Preparation Methods, Characteristics, and Prospects of α-Fe_2O_3/Graphene Supercapacitor Electrodes in a Green Chemistry Perspective

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Abstract

Supercapacitors are green energy storage devices featuring a long cycle and shelf life having high efficiency. The attainment of high-power density in combination with promising energy density is one of the main targets of developing hybrid supercapacitor electrode materials. Among the different electrical double-layer capacitance materials, graphene has an outstanding role due to its high surface area and high conductivity. In addition, it can act as an excellent matrix for the dispersion of a variety of nanomaterials. Among the various pseudocapacitor metal oxides, α-Fe_2O_3 has the auspicious features of cost-effectiveness, environment friendliness, and natural abundance together with its high theoretical capacitance. This review target to explore the preparation methods and the features of α-Fe_2O_3/graphene. A glance at the greener methods of graphene and its composite preparation is given in the review. The future of these materials and the directions for further studies are also briefly mentioned at the end.

Keywords—Supercapacitor electrode; α-Fe_2O_3/graphene; Eco-friendly preparation

I. Introduction to Supercapacitors

One of the biggest problems the energy sector faces is the creation of effective energy storage technologies. Supercapacitors are energy storage technologies that can meet today's energy demands. The limits of batteries and traditional capacitors are overcome by supercapacitors or ultracapacitors. Supercapacitors possess exceptional electrochemical characteristics such as their high cycle stability, shelf life, energy density, power density, quick charge-discharge rate, etc. Even though supercapacitors have a lower specific power than normal capacitors, they possess a higher energy density than conventional electrolytic capacitors[1–3]. Figure 1 depicts these features in the Ragone plot[4].

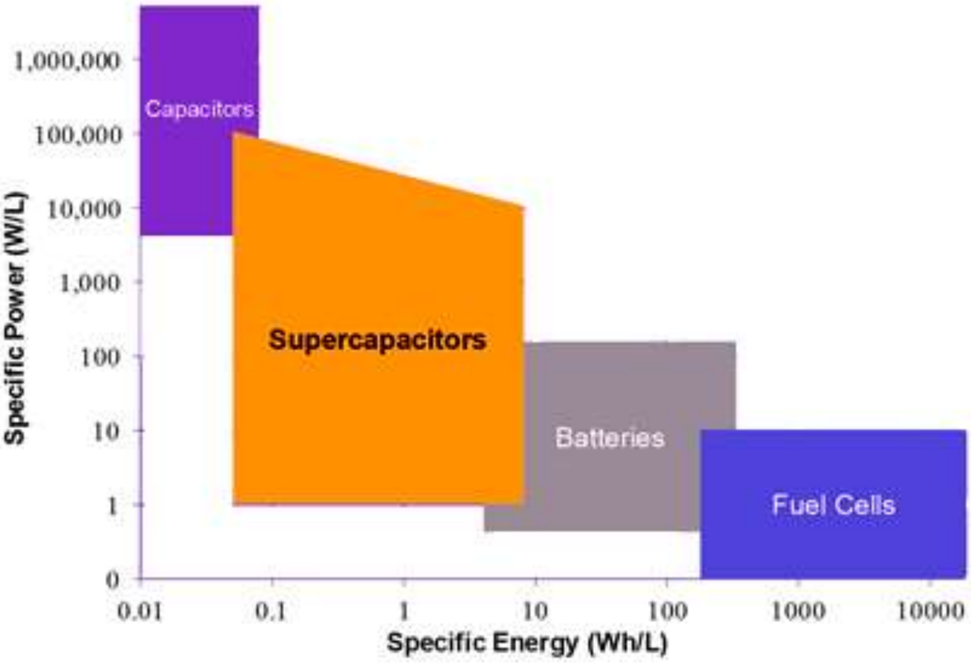

Figure 1. Ragone plot illustrating several energy storage devices.

Many charge-discharge cycles are possible with supercapacitors. The method for storing charges lengthens the cycle life. In contrast to batteries, the charge-storage process also utilises physical charge storage at the electrical double layer without the need for any chemical reactions.[3,5]. Because of their polarisation resistance, batteries' cycle life is shortened[3,6]. An ion-permeable separator dipped in an electrolyte and two electrodes make up the cell of a typical supercapacitor[7]. The electrodes in symmetric supercapacitors are formed of the same material combination, whereas they are different in asymmetric supercapacitors[8]. While using aqueous electrolytes in supercapacitors, the separators can be polymer/paper separators, while organic electrolytes performs better using fiber/glass separators[9,10]. Aqueous electrolytes typically operate at lower operating voltages, up to 1.2 V, while organic electrolytes run at potentials as high as 3 V[3].

Electrochemical double-layer capacitors (EDLC), pseudocapacitors, and hybrid capacitors are the three categories of supercapacitors according to their charge storage (Figure 2). Non-Faradaic, Faradaic, and a combination of the two are the respective mechanisms of charge storage. The typical components of an electrochemical double-layer capacitor (EDLC) are carbon-based electrodes with a large surface area[11,12]. Electrostatic electrical double layer formation is the storage mechamism in EDLC[1]. Here, when potential is supplied, charges are accumulated on the electrode surfaces, and then the electrolyte ions are transferred to electrodes having opposing charges[1, 6,13]. Carbon nanostructures are the electrode materials for EDLC's such as graphene, carbon nanotubes, carbon aerogels, graphene, etc., but activated carbon was also widely used for this purpose[2,3]. Between the electrode and the electrolyte in pseudocapacitors, the faradaic charge is stored through electrosorption, redox processes, under potential deposition intercalation, etc[14,15]. Even though the pseudocapacitor has a higher capacitance and energy density than EDLC, the power density is much lower because of the slower Faradaic processes[16]. Metal oxides and conducting polymers, showing pseudocapacitive nature displayed poor cyclic stability and mechanical stability[3].

The drawbacks brought on by individual EDLCs and pseudocapacitors are overcome by hybrid capacitors with electrodes displaying both EDLC and pseudocapacitance. Good power density, energy density, shelf life, etc. are all displayed by a hybrid capacitor without degrading the cyclic stability.[1,8,17]. A hybrid supercapacitor works by using composite electrodes, battery-style electrodes, and asymmetric electrodes[1]. The various charge-storage mechanisms used by EDLCs, pseudocapacitors, and hybrid capacitors are depicted in Figure 2.

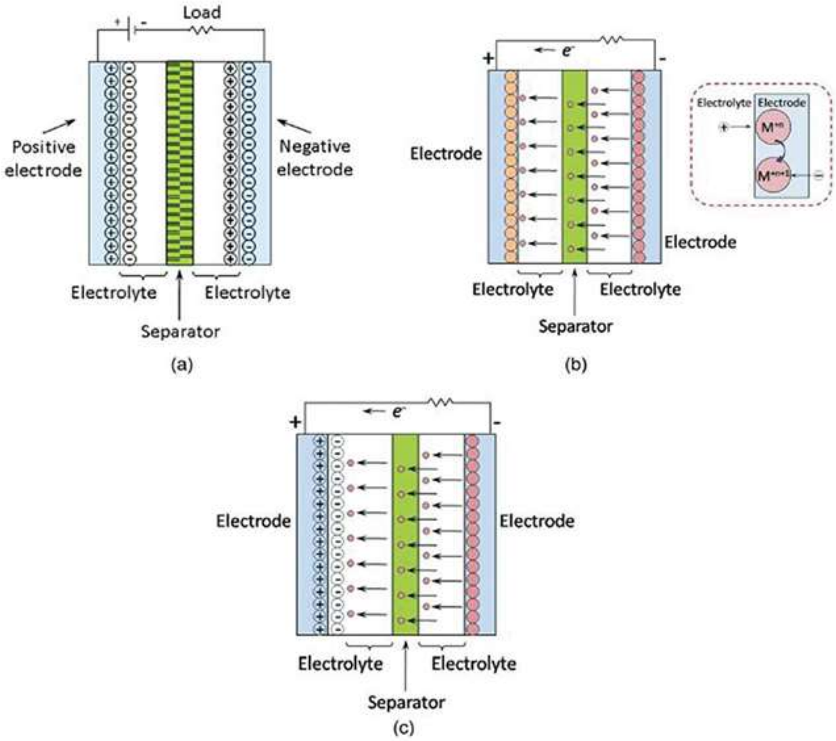

Figure 2. The charge storage principles of (a) an EDLC, (b) a pseudocapacitor, and (c) a hybrid capacitor are all shown. Reprinted with permission from https://www.greentechee.com/classification-and-energy-storage-principle-of-supercapacitors_n54[18].

The review here describes how graphene and Fe_2O_3 work as supercapacitor electrode materials. Graphene is now a widely used material for supercapacitor electrodes due to its high conductivity, EDLC nature, high surface area, and capacity to incorporate a variety of materials, whereas Fe_2O_3's main merits are abundant nature, good capacitance behaviour, low cost, and capacity to form non-covalent bonds with graphene. The review also describes the ease of making Fe_2O_3/graphene nanocomposite and their characteristics, particularly those important for electrode materials. The combination's supercapacitor performance is outlined, and the final section includes a well-written description of the combination's future prospects.

II. Graphene

Graphene, the most well-known EDLC nanomaterial, exhibits a theoretical capacitance of 550 F/g[19]. Graphene stands apart from conventional electrode materials due to its special characteristics, including high surface area, conductivity, electrical mobility, mechanical strength, and chemical stability. Here, the structure, background, characteristics, and production techniques of graphene are covered.

The extended π-conjugative network of graphene, a one-atom-thick planar sheet of sp2 hybridised carbon atoms, describes the majority of its features. Carbon atoms are arranged in a hexagonal structure with alternating single and double bonds[20]. The idealised structure of graphene is shown in Figure 3. Graphene may be wrapped into 0D fullerenes, rolled into 1D CNTs, and stacked into 3D graphite. It is the essential component of all other graphitic materials[21]. Wallace, McClure, and Semenoff conducted theoretical investigations on graphene in 1947, 1956, and 1984, respectively.[20,22,23]. Eizenberg and Blakely intercalated carbon to Ni surfaces to generate a monolayer of carbon in 1979[24]. In order to obtain FLG, highly oriented pyrolytic graphite (HOPG) was mechanically exfoliated in 1999. FLG was then detected using an atomic force microscope (AFM)[25]. Later, Zang and colleagues created FLG with a size of 10 nm[26]. Affoune et al. produced nano-sized graphene on HOPG in 2001 by thermally treating nanodiamonds at 1600 °C[27]. In a vital experiment conducted at the University of Manchester later that year, Andre Geim and Konstantin Novoselov isolated a single layer of graphene using a technique similar to a scotch tape called micromechanical cleavage[28]. Both of them received the 2010 Nobel Prize in Physics for their roles in the rediscovery of the extraordinary 2D substance graphene.

Single-layered graphene (SLG) is a single, isolated 2D hexagonal sheet of carbon atoms, whereas bi-layered and few-layered graphene (FLG) include two and ten layers of carbon atoms, respectively.

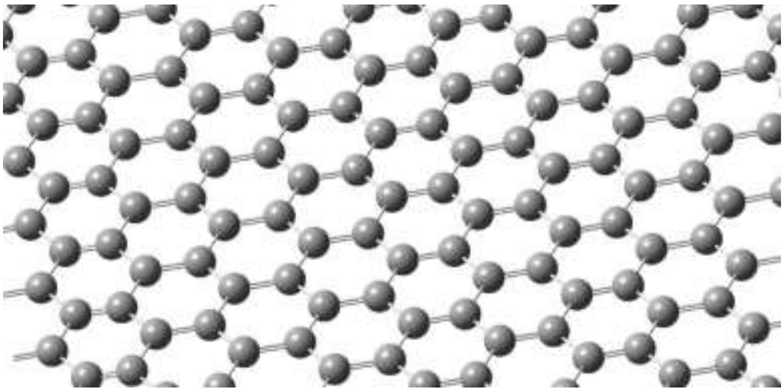

Figure 3. Idealized structure of single graphene sheet.

A. Properties of Graphene

The electronic, thermal, optical, mechanical, and chemical properties of graphene are particularly exciting. Graphene is a leading option for energy storage applications and other technological developments due to its futuristic traits[29]. Since it has received numerous reviews, a thorough analysis is not included here. In a nutshell it can be described as follows.

Graphene is a zero bandgap semiconductor[30]–[32], where the valence band and conduction bands meet at K and K_0 points, the so called Dirac/charge neutrality points[33]. The graphene band structure is depicted in Figure 4. The valence band is filled while the conduction band is empty in un-doped graphene. The production of massless quasi-particles is caused by the transmission of electrons via the conjugative π-network of graphene. At normal temperature, the pure graphene's electron mobility is 15000 cm^2V^{-1}/s^{-1}[28]. Graphene has distinct electron and hole mobility between 10 K and 100 K. At normal temperatures, the mobility is slightly constrained by the graphene's dominant scattering mechanism by acoustic phonons[34–36]. The special electronic structure and thus derived outstanding conductivity make graphene suitable for wide variety of applications including its use as supercapacitor electrode material[37].

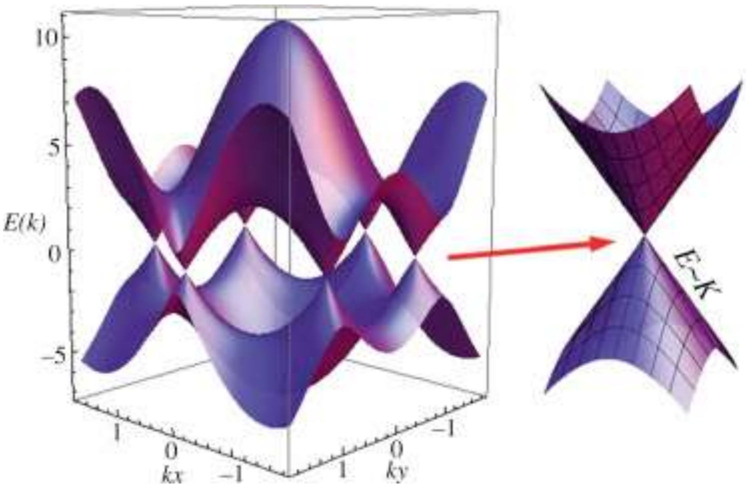

Figure 4. Graphene Band Structure. Reprinted with permission (Biro et al[38]) Copyright (2012) Royal Society of Chemistry.

One of the best materials for heat conductivity is graphene, making it useful for microelectronic applications. In comparison to pyrolytic graphite at room temperature, graphene has a substantially greater theoretical heat conductivity of 5300 $Wm^{-1}K^{-1}$[36]. The thermal conductivity additionally increase with the graphene flake size[39-41]. CVD graphene possess thermal conductivities from 1500 – 2500 $Wm^{-1}K^{-1}$[42], [43]. A layer of isolated graphene transmits 97.7% of the light that strikes it, and only 0.1% of the light is reflected off of the graphene. The optical transparency reduces with the number of layers[32,44,45].

Graphene has an intrinsic tensile strength of 130 GPa and a young's modulus of roughly 1 TPa, which is incredibly lightweight, flexible, and mechanically durable[46,47]. Even after being heated at 200 °C for four hours, graphene is highly resilient to chemical reactions, and it defends against hydrogen peroxide and prevents the oxidation of metal surfaces[48]. Graphene can interact via weak Van der Waal forces of attraction, which can further promote functionalization, in addition to covalent bonding[49]. By adding potassium ions to the surface of graphene, which is produced through epitaxial growth, Ohta et al. were able to demonstrate the n-type doping of graphene[50]. When an electron-accepting molecule is deposited on the surface of graphene, Chen et al. were able to demonstrate the p-type behaviour of the SiC-derived graphene. Graphene is a stand-alone substance as a result of all these peculiar qualities.

B. Preparation of Graphene

For the creation of graphene, various top-down and bottom-up techniques were used. Many reviews go into great length about them[51]–[60]. The various preparation techniques for graphene are shown in Figure 5.

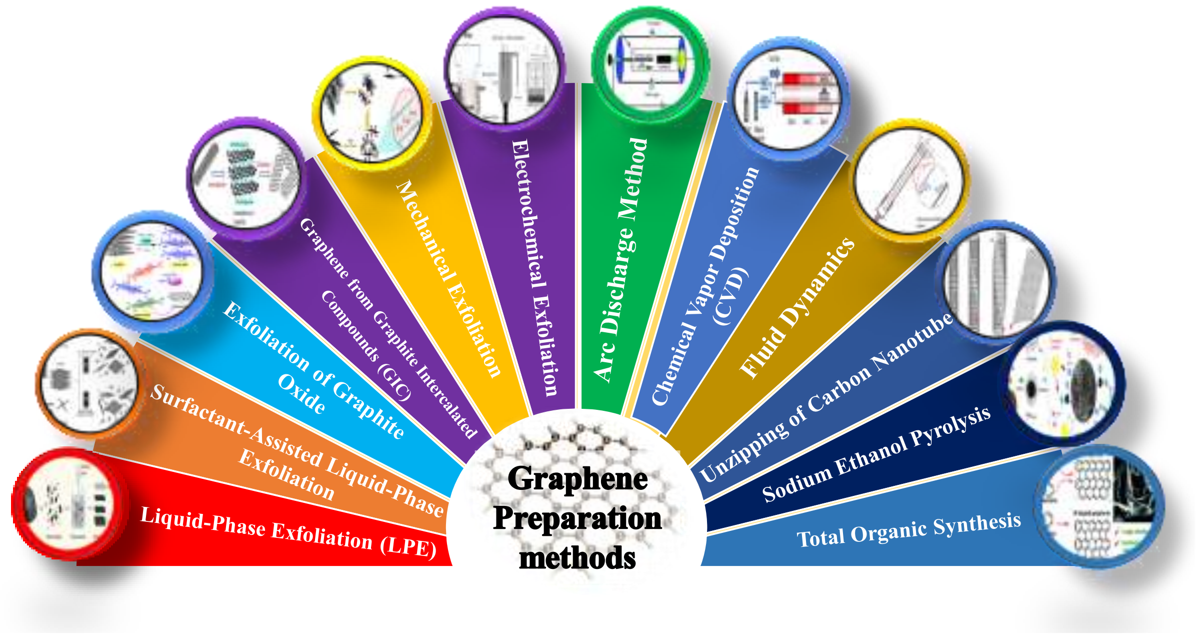

Figure 5. Various graphene preparation methods [51]–[60]

III. Graphene Nanocomposites

Due to its fascinating properties, graphene nanocomposites have a wide range of optical, thermal, electrical, and mechanical properties[21]. Pure graphene's use is constrained in a number of disciplines due to the lack of functional groups in it[61]. By adding functions via composite or hybrid creation, graphene sheets can be transformed into nanomaterials with a variety of uses in sensors, energy storage devices, photocatalysis, heterogeneous catalysis, solar cells, etc[62]–[65]. Hydrothermal/solvothermal processes, electrochemical deposition, physical deposition, photochemical reaction, ultrasonication, mechanical mixing, CVD, electrophoresis deposition, and other processes are used to create graphene nanocomposites. They can also be made through the non-covalent interaction of certain chemical and inorganic molecules with graphene[65]. Polymers, molecules, and nanomaterials are widely used to functionalize graphene[63], [66]. The schematic representation of graphene with the majority of the things listed is shown in Figure 6[65]. The use of polymers improves graphene's ability to disperse and results in outstanding conductivity and transparency[66]. The electrical and optical properties are additionally enhanced by the functionalization with nanoobjects. The development of bio-medical qualities including optical and electrical aspects occurs when graphene is coupled with molecules like DNA, RNA, proteins, etc[65]. The many functional groups in GO enable further functionalization[67].

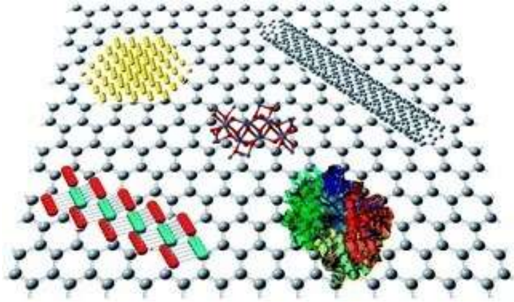

Figure 6. Pictorial depiction of graphene functionalized with many types of nanomaterials.

Consequently, graphene nanocomposites are prospective candidates in a variety of industries. With an improvement in their attributes, composite creation enhances each application's total performance[68]. For better performance, graphene can also be combined with other metal oxides. Additionally, dispersed metal oxides can prevent graphene from stacking its layers. Fe_2O_3 exhibits exceptional behaviour when compared to the other metal oxides that correspond to graphene. The characteristics of Fe_2O_3, as well as Fe_2O_3/graphene nanocomposites, are described in the sections that follow.

IV. Iron (III) Oxide

Among other iron oxides, such as iron (II) oxide (FeO) and iron (II, III) oxide (Fe_3O_4), Fe_2O_3 or iron (III) oxide is the most relevant iron oxide[69]. Natural ferromagnetism exists in Fe_2O_3[70]. The structure is made up of several crystalline phases, including the α, β, γ, and ε phases, the most prevalent of which is the α-phase[71].

A. Properties of Hematite (α-Fe_2O_3)

Hematite is a non-toxic, readily available, stable, environmentally benign, and corrosion-resistant n-type semiconductor (bandgap: 2-1 – 2.3 eV) substance with a variety of uses[69,71,72]. The reddish-brown-colored odorless solid is amphoteric with a rhombohedral crystal system having lattice parameters, a = 5.036 Å, b = 5.036 Å, and c = 13.749 Å [73,74]. The crystal structure of α-Fe_2O_3 is represented in the Figure 7.

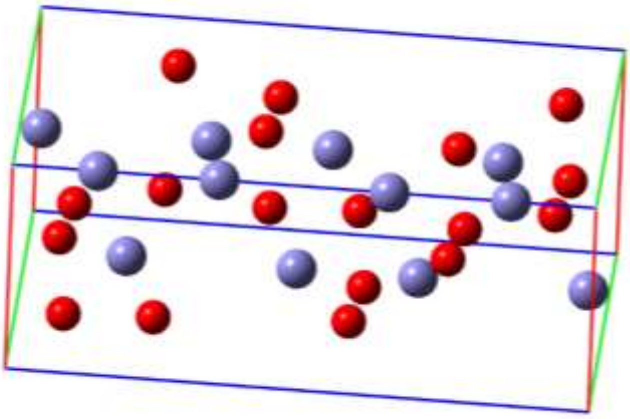

Figure 7. α-Fe_2O_3 cell[74].

Below its spin-flop transition temperature of 250 K, α-Fe_2O_3 exhibits antiferromagnetic behaviour, and it exhibits a weakly ferromagnetic nature both below and above its Neel temperature[75]. It possesses an extremely small 0.002 µB magnetic moment. [69,74].

B. Different Methods of Preparation of Hematite

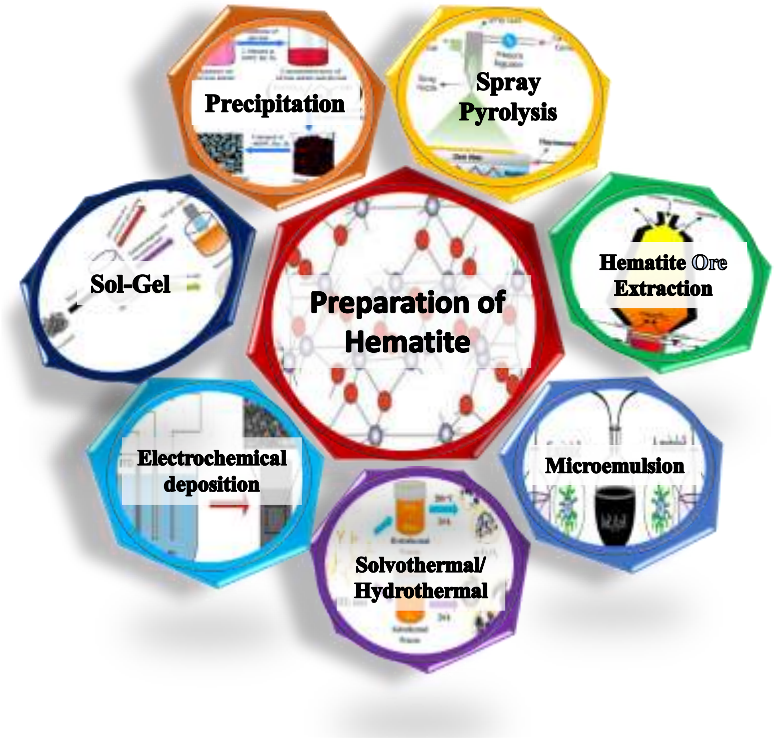

Figure 8. Various hematite preparation processes. [51,76–80].

Hematite is often synthesised using the standard methods for preparing metal oxides, such as electrochemical deposition, the sol-gel process, solvothermal/hydrothermal treatment, etc[51,76–80]. Figure 8 shows various hematite preparation techniques.

V. Fe_2O_3/Graphene Nanocomposites

Due to their complementary features, Fe_2O_3 in combination with graphene exhibit a conductive nature and redox behaviour that makes the highly stable composites suitable for a wide range of applications[81], [82]. Fe_2O_3 nanoparticles are prevented from aggregating by the graphene sheets, and Fe_2O_3 limits the ability of stacking graphene layers[81,82]. Due to their simplicity of synthesis and exceptional activity, Fe_2O_3/graphene nanocomposites are used in the manufacture of supercapacitor anodes, rechargeable batteries, gas sensors, fuel cells, electrochemical sensors, catalysts, and adsorbents, etc[81]. Effective approaches of the composite comprise hydrothermal/solvothermal treatment, the sol-gel method, thermal pyrolysis, electrodeposition, exfoliation of iron intercalated graphite (Fe-GIC), etc[76, 83, 84]. Normally, all synthetic techniques for Fe_2O_3 can also be employed to produce the composite in a way that includes adding the Fe_2O_3 precursor to the graphene dispersion. In the production of composites, some innovative Fe-GIC methods are also used, and here, the Fe precursor also serves as an exfoliant[85,86]. The $FeCl_3$-GIC method of making graphene nanolayers is depicted in Figure 9. The exfoliation of graphene sheets is improved by the intercalation of foreign species. Intercalant iron particles additionally decrease the interaction between the graphite sheets[83]. Anhydrous $FeCl_3$ was used as the precursor in a non-oxidation procedure by Qi et al. to create $FeCl_3$-GIC[87]. The interlayer gap between the graphene sheets gets wider with the intercalation process. Fe_2O_3/graphene was produced by high-pressure homogenization of Fe-GIC using the thermal annealing process, according to Qi and colleagues. They have created sandwich-structured α-Fe_2O_3/graphene[83]. This process typically demands inert, strict conditions for the growth of hematite nanoparticles. We have designed a simple substitute for Fe-GIC-assisted Fe2O3/graphene and thus derived graphene synthesis[88, 89].

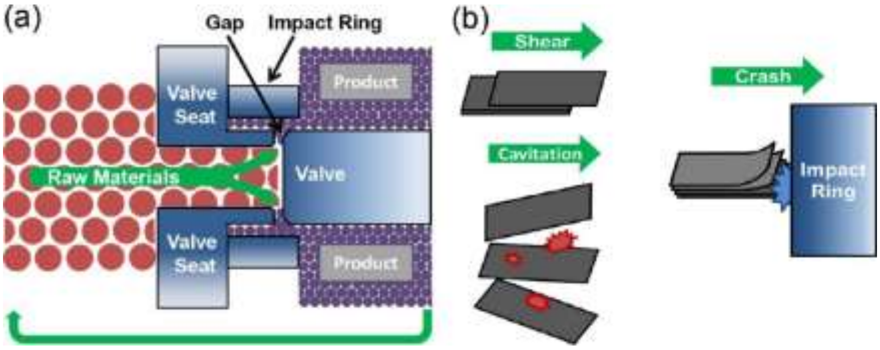

Figure 9. (a) High-pressure homogenization procedure illustrated in a diagram (b) Graphene preparation by $FeCl_3$-GIC exfoliation.Reprinted with permission (Qi et al[83]). Copyright (2017) American Chemical Society.

Song et al. synthesised Fe_2O_3-rGO aerogel using a hydrothermal process for supercapacitor applications[90]. By in-situ precipitation followed by chemical reduction, Xia and colleagues created rGO/Fe_2O_3/SnO_2 for lithium-ion batteries [91]. Thermal casting was used by Feng et al. to develop mesoporous Fe_2O_3/graphene nanosheets, which were used in Li-O_2 batteries. [92]. Likewise, many investigations looked into the use of Fe_2O_3/graphene nanocomposite.

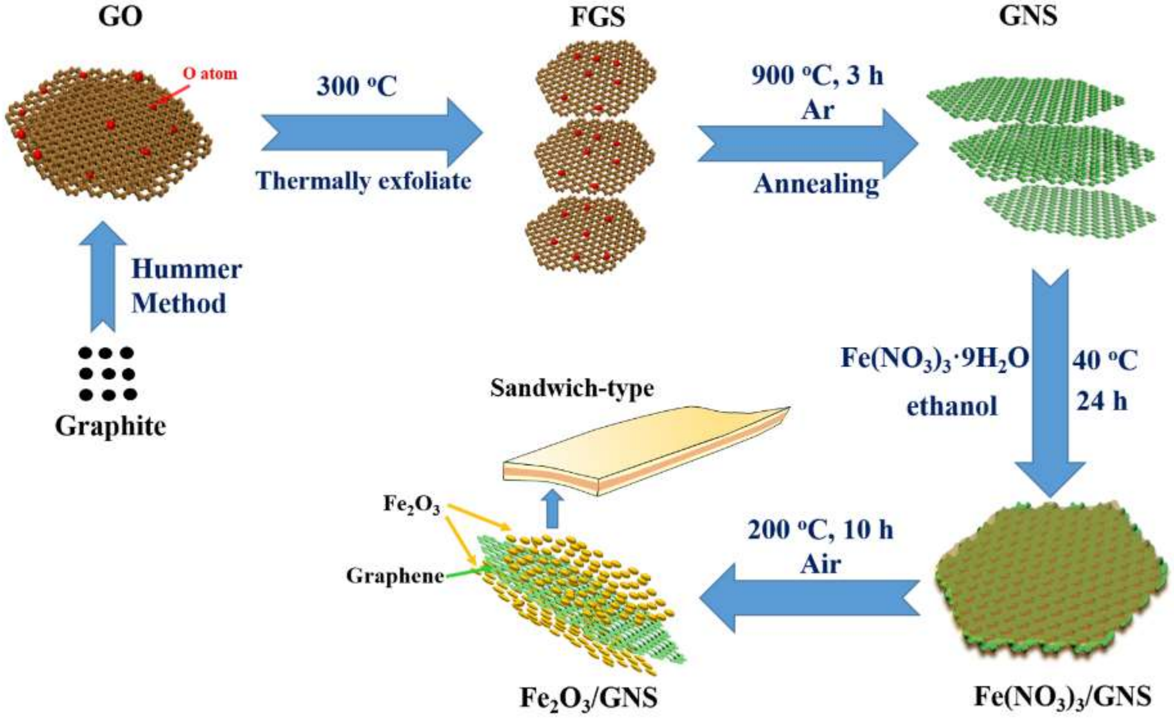

Figure 10. Thermal casting of Fe_2O_3/graphene nanosheets.Reprinted with permission[92]. Copyright (2013) American Chemical Society.

For use in photocatalytic applications to degrade Congo red, Kumar et al. produced a hydrothermal Fe_2O_3-graphene oxide nanocomposite at 102 °C[93]. Jedrzejewska conducted a study in ethanol to compare two pressure methods: microwave solvothermal reactor preparation and autoclaved solvothermal synthesis[94]. The developed Fe_2O_3/graphene composites' characteristics were examined, and it was found that they were similar. Thin films of Fe_2O_3/GO and powder Fe_2O_3/GO, which were produced using the electrodeposition method, were used to perform rhodamine B degradation. For the generation of powder catalyst, the impregnation method using drying of GO-$FeCl_3$ dispersion was used[95]. Wang et al. established a photo Fenton catalyst that is highly effective at degrading dye pollutants using a self-assembly approach for γ-Fe_2O_3 produced on Fe plates along with GO[96]. High-performing rGO/Fe_2O_3 composite was employed by Zhu et al. as an anode for lithium-ion batteries[97]. Urea and hydrazine were utilised as precipitating and reducing agents, respectively, while microwave irradiation was used to produce the composite. Excellent supercapacitor performance was achieved using the solvothermal approach to generate the Fe_2O_3/graphene gel, where the electrode was made over nickel foam[98]. Mokhtarifar et al. employed rGO and γ-Fe_2O_3 nanoparticles together to enhance the self-cleaning capabilities of TiO2[99]. From the studies, they found suitable amounts of rGO and γ -Fe_2O_3 nanoparticles in the TiO_2 composite for maximum performance.

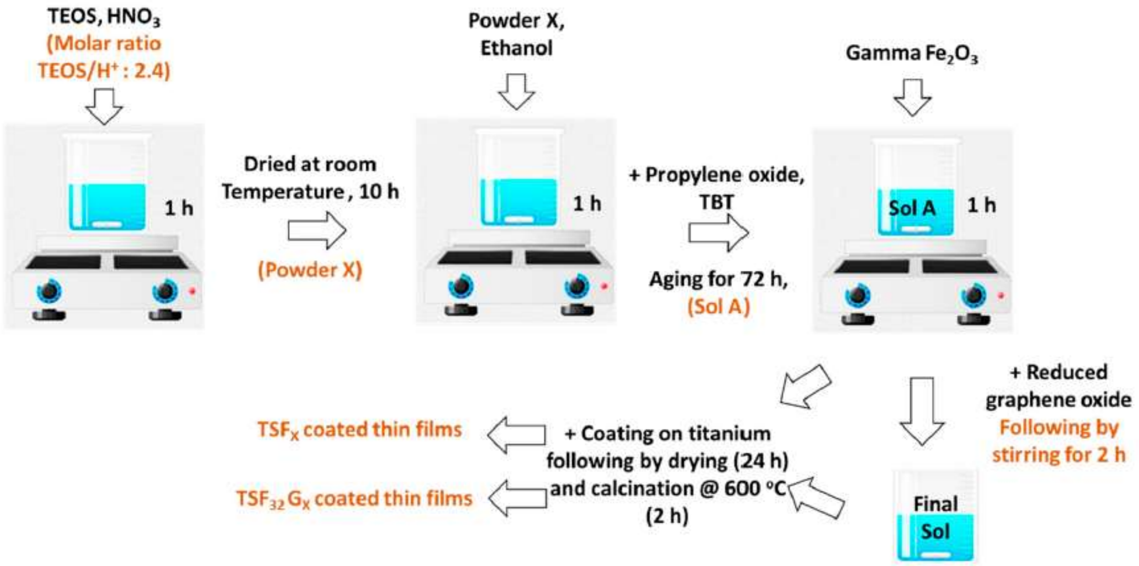

Figure 11. Preparation of a γ -Fe_2O_3 - rGO - TiO_2 composite film through the sol gel technique (Mokhtarifar et al[99]).

Utilising sodium alginate and chitosan or carrageenan as graphene precursors (by pyrolysis in an environment of argon), α-Fe_2O_3/graphene composites were made hydrothermally, and the systems worked well as photocatalysts for the breakdown of RhB.[100]. The researchers prepared the graphene using a more environmentally friendly technique than GO-based methods, and they came to the conclusion that alternative metal oxide/graphene-based systems may be developed in a more environmentally friendly manner. Figure 12 displays a few relevant uses for Fe_2O_3/graphene[81].

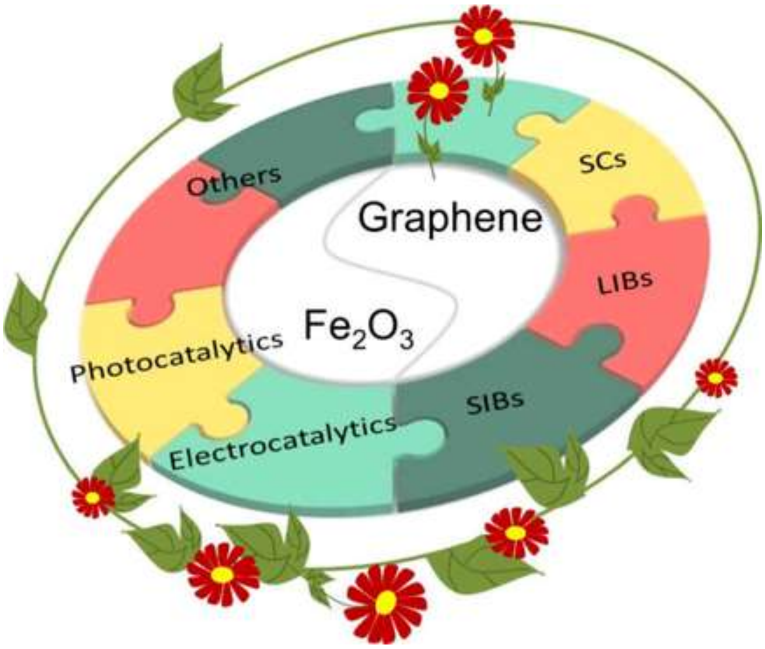

Figure 12. Various applications of Fe_2O_3/graphene where electron mobility is important. Reprinted with permission (Lu et al[81]). Copyright (2019) John Wiley & Sons, Inc.

VI. Graphene as a Supercapacitor Electrode

Graphene, the most well-known EDLC nanomaterial, has a theoretical capacitance of 550 F/g[19]. Graphene stands apart from conventional electrode materials due to its special characteristics, including high surface area, conductivity, electrical mobility, mechanical strength, and chemical stability. However, due to decreased conductivity, layer agglomeration, and re-stacking, practically bare graphene exhibits a lower capacitance than the theoretical value[19]. In an ionic liquid electrolyte, graphene was shown to have a specific capacitance value of 75 F/g, according to Vivekchand et al[101]. Chemically altered graphene was developed by Stoller and his team, and it displayed a capacitance value of 135 F/g in KOH and 99 F/g in $TEABF_4$/AN[102]. Re-stacking lowers the energy density and Coulombic efficiency, whereas metal oxides prevent these issues[3,93]. The electrochemical performance of graphene was much improved by the synergistic features obtained by combining with various metal oxides and other nanomaterials[103]. The well-distributed metal oxides additionally utilise graphene as a conducting network[104]. For supercapacitor investigations, Liu et al. developed cauliflower-like Co_3O_4/3D graphene that attained a specific capacitance value of 675 F/g[105]. Similar to these, a number of researchers reported several methods displaying the use of graphene in supercapacitors.

VII. Fe_2O_3/Graphene Supercapacitor Electrode Materials

The most crucial component of a high-performance supercapacitor is the electrode material. A hybrid supercapacitor that couples an EDLC and a pseudocapacitor could be a candidate for high performance[106]. The advantages of both work together to make energy storage highly effective. The supercapacitor's electrochemical stability and performance can be improved by graphene's EDLC behaviour and Fe_2O_3's pseudocapacitance, which can increase its specific power, specific energy, shelf life, conductivity, cyclic stability, etc[107]. Fe_2O_3 has a relatively high theoretical capacitance of 3625 F/g, however because of its weaker electrical conductivity, it performs electrochemically less well[107]–[110]. To solve the issue, an effective dispersion of Fe_2O_3 on a conductive matrix is required. Thus, the electrochemical characteristics can be strengthened by the conductive graphene network. Fe_2O_3 nanoparticles are also used in graphene sheets, which prohibits the re-stacking of graphene layers[111]. Additionally, the combination may allow for quick electrolyte ion transport towards the electrode, which allows high rate capability and cyclic stability overall[112]. Fe_2O_3/graphene can therefore function as a worthy competitor, displaying extremely high specific capacitance and noteworthy electrochemical performance. Colloidal electrostatic self-assembly followed by hydrothermal reduction enabled the synthesis of a Fe_2O_3/reduced graphene oxide composite with high specific capacitances of 908 Fg-1 and good cyclic stability retention of 69% and 714 Fg^{-1} @ 2 Ag^{-1} having 42.6% capacitance even at 30 A/g[113], [114]. With a very high cyclic stability, a microwave treatment produced a specific capacitance of 577.5 Fg-1 at 2 A/g[115].

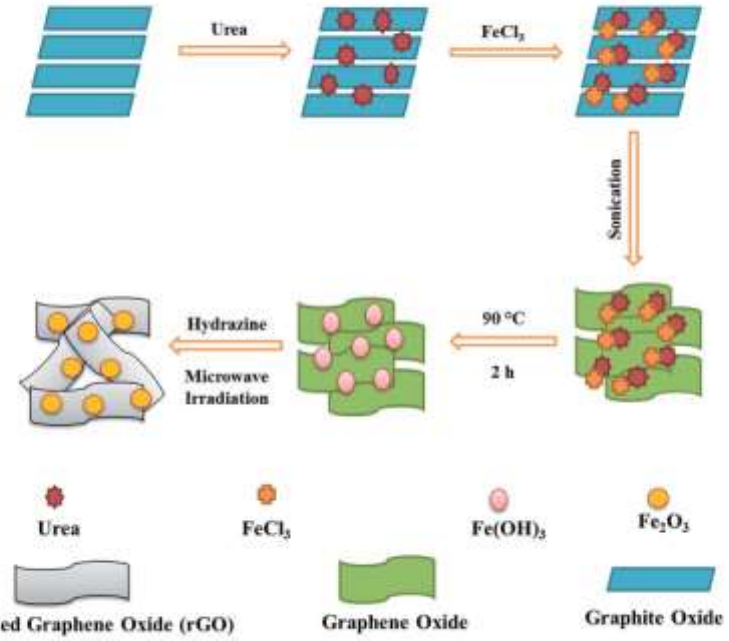

Figure 13. Microwave method for synthesising Fe_2O_3/reduced graphene oxide composite. Reproduced. from ref[115]. with permission from the Royal Society of Chemistry

Fe_2O_3 nanoplates were integrated into 3-dimensional porous GO, which displayed an areal capacitance value of 572 mF cm^{-2} at 1 mA cm^{-2}.[115] . Supercapacitors with Fe_2O_3 nanosheet films, nanotube arrays, etc. as electrode materials, with the addition of graphene resulted in an enhancement in their capacitive behaviour[115]–[118].

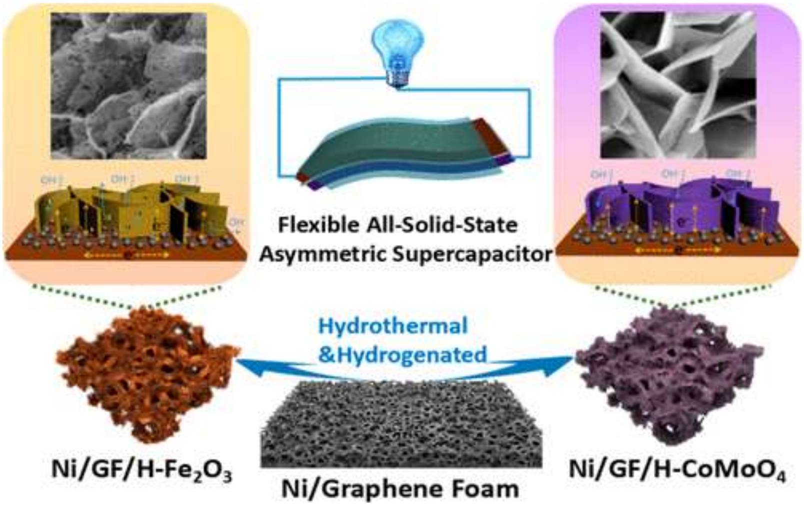

Figure 14. The asymmetric supercapacitor combination of Ni-graphene-Fe_2O_3 and Ni-graphene-$CoMoO_4$ is depicted schematically. Reprinted with permission (Chi et al[116]). Copyright (2017) American Chemical Society

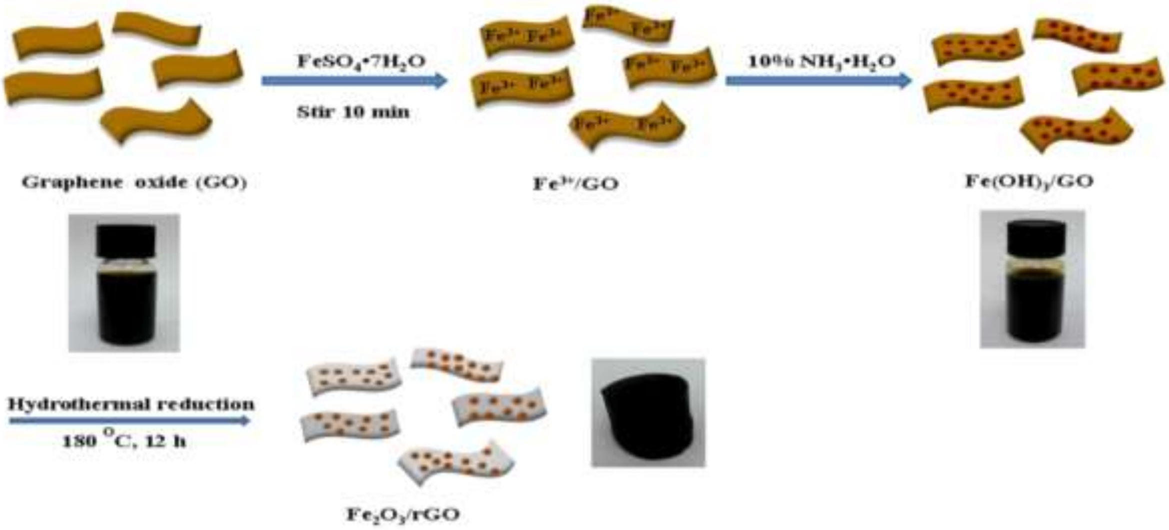

Figure 15. Fe_2O_3/rGO production through solvothermal method with improved specific capacitance is depicted schematically. Reprinted with permission (Ma et al[119]). Copyright (2014) American Chemical Society.

Phytic acid was utilised as the reductant in Gupta et al.'s environmentally friendly approach of GO reduction. They developed a composite using Fe_2O_3, GO, and polyaniline, and the development of a two-electrode device proved the composite's potential performance as a supercapacitor electrode[120].

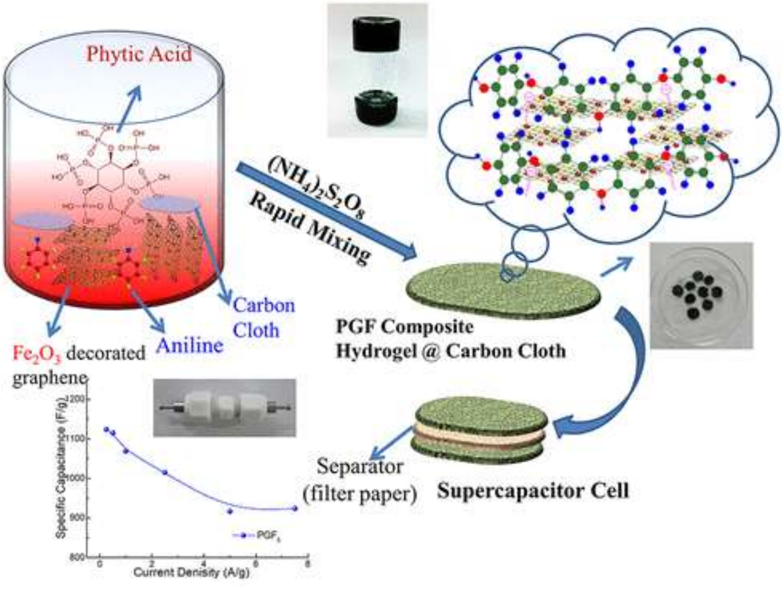

Figure 15. Fe_2O_3/graphene/polyaniline composite and two-electrode manufacturing aided by phytic acid. Reprinted with permission (Gupta et al[120]). Copyright (2020) American Chemical Society.

It is evident from the aforementioned literature search that the majority of investigations used the hydrothermal technique of preparation for the Fe_2O_3/graphene composite synthesis, with GO serving as the graphene source. Asymmetric supercapacitor construction was described by Tian et al. in order to examine the supercapacitor behaviour of individual electrodes in combination and to increase the potential window utilising an aqueous electrolyte[121].

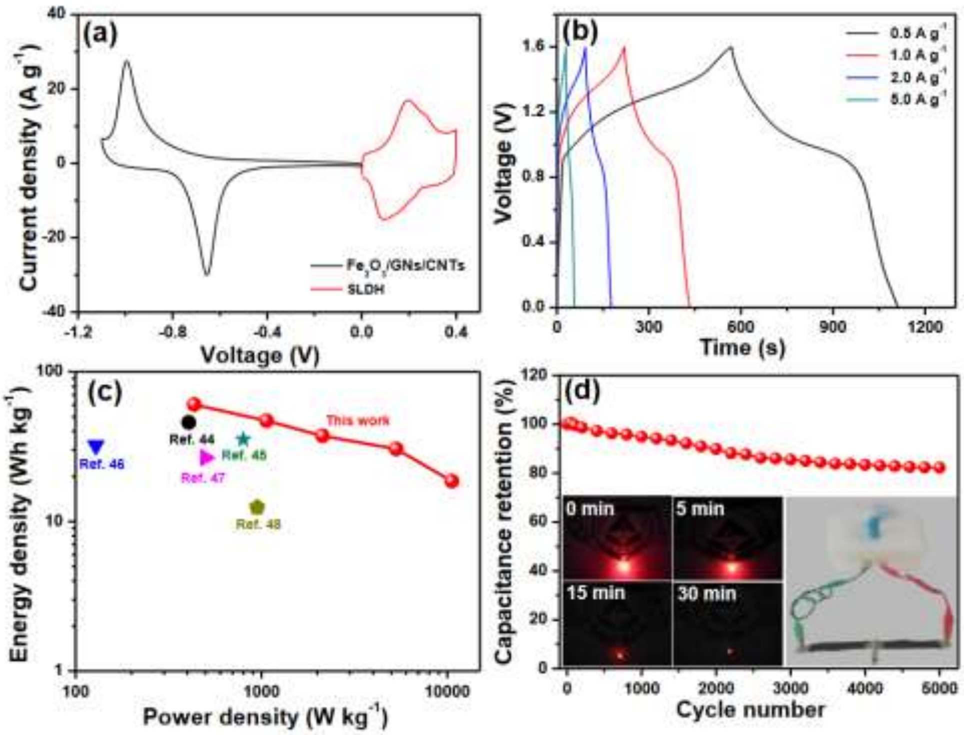

Figure. 16. Asymmetric supercapacitor combination of Fe_2O_3/graphene/carbon nanotube composite showing promising capacitance behaviour. Reprinted with permission (Tian et al[121]). Copyright (2019) American Chemical Society.

Table 1 gives the specific capacitance values at different current densities/scan rates of various Fe_2O_3/graphene-based nanocomposites in supercapacitor applications.

Table 1. Literature data on the electrochemical performance of Fe_2O_3/graphene-based systems

Electrode material	Specific capacitance (F/g)	current density	Electrolyte	References
Fe_2O_3@C-rGO	211.4 F/g	0.5 A/g	1 M Na_2SO_4	[122]
Fe_2O_3 nanotube/rGO	215 F/g	2.5mV/s	1 M Na_2SO_4	[123]
N-doped graphene/ Fe_2O_3	698 F/g	1 A/g	1 M KOH	[124]
Fe_2O_3/N-rGO	618 F/g	0.5 A/g	1 M KOH	[119]
N-rGO/ Fe_2O_3	268.4 F/g	2 A/g	1 M KOH	[125]
Fe_2O_3–graphene	226 F/g	1 A/g	1 M Na_2SO_4	[126]
Fe_2O_3/GNs/CNTs	675.7 F/g	1 A/g	6 M KOH	[127]
α-Fe_2O_3/graphene	306.9 F/g	3 A/g	1 M Na_2SO_4	[128]
Fe_2O_3/graphene	504 F/g	2 mA/cm^2	1 M Na_2SO_4	[129]
Fe_2O_3/graphene	151.8 F/g	1 A/g	2 M KOH	[130]
Fe_2O_3/graphene	224 F/g	25 mV/s	1 M Na_2SO_3	[131]
Fe_2O_3 nanodots@NG	274 F/g	1 A/g	2 M KOH	[132]
α-Fe_2O_3/rGO	903 F/g	1 A/g	1 M KOH	[133]
Polyaniline/Graphene/Fe_2O_3	1124 F/g	0.25 A/g	1 M H_2SO_4	[120]
α-Fe_2O_3/rGO	255 F/g	0.5 A/g	1 M Na_2SO_4	[134]
N-graphene/Fe_2O_3	260.1 F/g	2 A/g	1 M Na_2SO_4	[135]
rGO/Fe_2O_3	577.5 F/g	2 A/g	1 M Na_2SO_4	[115]
GNS/Fe_2O_3	320 mF/cm^2	10 mA/cm^2	6 M KOH	[136]
α-Fe_2O_3/graphene	343.7 F/g	3 A/g	1 M Na_2SO_4	[137]

Flower-like Fe_2O_3@multilple graphene aerogel	1119 F/g	1 A/g	3 M KOH	[138]
Fe_2O_3 nanodots/graphene	347.4 F/g	1A/g	2 M KOH	[139]
α-Fe_2O_3/graphene	551.5 F/g	1 A/g	6 M KOH	[140]
α-Fe_2O_3/rGO	894 F g^{-1}	0.5 A g^{-1}	1 M H_2SO_4	[141]
Fe_2O_3–graphene	226 F/g	1 A/g.	1 M Na_2SO_4	[142]
α-Fe_2O_3/RGO/Fe_3O_4	337.5 mF/cm^2	20 mA/cm^2	2 M KOH	[121]
Fe_2O_3/GNs/CNTs	675.7 F g−1	1 A g−1	6 M KOH	[143]
3D-Fe_2O_3/graphene	264 F/g	2.5 A/g	2 M KOH	[144]
RGO/Fe_2O_3	50 F/g	0.1 V/s	0.5 M H_2SO_4	[145]
Fe_2O_3/rGO	1083 F/g	2 F/g	1 M KOH	[146]
Fe_2O_3 graphene oxide/polypyrrole	442 F/g	1 A/g	1 M KCl	[147]
Iron oxide/RGO	406.5 mF/cm^2	10 mV/s	5 M LiCl	[148]
α-Fe_2O_3/graphene	815 mF/cm^2	0.5 mA/cm^2	2 M KOH	[88]

It is clear from the data in Table 1 that the researchers used diverse types of graphene, including GO, rGO, graphene aerogel, and less-defective graphene. The most extensively studied electrolytes for Fe_2O_3/graphene supercapacitors are KOH and Na_2SO_4. Due to the fact that graphene amounts frequently differ from the initial amounts of graphite used in preparation, only a small number of publications discuss the ratio of Fe_2O_3 to graphene[86], [106], [149]. They have been mainly used as anode materials in asymmetric supercapacitors.

VIII. Preparation Methods of Graphene in a Green Chemistry and Economical Perspective

As can be seen from the data in Table 1, the majority of the reported graphene/Fe_2O_3 systems function well as supercapacitor electrode materials. Graphene can be prepared using a variety of techniques, however most of the experiments included in the table used graphene that was obtained from GO. This is a result of the low cost, high yield, scalability, and regular practice of using established, well used technologies or processes for composite preparation. GO/rGO contains characteristics that make it easier to bind with metal oxides than pure graphene does. GO is also hydrophilic. These characteristics allow stable graphene-metal oxide composite materials to be developed. As a result, GO is used to manufacture 99.9% of metal oxide/graphene composites.

Modern chemists adhere to green chemistry principles while developing materials since they are more concerned with sustainable development. When graphite oxide (GrO) is made from graphite, dangerous oxidising combinations like concentrated H_2SO_4, $KMnO_4$, HNO_3, etc. are used, creating extreme oxidising conditions that result in the massive generation of toxic gases. For best outcomes, the GO preparation should be closely checked at all times and the temperature should be managed. Due to the integration of oxygen functions, the resulting GrO became aqueously processable, and during sonication, became exfoliated to GO. Hydrazine hydrate is a frequently utilised reductant for GO, which is also toxic. As a result, the entire process is risky, and alternatives are always favoured from an environmental standpoint. Even if many GO reductants today are safe for the environment and even derived from plants, the manufacture of GrO is still dangerous. Although rGO's functionalities and defects make it useful in a variety of applications, including membranes and catalysis, they can be problematic for those in which the aromatic conjugative π-network of graphene plays a significant role.

For purposes like supercapacitor electrodes, graphene should therefore be prepared under milder conditions. Some of those technologies, like CVD and epitaxial growth, are challenging to implement because of their low yield and high cost. However, there are effective eco-friendly, low-cost methods of exfoliating graphite that have a high yield of graphene, including surfactant-assisted liquid phase exfoliation, electrochemical techniques, ball-mill assisted techniques, and interlayer catalytic exfoliation of Fe-GIC, among others[52,54,58]. Although the aromatic π-conjugative network is intact in those, assuring good conductance, the lack of active sites for interaction between the components prevents these graphenes from forming composites without defects or functions. Here, there will be the least amount of interaction with alien organisms, including electrolyte ions. Thus, it is recommended to functionalize these graphene sheets without affecting the aromatic conjugative -network when using them as electrodes. The introduction of edge functionalities to graphene by ball-mill aided graphite exfoliation enables the covalent binding of metal oxides at the edges to generate useful hybrid materials.

The other approaches' extension of producing composites to achieve synergistic qualities is constrained since, in the absence of functional groups, covalent functionalization with graphene is not possible. However, Fe can combine strongly with aromatic moieties to yield stable compounds like ferrocene. Since less defective/defect-free graphene sheets can form stable complexes with α-Fe_2O_3, the combination can function as superior supercapacitor electrodes while keeping the conductivity of graphene. Additionally, the hydrophilic Fe_2O_3 can conduct redox reactions and interact strongly with electrolyte ions, which facilitates pseudocapacitance. Thus, these composites can exhibit exceptional specific capacitance and metallic conductance[88]. Recent studies using XPS analysis show the Fe-C interaction in α-Fe_2O_3/graphene[88]. Raman spectrum analysis provides clear evidence of those graphene samples' less defective character.[86], [150]–[152].

IX. Future Directions in the Fabrication and Use of α-Fe_2O_3/Graphene Nanocomposites

The search for more economical and environmentally friendly ways to prepare graphene for composite production is now more important than ever for the successful fabrication of graphene-based supercapacitor electrodes. Electron mobility and conductivity play a significant part in the uses of these materials, which can also be employed for other graphene applications. The introduction of Fe_2O_3, which is amphoteric and has redox characteristics for greater performance in addition to its affinity with aromatic species, can overcome the low affinity of less-defective graphene towards foreign species. Less defective graphene and Fe_2O_3 can be combined for developing a hybrid material that exhibits EDLC and pseudocapacitance.

High specific capacitance, power density, and energy density—three characteristics that are essential for supercapacitor materials—can result from this combination. The lightweight and flexibility of graphene-based composites, which can be investigated in the development of portable electronics and flexible devices, are an additional benefit of using them in supercapacitor formulations[88], [153], [154]. These devices can also be employed in health monitoring and other applications because even performance is unaffected by bending and twisting in graphene. Since Fe_2O_3/graphene supercapacitor electrodes combine high performance (in terms of specific capacitance, power density, energy density, rate capability, conductivity, etc.), low-cost methodology, and environmentally friendly preparation of a highly stable nanohybrid electrode material, upgrading them to devices and immediately exploring them in practical applications could change the face of graphene supercapacitor technology. Figure 17 depicts a pictorial summary of various preparation methods for graphene, as well as the performance characteristics of an electrode made of Fe_2O_3/graphene that is suitable for supercapacitor applications and the difficulties that Fe_2O_3/graphene resolves.

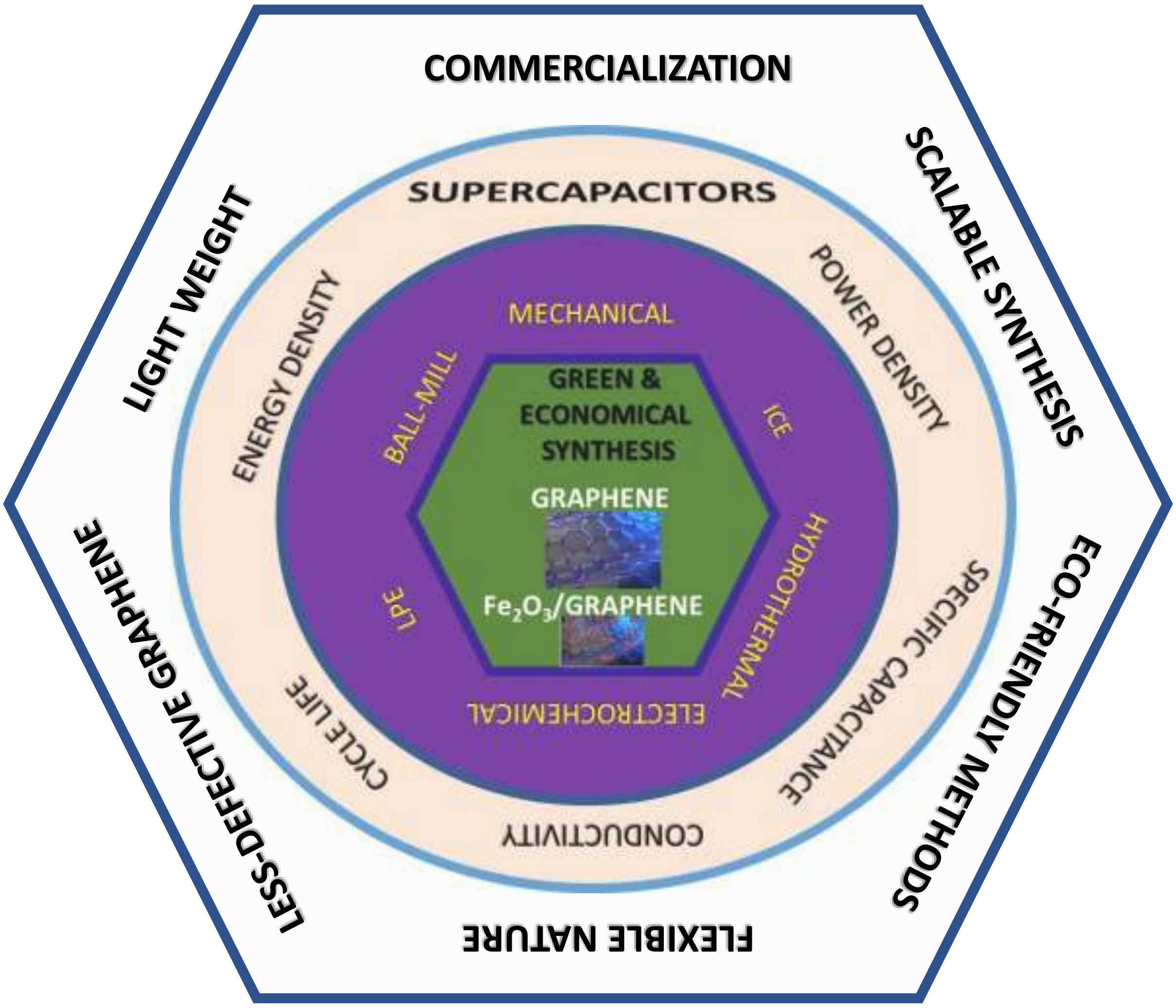

Figure 17. A diagram summarising the Fe_2O_3/graphene synthesis processes, supercapacitor performance metrics, and commercialization aspects.

X. Conclusions

This review focused on supercapacitors, which are promising energy storage devices with an electrode composition mostly composed of Fe_2O_3/graphene. Also briefly discussed the significance of graphene-based composite materials. Also emphasised Fe_2O_3, its value as a material for pseudocapacitors, and its role in the synthesis of composites with graphene. The review provides a clear explanation of the necessity for an economical, low-cost, and high-yielding method of producing graphene. At the conclusion of the review, the perspectives on the graphene preparation processes and the significance of Fe_2O_3 in the formation of hybrid nanomaterial are well-explained.

XI. Declarations

a) Availability of data and materials

All details associated with the review manuscript will be made available to the readers and reviewers upon demand.

b) Conflict of Interests

No conflict of interests is available associated with the present work

c) Acknowledgements

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