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# Progress on Free-Standing Graphene Hybrid: Advantages and Future Scenario

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## Abstract

Free-standing graphene (FSG) paper like electrodes has paid attention to the energy storage device application in the past decade. It befits to fabricate flexible devices due to its remarkable mechanical strength and offers high electrical conductivity. In this chapter, we explore the advantages and future prospects of FSG fresh candidate in rechargeable batteries. Herein, we summarized the synthetic strategies used for FSG fabrication and its properties, followed by its application in rechargeable batteries. Extensively, this chapter deals with fabrication of FSG hybrid composite papers for battery applications to understand the overall device performance. Specifically, we discuss the benefits of FSG electrodes over conventional electrode material and its fabrication in battery system. Ultimately, we conclude with the significance of FSG paper in battery application and forthcoming advantage for recycling purposes.

**Keywords:** free-standing graphene paper, electroactive, Li-ion battery, Na-ion battery, Li-S battery, Li-air battery

## 1. Introduction

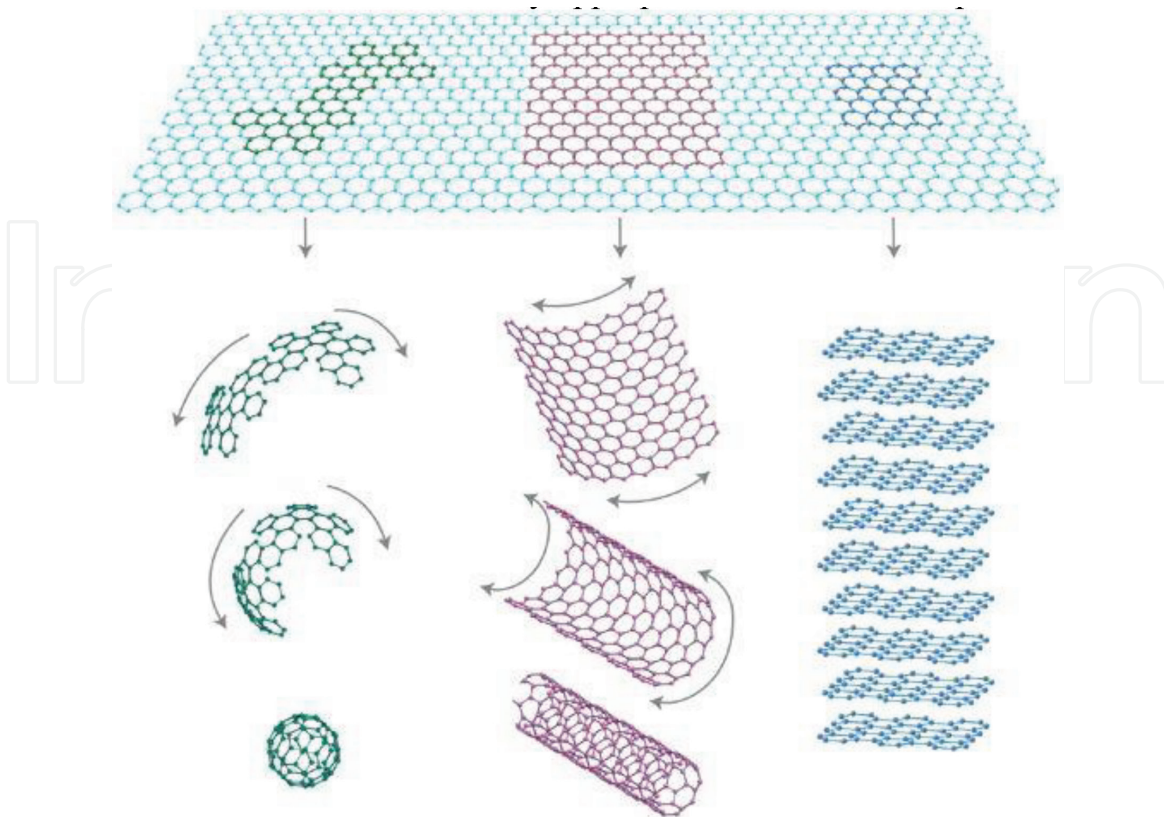
Pertaining to the day-to-day energy usage increases, various technologies were addressed to satisfy the current energy demand. Based on this circumstance, the electronic devices for energy conversion (solar cells and fuel cells) and energy storage (batteries and supercapacitors) were extensively studied throughout the world [1]. Basically, the performance of these devices depends on the materials' design with different nanostructures and material interfaces. In particular, advanced materials including carbon nanomaterials, viz., carbon black, carbon nanotubes, carbon nanofibers, graphene, and so on, play a vital role in an attempt to lead the breakthrough and challenges from laboratory scale to technology ideas [2].

Among them, graphene, since its discovery, has been stirring enthusiasm among the scientific community owing to its attractive properties. Properties such as high electrocatalytic activity, good conductivity with immense surface area, and low costs make it an ideal candidate to implement in electrochemical application. Subsequently, graphene has been utilized as a promising candidate in energy storage applications such as battery and supercapacitors (SCs) [3, 4]. Due to its high electrical conductivity, charge carrier mobility, and transparency, it has been potentially used as an electrode for electrochemical energy device application [5, 6]. Processing of graphene electrodes differs according to their application

by fabrication techniques and synthetic strategies. As graphene is an electrode focusing on rechargeable battery application, the device performance is based on the presence of electroactive sites in graphene sheets [7, 8]. Therefore, graphene sheets composited with suitable electroactive materials like metal chalcogenides, metal oxides/hydroxides, metal nanostructures, and even the heteroatom-doped graphene provide better activity for rechargeable batteries [9–11]. Conventionally, the electrode materials were deposited on metal foils by doctor-blade technique, drop-casting, spray-coating, or spin coating to construct the batteries. This electrode material was mixed with foreign materials (binders and conducting agent) to make into ink, paste, colloidal dispersion, etc., for deposition purposes. In the case of self-supported graphene foams or FSGs, the foreign materials are avoided, and on the whole, they act as electrodes directly [12]. This chapter outlines few reported literature on FSG performance for rechargeable battery applications. Moreover, we summarized the synthetic strategies and fabrication of free-standing graphene/hybrid functional materials for particular device application.

## 2. Graphene: properties and nomenclature

Graphene is a 2D one atom thin sheet that consists of hexagonal  $sp^2$  carbon, which is densely packed into honey-comb lattice and large benzene-like aromatic hydrocarbon. It is considered as fundamental basis for all carbon allotropes, and their conceptual depiction are shown in **Figure 1**. It represents that 2D graphene sheet can be enclosed into 0D like fullerene structure and rolled up into 1D-like carbon nanotube structure, and 10 layers of graphene can be stacked up into 3D graphitic-like structure. Hence, it is considered as “mother of carbon allotropes” [13]. The fabrication of graphene film by different synthetic routes was adapted accordingly to its required

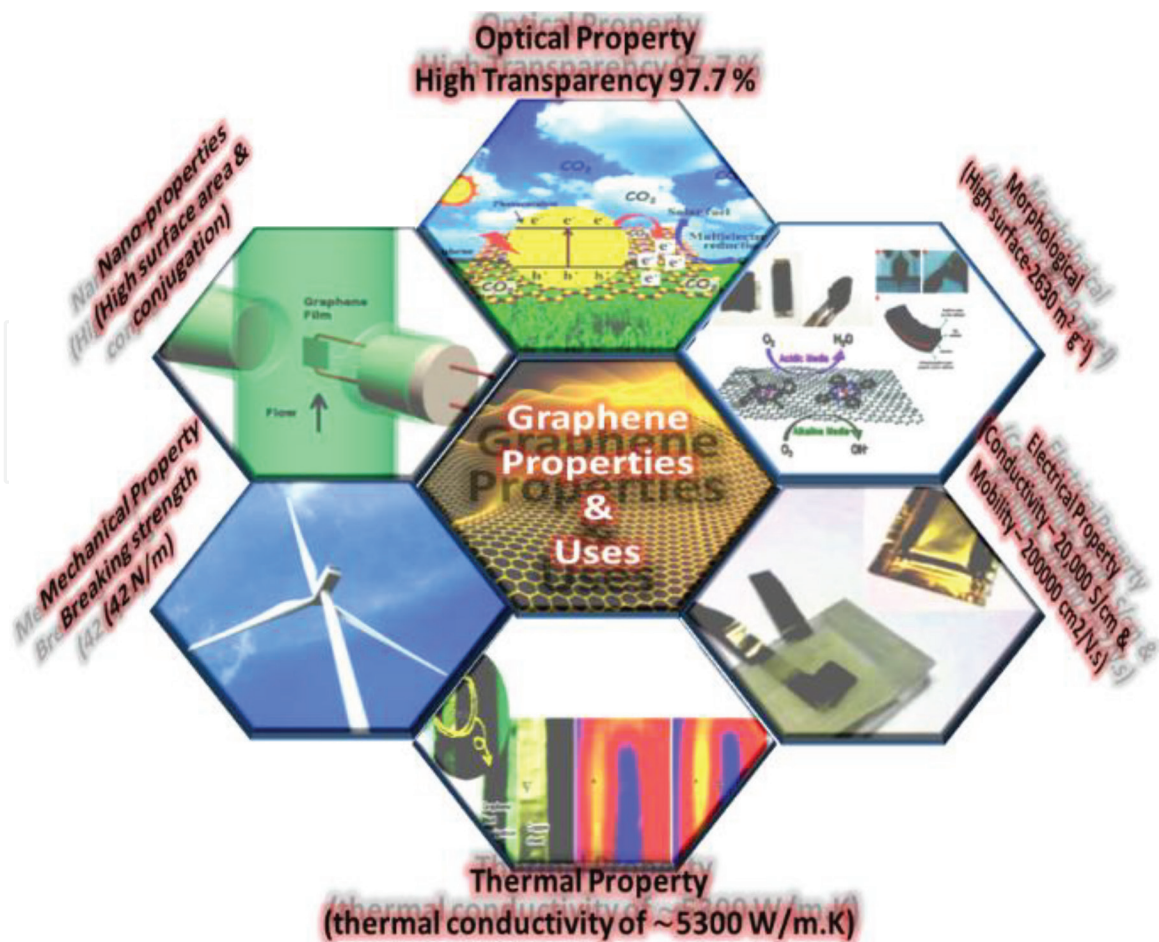


**Figure 1.** Carbon allotropes in different forms: 0D Bucky ball, 1D nanotubes, 2D sheets, and 3D graphite form (without permission from Ref. [13]).

properties for many applications. Current technologies addressed to synthesize graphene via several routes are as follows: mechanical exfoliation (liquid exfoliation and scotch tape method), epitaxial growth (chemical vapor deposition (CVD) and from organic molecules method), unzipping CNT (chemical and electrochemical methods), and wet chemical process (oxidation of graphite) [14].

## 2.1 Graphene: properties

Graphene possesses exclusive chemical, physical, mechanical, and thermal properties, which focuses on the field of electrochemical applications as an electrode material to enhance the stability and durability of the devices. Graphene application in any devices is adopted according to its properties as shown in **Figure 2**. Prominently, the conductivity of anode and cathode electrodes plays a vital role in batteries, which collect or disperse the electrons that tune up the performance to device. The conjugated  $sp^2$  carbon networks of 2D graphene sheet exhibit high conductivity around  $10^4$ – $10^6$  S/cm than any other carbon materials depending on the number of layers [15, 16]. Additionally, the electrode surface area is an essential part for batteries, which has high theoretical surface area of graphene, and is reported to be  $\sim 2600$  m<sup>2</sup>/g [17]. For suspended graphene sheets below 10 nm thickness, the spring constants were observed between 1 and 5 N/m, and pristine graphene exhibits Young's modulus of 1.05 TPa and intrinsic strength of 110 GPa, which has high mechanical property [18, 19]. The electrochemical property is a perspective for energy storage and generation technologies. The rate of heterogeneous electron transfer occurs on graphene materials; in the meantime, the rate of



**Figure 2.**  
Properties of graphene and its appropriate application.

reaction varies selectively at edges and basal plane according to their electroactive sites by adding impurities or doping. Graphene-based materials were potentially applied in electrochemical devices due to their inherent electrochemical activity nature [20]. These amazing properties of graphene such as electrical, mechanical, and electrochemical were attracted for rechargeable batteries.

## 2.2 Graphene: nomenclature

It is well known that graphene can be synthesized by several routes and named according to the recovered final product. Graphene research has elevated gradually in the past 5 years for its tremendous properties, but the scientific community ends up with the confusion in naming the material. Even though researchers have synthesized up to 100 layers of carbon sheets, they were naming them as graphene. This provides different changes in properties compared with the single-layer graphene sheet for their practical applications [21]. Hence, carbon journal community raised a nomenclature for graphene family, which is shown in (Table 1).

The descriptive term is an essential thing for researchers in the area of graphene material because the properties will change accordingly with recovered product with different synthetic strategies. For example, the graphene-based transparent conducting film adopted by the CVD method obtained 600 ohms/sq. at 96.5% transmittance at 550 nm, whereas solution processed graphene increases above 10 K ohms at the same transmittance [22–24]. Even the electrochemical behavior fluctuates according to the synthetic strategies; for instance, the presence of oxygen functional groups in graphene oxide (GO) shows an excellent electrochemical behavior rather than the pristine graphene [25]. Hence, the electrochemical device

Materials	Description
Graphene	Two-dimensional sheet with one atom thickness
Turbostratic graphene	Arrangement of graphene sheets in rotational fault structure
Bi-,tri-, or multilayer graphene	Stacking of graphene sheets (2 - bi, 3 - tri, & 4 - 10 - multi) in AB, ABA, or rotational order
Few layer graphene	Subset of multilayer graphene
Graphite nanosheets, nanoflakes, and nanoplates	Lateral/thickness of graphene sheets <100 nm.
Exfoliated graphite	Exfoliation of bulk graphite
Graphene nanoribbon	Length dimension in micron and width in the range of nanometer
Graphene quantum dots	Lateral dimension less than 10 nm with photoluminescence property
Graphene oxide	Graphene sheets that contain functional groups (epoxy, hydroxyl, and carboxyl)
Graphite oxide	Exfoliation of bulk graphite by strong oxidation process
Reduced graphene oxide	Reduction or restoration of sp <sup>2</sup> carbon of graphene oxide
Graphenization	Growth of graphene by small molecules (bottom-up approach)
Free-standing graphene, graphene foam, hydrogel, and aerogel	Graphene sheets arranged in 3D forms

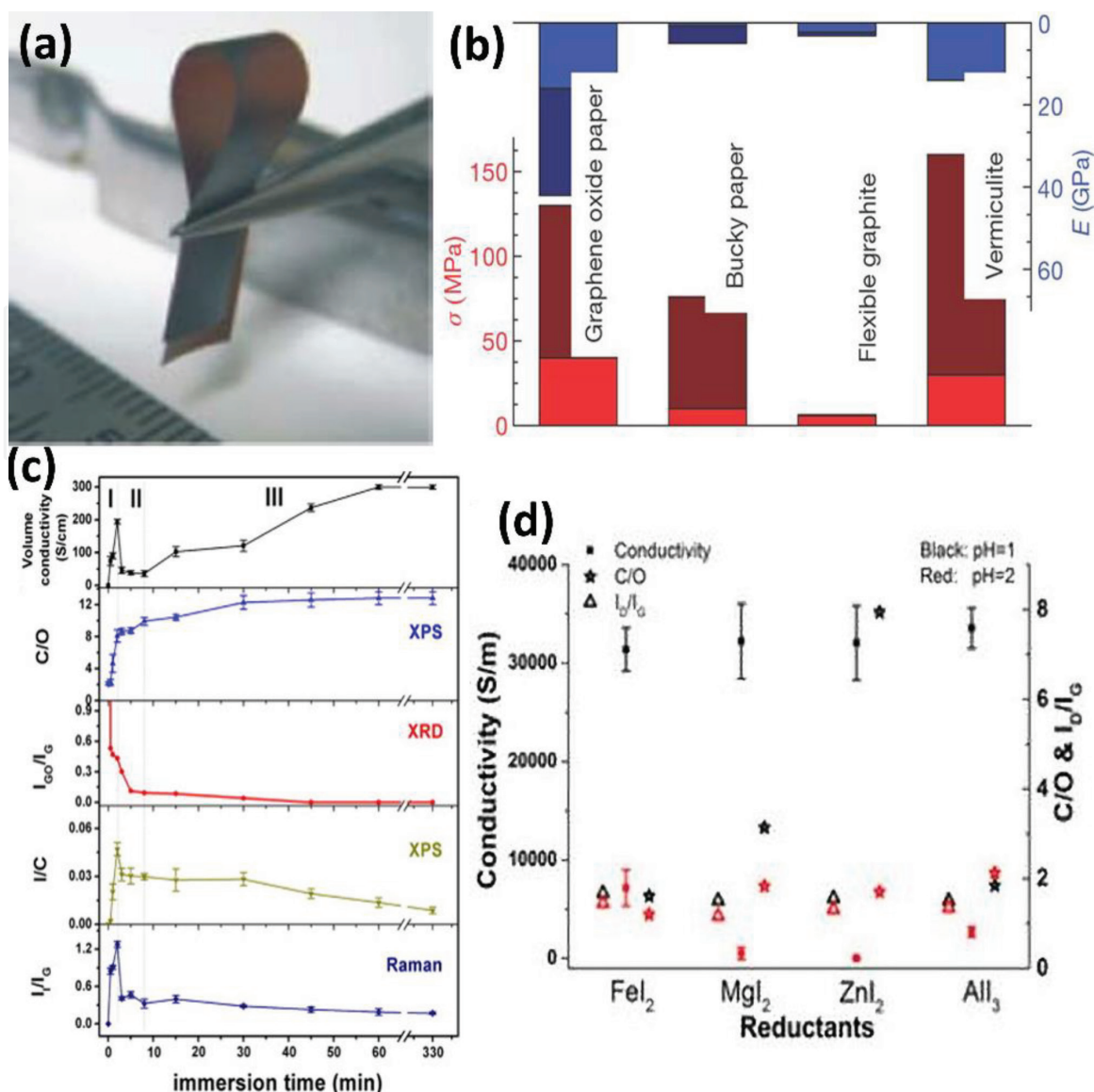
**Table 1.**  
*Nomenclature of graphene based on the structure.*

applications based on graphene electrodes depend on the architecture and hybrid composites to improve the active sites. Recently, 3D architecture like graphene materials such as foams, hydrogel, aerogel, and free-standing was utilized in electrochemistry-oriented topics.

### 3. Free-standing graphene: synthesis and its properties

For designing and fabricating large scale macroscopic or microscopic architecture like materials, the choice of precursor signifies the synthetic strategies. Graphene sheets synthesized by wet chemical process commenced for several applications due to the presence of functional groups. As discussed in the previous section, the methods utilized for the preparation of graphene sheets conclude their suitable application based on their properties. Noteworthy, there is a challenge for high dispersion of graphene either in aqueous or in organic solvents. It has been achieved by dispersing agent introduced into hydrophobic graphene sheets for good dispersion, whereas it submerges the graphene properties [26]. In the view of fact, large scale solution processable GO has several advantages such as cost effective, eco-friendly solvent and facile to introduce any foreign material due to the presence of functional groups [27, 28]. The copious amount of functional groups attached to the graphene surface contains hydroxyl and epoxy groups at basal planes and carboxyl groups at edges. This leads to affinity with water molecules, which provides a higher dispersion and further it assists with other inorganic or organic molecules for facile composite preparation. In the choice of precursor for free-standing material preparation, GO dominates as a building block due to its features of large scale solution processable with high colloidal dispersion. The resultant macroscopic FSG holds as an excellent mechanical, electrical, and light-weight material. Further, the 3D architecture of FSG enhances the surface area, porous nature, and structural active sites by merging with other functional host materials such as semiconducting material, metal nanoparticles, and polymers. The synergy of graphene sheets and functional host materials in the 3D macroscopic architecture attracted wide variety of applications due to the tuning of their properties.

In 1998, Smalley prepared CNT buckypaper by vacuum filtration, in prior it is well dispersed in Triton X-100 surfactant to break up the pi-pi interaction between the bundled ropes of CNT [29]. Further, CNT buckypapers were prepared by domino pushing technique, and they are strong, robust, and flexible. The obtained paper exhibits 26 micron thickness; the electrical conductivity was found to be  $2.0 \times 10^4$  S/m and thermal conductivity shows 153 W/mK [30]. These papers were directly applied for supercapacitor application. Thus, the carbon paper-like materials were potentially applied in a variety of applications due to their light-weight, highly flexible, robust, and eco-friendly nature. On the basis of cost, the CNT papers lag behind for the practical applications, and they have been replaced by graphene sheets. Similar to CNT buckypaper, GO paper was fabricated by flow-assisted vacuum filtration or evaporation techniques. **Figure 3a** and **b** shows the photograph of flexible GO paper and mechanical properties comparison chart of GO paper, buckypapers, vermiculite paper-like material, and graphite foil, respectively. Young's modulus is as high as in GO papers with 42 GPa for vacuum-assisted technique, and similar tensile strength but lowest Young's modulus (12.7 GPa) was obtained for evaporation-induced self-assembly technique [31, 34]. Thus, the high mechanical properties of GO paper can be used in several applications such as supercapacitors and other flexible substrates [35]. Moreover, the mechanical properties of GO papers depend on the alignment of GO sheets by any chemical modification between the layers and at the edges. The modifications are made either by crosslinking or grafting between



**Figure 3.**

(a) Photograph of flexible graphene oxide paper, (b) comparison chart of mechanical properties of GO paper with other flexible paper materials, (c) effect of FSG electrical conductivity changes w.r.t its properties upon HI treatment in different scale of time, and (d) electrical conductivity versus the Raman and XPS data of GO paper reduced by different metal halides (without permission from Refs. [31–33]).

the two sheets as GO has several functional groups that covalently attached to other molecules [36, 37]. The intercalation, functionalization, and interaction between the GO sheets provide high mechanical stiffness for paper-like material. Moreover, the atmospheric humidity affects the mechanical property of the GO paper, increase in the relative humidity to 100%, the GO colloidal solution absorbs water from moisture and it bulges to 70% which decreases the tensile strength [34]. The functionalization on graphene surface also affects the mechanical properties depending on the functional moieties as well as the bonding nature [38–40]. The electrical properties of GO papers depend on the synthetic methods as several changes were observed in structures and reduction ratios of C/O. Upon exposing to the hydrazine vapor, the conductivity of GO papers increased by four order of magnitude from  $8.5 \times 10^{-4}$  to 170 S/cm. Further enhancement in conductivities of GO paper was developed by treating the paper with mixture of argon/hydrogen/hydrazine vapors [41]. The removal of the oxygen group is the main factor to restore the  $sp^2$  carbon network by chemical or thermal treatment. The chemical reductive treatment efficiently removes the oxygen moieties from the GO paper, whereas the thermal treatment shows high restoration of  $sp^2$  carbon network but less removal of oxygen functional groups.

Recently, a rapid reduction treatment was proposed by immersing the GO papers in hydrohalic acids, viz., HI and HBr, which shows a remarkable electrical conductivity around 298 and 3220 S/cm, respectively [32, 42]. Based on the facile chemical treatment, the electrical conductivity of FSG improvement was shown by treating the GO papers in metal halides like  $MgI_2$ ,  $AlI_3$ ,  $ZnI_2$ , and  $FeI_2$  that exhibit 550 S/cm [33].

Owing to these attractive mechanical and electrical properties of FSG material, it played vital role in flexible device technologies based on electrochemical energy storage and generation, actuators, sensors, and catalysts. Based on the attractive graphene properties and its nomenclature, the graphene oxide has fascinating properties which has layered structure similar to graphene that containing oxygen functional groups such as carboxyl, hydroxyl and epoxy. These functional groups were highly dispersed in DI water; hence, it is well aligned over vacuum filtration process. The GO paper is peeled off after vacuum drying and subjected to reducing treatment, as synthesized FSG material is directly utilized as current collector in place of Al, Cu, Ni foam, etc., for energy storage applications.

#### **4. Free-standing graphene electrodes for batteries**

Battery is an electrochemical energy storage device that is cost-effective and eco-friendly and with cyclic durability, excellent overall performance, and long-term stability. In this decade, lithium ion battery (LIB) is successfully commercialized worldwide for portable electronic devices, and it has approximately 200 kWh scale for transportation and stationary storage [43]. On comparison with other secondary-based batteries such as sodium sulfur, redox flow, Ni-Cd, etc., Li ion cells have gathered the most commercial interest because they provide high energy and power densities, respectively. In contrast, other secondary batteries are under development stage for consideration in commercial package over LIB due to its major drawback as follows: large scale storage, cost of materials, toxicity, cyclic performance, or stability issues. However, the better system in secondary batteries credited for LIB because the redox potential of  $-3.04$  V vs. SHE (standard hydrogen electrode) for  $Li/Li^+$  which has high electropositive in periodic table and light weight material with small ionic radius. Henceforth, the charge-discharge rates enhance and power densities vary in the ranges of 500–2000 W/kg [44]. In commercialized LIBs, the existing negative electrode is a graphite-layered structure material coupled with the host material and  $LiCoO_2$  has positive electrodes. Similar to LIBs, the other systems were also focused since it lags behind to reach the theoretical specific capacity (400 Wh/kg) that requires for electric vehicles for long term usage. Hence, other kinds of secondary batteries have been discovered such as Li-sulfur, sodium-ion battery (SIB), sodium-sulfur, Li-air, Zn-air, and flow batteries.

##### **4.1 Li-ion battery**

Conventionally, LIBs are made up of graphite anode and  $LiCoO_2$  layered material as cathode sandwiched between  $LiPF_6$  (1.0 mol/L) as an organic electrolyte dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) in 1:1 volume ratio [45]. While LIB is charging, deintercalation happens at cathode, where the Li ions are removed from the layered  $LiCoO_2$  by releasing electrons to cathode. The released Li ions are transported to anode with the help of the electrolyte system and finally intercalated into graphite by gaining electrons. The same process is reversed during the discharging process.

Designing of anode materials for LIBs has focused much attention on retaining large reversible specific capacity. Beyond the graphite anode, few metal oxides and



metal alloys were developed as anode material, and the lithiation and delithiation processes were investigated. Specifically, FSG paper outpaces the other candidates such as carbon nanotube (CNT) paper or graphite foil due to their tremendous properties as discussed earlier. Importantly, the electrical and mechanical properties of FSG are potentially applied for flexible device application. However, the FSG electrode itself does not provide higher capacity (approximately 100 mAh/g), which is not applicable as anode in LIB; instead, it has good cycling stability. Therefore, the host material that has high electrochemical active sites is incorporated into FSG for improvement of capacity in the device. This extends the large volume expansion in FSG electrodes for an efficient Li ions intercalation. One of the advantages of this FSG hybrid electrode is that it excludes the nonconducting polymer binders as additives. Conventional electrode-based materials were obtained as powders and coated on the metal foils in the form of ink using additives like polymer binders and conducting additive, whereas the FSG hybrid electrode plays dual role as a current collector and conductive additive.

In 2005, LIBs were fabricated with free-standing electrode based on CNTs prepared by vacuum filtration method [46]. Significantly, the free-standing electrode fabrication is a facile route in comparison with the conventional electrode since the mixture of active material, polymer binder, and conductive additive in solvent coated on metal foils. The CNT free-standing electrode provides reversible discharge capacity of 200 mAh/g at 0.08 mA/cm<sup>2</sup>. Further, the specific capacity was enhanced by the CVD grown free-standing CNT that delivers 572 mAh/g at 0.2 mA/cm<sup>2</sup> [47]. This is a quite interesting result obtained for free-standing electrodes rather than the conventional electrodes. Meanwhile, the usage of high-cost material CNTs as free-standing electrodes lags behind manufacturing process. From this point of view, inexpensive material graphene prepared by chemical methods provides large scale production as dispersion in many solvents. This dispersion is readily subjected to vacuum filtration to prepare FSG paper with desired thickness. Usually, the discharge capacity of 298 mAh/g decreased to 240 mAh/g after 50 cycles for graphite electrodes with 81% retention capacity. But the FSG paper itself as anode provides huge irreversible discharge capacity, i.e., 680 mAh/g at initial cycle dropped to 84 mAh/g second cycle. The retention capacity is very poor compared to graphite electrode and therefore it is concluded to be not a suitable candidate for anode material [48]. This helps infer that solid electrolyte interface (SEI) formation is a significant parameter to reduce the storage capacity in FSG electrodes.

To potentially apply FSG as anode material in LIBs, the second phase material with highly electrochemical active sites should be composited to enhance the capacity. In this regard, Lee et al. composited Si NPs on GO sheets, vacuum filtered, and followed by thermal treatment to produce FSG/Si nanoparticle (NP) paper. This work delivers high Li ion storage when compared to pristine FSG electrodes. Si NPs intercalated between the graphene sheets of FSG paper that facilitates good 3D graphite-like framework and provides high Li ion storage even at high current density [49]. Another work has been reported with similar hybrid FSG/Si NPs, whereas a facile route has been introduced to fabricate. The specific capacity of 708 mAh/g was observed without any loss even after 100 cycles and this is mainly due to the larger volume change in graphene-Si composite. It also denotes the performance of device with an efficient electron and charge transfer contributed by graphene sheets that minimize the internal resistance of the electrodes [50]. Zhang et al. prepared Si hollow nanosheets using Mg as template and connected with graphene sheets to obtain free-standing electrodes by layer-by-layer method followed by HI reduction treatment. The specific capacity was examined during flat and bent state, which delivers similar results without any loss. Remarkably, Si/FSG paper anodes

retain high reversible capacities even at long cycles, which reveals their retention capacity. They exhibit specific capacity of 660 mAh/g at 0.2 A/g current density after 150 cycles with 99% coulombic efficiency [51]. As mentioned earlier, all the Si NPs are highly expensive in terms of manufacturing process and hence a low cost method plays a significant factor. To tackle this issue, Cai et al. prepared Si NPs on CNT surface using low-cost Al-Si alloy as starting material and further inserted with graphene sheets to form a self-standing hybrid anodes for LIBs. Comparing with bare Si/CNT or Si/Graphene anodes, Si-CNT/FSG hybrid electrode, it delivers 1100 mAh/g at 0.2 A/g current density after 100 cycles. Addition of CNT was involved to disperse the Si NPs on the surface and provide network between the graphene sheets for conductivity enhancement as well as improved Li ion intercalation for efficient charge transfer [52].

Metal oxides (MOs) play an important role in LIBs as anode material and their poor conductivity restricts their application. Hence, introducing the conductive phase into MOs provides high retention capacity with long-life cycling stability. The theoretical reversible capacity of SnO<sub>2</sub> is 782 mAh/g and its poor performance is due to low cycling with serious volume expansion. With this regard, SnO<sub>2</sub> NPs dispersed on GO surface, followed by vacuum filtration to obtain free-standing electrodes and used as two different LIB anodes by thermally reduced and chemically reduced respectively [53, 54]. The specific capacity of 438.5 mAh/g at 0.1 A/g and 700 mAh/g at 0.2 A/g has been delivered for the two different reduction methods for SnO<sub>2</sub> NPs/FSG electrodes. In both the cases, capacity fading is not observed even after the 50 cycles owing to the good anchoring of SnO<sub>2</sub> and graphene sheets. Further, other metal oxides TiO<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, and CuO nanostructured materials are incorporated into the FSG and are investigated for their performance in anode application for LIBs that delivers 269 mAh/g at 0.2 A/g, 692 mAh/g at 0.05 A/g, 544 mAh/g at 10 A/g, and 698.7 mAh/g at 0.67 A/g capacities, respectively [55–59]. Commonly, all these metal oxides' specific capacity shows a reasonable capacity with the long-life cycling after incorporating the MOs into FSG electrodes due to the following aspects: (1) Interaction of GO and MO precursors increases, which enhances the well dispersive growth of MO NPs on graphene sheets. (2) Anchoring of MOs and graphene enhances the volume expansion/contraction for lithiation/delithiation process. (3) The cycling stability increases compared to pristine MO anodes even after several cycles owing to its structural phase remain stable after alloying/de-alloying process of lithium ions. (4) MOs avoid the aggregation of graphene stacking that leads to larger void space to penetrate the electrolyte and make a strong interface with the electrochemical active MOs for an efficient Li ion storage.

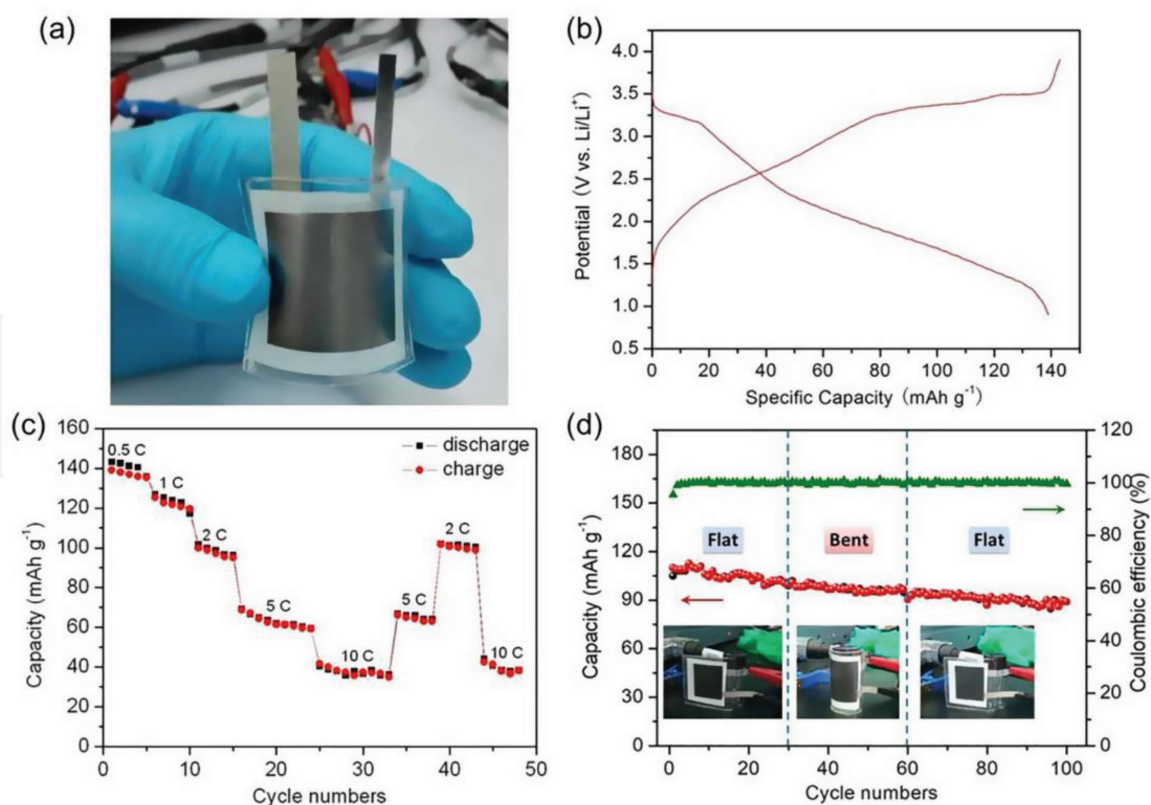
Further, with the controlled synthesis of oxygen, functionalized CNT/FSG electrodes were fabricated for anode application in LIBs. The battery performance is based on the oxygen functional groups in the electrodes that have been investigated. An optimization in weight ratios of CNT/FSG and heat treatment improves the volumetric and gravimetric capacitances. The CNT/GO hybrid at a ratio of 1:1 shows higher volumetric capacity of 260 mAh/cm<sup>3</sup> that reduced at 200°C, while lower capacity of 43 mAh/cm<sup>3</sup> for 900°C treated CNT/GO. Whereas, at high current densities, the role of oxygen in capacity role suppress for 200°C larger than the 900°C [60]. This implies the importance of CNT intercalation between the graphene sheets of FSG electrodes. Zhang et al. demonstrated the defect-rich MoS<sub>2</sub> NSs/graphene/CNT hybrid paper as anode material for LIBs. In this design, MoS<sub>2</sub> facilitates the lithium ion storage due to the high active sites at the edges and the electrical conductivity improved by the network of CNTs attached to the graphene sheets. In addition to the conductivity enhancement, the porosity of the FSG electrodes increased by the network of CNT sandwiched graphene sheets. On the

whole, the binder-free and substrate-free hybrid anode papers deliver high reversible capacity of 1137.2 mAh/g at 0.1 A/g current density with good cycling stability [61]. This framework induces a novel pathway to incorporate other host materials to understand the CNT/FSG electrodes. Recently, several transition metal oxides provide high reversible theoretical capacities compared with the commercialized graphite anode. To the CNT/FSG electrode network, transition metal oxides such as  $\text{Fe}_2\text{O}_3$  [62],  $\text{CuO}$  [63],  $\text{MnO}$  [64], and  $\text{CoSnO}_3$  [65] were incorporated as electrochemical active phase into the framework and investigated as anode material performance for LIBs. All these hybrid papers exhibit high reversible capacity of 716 and 600 mAh/g at 0.5 A/g current density more than 50 cycles for  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  nanobox, respectively. Apart from this, an enhanced capacity was observed for  $\text{CoSnO}_3$  and  $\text{MnO}$  NPs at high current density of 2 A/g, which delivers 676 and 530 mAh/g, respectively. Individually, the CNT/FSG and transition metal oxide anodes were found to have a drastic decrease of specific capacity upon increasing the current density, whereas a slight decrease of specific capacity was observed after hosting the metal oxides into CNT/FSG framework. Reasons for high reversible capacity and good cyclic stability of metal oxide-CNT/FSG electrodes are very similar due to the following merits: (1) incorporation of metal oxides improves the Li ion kinetics and enhances the charge transfer due to highly conductive CNT network between the graphene sheets; (2) 3D framework of CNT/FSG has highly porous nature, large specific surface area, and large volume change, which has well dispersion of metal oxide NPs onto the carbon surfaces; and (3) long cycling due to good attachment of metal oxide with CNT/FSG, whereas greater the volume expansion, higher the Li ion intercalation.

Interestingly, Cao et al. designed a unique layered nanostructure of porous ternary  $\text{ZnCo}_2\text{O}_4$  on graphene sheets and fabricated as flexible anode and investigated its electrochemical performance. And also they constructed full cell with  $\text{LiFePO}_4$  as cathode material that deposited on FSG paper as slurry by homogenous mixing of conductive additive and polymer binder [66]. **Figure 4a** shows the photograph of flexible Li-ion battery fabricated by FSG hybrid electrodes. The half-cell of  $\text{ZnCo}_2\text{O}_4/\text{FSG}$  anode delivers higher specific capacity of 791 mAh/g at 1 A/g after 1000 cycles with 97.3% of capacity retention and concludes that it has an excellent cycling stability. **Figure 4b** shows the rate capability of the flexible battery with different current densities ranging from 0.5 to 10 C. This full cell delivers 40 mAh/g even at 10 C rate and the specific capacitance remains the same after the current density decreased to 2 C, which shows a good reversibility. The full cell has FSG paper as current collector for both the anode and cathode that are composited with  $\text{ZnCo}_2\text{O}_4$  and  $\text{LiFePO}_4$  as host materials, respectively. It operates at 2 V with initial charge of 143 mAh/g and coulombic efficiency of 97.2%, which is comparable to existing LIB. The specific capacity is maintained at 90 mAh/g with high capacity retention under flat and bent states over 100 cycling process, which implies the flexibility of the device as shown in **Figure 4d**. It represents that graphene conductivity is unchanged while bending the device.

## 4.2 Sodium-ion battery

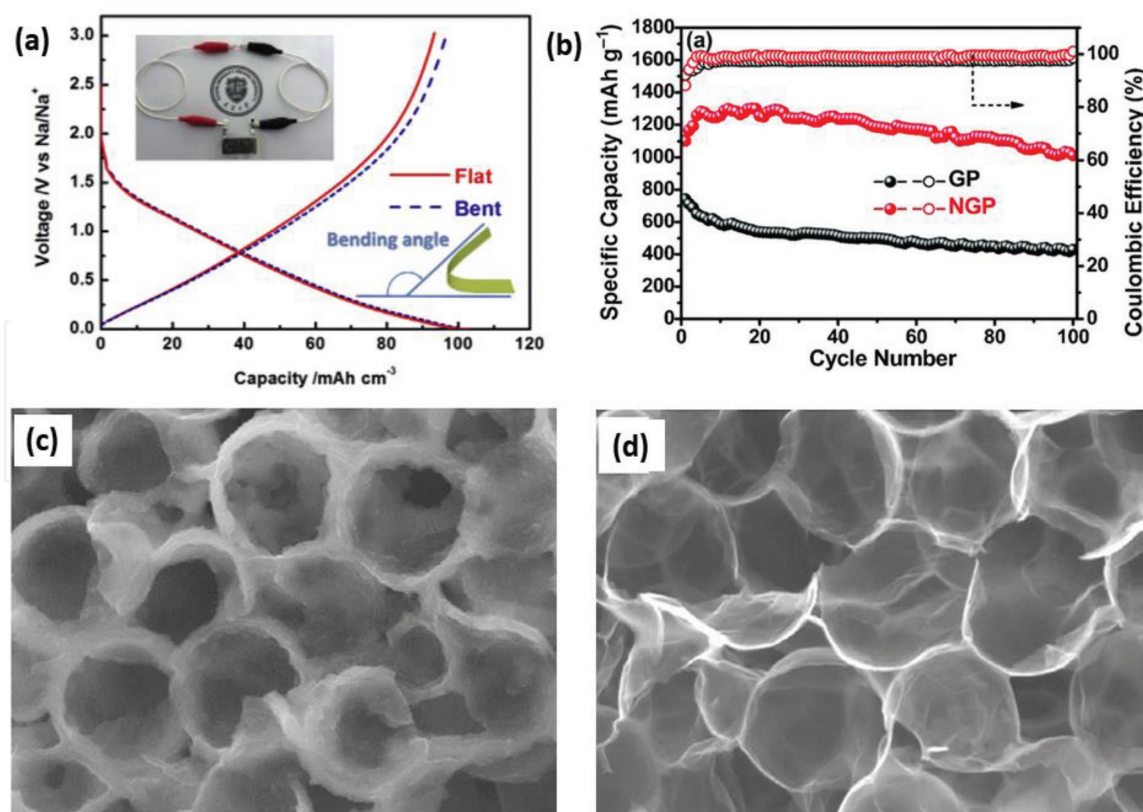
Ahead of LIBs, SIBs have attracted the research community as the resources of Na are inexhaustible across the globe. In comparison with LIBs, the redox potential is  $-2.71$  V vs. SHE and only the radius is 55% larger than the Li ions. Larger radius influences to focus on suitable material for insertion/extraction of Na ions effectively. The researchers focused on developing an efficient anode material for SIBs that involves carbon-based families and Na intermetallic compounds. The first cycle-specific capacity of sodium-antimony and sodium-phosphorous shows 600 and 2596 mAh/g,



**Figure 4.** (a) Photograph of flexible full cell Li-ion battery with FSG/ZnCo<sub>2</sub>O<sub>4</sub> as anode and FSG/LiFePO<sub>4</sub> as cathode, (b) charge-discharge curve of full cell at 0.5 C rate, (c) charge-discharge rate capability at different rates, and (d) capacity variation on flat and bent state during cycling at 2 C rate (without permission from Ref. [66]).

respectively [67–69]. Specific capacities drop after first cycles due to the internal cracking in the electrodes upon Na ion insertion. It leads to hinder the electrical properties and dissolution of electrode materials to electrolyte. The hard carbon with large interlayer distance that functions as anode material for SIBs and delivers more than 200 mAh/g of capacity even after 100 cycles was reported elsewhere.

The porous nature and structure of the FSG could facilitate the accommodation of host materials such as transition metal chalcogenides (TMCs), which are electrochemically active for the Na ions for alloying process. David et al. reported that the MoS<sub>2</sub>/FSG composite papers exhibit an excellent cyclic stability with high reversible capacity of 338 mAh/g at 0.025 A/g. It is the first report and opens the pathway to apply free-standing electrodes for SIB anode [70]. The cyclic stability was enhanced in flower-like MoS<sub>2</sub> incorporated on graphene foam prepared by one-step microwave-assisted synthesis. It offers stable capacity of 290 mAh/g at 0.1 A/g after 50 cycles compared to previous MoS<sub>2</sub>/FSG electrode. The cycling performance is enhanced due to highly conductive 3D graphene foam and well-dispersed MoS<sub>2</sub>, which shields as well as avoids the strain during the sodiation/desodiation process at anode [71]. With the significance of MoS<sub>2</sub> TMC for SIB anodes, further investigation was followed by incorporating other TMCs such as WS<sub>2</sub> and Co<sub>0.85</sub>Se into FSG [72, 73]. As mentioned in LIBs, the electrochemical behavior can be increased by introducing the heteroatoms into the graphene sheets. Heteroatom-doped FSG electrode performance was investigated for SIB anode, where the nitrogen improves the electronic conductivity and fluorine expands the interlayer for an efficient accommodation of Na ions. This delivers a reversible capacity of 56.3 mAh/g at 1 A/g for 5000 cycles. It indicates that the doping of heteroatoms enhances the cycling stability of SIB anodes. **Figure 5a** shows the discharge/charge profile before and after the bent state, which remains with the same capacity at current density



**Figure 5.**

(a) Discharge/charge profile of heteroatoms (N and F)-doped FSG electrode at bent and normal state for SIBs. (inset: The photograph of FSG pouch cell illuminated with LED), (b) comparison of specific capacity and coulombic efficiency of bare FSG and N-doped FSG for Li-S battery. Cross-sectional SEM images of (c) discharged and (d) re-charged macroporous FSG electrodes (without permission from Refs. [74–76]).

of 0.05 A/g. It reveals the mechanical strength of the FSG electrodes that is suitable to fabricate flexible pouch cell [74]. Even though the above said materials show an excellent cyclic stability, still it is necessary to improve the specific capacity of SIBs. It is well known that  $\text{Na}_3\text{P}$  has theoretical capacity of 2600 mAh/g, where its demerits are very similar to those of Si electrode in LIBs. Because of high pulverization, fast capacity fading and also it hinders the electrical contact which lags behind in the electrochemical stability. Lots of effort have been made by assembling red P into carbon matrix to overcome these problems. Red P was composited on carbon nanofibers (CNFs) and dipped in GO solution followed by HI treatment providing P-CNF/FSG electrodes. In this architecture, CNF network enhances the pathway of electron transport rapidly and the role of graphene sheets to improve the conductivity as well as to avoid the breakup of bonds P–P from electrodes. This work demonstrates a significant capacity of 406.6 mAh/g at 1 A/g after 180 cycles [77]. Moreover, the graphene sheets have been utilized as a multifunctional conductive binder, and hard carbon/FSG as anodes for SIBs was constructed. It delivers high reversible capacity of 372.4 mAh/g and shows capacity retention of 90% over 200 cycling. A superior performance is observed in the absence of PVDF binder with higher rate capabilities and converting the rigid nature of hard carbon into flexible graphene sheets [78].

### 4.3 Li-S battery

Akin to SIBs, FSG electrodes play a major role in other rechargeable secondary batteries such as Li-S, Li-air, and Zn-air. The higher specific energy is a significant parameter for transportation and stationary applications, and in that case, Li-S batteries offer advantages but it is limited with few challenges discussed later. The

highest theoretical capacity of Li-S system is 2600 Wh/kg, which is highest than the LIB due to highest capacity of Li-S cathode sulfur has 1675 mAh/g. The most challenging part is to improve the electronic conductivity of cathodes of Li-S as the sulfur exhibits poor conductivity of 10–17 S/cm as well as the formation of polysulfides at cathodes. These polysulfides oxidize the Li anode and get back to cathodes and re-oxidize, thus lowering the performance of Li-S system. An extensive effort has been made to improve the cathodes by incorporating the carbon additives to sulfur to minimize the unnecessary reactions. Initially, mesoporous FSG was prepared and the sulfur was deposited by vapor treatment and was utilized as cathodes for Li-S system. It delivers charging capacity of 1288 mAh/g with high coulombic efficiency that reveals the restriction of sulfur to dissolve polysulfides in mesoporous FSG framework [79]. Similar to LIB and SIBs, the electrochemical behavior of cathode in Li-S system enhanced for heteroatom-doped FSG electrodes. **Figure 5b** shows the comparison of FSG and N-doped FSG capacity and coulombic efficiency with different cycle number. The heteroatom-doped FSG shows superior performance than the bare FSG due to the high interaction of polysulfides with heteroatoms that increase specific capacity. The nitrogen doping effect in FSG minimizes the concentration of polysulfides and forms a uniform layer of  $\text{Li}_2\text{S}$  at cathode. This system delivers 1000 mAh/g at 0.335 A/g after 100 cycles [75]. In another work, Zhu et al. developed free-standing cathodes by CNTs that were interconnected with the sulfur-graphene walls and investigated the electrochemical behavior that delivers 1346 mAh/g at 0.17 A/g current density. It is due to sulfur at graphene walls that deals to provide dual response as follows: (i) hinder the dissolution of polysulfides minimizing the shuttle phenomenon and (ii) offer volume expansion even at high quantity of sulfur. Moreover, its capacity retention shows 40% when current density is increased to 16.7 A/g owing to the good electron pathway by CNTs connected with graphene nanosheets [80]. Further, nanosized  $\text{Li}_2\text{S}$  (25–50 nm) particles incorporated into FSG papers by vacuum filtration process demonstrated an excellent cycling and rate capability with reversible capacity of 816.1 mAh/g at 0.1675 A/g (150 cycles) and 597 mAh/g at 11.7 A/g (200 cycles). This shows excellent performance in electrochemical behavior due to the uniform distribution of  $\text{Li}_2\text{S}$  particles on graphene sheets that minimize the barrier for Li ion transport and particularly it has superior wetting nature to interconnect the polysulfides with graphene network into the paper electrodes [81]. Similarly, Chen et al. designed an efficient hierarchical nanostructure like nanobundled forest with  $\text{Li}_2\text{S}$ /few-walled CNTs at FSG obtained solution processing followed by self-assembly method as cathodes. In this design, CNTs assembled in shaft-like structure and  $\text{Li}_2\text{S}$  as active material, whereas the graphene sheets act as barrier for  $\text{Li}_2\text{S}$ . It achieves high capacity of 868 and 433 mAh/g at current density of 335 and 16.7 A/g, respectively. This originates from the good framework between CNTs and graphene sheets as well as the uniform distribution of  $\text{Li}_2\text{S}$ , and moreover, the barrier of graphene sheets for  $\text{Li}_2\text{S}$  reduces the dissolution of polysulfides. Overall, the influence of void space enhances the volume change and thus improves the cycling stability of Li-S battery [82].

#### 4.4 Metal-air battery

Recently, metal-air batteries have inspired much attention apart from the above said battery systems due to their high theoretical capacity than the metal-ion and Li-S batteries. The metal-air batteries can be operated in aqueous or nonaqueous medium based on the selection of metals. The nonaqueous medium is well suited for the Li-air batteries that deliver high capacity than in aqueous medium but still there are some issues when it comes to the practical application. The development of cathode in Li-air is significant as it is the main compartment to breathe oxygen

for delivering high capacity of the system. There are a lot of reports for cathode development based on metal oxides grown on Ni foam as binder-free electrodes. The role of FSG electrodes was also investigated as cathodes for Li-air batteries. First, Kim et al. developed graphene nanoplates (GNP)/GO composite paper-like electrodes as cathodes for Li-air battery system. The wrinkled nature of the paper electrodes induces the high surface area and also delivers higher discharge capacity of 9760 mAh/g at 0.1 A/g current density. This superior performance is due to the reduced overpotential, and the difference in consumption/evolution of O<sub>2</sub> is minimized. On the whole, the system exhibits higher efficiency in OER (oxygen evolution reaction)/ORR (oxygen reduction reaction) of 87% [83]. The same group developed macroporous FSG paper with surface area of 373 m<sup>2</sup>/g and pore volume of 10.9 cm<sup>3</sup>/g with 91.6% of porosity that exhibits a high specific capacity of 12,200 mAh/g at 0.2 A/g. The rate capability is enhanced where it shows high cycling performance even at higher current density of 0.5 and 2 A/g that delivers approximately 1000 mAh/g. This is attributed to the minimized volume expansion that limits the decomposition and formation of Li<sub>2</sub>O<sub>2</sub> at the macroporous nature of FSG. While discharging/charging the macroporous FSG, the nature of FSG electrode decomposes the discharge products completely that reveals its highly porous structure as shown in the **Figure 5c** and **d** [76]. Researchers investigated the effect of FSG cathodes in Li-air upon introduction of metal oxides, namely, α-MnO<sub>2</sub> and NiCo<sub>2</sub>O<sub>4</sub>. Upon insertion of α-MnO<sub>2</sub> into FSG electrodes, the overpotential decrease was caused during charge/discharge process. It delivers 2900 mAh/g for the higher content of α-MnO<sub>2</sub> that was reported and shows the catalytic improvement in this study [84]. And Jiang et al. reported an excellent reversible capacity of 5000 mAh/g at 0.4 A/g by incorporating mesoporous NiCo<sub>2</sub>O<sub>4</sub> into macropores of FSG. It also lowers about 0.18 and 0.54 V of overpotential for discharge and charge, respectively [85].

## 5. Conclusions

In this chapter, FSG electrodes in battery applications signify their potential advantages to the fabrication technology. The fabrication of FSG electrode is facile as well as it excludes some additives applied in conventional electrodes. At present, the electrode of spent batteries contains active materials, binder, and metal foil, which set hurdles for recycling process. Herein, the FSG hybrid electrodes provide good capacity and cycling for battery application without binder and metal current collector. This exclusion provides light weight and flexible batteries and also there is a pathway to discover a facile route to recover the materials from FSG hybrid-based spent batteries in future.

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## Conflict of interest

The authors declare that there is no conflict of interest.

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