Low- and high- magnified SEM (A, B) and TEM (C, D, E) images, SAED (inset of D) and HRTEM image (inset of E) of Fe\(_3\)O\(_4\)/rGO. f–g. Nyquist plots of the EIS for Fe\(_3\)O\(_4\)-C, rGO and Fe\(_3\)O\(_4\)/rGO composite. h. Schematic illustration for the preparation of Fe\(_3\)O\(_4\)/rGO composite.

2.6. Doped graphene
Doping graphene with heteroatoms can effectively tune its electronic structure and other intrinsic properties.\(^{110}\) Doping graphene with nitrogen or boron creates a band-gap and makes it a n-type or p-type material. Such chemically doped materials have unique properties, for example, nitrogen-doped graphene is a good electron-donor and these unique properties can be used in many energy-related areas.\(^{111}\) For instance, the doping of nitrogen atoms has at least three salient advantages. First, nitrogen atom has three valence electrons to form strong bonds whereas the extra loan pair of electron improves the overall conductivity.\(^{112}\) Also, the larger nitrogen atoms protrude among graphene sheets, affecting the hexagonal ring structure of graphene. This deviation from the planer geometry of graphene can facilitate charge accumulation at the electrode interface.\(^{113}\) Furthermore, doping induced changes in the symmetry of hexagonal structure is expected to reduce the stacking of graphene sheets, acting as an effective spacer.\(^{114}\) However, a limited loading percentage and low specific surface area have been the main obstacle to its widespread utilization. Legion ways have been
developed to address the problem. Wen et al. developed a simple way to fabricate highly crumpled nitrogen-doped graphene nanosheets using cyanamide (NH2CN) as N-dopant. Abundant wrinkled structures, high pore volume and nitrogen doping altogether contribute to the increased electrochemical performances, in which the specific capacitance was reported to be 245.9 F g⁻¹ at 1 A g⁻¹. V. Sahu et al. employed a novel and cheap method to dope graphene with non-mulberry silk cocoon membrane. By pyrolyzing the silk cocoon membrane at 400°C in argon atmosphere to produce graphene, they obtained graphene that is desirably heavily nitrogen doped (~15%). By means of a simple hydrothermal reaction, in which GO and ammonia are adopted as carbon and nitrogen source respectively, Sui’s group successfully prepared a highly porous (830 m² g⁻¹) nitrogen-doped graphene aerogel. Enhanced specific capacitance was measured to be 223 F g⁻¹ at 0.2 A g⁻¹ and long-term cycling performances were also achieved. Also using a hydrothermal method, Lu et al. achieved a higher specific capacitance 301 F g⁻¹ at 0.1 A g⁻¹ with o-phenylenediamine as N-dopant. In another hydrothermal reaction, Sun et al. utilized NH₃ released from urea to react with the oxygen functional groups of GO and then the nitrogen atoms were successfully doped into graphene skeleton. Large surface area (593 m² g⁻¹) and large proportion of nitrogen atoms (10.13%) play vital roles in the enhanced specific capacitance of 326 F g⁻¹ at 0.2 A g⁻¹.

Substitutions of carbon with boron in the graphene lattice shifts the Fermi level toward the valence band, thereby enhancing charge storage and transfer within the doped graphene structure. Moreover, the presence of boron dopants in graphene contributes to a space-charge-layer capacitance and/or pseudocapacitance, further increasing the apparent capacitance. Han et al. created a novel B-doped graphene nanoplatelets by reduction of graphene oxide with a borane (BH3)-tetrahydrofuran (THF) adduct under reflux via a one pot synthesis using a liquid process on a large scale. Such nanoplatelets contained small amounts of B components and, as a result, showed enhanced specific capacitance of 200 F g⁻¹ with a good rate performance using an aqueous electrolyte. Peng et al. described a simple and robust laser induction method, which does not require multiple steps and high temperature or high-vacuum environments, to prepare porous boron-doped graphene. The highest areal capacitance of as-prepared material reaches 16.5 mF cm⁻², 3 times higher than non-doped graphene.

When nitrogen and boron are combined together, even better electrochemical performances can be observed. Wu et al. created a 3D nitrogen and boron co-doped graphene aerogel and an all-solid-state supercapacitor based on it. The aerogel was prepared via hydrothermal reactions and freeze-drying processes with ammonia boron trifluoride (NH₃BF₃) and GO as precursors. The hybrid showed good specific capacitance of 239 F g⁻¹. The as-prepared supercapacitor also showed enhanced power density of 1600 W kg⁻¹ with respect to normal supercapacitor. Saha et al. used a hydrothermal method to develop hexagonal boron nitride (h-BN)/RGO composite (Figure 8 a). The presence of two different chemical species (B and N) in the sublattices of h-BN and the existence of inversion symmetry in the graphene backbone may result in the formation of electrochemically active h-BN/graphene composite. Boric acid and ammonia were chosen as the source of boron (B) and nitrogen (N). The band gap of the insulator h-BN was successfully reduced by increasing the amount of GO content in the composite (Figure 8 b). The precise amount of RGO content in the h-BN provided high specific capacitance of 824 F g⁻¹. The maximum energy density of 39.6 Wh kg⁻¹ was achieved in their asymmetrical supercapacitor.
3. Flexible supercapacitors

In recent years, attentions among energy-storage applications have been gathered around the field of flexible, portable supercapacitors, as an apt response to the fad of smart phones and VR technology. Such technology to construct supercapacitor can be very demanding, which requires, desirably, small size, flexibility, compactness, stability, high efficiency and high energy density. However, commercially available traditional supercapacitors always consist of a separator sandwiched between two electrodes with liquid electrolyte. Other contents are spirally wound and packaged into a cylindrical container or stacked into a button cell. Unfortunately, these device architectures often suffer from short life cycle, low energy density and even possible leakage of hazardous electrolytes. Most importantly, these ‘hard’ devices are incompatible with flexible electronic. Fortunate enough, scientists and engineers are actively designing different types of supercapacitors, including micro-supercapacitors and fiber-type supercapacitors, to alleviate these problems. These supercapacitors are based on novel electrode materials synthesized under the same tenets we discussed above.

3.1. Micro-supercapacitors

In addition to symmetric supercapacitors, in which anode and cathode have the same electrode materials, asymmetric supercapacitors are extensively studied for its salient advantages. They can make full use of the different maximum operating voltage of the cell system, leading to an obvious improvement in the specific capacitance and energy density of supercapacitors.

Solid-state electrolytes, also known as fast ion conductors or superionic conductors, are commonly used in micro-supercapacitors instead of conventional liquid electrolytes including aqueous electrolytes, organic liquid electrolytes and ionic liquid electrolytes. They conduct electricity due to the movement of ions through voids or defects in their crystal lattice. Solid electrolytes pose no threat of possible leakage to environment since they are well dispersed and bound into a polymer matrix. In addition, solid-state gel or polymer electrolytes offer dual functionality as they combine the separator and the electrolyte into a single layer. Most importantly, encouraging reports132, 133 showed the performance of solid-state gel electrolytes parallels their liquid counterparts, indicating the efficacy of such replacements. In order to meet the requirements of the design of small, thin, flexible and...
lightweight supercapacitors, many different types of solid-state electrolytes are developed, such as PVA/H2SO4, PVA/H3PO4 and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf2], C-TRI)/fumed silica nanopowder gel electrolyte and PVDF/ BMIM+BF4- ionic liquid polymer electrolyte.

Historically, the prototype of a flexible micro-supercapacitor was fabricated in 2003 by photolithography and an electrochemical polymerization technique with PPy as the active electrode material.134 However, the device only showed mediocre performances because of the high resistance and limited capacitance of the electrode. Inspired by their creative work, many research efforts have been dedicated to developing flexible micro-supercapacitors by focusing on graphene and its composites. Niu et al. combined photolithography with electrophoretic deposition to prepare graphene micro-electrodes, then fabricated these into flexible all-solid-state micro-supercapacitors.135 The open edges of the graphene micro-electrodes enhanced the infiltration of the electrolyte ions into the micro-patterned graphene electrodes, due to the shortened diffusion pathways. As a result, electrolyte ions could access more surface area of the graphene sheets compared with traditional large-area graphene film electrodes. Furthermore, the graphene micro-electrodes permits uptake of the electrolyte ions into or removal from the graphene layers with short diffusion pathways. Therefore, the graphene micro-supercapacitors exhibited a much better electrochemical performance than the conventional supercapacitor configuration. The specific capacitance of the graphene micro-supercapacitor was 285 F g⁻¹, which is about three times higher than that of a conventional graphene supercapacitor (86 F g⁻¹).

Xue and his co-workers136 fabricated flexible a solid-state microsupercapacitor by in situ electrodeposition of PANI nanorods on the surface of RGO patterns that are prepared by micromolding in capillaries (MIMIC). First, a flat PDMS substrate and a patterned PDMS stamp were pressed together to achieve conformal contact. A drop of well-dispersed GO aqueous solution was placed at each end of the PDMS stamp. After heating under vacuum with hydrazine solution and then degassing for 30min at room temperature, the system was then warmed to 70°C for 12h to form the patterned RGO electrodes. PANI was electrodeposited on the patterned GO interdigital electrodes using a three-electrode electrochemical system at a constant potential of 0.75 V vs. Ag/AgCl in a 0.05 M aniline solution with 0.5 M H₂SO₄ as the supporting solution. H₂PO₄-PVA gel electrolyte was used to coat the micro-supercapacitor device to achieve a solid-state flexible micro-supercapacitor. Compared with micro-supercapacitors that employ PANI deposited on bare gold micro-electrodes, the PANI/RGO-based micro-device showed slightly higher specific capacitance (970 F g⁻¹ at a current density of 2.5 A g⁻¹, as compared with approx. 940 F g⁻¹ for Au/PANI), better rate capability, and enhanced cycle stability (10% capacitance decay after 1700 charge/discharge cycles, as compared with 20% after less than 500 cycles for Au/PANI), which was ascribed by authors to the synergistic effect of RGO and PANI nanorod arrays.

What’s more, Wu et al. created a flexible all-solid-state graphene based micro-supercapacitor through micropatterning of high temperature RGO films.137 Owing to the relatively high electrical conductivity (345 S cm⁻¹) of the fabricated RGO films and the in-plane interdigitated geometry, the resultant micro-supercapacitor delivered a good electrochemical performance. The device exhibited a maximum areal capacitance of 80.7 mF cm⁻² and a volumetric capacitance of 17.9 F cm⁻³. More remarkably, the device showed a power density of 495 W cm⁻³, and an energy density of 2.5 mW h cm⁻³, which is comparable to that of lithium thin-film batteries. This device retained 98.3% of its initial capacitance after 100 000 cycles. Operation at high scan rates up to 1000 V s⁻¹ is possible, which illustrates the ultrafast charge and discharge capability and ultrahigh power density of the micro-supercapacitor. Recently, Kaner et al. introduced a scalable fabrication method for graphene micro-supercapacitors over large areas by using a commercially available LightScribe DVD burner.138 With this method, more than 100 micro-supercapacitors can be produced on a single disc in less than 30min. The flexible all-solid-state micro-supercapacitors exhibited an areal specific capacitance of 3.05 F cm⁻³ at 16.8 mA cm⁻³, and maintained 60% of this value when operated at a current density of 18400 mA cm⁻³. This is equivalent to the operation of the device at 1100 A g⁻¹, which is about 3 orders of magnitude higher than the normal current density used for traditional
supercapacitors. Furthermore, they introduced an experimental demonstration of an all-solid-state micro-supercapacitor by using an ionogel electrolyte that allows for an operational window of 2.5 V. The micro-supercapacitor also showed exceptional electrochemical stability under different bending and twisting conditions. These micro-supercapacitors exhibited an ultrahigh volumetric power density of 200 W cm\(^{-3}\) and excellent frequency response with an RC time constant of only 19 ms.

Furthermore, Wu et al. demonstrated the first fabrication of stacked-layer heterostructure films (denoted as TP/EG) from thiophene (TP) nanosheets and electrochemically exfoliated graphene (EG) for high-rate and flexible all-solid-state (ASSS) (TP/EG-ASSSs) and micro-supercapacitors (TP/EG-MSCs) with superior rate capability and enhanced volumetric capacitance. The heterostructure films with a thickness of about 105 nm are produced by alternating deposition of electrochemically EG nanosheets (\(\leq 3\) layers) and redox-active conducting TP nanosheets (thickness of 3.5 nm) in sequence, and exhibit large-area uniformity. Notably, the produced films were directly transferred on a polyethylene terephthalate (PET) substrate and served as free-standing electrodes for flexible supercapacitors. Remarkably, the resulting TP/EG-ASSSs exhibited a pronounced pseudocapacitance contribution which enabled fast ion diffusion and electron transport throughout the binder-free compact film electrode, and delivered an areal capacitance of \(\approx 3.9\) mF cm\(^{-2}\) and a volumetric capacitance of \(\approx 375\) F cm\(^{-3}\), energy density of 13 mWh cm\(^{-3}\) and power density of 776 W cm\(^{-3}\). Meanwhile, the TP/EG-MSCs can be operated at high rate of up to 1000 V s\(^{-1}\), offering ultrahigh rate capability, e.g., with a landmark areal capacitance of 1.30 mF cm\(^{-2}\) and volumetric capacitance of 123 F cm\(^{-3}\) at 100 V s\(^{-1}\), as well as unprecedented flexibility under different bending conditions.

Ramadoss et al. also fabricated a thin, lightweight, mechanically stable yet flexible paper-based all-solid-state flexible supercapacitor (FSC) using CVD-grown high quality 3D-graphene coated on a graphite-paper current collector. The 3D-graphene powder suspended in an aqueous media was deposited onto the graphite-paper-based current collector by a lift-off method, which allowed a facile, cost-effective, scalable, lightweight, binder and conductive additive-free electrode. The resultant paper-based symmetric all-solid-state flexible supercapacitor demonstrated a high device capacitance of 80 F g\(^{-1}\) (11.1 mF cm\(^{-2}\)), excellent cycle stability (112% capacitance retention even after 10 000 cycles), and high power (178.5 W kg\(^{-1}\); 24.5 mW cm\(^{-2}\)) and energy density (8.8 Wh kg\(^{-1}\); 1.24 mWh cm\(^{-2}\)). More importantly, the as-fabricated device well retained its electrochemical performance even under harsh conditions such as bending, rolling and twisting. Mondal’s group successfully synthesized a ternary rGO/Fe3O4/PANi (rGFP) composite for binder-free, semiflexible, thin, all-solid-state supercapacitor device. They adopted a scalable soft-template technique for the preparation of three-dimensional Fe3O4-decorated rGO-doped PANI nanorods. Figure 9a illustrates their design of a symmetric supercapacitor. They attributed the excellent electrochemical energy storage performance such as a high specific capacity, high energy density (47.7 Wh kg\(^{-1}\)), high power density (550 W kg\(^{-1}\)), and cycling stability (78% retention after 5000 cycles) to the synergistic effect of double-layer capacitance of rGO and the pseudocapacitance of Fe3O4 nanoparticles and PANI nanorods. Practically, they illuminated LEDs with their as-fabricated supercapacitor for 30min.
3.2. Fiber-type supercapacitors
Fiber-type supercapacitors have made promising progress in recent years. Compared with the 2D traditional planar structured supercapacitors, fiber-shaped supercapacitors have exhibited great potential in portable and wearable electronics due to their tiny volume, higher flexibility, and excellent deformability. A proper asymmetric design and appropriate electrolytes can further enhance its electrochemical performances as we discussed above. Here, we mainly concentrate on the design of electrode, by comparing different types of fibers and its fabrication process, and its performances and applications in fiber-type supercapacitors.

Besides proper paring with two positive and negative active materials, suitable fiber-shaped substrate is also a prime factor for the performances of fiber-type supercapacitors. A burgeoning of...
various fiber electrodes can be witnessed in recent years, including metal wires, carbon based fibers (CNT fibers, graphene fibers (GF)), and composite fibers.

3.2.1. Metal fiber supported electrodes
Metal wires, such as Au, Ni, and Ti, exhibit excellent conductivity, good mechanical strength and flexibility, which is very desirable as long as highly portable devices is considered. These metal wires can be served as both physical support for active materials and current collectors in fiber-type supercapacitor design. Wang et al. successfully fabricated an all-solid-state asymmetric supercapacitor based on titanium wire/Co3O4 nanowires and carbon fibers/graphene electrodes. First, they employed a facile hydrothermal method to deposit porous Co3O4 on nickel fibers instead of titanium wires. The composite, which is capable of a specific capacitance up to 560 F cm-3 with an alkaline electrolyte in a three electrode configuration, possessed a large, electrochemically active surface and short path for ion diffusion and electron transport. Then they fabricated a solid-state asymmetric supercapacitor by carefully entangling a bundle of carbon fibers coated with graphene around the nickel fiber coated with Co3O4 nanowires previously immersed in the PVA-KOH gel solution. However, when they realized, in time, nickle fibers are too heavy and too hard to be utilized in flexible devices, they changed their substrate of nickel to more soft titanium wires. Their strategy proved to be very successful, as shown in Figure 10. With an operating potential of 1.5 V, this newly fabricated asymmetric supercapacitor presented largely improved energy and power delivery as well as superior flexibility. In addition, their work successfully integrated supercapacitors with photodetector to realize a new flexible device with multifunctionalities. In addition, Wang et al. used a copper wire (CW), which is both highly flexible and cost-effective, as the substrate to be wrapped with 3D porous graphene hydrogel (GH). They directly immersed the CW in an aqueous GO suspension, upon which a spontaneous redox reaction between the CW and GO nanosheets occurs, leading to the formation of the 3D porous GH/CW electrode. Due to the synergistic effects of different components and advantages of nanoporous structured fiber electrodes, their as-fabricated fiber asymmetric supercapacitor based on MnO2/RGO/carbon fiber and GH/CW electrodes can be reversibly charged/discharged with a wide voltage range from 0 to 1.6 V, delivering a high areal energy density of 18.1 uWh cm-2 and volumetric energy density of 0.9 mWh cm-3.

Figure 10. a) Photographs of the fiber-based all-solid-state flexible asymmetric supercapacitor at different bending states, b) CV curves, and c) galvanostatic charge–discharge curves of the flexible supercapacitor. d) CV curves obtained at a scan rate of 100 mV s-1 at different bending states in their work.
3.2.2. Carbon materials based fiber supported electrodes

Fiber-type asymmetric supercapacitors based on metal wires current collectors exhibits promising performance for wearable electronics. However, metal wires occupied a large portion of total weight of the flexible devices, which inevitably leads to a dwindled gravimetric energy/power density of the resultant devices as a whole. To further increase the practicability and flexibility, carbon based fibers such as carbon fibers bundles, CNTs fibers, and graphene fibers (GFs), which have the advantages of low densities, slender structure, and good flexibility, are extensively studied in recent years. Here, we mainly discuss supercapacitors based on GF.

Cai et al. first fabricated GFs by reducing GO under the presence of ascorbic acid inside silicone tubing at low temperature of 80°C in a water bath. Then NiCo2S4 nanoparticles were deposited onto the GFs via a solvothermal deposition method. The obtained GF/NiCo2S4 hybrid fiber electrode exhibited a high volumetric capacitance up to 388 F cm⁻³ in a three-electrode cell at 2 mV s⁻¹. Using the GF/NiCo2S4 as the positive electrode and GF as the negative electrode, their as-fabricated asymmetric supercapacitor showed a high energy density up to 12.3 mWh cm⁻³ with a maximum power density of 1600 mW cm⁻³, outperforming that of the thin-film lithium battery. Negligible decrease in its electrochemical performances can also be seen when they tested their supercapacitors under different bending state and in water condition, suggesting a high stability. They further demonstrated its potential use in potable applications by powering a LED using 3 supercapacitors in series.

Wang et al. developed a novel self-healable supercapacitor based on self-healing materials, which are capable of healing damage partially or completely inflicted on them and restoring mechanical and structural properties. As shown in Figure 11j–k, first, they prepared spring-like RGO-based composite fibers (polypyrrole (PPy)-decorated RGO/multiwalled carbon nanotubes, denoted as MWCNTs) that are thick enough to reconnect the broken electrodes accurately by visual inspection. Then stretchable carboxylated polyurethane (PU) acting as a self-healing material was coated on the spring-like fiber electrodes. They believe hydrogen bond acceptors and donors in abundance in the supramolecular network of carboxylated PU give rise to self-healable properties. Once the spring electrodes were broken, as long as the separated parts are placed at suitable places, self-healing carboxylated PU can guide the reconnection process, leading to the restoration of the electrical properties. Their supercapacitor exhibited a 82.4% capacitance retention after a large stretch (100%), and 54.2% capacitance retention after the third healing (shown in Figure 11a–i). In the pursuit of high-rate performances of fiber-type supercapacitors, Yu et al. fabricated a graphene fiber made from chemical vapor deposition grown laminated graphene sheet. Then it was adopted to form a supercapacitor which exhibits an exceptional rate capability with an excellent relaxation time constant of 1.4 ms. In addition, it can be charged-discharged at a high scan rate of 100 V s⁻¹ while maintaining good capacitive behavior. When the scan rate increased by 5000 times, from 20 mV s⁻¹ to 100 V s⁻¹, the graphene fiber based supercapacitor maintained 38.6% of its initial capacitance.
Figure 11. Electrochemical measurements and application for as-prepared stretchable and self-healing supercapacitors. (a) Photographs, (b) cyclic voltammogram curves (c) evolutions of specific capacitance of the supercapacitor before and after stretching to 100% (d) Cyclic voltammogram curves, (e) galvonostatic charge–discharge measurements (f) Nyquist plots of the supercapacitor before after self-healings (g) Illustration of the supercapacitor driving a photodetector of perovskite nanowires. (h) Photographs of the supercapacitor before and after self-healing. (i) Photocurrent dependence on time of the photodetector under illumination of on/off states. (j–k). Schematic diagrams of the stretchable and self-healable mechanism, manufacturing process of PPy/RGO/MWCNT electrodes and self-healing supercapacitors.

4. Summery and future prospects
In recent years, graphene is renowned for its excellent properties including large specific surface area, high thermal and electrical conductivities, tough mechanical strength, and high optical transparency. However, pure graphene is less studied, due to its limitations of small-scale, high-cost preparation, and time-consuming processing, than its derivative GO which has been proven to be an ideal 2D nanoscale
building block for macroscopic assembly for the abundant oxygenated groups on its basal plane and edges, allowing it to be highly dispersed in polar solvents, especially in water. Intending to avoid re-aggregation of graphene sheets in the assembly process, activation process, spacers are used to obtain a larger surface area that enables fast ionic and electronic transport. Also, abundant 3D interconnected networks in porous graphene sponges and foams facilitate charge transfer. In addition, graphene gels like hydrogels and aerogels showed excellent mechanical strength and chemical stability. However, the large porous space and spacers are not conductive, leading to a moderate power density of the device as a whole. In recent years, there is a zeal among scientists in integrating the advanced properties of the individual graphene sheets, through the assembly of GO nanoscale building blocks into macroscopic architectures with hierarchical structure and extraordinary physicochemical properties. Various assembly techniques have led to the realization of many diverse structures and morphologies, with a unique collection of properties and fertile functionalities of the graphene architectures. Pseudo-capacitive materials like PPy and MnO2 are incorporated into graphene nanosheets, which showed extraordinary mechanical strengths and high electric conductivity. On the other hand, doping graphene assemblies is another effective way to achieve a highly conductive electrode which favors fast charge transfer.

Fabrication of 3D electrochemical supercapacitors is relatively new but rapidly growing endeavor when compared to more conventional supercapacitors. Fiber-type supercapacitors and micro-supercapacitors are two typical examples of highly flexible supercapacitors. They are promising energy storage devices for wearable electronics by virtue of its unique features in high flexibility, small size and light weight. We elaborated on their fabrication process, device design and electrochemical performances. Overall, more strategies to further improvements in power and energy performance are still needed, such as proper design of positive and negative materials electrode, gel electrolyte with high ion conductivity, large voltage window and safety.

To further enhance performances of supercapacitors, the following should be taken into consideration. First, it’s of tantamount importance to develop proper assembly strategies to avoid the thermodynamically-favorable re-aggregation of graphene sheets. Second, a deeper understanding of the assembly mechanism is imperative to achieve a precise control of the fabrication process in order to obtain uniform GO nanosheets in terms of size, shape and functional groups on the edges of its surface. Third, a firm grasp of interactions between graphene nanosheets and incorporated functional guests is necessary to achieve a more rational design of graphene composites. Fourth, more choices of solid-state electrolytes which are fast ion conductors, are required so that the cell voltage of a micro-device can be higher to further increase energy density. In addition, a unified evaluation system to compare different supercapacitors and characterize flexibility should be established as long as highly flexible supercapacitors are considered.

In conclusion, graphene-based materials for flexible supercapacitors have been extensively explored. The research results indicate that graphene based materials will play an important and perhaps irreplaceable role in flexible supercapacitors because of their intriguing features. Although many challenges remain, we believe that flexible graphene-based supercapacitors will be a norm in public’s everyday life in the near future.

References
[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Science, 2004, 306, 666–669.
[2] M. J. Allen, V. C. Tung and R. B. Kaner, Chem. Rev., 2009, 110, 132–145.
[3] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, Angew. Chem., Int. Ed., 2009, 48, 7752–7777.
[4] D. Chen, L. Tang and J. Li, Chem. Soc. Rev., 2010, 39, 3157–3180.
[5] C. Lee, X. Wei, J. W. Kysar and J. Hone, Science, 2008, 321, 385–388.
[6] J. Xia, F. Chen, J. Li and N. Tao, Nat. Nanotechnol, 2009, 4, 505–509
[7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Science, 2004, 306, 666–669.

[8] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First and W. A. de Heer, J. Phys. Chem. B, 2004, 108, 19912–19916.

[9] K. Yan, L. Fu, H. Peng and Z. Liu, Acc. Chem. Res., 2013, 46, 2263–2274.

[10] W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc, 1958, 80, 1339

[11] Huai-Ping Cong, Jia-Fu Chen and Shu-Hong Yu, Chem. Soc. Rev., 2014, 43, 7295

[12] Zhi, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, et al. Science 332 (2011) 1537e1541

[13] Kaisheng Xia, Qiyang Li, Lin Zheng, Kun You, Xiangle Tian, Bo Han, Qiang Gao, Zhiyuan Huang, Gang Chen, Chenggang Zhou. Microporous and Mesoporous Materials 237 (2017) 228e236

[14] X. Sun, P. Cheng, H. Wang, H. Xu, L. Dang, Z. Liu, et al. Carbon 92 (2015) 1e10

[15] S. Yun, S.-O. Kang, S. Park, H.S. Park. Nanoscale 6 (2014) 5296e5302

[16] D.-W. Wang, F. Li, M. Liu, G. Q. Lu and H.-M. Cheng, Angew. Chem., Int. Ed., 2008, 47, 373–376.

[17] L. L. Zhang and X. S. Zhao, Chem. Soc. Rev., 2009, 38, 2520–2531.

[18] Y. Tao, X. Y. Xie, W. Lv, D. M. Tang, D. B. Kong, Z. H. Huang, N. Nishihara, T. Ishii, B. H. Li, D. Golberg, F. Y. Kang, T. Kyotani and Q. H. Yang, Sci. Rep., 2013, 3, 2975

[19] Y. X. Xu, K. X. Sheng, C. Li and G. Q. Shi, ACS Nano, 2010, 4, 4324–4330

[20] Z. P. Chen, W. C. Ren, L. B. Gao, B. L. Liu, S. F. Pei and H. M. Cheng, Nat. Mater., 2011, 10, 424–428

[21] X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang and H. Zhang, Small, 2011, 7, 3163–3168

[22] F. Liu and T. S. Seo, Adv. Funct. Mater., 2010, 20, 1930–1936

[23] Barbaros Ozyilmaz, Orhan Kahya, Jonghak Lee. US 2015/0085424. PCT/SG2013/000230

[24] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, ACS Nano, 2010, 4, 4806–4814

[25] S. Park and R. S. Ruoff, Nat. Nanotechnol., 2009, 4, 217–224

[26] K. R. Koch, J. Chem. Educ., 1982, 59, 973–974

[27] Y. Zhao, C. Hu, Y. Hu, H. Cheng, G. Shi and L. Qu, Angew. Chem., Int. Ed., 2012, 51, 11371–11375

[28] Z. Niu, J. Chen, H. H. Hng, J. Ma and X. Chen, Adv. Mater., 2012, 24, 4144–4150

[29] S. Pei, J. Zhao, J. Du, W. Ren and H.-M. Cheng, Carbon, 2010, 48, 4466–4474

[30] J. J. Yoo, K. Balakrishnan, J. Huang, V. Meunier, B. G. Sumpter, A. Srivastava, M. Conway, A. L. M. Reddy, J. Yu, R. Vajtai and P. M. Ajayan, Nano Lett., 2011, 11, 1423–1427

[31] M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, Nano Lett., 2008, 8, 3498–3502

[32] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H. Cheng, Nat. Mater., 2011, 10, 424–428

[33] Juan Zhang, Bo Zhou, Bo Zhao, Ling Si, and Xiaoping Jiang, Chin. J. Chem. 2017, 35, 1601—1610

[34] Cuixian Liu, Gaoyi Han, Yunzhen Chang, Yaoming Xiao, Haihan Zhou, Gaoquan Shi, Chemical Engineering Journal 328 (2017) 25–34

[35] Harish Banda, David Aradilla, Anass Benayad, Yves Chenavier, Barbara Daffos, Lionel Dubois, Florence Duclairoir, Journal of Power Sources 360 (2017) 538e547

[36] H. Huang, L. Xu, Y. Tang, S. Tang, Y. Du, Nanoscale 6 (2014) 2426–2433

[37] Q. Wu, Y. Sun, H. Bai, G. Shi, Phys. Chem. Chem. Phys. 13 (2011) 11193–11198

[38] Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, X. Duan, ACS Nano 7 (2013) 4042–4049

[39] Y. Xu, G. Shi, X. Duan, Acc. Chem. Res. 48 (2015) 1666–1675

[40] F. Liu, S. Song, D. Xue and H. Zhang, Adv. Mater., 2012, 24, 1089–1094

[41] Kunfeng Chen, Fei Liu, Shuyan Song and Dongfeng Xue CrystEngComm, 2014, 16, 7771
[42] C. Gómez-Navarro, J. C. Meyer, R. S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern and U. Kaiser, Nano Lett., 2010, 10, 1144–1148.

[43] A. Lerf, H. He, M. Forster and J. Klinowski, J. Phys. Chem. B, 1998, 102, 4477–4482.

[44] Md Moniruzzaman Sk and Chee Yoon Yue, RSC Adv., 2014, 4, 19908.

[45] Yu Yu, Yongbin Sun, Changyan Cao, Shuliang Yang, Hua Liu, Ping Li, Peipei Huang and Weiguo Song, J. Phys. Chem. A, 2014, 2, 7706.

[46] B. G. Choi, J. Hong, W. H. Hong, P. T. Hammond and H. Park, ACS Nano, 2011, 5, 7205–7213.

[47] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong and Y. Li, Adv. Mater., 2013, 25, 267–272.

[48] J. L. Vickery, A. J. Patil and S. Mann, Adv. Mater., 2009, 21, 2180–2184.

[49] Yuanlong Shao, Maher F. El-Kady, Lisa J. Wang, Qinghong Zhang, Yaoang Li, Hongzhi Wang, Mir F. Mousavie and Richard B. Kaner, Chem. Soc. Rev., 2015, 44, 3639.

[50] J. Zhang, J. Jiang, H. Li and X. S. Zhao, Energy Environ. Sci., 2011, 4, 4009–4015.

[51] R.-R. Bi, X.-L. Wu, F.-F. Cao, L.-Y. Jiang, Y.-G. Guo and L.-J. Wan, J. Phys. Chem. C, 2010, 114, 2448–2451.

[52] C.-C. Hu, K.-H. Chang, M.-C. Lin and Y.-T. Wu, Nano Lett., 2006, 6, 2690–2695.

[53] B. G. Choi, S.-J. Chang, H.-W. Kang, C. P. Park, H. J. Kim, W. H. Hong, S. Lee and Y. S. Huh, Nanoscale, 2012, 4, 4983–4988.

[54] J. Mu, B. Chen, Z. Guo, M. Zhang, Z. Zhang, P. Zhang, C. Shao and Y. Liu, Nanoscale, 2011, 3, 5034–5040.

[55] R. Li, X. Ren, F. Zhang, C. Du and J. Liu, Chem. Commun., 2012, 48, 5010–5012.

[56] A. Pendashteh, M. F. Mousavi and M. S. Rahmanifar, Electrochim. Acta, 2013, 88, 347–357.

[57] Q. Lu, M. W. Lattanzi, Y. Chen, X. Kou, W. Li, X. Fan, K. M. Unruh, J. G. Chen and J. Q. Xiao, Angew. Chem., Int. Ed., 2011, 123, 6979–6982.

[58] C. Yuan, X. Zhang, L. Su, B. Gao and L. Shen, J. Mater. Chem., 2009, 19, 5772–5777.

[59] X. Xia, J. Tu, Y. Mai, R. Chen, X. Wang, C. Gu and X. Zhao, Chem. – Eur. J., 2011, 17, 10898–10905.

[60] M. Wei, X. Cui, W. Chen and D. G. Ivey, Chem. Soc. Rev., 2011, 40, 1697–1721.

[61] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya and L.-C. Qin, Carbon, 2011, 49, 2917–2925.

[62] S. Chen, J. Zhu, X. Wu, Q. Han and X. Wang, ACS Nano, 2010, 4, 2822–2830.

[63] Z.-S. Wu, W. Ren, D.-W. Wang, F. Li, B. Liu and H.-M. Cheng, ACS Nano, 2010, 4, 5835–5842.

[64] M. Toupin, T. Brousse and D. Be´langer, Chem. Mater., 2004, 16, 3184–3190.

[65] Z. Zhang, F. Xiao, L. Qian, J. Xiao, S. Wang and Y. Liu, Adv. Energy Mater., 2014, 4, 1400064.

[66] J. Liu, J. Jiang, C. Cheng, H. Li, J. Zhang, H. Gong and J. F. Fan, Adv. Mater., 2011, 23, 2076–2081.

[67] C. Yuan, L. Yang, L. Hou, L. Shen, X. Zhang and X. W. Lou, Energy Environ. Sci., 2012, 5, 7883–7887.

[68] L. Yang, S. Cheng, Y. Ding, X. Zhu, Z. L. Wang and M. Liu, Nano Lett., 2011, 12, 321–325.

[69] J. Li, W. Zhao, F. Huang, A. Manivannan and N. Wu, Nanoscale, 2011, 3, 5103–5109.

[70] M. Li, Z. Tang, M. Leng and J. Xue, Adv. Funct. Mater., 2014, 24, 7495–7502.

[71] Y. Li, Q. Zhang, X. Zhao, P. Yu, L. Wu and D. Chen, J. Mater. Chem., 2012, 22, 1884–1892.

[72] K. Sujith, A. M. Asaha, P. Anjali, N. Sivakumar, K. R. V. Subramanian, S. V. Nair and A. Balakrishnan, Mater. Lett., 2012, 67, 376–378.

[73] Q. Wu, Y. Xu, Z. Yao, A. Liu and G. Shi, ACS Nano, 2010, 4, 1963–1970.

[74] Y. Meng, K. Wang, Y. Zhang and Z. Wei, Adv. Mater., 2013, 25, 6985–6990.

[75] P. A. Mini, A. Balakrishnan, S. V. Nair and K. R. V. Subramanian, Chem. Commun., 2011, 47, 5753–5755.

[76] A. Laforgue, P. Simon, C. Sarrazin and J.-F. Fauvarque, J. Power Sources, 1999, 80, 142–148.

[77] G. A. Snook, P. Kao and A. S. Best, J. Power Sources, 2011, 196, 1–12.
[78] J. M. D’Arcy, M. F. El-Kady, P. P. Khine, L. Zhang, S. H. Lee, N. R. Davis, D. S. Liu, M. T. Yeung, S. Y. Kim, C. L. Turner, A. T. Lech, P. T. Hammond and R. B. Kaner, ACS Nano, 2014, 8, 1500–1510.
[79] Jang, J. Conducting Polymer Nanomaterials and Their Applications. Adv. Polym. Sci. 2006, 199, 189–259.
[80] D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G. Q. Lu and H.-M. Cheng, ACS Nano, 2009, 3, 1745–1752.
[81] Kai Zhang, Li Li Zhang, X. S. Zhao, and Jishan Wu Chem. Mater. 2010, 22, 1392–1401
[82] Huai-Ping Cong, Xiao-Chen Ren, Ping Wanga and Shu-Hong Yu Energy Environ. Sci., 2013, 6, 3985-3992.
[83] S. Park and R. S. Ruoff, Nat. Nanotechnol., 2009, 4, 217
[84] Yan Liu, Ruijie Deng, Zan Wang and Hongtao Liu J. Mater. Chem., 2012, 22, 13619–13624
[85] Xiaochen Dong, Jingxia Wang, Jing Wang, Mary B. Chan-Park, Xingao Li, Lianhui Wang, Wei Huang, Peng Chen Materials Chemistry and Physics 134 (2012) 576e580
[86] Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J. Y.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. Nature 2011, 475, 364-367.
[87] Li, J. T.; Ye, F.; Vaziri, S.; Muhammed, M.; Lemme, M. C.; Ostling, M. Adv. Mater. 2013, 25, 3985-3992.
[88] Kai Chi, Zheyue Zhang, Jiangbo Xi, Yongan Huang, Fei Xiao, Shuai Wang, and Yunqi Liu ACS Appl. Mater. Interfaces 6, 18, 16312-16319
[89] J. Zhang, Y. Yu, L. Liu and Y. Wu, Nanoscale, 2013, 5, 3052–3057.
[90] Hao-Hsiang Chang, Chih-Kai Chang, Yu-Chien Tsai, Chien-Shiun Liao, CARBON 50 (2012) 2331–2336.
[91] Yang Zhao , Jia Liu , Yue Hu , Huhu Cheng , Chuangang Hu , Changchong Jiang , Lan Jiang , Anyuan Cao , and Liangti Qu , Adv. Mater. 2013, 25, 591–595
[92] M. Skompska, J. Mieczkowski, R. Holze, E. Heinze, J. Electroanal. Chem. 577 (2005) 9.
[93] Farah Alvi, Manoj K. Ram, Punya A. Basnayaka, Elias Stefanakos, Yogi Goswami, Ashok Kumar. Electrochimica Acta 56 (2011) 9406–9412.
[94] Suvi Lehtimaki, Milla Suominen, Pia Damlin, Sampo Tuukkanen, Carita Kvarnstrom, and Donald Lupo ACS Appl. Mater. Interfaces 6, 18, 16312-16319
[95] Zhong-Shuai Wu, Wencai Ren, Da-Wei Wang, Peng Li, Bilu Liu, and Hui-Ming Cheng ACSNANO VOL. 4 • NO. 10 • 5835–5842 • 2010
[96] Jun Yan, Zhuangjun Fan, Tong Wei, Weizhong Qian, Milin Zhang, Fei Wei. CARBON 48 (2010) 3825–3833
[97] Sheng Chen, Junwu Zhu, Xiaodong Wu, Qiaofeng Han, and Xin Wan. ASCNANO. VOL.4 NO.5 2010.
[98] Guihua Yu, Liangbing Hu, Michael Vosgueritchian, Huiliang Wang, Xing Xie, James R. McDonough, Xu Cui, Yi Cui, and Zhenan Bao Nano Lett. 2011, 11, 2905–2911
[99] Hamid Reza Naderi, Parviz Norouzi, Mohammad Reza Ganjali Applied Surface Science 366 (2016) 552–560
[100] Xiaochen Dong, Xuewan Wang, Jing Wang, Hao Song, Xingao Li, Lianhui Wang, Mary B. Chan-Park, Chang Ming Li, Peng Chen. CARBON N 5 0 ( 2 0 1 2 ) 4 8 6 5 – 4 8 7 0
[101] Jin Ge, Hong-Bin Yao, Wei Hu, Xiao-Fang Yu, You-Xian Yan, Li-Bo Mao, Hui-Hui Li, Shan-Shan Li, Shu-Hong Yu.Nano Energy (2013) 2, 505–513
[102] Umakant M. Patil, Ji Soo Sohn, Sachin B. Kulkarni, Hyung Goo Park, Youngmo Jung, Kishor V. Gurav, Jae Hun Kim, Seong Chan Jun.Materials Letters 119 (2014) 135–139
[103] Yongmin He, Wanjun Chen, Xiaodong Li, Zhenxing Zhang, Jiecai Fu, Changhui Zhao, and Erqiang Xie. ACSNANO.VOL. 7 ’ NO. 1 ’ 174–182 ’ 2013
[104] Yiju Li, Guiling Wang, Ke Ye, Kui Cheng, Yue Pan, Peng Yan, Jinling Yin, Dianxue Cao Journal of Power Sources 271 (2014) 582e588
[105] Zhong-Shuai Wu, Da-Wei Wang, Wencai Ren, Jinping Zhao, Guangmin Zhou, Feng Li, and Hui-Ming Cheng. Adv. Funct. Mater. 2010, 20, 3595–3602.

[106] Chengcheng Xiang, Ming Li, Mingjia Zhi, Ayyakkannu Manivannan, Nianqiang Wu. Journal of Power Sources 226 (2013) 65e70

[107] Kamatchi Kamaraj Purushothaman, Balakrishnan Saravanakumar, Inbamani Manohara Babu, Balasubramanian Sethurama and Gopalan Muralidharan. RSC Adv., 2014, 4, 23485

[108] Hailiang Wang, Hernandez Sanchez Casalongue, Yongye Liang, and Hongjie Dai. J. AM. CHEM. SOC. 9 VOL. 132, NO. 21, 2010

[109] Xiao-Chen Dong, Hang Xu, Xue-Wan Wang, Yin-Xi Huang, Mary B. Chan-Park, Hua Zhang, Lian-Hui Wang, Wei Huang, and Peng Chen. ACSNANO.VOL. 6 ' NO. 4 ' 3206–3213 ' 2012

[110] L.S. Panchakarla, K.S. Subrahmanyam, S.K. Saha, A. Govindaraj, H.R. Krishnamurthy, U.V. Waghmare, C.N.R. Rao, Adv. Mater. 21 (2009) 4726—4730.

[111] C. Zhu, S. Dong, Nanoscale 5 (2013) 1753—1767.

[112] H.-L. Guo, P. Su, X. Kang, S.-K. Ning, J Mater. Chem. A 1 (2013) 2248–2255.

[113] L. Zhao, R. He, K.T. Rim, T. Schiros, K.S. Kim, H. Zhou, C. Gutiérrez, S.P. Chockalingam, C.J. Arguello, L. Pálová, D. Nordlund, M.S. Hybertsen, D.R. Reichman, T.F. Heinz, P. Kim, A. Pinczuk, G.W. Flynn, A.N. Pasupathy. Science 333 (2011) 999–1003.

[114] L. Qu, Y. Liu, J.-B. Baek, L. Dai. ACS Nano 4 (2010) 1321–1326

[115] Lei Li, Peng Gao, Shili Gai, Fei He, Yujin Chen, Milin Zhang, Piaoping Yang. Electrochimica Acta 190 (2016) 566–573

[116] Penghui Zhao, Weilong Li, Gang Wang, Baozhi Yu, Xiaojun Li, Jintao Bai, Zhaoyu Ren. Journal of Alloys and Compounds 604 (2014) 87–93

[117] Zhenhai Wen, Xinchen Wang, Shun Mao, Zheng Bo, Haejune Kim, Shumao Cui, Ganhua Lu, Xinliang Feng, and Junhong Chen. Adv. Mater. 2012, 24, 5610–5616.

[118] Vikrant Sahu, Sonia Grover, Brindan Tulachan, Meenakshi Sharma, Gaurav Srivastava, Manas Roy, Manav Saxena, Niroj Sethy, Kalpana Bhargava, Deepu Philip, Hansung Kim, Gurmeet Singh, Sushil Kumar Singh, Mainak Das, Raj Kishore Sharma. Electrochimica Acta 160 (2015) 244–253.

[119] Zhi-Yin Sui, Yue-Na Meng, Pei-Wen Xiao, Zhi-Qiang Zhao, Zhi-Xiang Wei, and Bao-Hang Han. ACS Appl. Mater. Interfaces 2015, 7, 1431-1438.

[120] Yanhong Lu, Fan Zhang, Tengfei Zhang, Kai Leng, Long Zhang, Xi Yang, Yanfeng Ma, Yi Huang, Mingjie Zhang, Yongsheng Chen. Carbon 6 3 ( 2 0 1 3 ) 5 0 8 – 5 1 6.

[121] Li Sun, Lei Wang, Chungui Tian, Taixing Tan, Ying Xie, Keying Shi, Meitong Li and Honggang Fu. RSC Adv., 2012, 2, 4498–4506.

[122] Jongwoo Han, Li Li Zhang, Seungjun Lee, Junghoon Oh, Kyoung-Seok Lee, Jeffrey R. Potts, Junyi Ji, Xin Zhao, Rodney S. Ruoff, and Sungjin Park. ACSNANO.VOL. 7 ' NO. 1 ' 19–26 ' 2013.

[123] Zhiwei Peng, Ruquan Ye, Jason A. Mann, Dante Zakhidov, Yilun Li, Preston R. Smalley, Jian Lin, and James M. Tour. ACSNANO.VOL. 9 ' NO. 6 ' 5868–5875 ' 2015.

[124] Zhong-Shuai Wu, Andreas Winter, Long Chen, Yi Sun, Andrey Turchanin, Xinliang Feng, and Klaus Müllen. Adv. Mater. 2012, 24, 5130–5135

[125] Sanjit Saha, Milan Jana, Partha Khanra, Pranab Samanta, Hyeyoung Koo, Naresh Chandra Murmu, and Tapas Kuila. ACS Appl. Mater. Interfaces 2015, 7, 14211-14222

[126] Zuo, Z.; Jiang, Z.; Manthiram, A. Mater. Chem. A 2013, 1, 13476–13483.

[127] Han, J.; Zhang, L. L.; Lee, S.; Oh, J.; Lee, K.-S.; Potts, J. R.; Ji, J.; Zhao, X.; Ruoff, R. S.; Park, S. ACS Nano 2012, 7, 19–26.

[128] Niu, L.; Li, Z.; Hong, W.; Sun, J.; Wang, Z.; Ma, L.; Wang, J.; Yang, S. Electrochim. Acta 2013, 108, 666–673.

[129] Wang, D.-W.; Li, F.; Chen, Z.-G.; Lu, G. Q.; Cheng, H.-M. Chem. Mater. 2008, 20, 7195–7200.
[130] Shiraishi, S.; Kibe, M.; Yokoyama, T.; Kurihara, H.; Patel, N.; Oya, A.; Kaburagi, Y.; Hishiyama, Y. Appl. Phys. A: Mater. Sci. Process. 2006, 82, 585–591.

[131] Kwon, T.; Nishihara, H.; Itoi, H.; Yang, Q. H.; Kyotani, T. Langmuir 2009, 25, 11961–11968.

[132] S. Nohara, H. Wada, N. Furukawa, H. Inoue, M. Morita, C. Iwakura, Electrochim. Acta 2003, 48, 749.

[133] M. Morita, J. L. Qiao, N. Yoshimoto, M. Ishikawa, Electrochim. Acta 2004, 50, 837.

[134] J.-H. Sung, S.-J. Kim and K.-H. Lee, J. Power Sources, 2003, 124, 343–350.

[135] Z. Niu, L. Zhang, L. Liu, B. Zhu, H. Dong and X. Chen, Adv. Mater., 2013, 25, 4035–4042.

[136] M. A. Q. Xue, F. W. Li, J. Zhu, H. Song, M. N. Zhang, T. B. Cao, Adv. Funct. Mater. 2012, 22, 1284.

[137] Z. S. Wu, K. Parvez, X. Feng and K. Müllen, Nat. Commun., 2013, 4, 2487.

[138] M. F. El-Kady and R. B. Kaner, Nat. Commun., 2013, 4, 1475.

[139] Zhong-Shuai Wu, Yijun Zheng, Shuanghao Zheng, Sen Wang, Chenglin Sun, Khaled Parvez, Taichi Ikeda, Xinhe Bao, Klaus Müllen, and Xinliang Feng. Adv. Mater. 2017, 29, 1602960.

[140] Ananthakumar Ramadoss, Ki-Yong Yoon, Myung-Jun Kwak, Sun-I. Kim, Seung-Tak Ryu, Ji-Hyun Jang. Journal of Power Sources 337 (2017) 159e165.

[141] Sanjoy Mondal, Utpal Rana, and Sudip Malik. J. Phys. Chem. C 2017, 121, 7573-7583.

[142] Y. Huang, H. Hu, Y. Huang, M. Zhu, W. Meng, C. Liu, Z. Pei, C. Hao, Z. Wang, C. Zhi, ACS Nano 9 (2015) 4766e4775.

[143] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, Nat. Commun. 5 (2014) 3754.

[144] X. Wang, B. Liu, R. Liu, Q. Wang, X. Hou, D. Chen, R. Wang, G. Shen, Angew. Chem. Int. Ed. 53 (2014) 1849e1853.

[145] Zheye Zhang, Fei Xiao and Shuai Wang. J. Mater. Chem. A, 2015, 3, 11215.

[146] W. Cai, T. Lai, J. Lai, H. Xie, L. Ouyang, J. Ye, C. Yu. Sci. Rep. 6 (2016) 26890.

[147] Siliang Wang, Nishuang Liu, Jun Su, Luying Li, Fei Long, Zhengguang Zou, Xueliang Jiang, and Yihua Gao. ACS Nano 2017, 11, 2066-2074.

[148] Jiali Yu, Mei Wang, Ping Xu, Seung-Hyun Cho, Jonghwan Suhr, Ke Gong, Linghui Meng, Yudong Huang, Joon-Hyung Byun, Youngsook Oh, Yushan Yan, Tsu-Wei Chou. Carbon 119 (2017) 332e338.

[149] Maher F. El-Kady, Veronica Strong, Sergey Dubin, Richard B. Kaner. Science, 2012,335(6074): 1326-1330.

[150] Ruquan Ye, Xiao Han, Dmitry V. Kosynkin, Yilun Li, Chenhao Zhang, Bo Jiang, Angel A. Marti, and James M. Tour. ACS Nano 2018, 12, 1083-1088.

[151] Stoller MD, Park S, Zhu Y, An J, Rouff RS. Nano Letter 2008;8:3498–502.

[152] Wang G, Yang J, Park J, Gou X, Wang B, Liu H, et al. J Phys Chem C 2008;112:8192–5.

[153] Stankovich S, Dinkin DA, Greffrey HBD, Kohlhaas KM, Zimney EJ, Stach EA,et al. Nature 2006;440:282–6.

[154] Du V, Surwade SP, Ammu S, Agnihotra SR, Jain S, Roberts KE, et al. Angew Chem Int Ed 2010;122:2200.

[155] Ramachandran R, Felix S, Joshi GM, Raghupathy BPC, Jeong SK, Grace AN. Mater Res Bull 2013;48:3834-42.

[156] Rajendran Ramachandran, Murugan Saranya, Venugopal Velmurugan, Bala P.C. Raghupathy, Soon Kwan Jeong, Andrews Nirmala Grace. Applied Energy 153 (2015) 22–31.

[157] M.D. Levi, Y. Gofer, D. Aurbach, M. Lapkowski, E. Vieil, J. Serole, J. Electrochem. Soc. 147 (2000) 1096.