Review on Graphene Nanoparticle Composites

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Abstract

In recent years, graphene has attracted attention. Grapheneis a thick planar sheet of sp^2 bonded carbon atoms. Its lattice is honey comb structure. Graphene is one of the most rising material due to its various fascinatingl properties.From recent study it is proved that graphene based composites with different nanoparticle show extensive application. In this review we focus on recent developement in the synthetic approach, properties and the facilities of use of graphene nanoparticle composites.The advantages of graphene-nanoparticle composites are specifically observed in catalytic reactions,electrochemical sensing, detection by surface enhanced Raman spectroscopy, purification of waterusing adsorbent and other applications are discussed here.

Keywords:Graphene, nanoparticles, composites, catalysis

Introduction

Graphene is a single layer of carbon atoms connected in a hexagonal structure[1]. Each of these carbon atoms is sp^2-hybridised. Graphene has high conductivity, large surface area, high mechanical and thermal stability [2]. Because of such properties graphene has shown a great promise in a wide range of applications .Especially, high charge carrier mobility (up to 10^5 cm^2 V^{-1} S^{-1}), high intrinsic strength(130 GPa), high thermal conductivity at room temperature (10^3 Wm^{-1} K^{-1}) and large surface area (>2000 m^2 g^{-1}) compared to graphite (10 m^2g^{-1}) or carbon nanotube (1300 m^2 g^{-1}) have been utilized to make graphene based nanocomposite for optical and electronic application [3]. The working efficiency of graphene based materials is generally higher than other.

Due to hydrophobic in nature, does not dissolve in hydrophilic solvent. Highly colloidally stable exfoliated sheets of GO is produced by the chemical exfoliation method. GO contains sp^2 hybridised carbon and with oxygenas hydroxyl, epoxy, carbonyl and carboxyl etc functional groups. However, unique properties of graphene are compromised in GO, that limits its use. Reduced graphene oxide (RGO) increases the number of sp^2 hybridised carbon atoms and the lost properties of graphene are recovered. Self-aggregation process, lower solubility but with enhanced conductivity, light absorption property, mechanical and thermal stability are increased by RGO. Similar to GO, RGO is used in synthesis of graphene based nanocomposites [3-11].

Nanoparticles are widely used in optical, biomedical and electronic application. Metal/metal oxide nanoparticles (e.g., Pt, Pd, Co_3O_4, Au, Ag), semiconductor nanoparticles (e.g., TiO_2, CdSe, ZnS, ZnO) and magnetic nanoparticles (e.g., Fe_2O_3, Fe_3O_4).Metal/metal oxide/hydroxide nanoparticle acts as active centre for chemical/electrochemical reaction (e.g., O_2 reduction, biofuel oxidation, organometallic reaction). The semiconductor nanoparticles have definite energy band gap. It act as photocatalyst.The magnetic nanoparticles have been used in magnetic separation and magnetic resonance imaging applications. In biosensing application Ag, Au, Pt; in photocatalytic application Pt, Pd, Si, SnO_2, MnO_2, $Ni(OH)_2$ and Fe_3O_4, γ-Fe_2O_3 based nanoparticles are mainly used in magnetic separation application [12-17].

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Graphene-nanoparticle compositesshows the property of both component and removes some of the limitations and enhances the performance of individual component.

Synthesis of Graphene-Nanoparticle(G-N) Composites:

Synthesis of high quality graphene helps to control its physical and chemical property.In Figure1 chemical structure of graphene, GO, RGO, G-N composites are shown. Graphite is the natural choice as a starting precursor to produce graphene as graphiticlayers are already present within graphite structure and graphene canbe obtained by simply "peeling off" these graphite layers via mechanical and/or chemical means [23-24]. By micromechanical exfoliation on silicon substrate or chemical vapour decomposition(CVD) on transition metal surfaces, high quality graphene is synthesized but these methods have low production efficiency [25-26]. Figure 2 shows summarized different syntheticapproaches and Figure 3 summarizes the methods (as well as costs associated with the methods).

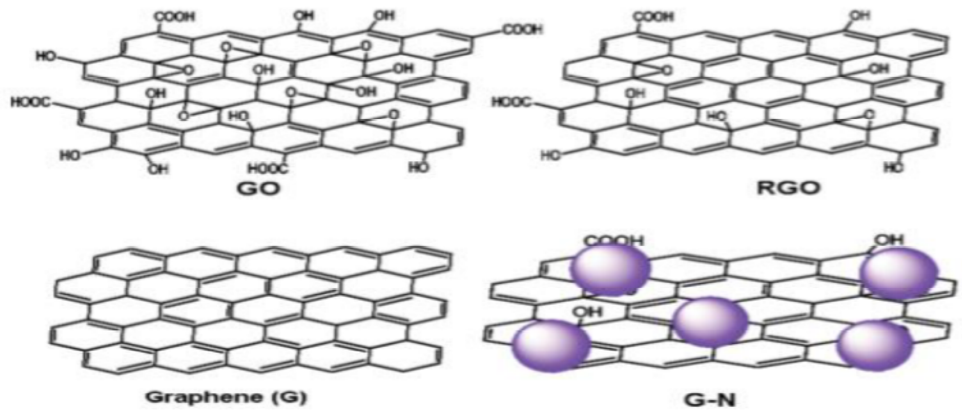

Fig. 1. Chemical structure of graphene oxide (GO), reduced graphene oxide (RGO), graphene and graphene-nanoparticle (G-N) composites.

Figure 1 adapted from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

By modified Hummer's method colloidal GO is synthesized from graphite flakes . G-N composites are synthesized by in-situ reduction of metal ions in presence of colloidal graphene oxide.

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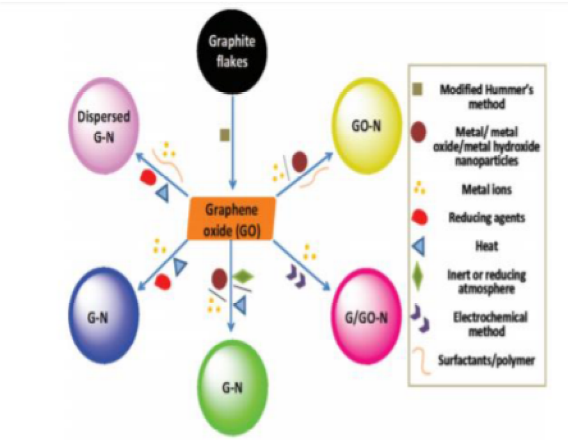


Fig. 2. Schematic illustration of synthetic strategies for graphene/GO based composites with different nanoparticles.

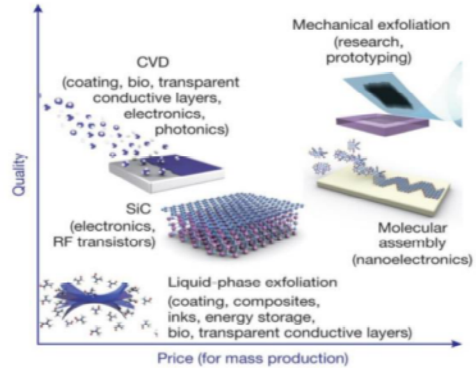


Fig 3 Common methods used for graphene production.

Fig 2. adapted from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

Fig 3. adapted formQing Li, Nasir Mahmood, Jinghan Zhu, Yanglong Hou and Shouheng Sun, Graphene and its Composites with Nanoparticles for Electrochemial energy applications, Brown University and Peking University.

Research on Graphene and Graphene Nanocomposites

Graphene has revolutionized modern day technology with its remarkable and unique properties. The research has exponentially grown by numerous universities, R & D establishments and many more private and governmental bodies around the world. Research on Graphene can be found in every aspect .

Quantity of publications in Graphene since 2000

Using the web science tool, a clear representation of the publication trend on graphene is shown. The publication trend since the year 2000 (January) that the amount of research has grown exponentially from 106 articles in the year 2000 to 8,169 articles in the year 2012 (December) in Figure4.As Figure 5 shows, physics (record count: 13,756) is the most often research area, followed by chemistry (9,231), material science (8,458), science and technology (5,779) engineering (1,677), electrochemistry (932), and so on [35-36].

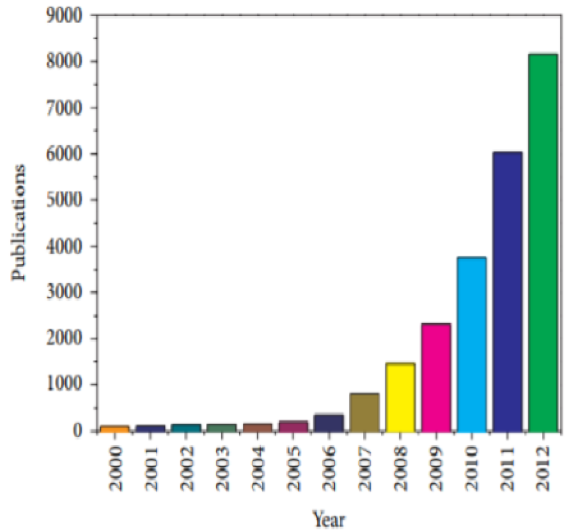


Fig 4: Publication trend in graphene 2000-2012

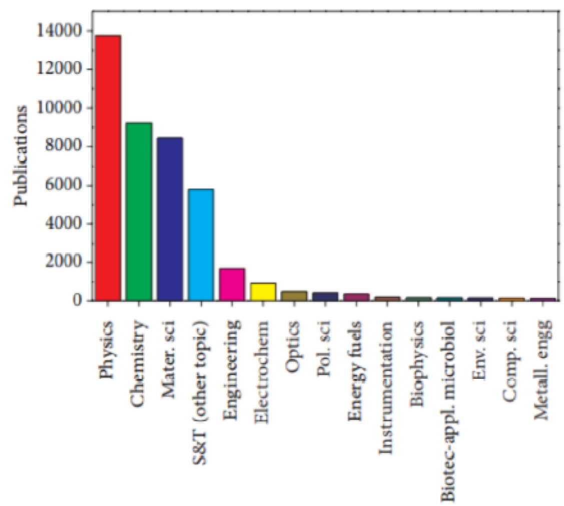
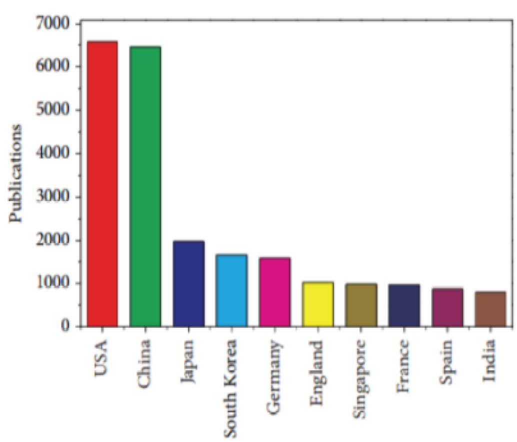


Fig5.Top 15 research areas in graphene is chronology since extensively used since 2000-2012

Fig 4,5 adapted from Vivek Dhand, Kyong Yop Rhee, Hyun Ju Kim and Dong Ho Jung, Journal of nanomaterials, Vol. 2013

A country wise search was conducted to find number of publication in graphene research since 2000. Figure 6 showsthat the United States takes highest position in the chart with highest number of publications, 6,500 followed by China with 6,400, Japan with 1,979 and so on. This indicates the importance given to graphene research and the quantity of research around the globe.Competition will intensify among various countries for thehighest position, quality, applications, patents, commercial products and future markets of graphemc [37-39].



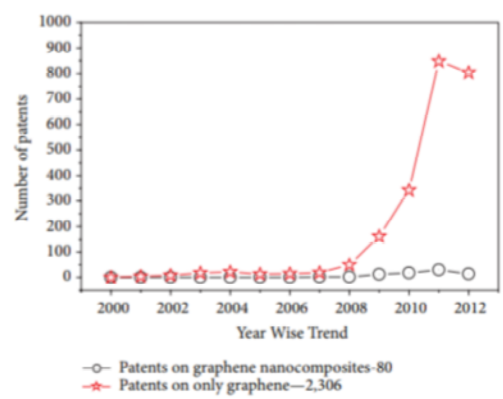


Fig6. country wise publication in graphene graphene nanaocomposite since 2000-2012

Fig7. Patent trends of graphene andsince 2000-2012

Fig 6,7 adapted from VivekDhand,Kyong YopRhee,Hyun Ju Kim and Dong Ho Jung, Journal of nanomaterials, Vol. 2013

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Patents on Graphene since 2000

Patents play a major roleon the scientific and industrial platform. According to the data provided by Lv et al. (2011),more than 50 countries have filed nearly 823 patents on graphene from January 2000 to December 2010, in 15 different disciplines. These data show that the top countries obtaining and applying for patents are the USA, followed by Asian nations. China, Japan and South Korea contribute almost 25% of all the patentpublished in Asia.In the last ten years, Asian countries have recorded an explosive patent growth of almost 87% in the field of graphene. Fromthe graph (Figure 7), it is evidentthat the future of R & D for graphene-based nanocomposites is very bright with high prospects. Since the average annual number of patents and publications for graphene is very high and increasing dramatically, it appears that investigations of graphene's properties are likely to focus in the near future on nanocomposites as the primary area of application [40-45].

Properties of Graphene-Nanoparticle (G-N) Composites

Chemical modification of graphene with other elements has been explored extensively to improve intrinsic properties, of graphene derivatives.Doping heteroatoms (e.g. N,B,P or S) into the graphene lattice enhance the electronic and geometric features of the resultant graphene. In this case number of active sites increases for stronger molecular adsorption. For electrolytic reaction such doping is important to further controll the graphene properties [46-47].

Because of graphene's exceptional thermal, mechanical, and electronic properties, it stands out as the most promising candidate to be a major filling agent for composite applications. Graphene nanocomposites at very low loading show substantial enhancements in their multifunctional aspects, compared to conventional composites and their materials. This makes the material lighter with simple processing and stronger for various multifunctional applications.Therefore the graphene –nanoparticle junction area can become catalytically "hot" spots to catalyze the reactions.

In GO, the π-π^* transition is not observed due to lower percentage of conjugated double bonds. Ifthe chemical reduction of graphene oxide is done by hydrazine, percentage of conjugated double bond and appearance of π-π^* transition band at 260 nm increases.In G-N composites both components shows optical property. Figure 8 G-N composites with plasmonic silver or gold nanoparticles shows respective plasmonic band along with graphene band. However, plasmonic band is extensively damped by graphene. The plasmonic bands for silver and gold nanoparticles are observed at ~ 400 nm and ~ 530 nm, respectively, along with the π-π^* transition band at ~ 300 nm[51-56].

Raman spectroscopy is a non-destructive tool for the analysis of order and disorder of the crystallized carbon samples. In pure form graphene has ordered structure.Due to scattering of the E1g photon of the sp^2hybridised carbon an intense graphitic bands (G) at 1600 cm^{-1} is observed.Figure 9. As the disorder arises on graphene surfaces a new detective band (D) at 1300 cm^{-1} arises from breathing mode of point photons of A1g symmetry. Disordering on graphene surface occur due to chemical oxidation, doping and thermal annealing and results the disruption of sp^2 domain of graphene surfaces. The ratio of intensity of defective band to graphitic bands (I_D/I_G) elucidate the intensity of defective band to graphitic band.I_D/I_G ratio is > 1 indicates the prominant defective nature of graphitic structure. It becomes 1.9-2.1 by incorporation of nanoparticles on graphene surface [57-64].

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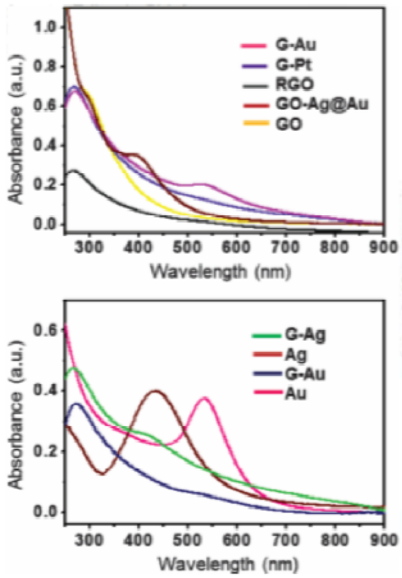

Fig.8

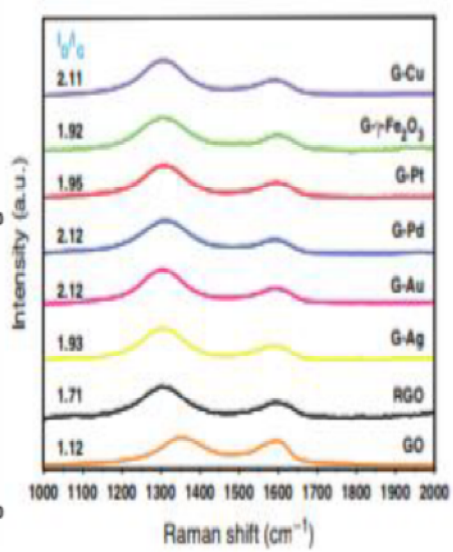

Fig.9

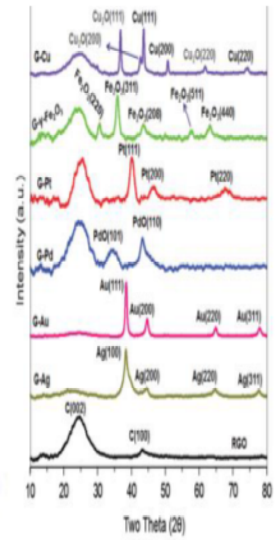

Fig.10

Fig.8 UV visible absorption spectra of GO, RGO and different G-N composites madeof silver nanoparticle (G-Ag), gold nanoparticle (G-Au) and platinum nanopaticle (G-Pt).

Fig.9 Characteristic Raman spectra of different G-N composites, G-Ag, G-Au, G-Pt, G-Cu and G-γ-Fe_2O_3; showing the G-band and D-bands of graphene..

Fig.10 Characteristic XRD spectra of different G-N composites, G-Ag, G-Au, G-Pt, G-Pd, G-Cu and G-γ-Fe_2O_3; showing the reflections from nanoparticle and carbon. Fig 8,9,10 adapted from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

Characteristic reflection from both components can be observed from XRD ofG-N composites.Figure 10 The RGO of two broad reflections of graphitic planes of carbon (002) and carbon (100).The number of layers and d spacing between the planes can be derived from Scherer equation as the number of stacking layers increases the reflection from crystalline carbon becomes sharper. G-N composites show respectivereflections from nanoparticle componentsalong with reflection for graphene component. (**Fig. 10**) For example, G-N compositeswith silver nanoparticle shows reflections due to silverplanes of (100), (200), (220) and (311) along with reflection at graphitic plane. G-Pt composites shows the broad reflections of platinumplane at (111), (200), (220) along with graphite plane at (002).When less noble metal is used the reflection of the respective metal oxide dominates. For example copper and paladium based nanocomposites show reflection of metal oxides.The G-Cu composites showthe reflection of Cu metal at (111), (200), (220) and reflections of copper oxide at (200), (111), (220). G-Pd composites shows the reflections of palladium oxide at (101), (110) along with the signature of graphite.

Application of Graphene-Nanoparticle (G-N) Composites

Graphene nanoparticle compositeshave versatile applications. presence of nanoparticle lowers the aggregation property of graphene and thus its high surface area and other properties are

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largely remain intact.As a result G-N based composites have combined property of both coponents suitable for various applications. In following sections we will discuss some of the emerging areas they have been used highlighting their advantages.

Enhanced Catalytic Property

In various organic transformation reactions, metal or metaloxide nanoparticles are used as heterogeneous catalyst. For better performance of different types of organic conversion reaction graphene based materials used as catalyst support. Table 1 and Figure 11In general G-N composites offer high conversion yield. composites catalysts are stable under repeated use. Silica coated positively charged iron oxide and silver nanoparticles have been used to electrostratically interact with colloidal GO followed by chemical reduction to produce graphene based composites.For click reaction, A^3 coupling reaction and alcohole oxidation reaction, this composites have been used. The mixture of copper salt and GO are simultaneously reduced to form G-N composites and showed high catalytic activity for O/N-arylation. The TEM study shows that the copper nanoparticle of size 2-3 nm and sillica coated silver nanoparticles of size 7-8 nm are uniformly distributed on the graphene surfaces.Figure 11(b) The graphene surfaces not only stabilize the active γ-Fe_2O_3/Ag/Cu nanoparticlesbut it can also provide a suitable platforms or medium for reacting molecules to carry out reaction smoothly and with higher efficiencies.

Table1Summery of application of G-Ncomposites as heterogeneous catalyst

Composites	Application	Advantage
GO-Pd. G-Pd	suzuki copling, suzuki-Miyaura coupling, Heck eaction	GO/ graphene as better supportthan carbon black
G-Fe_3O_4-Au, G-γ-Fe_2O_3	O-nitroaniline to benzediamin, triazoles synthesisvia click chemistry	Graphene as better support and magnetic separation
GO-Ag, G-Ag	decarboxylative cycloaddition, A^3 - coupling	High catalyst stability, efficient catalysis
G- Cu, G- CuO	Arylation	Graphene as conductive support, stabilize Cu / CuO
G-Ru	Arene hydrogenetion	High catalyst stability

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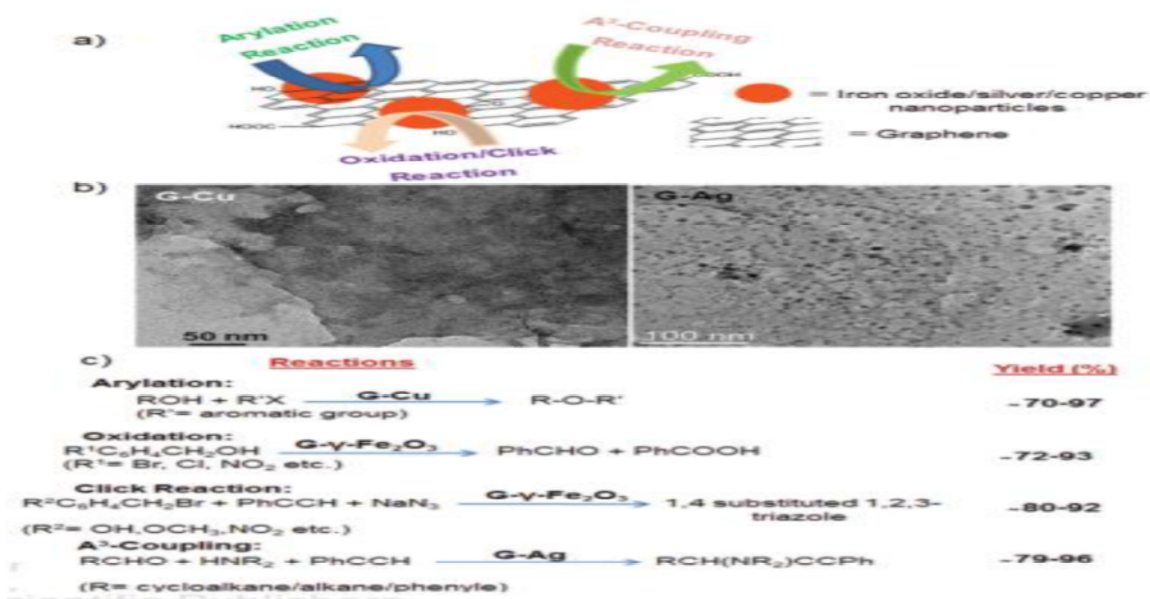

Figure-11(a) Schematic representation of G-N composites catalyzed different organic reactions, (b) TEM images of G-N composites made of copper nanoparticle (G-Cu) and silver nanoparticle (G-Ag) and (c) G-N composites based catalytic arylation, oxidation, click reaction.Fig. 11 adapted from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

Due to large surface area and high local concentration of electrons on the nanoparticles, large number of reactant molecules can easily adsorb on the graphene surfaces and fascilate the A^3 coupling, arylation and click reactions.The oxidation reaction of alkyl/nitro substituted benzyl alcohol molecules is catalyzed due to presence of oxygen functionality on the graphene surface. The number of catalytic centres can be increased by the decoration with smaller size and uniformly dispersed nanoparticles on graphene surfaces which results in better catalytic conversion. The stabilization of nanoparticles on graphene surfaces give higher catalytic performance [82-86].

Enhanced Electrochemical Detection Sensitively and Selectively

For diagonosing different types of biomolecules, toxic materials and explosive materials, electrochemical technique is an important tool. Graphene has been used in electro chemical sensing application of different biomolecules. Graphene oxidizes at high positive potential (2.5 V in mM phosphate buffer solution), so the molecule having high reduction or oxidation potential can be detected by electrochemical technique. The edges and defects in few layer RGO are considered as superior part for electrochemical activity.Different types of G-N composites are used for electrochemical biosensingwhich are abridged inTable 2**.**

To enhance the selectivity or sensitivity, G-N composites are designed. The selectivity comes from surface charge present in composites or selective affinity of analyte to any component of

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composites. The sensitivity arises from large surface area, high loading of nano particle and high conductivity of graphene. These factors facilate high adsorption of analyte and eletron shuttling from analyte to electrode or vice versa [92-96]

Representative example of graphene based composites with gold nanoparticle (G-Au) and their electrochemical detection is shown in Figure 12. TEM imageshows bright round spot observed on graphene surface as gold nanoparticle and similar morphology is expected when they are used to modify the working electrode.For resolution of individual redox signals, finer optimization of loading of Au nanoparticles on graphene surface is important.Thus, sensitive and selective detection of ascorbic acid , dopamine, uric acid or DNA bases can be performed from mixture. In most of the cases ascorbic acid supress the redox signals of dopamine/uric acid. The oxidation peak potential of ascorbic acid is shifted by G-Au towards lower potential and thus signal is isolated [97-113]

Table2 Summary of application of G-N composites in electrochemical sensing.

Composites	Detection Application	Advantag
G-Pt-PVP[1],	Glucose	High Sensitivity
G-Pt	H_2O_2, cholesterol, arsenic, ascorbic acid-dopamine-uric acid mixture	High Sensitivity, simultaneous detection of analyte from mixture
G-Au-chitosan	Glucose, uric acid, uric acid-adrenaline mixture	Simultaneos detection of analyte from mixture
G-Au	Ascorbic acid-dopamine-uric acid mixture, guanine-adenine-thymine-cytosine mixture	High sensitivity, simultaneous detection of analyte from mixture
G-Au-PDDA[2]	Organophosphates	High sensitivity
Notes : [1]polyvinyl pyrrolidone, [2]poly diallyldimethylammonium chloride		

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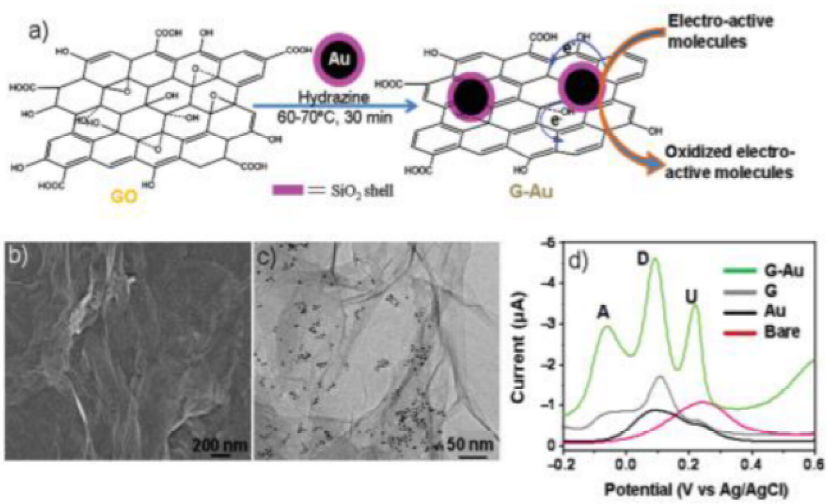

Figure-12 (a) schematic representation of synthesis of G-N based composites with gold nanoparticles (G-Au) and mechanism of electrocatalysis, (b)FESEM image of G-Au (c) TEM imageof G-Au and (d) differential pulse voltametry response of mixture of ascorbic acid (A), dopamine (D) and uric acid (U) by differently modified glassy carbon electrode. Fig. 12 adapted from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

Enhanced SERS Detection Sensitivityand Reproducibility:

For the detection of low concentration of molecules SERS is a highly sensitive technique. The electromagnetic enhancement is responsible more than chemical enhancement for the sensitive detection. Graphene and GO based composites with plasmonic nanoparticle have been used to improve the detection sensitivity and signal reproducibility. (Table 3, Figure 13) At the surface of graphene/GO, large number of nanoparticles are attached and control their aggregation (dimmers / oligomers). For this reason more number of electromagnetic hot spots are formed that are responsible for SERS. The SERS signal intensity is enhanced due to adsorption of Raman probes on those hot spots[115-119]. (Fig 13(d)) Surface of GO/ graphene help for adsorption of Raman probes which are commonly having π- ring structures. The electrostatic interaction, π-π stacking or H- bonding interaction between Raman probe and G-N composites can induce their positioning at hot spots. Using this approach various dye molecule, toxic metal ions and biomolecule are efficiently detected [120,121]

Reproducibility of SERS signal can be significantly enhanced. Very poor reproducibility of SERS signal is obtained in salt induced uncontrolled aggregation of plasmonic nanoparticle because it generates electromagnetic hot spot at intermediate stage. Thus limits for reliable detection application.Stable aggregates is generated by G-N composites and thus reproducibility of SERS signal is enhanced. (Fig. 13) For example, plasmonic hot spots have been stabilized by GO liquid crystals that significantly enhance the SERS signal reproducibility. (Fig. 13(c)) approach have been used for sensitive detection of different biomolecule suchas adenine, biotin and thaimine[122-126].

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Table 3 G-N Composites used in SERS based detection

Composites	Detection Application	Advantages
G-Ag	Allura red, ponceau, erythrosine colourants in foods	High detection sensitivity
GO-Ag	Folic acid	High sensitivity due to formation of more electromagnetic hot spots
RGO-Au	Hg(II)	Ultrasensitive detection
GO-Au	Malachite green	High sensitivity due to chemical and electromagnetic nhancement effect
GO-Ag@Au	Rhodamine 6G, 4-mercaptopyridine, biomolecules	High sensitivity due tostabilization of electromagnetic hot spots byliquid CRYSTALLINE go
GO-Ag@Au	Glucose	High detection sensetivity

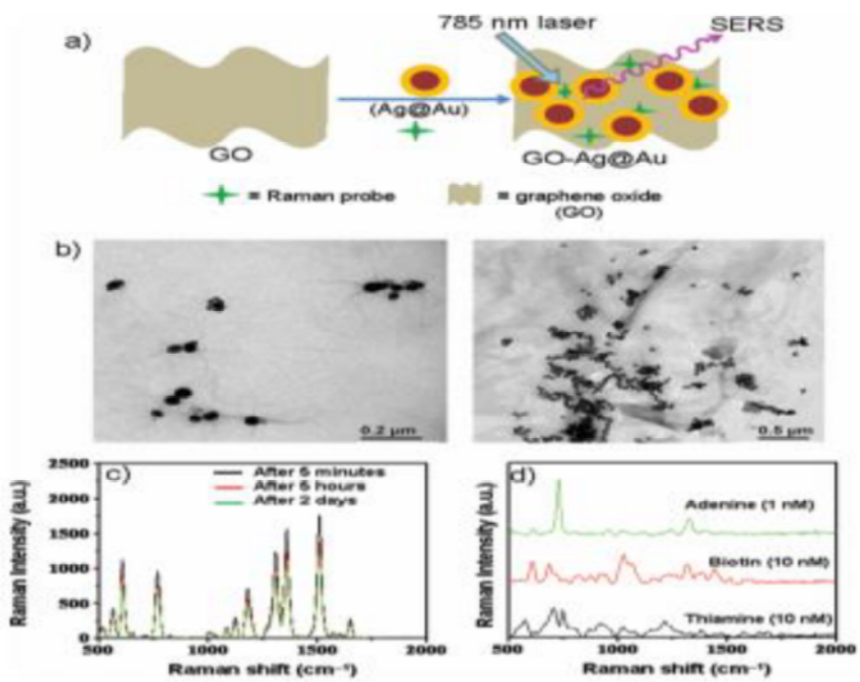

Figure-13 (a)Schematic representation SERS approach using G-N composites with silver coated gold nanoparticle (G-Ag@Au). (b) TEM image of representative G-Ag@Au composites, (c) reproducible SERS signal of 2-marcapto pyridine using G-Ag@Au composites and (d) SERS detection of biomolecules using G-Ag@Au composites. Fig. 13 adapted fromfrom A. Mondal and N.

R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy,Environmental and and Biomedical Science, Vol. 3, pp. 177-192, 2014

High Performance Fuel Cell Catalyst

For fuel cell application, Graphene-metal hybride materials are used as alternative electrode materials.The aim of fuel cell research is to get green energy from chemicals using electrochemical approach. The reactions are performed on electrode surface. Current is generated for these reactions [127-130]. We know direct four electron reduction of oxygen to H_2O is more efficient and desired compared to two electron reduction which leads to the formation of H_2O_2 [131]. Various electrocatalyst such as metal nanoparticles (e.g. Pt, Pd, Au), bimetallic nanoparticles (e.g. PtAu, PtAg, PtCu, PdCu) and metal oxides are used due to low efficiency. But the problem is generation of poisoning intermediate such as CO in many of these catalytic fuel cell reaction. It hampers the long term stability of the catalyst.In order to solve these issues the G-N based composites have been used as electrocatalyst.The poisoning effect is decreased by using graphene as support and gives longer life time to the catalyst [132-138].

The main criteria of the G-N composites based catalyst are uniform loading capacity of nanoparticles which gives high surface area, intact binding between two components and minimum use of stabilizers. The advantages of G-N composites based catalyst are minimization of catalyst poisoning, maximization of catalytic current and stable catalytic current with repeated cycles[139,140]. (Table 4, Figure 14).

Table 4 Summary of application of G-N composites as fuel cell catalyst

Composites	Fuel cell reaction	Advantages
G-Pt, RGO-Pt	O_2 reduction, HCOOH oxidation, methanol oxidation	High cataytic current, high catalyst stability, more carbon monoxide tolerance
GO-Pd, G-Pd	HCOOH oxidationmethanol oxidation, ethanol oxidation	Highcatalytic current, stable catalytic current to repeated cycles
RGO-Au	O_2 reduction	High onset potential, high catalyst stability
G-PtPd	Methanol oxidation	Low carbon monoxide poisoning
G-PtAu	HCOOH oxidation	Low carbon monoxide poisoning, high catalyst stability
G-noble metal	Ethanol oxidation, HCOOH oxidation	Stable catalytic current
G-Co_3O_4	O_2 reduction	High catalyst stability

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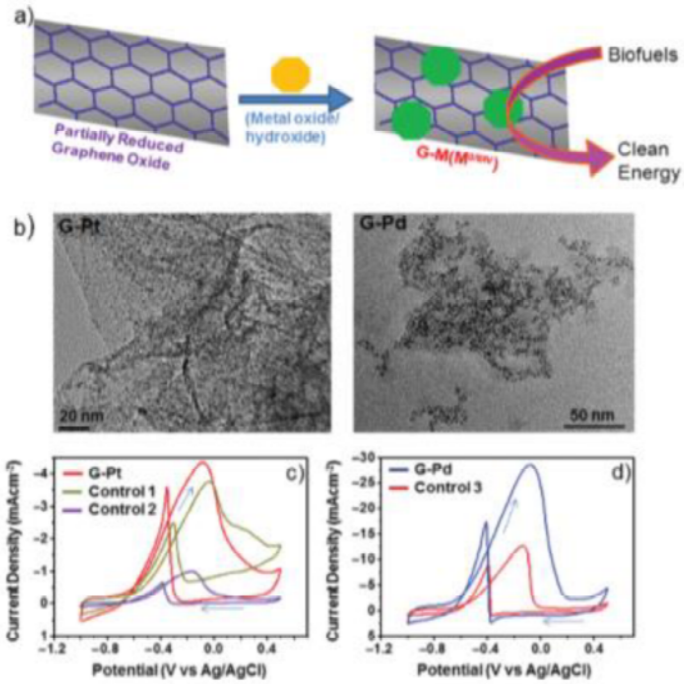

Figure-14 (a) Schematic representation ofsynthesis and fuel cell catalytic application of G-N composites, (b) TEM image of platinum nanoparticle (G-Pt) and palladium nanoparticle (G-Pd), (c) electrochemical oxidation of 0.5 M ethanol in 1 M KOH using G-Pt composites with respect to control 1 (G-N composites produced by reduction of platinum salts and GO) and control 2 (20% wt% Pt on graphitized carbon) and (d) electrochemical oxidation of 0.5 M ethanol in 1 M KOH using G-Pd with respect to control 3 (G-N composites produced by reduction of palladium salts and GO. Fig 14 adapted from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

The active surfacearea is decreased due to commonly used surfactant and polymeric stabilizers. In G-N composites based approach, using graphene as nanoparticle stabilizer and supported catalyst this problem can be solved. G-Pt and G-Pd composites are prepared by using this approach. Colloidal platinum oxide/palladium oxide nanoparticles are treatedwith partially reduced GO[143-148]. (Fig. 14) The Pt Nanoparticles with average size 2.3 nm and palladium oxide nanoparticles with average size 3.5 nm are uniformly distributed on graphene surfaces as seen in the TEM image. (Fig. 14(b))The current density(based on the actual surface area) for ethanol electro-oxidation using this G-Pt composites is higher than control 1(G-Pt prepared by insitu reduction of platinum salts in presence of GO and control 2 (20% wt% Pt on graphitized carbon).(Fig. 14(c)) Similarly, the current density for ethanol oxidation by G-Pd is higher than the control catalyst produced by the in situ reduction of salt in presence of GO (Fig. 14(d)).In addition no CO oxidation peak is observed in the forward reaction using the G-Pt /G-Pd composites. Overall, the performance of these catalyst toward electrochemical oxidation of ethanol and formic acid is very good and they produce high current density with low poisoning effect and catalytic current is stable to repeated catalytic cycles.

High Performance Adsorbent for Water Purification:

There are various methods for waste water treatment such asmembranebasedfiltration,ionexchange, adsorption, precipitation and amalgamation. Among all methods the adsorption based method is cost effective and mostly widely used for removal of various pollutants.For such purpose activated carbons and porous carbons are commonly used. The magnetic metal oxide nanoparticle are also used as adsorben. There are few limitation such as limited functionalization and stability issues, poor dispersibility in the commomly used adsorbent.Most of the limitation are removed by using G-N composites. G-N composites made of magnetic nanoparticle (e.g. Fe_3o_4 / γ-Fe_2O_3) can solve most of the limitations of magnetic nanoparticles and graphene. Such composites have high surface are, magnetic property and high separation efficiency. Table 5. The different organic substrates are efficiently adsorbed on graphene surfaces through π-π interactions, electrostatic interactions andweak interaction. . The positively charged silica coated γ-Fe_2O_3 nanoparticles are treated with negatively charged GO followed by hydrazine reduction that results magnetic G-γ-Fe_2O_3 composites. The γ[159]-Fe_2O_3 nanoparticles with average size of 15 nm are well distributed on the graphene surfaces as observed in the TEM images. (Fig. 15b)) Endocrine disruptors can be removed by mixing G-γ-Fe_2O_3 composites with waste water followed by magnetic separation of G-γ-Fe_2O_3 composites to get clean water. (Fig. 15(a)) These endocrine disruptors are adsorbed on the graphene surfaces throughthe π-π interactions, hydrophobic interaction and electrostatic interaction. Typicalresults are shown in Fig. 15(c) for G-γ-Fe_2O_3- based separation of bisphenol A. It is shown that performance of bisphenol A. It is shown that performance of bisphenol A separation by G-γ-Fe_2O_3 is better than commercially available activated carbon.

Table 5 Application of G-N composites in water purification.

Composites	Removed pollutant	Advantages
GO-Fe_2O_4	Cu(II), Co(II), fulvic acid, rhodamine B, acid blue, malachite green	Easy and efficient separation, magnetic separation
RGO-Fe_2O_4	As(III), As(V)	High adsorption capacity
G-Fe_3O_4	Safranine T, neutral red, victoria blue	Efficient separation
G-γ-Fe_2O_4	Endocrine disrupters	Efficient separation
RGO-ZnO	Rhodamine B	Adsorption and photodegradation

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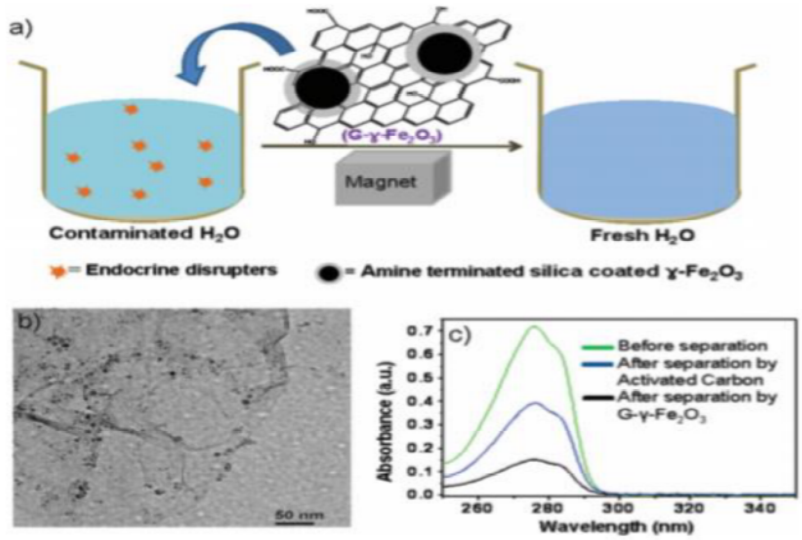

Fig.15(a) Schematic representation of separation of endocrine disruptors from water using G-N composites made of γ-Fe_2O_3**(G-γ-Fe_2O_3), (b) TEM image of** G-γ-Fe_2O_3 **and (c) comparative separation efficiency of bisphenol A by activated carbon and G-γ-Fe_2O_3 as observed by UV- visible absorption spectra of bisphenol A. Fig. 15 adapted** from A. Mondal and N. R. Jana, Reviews in Nanoscience and Nanotechnology, Graphene-Nanoparticle Composites and Their Applications in Energy, Environmental and Biomedical Science, Vol. 3, pp. 177-192, 2014

Efficient Photocatalyst

The G-N composites contained semiconductor nanoparticle used in photocatalytic applications [160]. Graphene nanoparticle composites reduce CO_2 into reactive carbon forms.(Table 6) .Due to chemical stability, nontoxicity and low cost, TiO_2- based nanomaterials are widely used as photocatalyst.Photocatalytic efficiency of Graphene-TiO_2 composites is higher than bare TiO_2. A significant limitation of TiO_2 based materials is that it has large band gap. It is active only under UV light. To expand photocatalysis under visible light, materials that absorb in the visible range and offers photocatalysis under sunlight are developed. The graphene based composites with Ag_3PO_4, CdS have been used for such visible light photocatalytic degradation and photocatalytic conversion reactions [161-165.]

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Table 6 Summary of application G-N composites as photocatalyst

Composites	Molecule degraded	Advantagea
RGO-Ag_3PO_4	Methyl orange, methylene blue	Efficent degradation under visible light
GO-Ag_3PO_4	AO7 dye, phenol	Efficient degradation under visible light
G-TiO_2	Methyl orange, alkyl phenol, butane	Efficient degradation under UV light
G-ZnS	Conversion of alchole to aldehyde	Graphene capture visible light and act as photosensitizer
G-CdS	Rhodamine B	Efficient degradation under visible light

Table 7 G-N composites used for supercapacitor application

Composites	Advantages	Reason
G-ZnO	Reversabie charging-discharging, high capacitance	Intercalation of ZnO between graphene
G-$Ni(OH)_2$	High energy densities, high power densities long cycle life	Intercalation of nanocrystalline $Ni(OH)_2$ between graphene
G-SnO_2	High capacitance	Synergistic effect of SnO_2 and graphene
G-MnO_2, GO-MnO_2, G-Mn_3O_4	Flexible, light weight, high performance, high charge-discharge rate, long cycle life	High surface area, porous structure and conductive matrix promote fast Faradic charging and discharging
G-RuO_2, G-TiO_2, G-Fe_3O_4	High capacitance	Minimum agglomeration of metal oxide helps efficient Faradic chrge transfer
G-$Co(OH)_2$	High capacitance	Stabilization of graphene and $Co(OH)_2$

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Various oxidative species (e.g. $O^{\cdot}_2$, O^{-}_2, OH free radical) which causes oxidation of different aromatic compounds are generated by these photogenarated holes in the valence band and conduction band [166].Graphene-Cu nanopartcle composite is used as active photocatalyst for transforming aromatic nitro compounds into azoxy or azo compounds. It follow a green photocatalytic route for the reduction of aromatic nitro compounds. Due to fast recombination process of electron-hole pair the photocatalytic efficiency of semiconductor is quite low. To increase efficiency graphene is used as catalyst support delay the electron-hole pairrecombination process. Graphene accepts the electrons situated in semiconductors conduction bands and shuttle the electrons through the conjugated π domains in graphene surfaces. Graphene can also act as electron reserviorand photosensitizer to capture the visible light [167-171]

Improved Supercapacitor

Supercapacitors are electrochemical energy storage devices. They work by the process reversible adsorption and desorption of ions. Graphene based materials , especially graphene metal oxide hybrid materials are used for this purpose [172] Electrochemical double layer capacitors(EDLCs) is a common type of supercapacitor. It store energy by accumulation of charges in the electrical double layer via electrostatic interactions at the electrode-electrolyte interface. The capacitance of graphene nanosheet, used as supercapacitors, is not high. RuO_2 has high specific capacitance and longer cyclic life time .But use of these oxide is not cost effective. Other metal oxides or hydroxides havelow specific capacitance. In graphene based hybrid material with metals oxide show both supercapacitive and pseudocapacitive nature simultaneously. These composites have high specific capacitance and faster charge-discharge ability. Due to the high conductivity of graphene as support, high overall surface area, high mechanical and chemical stability and flexibility of the composites graphene based composites show high performance |174-177|. Table 7 abridges the composites materials along with their advantages.

Efficient Li – Ion Battery

Li-ionbatteryisfirstintroduced in 1991. For today's mobile electronic devices Li-ion battery witha high energy density (150Wh/kg) has become a major power source. Rechargable Li-ion batteries (RLBs) have high charge density which means they last longer than any other batteries. It can hold more power. They are used in different devices. Energy is stored and released respectively by insertion of Li-ion into the anodic substances during charges and release during discharging occurs for energy storing and release, respectively. In Li ion battery metal Li used as an anode. Different metal or metal oxide or carbon coated material used in formation of anode. Due to high mechanical and electronic properties of graphene, it is used as alternative anode material. Graphite based Li ion battery has some problem. lowering of Li insertion, long diffusion distance for lithium ion and slow charge-discharge cycling of life time are the main limittations of Li ion battery.[178-183]. Figure 16 Co_3S_4 nanotubes are made to deposit on graphene by using pre-synthesized $Co(CO)_{0.35}Cl_{0.20}(OH)$ nanowires and thioacetamide as sacrificial template and S source, respectively. The composites show better cycling performance and higher reversible capacity than pristine Co_3S_4 electrode[184,185]. Conductive graphene reduce the volume expansion/contraction during charge-discharge period leading to higher life cycle and shorter

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transport length for Li-ion. In addition presence of nanoparticle prevents the dense packing of the graphene sheets that offers high adsorption of Li-ion [186,187]. The various combinationsof graphene based composites with metal/metal oxide are summarized Table8.

Table 8. G-N composites used for Li-ion battery application.

Composites	Advantage	Reason
G-Si, G-porous Si	High storage capacity, stable performance over repeated cycles	Graphene provide conductive network and elastic buffer
G-Co_3O_4	Stable performance over repeated cycles	Prevent volume expansion/ contraction and aggregation of Co_3O_4
G-SnO_2	High performance	High loading of SnO_2
RGO-Sn, G-Sn	High specific capacity, high reversibility	Sn nanoparticles act as spacer for separation of graphene sheets and induce efficient electron transfer
G-TiO_2	High charge discharge rate	Percolated graphene network inmetal oxide electrode

Fig.16

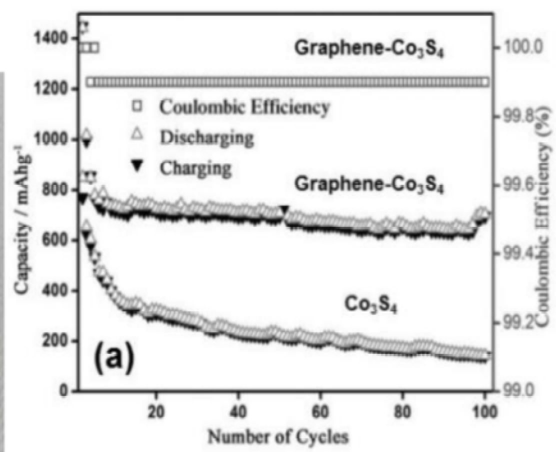

Fig17

Fig. 16 is taken from Qing Li, Nasir Mahmood, Jinghan Zhu, Yanglong Hou and Shouheng Sun, Graphene and its Composites with Nanoparticles for Electrochemial energy applications, Brown University and Peking University. Figure 17 cyclic behaviour of Co_3S_4 and the graphene-Co_3S_4 with a columbic efficiency at a rate of 0.2 C between 0-3 V vs Li^+/Li.

Conclusion and Future Direction

Unique chemical structure andexcellent conductivity, transparency, mechanical strength, porosity and electrochemical properties of graphene bring a new era in nanotechnology. G-N composites has been extensively studied for various applications, especially for electrochemical

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energy conversion and storage. Graphenebased composites havebeen used as super material. In the world of material science graphene nanoparticle composites is a masterpiece.

Despite of significant work donein this area, more work should be done on graphene nanoparticle composites for advancement of the field.

(1)In the synthetic process , more advanced technique must be used.

(**2**) It is required to develope the techniques by which different molecules can be involved in formation of different graphene based composites. It helps to increase its versatility.

(**3**) Contolled loading of nanoparticle is very essential. If the process will be according to this, it helps to functionalize the composites more in different applications.

(4) To produce clean composites we avoid the method where large molecule or polymer is used. With the help of these advancements it is expected further developmentoccur on graphene nanoparticle composites of in coming years.

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