Advances in research on 2D and 3D graphene-based supercapacitors*

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Abstract

Graphene-based materials in two-dimensional (2D) and three-dimensional (3D) configurations are promising as electrode materials for supercapacitors due to their large surface area, excellent electrical conductivity, high electrochemical activity and high stability. In this article recent advances in research on 2D and 3D graphene-based materials for supercapacitor electrodes are reviewed extensively in aspects of fabrication methods and electrochemical performances. From the survey, the performance of 2D and 3D graphene-based materials could be significantly enhanced by employing nanostructures of metal oxides, metals and polymers as well as doping graphene with hetero atoms such as nitrogen and boron. In addition, the charge storage performances were found to depend greatly on materials, preparation method and structural configuration. With similar material components, 3D graphene-based networks tended to exhibit superior supercapacitive performances. Therefore, future research should be focusing on further development of 3D graphene-based materials for supercapacitor applications.

Keywords: 2D graphene, 3D graphene, supercapacitors, electrode materials

Classification numbers: 2.07, 5.15, 5.18

1. Introduction

Capacitors are passive electrical devices that store energy on two conducting metal plates sandwiched around a dielectric. In comparison with batteries, capacitors weigh less and do not carry toxic metals or toxic chemical. In addition, charging and discharging can be repeated numerous times without breaking down. However, dielectric capacitors can store much less electrical energy than batteries. Electrochemical capacitors or supercapacitors (SCs) have thus been developed in order to improve electrical energy storage in capacitors. Unlike conventional capacitors, a supercapacitor comprises two electrodes submerged in an electrolyte and separated by an ion-permeable membrane, typically referred to as a separator. The electrodes of supercapacitors are made of a conductive, porous material, providing a much larger surface area for...
charge storage. In addition, SCs can offer much higher power density than batteries due to faster charge-discharge process within seconds while their energy densities can be more than 10 Wh kg$^{-1}$, which is satisfactory for several applications. Moreover, SCs exhibit an outstanding cycle ability more than 100 times that of batteries and low self-discharging. Thus, SCs have garnered high interest by scientists of related disciplines due to their potential for complementing and/or replacing more conventional batteries.

Typically, SCs can be classified according to the energy storage mechanism into two distinct categories, i.e. electrochemical double layer capacitors (EDLCs) and pseudocapacitors (PCs). EDLCs accumulate charge by electrostatic ion adsorption at the interface between electrodes and electrolyte on both sides of the separator. EDLC’s energy capacity may be effectively enhanced by increasing the available specific surface area, pore size and electrical conductivity [1]. PCs, on the other hand, store energy by additional reversible faradic processes (redox reactions) at characteristic potentials. PCs can provide higher specific capacitances and energy densities than pure EDLCs [2, 3]. However, pseudocapacitive materials tend to suffer from low conductivity, which causes high equivalent series resistance and limited specific capacitance. Moreover, some PC materials, particularly conducting polymers, exhibit low cycling stability [4].

Graphene, the atomically thin 2D layer of sp$^2$-hybridized carbon atoms arranged in a honeycomb crystal lattice, is one of the most intensively researched electrode materials for SCs due to its high carrier mobility, large electrical conductivity, high specific surface area (~2700 m$^2$ g$^{-1}$) as well as high mechanical strength (~1 TPa) and chemical resilience [5–10]. It has been predicted that graphene’s high specific surface area can lead to a large theoretical double layer capacitance of up to 21 μF cm$^{-2}$ or 550 F g$^{-1}$ [11]. Thus, graphene can exhibit superior energy storage performances compared with graphite, carbon nanotubes (CNTs) and other carbon nanostructures. Moreover, graphene can be synthesized from graphite at low cost by several physical and chemical techniques. With the aforementioned attributes, graphene is considered a very promising candidate for SC applications in a wide range of electronic devices such as portable systems, hybrid electric vehicles, memory protection in CMOS logic circuits, home electronics, PCs, uninterruptible power supplies (UPS) in security alarm systems, remote sensing, smoke detectors, etc.

However, self-agglomeration of graphene due to strong attractive forces between sheets is a challenging obstacle in the way of large scale production of high quality graphene-based supercapacitors. Various methods of graphene surface modifications have been developed to allow stable molecular dispersion of individual (or at least few layer) graphene sheets while retaining most of desirable intrinsic properties. For instance, covalent functionalization of graphene with oxygen-containing groups, graphene oxide (GO) has been shown to significantly improve their dispersability [12, 13]. However, several of these methods negatively impact graphene’s overall electrochemical performance. Thus, it is still a great challenge for scientists to devise new ways to improve the structures of graphene-based materials for supercapacitor applications. The combination of highly conductive graphene and pseudocapacitive materials is a way to augment the inferior electrochemical properties of PCs. Therefore, SCs based on graphene-conductive polymer or graphene-metal oxide and hydroxide nano-particles have recently been widely investigated. In these composite materials, graphene can provide conducting pathways for the redox reactions of the pseudocapacitive species and enhancing the electrical conductivity [14–17].

Another important approach is to construct 3D graphene structures, which are groups of 2D graphene formed or connected into well-defined 3D architectures. Important examples of 3D graphene include graphene foams, graphene aerogels and graphene networks. The key advantages of 3D graphene structures include high effective surface area, high electrical conductivity and good reproducibility. In addition, they can act as conductive skeletons supporting other electrochemically active materials added to enhance the supercapacitive performances. 3D graphene has been compositied with various types of materials including other carbon nanostructures such as carbon nanotubes (CNTs), conductive polymers such as polyaniline and metal oxides such as MnO$_2$ for SC applications. In this review, recent advances in the field of SCs based on 2D and 3D graphene-based materials are broadly covered. In addition, the preparation methods and structural properties as well as electrochemical performances of graphene-based materials are discussed.

2. 2D graphene-based supercapacitors

The 2D sheet structure of graphene makes it a nearly ideal candidate for thin film supercapacitors. Graphene sheets can be facilely assembled into free-standing thin-film electrodes [18, 19]. In 2008, Ruoff et al [1] pioneered the development of chemically modified graphene (CMG) made by chemical functionalization of monolayer graphene. CMG electrode materials exhibited a high specific surface area of 705 m$^2$ g$^{-1}$ as well as specific capacitances of 135 F g$^{-1}$ in a 5.5 M KOH aqueous solution and 99 F g$^{-1}$ in a 1 M tetraethylammonium tetrafluoroborate (TEABF$_4$)/acetoni­trile (AN) electrolyte, respectively. To enhance the capacitive performance of graphene-based materials, Peng et al [20] introduced oxygen-rich in-plane pores into graphene backbones through sonochemical etching of GO and subsequent chemical reduction. The fabricated electrodes held maximum energy and power densities of 47 Wh kg$^{-1}$ and 100 kW kg$^{-1}$, respectively, which were almost three times as high as those of reduced GO (rGO) without etching treatment.

Another important form of graphene electrodes is 2D graphene papers. With this approach, Ruoff et al [21] prepared highly conductive, free-standing, and flexible porous carbon thin films by KOH activation of rGO paper without conductive additives and binders. The graphene papers exhibited a high specific surface area of ~2400 m$^2$ g$^{-1}$, a high electrical conductivity of 5880 S m$^{-1}$ and a high specific capacitance of 120 F g$^{-1}$ at a current density of 10 A g$^{-1}$ in TEABF$_4$/AN electrolyte. Alternatively, Liu et al [22] devised a facile template approach to prepare highly conductive and flexible
rGO paper with hierarchical porous structures that possesses large ion-accessible surface area and efficient electrolyte-ion transport pathways. Porous rGO electrodes delivered specific capacities of 173.5 F g\(^{-1}\), \(\sim 1.8\) times higher than packed rGO. Also, porous electrodes exhibited good electrochemical performance with energy and power densities of 28.5 W h kg\(^{-1}\) and 4 kW kg\(^{-1}\), respectively, as well as excellent cycling stability, retaining 101.5% of its initial capacitance after 2000 cycles at 5 A g\(^{-1}\). Additionally, graphene-based thin-film micro-supercapacitors fabricated by spin-coating achieved high area capacities up to 80.7 µF cm\(^{-2}\) [23]. Furthermore, methods such as vacuum-filtration, interfacial self-assembly at oil/water interfaces, layer-by-layer stacking and Langmuir–Blodgett deposition have been used to prepare 2D graphene structures for energy storage applications [24–27].

One of the main problems concerning the processibility of single- or few-layer graphene is the tendency to restack and agglomerate due to the strong \(\pi-\pi\) interactions between individual sheets and thereby negatively affecting the surface area to volume ratio and limiting the surface available for electrochemical double layer formation. This, in turn, leads to drastically diminished electrochemical energy storage performances. A potential way to inhibit restacking is to incorporate atoms or molecules which are chemically or physically bonded to graphene sheets, preventing agglomeration via either steric hindrance or soluble functional groups. Suitable materials for this purpose include metal oxides (e.g. SnO\(_2\), MnO\(_2\) and NiO), metal particles (e.g. Au, Ag and Pt), organic compounds (e.g. water-soluble polymers and surfactants) and conducting polymers [3, 12, 28–36]. For instance, Wang et al [31] developed graphene paper pillared with carbon black nanoparticles using a simple vacuum filtration method. The inclusion of these particles greatly mitigated the restacking of graphene sheets during the filtration process. The material exhibited a good specific capacitance value of 138 F g\(^{-1}\) in an aqueous electrolyte at a scan rate of 10 mV s\(^{-1}\) and specific capacitance retention of 96.15% after 2000 cycles at a current density of 10 A g\(^{-1}\). Alternatively, Li et al [37] prepared bendable graphene film electrode materials based on pseudo-capacitive Ni(OH)\(_2\) nano-platelets intercalated between graphene sheets via an extended filtration assisted method. The method could effectively prohibit self-restacking of graphene, resulting in enhanced electrochemical performances with a high specific capacitances of 537 F g\(^{-1}\) (corresponding to 655 F cm\(^{-3}\) volumetric capacitance). Similarly, Choi et al [38] developed a graphene/MnO\(_2\) composite film electrode by a filtration method, achieving a good specific capacitance of 389 F g\(^{-1}\) in 1 M NaSO\(_4\) and a 95% capacitance retention after 1000 cycles. Moreover, high energy- and power-density supercapacitors using an asymmetric configuration of Fe\(_2\)O\(_3\) and MnO\(_2\) nanoparticles embedded in macroporous graphene film electrodes were fabricated by performing vacuum filtration of metal-ion containing GO sheets and converting them into metal nano-particle/rGO films by microwave irradiation, which can be operated in a safe and low-cost aqueous electrolyte [39]. The asymmetric configuration resulted in a large potential window of 1.8 V, a good energy density of 41.7 W h kg\(^{-1}\), a high power density of 13.5 kW kg\(^{-1}\) and a good energy/power retention for over 5000 cycles at a high current density of 16.9 A g\(^{-1}\). Furthermore, Liu et al [40] prepared CuO nanosheets (NSs)/rGO hybrid films by vacuum filtration of CuO NSs/rGO composite dispersions, followed by hydrothermal reduction. The CuO NSs/rGO hybrid lamellar films exhibited a specific capacitance of 163.7 F g\(^{-1}\), which was higher than those of CuO NSs (69.7 F g\(^{-1}\)) and rGO (66.0 F g\(^{-1}\)). CuO NSs/rGO films retained an effective capacity of 82.5 F g\(^{-1}\) after 1000 cycles.

In another approach based on organic materials, Yang et al [41] developed a flexible, porous and yet dense chemically converted graphene gel film via capillary compression of graphene in the presence of volatile and non-volatile liquid electrolytes, attaining a high volumetric capacitance values of 255.5 F cm\(^{-3}\) in aqueous electrolytes. In addition, Mao et al [3] stabilized aqueous graphene dispersions by reducing GO in the presence of surfactants such as tetrabutylammonium hydroxide (TBAOH) and sodium dodecyl benzene sulphonate (SDBS). Polyaniline (PANI) was then polymerized in situ in these stable graphene/surfactant dispersions. The resulting material, consisting of PANI and graphene stabilized with TBAOH (weight ratio 9:1), showed high specific capacitance of 526 F g\(^{-1}\) at a current density of 0.2 A g\(^{-1}\) with a good cycle life. Likewise, PANI-coated graphene sheets (~15 wt%) prepared via chemical routes exhibited a large specific capacitance of 1046 F g\(^{-1}\) and retained 96% of this value even at higher current densities of 10–100 A g\(^{-1}\) [42, 43]. Also, Wang et al [44] prepared PANI nanowire arrays on flexible polystyrene microsphere/reduced graphene films via dilute polymerization and then removed the microspheres to form a free-standing rGN/PANI nanocomposite film. A high specific capacitance value of 740 F g\(^{-1}\) (corresponding to 581 F cm\(^{-3}\)) at a current density of 0.5 A g\(^{-1}\) and the capacitance retention of 87% after 1000 cycles at 10 A g\(^{-1}\) were achieved. The maximum energy density and power density were found to be 65.94 W h kg\(^{-1}\) and 0.2 kW kg\(^{-1}\), respectively. Moreover, Zhang et al [45] reported a graphene-based film with inserted hollow polypyrrole (PPy) spheres between graphene sheets, realizing a specific capacitance of up to 500 F g\(^{-1}\) at current densities of 5 A g\(^{-1}\) that remained stable even after 10\(^6\) charge/discharge cycles. Furthermore, Lehtimäki et al [46] combined poly(3,4-ethylenedioxythiophene) (PEDOT) and GO by a simple electropolymerization process on flexible substrates followed by further electrochemical reduction of GO into rGO. The PEDOT/rGO composite offered a high areal specific capacitance value of 14 F cm\(^{-2}\), which was ascribed to the largely accessible surface area of rGO combined with the pseudocapacitance of PEDOT.

Doping graphene’s sp\(^2\)-hybridized crystal lattice with hetero-atoms such as N, B, S and P is another promising way to alter its molecular structure and effectively enhance graphene’s supercapacitive performance. Among these hetero-atoms, nitrogen (N) received the most attention due to its high electro-negativity, comparable atomic size to the carbon atom and ability to donate additional free electrons [47–50]. Firstly, Śliwak et al [51] synthesized N-doped rGO (N-rGO) by a facile hydrothermal route involving the doping of an aqueous graphene oxide dispersion with 3-amino-1,2,4-triazole (amitrole). N-rGO,
with exceptionally high nitrogen contents ranging from 10.9 to 13.4 at%, showed capacitance values of 244 F g$^{-1}$ at a scan rate of 100 mV s$^{-1}$ in 6 M KOH and a good capacitance retention of 92% after 5 × 10$^3$ cycles due to the high stability of the electrochemically active nitrogen moieties. Similarly, Chen et al. [49] prepared N-doped graphene nanosheets by reduction of graphene oxide with NH$_2$H$_2$PO$_4$ (NGC) and (NH$_2$)$_2$HPO$_4$ (NGL) in a mild hydrothermal process. Nanosheets grown using NGC were found to have lower nitrogen but higher oxygen content than those using NGL. N-doped graphene nanosheets prepared by NGC exhibited relatively high specific capacitance, energy density and capacitance retention (383 F g$^{-1}$ at 1 A g$^{-1}$, 12.21 Wh kg$^{-1}$ at 0.25 A g$^{-1}$ and 8.81% after 10$^4$ cycles) compared with those prepared by NGL (356 F g$^{-1}$ at 1 A g$^{-1}$, 9.28 Wh kg$^{-1}$ at 0.25 A g$^{-1}$ and 4.80% after 10$^4$ cycles). Nitrogen-rich graphene nanosheets (NGN) with crumpled, stacked, and cross-linked sheet structures were developed using hydrothermal treatment and formaldehyde polymerization. The cross-linked NGN structure with 14.7 at% N content and 88 m$^2$ g$^{-1}$ specific surface area displayed the specific capacitance of 201 F g$^{-1}$ at 50 mA g$^{-1}$ in 1 M H$_2$SO$_4$ electrolyte with the capacitance retention of 96.2% after 10$^4$ cycles at 5 A g$^{-1}$ [52]. In addition to nitrogen, phosphorous (P) was doped into graphene by annealing the mixture of graphene and phosphoric acid. Results showed that P-doping of graphene led to significantly improved specific capacitance and cycling stability in an aqueous electrolyte of 1 M H$_2$SO$_4$, compared with undoped graphene electrodes. The P-doped graphene electrode could withstand a wide voltage window of 1.7 V with only 3% performance degradation after 5000 cycles at a current density of 5 A g$^{-1}$, providing a high energy density of 11.64 W h kg$^{-1}$ and a high power density of 831 W kg$^{-1}$ [53]. Furthermore, sulfur was doped into 3D porous rGO hollow nanoparticle frameworks by directly annealing graphene oxide-encapsulated amino-modified SiO$_2$ nanoparticles with dibenzyl disulfide, followed by hydrofluoric acid etching. The as-prepared products showed a high specific capacitance of 343 F g$^{-1}$, good rate capability and excellent cycling stability in an aqueous electrolyte [54].

Doping graphene with boron (B) is also feasible due to its comparable atomic size and electronic properties. The B atoms, with three valence electrons, act as p-type dopants in the carbon lattice, leading to the shift of Fermi level towards the valence band and a change of graphene electronic structure. This structural change effects the electrochemical properties of the resultant B-doped graphene, which can be prepared by several methods [19]. For instance, boron was doped into thermally reduced graphene nanosheets by hydrothermal treatment using H$_3$BO$_3$. The B-doped graphene electrode exhibited a specific capacitance of 113 F g$^{-1}$ at 1 A g$^{-1}$, about twice as high as that of undoped one (53 F g$^{-1}$) [55]. In addition, boron-doped graphene structures with porous morphologies were developed by an easy and efficient approach based on the ‘Fried-Ice’ concept. The porous graphene structures were produced via the steam etching effect, exhibiting a high specific surface area of 622 m$^2$ g$^{-1}$ and a good specific capacitance of 281 F g$^{-1}$ with a long cycle life in an aqueous electrolyte [56].

Lastly, codoping graphene with two types of dopants can also greatly benefit electrochemical performance [57–59]. For example, a novel strategy for synthesis of highly porous nitrogen-sulfur co-doped graphene nanoribbons (NS-GNRs) with enhanced active sites was developed by Gopalsamy et al. [57]. The highly porous NS-GNR provided efficient ion transport paths, thereby enhancing the conductivity and stability of electrode material. NS-GNR exhibited a high specific capacitance of 442 F g$^{-1}$ at 0.5 A g$^{-1}$, a wide operating voltage window of ~1.8 V, a good energy density of ~23.85 Wh kg$^{-1}$, a high power density of ~8753 W kg$^{-1}$, excellent rate capability and cycling performance with capacitance retention of ~98.6% after 10$^4$ cycles. Also, a novel flexible architecture of nitrogen and sulfur co-doped graphene structures was synthesized via a thermal treatment in the mixture of liquid crystalline graphene oxide and doping agents followed by a soft self-assembly approach, resulting in a high surface area macro- and nanoporous free-standing material. A good gravimetric capacitance of 305 F g$^{-1}$ (at 100 mV s$^{-1}$), a volumetric capacitance of 188 F cm$^{-1}$ (at 1 A g$^{-1}$), an outstanding energy density of 28.44 W h kg$^{-1}$ and a long cycle life of 10$^4$ cycles were obtained [58]. In another approach using phosphorous (P) codopant, a phosphorus and nitrogen co-doped carbon material (PNDC) was synthesized from aminated tannin and polyphosphoric acid by a rapid and highly efficient microwave synthetic technique. Specific capacitance in 6 M KOH was determined to be 161 F g$^{-1}$ [59]. Also, melanine phosphate, as a sole precursor, was used to synthesize nitrogen/phosphorous co-doped graphene (N/P-G) monoliths by a facile hydrothermal method. The N/P-G materials exhibited excellent electrochemical performances as electrodes for supercapacitors with specific capacitances of 183 F g$^{-1}$ at 50 mA g$^{-1}$ and a high energy density of 11.33 W h kg$^{-1}$ at 1.6 V in 1 M H$_2$SO$_4$ aqueous electrolyte [60].

3. 3D graphene-based supercapacitors

3D graphene based architectures have attracted huge attention owing to the combination of the structural interconnectivities and the outstanding properties of graphene, resulting in functional structures with low density, high porosity, large surface area, high electrical conductivity and improved structural stability [61, 62]. To date, different strategies have been developed to obtain different 3D graphene architectures including hydrogels [63], aerogels [64], foams [62, 65] and sponges [66]. In addition, 3D graphene has been combined and modified with various types of nanomaterials including metal oxide nanostructures, metal nanoparticles and conductive polymers for supercapacitor applications. For example, CoO nanobundle-3D graphene foam (CoO NB@GF) composite was fabricated by chemical vapor deposition (CVD) on Ni foams using ethanol as a carbon source, acid etching and hydrothermal treatment using cobalt nitrate and urea. CoO NB@GF exhibited a high specific capacitance of 352.75 F g$^{-1}$ at 1 A g$^{-1}$ in 3 M NaOH, a low equivalent series resistance (ESR) of 2.12 Ω and a low charge transfer resistance (Rct) of 4.78 Ω, indicating consistent interfacial contacts between
the CoO and 3D graphene foams [67]. Likewise, Ni(OH)\(_2\) nanoflakes were synthesized on 3D CVD graphene foam by a hydrothermal method using NiCl\(_2\)-6H\(_2\)O and KOH solutions. The specific capacitances of Ni(OH)\(_2\)/3D graphene foam were as high as 1450 F g\(^{-1}\) at 5 A g\(^{-1}\) and 1196 F g\(^{-1}\) at 60 A g\(^{-1}\) with the capacitance retention of 78% after 1000 cycles in 6 M KOH [68]. Also, Co\(_3\)O\(_4\) nanosheet arrays were produced by a hydrothermal technique using a solution containing Co(NO\(_3\))\(_2\)-6H\(_2\)O, NH\(_4\)F and Co(NH\(_2\))\(_2\) on 3D graphene/nickel foam, which was prepared by electrophoretic deposition/annealing in argon gas. Electrochemical measurements in three-electrode configuration demonstrated an ultrahigh specific capacitance of 3533 F g\(^{-1}\) at 1 A g\(^{-1}\) and 2222 F g\(^{-1}\) at 20 A g\(^{-1}\). The superior pseudocapacitive performances could be attributed to its unique structural characteristics [69]. In another study, manganese dioxide (MnO\(_2\)) was grown in situ on 3D graphene using reverse microemulsion (water in oil method) reaction under ultrasonication. The MnO\(_2\)/3D graphene exhibited a high specific capacitance of 659.7 F g\(^{-1}\) at 0.3 A g\(^{-1}\) with a capacitance retention of 106% after 1000 cycles using three-electrode system in 1 M Na\(_2\)SO\(_4\) [70]. Moreover, CoMoO\(_4\) nanoplatelets/CVD 3D-graphene was prepared by a facile two-step hydrothermal method. From electrochemical measurement using three-electrode configuration in 2 M KOH, the specific capacitance of the CoMoO\(_4\)/3D-graphene was 1255.2 F g\(^{-1}\) at 1 A g\(^{-1}\) with a cycling stability of 91.3% after 3000 cycles at 1 A g\(^{-1}\). The 3D-graphene/CoMoO\(_4\) electrode was then assembled in all-solid state asymmetric supercapacitor with activated carbon as the other electrode and PVA/KOH gel as electrolyte. The specific capacitance of the asymmetric configuration was 109 F g\(^{-1}\) at 0.2 A g\(^{-1}\) with a low capacitance attenuation of 12.1% after 3 \times 10\(^5\) cycles at 1 A g\(^{-1}\) [71]. In another investigation, silver nanoparticles (AgNPs) were decorated on CVD 3D graphene foam by a simple and rapid microwave-assisted growth using AgNO\(_3\) and silver citrate. From electrochemical measurements in three-electrode system in 4 M KOH, the specific capacitance of GNs/AgNPs was 528 F g\(^{-1}\) at 1 A g\(^{-1}\) with an excellent retention of 93% after 3000 cycles [72].

Conductive polymers have also been widely applied on 3D graphene to enhance the supercapacitor performances. For instance, 3D rGO/PANI nanocomposite films were prepared by diffusion driven layer-by-layer (dd-LbL) assembly. Graphene oxide was assembled into a 3D-rGO framework with an aqueous ammonia solution. The 3D NG exhibited a hierarchical and interconnected porous network, offering favorable pathways for electrolyte penetration and transportation. The 3D NG gave the specific capacitance of 334 F g\(^{-1}\) at 1 A g\(^{-1}\) in 1 M H\(_2\)SO\(_4\), corresponding to the energy and power densities of 28.06 Wh kg\(^{-1}\) and 0.25 kW kg\(^{-1}\), respectively [75]. Furthermore, 3D rGO-carbon nanotubes-polyaniline hybrids (rGO-CNTs-PANI hybrid) on Ni foam was fabricated by electrophoretic deposition of GO onto Ni foams and the growth of uniformly aligned CNTs on rGO via floating catalyst chemical vapor deposition (FCCVD), followed by in situ anodic electrochemical polymerization of aniline monomer onto rGO-CNTs. The results revealed that the as-prepared hybrid assembled in the two-electrode configuration showed a high specific capacitance of 741 F g\(^{-1}\), a good energy density of 92.4 W h kg\(^{-1}\), a high power density of 6.3 kW kg\(^{-1}\) and good cycling stability with a retention of 95% after 5000 cycles at a scan rate of 10 mV g\(^{-1}\) [76].

Moreover, supramolecular chemistry has been introduced to modify 3D-graphene to enhance electrochemical performance of SC electrodes. For instance, supramolecular \(\beta\)-cycloglutathione polymers (\(\beta\)-CDP) assembled 3D graphene hybrid (called rGO@\(\beta\)-CDP@PEG-AD) was synthesized by mixing \(\beta\)-CDP with graphene oxide (GO) in aqueous solution and reduction by hydrazine in KOH. Then, adamantane end-capped poly(ethylene oxide) (PEG-AD) was introduced into rGO sheets to increase the interlayer spacing of rGO sheets to form 3D structure, providing efficient 3D electron transfer pathways, ion diffusion channels and infiltration of gel electrolyte. The attained specific capacitance was 163 F g\(^{-1}\) at 1 A g\(^{-1}\) with 80% of retention after 10\(^4\) cycles at 1 A g\(^{-1}\) and 82% after 5 \times 10\(^5\) cycles at 2 A g\(^{-1}\) in 6 M KOH [77].

Nitrogen doping has also been widely applied to 3D-graphene in order to enhance the electrochemical properties. For example, 3D porous nitrogen-doped graphene hydrogel (N-rGOH) was synthesized hydrothermally from graphene oxide mixed with poly dimethyldiallylammonium (PDDA) chloride and ammonium bicarbonate in aqueous solution. The chains of PDDA could bind two or more GO sheets through hydrogen bonding or electrostatic forces, which were the driving force for the 3D GO hydrogel formation, providing larger specific surface area (335.6 m\(^2\) g\(^{-1}\)), higher nitrogen content (10.8 at%), higher electrical conductivity, lower density and better electron transfer channels. The N-rGOH based supercapacitor device displayed a specific capacitance of 48.6 F g\(^{-1}\) at 0.5 A g\(^{-1}\) over a potential window of 3.2 V in an ionic liquid electrolyte, corresponding to a high energy density of 94.5 W h kg\(^{-1}\). The retention of 87% after 5000 cycles at scan rate of 100 mV s\(^{-1}\) was also observed [78]. In another study [79], 3D nitrogen-doped graphene (3D NG) was fabricated via one-pot hydrothermal reduction by reacting graphene oxide with an aqueous ammonia solution. The 3D NG exhibited a hierarchical and interconnected porous network, offering favorable pathways for electrolyte penetration and transportation. The 3D NG gave the specific capacitance of 334 F g\(^{-1}\) at 0.5 A g\(^{-1}\) with an excellent cycling stability of 95% after 2 \times 10\(^5\) cycles at 10 A g\(^{-1}\) in 6 M KOH. The high capacitive...
performance could be attributed to N-configurations with a high N-content. In a more recent work [80], 3D NG was produced by carbonization of poly-o-phenylenediamine under N2 atmosphere using Ni nanoparticles as templates and catalyst. The 3D NG showed interconnected porous structure with high nitrogen doping content and had high ensuring large electrolyte-accessible surface area, rapid ion transportation and fast electron transport. From electrochemical measurement using three-electrode system, large and reversible redox reactions were observed implying a great pseudocapacitance of N/O-containing surface. The specific capacitance of 3D NG was 345 F g\(^{-1}\) at 1 A g\(^{-1}\) in 1 M H\(_2\)SO\(_4\), which was higher than that in 1 M KOH (312 F g\(^{-1}\) at 1 A g\(^{-1}\)) due to the larger pseudocapacitance. The excellent retention of 96% after 5000 cycles at 2 A g\(^{-1}\) was obtained in H\(_2\)SO\(_4\).

4. Conclusion and outlook

In summary, the electrochemical performances of 2D and 3D graphene-based materials prepared by various methods were reviewed. For 2D graphene-based materials, most reports employed additive materials including metal oxides, metal and polymer nanostructures between graphene sheets as molecular spacers to prevent self-restacking and provide additional stored charges via pseudocapacitance mechanism. Incorporation of hetero atoms such as N, P, S and B were shown to be another effective means to enhance the supercapacitive behaviors of 2D graphene. In the case of 3D graphene including hydrogels, aerogels, foams and sponges, metal oxide, metal and polymer nanostructures as well as N-doping were also employed to increase capacitance via effects of surface area, electronic conductivity and pseudocapacitance. In addition, the charge storage performances were found to depend greatly on materials, preparation method and structural configuration. With similar material components, 3D graphene-based network tended to exhibit superior supercapacitive performances. Thus, 3D graphene networks with interconnected porous structure compositing with other nanocarbon structures and pseudocapacitive nanomaterials should be further explored to achieve supercapacitors with high power density and energy density. In addition, mechanically flexible graphene-based materials for supercapacitors and other energy storage devices should be developed to accommodate the rapid development of flexible electronics.

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