Graphene Based Aerogels: Fundamentals and Applications as Supercapacitors

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ABSTRACT

Super Capacitors have attained a huge amount of attention due to their outstanding features and characteristics such as high-power density, excellent charge/discharge routine, and tendency of a longer lifetime. Graphene, a single layer of hexagonally crammed carbon atoms, has always been considered as an outstanding material for super capacitor fabrication due to its higher theoretical surface area, high electrical conductivity, stable thermal properties, and its mechanical and chemical properties. Super capacitor electrode resources which are based on 3D network/aerogel structures are resultant of graphene is a prime area of research due to their porous structure and lattice which meets the expense of rapid electron transport, higher stability, and a good cycle performance. This review intents to summarize the fundamentals and the fabrication strategies of 3D graphene aerogels.

1. Introduction

Supercapacitors, also known as the electrochemical capacitors or ultra-capacitors, have attained huge attention and recognition due to their outstanding characteristics such as the high specific power (500-10,000 W/kg), exceptional charge/ discharge performance and the tendency for a longer lifetime (>500,000 cycles) [1]. The supercapacitors are engaged together with the fuel cells or batteries in electric vehicles, power equipment, memory back-ups and some renewable energy devices [2]. They can be characterized as Electrical Double-Layer Capacitors (EDLC) and Pseudocapacitors based on the feature of charge storing mechanism [3]. Materials such as conducting polymers [4,5], carbon based porous materials [6], and transition metal oxides [7], etc. were extensively stated for fabricating a high-performing supercapacitor which attains a high energy storing capacity. Nonetheless, conducting polymers and metal oxides-based supercapacitors exhibit a rather poor stability and rate capability. The materials with high specific surface area, high porosity and a high electronic and ionic conductivities are required for the job of a supercapacitor with improved specific energies.

Graphene is a single layer of hexagonally packed carbon atoms, and has been deliberated to be an outstanding material for supercapacitor fabrication due to its features like high theoretical surface area (2630 m²/g), high electrical conductivity (2×10^3 S/cm), stable thermal properties and mechanical & chemical properties [8–15]. The charge storing mechanism in graphene is based on EDLC, thus, supercapacitors based on graphene shows a higher specific power and capacity retention paralleled with the pseudocapacitors [16]. Graphene has been generally reported as a supercapacitor electrode material by means of flexible free-standing layered structure [17,18], aerogels [19,20], hybrids [21], etc. to boost the energy density and the specific capacitance. Graphene is reflected as a superior material for supercapacitor applications because it has a high theoretical specific capacitance, estimated around to be of 550 F g^{-1} [22–24]. Nonetheless, the anticipated theoretical specific capacitance of graphene has not been accomplished so far due to self-restacking of graphene sheets, which eventually leads to a reduced surface area and ionic pathways [25]. Subsequently, the restacked graphene is not a very good option for a supercapacitor electrode, graphene centered aerogels with open pore structure have been hosted due to their three-dimensional interconnected networks for the electronic and ionic pathways for the operational charge/discharge [25–27].

Graphene aerogels exhibited great application as electrodes for the energy storing devices due to their characteristics like light weight nature, porosity, astonishing electrical conductivity and the chemical stability [28,29]. This review mainly focuses on the fundamentals,

fabrication, and the consumption of graphene-based aerogels for supercapacitor applications.

2. Fundamentals of Supercapacitors

The structure of a supercapacitor is like that of a battery. Usually, a supercapacitor contains two electrodes which are immersed in an electrolyte and alienated by any porous membrane. The job of the separating membrane is to allow the channelling of electrolyte ions and the electrically isolated electrodes. All the constituents of super capacitor such as the electrodes, the electrolyte, the separator, and the current collector affects the overall performance of the device. As mentioned, super capacitors can be classified into pseudocapacitors and Electric-Double-Layer Capacitors (EDLC) according to the charge storage mechanisms.

The EDLC stores energy through the adsorption of electrolyte ions on the surface of electrode whereas pseudocapacitors stores energy through the fast-Faradaic redox reactions between the electrode materials. Conducting polymers and metal oxides are generally used as electrode materials for the pseudocapacitors because they can undergo reversible redox reactions very easily [30]. Materials having high specific surface areas such as graphene is suitable for EDLC because of its property of absorbing the electrolyte ions. The major mechanisms for the EDLC ascends from the reversible adsorption of the electrolyte ions on the surface of the electrode materials. In charging, the anions transport to the positive electrode surface and cations conveyance is towards the negative electrode which formulates an electrical double layer at the interface. Upon releasing the already stored energy, the adsorbed electrolyte ions will discharge into the solution. For EDLC, the specific capacitance C (F g^{-1}) of each electrode is generally presumed to follow that of a parallel-plate capacitor [31] which is as follows

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$ (1)

where "ε_r" is the relative permittivity, "ε_0" is the vacuum permittivity, "A" (m^2 g^{-1}) is the specific surface area of the electrode, which is accessible to the electrolyte ions, and "d" (m) is the effective thickness of the EDLC. The total capacitance of a supercapacitor cell, C_{cell} can be calculated by each of the individual electrode of C_1 and C_2 using equation (2) as follows

$$\frac{1}{C_{cell}} = \frac{1}{C_1} + \frac{1}{C_2}$$ (2)

Here, C_1 and C_2 are the capacitance of the positive and negative electrodes, respectively. The performance and outcomes of a supercapacitor is majorly assessed on the basis of the following criteria: (1) power density substantially greater than batteries with reasonably high specific energies (> 10 Wh kg^{-1}), (2) an outstanding cycle ability (more than 100 times than the batteries), (3) fast charge-discharge procedure (within seconds), (4) low rate of self-discharging, (5) safer to operate, and (6) low cost. It must be highlighted that the time constant which is expressed as resistance (R) times capacitance (C) is another important consideration in evaluating and judging the overall performance of a supercapacitor.

The electric energy (E) of a supercapacitor is related to the capacitance, C, and the applied voltage, V as follows

$$E = \frac{1}{2}CV^2$$ (3)

The power, P, of a supercapacitor can be calculated by the following equation:

$$P = \frac{V_2}{4R_s}$$ (4)

Here, V is the maximum cell voltage in volts and Rs is the equivalent series resistance (ESR) in ohms.

Each of the element is fundamentally crucial to the final performance and outcomes of a supercapacitor. A large capacitance value, high operating cell voltage and a minimum ESR are the requirements for an exceptionally performing supercapacitor. The advancement of electrode material and the electrolyte solutions are also critical to enhance the overall performance of the setup. The supercapacitor electrode must showcase a high surface area and proper pore size. It ought to be electrically conductive with optimum stability and having high density to give a better and high volumetric energy density. As an alternative, a non-aqueous electrolyte with low resistivity is a better option for the architecture of a high-power and high-energy density supercapacitor because the non-aqueous electrolyte can be functioned with, at high voltages (up to 3.5 to 4 V).

3. Fabrication of Graphene based aerogels

Generally, an aerogel is a 3D network consisting of an interconnected micro or nanosheets which are having pores on micro, meso, and macro in contrast to 2D films. The micro and mesopores assemblies subsidize to the high special surface area and the macropores generates approachability for the active surfaces. The ultralow density and flexibility of 3D aerogels makes them an outstanding candidate for the portable electronics, affording high flexural strength and excellent mechanical stability too [32,33]. Owing to their plentiful conductive interconnecting networks between 2D nanosheets and graphene aerogels are encouraging for supercapacitor applications. The robust graphene aerogel supplements physical and chemical stability during repeated ion intercalation and deintercalation which empowers long cycle lifetimes for graphene aerogel-based devices. This section details the noteworthy reports, dealing with the enhancements in the fabrication of graphene layers.

The groundwork of graphene-based aerogels depends majorly on the self-assembly of graphene or graphene oxide sheets [34]. Oxidation-reduction [35], chemical vapor deposition (CVD) [36], and mechanical stripping [37], are majorly used techniques for the fabrication of graphene nanosheets. In the oxidation-reduction method, graphite will first transfigure into graphite oxide by Hummers' method and then through the exfoliation or ultrasonication, graphene oxide (GO) will be produced. The GO is then reduced by a reducing agent such as hydrazine hydrate, isocyanic acid Vitamin C, or thermally or any other method to yield graphene. In the CVD process, any carbon source is utilized to grow graphene on a variety of substrates such as metallic (Cu, Ni, Co, Fe) or planar non-metallic surfaces (SiO$_2$, Si$_3$N$_4$, SrTiO$_3$, NaCl). In a regular CVD treatment, hydrocarbon precursors are pyrolyzed to carbon radicals and then deposited on the surface to form a single-layer or a few-layers of graphene. Though CVD growth consequences an ordered graphene structure with excellent electronic properties in comparison to the oxidation-reduction technique, it requires an extra process of transferring the graphene layer onto other desired substrates.

In contrast to conventional film, graphene-based aerogels have a stable 3D network and higher pore volumes. For the manufacture of graphene-based aerogels, self-assembly approaches are a common "bottom-up" tactics. Graphene nanosheets serve as the building block units for self-assembly to obtain 3D porous networks. Xu et al. fabricated an electrically conducting, mechanically durable, and thermally stable self-accumulated graphene hydrogel with high specific capacitance through a hydrothermal methodology as shown in fig. 1 [38]. Yan et al. developed a simplified method for the fabrication of 3D graphene aerogel via in situ self-assembly of graphene by mild chemical reduction processes [39]. The fabricated 3D graphene aerogels demonstrate higher mechanical and electrical properties, high specific capacitance, thermal stability, and lower densities. The plenty of oxygen-containing functional groups on the surface of graphene oxide enhance the π-π stacking amongst the graphene layers and enables the collaboration between nanosheets and makes the self-assembly procedure possible.
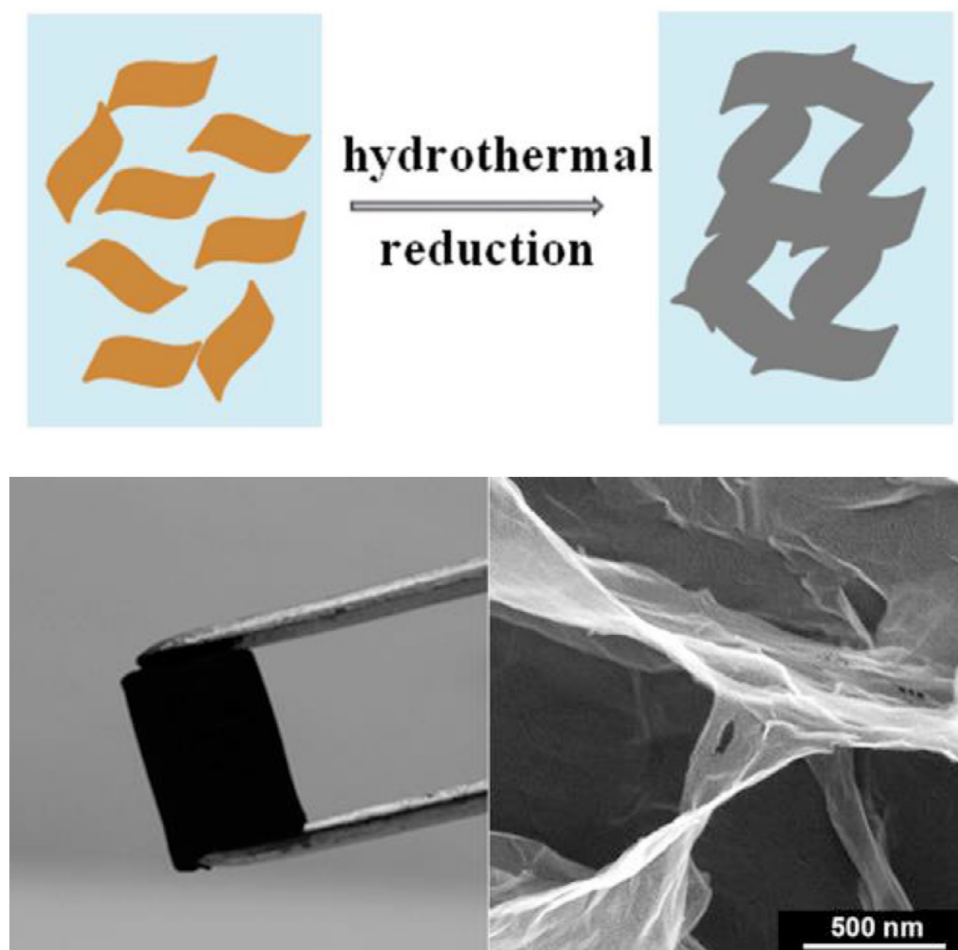
Figure. 1. Schematic illustration of the construction of graphene aerogels through hydrothermal reduction self-assembly with corresponding image and SEM. "Reprinted with permission from ref [38]. Copyright (2010) American Chemical Society."

Yu and his group developed macroscopic multifunctional graphene-based aerogels by a ferrous ion induced self-assembly procedure by in situ simultaneous deposition sheets [40].

Generally, self-assembly methodologies offer a suitable and scalable procedure to fabricate graphene aerogels with good electrical conductivity, and thermal stability as well. Recently, Tang and his group demonstrated a ZIF-8 metal–organic framework /reduced graphene-oxide aerogel through a self-assembly process with the synergistic effects of a chemical reduction and the process of cross-linking by metal ions [41]. Cross-linkers can also engage in linking the graphene layers to form 3D aerogels through the hydrogen bonding, electrostatic interaction, and covalent bonding. Sun et al. graphene constructed aerogels with ultralow density and super-elasticity by accumulating carbon nanotubes and chemically-converted giant graphene sheets using sol cryodesiccation and carbonization process [42].

There are reports for the fabrication of graphene aerogels with biopolymers as cross linkers cause of their elasticity and fatigue resistance in resultant aerogels. Gao et al. validated chitosan cross-linkers with the graphene oxide (CS-GO) forms a homogeneous concoction through bidirectional freezing and annealing as depicted in figure 2 [43]. The resultant material preserves structural integrity even after more than 106 cycles at 20% strain and 2.5×105 cycles at 50% strain. Moreover, the final material showcases features like super-elasticity, high compressibility, and an outstanding resistance towards fatigue.

Li and his group designed graphene aerogel by foaming a graphene oxide scattering with the support of a surfactant, sodium dodecyl sulphate, followed by lyophilization and the thermal reduction as well [44]. The resulting aerogel demonstrates properties such as ultra-low density, good electrical conductivity, high porosity, and an excellent elasticity. Worsley et al. testified graphene aerogel with high levels of electrical conductivity and ultra-low-density invented over supercritical drying and thermally reducing of monolithic solids of the single-layer graphene oxide [45]. This fabrication scheme operates covalent carbon bonding in between the graphene sheets in contrast to the physical cross-linkage. Cellulose nanofibers (CNF)-reduced graphene oxide (RGO) aerogels were also described with features like higher porosities and conductivities [46,47].

CVD-growth is another stratagem for the fabrication of graphene aerogels via Ni- foam templates with the assistance of ethanol reported by Zhang and his group [48]. Wang et al. fabricated a 3D graphene aerogel devising a bubble like network (fig. 3) with a template-free methodology [49]. The 3D network comprises of tightly compacted single or a few-layered graphitic sheets which delivers an intimate structural interconnectivity, huge accessible surface area, freeway for electron/phonon transportation, as well as the robust mechanical assets. 3D printing procedure is also established for the fabrication of 3D graphene aerogel networks by Worsley et al. by a graphene-based direct ink writing procedure [50]. The consequential aerogels exhibit high conductivity and lightweight nature with high compressibility.

4. Graphene based aerogels for Supercapacitors

Supercapacitors fills up the gap between the batteries and the conventional capacitors retaining higher energy densities than the conventional capacitors and higher power densities than the batteries. Electrochemical adsorption/desorption and redox reactions subsidize to
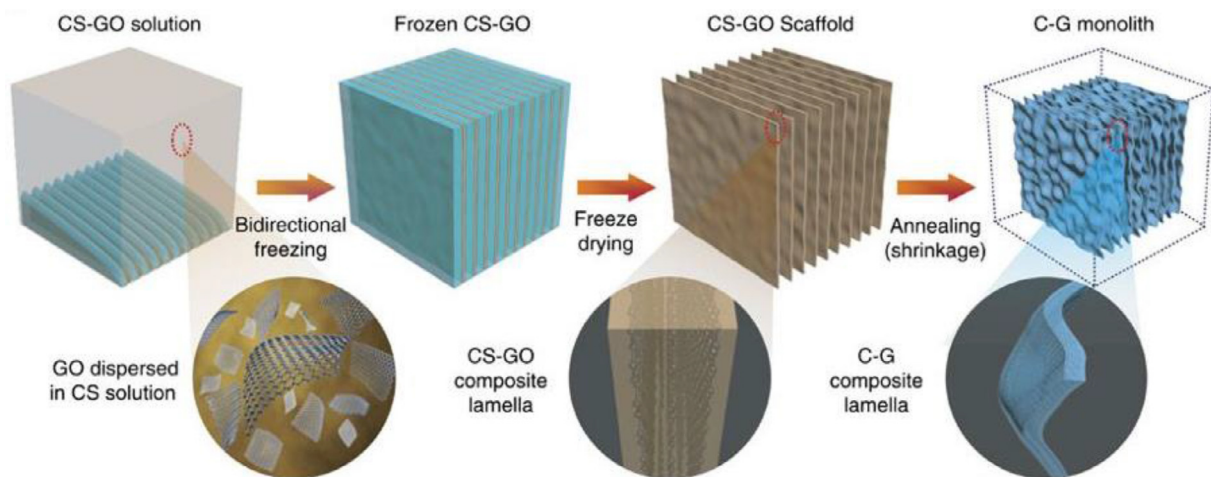
Figure. 2. Schematic diagram showing the construction of chitosan-graphene oxide (CS-GO)aerogels via bidirectional freezing and annealing [43].

the process of energy storage in supercapacitors. This section details the recent progresses in various types of graphene-based aerogels for EDLC and pseudocapacitors.

4.1. Electric Double Layer Capacitors (EDLCs)

For the process of charge storage, Electric Double-layer capacitors (EDLCs) retains a double electric layer interface in between the electrode materials and the electrolyte [51]. Upon a functional electrical field, the positive and negative electrodes accumulate the opposite ions from the present electrolyte to balance off the electric fields and the potential difference as a result of the relocation of ions is the basic mechanism for the energy storage. This is a conventional physical model of the supercapacitors. There are so many available factors that are affecting the supercapacitors such as electrode interfacial contact, electrode active material types, and their Brunauer-Emmett-Teller specific surface (BET) [52].

Graphene is a favourable electrode material due to its high BET and conductivity features [53]. If the materials specific surface area is high, the operational contact area between the electrolyte and the electrode materials would be amplified. This would boost the power density and the process of the transfer of charges. If BET is amplified, activation of graphene aerogel would increase the feature of porosity. Zhu et al. synthesized porous aerogel with a BET surface area of 3100 m^2g^{-1} by the usage of the chemical activation of exfoliated graphite oxide [54]. Ye et al. fabricated graphene aerogel-nickel foam having a BET of 463 $m^2\,g^{-1}$ and conductivity of 71.4 S m^{-1}. The concluded hybrid aerogel exhibits properties like good electrochemical cyclic stability, high rate capability, and a high specific capacitance of 366 F at 2 A g^{-1} [55].

The size and pore distribution in the graphene aerogels are one major key factor verbalizing their overall performance. Usually, pores in the graphene aerogels are divided into different pore sizes like macropores (greater than 50 nm), mesopores (2-50 nm), and

micropores (less than 2 nm). Every pore size has particular roles in the supercapacitor performance. Macropores are responsible for storing electrolyte ions and mesopores offer electrolyte ion transportation while the micropores enable the charge accommodation processes [1]. Lee et al. fabricated porous graphene aerogel by a chemical activation with K_2CO_3 which has exhibited outstanding specific capacitance value of 300 F g^{-1} [56]. Yun et al. revealed CO_2-activated macroscopic graphene aerogels which contains a 3D inter-networked macroporosity ascending from the self-assembly, mesoporosity rising from the intervoids of nanosheets, and microporosity via the activation of CO_2 [57]. The resulting graphene aerogel showcases a good cycle stability and rate capability with a specific capacitance of 278.5 F g^{-1}. Zu et al. fabricated 3D periodic graphene combined aerogel microlattices via a 3D printing practise of direct graphene oxide-based composite ink writing (fig 4) [58]. The supercapacitor electrode aerogel with thickness in the order of millimeters supplied a maximum specific power of 4079.9 W kg^{-1} at a specific energy of 0.26 Wh kg^{-1} and displayed a capacitive withholding of (ca. 90% from 0.5 to 10 A•g^{-1}). Three-dimensional graphene aerogels with macro- and meso-porous structures were offered by Wu et al. by adding tetraethoxysilane silica source (TEOS) and annealing at 800°C [59]. The resulting 3D network unveils features like high surface area, and low mass density with an excellent specific capacitance of 226 Fg^{-1} inclusive of high rate capability, and excellent cycling stability.

The surface area of a single graphene sheet is 2630 m^2/g. Mechanically resilient and feature of electrically conducting graphene aerogels with specific capacitance of 128 F g^{-1} with advanced rate performances were described by Zhang and his group through supercritical drying of hydrogel from the reduction of graphene oxide with L-ascorbic acid [60]. Stoller et al. designed and manufactured an ultracapacitor with chemically modified graphene having a BET of 705 m^2g^{-1} and a specific capacitance of 135 Fg^{-1} [51]. Xu et al. reported a specific capacitance value of 160 Fg^{-1} for graphene aerogel arranged
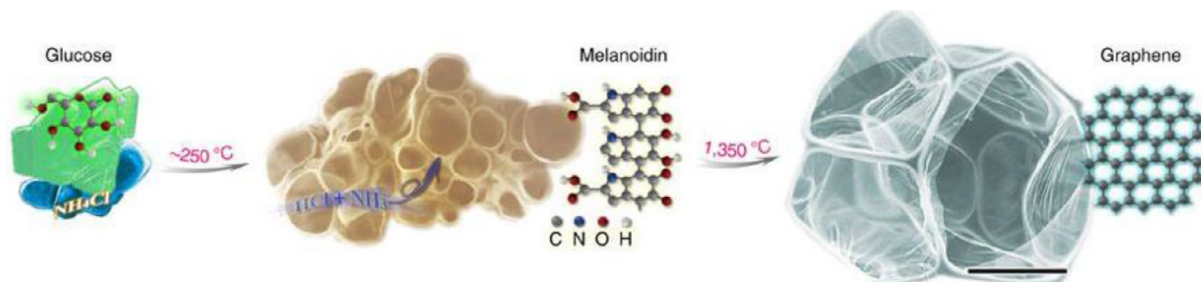

Figure. 3. Schematic diagram showing the growth process of template free sugar blowing CVD fabrication of 3D graphene aerogel [49].
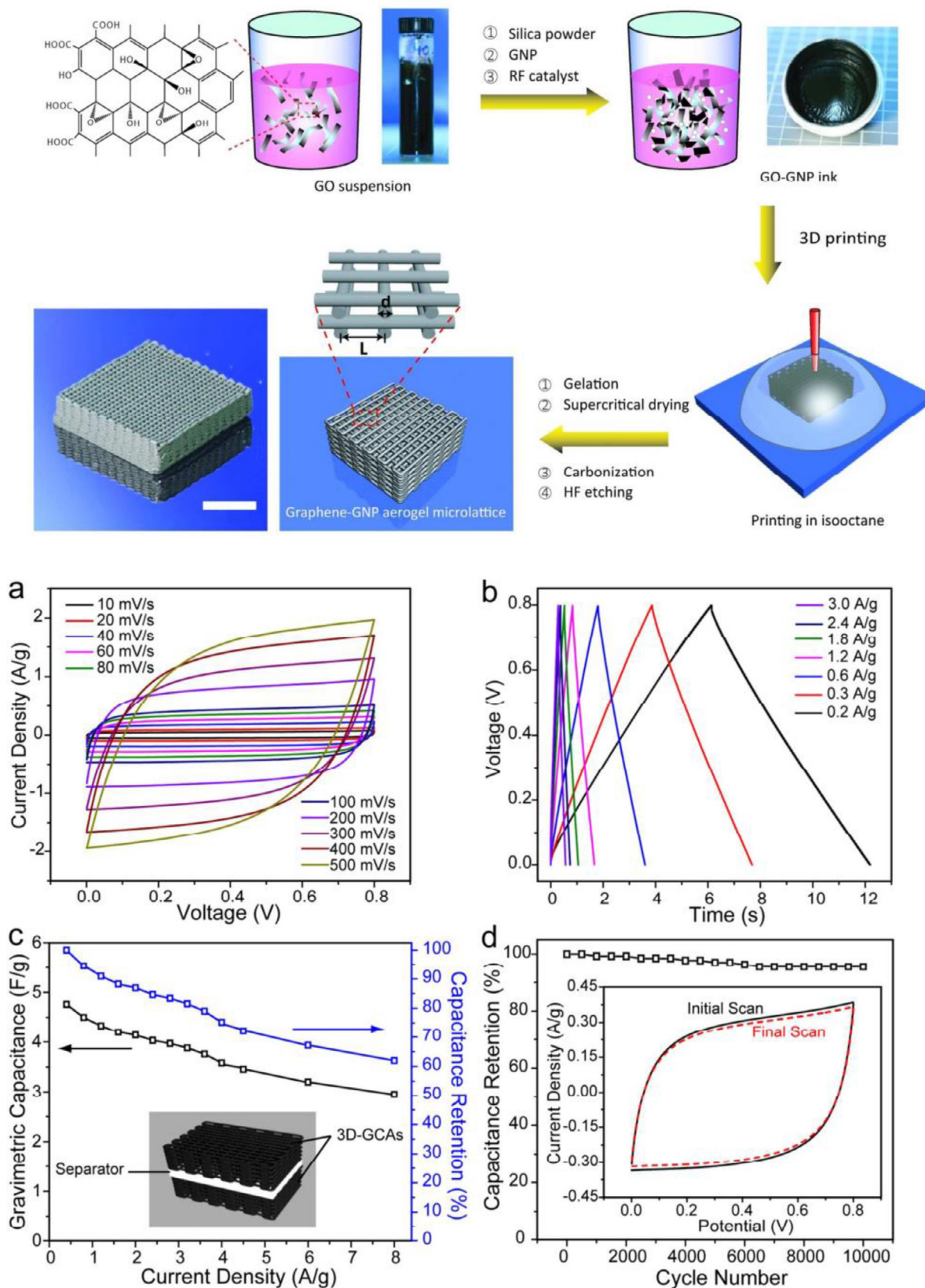
Figure. 4. Schematic illustrations of the fabrication process of 3D periodic graphene composite aerogel microlattices via a 3D printing technique of GO-GNP composite ink writing and the electrochemical performance(a) Cyclic Voltammetry for different scan rates in 3 M KOH (b) Charge-discharge curves (c) Gravimetric capacitance and capacitance retention (d) Cycling performance at a scanning rate of 200 mV s⁻. "Reprinted with permission from ref [58]. Copyright (2016) American Chemical Society."
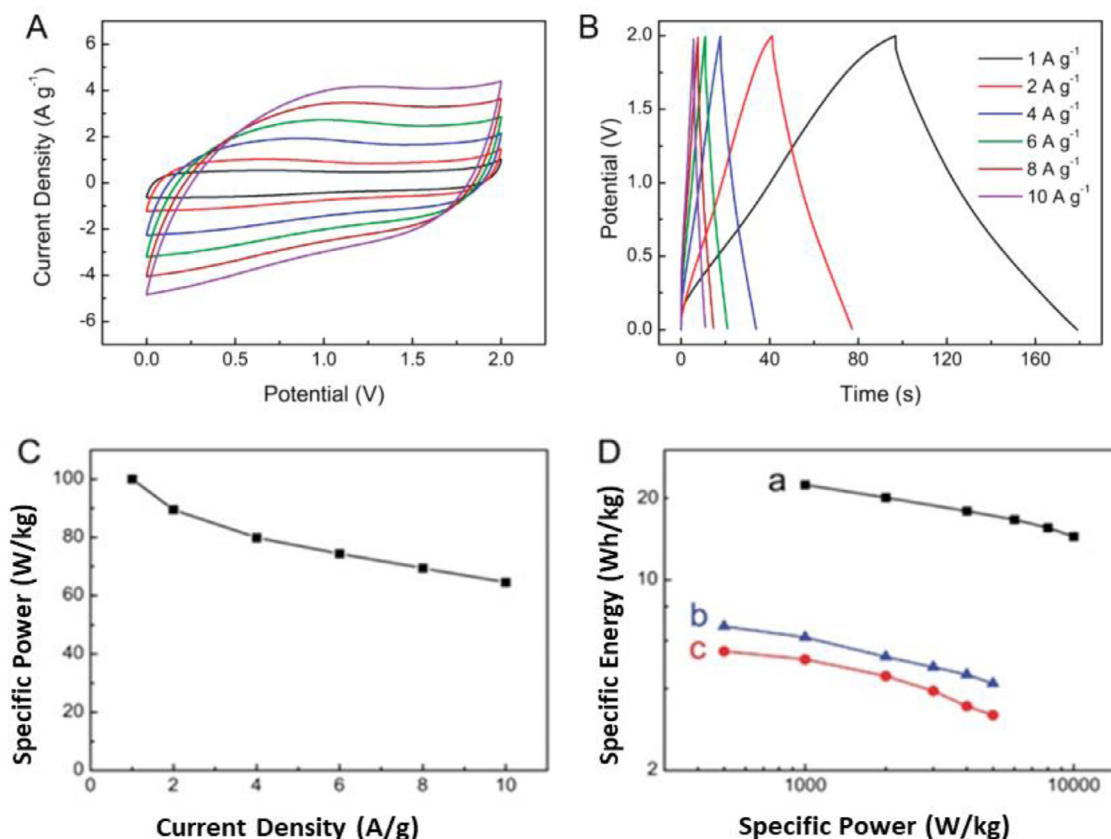
Figure. 5. Electrochemical performance of the pseudo-capacitor of graphene aerogel-MnO$_2$-Ni foam. (A) Cyclic voltammograms at different scan rates of 10, 20, 40, 60, 80, and 100 mV s^{-1} (from inner to outer). (B) Galvanostatic charge/discharge curves at different current densities of 1, 2, 4, 6, 8, and 10 A g^{-1}. (C) Capacitance retention ratio as a function of discharge currents. (D) Ragone plots of the pseudo-capacitor of graphene aerogel-MnO$_2$-Ni foam (a) and pseudo-capacitors of MnO$_2$-Ni foam//MnO$_2$-Ni foam (b) and graphene aerogel/graphene aerogel (c) "Reprinted with permission from ref [98]. Copyright (2012) American Chemical Society."

by hydrothermal procedure [38]. Enhanced conductivity of 1.3–3.2 Sm^{-1} and a specific capacitance of 220 F g^{-1} high power density and a longer cycle life for a graphene aerogel were achieved after reducing with hydrazine were reported by Zhang et al. [61]. This enhancement would be recognized for the reduction of oxygen- bearing functional groups. Luan et al. validated a conductive 3D graphene oxide aerogel with ethylenediamine (EDA) via cross-linking method trailed by a hydrazine reduction and showcased an electrical conductivity of 1351 S m^{-1} and a specific capacitance of 232 F g^{-1} [62]. Excellent capacitance with outstanding stability features for 3D porous aerogel electrodes by mingling 0D carbon onions, 1D carbon nanotubes, and 2D graphene oxide were validated by Song and his group [63].

There are several reports which were accessible for the doping of graphene with one or various several elements such as the N, S, B, and P for rearrangement of the graphene crystal lattice and, hence influencing the electronic structures. This reconstruction and influencing, offer both chemical and physical dissimilarities that can enhance the performances of the concluding material [63]. Nitrogen is a highly doped element with graphene because of its ease of integration and abundance in nature. When compared with the carbon atom, boron and nitrogen possess similar sizes and electronic configuration [64,65]. This makes it easier to dope graphene either with boron/nitrogen, which interns results in the modification of graphene electronic structure. Nitrogen having extra valence electron assists a new energy level is the conduction band of graphene [66,67]. The catalytic and electrochemical activity of the graphene is enhanced with the introduction of these new energy levels, as a result the material performance increases [66,67]. Along with the electronic activity the nitrogen doping also influences the surface activity, which inter improves the wettability of the carbon electrode. Thus, interaction of electrolyte with carbon electrode

improves at electrolye/electrode interface and higher capacitive value is achieved compared to un-doped electrodes [68]. Hao et al. fabricated N-doped porous graphene-based carbon aerogels having macropores and mesopores demonstrates a higher specific capacitance of about 197 F g^{-1} at a current density of 0.2 A g^{-1} [69]. Chen et al. demonstrated nitrogen doped graphene aerogel by hydrothermal synthesis with organic amine as the nitrogen basis [70]. The N-doped aerogel exhibits a high specific power of 205.0 kW/kg at 185.0 A g^{-1} and at a current density of 100.0 A/g, 95.2% of its capacitance was engaged for 4000 cycles. On the other hand, boron acts as charge acceptors in the carbon lattice. Thus, doping with boron having three valance electrons introduces uneven charge distribution and facilitates charge transfer among adjacent atoms by acting as charge acceptors. This type of charge transfer results in pseudo-capacitive contribution and improves the electrochemical activity and surface chemistry of the graphene [71]. Phosphorus has larger atomic radius and exhibits similar chemical properties, but higher charge transfer capability compared to boron and nitrogen. Along with this, improved electrical conductivity and electron donor ability of phosphorus together enhances the charge storage capacity of material by offering pseudo-capacitive component in addition to electric double layer [72]. The electrochemically active electrolyte surface functional groups and oxygen surface functionalities produces instability and deteriorates capacitor performance. This issue can be addressed by phosphorous doping where it acts as oxidation protector. Thus P-doping not only assists improved capacitive performance but also establishes a wider operating voltage range by preventing oxidation [73,74]. Compared with other hetero atom dopants, sulphur doping of graphene for supercapacitor application is still not studied to its fullest. Sulphur as electron donor, modifies the charge distribution and improves the electronic activity of the material. This intern
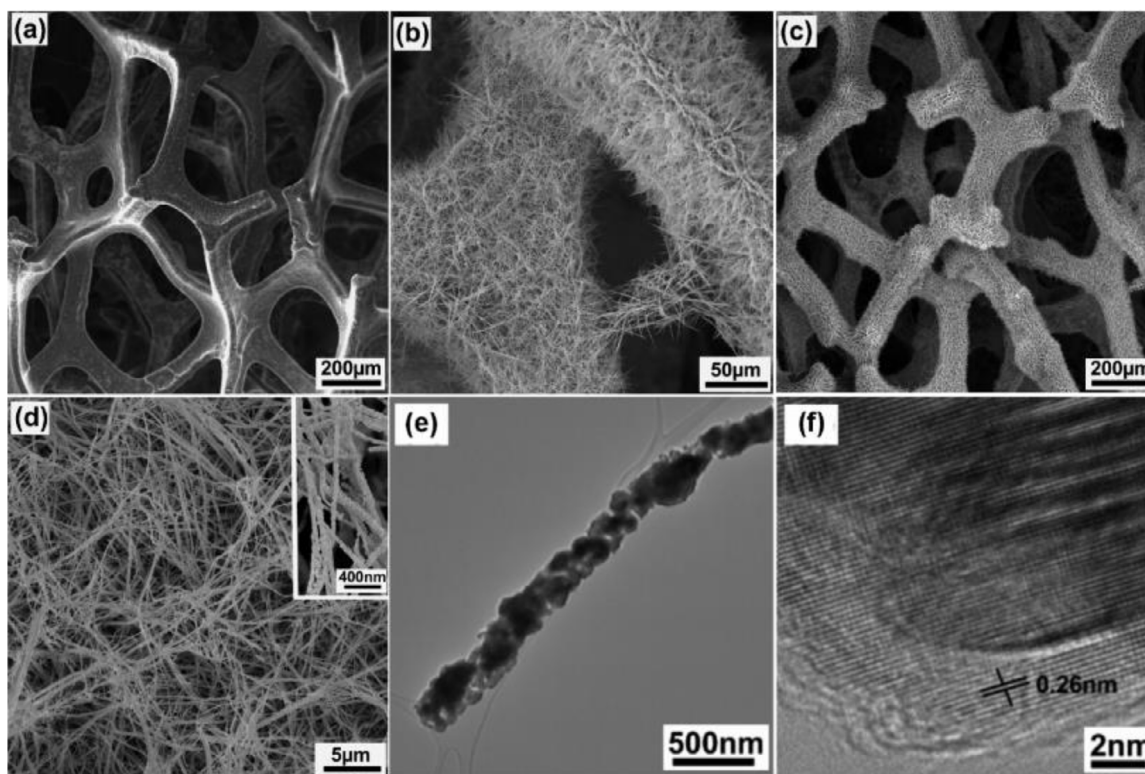
Figure. 6. SEM images of (a) 3D graphene aerogel, (b) 3D graphene aerogel/Co_3O_4 nanowire. (c,d) Low- and high magnification SEM images of graphene aerogel/Co_3O_4 nanowire. Inset panel d shows an enlarged view. (e,f) Low- and high-resolution TEM images of Co_3O_4 nanowire grown on the surface of 3D graphene aerogel."Reprinted with permission from ref [102]. Copyright (2012) American Chemical Society."
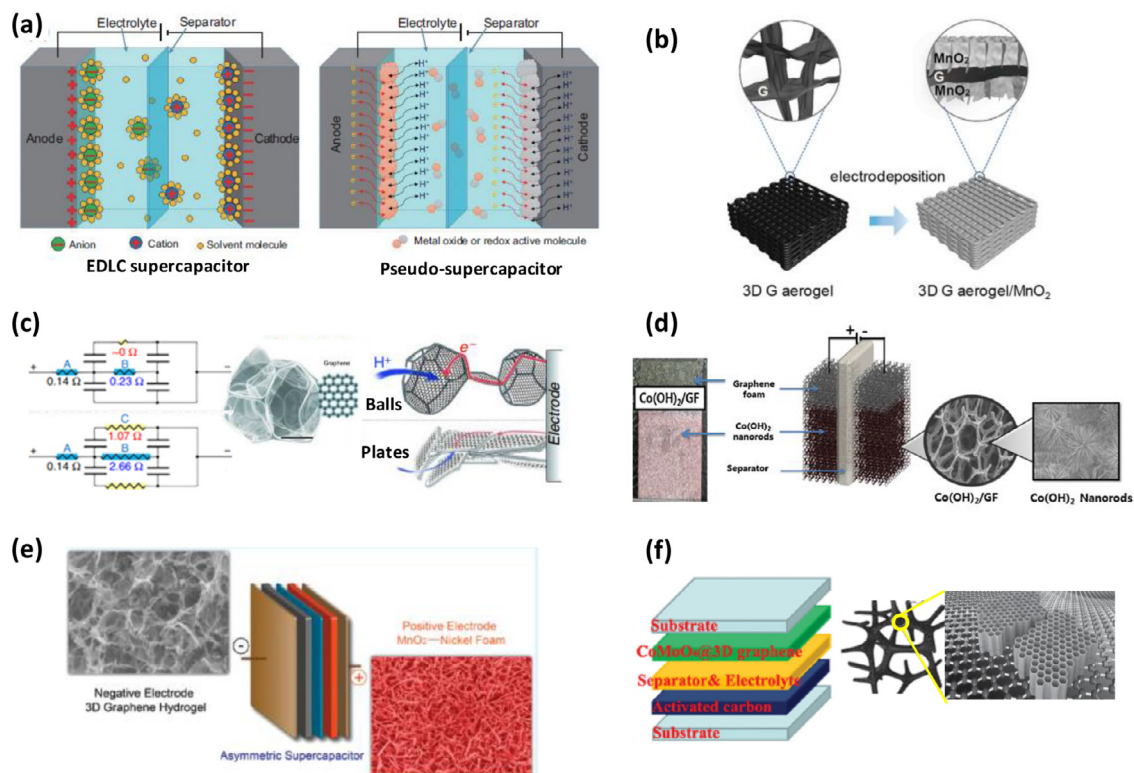

Figure. 7. Schematic illustration of supercapacitor. (a) Device structure for EDLCs and pseudo supercapacitor [119]. (b) 3D printed graphene aerogel for supercapacitor application [116]. (c) Graphene balls by substrate-free sugar blowing effect for application in pseudocapacitor [49]. (d) Graphene foam with hierarchical Co $(OH)_2$ nanorods [82]. (e) Pseudo-capacitors using graphene aerogel consisting of 3D interconnected pores as anode and vertically aligned MnO_2 nanoplates [80]. (f) Nano-honeycomb 3D Graphene- $CoMoO_4$ hybrid electrodes for pseudo-capacitors [83].

Table 1

Performance characteristics of Electric Double Layer Capacitors (EDLCs) based on graphene aerogels.

Materials	Fabrication method	Current density	Specific Capacitance	Cycle retention	Reference
Graphene nanosheet	Modified hydrothermal method	$1\ A\ g^{-1}$	$245\ F\ g^{-1}$	92%	[85]
N-doped holey graphene	Two-step hydrothermal treatment	$0.5\ A\ g^{-1}$	$318.3\ F\ g^{-1}$	98.4%	[86]
glucose/graphene	hydrothermal reduction and CO2 activation method	$1\ A\ g^{-1}$	$305.5\ F\ g^{-1}$	98.5%	[87]
manganese oxide/graphene	rapid microwave reduction process	$0.5\ A\ g^{-1}$	$240\ F\ g^{-1}$	90%	[88]
Graphene-coated Carbon Nanotube	From single-walled carbon nanotubes		$60\ F\ g^{-1}$	90%	[89]
graphene/polyaniline	Hydrothermal route	$1\ A\ g^{-1}$	$520.3\ F\ g^{-1}$		[90]
MoS2/chemically modified graphene	Hydrothermal route	$1\ A\ g^{-1}$	$268\ F\ g^{-1}$	93%	[91]
MoS2/graphene	in-situ thermal decomposition-reduction method	$0.1\ A\ g^{-1}$	$862.5\ mAh\ g^{-1}$	109.6%	[92]
boron-doped graphene	Hydrothermal method	$1\ A\ g^{-1}$	$308.3\ F\ g^{-1}$	92%	[93]
nitrogen and sulfur co-doped graphene	Hydrothermal method,	$1\ A\ g^{-1}$	$182.3\ F\ g^{-1}$		[94]

Table 2

Performance characteristics of pseudocapacitors based on graphene aerogels.

Materials	Fabrication method	Current density	Specific Capacitance	Cycle retention	Reference
graphene/polypyrrole	electrochemical deposition	$1\ A\ g^{-1}$	$335\ F\ g^{-1}$	97%	[107]
Graphene/Ruthenium Active Species	hydrothermal synthesis		$238\ Fg^{-1}$		[108]
Graphene-Poly (3,4- Ethylenedioxythiophene)/MnO2	electrochemical deposition		$343\ Fg^{-1}$	80%	[109]
Tunable Layered Double Hydroxide Precursors/Graphene	hydrothermal treatment	$1\ A\ g^{-1}\ 2\ A\ g^{-1}\ 10\ A\ g^{-1}$	$2165\ Fg^{-1}\ 2055\ Fg^{-1}\ 1478\ Fg^{-1}$	78.5%	[110]
Cobalt Sulfide/Graphene	hydrothermal treatment	$1\ A\ g^{-1}$	$564\ Fg^{-1}$	94.8%	[111]
Graphene Oxide-Co3O4		$1.67\ A\ g^{-1}$	$63.7\ Fg^{-1}$	94.8%	[112]
Nitrogen and phosphorous dual-doped graphene	hydrothermal treatment	$50\ mA\ g^{-1}$	$330\ m\ Ah\ g^{-1}$	100	[113]
Sulfur and Phosphorus Co-doping of Hierarchically Porous Graphene	Electrochemical deposition method	$1\ A\ g^{-1}$	$381\ Fg^{-1}$	87.2%	[83]
The robust 3D porous α-Fe2O3@3DrGO	hydrothermal self-assembly process	$5\ A\ g^{-1}$	The robust 3D porous α-Fe2O3@3DrGO aerogel	-	[114]
V2O5/graphene	hydrothermal synthesis	$0.6\ A\ g^{-1}$	$484.0\ F\ g^{-1}$	80%	[115]

increases the specific capacitance and electrode polarization via reversible faradic capacitance process [75,76]. Like nitrogen doping sulphur also increases the wettability of the electrode material. Sulphur doping assists an improved energy density without sacrificing the power density [77]. This is due to improved electronic conductivity offered by sulphur, which along with electric double layer capacitance also gives pseudo-capacitive contribution. Thus, hetero atom doping is an efficient way to improve the electrochemical and physical properties like power/energy density, charge transfer, stability, capacitive performance, and wettability, which inter has positive impact on supercapacitor performance. To incorporate different properties offered by doping of individual element in improving the system performance, co-doping of these hetero atoms is also studied. A graphene aerogel co-doped with sulphur and nitrogen offered current density of $1\ Ag^{-1}$, specific capacitance of $203\ Fg^{-1}$ and energy density of $101\ WhKg^{-1}$ [78]. The boron and nitrogen co-doped monolithic graphene aerogels and active materials shows improve electrochemical performance [79–81]. In a similar study a specific capacitance of $337\ Fg^{-1}$ at $0.5\ Ag^{-1}$ by phosphorus and nitrogen doping was reported by chen et al [82]. Park et al. displayed a co-doping of sulphur (S) and phosphorus (P) atoms into the 3D activated graphene aerogel with a microporous environment and attained a specific capacitance of $438\ Fg^{-1}$ at $10\ mVs^{-1}$ and also achieved a greater electrochemical stability [83]. Recently, the efforts are going on to introduce the synergetic effects of more than two hetero atoms in highly porous carbon to improve the capacitive performance [84].

4.2. Pseudo-capacitors

For charge storing features, pseudo-capacitors are influenced by reversible electrochemical adsorption/desorption procedures or oxidation-reduction reactions. These reactions initiates towards the deposition of materials onto various surfaces and sub-surfaces [95]. Pseudo-capacitors are generally asymmetric supercapacitors whose cathodes

are stereotypically carbon materials and anodes are the conducting polymers or metal oxides.

A 3D graphene aerogel consisting of hexagonally bonded sp^2 C atoms having higher surface areas, and larger pores which inhibits the aggregation of graphene sheets and enables the process of ion diffusion [96]. Luan et al. fabricated high energy density pseudo-capacitors with the help of a nickel oxide as cathode and a reduced graphene aerogel acting as an anode [97]. The consequential capacitor exhibits excellent charge/discharge cycling presentation with an aerial capacitance of $248\ mF\ cm^{-2}$ and a specific energy of $39.9\ Wh\ kg^{-1}$ at a current density of $1\ mA\ cm^{-2}$. Gao et al. fabricated Pseudo-capacitors using graphene aerogel consisting of 3D interconnected pores as anode and vertically aligned MnO_2 nanoplates on nickel foam as cathode [98]. The resultant device showcased a wide potential window of $0-2.0$ V with a higher specific energy of $23.2\ Wh\ kg^{-1}$ and a specific power of $1.0\ kW\ kg^{-1}$. The pseudo-capacitor also depicts a stable cycling performance with 83.4% capacitance retention after 5000 cycles.

Transitional metal oxides or hydroxides were also described in pseudo-capacitor reversible redox reactions due to their exciting electronic, and electrochemical assets to accomplish higher specific capacitances. Due to the lower electrical conductivity and cycle stability of metal oxides and hydroxides, their amalgamation with graphene aerogels can augment the electrical conductivity, charge transfer, and the structural stability [99]. Patil et al. manufactured graphene/Co$(OH)_2$ aerogels have achieved a higher specific capacitance of $1139\ F\ g^{-1}$ at $10\ A\ g^{-1}$ charge-discharge current density. The resultant aerogel electrode in pseudocapacitor device exhibits a higher specific energy of $\sim13.9\ Wh\ kg^{-1}$ and specific power of $\sim18\ kW\ kg^{-1}$ [100]. Yu et al. collective 3D graphene networks and $CoMoO_4$ for generating super long-life pseudo-capacitors which delivers a high specific capacitance of $2098\ F\ g^{-1}$ at $5\ A\ g^{-1}$ with long-term cycle stability and higher energy densities [101]. Dong et al. in situ synthesized cobalt oxide (Co_3O_4) nanowires on CVD created 3D graphene aerogels for free-standing electrodes for supercapacitor applications [102]. The aerogel composite

provided a high specific capacitance of ~1100 F g^{-1} at a current density of 10 A g^{-1} with an outstanding cycling stability.

Due to their synthetic flexibility, stability and high redox pseudo-capacitance, conducting polymers are noteworthy vigorous materials for supercapacitors [103]. Still, ordinary conductivity and poor cycling stability are few of their disadvantages. Zhao et al. fabricated an extensively compressible supercapacitor by using polypyrrole-graphene aerogel as the electrode [104]. The device demonstrated a volumetric capacitance of 14 F cm^{-3} for uncompressed electrode and 28 F cm^{-3} for the compressed one by 50%. The supercapacitor attains superb compression tolerance without the significant variation of capacitances under the long-term compressive loading and unloading procedures. chi et al. fabricated 3D porous polyaniline-graphene flexible all-solid-state supercapacitor hybrids with faster ionic conducting channels [105]. The supercapacitor showcased higher cycling performance with a gravimetric specific energy of 24.02 Wh kg^{-1} at a specific power of 400.33 W kg^{-1}.

Since carbon materials are generally explored due to their relatively low price, remarkable chemical stability, and desirable electric conductivity, 3D graphene aerogel exhibits numerous intriguing features including large specific surface area, high porosity, mechanical strength, chemical stability, and high electrical conductivity, thus providing exceptional potential as an electrode for supercapacitors. The main advantage of 3D network structure of graphene is its inhibition on the stacking of graphene sheets that largely limits its performance as supercapacitors. The interconnected pores, micro or meso, of 3D graphene aerogel framework generally prevents this agglomeration. This unique 3D architecture assimilates multidimensional electron transport and effective ion accessibility [106].The excellent properties with the unique structure of graphene aerogel benefits their application in supercapacitors as for both the electrode and electrolyte materials.

5. Device structure

The schematic of the EDLC and pseudo supercapacitor is shown in fig 7a. The key element of the supercapacitor is electrodes, electrolyte, and separator, which synergistically contributes to its performance. For effective working of supercapacitor, the separator in the device should be ultra-thin, highly porous, chemically inert and possess high dielectric strength. The working electrodes must have high chemical stability, high surface area which can be achieved by highly porous material and should offer negligible resistance. The two working electrodes are kept in a proximity with a separator in between and the setup is impregnated within an electrolyte. The electrolyte provides insulation between the electrodes and allows transfer of ions. Among various available factors, electrode material majorly affects the supercapacitors performance. Graphene aerogels are highly porous material which significantly increases the specific area of the electrode and intern its interaction with the electrolyte. To further increase the specific surface area, efforts are going on to tailor the dimension/morphology/texture of the graphene aerogel. Recently, Yo et al. synthesized a 3D printed graphene aerogel based supercapacitor with ultra-thin MnO_2 loading and reported capacitance of 44.13 F cm^{-2} [116]. A high specific area graphene balls by substrate-free sugar blowing effect was reported by Wang et al [49]. The high porosity in the graphene aerogel usually results in higher inter sheet resistance which inter decreases the conductivity of material. Doping graphene aerogels with hetero atoms not only improves the wettability and ion diffusion but also enhances the conductivity of the materials [117]. The co-doping of the hetero atoms has further improved the performance of the supercapacitor [78]. Despite such a major impact, not much is known with respect each of these functionalities. Thus synergetic effect of multiple hetero atoms doping in graphene aerogel can be studied to enhance the supercapacitor performance [84]. Compared to EDLC, pseudocapacitors rely on highly reversible electrochemical adsorption/desorption processes or oxidation-reduction reactions for storing energy. The major issues with the

pseudocapacitors are low electrical conductivity of the electrode and low cycle life. These limitations can be addressed by combining graphene aerogel as an electrode and even incorporating them in a hybrid supercapacitor device configuration. Patil et al. anchored graphene foam with hierarchical Co (OH)$_2$ nanorods and studied the capacitance in symmetric device configuration as shown in fig 7d. Where graphene foams offered improved conductivity, high porosity and high specific surface area, while Co (OH)$_2$ nanorods assisted in high power density and specific capacitance. The resultant pseudocapacitor device exhibits specific capacitance of 1139 F g^{-1} at 10 A g^{-1} and specific power of ~18 kW kg^{-1} [82]. Gao et al. fabricated asymmetric pseudo-capacitors using graphene aerogel consisting of 3D interconnected pores as anode and vertically aligned MnO_2 nanoplates on nickel foam as cathode in a neutral aqueous Na_2SO_4 electrolyte as shown in fig 7e. The supercapacitor exhibited potential range of 0-2 V with an energy density of 23.2 Wh kg^{-1} and power density of 1.0 kW kg^{-1} [80]. To address the stability and low cycle life of the psuedocapacitor, Yu et al. synthesised nano-honeycomb 3D Graphene- $CoMoO_4$ hybrid electrodes as shown in fig 7f. The fabricated capacitors delivered a high specific capacitance of 2098 F g^{-1} at 5 A g^{-1} with long term cycle stability and higher energy densities [83]. The supercapacitor are promising devices and needs improvements for its widespread use in various applications for energy storage. The use graphene aerogels as electrode materials has shown tremendous improvement in the performance of supercapacitors and created a new spark in this emerging field. Still various issues like high conductivity, thermal stability for its operation at high temperatures and cost effectiveness needs to be overcome to implements its commercialization at larger scale. Kim et al. addressed the thermal stability up to 200°C by integrating meso–macroporous graphene aerogel with a composite polymer electrolyte of ionic liquid-fumed silica nanoparticle [118]. The conductivity of the aerogels can be improved by doping with conducting fillers and multiple hetero atoms. The cost effectiveness of the fabricated supercapacitor can be addressed by cheaper electrode preparation and processing methods using low-cost carbon precursors as source materials.

6. Summary and perspectives

Graphene is a rapidly industrialized nanomaterial over the past decade into miscellaneous range of structures, types, mixtures, and composites for endless applications and procedures. Out of these, much consideration has centred on developing and fabricating numerous graphene-based 3D porous structures often nomenclatured as aerogels, owning excellent properties and features of high surface areas, and larger internal spacings. The demonstration of the direct development of 3D graphene aerogels as well as the amalgamation of 2D graphene with 3D porous networks have fascinated a lot of consideration.

In this review, we detailed the fundamentals and the recent developments and fabrications of graphene aerogels for supercapacitor applications and procedures. Fabrication techniques of graphene aerogels such as self-assembly, cross-linking, CVD-growth, and 3D printing were discussed and explained. In the case of EDLCs, graphene aerogels, directly or else, incorporated with other carbon materials, can be engaged as electrode materials as well. Besides, the electrochemical enactment improvement of graphene aerogels, by increasing the electrical conductivity, raising the specific surface area, increasing the porosity, and doping/co-doping with various available non-metals including N, P, S, and B were revised and concluded. In pseudocapacitors, graphene aerogel was engaged as an anode. The modifications of graphene aerogels with metal compounds and conducting polymers can be demonstrated, to enhance the capacitor properties and features compared to the double layer capacitors.

There are few technical and commercial challenges in the preparation and implementation of the graphene aerogels which needs to be addressed and are as follows: (i) the preparation of 3D graphene aerogels presently limited to the laboratory scale and should be

enhanced and optimized for industrial scale applications, (ii) the accuracy and precision of the size of graphene aerogels should be improved for the end use applications, (iii) development of graphene aerogels of various shapes with unique functionalities and improved mechanical properties are yet to be explores, and (iv) the major challenge is to implement more accurate and cost-effective fabrication strategies.

Figure. 5, Figure. 6, Table 1, Table 2,

Declaration of Competing Interest

The manuscript entitled "Graphene Based Aerogels: Fundamentals and Applications as Supercapacitors" and authors: Yasir Beeran Pottathara, Hanuma Reddy Tiyyagura and Kishor Kumar Sadasivuni submitted as a Mini Review to Journal of Energy Storage, has not been published previously by any of the authors and/or is not under consideration for publishing in another journal at the time of submission. All authors have seen and approved the submission of the manuscript and there is no conflict of interest.

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Supplementary materials

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