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Synthesis Technique of Graphene Composite for Energy Storage Devices

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Abstract

With the rising needs of the energy resources, a lot of work has gone into the growth of the energy storage devices and its technologies. Graphene is known to be the carbon nanomaterial having two dimensional structure (2D), high specific surface area, good mechanical strength, good optical transmittance, larger electronic mobility, ultrahigh electrical conductivity, and exceptional electronic and thermal conductivity. As a result, it is very appealing material for basic energy storage unit for electrochemical devices like supercapacitor, solid-state batteries and flexible electronic devices. Addition of graphene can improve the efficiency, capacity, durability and cyclicity of energy devices. In terms of applications, the benefits of graphene have expanded its use in electroanalytical and electrochemical sensors. However, there is huge literature based on the graphene synthesis by using various techniques and for their application in basic storage unit (cell) are in progress to innovate the graphene structure and its morphologies. In this article, the recent growth in graphene and its materials for the storage devices and conversion applications is reviewed. Also, it predicts the future development in scalable manufacturing as well as other additional energy storage related applications.

Keywords: *Graphene; Lithium; Electrochemical; Storage; Supercapacitor; Electroanalytical*

1.0 Introduction

Global population growth has resulted in increased energy demand from global power consumption anticipated to rise in the coming years. As a result, scientists and researchers must create cost-effective and ecologically friendly sustainable, clean, and renewable energy solutions to meet our society's expanding energy demands and difficulties[1-6]. Supercapacitor and lithium-ion batteries (Li-ion) offering high power density, high specific energy, high cyclicity, and flexibility[7,8]. With this hydrogen (H_2) also becoming the energy system which is in use in sustainable energy without creating hazardous byproducts. Power density of lithium ion cell depends on the internal resistance and mobility of the charge. Graphene is having large surface area and low electronic resistivity which make it suitable for fast charging devices of the material.

Graphene is known to be an allotrope of carbon which is densely packed in a honeycomb lattice structure contains single layer C-C bond length of 0.142nm having sp^2 hybridized carbon atom which attains research motives for its versatile properties[9]. In 2004, the discovery of graphene has reached its enormous properties. It shows the various properties like large specific surface area, high intrinsic mobility, Young's modulus, thermal conductivity, optical transmittance and good electrical conductivity with current density of $1\text{-}2*10^8$ A/cm^2 [10-16].

Different researchers have given different synthesis techniques for graphene like mechanical exfoliation of graphite, arc-discharge method, Hummer's method and modified Hummer's method, chemical-vapor deposition

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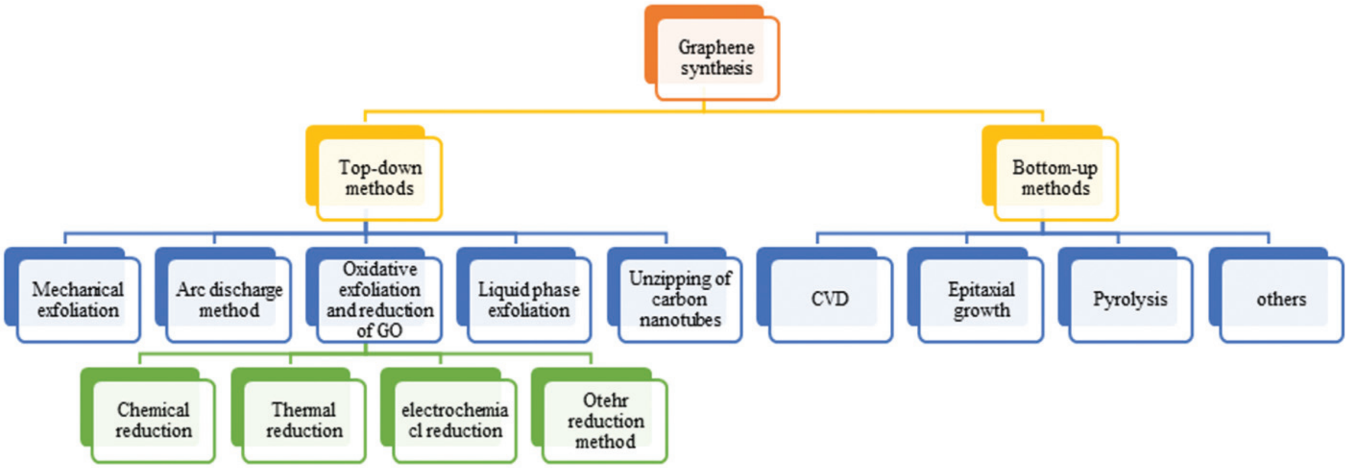

Figure 1: Representation of synthesis techniques of graphene[18]

Table 1: Overview of graphene properties

Properties	Graphene	References
Specific surface area	2600–2620 m2 g–1	[11]
Typical electron mobility	200,000 cm2 V–1 s	[12]
Thermal Conductivity	~5000$Wm^{-1}K^{-1}$	[13]
Thermal Resistance	~4*$10^{-8}Km^2W^{-1}$	[14]
Young modulus	1Tpa	[15], [16]

method (CVD)[17]. Flow chart of graphene synthesis techniques given in Fig.1.

The first attempt of graphene synthesis has been done in the year 1975, the monolayer of graphene synthesis was first discovered. Further, Lang and his team fabricated the graphene with single and double layers by using chemical thermal decomposition method on single platinum (Pt) substrates[19]. But, the inconsistency between the graphene sheets on Pt surface, leads to the failure of its applications. Nevertheless, various efforts of graphene have been taken place in 1999[20,21]. In 2004, Novoselov et al[22] discovered the synthesis of graphene by using exfoliation process in their first revelation. This method developed the new techniques and fundamentals for the large scale production of graphene. Summary of synthesis of graphene i.e. top-down method and bottom-up method given in Table 2.

Furthermore, graphene and its composite have been studied in wide research area of industrial application which includes the transistors, sensors, solar cells, and electrochemical devices like supercapacitor, solid-state batteries and flexible electronic devices. In the designing of nanocomposite, graphene found more appreciable. While using transition metal oxides (TMO) to construct the graphene, its specific capacity increases which leads in good electrical conductivity, thermal conductivity and great cyclic stability in lithium ion battery. For high-end electronic applications, i.e. lithium ion battery, the concept of synthesizing graphene utilizing nanocomposites gives long-term cost-effectiveness and breakthroughs in the charging and discharging process[17]. Several articles have been published in the development of graphene and C-based materials[25-31]. This research focuses on graphene its derivatives for EES devices such supercapacitor, lithium air batteries, lithium sulfur batteries (Li-S), and Li-ion batteries (LIB). This review is arranged as follows: First, we'll go through some current research findings on the utilization of graphene and its derivatives in supercapacitor and Li-ion cell in the literature. After that, we'll go through some of the current efforts to commercialize graphene-based composites in storage devices (ESS). Lastly, we go through the issues and concerns that this discipline is dealing with, as well as a summary, findings, and recommendations and possibilities for future study.

2.0 Graphene Metal Composites for Li-ion cell

The most popular energy storage device is LIB. It contains tremendous different physical and chemical properties which includes high density, voltage stability, longevity, environmental security and low self-discharge rate. The positive electrode (cathode), negative electrode(anode), electrolyte, and separator are the four major components[32-34]. Because of its exceptional qualities, graphene and graphene-based composites have gained favour in the usage of rechargeable Li-ion batteries. In this regard, graphene has a high potential to store lithium, demonstrating that lithium may be bonded on the both sides of graphene edges, graphene

Table 2: Summary of graphene synthesis routes [23,24]

Synthesis method	Layers	Dimensions	Advantages	Disadvantages
Top-Down Method				
Mechanical exfoliation	Many layers	µm to cm	Large size	Low yield
Sonication of graphene	Mono and Multiple	µm	Low-cost	Low yield
Electrochemical exfoliation/ functionalization of graphene	Mono and Multiple layer	500-700 nm	high electrical conductivity, One step functionalization and exfoliation	Require ionic solids
Graphene acid dissolution	Mono layer	300-900 nm	Unusual graphene	Use of dangerous acid
Bottom-Up Method				
CVD method	Multiple layer	100nm	Large size	Difficult to scale up
Arc discharge	Mono and multiple layer	100 nm to µm	Graphene production rate of 10 g/h	Carbonaceous impurities
Unzipping of CNTs	Multiple layer	few µm long nanoribbons	Nanotubes are chosen to manage the size	Expansive raw material
Epitaxial growth on SiC	Multiple layer	Upto cm size	High surface area	Time consuming
Reduction of GO	Multiple layer	Sub-µm	Unoxidized graphene layers	Contaminated by aluminium sulphide or aluminium oxide

sheets, and other sorts of defect sites. When used as a conductive matrix, graphene may significantly increase electron conduction in Li-ion batteries when in contact with electrochemically active materials and efficiently check material collection during the lithiation and delithiation method[35,36]. As a result, graphene-based nanostructured materials provide an interesting explanation to present gravimetric energy density restrictions and problems[37]. The author would like to address some experimental findings by using graphene and its nanocomposites as an anodes and cathodes materials.

2.1 Anodes

In lithium ion battery, the graphite anode having a specific capacity of 372 mAh/g[1]. In 2008, Yoo[38] and his colleagues produced graphene nanosheets (GNS) to improve lithium storage capacity, achieving a specific capacity of 540 mAh/g by controlling the layered structure of GNS. Carbon nanotube (CNT) and C_{60} were added to the graphene nanosheets to increase the capacity to 730 mAh/g respectively. The improved performance is attributed to an improvement in the electrical of the new anode material, which can accommodate more lithium[38-42]. Cheng et al. reported high energy density of Nitrogen doped graphene and Boron doped graphene electrode at low charge/discharge rate, the doped graphene electrodes exhibits high capacity of 1043 mAh/g for N-doped graphene and 1540 mAh/g for B-doped graphene[65]. Doped graphene has the capacity to quick charge and discharge for a short time (approximately 1h to seconds), allowing it to achieve both rate capability and long-term cycles. In Table 3 anode made of graphene or graphene as anode composite is summarized[43].

2.2 Cathodes

In recent years, many researchers have given attention to improve the energy density and power density of Li-ion battery. Hence, graphene and its derivatives have been presented for use in the cathode material to address deficiencies in typical cathode materials such as low electrical

Table 3: Electrochemical performance of anode made of graphene or graphene composite for li-ion battery

Materials	Specific capacitance ($mAhg^{-1}$)	Current density (Ag^{-1})
Graphene nanosheet (GNS) [38]	540	0.05
GNS/Carbon nanotube (CNT) [38]	730	0.05
GNS/C_{60} [38]	784	0.05
Graphene/SnO_2 [44]	1996	1
Co_3O_4/rGO [45]	860	40
Mn_3O_4/reduced graphene oxide (rGO) [46]	390	1.6
rGO/Fe_3O_4 [47]	1000	0.074

Table 4: Electrochemical performance of cathode made of graphene or graphene composite for li-ion batteries

Materials	Specific capacitance ($mAhg^{-1}$)	Current densities (Ag^{1})
LiMn 1-xFe xPO4/rGo [52]	65 155	17000 85
3D porous LiFePO4 [53]	146	17
V2O5/graphene [54]	94.4	10000
LiFePO4/ graphene flakes [55]	208	17

conductivity, low specific capacity, and so on[43]. Like, olivine-structured of $LiMPO_4$ where M is used for iron, manganese, cobalt (Co), or nickel (Ni) have been designed in such a way that it is used as the promising cathode material for rechargeable Li-ion batteries showing high capacity, cyclicity, etc[48-51]. Some other graphene cathode material like rGO/$LiFePO_4$ shows the specific capacity of 146mAh/g and current density of 17 mA/g. Likewise, $LiMn_{0.75}Fe_{0.25}$ Po_4/rGo (reduced graphene oxide) having the excellent Li-ion storage[52]. In Table 4 cathode made of graphene or graphene aa cathode composite is summarized.

3.0 Graphene based Material for Supercapacitor

Supercapacitor are known to be the electrochemical capacitors (ECs) or ultracapacitor which provide the facility of power transfer at higher current rates. Supercapacitor can be classified as hybrid/asymmetric capacitors, electrical double-layer capacitors (EDLC), and pseudo-capacitors[37]. As a result, ECs having energy density of 5-10 Wh/kg in comparison with batteries, which vary from 120-170 Wh/kg for lithium ion cell[56]. Hence, table 5 summarizes the current achievements and challenges in attaining high power and high energy density in supercapacitor depends on graphene and graphene-based composites.

Table 5: Specific capacitance and current densities of supercapacitor made of graphene based composite materials

Materials	Specific capacitance ($mAhg^{-1}$)	Current densities (Ag^{-1})
Chemically modified graphene [57]	130	1.3
Hydrazine rGO [58]	264	0.1
Exfoliated GO [59]	120	0.83
N-doped rGO [60]	282	1
PANI graphene [61]	970	2.5
Graphene/CNTs [62]	$2.8mF/cm^2$	50V/s
Vertically oriented graphene [63]	130	600
Solvated graphene films [64]	156.5	1080

4.0 Conclusion and Future Aspects

Graphene and graphene-based composite shows the promising result to fulfil current demand of energy storage systems. As discussed, graphene-based cathode, anode and supercapacitor shows excellent results, but commercialization of these devices is still a challenge. Graphene composite material used in these devices improve their electrical parameter such as high electrical conductivity, high energy, and power density. Further optimization of electrode for battery technologies Li-ion, Li-Air, Li-S having graphene composite can give promising result in smart electronics gadgets. While synthesizing graphene, avoiding restacking is challenging task. Cost-effective, standard procedure for scalable amount of graphene or graphene composite are some challenging areas future research work.

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