

Advances in graphene based nanocomposites as a high capacity anode material for Lithium ion batteries

Bakht mand khan, Hasnain khan, Sajjad khan, Kefayat Ullah*

Department of Applied Physical & Material Sciences, University of Swat, Pakistan

Abstract: This review studied different composites of lithium ion batteries based on graphene as support materials. We study different problems such as charge mobility, thermal and chemical stability due to high temperature and nontoxicity behaviors. These graphene based composites achieved with very low production costs, which makes them commercially attractive. We also concluded that graphene-based Li-ion batteries soon become part of energy harvesting devices to limit fossil fuel dependence. Besides their limitations, these anode materials have the potential to make them efficient. More research is needed to make these materials more efficient, sustainable, and less harmful to nature and human health.

Keywords: Graphene, Nanocomposites, Anode, Lithium ion batteries

1. Introduction

Batteries are gaining a lot of interest for utilization of renewable energy resources due to their capacity to store intermittent energy [1]. Among all rechargeable batteries, lithium ion batteries are mostly studied as attractive energy storing devices due to its storage capacity and large energy density, which is beneficial for wide variety of applications and needs for daily life. [2]. Presently, LIB is commonly used in cameras system [3], mobile phones [4], laptops [5], electric vehicles [6] and hybrid electric vehicles [7]. Lithium ion batteries have got a lot of interest as a new generation of energy storage devices due to their benefits such as no memory effect [8], high energy-density [9], long lifetime [10], light in weight [11], and quick charge/discharge ability [12]. Goodenough et al. discovered in 1980 that layered lithium cobalt oxide (LiCoO_2) material allows reversible intercalation/deintercalation of lithium ions at a strong potential, which was a turning point in the development of LIBs. Researchers noted that lithium ions may be injected and ejected from graphite structures continuously at a low voltage. Reversible charging/discharging operations may be obtained in LIBs using graphite as the anode and lithium cobaltate as the cathode by continuous migration of lithium ions between cathode and anode. [13]. Since the early 1990s, Sony has been commercially launching LIBs.

* Corresponding author: kefsayed@uswat.edu.pk (Kefayat Ullah)

have emerged as the most useful rechargeable battery technologies available in the market to date [14]. Goodenough, Yoshino, and Whittingham were awarded the Nobel Prize in Chemistry in 2019 for their significant contributions to the invention of LIBs, which is a major step towards the production of rechargeable batteries. [15]. Lithium ion batteries are consist of four essential components including an anode, cathode, separator, and conductive electrolytes. The charging process happens when the lithium-ion travels through the separator from lithium cobalt oxide (cathode) to graphite (Anode) by conducting electrolyte. Discharging process occurs when a load like a light-emitting diode is connected to the battery, the lithium-ion atoms in the anode lose electrons and becomes lithium ions, which move toward the cathode. [16]. As a necessary component of lithium-ion batteries, anode material plays important role for the electrochemical-performance of lithium ion batteries. Graphite is presently the most generally used anode material in LIBs, but it contain a very less theoretical capacity about just 372 mAh/g. [17]. Due to the limited capacity of a graphite anode, it will no longer be able to meet the requirements of the fast-growing industries [3]. Research is needed to prepare a new kind of anode materials in which capacity is higher than graphite anode to enhance energy density and performance of LIBs. [18].

Graphene as a single layer of graphite with a higher capacity three times of that graphite, get a lot of interest to use as anode material due to their properties such as large specific-surface area and more lithium ions [19]. Graphene is very well suited for LIB anode applications because of its high energy storage capacity of 669 mAh/g, good cycle stability, longer interlayer-distance of 0.615 nm with weak van der-Waals forces, that allow for easy intercalation/deintercalation process [20]. Graphene has high chemical stability, good mechanical flexibility and superior electrical conductivity. These properties make graphene an good electrode material to prepare highly conductive composite materials and improve electrochemical properties [21]. Silicon (Si) is the most promising negative electrode material for LIBs [22] because of its high lithium-ion storage capacity of 4200 mAh g⁻¹ [23] which is ten times that of currently used graphite [24]. Due to its high power and energy density, silicon-graphene composite material have been investigating as potential anode materials for LIBs [25]. The sandwich structure graphene- silicon composites show a long cycling performance and excellent electrochemical performance. After 500 cycles, at 100 mA/g it shows very large capacity of 1085.6 mAh/g [26]. To improve the cycling performance, researchers have proposed a variety of silicon-graphene composites [27]. SiO₂-GA is used as anode material to increase the performance of LIBs, a specific capacity of 300 mAh/g was achieved at a current-density of 500 mA/g [28]. TiO₂ has also attracted a lot of interest as a good and safe anode material for LIBs [29]. Furthermore, TiO₂ has exceptional characteristics like large theoretical capacity of 335 mAh/g, low toxicity, low in price, chemical stability, and compatibility with a variety of nanostructures [30]. According to Liang et al., graphene doped TiO₂ nanocomposite has improved mobility of electron and longer electronic mean free path with a lower defect density in graphene, which allows photogenerated electrons to diffuse further from the graphene doped TiO₂ interface, extending the lifetime of photoexcited holes and electrons in Titanium dioxide [31]. The

use of graphene in TiO_2 -graphene composites can improve the thermal conductivity and excellent topological features [32]. By using the aerosol-assisted spray drying method, the prepared TiO_2 -RGO nanocomposites which show good performance, at a current density of 3.74 A/g shows a reversible capacity of 109 mAh/g and at a current density of 0.94 A/g after 800 cycles with a 97% of capacity retention shows good cycling stability [33]. Tin oxide (SnO_2) is also considered best anode materials for future generation LIBs due to its safe operating voltage, low cost, large theoretical capacity, environmentally friendly, and natural availability [34]. SnO_2 has a large theoretical capacity (782 mAh g^{-1}) and a low discharging voltage (1.5V), making it an attractive anode candidate for the excellent performance of future lithium ion batteries [35]. In SnO_2 -graphene nanocomposites, the layer of graphene not only limits the contact between electrolyte and SnO_2 components, also it reduces graphene flexibility which affects its capacity to accommodate the volume-expansion of tin dioxide (SnO_2) [36]. Zhou and his group member obtained SnO_2 /Nitrogen-doped graphene hybrid composite, at 500 mA/g after 500 cycles it shows outstanding cycling-performance of 1021 mAh/g [37]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is also considered to be good anode material for the next generation of lithium ion batteries because it does not have disadvantages like graphite [38]. Furthermore, due to its zero-strain nature, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has large cycle stability. As a result, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ becomes one of the most attractive anode for high-performance LIBs [39]. LTO doped graphene composites improve electrical conductivity and also enhance the structural stability of LTO throughout the discharge and charge process. [40]. Molybdenum disulfide (MoS_2) has also received much interest for next-generation LIBs anode material because of its layered structure, which facilitates the insertion-deinsertion of Li^+ ion [41], and has large theoretical capacity of 669 mAh g^{-1} [42]. 2D structure and high conductive behavior of graphene provide a large surface area which provides an easy path for the charge transport process [20]. Because of its high capacity of 1290 mAh g^{-1} , graphene- MoS_2 composite is a good electrode for LIBs [43]. Zinc oxide is considered to be one of the useful transition metal oxide anode for LIBs [44], because it has a large theoretical storage capacity of 987 mAh g^{-1} , low-cost production, and large lithium ion diffusion coefficient [45]. For example, ZnO /graphene electrodes have been prepared by ball-milling method, although that the unequal distribution of graphene and zinc oxide, as well as major defects in zinc oxide crystals, have sometimes resulted generating difficulties [46]. At 0.1 C , the ZnO /graphene anode has a storage capacity of 850 mAh g^{-1} and after 50 cycles with the capacity rate decay $\sim 8\%$ deliver good cycling stability [47]. Fe_3O_4 is considered to be a useful anode in LIBs due to its large theoretical capacity of 926 mAh g^{-1} [48], low in cost, and environmentally friendly [49]. Combining Fe_3O_4 nanomaterials with graphene has recently become a popular strategy for improving cycle stability [50]. Much research on Fe_2O_3 -Reduced graphene oxide has recently been investigated., Xu et al. [23] prepared porous Fe_2O_3 /graphene nanocomposites as an anode which shows a better rate performance [51]. Y.-H. Shi, et al [52] prepare Fe_3O_4 -RGO composites, it shows good capacity of 925.3 mAh g^{-1} at a current density of 100 mA g^{-1} and at 500 mA g^{-1} it maintained about 636.1 mAh g^{-1} . MoO_2 is also well-known for its large theoretical capacity of 838 mAh g^{-1} and better conductivity [53]. As a result, MoO_2 seems to have

the potential to be utilized as a durable and safe anode for LIBs [54]. MoO₂-RGO nanocomposites showed superior lithium storage capability with an outstanding discharge capacity of 765.1 mAh/g and also it exhibited good stability at current density of 100 mA/g [55] SnS₂ is also believed as a good anode for LIBs due to its large theoretical capacity of 1232 mAh g⁻¹ [56]. Chang et al. discovered few-layer SnS₂-graphene hybrid materials produced in the solution-phase technique using L-cysteine as a ligand and at a current density of 100 mA/g it showed a reversible specific capacity up to 920 mA hg⁻¹ at a current density of 100 mA/g [57]. Zinc ferrite (ZnFe₂O₄) is a potential anode material because of his low cost, high theoretical capacity (1000 mA hg⁻¹), environmentally friendly and natural availability [58]. ZnFe₂O₄-RGO composite electrode has an impressive lithium-ion storage capability, for 200 charge-discharge cycles it shows a reversible-capacity (760 mAh/g) and at a current rate of 1.0 A/g and after 700 cycles the capacity was decreased to 603 mAh/g [59].

In this review, we discuss synthesis techniques of graphene based anodes for lithium ion batteries. The stability factors, composite selections, and efficiencies were discussed in detail. The limitation was also discussed to overcome the various problems during the designing of new materials for anode materials.

2 Experimental

In the experimental sections, a few graphene materials and their synthesis were discussed in detail. Si-doped GA composite was prepared by a simple hydrothermal process as shown in Fig 1. After surface-modifying silicon nanoparticles (SiNPs) with phytic acid, 2 mg ml⁻¹ produced graphene oxide (GO) was introduced to the ultrasonic-disruptor, then agitated for 30 minutes. Various hydrophilic functional groups develop on the surface of silicon nanoparticles after phytic acid treatment, with various phosphoric acid groups hydrogen bonding with SiO₂. As a result, silicon nanoparticles and graphene oxide binding can be improved. The combined solution is then hydrothermally treated to produce an aerogel structure. Two types of negative electrode materials designated Si doped GA-1 and Si doped GA-2 having mass ratio of graphene oxide to silicon is 1:10 and 2:10 are produced through freeze drying and by heat treatment to decrease graphene oxide in a tube furnace [60].

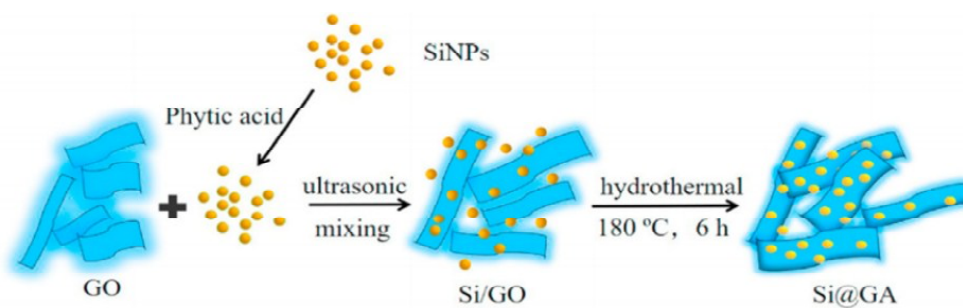


Fig 1: Synthesis procedure of Si doped GA-1 and Si doped GA-2 composite [60].

The modified Hummers technique was used to produce a graphene oxide (GO) sample from pure graphite flakes. After treatment by annealing, an R-TiO₂ doped RGO composite was created using the hydrothermal technique as shown in Fig 2. By magnetic-stirring, a solution is produced by mixing 2mgml⁻¹ and 3ml TiCl₃ solution with 30ml graphene oxide (GO) and by rapid stirring a solution of 30 ml sodium hydroxide (NaOH)~2.5 mol/l is added with the above-prepared solution. After keeping the temperature up to 180 °C for 12 hours, a 20 g of sodium hydroxide (NaOH) powder and the uniform mixture are shifted to a Teflon lined -stainless autoclave of 100ml with the help of a magnetic stirrer. Later in the reaction, by centrifugation, the precursor is obtained and washed multiple times with t 0.1M of dilute HNO₃ solution and deionized water. The precursor is heated at 500 °C in a nitrogen atmosphere (N₂) for 4 hours and obtained R-TiO₂ doped rGO composite. Fig 2 shows the method to produce R-TiO₂ doped rGO composite [61].

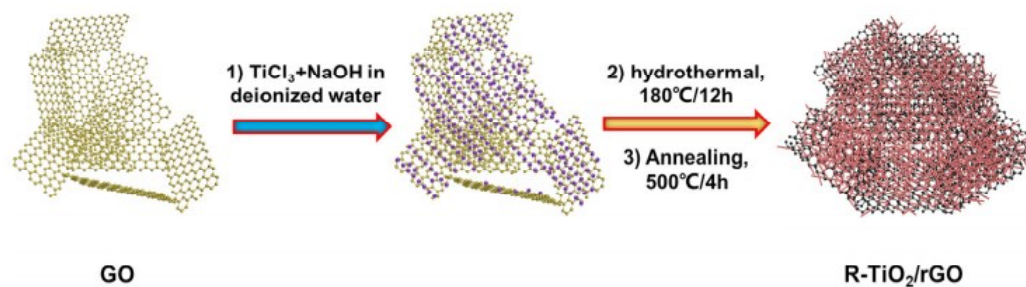


Fig 2: Schematic diagram for the preparation of R-TiO₂/rGO composite [61].

Fig 3 shows the production process of SnO₂-monodispersed graphene(MG) nanocomposites. First, Sn(OH)₄ nanoparticles was produced using simple solvothermal technique using Poly-vinylpyrrolidone PVP and DMF. The nanoparticles Sn(OH)₄ were equally distributed in a graphene oxide solution and heated at a temperature of 80°C before being poured in liquid nitrogen. As graphene oxide is a large surface-energy material that is easily washed by water and when the hot solution was rapidly reached to 196°C, and surface-tension of graphene oxide increased significantly due to low temperature and decreasing of the solid to liquid interface. This can cause graphene oxide sheets to shrink to reduce their surface-energy and anisotropy of solid surfaces would cause unequal distortion. This characteristics, together with arbitrary phase-transformation of H₂O to ice because of quick cooling, each contribute folding and bending of graphene oxide sheets. As a result, curved-surface structure, which may prevent direct and parallel connection with neighboring sheets were obtained. The freeze drying procedure can then keep stable structure while the solvent is being removed. Finally, the SnO₂-monodispersed (MG) nanocomposites was produced following a heat treatment capable of dehydrating Sn(OH)₄ and reducing GO concurrently [36].

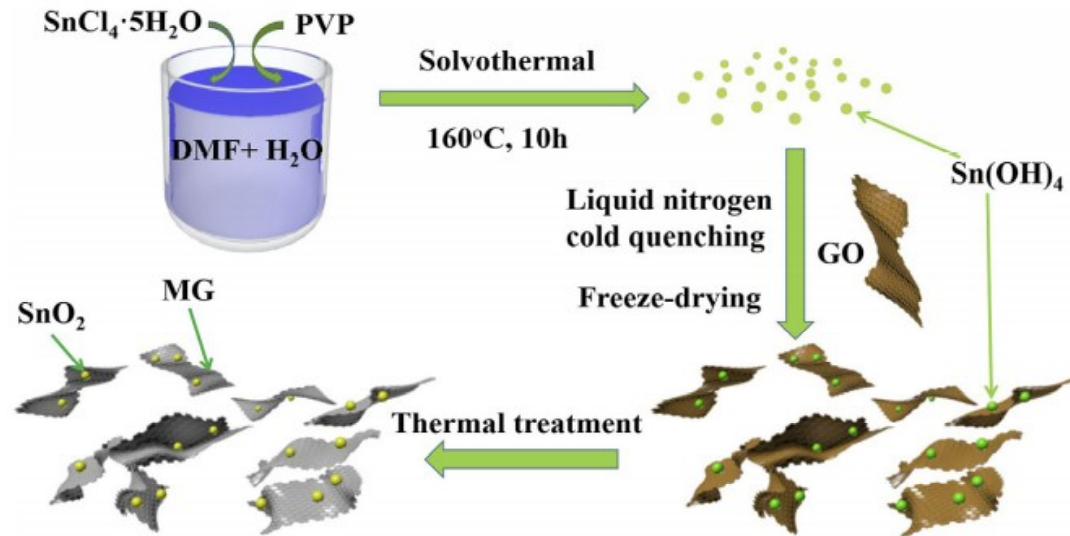


Fig 3: Schematic diagram for the synthesis of the SnO_2 -monodispersed graphene (MG) nanocomposites [36].

Using capillary evaporation process holey graphene framework (HGF)-nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocomposite was prepared. For the preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ two sources can be used. $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was utilized as a source of titanium and $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ as a source of lithium. Using the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -HGF composite as an example, the typical preparation processes could be as follows. In a 2 mg mL^{-1} holey graphene oxide aqueous solution, $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ and iced ethylic were added. Then iced ethylic-acid and source of titanium $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dispersed in ethanol to make a homogeneous mixture, which was dissolved in a combination of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ and holey graphene oxide to make a grey suspension. The dispersed suspension is heated at the temperature from 70 to 80 °C for 2 hours after the reaction up to the suspension is completely dried to obtain the precursor of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -holey graphene framework composite. After that precursor of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -holey graphene framework composite was then heated for 2 hours at 750°C in an Ar atmosphere to produce a $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ composite. To test the mechanisms of tap density change throughout the evaporation drying procedure, many $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -holey graphene framework (HGF) composites with different initial stoichiometric ratios of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to holey graphene oxide (HGO) were produced. The same stoichiometric ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to GO of 1:1, which is termed as LTO-graphene (GF) composite. [39].

Graphene doped MoS_2 alternatively-stack structure (GMASS) is produced by chemical vapour deposition (CVD). Through layer by layer stacking, GMASS was successfully produced as shown in Fig 4. The substrate was made of copper foil, which is mostly used as a current collector in lithium ion battery electrodes. The initial step was to pick up PMMA doped graphene-film with copper foil and dry it in an electric oven at 100°C

for 4 hours to eliminate water and graphene layers are attached to the copper foil surface, then removed the layer of PMMA. The film was washed in acetone three times at room temperature before being washed in acetone in a closed container at 100°C. It was then heat-treated for 4 hours at 400°C in an H₂ atmosphere. The obtained product was used as a substrate to take up PMMA/MoS₂ film and then went through the same PMMA removal technique as in the first stage. The first two processes were repeated up to 5 times to produce a GMASS with 5 layer graphene layers and 5 layer MoS₂ [19].

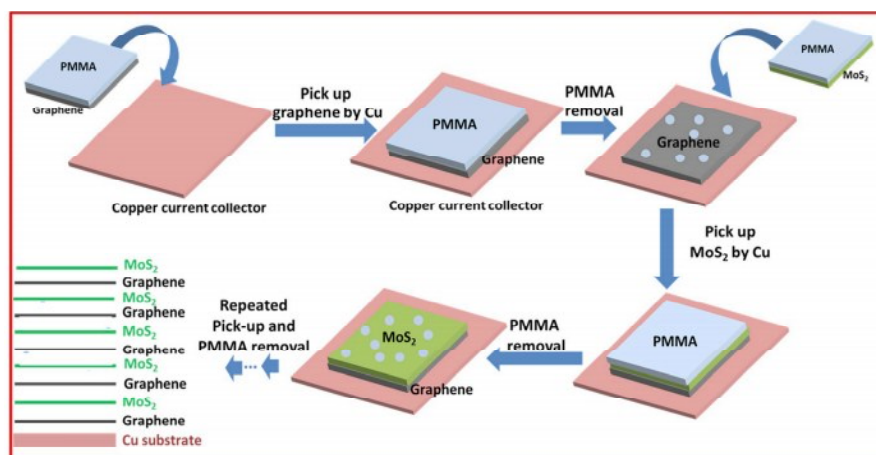


Fig 4: Schematic diagram for the synthesis of graphene/MoS₂ composite [19].

In a typical procedure, raw materials for zinc oxide were initially produced directly utilizing sodium hydroxide (NaOH) and zinc acetate in a precipitation technique. The graphene powders and zinc oxide (ZnO) were then milled at 800 rpm for 12 hours in a planetary machine with different mass ratios (10:90 and 15:85), producing ZnO doped graphene-10 and ZnO doped graphene-15, as shown in Fig 5. The graphene powders having a graphene layer greater than ten were chosen as a raw material for the decrease cost ZnO doped graphene composites. Then the surface of zinc oxide was changed by using the ball-milled method and graphene powders was breakdown into few layers graphene. The ratios of ZrO₂ grinding balls along with different diameters (5, 8, and 10 mm) were chosen to the ratio of 1:1:1 for the obtaining best ball-milling result.[62].

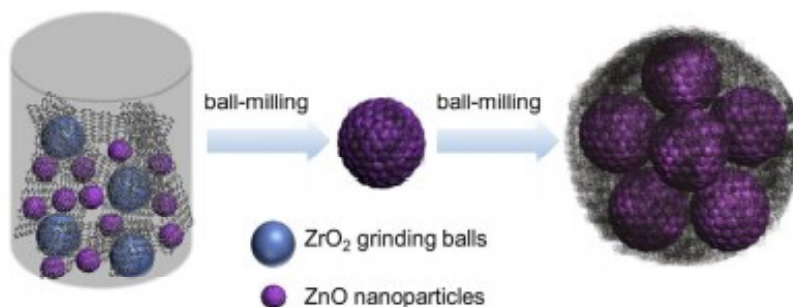


Fig 5: Synthesis procedure of ZnO/G composite by ball-milling method [62].

Fe_3O_4 -Reduced graphene oxide composite was prepared by using broccoli shape FeCO_3 -NPs as shown in Fig. 6. With natural graphite powder, a modified Hummers' technique was used to produce cross-linked 3D network graphene. The FeCO_3 was used as a precursor and assembled with graphene in the existence of hydrazine hydrate. 0.013 L graphene oxide (1 g/L) was allowed to treat ultrasonically for 3 hours. Also, 0.05 g of FeCO_3 solid was inserted in the solution of graphene oxide, and then stirred for 2 hours to create a homogenous suspension liquid. The suspension was then injected with 2.5 liters of hydrazine. For 3 hours, the mixture was maintained at the temperature of 100°C under reflux. Fe_3O_4 /Reduced graphene oxide (rGO) composites were centrifuged and washed many times before being used. Finally, the sample was dried overnight at 60°C [52].

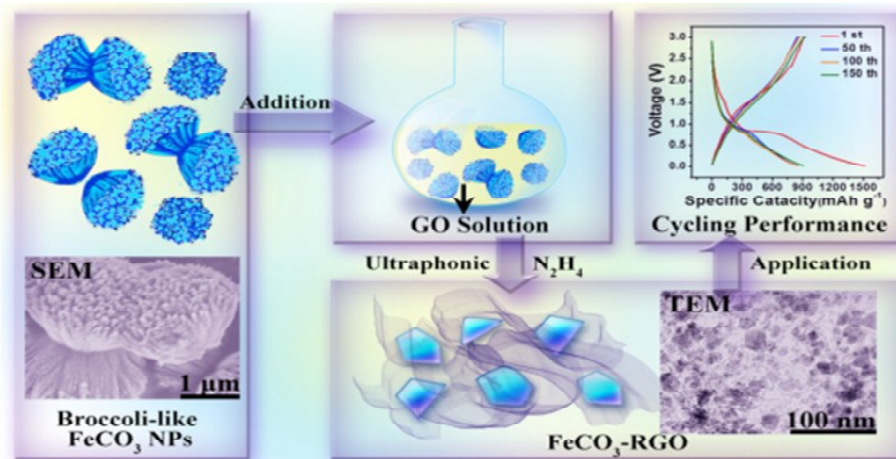


Fig 6: Schematic diagram for the fabrication of Fe_3O_4 -RGO composites [52].

The following process was used to make a MoO_2 /graphene composite using the plasma-enhanced electrochemical exfoliation method as shown in Fig 7. The electrolyte was 1.5 mol $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was added to 150 mL H_2SO_4 solution with concentrations of 1M, 3M and 0.5M. As cathode and anode, graphite and Pt electrodes were chosen. The cathodic graphite tip was sharpened to 1 mm in diameter and immersed in the solution for about 1 mm, while the Pt electrode was immersed deeply. Then, a constant voltage of 70 V was supplied between two electrodes through a DC source (110V-3A, Kikusui Electronics Corp., Japan), and current intensity was regulated in the range of 0.4 to 0.6 A. In an ultrasonication bath at ambient conditions, the reaction continued for one hour. To maintain the sharper tip, the graphite electrode must be re-sharpened every 15 minutes. The resulting suspension was thoroughly filtered and rinsed with distilled water and ethanol using a vacuum filtering system with a polyvinylidene fluoride membrane (pore size of 0.2 μm) until it reached neutral pH is equal to 7. The complete products were then collected after one hour of drying at the temperature of 60°C . The same procedure was used with varying precursor concentrations. The starting concentrations of ammonium molybdate in samples GMo1, GMo5, and GMo10 are 1 mM, 5 mM, and 10 mM, respectively.[63].

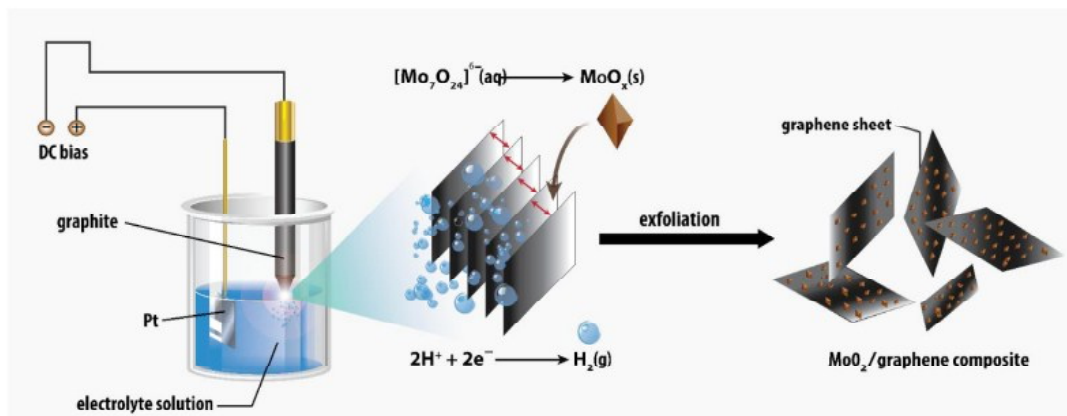


Fig 7: synthesis procedure of MoO_2 doped graphene composites [63].

SnS_2 -nanoparticle doped graphene nanosheet was prepared by simple method. At first step, concentration of 1 mg/ml GO is distributed in solution of ethylene glycol solution through ultrasonication and by stirring. The solution-1 and solution-2 are formed from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (280.5 mg) and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (384.3 mg) mixed in 10 ml of ethylene glycol solution. The solution-1 was then added drop by drop to the ethylene oxide solution including graphene oxide and stirred it overnight. The solution-2 was then added to the prepared solution and stirred for 30 min. Lastly, the ash-green mixture was then transferred from beaker to a Teflon liner, then to react at 180°C for 24 hours. The sample preparation procedure is depicted in Fig. 8 [56].

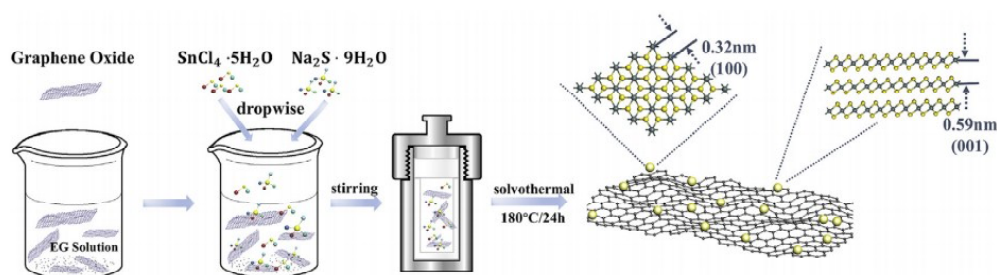


Fig 8: Schematic diagram for the preparation of SnS_2/GNS composite [56].

3. Result and discussions:

In this review, we have discussed some synthesis methods of graphene based anodes nanocomposites for high performance of lithium ion batteries (LIBs). Different materials and their composites with graphene can be prepared to obtain the high-capacity anode materials. In recent developments in high-performance graphene and its composite is used as an anode material for LIBs. The electrochemical performance of each synthesized composite is tested for LIBs. Graphene has unique properties like high surface area, chemical diffusivity, mechanical strength, large theoretical capacity and excellent electrical conductivity make graphene a suitable anode material for lithium ion batteries. In this study graphene is doped with other anode material to make composite which is used in LIBs anodes.

Using a hydrothermal method, silicon-doped graphene aerogel composites were synthesized. Two types of anode material were prepared for lithium ion Batteries, named (Si doped GA-1 and Si doped GA-2). These anode materials for lithium ion batteries have been investigated, and they exhibit good cycle and rate performance. At a current density of 0.2 A g^{-1} , an excellent reversible specific capacity was maintained above 1330 mAh g^{-1} after 100 cycles and while operating at high current density of 2 A g^{-1} , its reversible specific capacity is obtained more than 600 mAh g^{-1} . The unique structure and use of graphene in the Si doped GA-2 anode can improve the composite electrical conductivity and also prevents the Si structure from collapsing, resulting in the electrochemical properties of the composite enhanced [60]. R-TiO₂ doped rGO composites are simply prepared by a hydrothermal technique using graphene oxide solution, NaOH solution, and TiCl₃ under magnetic stirring. The precursor was heated in a nitrogen (N₂) oven. Lithium ion (Li⁺) diffusion movement is improved due to TiO₂-nanorods like structure, also reduced graphene oxide enhanced the composite electronic conductivity and transfer rate of electrons /lithium ions (Li⁺) during repetitive lithium-cycling. R-TiO₂ doped rGO composite anode shows good electrochemical characteristics due to its specific storage capacity, after 100 cycles at 1C a specific capacity can be obtained of 267 mAh g^{-1} which shows large rate capability, and after 500 cycles at 10 C it shows long-period cycle stability of 151 mAh g^{-1} . At a large-current density of 30 C the sample of R-TiO₂ doped rGO composite has a large reversible- capacity (55 mAh g^{-1}), at 1-3 V shows a good discharge capacity of 96 mAh g^{-1} . Due to this properties, the R-TiO₂ doped rGO composite is good anode material for future LIBs [61]. A simple cold-quenching induced self-assembly technique is used to effectively construct a new type of high mono-dispersed and wrinkled graphene nanosheets (GNs) attaching with SnO₂ nanoparticles to prepare SnO₂/MG composite. Result of increased conductivity and reducing volume change, the foldable structure of monodispersed graphene nanosheets can limit restacking and restrict the movement and aggregation of SnO₂ nanoparticles on the surface GNs. Moreover, during the production procedure, a synergistic interaction between GNs and SnO₂ nanoparticles is induced. Due to this interaction, the SnO₂/MG nanocomposite achieves good electrochemical performance for LIBs anode. After 200 cycles at a current density of 100 mA g^{-1} , it shows large reversible capacity of 1147 mAh g^{-1} and at a current density of 1000 mA g^{-1} large rate capability (759 mAh g^{-1}) can be obtained and also at 2000 mA g^{-1} after 600 cycles it showed a long cycle life of 662 mAh g^{-1} [36]. Through a capillary evaporation technique, a mesopore-oriented holey graphene Framework (HGF) attached with Li₄Ti₅O₁₂ nanoparticles was effectively produced HGF/Li₄Ti₅O₁₂ composite. Holey graphene consists of a huge amount of in-plane nanopores having 5 nm diameter. These nanopores might allow Li ions to shuttle graphene sheets as well as reduce Li-ion diffusion resistance in Li₄Ti₅O₁₂-HGF composites, which is essential for achieving superior power capability. The porous-like structure of the Li₄Ti₅O₁₂-HGF composite can be accurately adjusted by varying the initial ratio of Li₄Ti₅O₁₂-HGF. A large tap density may be produced by accurately adjusting the porous-like structure, which is useful for getting improved volumetric-power capability. The holy doped graphene is highly stable and Li₄Ti₅O₁₂ a type of zero strain material. LTO/

HGF-1 also seems to have a good volumetric-power capability, at 17.5 A g^{-1} delivering good volumetric specific capacity of 98 mAh cm^3 after 1000 cycles with 84% of capacity retention, shows long-cycle stability and high rate performance of anode material [39]. CVD growth techniques have also been used to prepare graphene and MoS_2 . A graphene/ MoS_2 alternately stacked structure (GMASS) was then produced using 5 layers of MoS_2 and 5 layers of graphene. The CVD-produced MoS_2 and films have few defects, for electrochemical characteristics, the as-fabricated GMASS-structure is an excellent platform for studying the influence of MoS_2 and graphene interactions. When compared to monolayer graphene electrodes (1.46 V), GMASS has a lower average operating voltage (1.31 V) when it used as a LIBs anode. As compared to the graphite anode (461 cm^3), its volumetric capacity was considerably increased (1260 mAh cm^3). These electrochemical characteristics are advantageous for achieving large energy density in Lithium ion Batteries. graphene/ MoS_2 heterostructure composite is used to be good performance LIBs anode in the future [19]. ZnO/G composite is produced by a simple ball milling technique and it shows a good performance for lithium ion batteries. Graphene is doped with ZnO nanoparticles, a 3D conductive network produces for zinc oxide nanoparticles due to the excellent mechanical strength and large conductivity of graphene which can reduce the volume changes, also graphene layer present on the surface drive electrons to the conductive-network from zinc oxide inside the electrode which limits its side reaction. The electronic mobility and ion-diffusion coefficient will be enhanced due to the produced defects and cracks through the bead hit on the surface of graphene. The electrochemical performance will be tested for full lithium ion battery, in which ZnO/G is used as an anode and lithium cobalt dioxide (LiCoO_2) used as a cathode, at 100 mA g^{-1} it indicates a good reversible capacity of 400 mAh g^{-1} and large energy-density (1478 Wh kg^{-1}) [62]. Fe_3O_4 nanoflakes-Reduced graphene oxide composites were made from a FeCO_3 hierarchical-microstructure, without the calcination of high temperature. It is a low-energy technique for fabricating Fe_3O_4 nanoflakes-Reduced graphene oxide composites. FeCO_3 to Fe_3O_4 , there was an impressive morphological and phase transition. The Fe_3O_4 -Reduced graphene oxide composites as-prepared were produced from a multichannel-material of FeCO_3 -microspheres that benefitted from alkaline solution permeation, which enhanced Fe_2^+ dispersion and makes up Fe_3O_4 uniformly attached on RGO sheets. Reduced graphene oxide sheets have a large surface area, which provided a path for Lithium ions movement and buffered volumetric expansion of Fe_3O_4 -material. At current density of 100 mA g^{-1} , the Fe_3O_4 -RGO composites offer a good capacity of 925.3 mAh g^{-1} when it tested as anode for LIBs. Even at current density of 500 mA g^{-1} , the capacity remains at 636.1 mAh g^{-1} after 1000 cycles [52]. MoO_2 doped graphene composites are effectively produced in a single-step technique having a piece of low price equipment and a basic setup with the ambient condition. The findings show that MoO_2 - nanoparticles having sizes less than 30 nanometers are arranged randomly on the multi-layer graphene sheets(MG) surface [63]. An inexpensive and simple approach is used to produce an SnS_2 nanoparticle-graphene nanosheets composite. Due to the unusual structure of graphene nanosheets and SnS_2 , it is linked by covalent bonds, which exhibit good performance in Lithium ion Batteries. It shows a

capacity of 1250.8 mAh g⁻¹ in Lithium ion Batteries, which is significantly higher than Sn-based material. After the rate is raised to 0.5 A g⁻¹, it retains a capacity of about 798.6 mAh g⁻¹. These findings show that doped graphene not only reduces the volume changes are mostly due to the inclusion of faulty graphene, which not only reduces volume changes but also offers additional active sites for the transport of electrons and more ion storage [56].

Production of silicon (Si) from silicon dioxide (SiO₂) may pollute the environment and also consumed a lot of energy. Using reductants like carbon-based materials, the reduction of silicon dioxide is difficult to produce high-quality silicon in a large amount. [64]. TiO₂ doped graphene composites are difficult to make because they require a costly organic source. [61]. In the long cycle process, the capacity of the SnO₂-graphene composite is decreased which is a typical problem. This is because the SnO₂-nanoparticles doped on the graphene surface agglomerated where graphene cannot encapsulate it, causing falling off the active material during the charging/discharging process [65]. There is well dispersed graphene based nanocomposites are required to obtain high capacity with low production cost.

4. Conclusion

The outstanding chemical and physical properties of graphene make graphene as a potential material for energy storage and conversion devices. Presently among all the energy storage devices, lithium ion batteries has an excellent electrochemical energy storage device which convert chemical energy into electrical energy. As a major component of LIBs anode material plays a major role in the storage capacity of LIBs. Graphite is used as anode component in LIBs, but the graphite anode is very limited theoretical capacity and cannot achieve the industries requirements. To enhance the performance of LIBs graphene is considered one of the best anode due to its excellent characteristics. Also graphene ability to doped with other materials to reduce its volume changes and improve its electrical conductivity. Graphene based nanocomposites seem to be best anodes for future LIBs.

References

1. Xiong, R., et al., *Lithium-ion battery aging mechanisms and diagnosis method for automotive applications: Recent advances and perspectives*. 2020. **131**: p. 110048.
2. Zhao, X., et al., *High-performance Li-ion batteries based on graphene quantum dot wrapped carbon nanotube hybrid anodes*. 2020. **13**(4): p. 1044-1052.
3. Lin, H., et al., *Janus MoSSe/graphene heterostructures: Potential anodes for lithium-ion batteries*. 2021. **854**: p. 157215.
4. Mossali, E., et al., *Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments*. *Journal of Environmental Management*, 2020. **264**: p. 110500.
5. Koleti, U.R., T.Q. Dinh, and J.J.J.o.P.S. Marco, *A new on-line method for lithium plating detection in lithium-ion batteries*. 2020. **451**: p. 227798.
6. Liu, J., et al., *Aging mechanisms and thermal stability of aged commercial 18650 lithium ion battery induced by slight overcharging cycling*. *Journal of Power Sources*, 2020. **445**: p. 227263.

7. Kosai, S., U. Takata, and E. Yamasue, *Natural resource use of a traction lithium-ion battery production based on land disturbances through mining activities*. Journal of Cleaner Production, 2021. **280**: p. 124871.
8. Xu, J.-L., et al., *Ni-doped Ni₃S₂ nanoflake intertexture grown on graphene oxide as sheet-like anode for high-performance lithium-ion batteries*. 2020. **835**: p. 155418.
9. Sun, J., B. Mao, and Q.J.F.S.J. Wang, *Progress on the research of fire behavior and fire protection of lithium ion battery*. 2021. **120**: p. 103119.
10. Ershadi, M., et al., *Preparing graphene-based anodes with enhanced electrochemical performance for lithium-ion batteries*. 2020. **26**(10): p. 4877-4895.
11. Majeed, M.K., et al., *Clay-derived mesoporous Si/rGO for anode material of lithium-ion batteries*. 2020. **848**: p. 156590.
12. Hou, C., et al., *Recent Advances in Co₃O₄ as Anode Materials for High-Performance Lithium-Ion Batteries*. Engineered Science, 2020. **11**: p. 19-30.
13. Fang, Z., et al., *Progress and challenges of flexible lithium ion batteries*. 2020. **454**: p. 227932.
14. Chen, T., et al., *Applications of lithium-ion batteries in grid-scale energy storage systems*. 2020. **26**(3): p. 208-217.
15. Deng, Z., et al., *Recent Progress on Advanced Imaging Techniques for Lithium Ion Batteries*. 2021. **11**(2): p. 2000806.
16. Zhang, L., et al., *Advanced Matrixes for Binder Free Nanostructured Electrodes in Lithium Ion Batteries*. 2020. **32**(24): p. 1908445.
17. Li, X., et al., *Review on comprehending and enhancing the initial Coulombic efficiency of anode materials in lithium-ion/sodium-ion batteries*. Nano Energy, 2020. **77**: p. 105143.
18. Dhar, S., et al., *Silicon-graphene composite synthesis: Microstructural, spectroscopic and electrical conductivity characterizations*. 2020. **33**: p. 5136-5142.
19. Yu, X., et al., *Fabrication of graphene/MoS₂ alternately stacked structure for enhanced lithium storage*. 2020. **239**: p. 121987.
20. Chodankar, N., et al., *Graphene and molybdenum disulphide hybrids for energy applications: an update*. 2020. **6**: p. 100053.
21. Huang, G., et al., *Two-dimensional Material as Anode for Lithium Ion Batteries: Recent Progress*. 2020. **15**: p. 5416-5429.
22. Jamaluddin, A., et al., *Control of Graphene Heteroatoms in a Microball Si@Graphene Composite Anode for High-Energy-Density Lithium-Ion Full Cells*. ACS Sustainable Chemistry & Engineering, 2020. **8**(51): p. 18936-18946.
23. Han, M., et al., *Growth of flexible and porous surface layers of vertical graphene sheets for accommodating huge volume change of silicon in lithium-ion battery anodes*. 2020. **17**: p. 100445.
24. Jamaluddin, A., et al., *Facile synthesis of core-shell structured Si@ graphene balls as a high-performance anode for lithium-ion batteries*. 2020. **12**(17): p. 9616-9627.
25. Ma, M., et al., *Rational design, synthesis, and application of silica/graphene-based nanocomposite: a review*. 2020: p. 109367.
26. Liu, X., et al., *Enhancing lithium storage performance by strongly binding silicon nanoparticles sandwiching between spherical graphene*. 2021. **539**: p. 148191.
27. Han, X., et al., *On the Interface Design of Si and Multilayer Graphene for a High-Performance Li-Ion Battery Anode*. 2020. **12**(40): p. 44840-44849.
28. Dong, X., et al., *SiO₂/N-doped graphene aerogel composite anode for lithium-ion batteries*. 2020. **55**(27): p. 13023-13035.
29. Tian, Q., et al., *Hierarchical carbon-riveted 2D@0D TiO₂ nanosheets@SnO₂ nanoparticles composite for a improved lithium-ion battery anode*. Applied Surface Science, 2020. **511**: p. 145625.

30. Subaþý, Y., et al., *Surface modified TiO₂/reduced graphene oxide nanocomposite anodes for lithium ion batteries*. Journal of Solid State Electrochemistry, 2020. **24**.
31. Yang, J., et al., *Preparation of TiO₂/single layer graphene composite films via a novel interface-facilitated route*. 2020. **503**: p. 144334.
32. Huang, P., et al., *Effect of graphene concentration on tribological properties of graphene aerogel/TiO₂ composite through controllable cellular-structure*. 2020. **188**: p. 108468.
33. Han, M., et al., *Vapor pressure-assisted synthesis of chemically bonded TiO₂/C nanocomposites with highly mesoporous structure for lithium-ion battery anode with high capacity, ultralong cycling lifetime, and superior rate capability*. Journal of Power Sources, 2020. **465**: p. 228206.
34. Lu, Z., et al., *Porous SnO₂/Graphene Composites as Anode Materials for Lithium-Ion Batteries: Morphology Control and Performance Improvement*. Energy & Fuels, 2020. **34**(10): p. 13126-13136.
35. Liu, X., et al., *Mechanical simulation informed rational design of a soft-and-hard double-jacketed SnO₂ flexible electrode for high performance lithium-ion battery*. 2021. **35**: p. 520-529.
36. Li, Y., et al., *Highly monodispersed graphene/SnO₂ hybrid nanosheets as bifunctional anode materials of Li-ion and Na-ion batteries*. 2020. **821**: p. 153506.
37. Liang, B., et al., *Hybrid of Co-doped SnO₂ and graphene sheets as anode material with enhanced lithium storage properties*. 2020. **533**: p. 147447.
38. Zhang, F., et al., *Interfacial electrostatic self-assembly in water-in-oil microemulsion assisted synthesis of Li₄Ti₅O₁₂/Graphene for lithium-ion-batteries*. Journal of Alloys and Compounds, 2020. **819**: p. 153018.
39. Xiang, Y., et al., *Nano-Li₄Ti₅O₁₂ particles in-situ deposited on compact holey-graphene framework for high volumetric power capability of lithium ion battery anode*. Journal of Power Sources, 2020. **447**: p. 227372.
40. Wang, D., et al., *Nitrogen, sulfur Co-doped porous graphene boosting Li₄Ti₅O₁₂ anode performance for high-rate and long-life lithium ion batteries*. Energy Storage Materials, 2020. **27**: p. 387-395.
41. Choi, J.-H., et al., *Enhanced electrochemical performance of MoS₂/graphene nanosheet nanocomposites*. 2020. **10**(32): p. 19077-19082.
42. Stolyarova, S., et al., *Anode materials from MoS₂ and multilayered holey graphene for Li-ion batteries*. Fullerenes, Nanotubes and Carbon Nanostructures, 2020. **28**: p. 1-7.
43. Xu, K., et al., *Atomic investigation on structural rearrangement of MoS₂/graphene heterostructure upon electrochemical lithiation and delithiation*. 2021. **282**: p. 128846.
44. Lavagna, L., et al., *Graphene and lithium-based battery electrodes: A Review of recent literature*. 2020. **13**(18): p. 4867.
45. Wu, D., et al., *Controllable synthesis of zinc oxide nanoparticles embedded holey reduced graphene oxide nanocomposite as a high-performance anode for lithium-ion batteries*. Powder Technology, 2020. **367**: p. 774-781.
46. Song, J., et al., *Porous ZnO/C microspheres prepared with maleopimaric acid as an anode material for lithium-ion batteries*. 2020. **165**: p. 55-66.
47. Thauer, E., et al., *Novel synthesis and electrochemical investigations of ZnO/C composites for lithium-ion batteries*. 2021: p. 1-16.
48. Wu, Q., R. Jiang, and H.J.C.I. Liu, *Carbon layer encapsulated Fe₃O₄@ Reduced graphene oxide lithium battery anodes with long cycle performance*. 2020. **46**(8): p. 12732-12739.
49. Simamora, P., J. Al Khalil, and J. Rajagukguk. *Synthesis and characterization Fe₃O₄/GOnanocomposites as lithium-ion battery anodes (LIBA)*. in *Journal of Physics: Conference Series*. 2020. IOP Publishing.
50. Liang, Y. and W.J.J.o.M.S.M.i.E. Lu, *Gamma-irradiation synthesis of Fe₃O₄/rGO nanocomposites as lithium-ion battery anodes*. 2020. **31**(19): p. 17075-17083.
51. Zhang, X., et al., *Porous α -Fe₂O₃ nanoparticles encapsulated within reduced graphene oxide as superior anode for lithium-ion battery*. 2020. **31**(14): p. 145404.
52. Shi, Y.-H., et al., *Fe₃O₄ nanoflakes-RGO composites: A high rate anode material for lithium-ion batteries*. 2020.

- 511: p. 145465.
53. Zhang, Q., et al., *First-principles calculations of an asymmetric MoO₂/graphene nanocomposite as the anode material for lithium-ion batteries*. 2020. **10**(71): p. 43312-43318.
 54. Feng, Y. and H. Liu, *One-step for in-situ etching and reduction to construct oxygen vacancy modified MoO₂/reduced graphene oxide nanotubes for high performance lithium-ion batteries*. *Applied Surface Science*, 2021. **538**: p. 147992.
 55. Geng, Q., et al., *Two-phase Solvothermal Synthesis of MoO₂/RGO Nanocomposites for Lithium-Ion Battery Anodes*. *IOP Conference Series: Earth and Environmental Science*, 2021. **706**(1): p. 012043.
 56. Wu, Y.-Q., et al., *SnS₂ nanoparticle-integrated graphene nanosheets as high-performance and cycle-stable anodes for lithium and sodium storage*. *Journal of Alloys and Compounds*, 2020. **822**: p. 153686.
 57. Mou, H., et al., *Tin and tin compound materials as anodes in lithium-ion and sodium-ion batteries: A review*. 2020. **8**.
 58. Perumal, P., et al., *Tamarind seed polysaccharide biopolymer-assisted synthesis of spinel zinc iron oxide as a promising alternate anode material for lithium-ion batteries*. *Journal of Materials Science: Materials in Electronics*, 2020. **31**(13): p. 10593-10604.
 59. Xu, B., et al., *Simple and effective synthesis of zinc ferrite nanoparticle immobilized by reduced graphene oxide as anode for lithium-ion batteries*. *Journal of Colloid and Interface Science*, 2021. **584**: p. 827-837.
 60. Tang, F., et al., *Preparation and electrochemical performance of silicon@ graphene aerogel composites for lithium-ion batteries*. 2021. **854**: p. 157135.
 61. Fu, Y.-X., et al., *TiO₂ nanorods anchor on reduced graphene oxide (R-TiO₂/rGO) composite as anode for high performance lithium-ion batteries*. 2019. **497**: p. 143553.
 62. Yang, X., et al., *A surface multiple effect on the ZnO anode induced by graphene for a high energy lithium-ion full battery*. 2020. **824**: p. 153945.
 63. Dang, M.N., et al., *One-step Synthesis of Molybdenum Oxide/graphene Composites*. 2021. **37**(1).
 64. Xu, H., Z. Sun, and J. Chen, *Graphene-based anode materials for lithium-ion batteries*, in *Emerging 2D Materials and Devices for the Internet of Things*. 2020, Elsevier. p. 139-164.
 65. Lu, Z., et al., *Porous SnO₂/Graphene Composites as Anode Materials for Lithium-Ion Batteries: Morphology Control and Performance Improvement*. 2020. **34**(10): p. 13126-13136.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>